

INORGANIC CHEMISTRY

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THE MODERN PERIODIC TABLE

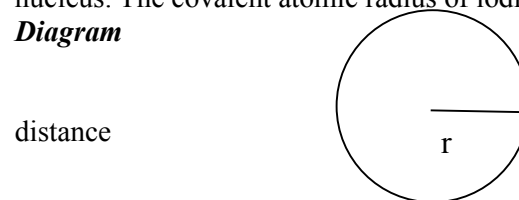
The modern periodic table consists of two major divisions. The horizontal arrangement of element called periods while the vertical arrangement is called group. The modern periodic table was derived directly from the electronic configuration of the atoms based on their atomic numbers and shows the relationship between the elements.

VARIATION OF PROPERTIES IN PERIODIC TABLE

1. SIZE OF ATOMS AND IONS

The radius of an atom is defined as the distance of closed approach to another nucleus. The covalent atomic radius of iodine atom =0.133nm.

Diagram



distance

Where r = atomic

Atom radius is equal to half the distance between the two nuclear in bonded iodine atom

Factors which affect atomic radius

i) Nuclear charge

The greater the nuclear charge the more strongly are outermost electrons attracted and all the closed they are to the nucleus and hence the smaller the atomic radius electrons attached to the nucleus. If the outermost electrons are far away from the nucleus the experience less nucleus attraction thus the atomic size increases

ii) SCREENNG EFFECT OR SHIELDING EFFECT

Screening effect is the repulsion of the outer most electrons by those in the innermost energy levels. The greater the screening effect, the less closely are outermost electrons attract and further they are from the nucleus and hence the greater the atomic radius. For small screening effect the outmost electrons are closely attracted by nucleus and the smaller the atomic radius

a) Variation of atomic radius across the period

Period II

Element	Li	Mg	B	C	O	F
Radius/nm	0.123	0.089	0.082	0.07	0.066	0.064

Period III

Element	Na	Mg	Al	Si	P	S	Cl
Radius/nm	0.156	0.136	0.125	0.117	0.110	0.104	0.099

Electronic configuration

Na $1s^2 2s^2 2p^6 3s^1$ Mg $1s^2 2s^2 2p^6 3s^2$, Al $1s^2 2s^2 2p^6 3p^1$
 S $1s^2 2s^2 2p^6 3p^2$ P $1s^2 2s^2 2p^6 3p^3$ Cl $1s^2 2s^2 2p^6 3p^4$

Cl $1s^2 2s^2 2p^6 3p^5$

Note

The size of an atom is determined by

- The attraction of the positively charged nucleus for electrons which tend to decrease the size of the atom.
- Screening of the outer electrons from the nucleus by the inner most electrons, this is called screening effect which is the repulsion of the outmost electrons from the nucleus by those in the inner shell. This tends to increase the size of the atom.

Trend across the period

Atomic has decreases from left to right across a period.

Explain: In moving from one element to the next across a period, an electron is added to the same shell and a proton added to the nucleus. Therefore, cross a period nuclear charge increases such that electrons are pulled closer tom the nucleus. The size of the atoms therefore decreases.

b) Variation of atomic radius down group

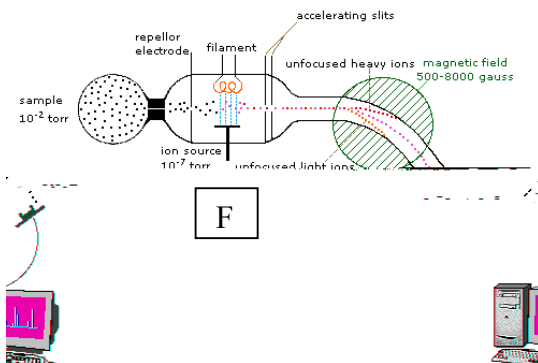
	RADIUS A	Electronic Configuration (OUTER)
Li	1.23	$1s^2 2s^1$
Na	1.57	$1s^2 2s^2 2p^6 3s^1$
K	2.03	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rb	2.16	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^1$
Cs	2.35	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2 5p^6 6s^1$

Trend

Atomic radius increases on descending any group in the periodic table for example group

Explanation

Down the group both nuclear charge and the number of electrons are increasing in each case there is addition of an electron on an extra added shell and a corresponding addition of a proton in the nucleus. But the increase in screening effect outweighs the increase in nuclear-charge. Therefore, effective nuclear attraction decreases such that electrons are less attracted by the nucleus resulting in the size of atoms.



Variation among transition elements

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Radius / nm	0.16	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.13	0.13

Trend

Among the transition element, the atomic radius remains almost the same.

Explanation:

This is because the effect of the increased nucleus charge is roughly balanced by the greater screening effect produced by adding an extra electron to the penultimate shell.

IONS

A positive ion (cation) is formed by the removal of one or more electrons from an atom. A cation is smaller than the atom from which it is formed. This is because after the removal of the electrons the nuclear attraction of the remaining few electrons increases so that the electrons are now more strongly attracted towards the nucleus thus reducing the atomic size.

For example;

	Radius
Fe (atom)	1.17A

Fe²⁺

0.760 A

A Negative Ion (anion) is formed by addition of one or more electrons to natural atom, addition of electrons increases the number electrons and thus reduces the effective pull of electrons by the nucleus so that electrons are now weakly held. Therefore, anions are bigger in size than the corresponding atoms.

For example

Radius

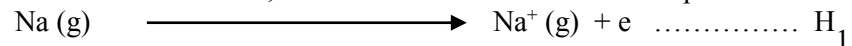
Cl	1.140A
Cl ⁻	1.18A

IONIZATION ENERGY

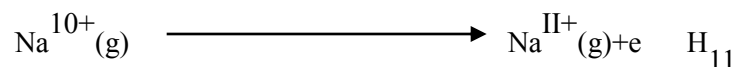
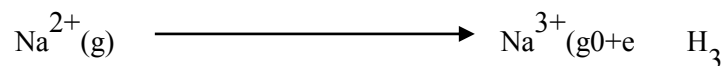
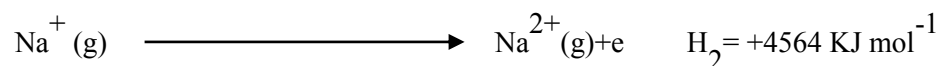
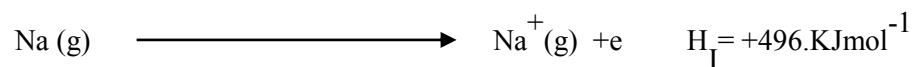
Ionization energy is defined as minimum amount of energy required to remove one mole of an electron from one mole of a gaseous atom or ion against the attractive forces of nucleus to form one mole of a positively charged ion.

The first ionization energy is the minimum amount of energy required to remove the most loosely held electron from a gaseous atom against the nuclear attractive forces.

For sodium atom, the first ionization is represented as below



Usually there can be H₂, H₃ etc. depending on whether there is 1, 2, 3 etc. are electrons.



Ionization energy is measured in KJ mol⁻¹ and is determined from mass spectra.

Determination of Ionization

It is composed of the following chambers;

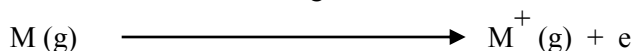
Vaporization/atomization

Ionization

Acceleration
Deflection chamber.

A solid in the atomization chamber is super-heated to give gaseous atoms of element and forced into the ionization chamber, the filament (F), is heated and gives off electrons. The grid Y of the filament is charged positively to different potentials while slits M are negatively charged.

The potential of Y is now increased and the electron emitted by the filament are now attracted and accelerated by F. In the process of traveling, the electron collides with atoms of the elements and cause ejection of an electron from the atom occurs hence causing ionization.



The electron ejected from the atom is attracted to the grid Y while the positive ion, M^+ formed is attracted by the slits. Current thus will flow and the minimum grid potential required for the ionization to occur is measured and recorded. This is known as ionization potential which is expressed in eV where $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$.

The grid potential is gradually increased so that 2nd, 3rd etc. electron is ejected.

NOTE:

Current does not flow if the potential on grid Y is Zero.

Ionization energy increases as electrons are removed.

Consider the ionization energies of beryllium

1 st I.E	2 nd I.E	3 rd I.E	4 th I.E
900	1758	14905	21060

Where I.E. = ionization energy

Trend:

Ionization energy increases from 1st to the 4th ionization energy. The first two electrons are easily removed but the last two electrons are difficult to remove.

Explanation:

a) The 2nd ionization energy is greater than 1st ionization energy because after

the removal of the first electron, the proton to electron ratio increases so that the nuclear attraction for the remaining few electrons increases. Since the remaining electrons are now strongly attracted towards the nucleus, it requires more energy to remove the next electron than the first electron.

b) The ionization energy to remove 2nd electron is about twice the first one and to remove the 3rd electrons requires about the 8 times more energy required to remove the 2nd electron. This is because the 3rd electron came from another energy level which was near the nucleus.

c) The energy to remove the 4th electron is about 1 ½ times more than the 3rd Ionization energy.

Therefore in beryllium atom, there are four electrons, two of which are very easy to remove and two which are difficult to remove.

Since to remove the 3rd electron, there is a very big rise in energy, therefore the 3rd electron comes from **different energy level** of electrons. From the electronic configuration of beryllium $1s^2 2s^2$. Beryllium therefore has two electrons in its lower energy level which are very near to the nucleus and difficult to remove and two others in the higher energy level which are easily removed.

Factor affecting the magnitude of ionization energy:

i) Atomic size: In small atoms, electrons are **strongly held tightly** and are difficult to remove while in large atoms, electrons are **less tightly held** towards the nucleus since they are far away from the nucleus and hence are easy to remove.

ii) Nuclear charge: The greater the nuclear charge, the more tightly electrons are held and the more difficult to remove against nuclear attractive forces.

iii) Screening effect: Ionization energy **decreases** with increase in screening effect. This is because screening effect makes electrons loosely attracted by the nucleus thus reducing the nuclear attraction.

iv) Penetrating power of valence electrons. For a given energy (quantum), the penetrating power increases in the order $f < d < p < s$. The greater the penetrating power of the valence electron the more closely is an electron attracted and the greater the ionization energy. Electrons in the f orbital **experience less nuclear attraction** than electrons in the s orbital therefore electrons located in the s orbital have a higher ionization energy than electrons in the p or d and f orbital.

Variation of 1st I.E across the period

Period II

Element	Li	Be	B	C	N	O	F	Ne
I.E.KJmol ⁻¹	520	899	801	1086	1403	1310	1681	2080

Trend

Graphically, the variation is represented by a plot of the 1st ionization energy against atomic number. (see the graph below)

Trend:

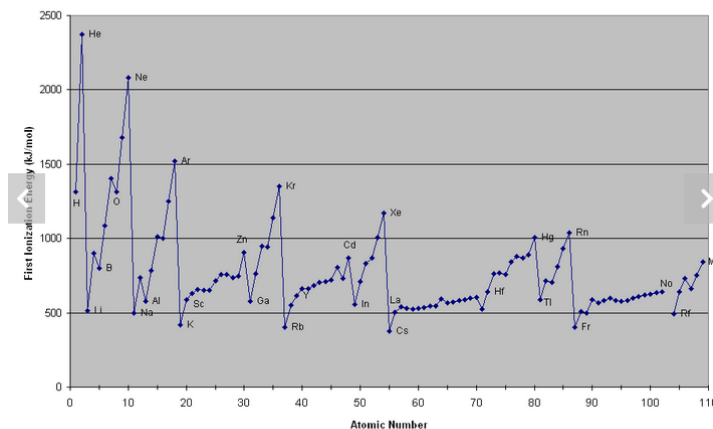
Generally, the 1st ionization energy increases across period with abnormal behavior shown by Mg and P for period III while be n for period II

Explanation

Moving from left to right one element to the across the period table, an electron is added to the same shell and a proton is added to the nucleus. The nuclear charge increases and the electrons are now more tightly held towards the nucleus thus requiring a lot energy to be removed.

In moving from left to right across a period, 1st Ionization energy of Be and Mg are unexpectedly higher than Boron and aluminum respectively. This is because a single electron is being removed from full 2S and 3S subshell respectively which is thermodynamically very stable and thus requires more energy.

Periodic Trends in First Ionization Energy



charts illustrate the general trends in the first ionization energy



Similarly ($1s^2 2s^2 2p^3$) and P ($1s^2 2s^2 2p^6 3s^2 3p^3$) have unexpected higher 1st ionization energy because their electrons are being removed for half full 2P and 3P sub shell respectively. Any half- full or full shell is thermodynamically stable and requires more energy.

Variation of ionization energy down group

Element	
1 st I.E/KJ mol ⁻¹	
Be	899
Mg	737
Ca	590
Sr	549
Ba	503

Trend

Generally, 1st Ionization Energy decreases down the group.

Explanation: On descending a group both the nuclear charge and screening effect increase but the increase in screening effect as a result of an extra shell of

electrons added outweighs that of the nuclear charge. Therefore, effective nuclear charge decreases so that electrons are less strongly held down the group and is easy to remove

APPLICATION OF IONISATION IN THE DETERMINATION OF THE CHEMISTRY OF ELEMENT

I. Atomic Number

The number of successive ionization energies indicates the number of electrons presents in atom .Sodium has 11 successive ionization energies indicating that the atomic number of sodium is 11

II. Arrangement of electrons and distribution of energy levels.

A plot of successive ionization energies of potassium shows distinct breaks. The arrangement starts with 2 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 the ionization energies. These have less ionization energies than the first 2 electrons. The next are 8 electrons also with similar energies but are easily removed than the previous. Finally, there is a single election which is easily removed. This group of electrons is called energy shell. In potassium atom, there are 4 energy levels and the electrons arrange as

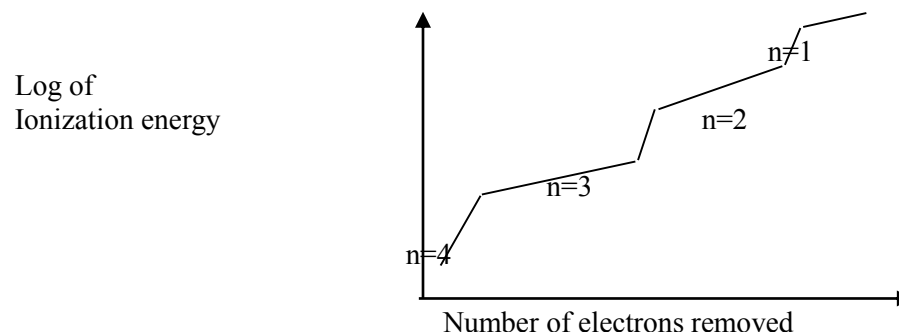
Energy level	n=1	n=2	n=3	n=4
No of electrons	2	8	8	1

Since potassium atom has four energy levels, it therefore belongs to period 4. Ionisation energies also provide information about the presence of sub-energy levels.

A careful plot of successive ionization energies in the 2nd energy level of potassium shows that there are 2 electrons with fairly similar ionization energies which are nearer to the nucleus and they are followed by 6 electrons with less energy but similar. This shows that the electrons in the 2nd energy level are arranged as

Sub energy	s	p
No, of electrons	2	6

Graph of Ionization Energy Potassium Atom against Number of Electrons Removed



III. Determination of metallic or non- metallic character.

The magnitude of ionization energy is used as a measure of the metallic character of an element. The first ionization energies of metals are all nearly below 800 KJ mol⁻¹ while those of non- metals are all nearly above 800 KJ mol⁻¹. Down the group ionization energy decreases so that the elements become more metallic. In group (IV), (v) there is change from non-metallic to metallic character.

Across a period 1st ionization energy increases in moving across a period, the elements become less metallic but more non- metallic.

The use of ionization energy to predict the properties of elements

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

	First I.E	Second I.E	Third I.E
A	780	1500	7730
B	500	4560	6900
C	580	1815	4620
D	1310	3460	5300

a) From the 1st ionization energies of the elements it can be elements b and c have typical metallic properties since their 1st ionization energies are all nearly below 800 KJ mol⁻¹.

b) Element with 1st ionization energy near 800 KJmol⁻¹ also would show some metallic properties.

c) Moving from 2nd to 3rd ionization energy for A there is an increase of about 5 Times. This means the 3rd electron of A comes from a different shell hence A has 2 electrons on its outer shell. A is therefore a group 2 elements with charge of +2.

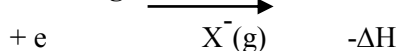
For element B there is an increase of about 9 times from 1st to 2nd I.E. and an increase of about 1½times from 2nd to 3rd I.E. Therefore element B has one electron on its outermost shell and thus is a group 1 element and would have a charge of +1

In element C, from 1st to 2nd Ionization energy increase is about 3 times and from 2nd to 3rd I.E. by about 2½times. Therefore there is similar rise in ionization energy. This implies that the 3 electrons in C are from the some shell and C therefore would form three positive charges and hence belongs to periods 3.

Element D with its first Ionization energy well over 800 KJ mol⁻¹ is anon metal
The following compounds therefore would be formed between
A and D = AD₂ B and D = BD, C and D = CD₃

ELECTRON AFFINITY

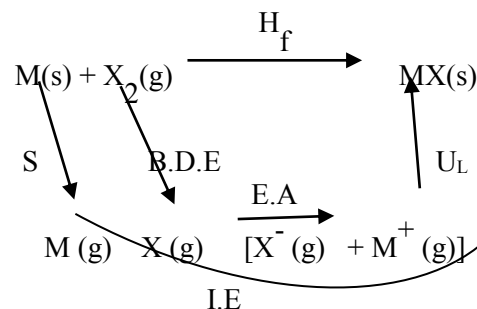
Electron affinity is the reverse of ionization energy. Electron affinity is defined **as energy change** that occurs when **one mole of electrons** combine with **one mole of gaseous atom** to form *one mole of gaseous negatively charge ion*. X (g)



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

(+ΔH) to affect it. The 2nd electron affinity is therefore positive (i.e. an endothermic process)

Electron affinity is estimated by an indirect method based on Born Haber cycle e.g. for a binary compound MX.



Where

S – Sublimation energy

BDE: Bond dissociation Energy

E.A. – Electron Affinity

I.E. – Ionization energy

H_f – Heat of formation

U_L – lattice energy

By Hess's Law

$$H_f = S + B.D.E + I.E + E.A + U_L$$

$$E.A = H_f - (S + B.D.E + I.E + U_L)$$

Electron affinity of some of the atoms and ions

Cl (g) + e	→	Cl ⁻ (g)	E.A= -364 KJ Mol ⁻¹
Br (g) + e	→	Br ⁻ (g)	E.A= -342 KJ mol ⁻¹
I (g) + e	→	I ⁻ (g)	E.A= -295 KJ mol ⁻¹
O (g) + e	→	O ⁻ (g)	E.A= -142 KJ mol ⁻¹
O ⁻ (g) + e	→	O ²⁻ (g)	E.A= +971 KJ mol ⁻¹
S (g) + e	→	S ⁻ (g)	E.A= -200 KJ mol ⁻¹
S ⁻ (g) + e	→	S ²⁻ (g)	E.A= +650 KJ mol ⁻¹

Note:

The more exothermic (more negative) the electron affinity, the more stable is the anion formed. Therefore, among the halogens above Cl⁻ is the most stable ion while I⁻ is the stable.

Formation of divalent ion is endothermic which shows that a univalent ion is more stable than a divalent one

FACTORS AFFECTING AFFINITY

Atomic radius

The smaller the atomic radius the more strongly attracted is the electron and the greater the electron affinity. For larger atomic radius nuclear attraction for

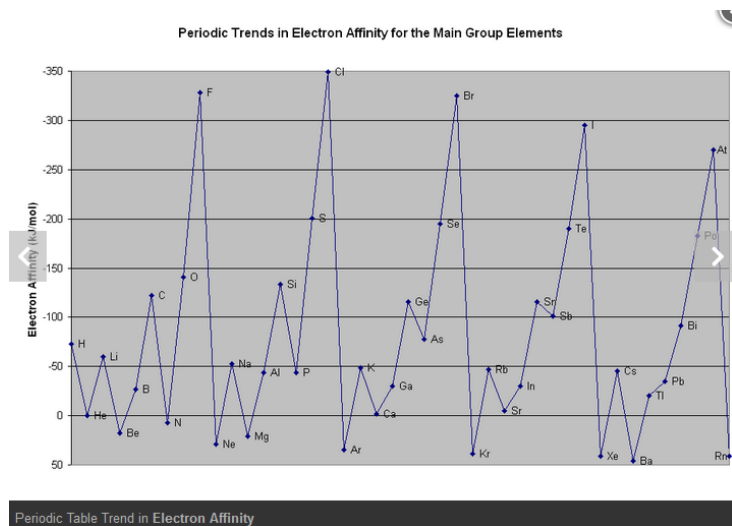
incoming electron is low leading to small electron affinity.

Nuclear charge

The greater the nuclear charge the more strongly is the incoming electron attracted, and the greater the electron affinity. The smaller the nuclear charge the less strongly is the electron added attracted and the lower the electron affinity.

Screening effect

The greater the screening effect the less strongly is the electron added attracted and the lower the electron affinity. The smaller the screening, the more strongly attracted is the incoming electron and the greater the electron affinity.



Variation of electron affinity across a period

Period 3

	Na	Mg	Al	Si	P	S	Cl
Electron affinity/ KJ mol ⁻¹	-20	+67	-30	-135	-60	-200	-364

Trend: Generally, Electron affinities across a period increase.

Explanation Effective nuclear charge increases across a period so that the nuclear attraction for the incoming electron increases.

The electron affinity of Mg is more positive than expected because in Mg, the electron is being added to full ($1s^2 2s^2 2p^6 3s^2$) sub-energy level which is **thermodynamically stable** and **resist** the addition hence energy should be put into effect it.

Similarly, the electron affinity of P is less negative than expected because in P, the electron is being added to a half full 3p sub-energy level which is also stable and resists the addition hence less energy is released, i.e. $P-1s^2 2s^2 2p^6 3p^3$

Variation of Electron affinity down a group

Group VII

Elements	Electron affinity KJmol ⁻¹
F	-323
Cl	-364
Br	-324
I	-295

Trend: Electron affinity generally decreases down the group.

EXPLANATION:

Down the group because of an extra energy level of electrons added, the increase in screening effect outweighs that of the nuclear charge so that effective nuclear charge decreases. There is therefore decrease ability attract electrons hence, decrease in electron affinity.

ELECTRO NEGATIVITY

Electro negativity is the tendency of an atom to become negatively charged in its covalent compound.

Or

Electro negativity is the tendency of an atom to attract an electron in it's a covalent bond.

Factor that affect electro negativity

Nuclear charge

The greater the nuclear charge the more strongly are the bonding electrons attracted and the greater the electronegativity. For small nuclear charge the bonding electrons less strongly attracted and the smaller the electronegativity.

Screening effect

For low screening effect the bonding electrons have high nuclear attraction leading to high electro negativity. The greater the screening effect the less attracted are the bonding electrons and the lower the electro negativity.

Atomic radius

The smaller the atomic radius the more strongly are the bonding electrons attracted and the greater the electronegativity. For large atomic radius the bonding electrons are less attracted by the nucleus leading to low electronegativity.

Two atoms with similar tendency to attract electrons will form pure covalent bond in homo nuclear molecules for example O_2 Cl_2 .

Electronegativity is obtained from the formula $\frac{I.E + E.A}{2}$. Where I.E and E.A are in $KJ\ mol^{-1}$

Variation of electronegativity across a period 3

Elements	Na	Mg	Al	Si	P	S	Cl
Electron egativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Trend: Electronegativity increases across a period.

Explanation: In moving from left to right across a period, from one element to the next, the nuclear charge increases by one unit and an electron is added to the outer shell. As the nuclear charge increases across, the atoms have an increasing electron attracting power and therefore an increase in electronegativity

Variation of electronegativity down the group VII

Electronegativity/ $KJmol^{-1}$	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5

Trend: Electronegativity decreases down a group.

Explanation: Down the group as a result of an extra shell of electrons added, the increase in screening effect outweighs that of the nuclear charge. Therefore, effective nuclear charge decreases and hence the atoms develop a decreasing power to attract electrons.

What happens if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B.



If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found *on average* half way between the two atoms. To get a bond like this, A and B would usually have to be the same atom. Such bonds are in, H_2 or Cl_2 molecules. This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms

What happens if B is slightly more electronegative than A?

B will attract the electron pair rather more than A does.



That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so $\delta+$ means "slightly positive".

Polar bonds

A polar bond is a *covalent bond* in which there is a *separation of charge between one end and the other*. i.e. one end is slightly positive and the other slightly negative. Examples include most covalent bonds. HCl , H_2O , H_2S

What happens if B is a lot more electronegative than A?

In this case, the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed.

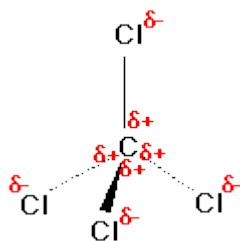
In Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Polar bonds and polar molecules

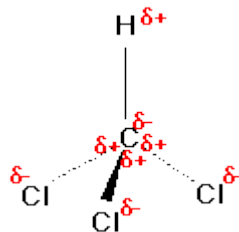
In a simple molecule like HCl, if the bond is polar, so also is the whole molecule. In CCl₄, each bond is polar.

The molecule as a whole, however, isn't polar because it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.



By contrast, CHCl_3 *is* polar.

The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.



A polar molecule will need to be "lop-sided" in some way.

Diagonal relationships in the Periodic Table

What is a diagonal

What is a diagonal relationship?

relationship?

This is a case where an element at the top of one group has some similarities with an element in the next group.

For example, boron and silicon. Unlike the rest of Group 2, beryllium and aluminium, lithium and magnesium.

There are several reasons for this, but each depends on the way atomic properties like electronegativity vary around the Periodic Table.

Explaining the diagonal relationship with regard to electronegativity

Electronegativity increases across the Periodic Table. i.e., the electronegativities of beryllium and boron are: Be (1.5) and B (2.0)

Electronegativity falls as you go down the Periodic Table. i.e., the electronegativities of boron and aluminium are: B(2.0) and Al (1.5), So, comparing Be and Al, you find the values are (by chance) exactly the same.

The increase from Group 2 to Group 3 is offset by the fall as you go down Group 3 from boron to aluminium.

Something similar happens from lithium (1.0) to magnesium (1.2), and from boron (2.0) to silicon (1.8).

In these cases, the electronegativities aren't *exactly* the same, but are very close.

Similar electronegativities between the members of these diagonal pairs means that they are likely to form similar types of bonds, and that will affect their chemistry.

The polarizing ability of positive ions

What do we mean by "polarizing ability"?

Solid aluminium chloride is covalent. Imagine instead that it was ionic. It would contain Al^{3+} and Cl^- ions.

The aluminium ion is *very small* and is *packed* with three positive charges (charge density) is therefore very high. That will have a considerable effect on any nearby electrons.

We say that the aluminium ions polarize the chloride ions.

In the case of aluminium chloride, the electron pairs are dragged back towards the aluminium to such an extent that the bonds become covalent. But because the chlorine is more electronegative than aluminium, the electron pairs won't be pulled half way between the two atoms, and so the bond formed will be polar.

Factors affecting polarizing ability

Positive ions can have the effect of polarizing (electrically distorting) nearby negative ions. The polarizing ability depends on the charge density in the positive ion.

Polarizing ability increases as the positive ion gets smaller and the number of charges gets larger.

As a negative ion gets bigger, it becomes easier to polarize. For example, in an iodide ion, I^- , the outer electrons are in the 5-level - relatively distant from the nucleus.

A positive ion would be more effective in attracting a pair of electrons from an iodide ion than the corresponding electrons in, say, a fluoride ion where they are much closer to the nucleus.

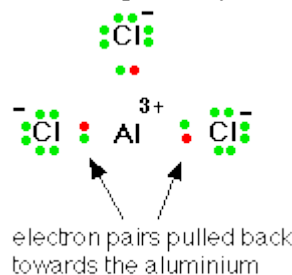
Aluminium iodide is covalent because the electron pair is easily dragged away from the iodide ion. On the other hand, aluminium fluoride is ionic because the aluminium ion can't polarize the small fluoride ion sufficiently to form a covalent bond.

ELECTROPOSITIVITY

Electro positivity is the tendency of an atom to become positively charged in its metallic compound.

Or

Electro positivity is the tendency of an atom to lose an electron in it's a covalent bond.



Factor that affect electro positivity

Nuclear charge

The greater the nuclear charge the more strongly are the bonding electrons attracted towards the nucleus and the lower the electro positivity because it is difficult for an atom to lose bonding electrons. For small nuclear charge the bonding electrons less strongly attracted and the greater the electro positivity.

Screening effect

For low screening effect, the bonding electrons have high nuclear attraction leading to the less ability to lose electrons. The greater the screening effect the less attracted are the bonding electrons and the higher the electro positivity.

Atomic radius

The smaller the atomic radiuses the more strongly are the bonding electrons attracted and the lower the electro positivity. For large atomic radius, the bonding electrons are less attracted by the nucleus due to the high screening effect thus leading to higher electro positivity.

Two atoms with similar tendency to lose electrons will form pure metallic bond in homo nuclear molecules for example Na , Al .

Two atoms with large difference in their electro positivity's develop some ionic bond character.

Ionic charge

For anions, as the ionic charge increases there is an increases in the screening effect that increases the tendency of the ion to lose bonding electrons, for cations, as the ionic size increases, there is a decrease in the ionic size due to the increase in the nuclear attraction.

Variation of electro positivity across a period 3

Trend: Electro positivity decreases across a period.

Explanation: In moving from left to right across a period, from one element to the next, the nuclear charge increases by one unit and an electron is added to the outer same shell. As the nuclear charge increases across, the atoms have a decreasing electron losing power and therefore a decrease in electro positivity

Variation of electro positivity down the group VII

Trend: Electro positivity increases down a group.

Explanation: Down the group as a result of an extra shell of electrons added, the increase in screening effect outweighs that of the nuclear charge, electrons are loosely attracted towards the nucleus and hence the atoms develop an increasing power to lose electrons.

ATOMIC STRUCTURE, ORBITS AND ENERGY

LEVELS

Orbitals is regions of space that electrons inhabit. The orbitals have levels of existence known as energy levels. Each orbital has a name that is;

The **S** (shape) orbital: it tells us about the shape of the orbital. **s** orbitals are spherically symmetric around the nucleus.

P (principle) orbital: This is arbitrarily divided into P_x , P_y and P_z . where x, y or z is the direction change as the atom tumbles in space.

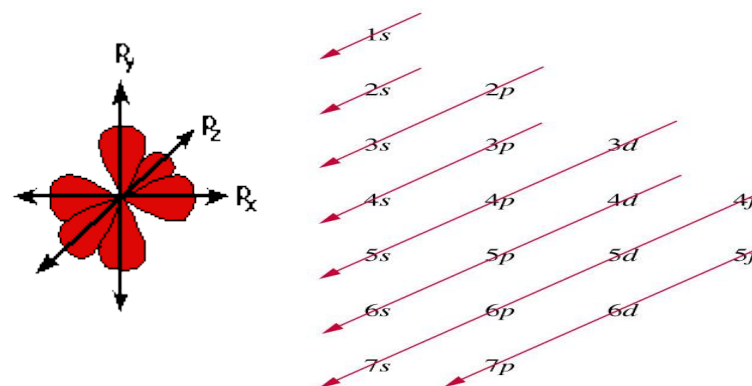
d (diffuse), and **f** (fine or fundamental) orbitals which are at a high energy level than the s and p.

Electron Energy Levels

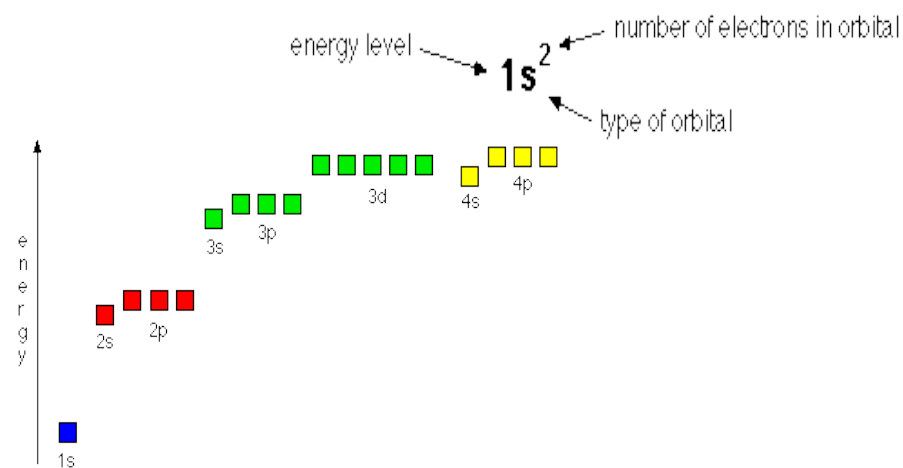
The electrons in an atom are located at specified distances from the nucleus and are found to have different amounts of energy. The maximum number of electrons that can occupy a specific energy level can be calculated by using the formula $2n^2$, where **n** is the number of the principal energy level.

Principal energy levels are broken down into sublevels. Theoretically there are an infinite number principal energy levels and sublevels.

The Principal Energy Level only holds a given number of sublevels/orbitals.



Principal Energy Level	number of Sublevels	Sublevels/orbitals
1	1	1s
2	2	2s 2p
3	3	3s 3p 3d
4	4	4s 4p 4d 4f
5	5	5s 5p 5d 5f 5g



sublevel	number of electrons in each sublevel
s	2
p	6
d	10
f	14
g	18



Order of Filling of Electron States

The electrons will take the lowest energy consistent with the Pauli Exclusion Principle. Each orbital can only hold 2 electrons.

Hund's Rule: states that when electrons fill orbitals within a sublevel, each orbital is occupied by a single electron before any orbital has two electrons, and all electrons in singly occupied orbitals have the same direction of spin.

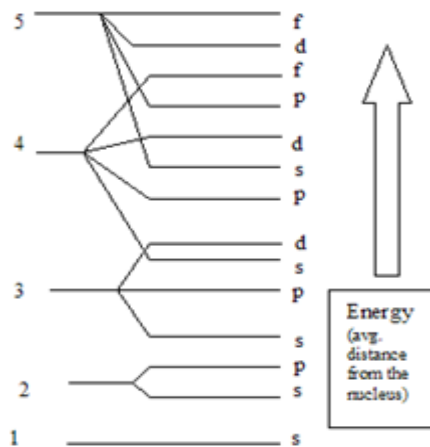
NOTE-Some Principal Energy Levels start to fill before previous ones finish. That is, the 4s fills before 3d, because 4s has less energy than 3d. It must fill first.

Electrons fill the sublevels in energy order 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

If we add the number of electrons that each sublevel holds it looks like this:
 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^6$

The diagram really shows the overlap of the Principal Energy Levels

K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$



Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

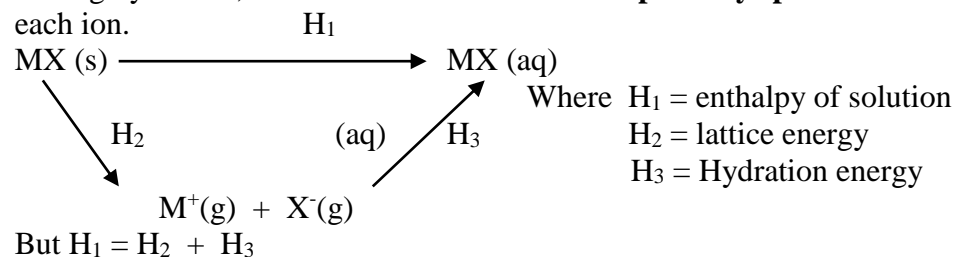
SOLUBILITY OF IONIC SALTS

Ionic salts are formed by electrostatic forces of attraction (electrovalent bond). They have polar bonds which make the compound polar thus they are soluble in polar solvents. Their solubility involves;

Break down of the ionic bond (crystal lattice) into free gaseous ions this involves lattice energy as shown below in the Born *Harbor* cycle.

The free gaseous ions are then hydrated by the solvent that is the solvent surrounds the ion making it aqueous. This involves hydration energy.

During hydration, the solvent molecules make a **primary sphere** around each ion.



For the system to be stable, energy must be released that is H_1 is **more negative** and thus the **more soluble** a compound is.

Lattice energy is **positive** because energy is needed to break bonds, hydration energy is **negative** because energy is given out when bonds are forming. Hence we need a high hydration energy than lattice energy for a compound to be more soluble than another.

Factors that determine solubility of a compound

Ionic radius

Small ions have a high charge density and more polar thus they **provide less surface area** for the attraction of the solvents in the primary sphere which determines the hydration energy but have more power to attract more solvent molecules in the secondary sphere.

Big ions provide enough surface area for the formation of more solvent bonds in a primary sphere, the solvent bonds formed in the primary sphere are the one responsible for hydration energy. Therefore the bigger the ionic radius, the greater the hydration energy and the more soluble the compound become.

NOTE:

Down the group in a periodic table, solubility increases and across the period, solubility decreases. Or down the group, hydration energy increases as lattice energy decreases.

CHAPTER 2

GROUP I ELEMENTS

Discusses trends in atomic radius, ionization energy, electronegativity, melting and boiling points of the Group 1 elements.

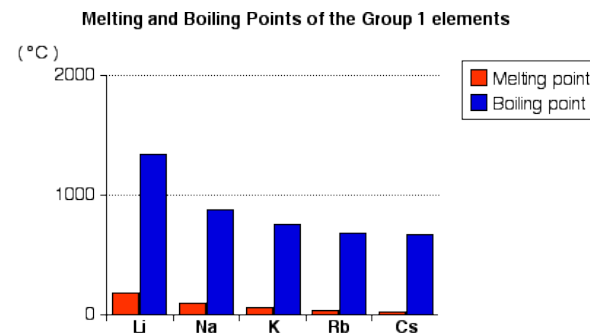
Trends in Melting and Boiling Points

Both the melting points and boiling points fall as you go down the Group.

Explaining

When you melt any of these metals, the metallic bond is weakened enough for the atoms to move around, and is then broken completely when you boil the metal.

The fall in melting and boiling points reflects the fall in the strength of the metallic bond.



The atoms in a metal are held together by the attraction of the nuclei to the delocalized electrons. As the atoms get bigger, the nuclei get further away from these delocalized electrons, and so the attractions fall. That means that the atoms are more easily pulled apart to make a liquid and finally a gas.

Each of these atoms has a net pull from the nuclei of $1+$. The increased charge on the nucleus as you go down the Group is offset by additional levels of screening electrons.

There are many factors that influence melting and boiling points, they include;

Intermolecular forces are the interactions *between* rather than *inside* molecules.

In pure substances, there are 3 important intermolecular forces which may be present:

□ **Dipole – dipole forces.** The dipole moment in a molecule will tend to align with those in its neighbors. This type of interaction is only possible if the molecule possesses a dipole.

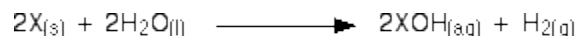
□ **Hydrogen bonds.** This is a particularly strong dipole – dipole interaction involving the interaction between the δ^+ H atoms in very polar bonds and lone pairs on very electronegative atoms. Hydrogen bonding therefore requires the presence of both δ^+ H atoms *and* electronegative atoms.

□ *Dispersion forces*. These forces are present in *all* molecules and atoms. At any moment in time, the electron density in a molecule or atom may not be symmetrical and this leads to a dipole moment. This momentary or *instantaneous* dipole moment *induces* a matching dipoles in neighboring molecules or atoms by polarizing their electron density.

Dispersion forces increase with the number of electrons in a molecule.

REACTIONS OF THE GROUP 1 ELEMENTS WITH WATER

All of these metals react vigorously or even explosively with cold water. In each case, a solution of the metal hydroxide is produced together with hydrogen gas.



Lithium floats on the surface, gently fizzing and giving off hydrogen and a colourless solution of lithium hydroxide. The reaction generates heat too slowly and lithium's melting point is too high for it to melt

Sodium

Sodium also floats on the surface, but enough heat is given off to melt the sodium. it melts almost at once to form a small silvery ball that dashes around the surface. A white trail of sodium hydroxide is seen in the water under the sodium, but this soon dissolves to give a colourless solution of sodium hydroxide. The sodium moves because it is pushed around by the hydrogen which is given off during the reaction.

Potassium

Potassium behaves rather like sodium except that the reaction is faster and enough heat is given off to set light to the hydrogen. This time the normal hydrogen flame is contaminated by potassium compounds and so is colored lilac (a faintly bluish pink).

Rubidium

Rubidium is denser than water and so sinks. It reacts violently and immediately, with everything spitting out of the container again. Rubidium hydroxide solution and hydrogen are formed.

Caesium

Caesium explodes on contact with water, quite possibly shattering the container. Caesium hydroxide and hydrogen are formed

In summary, The Group 1 metals become more reactive towards water as you go down the Group.

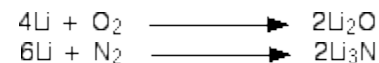
Explanation

Looking at the enthalpy changes for the reactions

The reactions become easier as the energy needed to form positive ions falls (ionization energy). This is in part due to a decrease in ionization energy as you go down the Group, and in part to a fall in atomization energy reflecting weaker metallic bonds as you go from lithium to Caesium. This leads to lower activation energies, and therefore faster reactions.

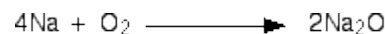
REACTIONS OF THE GROUP 1 ELEMENTS WITH Oxygen AND Chlorine

Lithium

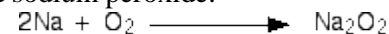


Lithium burns with a strongly red-tinged flame if heated in air. It reacts with oxygen in the air to give white lithium oxide. With pure oxygen, the flame would simply be more intense. diagonally it also reacts with the nitrogen in the air to give lithium nitride. Lithium is the only element in this Group to form a nitride in this way.

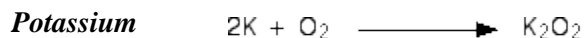
Sodium



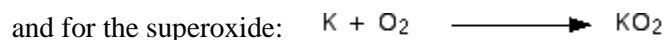
Small pieces of sodium burn in air with an orange glow forming a white solid mixture of sodium oxide and sodium peroxide.



The peroxide equation is:



Small pieces of potassium heated in air tend to just melt and turn instantly into a mixture of potassium peroxide and potassium superoxide without any flame being seen. Larger pieces of potassium burn with a lilac flame.

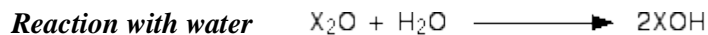


Rubidium and Caesium

Both metals catch fire in air and produce superoxides, RbO_2 and CsO_2 . The equations are the same as the equivalent potassium one.

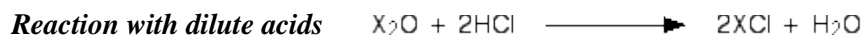
REACTIONS OF THE OXIDES

The simple oxides, X_2O



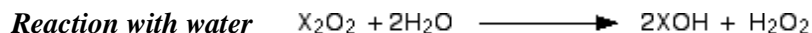
These are simple basic oxides, reacting with water to give the metal hydroxide.

For example, lithium oxide reacts with water to give a colourless solution of lithium hydroxide.



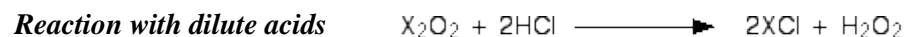
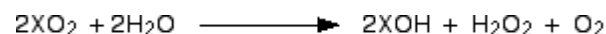
These simple oxides all react with an acid to give a salt and water. For example, sodium oxide will react with dilute hydrochloric acid to give colourless sodium chloride solution and water.

The peroxides, X_2O_2



If the reaction is done in ice, a solution of the metal hydroxide and hydrogen peroxide is formed.

If the temperature is high, the hydrogen peroxide produced decomposes into water and oxygen. The reaction can be very violent



A solution containing a salt and hydrogen peroxide is formed. The hydrogen peroxide will decompose to give water and oxygen if the temperature rises

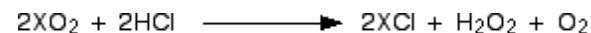
The superoxides, XO_2

Reaction with water

A solution of the metal hydroxide and hydrogen peroxide is formed, but oxygen gas is given off as well.

Reaction with dilute acids

A solution containing a salt and hydrogen peroxide is formed together with oxygen gas. The hydrogen peroxide will again decompose to give water and oxygen as the temperature rises.

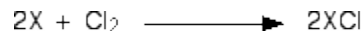


NOTE; if temperatures rise, hydrogen peroxide decomposes into water and oxygen.

The Reactions of the elements with Chlorine

Sodium, burns with an intense orange flame in chlorine in exactly the same way that it does in pure oxygen. The rest also behave the same in both gases.

In each case, there is a white solid residue which is the simple chloride, XCl.



Test for group I elements

CHAPTER 3

GROUP II A ELEMENTS (ALKALINE EARTH METALS)

Objectives

Discuss trends in atomic radius, ionization energy, electronegativity and melting point of the Group 2 elements.

	E.C ns ²	st 1 I.E /KJ mol ⁻¹	S.E.P	Ionic radius / ⁰ A	M. point / ⁰ C	Hydration energy /KJmol ⁻¹
Be		899	-1.70	0.31	1278	-498
Mg		738	-2.30	0.65	649	-393
Ca		589	-2.87	0.97	839	-310
Sr		549	-2.89	1.13	769	-284
Ba		502	-2.90	1.35	729	-251

General properties:

? The elements of group II are metallic and are similar in properties to those of group I. They have, however, less electropositive than group (I) elements. The elements are good reducing agent.

? The elements are similar in properties but Be show significant difference in its properties with the rest of the group members. This is because of its small size giving it the highest polarizing power. Because of this, compounds of Beryllium are essentially covalent. The other members form ionic compounds.

? All the members have two electrons in their outer shell and in chemical reaction these two electrons are transferred giving dispositive mental ion forming stable electronic structure of noble gases.

? Group II elements have higher melting and boiling points than group I A

member which contribute only one.(Among metals, the greater the number of electrons contributed to the charge cloud, the stronger the metallic bond and the greater the melting point).

? Melting point of group II elements generally decrease down the group. This is because, as the atomic radius increase down the group, the bonding electrons become spread further away from the nucleus and this reduces the forces of attraction between the bonding electron and nucleus.

? As atomic number increases more shells of electrons are added and so ionization energy decreases and hence standard electrode potential becomes more negative down the group.

Qn. Explain why Beryllium compounds are covalent yet others compounds in group two are ionic.

Give reasons why beryllium shows different chemical properties from its members.

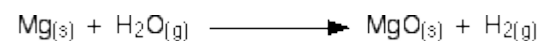
REACTIONS OF GROUP (II) ELEMENTS

With Water

Beryllium

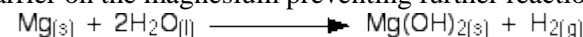
Beryllium has no reaction with water or steam even at red heat.

Magnesium



Magnesium burns in steam to produce **white** magnesium oxide and hydrogen gas.

Very **clean magnesium** ribbon has a **very slight** reaction with cold water. After **several** minutes, some bubbles of hydrogen form on its surface, and the coil of magnesium ribbon usually floats to the surface. However, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and forms a barrier on the magnesium preventing further reaction.



Calcium, strontium and barium



These all react with cold water with increasing vigor to give the metal hydroxide and hydrogen.

Calcium, reacts fairly vigorously with cold water in an exothermic reaction. Bubbles of hydrogen gas are given off, and a white precipitate of calcium hydroxide is formed,

The hydroxides aren't very soluble, but they get more soluble as you go down the Group. The calcium hydroxide formed shows up mainly as a white precipitate (although some does dissolve).

In summary, The Group 2 metals become more reactive towards water as you go down the Group.

Explanation (enthalpy change of solution, ionization and activation energy)

Beryllium as a special case

Beryllium *has a strong resistant* layer of *oxide* on its surface which lowers its reactivity turning it out to be very unreactive.

The enthalpy change of a reaction is a measure of the amount of heat absorbed or evolved when the reaction takes place. An enthalpy change is negative if heat is evolved, and positive if it is absorbed.

The activation energy for a reaction is the minimum amount of energy which is needed in order for the reaction to take place. It doesn't matter how exothermic the reaction would be once it got started - if there is a high activation energy barrier, the reaction will take place very slowly.

When Group 2 metals react to form oxides or hydroxides, metal ions are formed, the formation of the ions from the original metal involves various stages all of which require the input of energy - contributing to the activation energy of the reaction. These stages involve the input of:

- The atomization energy of the metal. This is the energy needed to break the bonds holding the atoms together in the metallic lattice.
- The first + second ionization energies. These are necessary to convert the metal atoms into ions with a 2+ charge.

After this, there will be a number of steps which give out heat again - leading to the formation of the products, and overall exothermic reactions

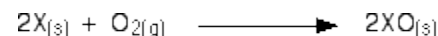
In summary, the reactions become easier as the energy needed to form positive ions falls. This is mainly due to a decrease in ionization energy as you go down the Group. This leads to lower activation energies, and therefore faster reactions.

Reactions with oxygen

Formation of simple oxides

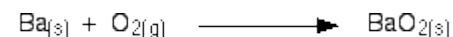
The metals burn in oxygen to form a simple metal oxide.

Beryllium is reluctant to burn unless it is in the form of dust or powder. Beryllium has a very strong layer of beryllium oxide on its surface, and this prevents any new oxygen getting at the underlying beryllium to react with it.



- *Beryllium* burns with silvery sparkles
- *Magnesium*, calcium, strontium and barium burns with a typical intense white flame

Formation of peroxides



Strontium and barium will also react with oxygen to form strontium or barium peroxide.

Strontium forms this if it is heated in oxygen under high pressures, but barium forms barium peroxide just on normal heating in oxygen. Mixtures of barium oxide and barium peroxide will be produced. The strontium equation would look just the same.

The reactions with air



Group 2 metals with air rather than oxygen with nitrogen to produce nitrides. In each case, a mixture of the metal oxide and the metal nitride.

White ash as a mixture of magnesium oxide and magnesium nitride is formed.

REACTIONS OF THE GROUP 2 ELEMENTS WITH COMMON ACIDS

Reactions with *dilute* hydrochloric acid

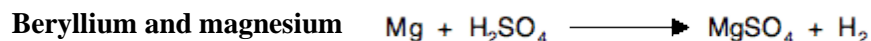
All the metals react with dilute hydrochloric acid to give bubbles of hydrogen and a colourless solution of the metal chloride.



The reactions get more vigorous as you go down the Group.

Reactions with *dilute* sulphuric acid

They form insoluble sulphates.



Bubbles of hydrogen are formed, together with colourless solutions of beryllium or magnesium sulphate.

Calcium, strontium and barium

Calcium sulphate is sparingly soluble, strontium and barium sulphates are insoluble. They form a layer of insoluble sulphate on all of these which will slow down the reaction or stop it entirely. For, calcium, some hydrogen is produced together with a white precipitate of calcium sulphate.

Reactions with *dilute* nitric acid

Beryllium

Beryllium does not react with nitric acid. Beryllium has a strong oxide layer (rather like the more familiar aluminium) which slows reactions down until it has been removed.

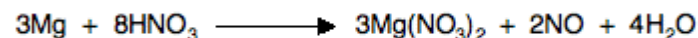
The other Group 2 metals

These will produce hydrogen from dilute nitric acid. Forming colourless solutions of the metal

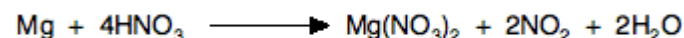
nitrate. Taking magnesium as an example, if the solution is very dilute:



At moderate concentrations nitrogen monoxide is formed, which can then readily be oxidized to nitrogen dioxide.

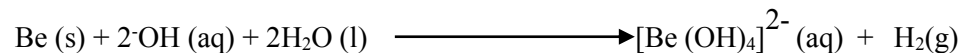


And with concentrated acid, nitrogen dioxide is formed,



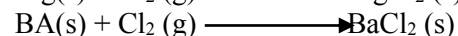
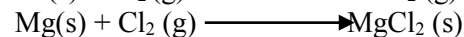
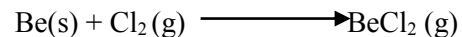
Reaction with alkalis

All the elements except beryllium do not react with alkalis. Beryllium reacts with aqueous alkalis forming complex called beryllate.



Reaction with halogens (chlorine)

All the metals react with chlorine when reacted to form dihalides.



Electro positivity of group II elements

Electro positivity is the tendency for an atom to lose its outermost electrons. Down

the group, electro positivity of the elements increases .This is because as the group is descended an extra shell of electrons is added from one element to the next. Because of this extra shell the increase in screening the increase in nuclear charge and as a result of decreased effective nuclear charge, the attraction of the nuclear for the outer electrons decreases and are thus easily lost.

The effect of increasing ionic radii of group II ion on the properties of the compound formed

The ion of group II element are more highly charged and are smaller than their corresponding ions of group I elements. Because of this, cations of group II elements have higher charge densities (polarizing power) **than** the ions of group I elements. And as a consequence of this;

Group II elements form compounds which are less ionic in character than those of group I elements

Group II elements have higher melting and boiling point than their corresponding elements in group I.

The lattice energies of group II compounds are higher than those of group I and because of this group II compounds are less soluble in water than group I compounds.

The compounds of group II are less stable to heat than group I compounds whereas carbonates of group II can be decomposed, those of group I are not.

Because of high polarizing power, group II cations form more stable complexes than cations of group I.

The metals of group II form ions less easily than those of group I

Because of the stability associated with full S orbital, group II elements have higher first ionization energies.

All elements of group (II) have a characteristic oxidation state of +2. This combined with their small size gives very high polarizing power and consequently their cations cause greater polarizing of the accompanying anions. Their compounds therefore, tend to be less ionic in nature than those of group (I) with smaller polarizing power.

Group (I)		Group (II)	
Li ⁺	0.060nm	Be ²⁺	0.031
Na ⁺	0.095nm	Mg ²⁺	0.062
K ⁺	0.133nm	Ca ²⁺	0.099

The enthalpies of hydration of group (II) ions are very much greater than those of group (I) ions

	Hydration		Hydration
Na ⁺	406 KJ mol ⁻¹	Mg ²⁺	1920 KJ mol ⁻¹
K ⁺	322 KJmol ⁻¹	Ca ²⁺	1650 KJ mol ⁻¹
Rb ⁺	301 KJmol ⁻¹	Sr ²⁺	1480 KJ mol ⁻¹

The lattice energies of salts of group (II) elements are so much greater than those of the salts of group (I) element. Therefore, generally, the alkaline earth metals are less soluble than the corresponding alkali salt.

NOTE:

In many respect, Li is a typical group (I) element which shows similarities with magnesium a typical group (II) element.

Similarly, **Be** a typical group (II) element resembles Al which is a group (II) element.

The similarities in properties between Li and Mg and between **Be** and **Al** is because both **Li** and **Mg** have similar polarizing power and **Be** and **Al** also have similar polarizing power'

DIAGONAL RELATIONSHIP

A relationship within the periodic table by which certain elements in the *second period* have a *close chemical similarity* to their diagonal neighbours in the *next group of the third period*. This is particularly noticeable with the following pairs.

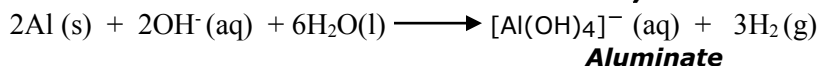
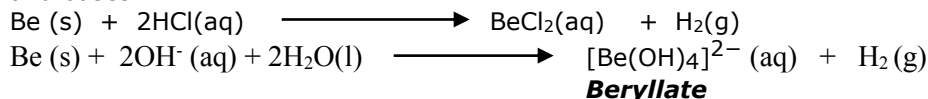
Lithium and magnesium:

- (1) Both form chlorides and bromides that hydrolyze slowly and are soluble in ethanol;
- (2) Both form colourless or slightly coloured crystalline nitrides by direct reaction with nitrogen at high temperatures; $6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$
- (3) Both burn in air to give the normal oxide only;
 $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
- (4) Both form carbonates that decompose on heating.
 $Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$
- (5) They burn in air to form normal oxides that dissolve in water to form hydroxides
 $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
 $MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(s)$

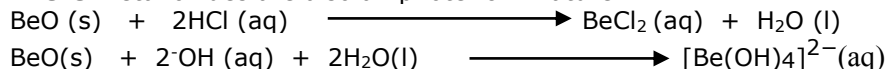
Beryllium and aluminium:

Both form highly *refractory oxides with polymorphs*;

both the metal elements are *amphoteric* that is they both react with acids and bases



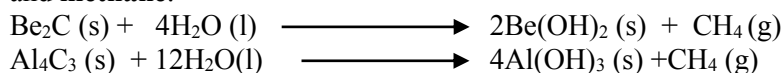
There metal oxides are also amphoteric in nature



Both form covalent halides and covalent alkyl compounds that display bridging structures;

Be like Al is rendered inactive by concentrated nitric acid that is do not react with nitric acid.

Both elements react with carbon forming **carbides** that hydrolyze into **hydroxide** and **methane**.



Boron and silicon:

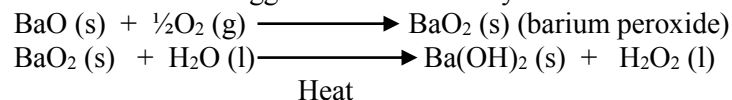
(1) both display semiconductor properties;

(2) both form hydrides that are unstable in air and chlorides that hydrolyze in moist air.

(3) Both form acidic oxides with covalent crystal structures, which are readily incorporated along with other oxides into a wide range of glassy materials.

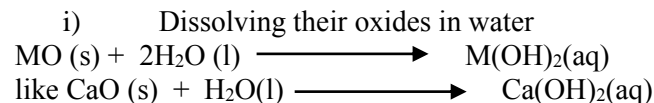
NOTE:

Group (II) elements form few peroxides because their ions are too small to form a stable lattice. However, Sr and Ba like group (I) elements form peroxide because their ions are bigger to form stable crystal lattice.

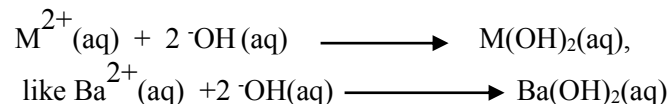


GROUP II HYDROXIDES

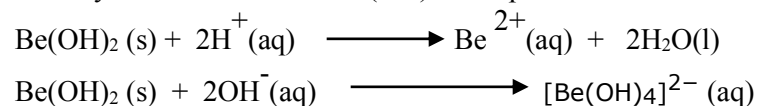
They are prepared by:



ii) Addition of aqueous sodium hydroxide (NaOH) or ammonia (NH₃) to a soluble salt of the ion.



All other hydroxides are basic. Be(OH)₂ is amphoteric.



SOLUBILITY OF GROUP II ELEMENTS (hydroxides and nitrates)

Group II elements generally form ionic salts whose solubility depend on two energy terms that is lattice energy and hydration energy.

The elements of group II form doubly charge cations (M²⁺) with smaller ionic radii than the corresponding group (I) cations

The lattice energies of group II cations however, increases much more than the hydration energies. Because of this the lattice energies of group (II) cations cannot be easily overcome by their hydration energies.

The *lattice energies of group I cations* are low are easily overcome by their hydration energy hence group II salts are less soluble.

	Lattice energy	Hydration energy	Enthalpy of solution
MgF ₂	+2908	-1910	+998
NaF	+918	-393	+525

Because of less endothermic enthalpy of solution, Solubility of group (II) hydroxide solubility in g/100g of water at 25°C

Mg(OH) ₂	0.01,	Sr(OH) ₂	0.89
Ca(OH) ₂	0.15	Ba(OH) ₂	3.32

Trend: Solubility increases down the group.

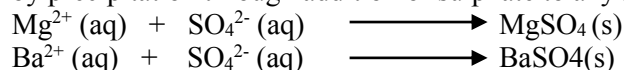
Explanation:

This is because lattice energy decrease more rapidly than hydration energy.

Note The solubility of the nitrate of group (II) is similar to that of their Hydroxide.

GROUP II SULPHATES:

Sulphates of group II elements are insoluble in water, therefore they are prepared by precipitation through addition of sulphate to any soluble salt



Solubility of Sulphates Solubility/100g of H₂O At 25°C

BaSO ₄	43
MgSO ₄	36
CaSO ₄	0.20
SrSO ₄	0.011
BaSO ₄	0.0024

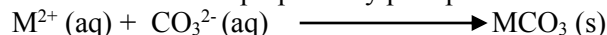
Trend: Solubility of the sulphates of group (II) elements decreases down the group.

Explanation: This is because down the group, hydration energy decrease more rapidly than lattice energy.

Note: The trend insolubility of CO₃²⁻, CrO₄²⁻ is similar to that of the sulphate.

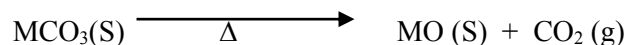
Thermal stability of carbonates

The carbonates are prepared by precipitation method.



Decomposition Temperatures of The Carbonates

Compound	BeCO ₃	MgCO ₃	CaCO ₃	SrCO ₃	BaCO ₃
Temp. °C	100	350	900	1290	1350



Explanation

The thermal stability of an ionic salt depends on;

- Size of its ion.
- Charge on the ions

The greater then, the more strongly will the ions attract and the more stable will be the salt, the smaller the ions, the greater will be their degree of approaching each other in the lattice and the more stable will be the salt.

In moving from Be²⁺ to Ba²⁺ the charge remains the same but the size of the ions increase. The charge and size of CO₃²⁻ is the same down the group, the degree of approaching each other in the lattice decreases and consequently the carbonate are expected to become less stable down the group but that is not the case.

Down as the size of the cations increases, their charge/ radius ratio (polarizing power) decreases such that the compounds become more ionic down the group and therefore, the ions will be strongly held. Therefore, decomposition temperature for the carbonates increases down the group that is to say in the order BeCO₃ < MgCO₃/SrCO₃ < BaCO₃. Hence BeCO₃ is less stable than BaCO₃.

Note

The trend is true for the nitrate

Compounds of group (II) are less stable than corresponding compounds of group (I) that is Na₂CO₃ is more stable than MgCO₃. This is because of the smaller size and high charge of Mg²⁺ compared to Na⁺. This gives Mg²⁺ greater polarizing power than Na⁺ thus MgCO₃ is less stable than Na₂CO₃ and therefore, is easily decomposed.

Decomposition is likely when a compound with small cation and large anion is converted to one with same cation but smaller (or more highly charged) anion.

Complex formation

Group (II) elements are noted for their **inability** to form complexes. Complex formation is favored by

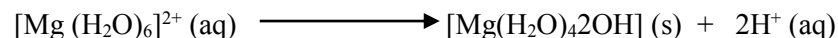
- ✓ Small and highly charged cation
- ✓ Presence of suitable empty orbital.

They therefore, form very few complexes because of the absence of empty orbitals. The tendency to form complexes decrease down the group because down the group, the ions become bigger and thus will have less attraction with lone pairs of electrons present for donation. Hence, Be forms more complexes than Barium. That is

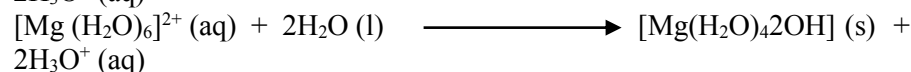
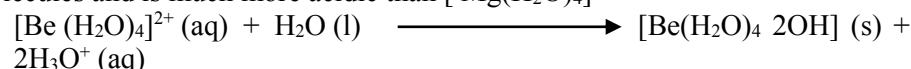
[Be (H₂O)₄]²⁺, [Mg (NH₃)₆]²⁺. Complex formation is favored by a small and highly charged cation.

HYDROLYSIS OF GROUP (II) SALTS

Soluble salts of strong acid (Cl⁻ and NO₃⁻) of Sr and Ba are neutral in solution while those of Mg and Ca are only slightly acidic.



The corresponding salts of Be are hydrolyzed and show acidic behavior. Although most Be salts are covalent, Be^{2+} in solution exists as $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and is much smaller than $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and because of its small size attracts water molecules and is much more acidic than $[\text{Mg}(\text{H}_2\text{O})_4]^{2+}$

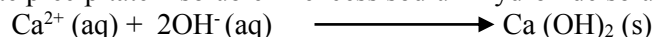


The degree of Hydrolysis decreases down the group because of the decreasing polarizing powers of the cations as the ionic radii increase.

2. Analysis of Calcium Ions in Solution

Sodium hydroxide solution.

A white precipitate insoluble in excess sodium hydroxide solution



Ammonia solution.

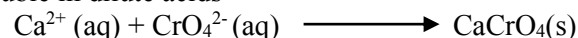
No reaction occurs that is no observable change occurs. This is because the concentration of OH^- from the weak base NH_4OH is insufficient to for the K_{sp} value of $\text{Ca}(\text{OH})_2$ to be reached,

Disodium hydrogen phosphate solution

A white precipitate is soluble in dilute acids.

Potassium chromate (IV) solution.

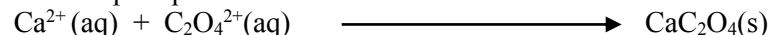
Yellow precipitate formed from concentrated solution only. This precipitate is soluble in dilute acids



Note. No precipitate is formed with dilute solution of Ca^{2+}

Ammonium ethanoate (oxalate) solution.

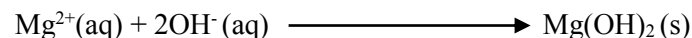
A white precipitate insoluble in ethanoic acid but soluble in mineral acids



2. Analysis of magnesium ion is solution

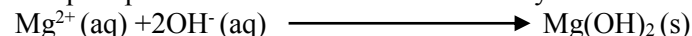
Sodium hydroxide solution

White precipitate insoluble in excess sodium hydroxide solution.



Ammonia solution

A white precipitate insoluble in excess sodium hydroxide solution.



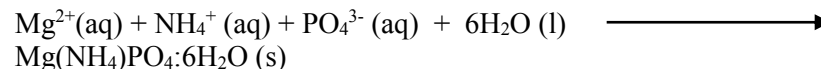
Note .The precipitate is not formed in the presence ammonia chloride because of common effect.

Ammonium ethanoate (oxalate) solution

A white precipitate formed in only in the presence of ethanoic acid.

Disodium hydrogen phosphate solution

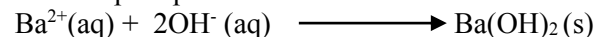
A white precipitate formed in the presence of ammonia solution together with ammonium chloride.



3. Analysis of barium ions in solution.

Sodium Hydroxide solution.

A white precipitate formed from concentrated solution only



Ammonia solution

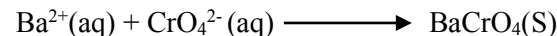
No reaction occurs i.e. No observable change occurs.

NOTE:

No precipitation occurs because the concentration of hydroxyl ions from the weak base (NH_4OH) is insufficient for the K_{sp} value of $\text{Ba}(\text{OH})_2$ to be reached.

Ammonium ethanoate (Oxalate) solution

White precipitate solution in ethanoic acid and mineral acids (Distinction from Ca^{2+})



Disodium hydrogen phosphate solution

A white precipitate insoluble in acids

Note: Ca^{2+} , Mg^{2+} and Ba^{2+} all form insoluble carbonate with sodium or ammonium carbonate solution.

Quantitative Analysis of Ca^{2+}

This is done by precipitating Ca^{2+} as calcium ethanoate (oxalate) by adding a solution of ammonium ethanoate to a solution of Ca^{2+}

The precipitate is then filtered and dissolved in excess dilute sulphuric acid to form ethanoic acid. The acid is then heated to 70°C and then titrated with standard potassium permanganate.

CHAPTER 3

Group IV elements

Element	Electronic configuration	Atomic radius	M. Point ($^\circ\text{C}$)	B. Point ($^\circ\text{C}$)
C	$1s^2 2s^2 2p^2$	0.77		3850 (sublimes)
Si	$2s^2 2p^6 3s^2 3p^2$	1.77	1410	2680
Ge	$3s^2 3p^6 3d^{10} 4s^2 4p^2$	1.22	937	2890
Sn	$4s^2 4p^6 4d^{10} 5s^2 5p^2$	1.41	232	2687
Pb	$5s^2 5p^6 5d^{10} 6s^2 6p^2$	1.54	327	1751

GENERAL PROPERTIES

Carbon occurs naturally as graphite and diamond (allotropic). Diamond has very high refractive index and dispersing power hence useful as jewelry. Besides, it's the hardest known substance used for drilling, cutting or grinding. Graphite is a good conductor of electricity because of the presence of mobile electrons in its layers. Graphite is also used as a lubricant because the layers slide over one another.

- ? Silicon occurs as SiO_2 in sand and as silicate in rocks and clays.
- ? Silicon and germanium are useful as semi-conductors and are extracted from their oxides SiO_2 and GeO_2 respectively.
- ? Tin and lead are rather inert. Tin is used to make tin plate sheets while

lead is used for making water pipe. Lead is extracted from its ore called galena in process similar to the of zinc

METALLIC PROPERTIES

Carbon is a non-metal while silicon is metalloids, Tin and lead show typical metallic properties. Therefore, the elements become more metallic down the group.

Allotropy

Allotropy

Allotropy is the existence of an element in two or more different physical states. Both carbon and tin show allotropy. Carbon exists as graphite and diamond while tin exists as grey tin (stable below 13.2°C). White tin (stable between $13.2-161^\circ\text{C}$) and Bristle tin stable above 161°C

Valence

The group members have a characteristic covalence of 4. Due to increasing electropositivity down the group, an electrovalency of 2 becomes more pronounced down the group.

Therefore the group members exhibit two oxidation states of +2 and +4. The stability of +2 oxidation states increases the group thus Pb is a strong oxidizing agent. The increase in stability of +2 oxidation state is due to inert pair effect. Inert pair effect being the inability of the s electrons to participate in bonding i.e. $ns^2 np^2$. The +4 oxidation state decreases in stability down the group. All the 5 elements can be their group state electronic configuration $ns^2 np^2$ promoted to $ns np^3$ and thus they are able to form 4 covalent bonds with the structure of their resultant compound being tetrahedral.

Note:

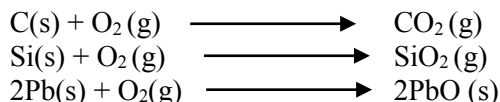
Carbon behaves differently from the rest of the group members because of its small size, high electronegativity and non-availability of d-orbital electrons. Some of the properties in which carbon differs from the rest of the group members include

- i. It is limited to a coordination number of 4 while the others can have 6.
- ii. Carbon can form multiple bonds with itself and other elements that is $\text{C}=\text{C}$, $\text{C}-\text{O}$, $\text{C}=\text{N}$
- iii. Carbon can form long chains or rings in which its atoms are bonded together in the process known as catenation.

Reactions of metalloids

a) With oxygen

They all react with oxygen on heating to form dioxides except lead which forms a monoxide.

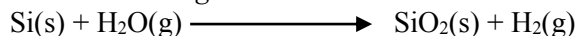


b) With Water

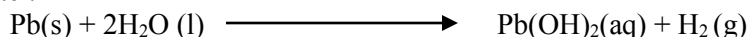
White hot cake (carbon) react with *steam* to mixture of carbon monoxide and hydrogen a mixture of water gas



Silicon react with *boiling water* or steam to form silicon (IV) oxide.



Germanium and tin do not react with water in any form. Lead reacts slowly with soft water.

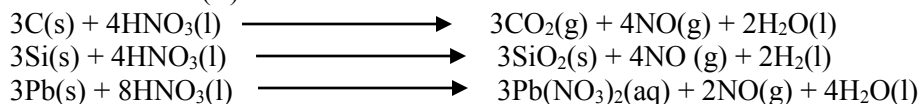


c Reaction with Acids

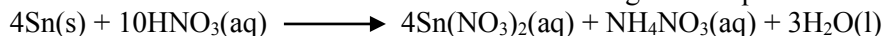
All do *not* react with dilute mineral acids except tin which reacts with dilute nitric acid.

With nitric acids:

Concentrated nitric reacts with all the elements to form monoxides except lead with forms lead (II) nitrate.

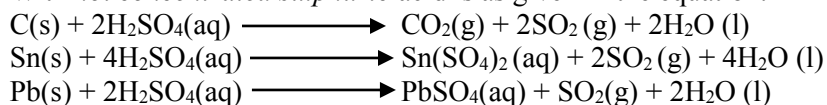


Note: Tin reacts with cold dilute nitric acid according to the equation.



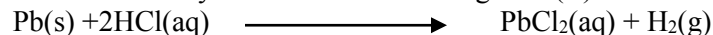
With Concentrated Sulphuric acid:

With *hot concentrated sulphuric acid* is as given in the equation.



With Hydrochloric acid:

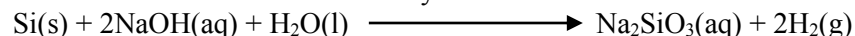
Concentrated Hydrochloric acid forming lead (II) chloride.



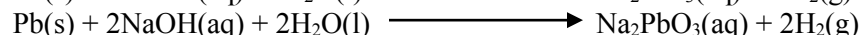
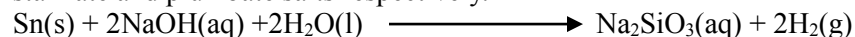
Note: Silicon does not react with any mineral acid

Reaction with alkalis: All the elements except carbon react with alkalis .

Silicon reacts with dilute sodium hydroxide solution to form sodium silicate.



Tin and lead react with hot concentrated solution of sodium hydroxide forming stannate and plumbate salts respectively.



COMPOUNDS OF GROUP (IV) ELEMENTS:

Unlike C and Si, the last three elements Ge, Sn and Pb exhibit +2 and +4 oxidation states in their compounds. The +2 oxidation state in Ge and Sn is unstable and revert to +4 state.

Electronegativity increase down the group as extra shell of electrons are added from one elements to the next down the group resulting in reduced nuclear attraction as screening effect become greater.

Lead is predominantly +2 and the +4 is very unstable reverting to +2 state.

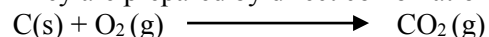
OXIDES: (MO₂ MO)

The elements form two types of oxides in both +2 and +4 oxidation states

(a) MO₂ (dioxides)

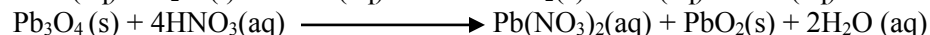
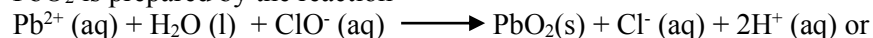
These are dioxides of C, Si, Ge and Sn.

They are prepared by direct combination on heating.



NOTE:

PbO₂ is prepared by the reaction



The boiling points of the dioxides are as

	CO ₂	SiO ₂	GeO ₂	SnO ₂	PbO ₂
B.Pt (°C)	-78	2590	1200	1900	

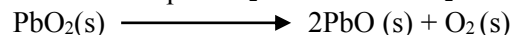
Explanation

CO₂ adopts a simple molecular structure.

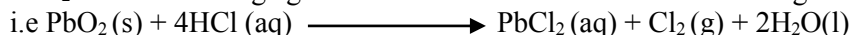
SiO₂ has a giant molecular while GeO₂.

SnO₂ and PbO₂ adopt intermediate molecular and ionic structure.

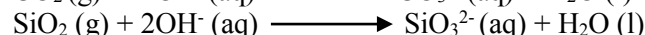
All other oxides except PbO₂ are stable. PbO₂ on heating decomposes as below,



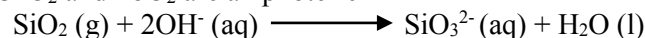
PbO₂ is an oxidizing agent which oxidizes warm HCl to chlorine gas.



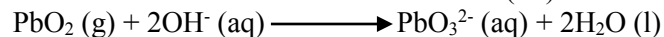
CO₂ and SiO₂ are acidic



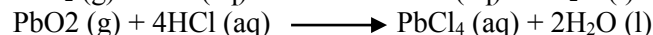
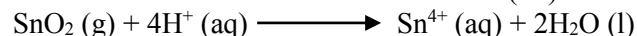
GeO₂, SnO₂ and PbO₂ are amphoteric



Stannate (IV)



Plumbate(IV)



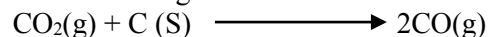
Note:

Therefore the oxides *become more basic down the group*.

(b) MO (monoxides)

Carbon monoxide is prepared by:

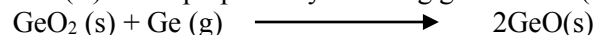
i) A reducing of Carbon dioxide with C



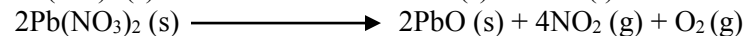
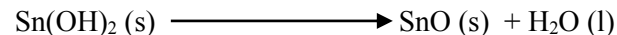
ii) Dehydrating methanoic acid with concentrated sulfuric acid.



Germanium (II) oxide prepared by reducing germanium (IV) oxide with Ge.

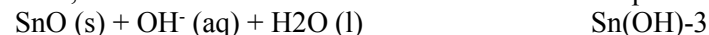


Tin (II) oxide and lead (II) oxide are prepared by action of heat on their hydroxides or nitrates.



Carbon monoxide and silicon (II) oxide have simple molecular structure and are neutral oxides

GeO, SnO and PbO have ionic structures and are amphoteric.

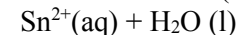
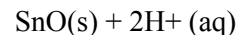


Stannate (II)



Pb(OH)-3

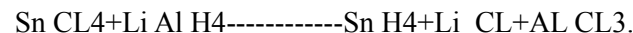
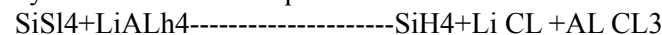
Plumbate(II)



The oxide also become more basic down the group

Hydrides

The hydrides of group (IV) elements are characterized by being covalent. They are prepared by reduction of their tetrachlorides with lithium aluminium hydride at 0°C in the presence of other



The hydrides have simple molecular structure and are tetrahedral in shape.

DIAGRAM

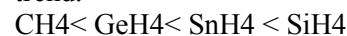
Thermal stability

Thermal stability decreases with their decomposition temperature as shown below:

CH ₄	SiH ₄	GeH ₄	SnH ₄	PbH ₄
800°C	450	285	150	0°C

The decrease in stability down the group is due to the changing character down the group with the +2 oxidation state becoming more stable.

Hydrolysis. The hydrolysis of these hydrides is base catalysed following the trend.



The trend in the hydrolysis is in accordance with their electronegativity values

C = 2.6, Si = 1.9, Ge = 2.0, Sn = 1.9

The greater the electronegativity of the element the less the hydrolysis the hydrolysis equation is as $\text{SiH}_4 + 2\text{OH}^- + \text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{H}_2$

$3+4H_2(g)$

$SnH_4+2OH^-+H_2O \rightleftharpoons SnO_2+3H_2(g)$

Halides (chlorides)

The elements form two types of halides

i) Mx_4 and (ii) MX_2

ii) Mx_4

Formed by all the elements except that PbI_4 and $PbBr_4$ do not exist due to reduction $Pb^{+4} \rightleftharpoons Pb^{+2} + 2e^-$

Preparation: $SiCl_4$, $GeCl_4$ are prepared by direct combination with chlorine.

$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$

$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(s)$

CCL_4 is prepared by action of conc. Cold HCl on PbO_2

$PbCl_4$ is unstable and revert to stable $PbCl_2$

The halides have simple molecular structure and are tetrahedral in shape

Diagram

Thermal stability

CCL_4	$SiCl_4$	$GeCl_4$	$SnCl_4$
---------	----------	----------	----------

$PbCl_4$

Boiling 76.4	57.0	86.5	115
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decomposes

Point 0°C

Decreases with the size of the elements because M-Cl bonds become longer and weaker.

CCL_4 , $SiCl_4$ and $GeCl_4$ are stable but $SnCl_4$ and $PbCl_4$ are decomposed by heat.

$PbCl_4 \rightleftharpoons PbCl_2 + Cl_2$

Hydrolysis

The halides except CCL_4 are Hydrolysed to form hydroxyl compounds and their solutions are acidic. CCL_4 is not hydrolysed because it lacks the vacant orbital needed to accommodate lone pair of electron donated by water molecules and besides, the C-Cl bond is strong.

$SnCl_4(aq) + 2H_2O \rightleftharpoons SnO_2(s) + 4HCl(g)$

The hydrolysis of $SiCl_4$ is so rapid that it even fumes in damp air

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

MX_2

Only formed by Ge, Sn and Pb and those of Ge and Sn are less stable while $PbCl_2$ is very stable.

$Pb(s) + Cl_2 \rightarrow PbCl_2(s)$

$Sn(s) + 2HCl(g) \rightleftharpoons SnCl_2(s) + H_2(g)$

$SnCl_2$ is hydrolysed becoming milky with formation of amphoteric oxide.

$PbCl_2$ is ionic and is less soluble in water but dissolves more in conc. HCl because of the formation of a soluble complex $PbCl_2+4$

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$PbCl_2(s) + 2Cl^-(aq) \rightleftharpoons PbCl_4^{2-}(aq)$

$SnCl_2$ is ionic and is less soluble in water but dissolves more in conc. HCl because of the formation of a soluble complex $PbCl_2+4$

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$PbCl_2(s) + 2Cl^-(aq) \rightleftharpoons PbCl_2^{2-}(aq) + \text{from conc. HCl}$

TEST FOR Pb^{2+}

Using NaOH (aq)

A white NaOH(aq)

A white precipitate is formed which dissolves in excess

$Pb^{2+} + 2OH^-(aq) \rightleftharpoons Pb(OH)_2(s)$

$Pb(OH)_2(s) + 2OH^-(aq) \rightleftharpoons [Pb(OH)_4]^{2-}(aq)$

Using NH_4OH

A white precipitate is formed insoluble in excess $Pb^{2+} + 2OH^-(aq) \rightleftharpoons Pb(OH)_2(s)$

$Pb(OH)_2(s)$

$Pb(OH)_2(s) + 2OH^-(aq) \rightleftharpoons [Pb(OH)_4]^{2-}(aq)$

Using $dilH_2SO_4$

A white ppt of $PbSO_4$ IS FORMED

$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s)$

Using $dil.HCl$

A white ppt of $PbCl_2$ is formed which dissolves on heating

$Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$

Using KI

A yellow ppt of PbI_2 is formed soluble in boiling water to give a colourless solution

$Pb^{2+}(aq) + 2I^-(aq) \rightleftharpoons PbI_2(s)$

Using K_2CrO_4

A yellow ppt of $PbCrO_4$ is formed

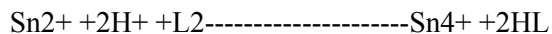
$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons PbCrO_4(s)$

Volumetric estimation of tin and lead

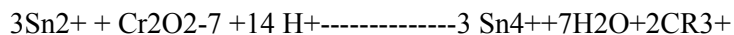
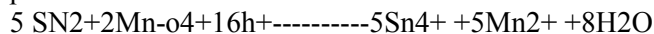
Tin alloys and compounds may be determined by

(i) Dissolving the metal in conc. HCl and the resultant solution titrated with

standard iodine solution



Dissolving solution with standard solution of potassium permanganate or potassium dichromate.



Appendix

Lead is estimated by ppt of its chromate

Procedure

To the slution of Pb^{2+} is added a buffer solution of ethanoic acid sodium ethanote, The mixture is then boiled and while boiling a fixed volume of a stsndard potassium dichromate is added. The content is cooled and the solution made to 250cm³, Then aliquate portions are then titrated with a standard solution of ammonium iron(II) sulphate to determine the amount of unreacted $\text{Cr}_2\text{O}_7^{2-}$ and hence amount which reacted with Pb^{2+}

Note In the presence of OH^- (BUFFER OF $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$), the

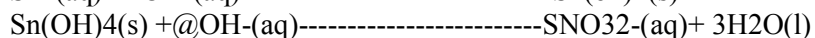
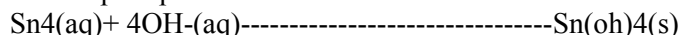
$\text{Cr}_2\text{O}_7^{2-}$ is converted to CrO_4^{2-}



ANALYSIS OF Sn^{2+}

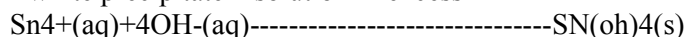
1. Using sodium hydroxide solution

A white precipitate formed which dissolves in excess



2. Using ammonia solution

A white precipitate insoluble in excess



Note; Sn^{4+} unlike Sn^{2+} gives no precipitate with mercury (II) chloride solution and also gives no colouration with ammonium molybdate solution.

Therefore one of these reagents can be used to distinguish between Sn^{2+} and Sn^{4+}

Note: the elements of group (ii) and Zinc

E.G (I) Like group (ii) elements, Zinc has also a fixed oxidation state of 2+

(ii) Both elements of group (ii) and Zinc do have complete inner shells

E.g .Mg= $1s^2 2s^2 2p^6 3s^2$

(Zn= $1s^2 2s^2 2p^6 3p^6 4s^2$)

(iii) compounds of group (ii) elements and those of zinc form colourless compound.

Zinc like beryllium dissolves in alkalis

Both BeO and ZnO are amphoteric

Both Be and Zn react with acids

Zinc however differs from group (ii) elements.

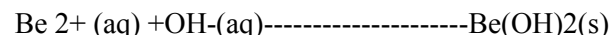
(a) Zinc ions form more complexes than group (ii) ions

(b) Zinc unlike Be reacts with dilute acids

Zinc unlike Be does not form hydride or nitrides.

Zinc unlike Be reacts with steam.

Note: Distinctive behavior of Be $^{2+}$



Chapter 4

ELEMENT			
FLUORINE	CHLORINE	BROMINE	IODINE
Atomic number	9	17	35
Electronic configuration	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6 3s^2 3p^5$	$1s^2 2s^2 2p^6 3s^2 3p^5 4p^5$
Atomic radius A ₀	0.72	0.99	1.14
Boiling point C ⁰	-188	-34.5	59
Electronegativity	4.10	2.85	2.75
First ionization energy, KJ	1681	1255	1142
Electron affinity KJ	333	348	340
Oxidation states	-1	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7
Colour and physical states at 25C ⁰	Pale yellow gas	Greenish yellow gas	Red brown solid
Lattice energy of potassium salt KX, KJ	817	718	656

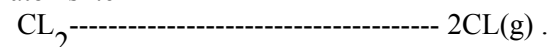
BOND ENERGY kJ	158.1	242	193	from the nine electrons already closely shielding the nucleus.
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General properties

All the element exist as diatomic molecules i.e. F_2, Cl_2, Br_2 and I_2 . The two atoms in each atomic molecules being joined by covalent bond.

The elements are generally very reactive. The high reactivity of the elements is due to

Low bonds dissociation energy of the molecules which allow easy formation of atoms i.e

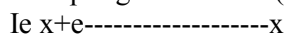


High electron affinity of the individual atoms which allows easy formation of ions.

The elements all have 7 electrons on their outer shell with one electron less than those of inert gas. The outer most general electronic configuration is $NP5$. They attain stable octet of noble gases by either.

Sharing of electrons (covalency) between themselves (Cl_2) or other atoms ($H-Cl$)

Accepting an electron (electrovalency) to form univalent ion



Their melting or boiling points increase down the group. This is because of increasing magnitude of van der Waal's forces as the molecules become bigger in size.

Because of small sizes, F_2 and Cl_2 molecules have weaker van der Waal's forces and can easily be overcome at room temperature hence they exist as gases. The forces however in Br_2 and I_2 are strong enough to hold them as liquids and solids respectively.

The bond energies generally decrease down the group except for fluorine

The decrease in bond energy from Cl_2 to I_2 is due to the increase in the sizes of the atoms which results in weaker attraction between the atoms in the molecule. The abnormally low bond energy for fluorine is because there is stronger repulsion between the non-bonding electrons in the combined atoms in the fluorine molecule due to its small size. This strong repulsion tends to force the atoms apart and thus assisting dissociating the molecule.

Electron affinity decreasing effective nuclear attraction for the incoming electron by the nucleus as the increase in screening effect outweighs that of the nuclear charge due to addition of an extra shell of electron from one element to the next down the group. The abnormally low value for fluorine is because of its small size which causes greater repulsion encountered by the incoming electron

Preparation of the halogens

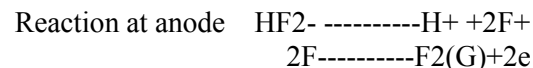
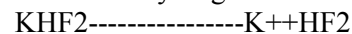
Chlorine, bromine and iodine are prepared in the laboratory by heating the solid halide salt with concentrated sulphuric acid in the presence of an equal bulk of manganese (iv) oxide. $2X(s) + 4H^+(aq) + MnO_2(s) \longrightarrow Mn^{2+}(s) + 2H_2O(l) + X_2$

Solid potassium manganate (vii) can be used instead of MnO_2 and reaction occurs in the cold



Fluorine is obtained by electrolysis of molten potassium hydrogen fluoride in the presence of anhydrous hydrofluoric acid and lithium fluoride.

Potassium hydrogen fluoride ionizes



Fluorine behaves differently from its group members because of its small size, low bond dissociation energy and its being the most electronegative. Some of the important differences between fluorine and the other halogens are Fluorides are usually more ionic than other halides because of its great electronegativity

Fluorides are usually more ionic than other halides because of its great electronegativity.

Fluorides form very strong hydrogen bonds because of its electronegativity.

Fluorine is the most reactive because of low bond dissociation energy.

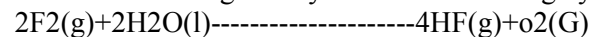
It forms very stable compound.

Tends to bring out the maximum covalency in other elements e.g. PF_5, SF_6, IF_7

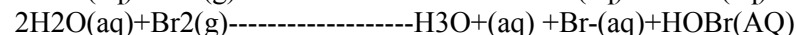
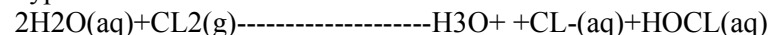
Reaction of the Halogens

With water

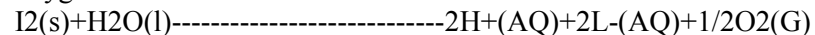
Fluorine reacts vigorously with water forming hydrogen fluoride and oxygen.



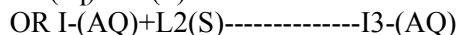
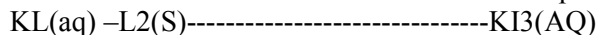
Chlorine and bromine react forming the halide ion hydroxyl ion and hypohalous acid.



Iodine is very sparingly soluble in water and the reaction is reversible in which oxygen oxidises the iodine ion back to iodine.

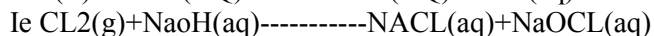
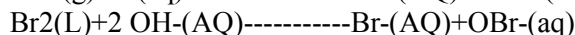
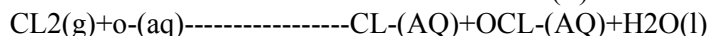
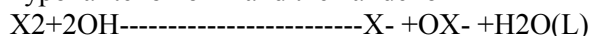


Note: Iodine is however very soluble in potassium iodine because of the formation of a soluble and stable triiodide complex



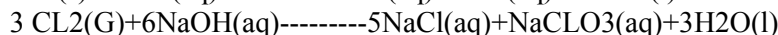
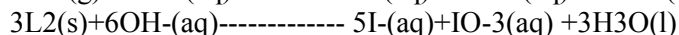
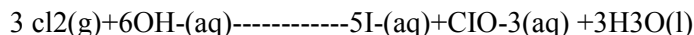
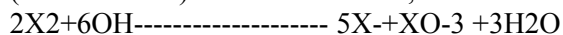
Reaction with alkalis

Chlorine, bromine and iodine react with cold dilute alkalis forming both the hypohalite ion OX^- and the halide ion X^-



(Sodium hypochlorite)

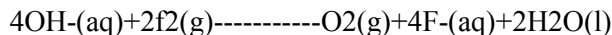
Chlorine, bromine and iodine react with hot concentrated alkaline (KOH or NaOH) to form halide ion, X^- and halite ion XO_3^-



Note: Fluorine reacts with cold dilute alkali to form oxygen difluoride

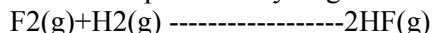


Fluorine reacts with warm concentrated solution of alkali to form oxygen

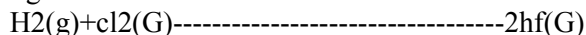


Reaction with hydrogen

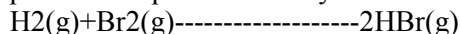
Fluorine explodes in hydrogen even in the dark forming HF



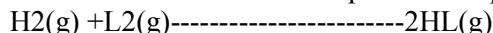
Chlorine only reacts with hydrogen in the presence of sunlight or ultraviolet light



Bromine reacts with hydrogen on heating to a temperature of 200°C in the presence of platinum catalyst.



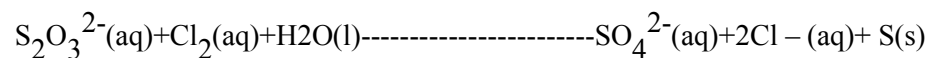
Iodine reacts at 400°C in the presence of Pt catalyst



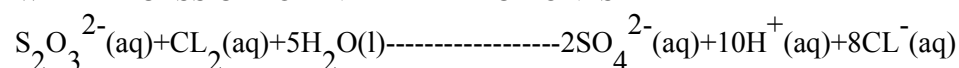
This reaction of H_2 with halogen demonstrates the reactivity of the halogens. F_2 is most reactive.



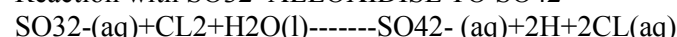
With sodium thiosulphate: chlorine reacts with sodium thiosulphate to form sulphate ion with deposition of sulphur



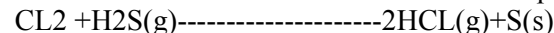
WITH EXCESS CHLORINE THE REACTION IS



Reaction with SO_3^{2-} - ALLOXIDISE TO SO_4^{2-}



Reaction with H_2S All react with H_2S to deposit yellow deposit of sulphur



Compounds of group VII elements

Hydrides of the halogens HX

Bond energy in K.J mol

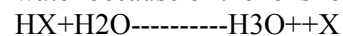
	556	431	336	299
--	-----	-----	-----	-----

Boiling point $^\circ\text{C}$

	19.9	-85.0	-66.7	-35.4
--	------	-------	-------	-------

Bond energy decrease down the group because Electronegativity decreases down the group Fluorine being most electronegative forms the strongest H-F while I being the electronegative forms the weakest H-I bond.

Pure hydrogen halides are covalent compounds are hence non-conductors of electricity. They are however, good conductors of electricity when dissolved in water because of the ions formed



Solutions of the hydrides in water are therefore acidic. Acidic strength increases from HF

, HI

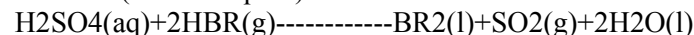
Percentage ionization of 0.1M HX

The dissociation of the halides in water depends on the bond strength between H and because of the very high Electronegativity of F, it forms very strong H-F bond and in water it therefore slightly dissociates hence few H^+ are present in solution.

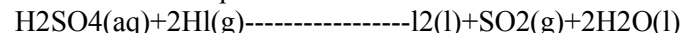
NOTE Acidic strength is affected by i) bond energy - down the group B.E decrease therefore the tendency to form H^+ increases down the group. This is because the Van Der Waals forces increase with size. HF has highest boiling point because of strong hydrogen bond formed due to the high Electronegativity of the fluorine atom.

Reaction of the hydrides with concentrated sulphuric acid

Concentrated sulphuric acid has no effect on HF and HCl. It oxidizes HBr to bromine (brown liquid) and is itself reduced to SO_2



concentrated sulphuric acid oxidizes HI to brown solution of iodine



OXIDES

The halogens form various oxides e.g. F_2O , Cl_2O , BrO_3 , Cl_2O_7 , I_2O_5 ETC. Because oxygen is more electronegative than Cl, Br and I on combination with oxygen, the halogen assumes a positive oxidation state. E.g. the oxidation state of F in F_2 is -2

Oxo acids

All the other halogens except F form the following oxo acids

Hypochlorous acid HClO , E.g. HClO (hypochlorous acid)

$\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl}(\text{l}) + \text{HOCl}(\text{l})$

The salts from hypochlorous acids are called hypochlorites e.g. hypochlorine

Bleaching powder contains calcium hypochlorites made by passing Cl_2

through a solution of calcium hydroxide. Bleaching powder is made by passing chlorine gas through slaked lime, solid $\text{Ca}(\text{OH})_2$

i.e. $\text{Ca}(\text{OH})_2(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaOCl}_2(\text{s}) + \text{H}_2\text{O}$

Note Addition of ethanoic acid or hydrochloric acid liberates chlorine gas

$\text{CaOCl}_2(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{Cl}_2(\text{g})$

This reaction is used to estimate the percentage of available chlorine in bleaching powder. The chlorine evolved is used to displace iodine from a solution of potassium iodide. The iodine is then titrated with a solution of sodium thiosulphate of known molarity

$\text{Cl}_2(\text{g}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{aq})$

$\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$

A similar reaction is used to determine the percentage of available chlorine liquid bleaches e.g. Jik which contains some sodium hypochlorite, Sodium chlorate (I)

In the presence of H^+ (from ethanoic acid) chlorate (I) ion reacts with iodide ion according to the equation

$\text{ClO}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq})$

$+ \text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$

SEE APPENDIX 1.3

On heating, sodium chlorate (I) decomposes in a disproportionation reaction as

$3\text{ClO}^-(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$

Halous acid HClO_2 e.g. HClO_2

Halic acid HClO_3 e.g. HClO_3 (Salts are called chlorate (IV))

$\text{Ba}(\text{ClO}_3)_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HClO}_3 + \text{BaSO}_4$

Prep

Chlorate (VI) ion is a strong oxidizing ion and in acid medium behaves as

$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

The following are some of the reactions

Oxidises Fe^{2+} to Fe^{3+}

$\text{ClO}_3^-(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 6\text{Fe}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + \text{Cl}_2(\text{aq})$

Oxides SO_3^{2-} to SO_4^{2-}

$\text{ClO}_3^-(\text{aq}) + 3\text{SO}_3^{2-}(\text{aq}) \rightarrow 3\text{SO}_4^{2-}(\text{aq}) + \text{Cl}^-(\text{aq})$

Oxides I⁻ to I_2

i.e. $\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{I}^-(\text{aq}) \rightarrow 3\text{I}_2(\text{aq}) + \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

IV) PERHALIC ACID HClO_4 e.g. HClO_4

Note The greater the number of oxygen the acid has, the greater the acidity. Therefore perchloric acid is the most acidic. THIS IS BECAUSE THE GREATER THE NUMBER OF OXYGEN ATOMS THE GREATER IS THE ELECTRON DISPLACEMENT TOWARDS THE OXYGEN AND THE WEAKER WILL BE THE H-Cl BOND. The acidic strength of the oxo-acids of chlorine increases with increase in the number of oxygen atoms

i.e. $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

This is due to oxygen atom being more electronegative than chlorine atom and this pulls electrons more strongly away from chlorine atom and effect weakens the H-Cl such that H^+ IS EASILY LOST TO THE SOLUTION. The greater the number of oxygen atoms the greater the effect and the greater the acidity.

INTER HALOGENS

These are covalent compounds formed when halogens combine with one another

They form compounds of the types AB , AB_3 , AB_5 , AB_7 .

The electronegative atom carries a partial negative charge e.g. ClF , ClF_3

BrF_5 , IF_7 , In IF_5 the oxidation number of iodine atom is +5 (F more

electronegative than I) Bromine trifluoride conducts electricity because of slight ionization.

$2\text{BrF}_3 \rightarrow \text{BrF}_2 + \text{BrF}_4$

Structure

XF_3 adopts T-shaped structure

E.g. ClF_3 or BrF_3

Test for Cl, Br and I

Using conc sulphuric acid

Addition of conc sulphuric acid to any chloride, bromide or iodine produces

HCl , HBr and HI gases respectively

Using silver nitrate solution

A white ppt of silver chloride is formed with a chloride.

CL-(aq)+AG+(aq)-----AGCL(s)

APale yellow ppt of silver bromide is frmed with bromide

Br-(aq)+Ag+(aq)-----AgBr(s)

Apale yellow ppt of silver bromide is formed with bromide

Br-(aq)+AG+(aq)-----AgBr(s)

With iodine a yellow ppt of silver iodine is formed

I-(aq)+Ag+(aq)-----AgI(s)

Using a mixture of conc.H₂SO₄ and manganese (IV) oxide

Additon of MnO₂ followed by conc.H₂SO₄ produces greenish chlorine gas from chloride, brown reddish vapour of bromine from bromides and dark solution of iodine from iodide

Using a lead ethanote solution

With Cl- a white ppt of lead chloride soluble on warming with Br- a white ppt of Pb Br₂ soluble inhot water.

With I- a yellow ppt of pb I₂ formed which dissolves in hot water to give a colourless solution.

Using a solution of Cl₂ in CCL₄

With Br, brown br₂ given off which dissolves in ccl₄ layer to give a brown layer. With I,iodine is liberated which dissolves in CCL₄ layer to give a violet coloration.

Using dilute ethanoic acid and sodium nitrite solution

No observable change occurs with CL- and Br- but I librates iodine which gives a violet solution in the CCL 4 layer.

Champter 5

PERIOD 3

Element						
Na	Mg	Al	Si	P	S	Cl
Atomic number	11	12	13	15	16	17
Atomic radius,nm	0.156					0.099
Ionic radius nm						0.181
Melting point oC						101
First ionization energy , KJ	496	737	527	786	1012	999
Electron affinity	-20	+67	-30	-135	-60	-364
Electronegativity	0.9	1,2	1.5	1.8	2.1	2.5

General properties

Na, Mg and Al are metals which adopt giant metallic structures.Silicon is metalloid with agiant covalent structure.

p.s AND CL are non-mentals which adopt simple molecular structures.Bonding : Na,Mg and Al adopt metallic bonding and this bonding increase strength from Na through Mg to Al.This is because of the increasing number of valence electron lost to the charge cloud of the metal.The mates conduct electricity due to presence of mobile delocalized electrns in their lattices.

Silico has a gaint covalent structure in which strong and many covalent bong=ds link one atom to the next throughout the whole lattice forming a three dimension giant structure .Because strong covalent bonds hold the atom tightly close to one another silicon has a very high melting and boiling point.

Non –metals P<S and Cl exist as molecules are held to one another by weak van dewaal's forces.The magnitude of these forces depends on the size of the molecule and increase with increasase in size of the molecules.

The force increase in the order Cl₂<P₄<S₈

Variation of properties

Atomic radius

Across the period from Na to Cl atomic radius decreases. In moving across from one element to the next a proton is added to the nucleus and an electron is added to he nucleus and an electron is added to the same shell

Addition of a proton increases nuclear charge while addition of electron to the same shell decreases screening effect with the result that effective nuclear charge increases and therefore the electron are trongly pulled towards the nucleus resulting in a decrease of the atomic radius.

Electropostivity

Electropositivity is the tendency of an atom of an element to lose its valence electrons to become positivity charged

Electropositivity sharply decreases across a period as anumber of electrons or the same shell increases. Because electrons in the same shell screen themselves poorly from the nucleus, the effect of increasing nuclear charge due to extra proton added from one elements to the next results in strong attraction for the outermost electrons by the nucleus and become therefore increasingly difficult to remove them.

Melting point

a) Among the metals.Melting point increases from Na through Mg to AL.

Among the metals, melting point depends on the strength of the metallic bond formed which in turn depends on the number of valence electrons a metal contributes for bonding. The greater the number of electrons a metal contributes for bonding the stronger the metallic bond and the higher the melting point. Therefore the sharp increase in melting point from Na to Mg is because Mg contributes more electrons (two) for bonding than sodium (contributes only one). The large increase, however, is not maintained from Mg to Al probably due to the fact Al seems not to contribute all its three electrons for bonding.

b) Silicon has a very high melting point because of the three dimensional net work of strong covalent bonds which hold the atoms closely together in a giant covalent structure.

c) Among non-metals

The molecules of these non-metals are held together to one another by weak van der Waals forces whose magnitude depends on the size of the molecules.

Sulphur has a higher melting point than phosphorus because sulphur forms bigger S₈ molecules than phosphorus which forms P₄ molecules. Chlorine forms small discrete Cl₂ molecules with very weak van der Waals forces.

First ionization energy;

First ionization energy is defined as the minimum energy required to remove one mole of electrons from one mole of a gaseous atom to form one mole of a univalent gaseous ion.

i.e



There is a general increase in the first ionization energies from Na to Cl except for the abnormal values obtained in Mg and P.

The general increase is because of increasing effective nuclear attraction for the outermost electrons. In moving from one element to the next across the period a proton is added to the nucleus of each element which increases the nuclear charge and also an electron is added to the same outermost shell therefore experience increasing nuclear attraction hence the increase in ionization energy.

The abnormally high value for Mg and Phosphorus is because the single electron here is being removed from a full 3s sub-energy level and a half filled 3p sub-energy level respectively which are thermodynamically more stable.

ELECTRON AFFINITY

Elements				
Na	Mg	Al	Si	P
Electronegativity	-20	+67	-30	-135

Tend Generally electron affinity increases across the period with Mg and P showing abnormal values.

Explanation: Across, in moving from one element to the next, the nuclear charge increases by one unit so that the nuclear attraction for electrons increases hence more energy is released.

The electron affinity for Mg is more positive than expected because here an electron is being added to a full 3s sub-shell which is stable and therefore resists addition of the electron so to add it requires energy.

Similarly in P the value of the electron affinity is less negative than expected because here the electron is being added to a half filled 3p sub-shell ($1s^2 2s^2 2p^6 3s^2 3p^3$) which is stable and therefore also resists any addition.

Compounds of period 3 element

a) Chloride

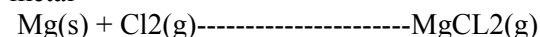
Elements					
Na	Mg	Al	Si	P	S
Chloride	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅
Physical state	S	S	S	I	I
Structure	G.I	G.I	G.I	C	S.m
Bonding	I	I	I	C	C
Melting point	801	715	180	-68	Pcl3

S=Solid l=liquid g = gas I= ionic C= Covalent G>I= giant ionic

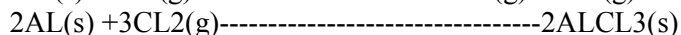
S.m= Simple molecular.

PREPARATION OF CHLORIDES

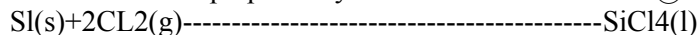
Chlorides of Na, Mg and Al are prepared by passing chloride gas over heated metal



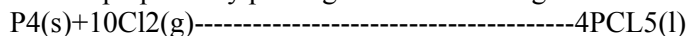
AlCl₃ prepared by passing either dry hydrogen chloride gas or chlorine gas over heated aluminium



Chloride of Si is prepared by direct combustion with Cl₂



PCl₅ is prepared by passing excess chlorine gas over heated phosphorus



STRUCTURE AND BONDING

NaCl and MgCl₂ are giant ionic structure where there is strong electrostatic force of attraction between the oppositely charged ions hence they have high melting points and boiling points.

Note Melting and boiling points decrease from NaCl through MgCl₂

to AlCl₃. This is because in moving from Na⁺ through Mg²⁺ to Al³⁺, the size of the cations decreases. i.e. $\frac{1}{0.095}$

Mg²⁺ = 0.065, Al³⁺ = 0.05. The charge on the cation increases. i.e. Na⁺ to +3 in Al³⁺. This results in Al³⁺ having the greatest charge/radius ratio (polarizing power).

$$\text{Polarizing power of Na}^+ = \frac{1}{0.095} = 10.5$$

$$\text{Polarising power of Mg}^{2+} = \frac{2}{0.065} = 30.7$$

$$\text{Polarizing power of Al}^{3+} = \frac{3}{0.050} = 60$$

Therefore Al³⁺ greatly polarizes the Cl⁻ ion more than Mg²⁺ and Na⁺ hence AlCl₃ is more covalent than MgCl₂ and NaCl.

The other chlorides adopt simple molecular structure consisting of small discrete molecules held together by weak Van der Waals' forces.

Thus they have low melting points

Reaction with water

Ionic chlorides dissolve in water to give neutral solution with a pH of 7. A solution of NaCl(aq) ----- Na⁺(aq) + Cl⁻(aq)

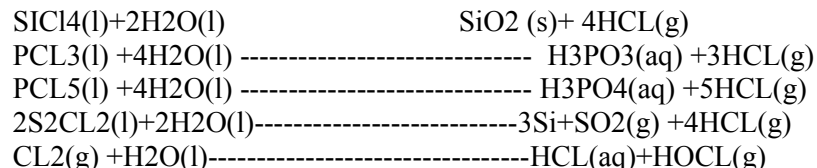
The ions attack around them water molecules

A solution of AlCl₃ however in water is not neutral but has a pH of 3. The acidic nature of the solution is due to the charge on Al³⁺ and its small radius. This causes Al³⁺ to form a strong bond with the OH- of water molecules and releasing H⁺ in solution which makes the solution acidic.



i.e. This is because of the high polarizing effect of Al³⁺ and its tendency to form strong bonds with oxygen which weakens the O-H bond of water molecules in the [Al(H₂O)₆]³⁺ so that the hydrated ion dissociates and acts as an acid.

The other chlorides of Si, P and S dissolve to give acidic solutions.



oxides

Elements

Na	Mg	Al	Si	P	S
Formula of Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	

STRUCTURE AND BONDING

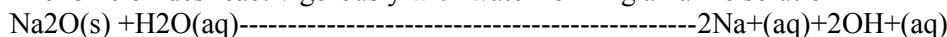
The oxides Na₂O, MgO and Al₂O₃ are giant ionic structures and their molten solutions conduct electricity. They have high melting and boiling points. SiO₂ has a giant molecular structure with a 3-dimensional network of covalent bonds. It does not conduct electricity.

P₄O₁₀, SO₃, Cl₂O₇ consist of small discrete molecule which are volatile and will low melting and boiling points. Therefore in moving from Na to Argon there is a steady change in the structure of the oxides from ion through giant molecular to simple molecular.

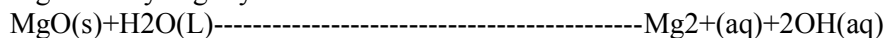
REACTION WITH WATER.

The change in the structure across the period influence the reactions of the oxide with water.

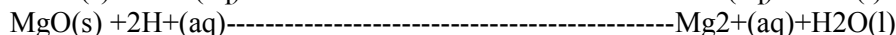
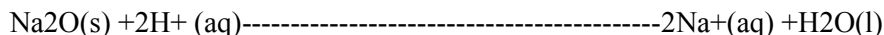
The ionic oxides react vigorously with water forming alkaline solution



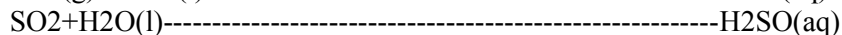
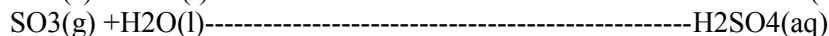
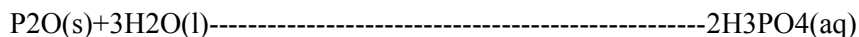
MgO is only slightly soluble in water



Na₂O(s) and MgO react with acids



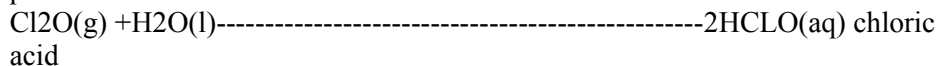
Al₂O₃ does not react with water but just Like BeO, Al₂O₃ is amphoteric. The rest of the oxides dissolve in water to form acidic solution.



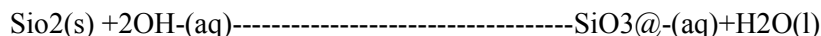
By these reactions P₂O₅ and SO₃ are called anhydrides of phosphoric and sulphuric acids respectively



perchloric acid



NOTE SiO₂ does not react with water but react with conc alkalis to form silicates.



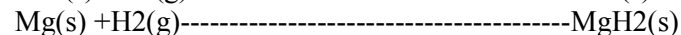
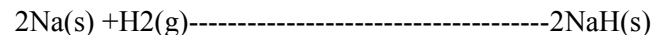
Hydrides

Elements

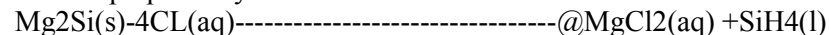
Na	Mg	AL	Si	P	S	CL
Formula of hydride	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂

Preparation of hydrides

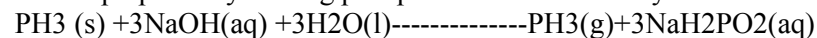
NaH, MgH₂ and AlH₃ are prepared by heating the metal in a stream of hydrogen gas at about 350°C



SiH₄ is prepared by reaction

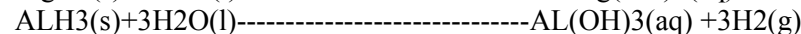
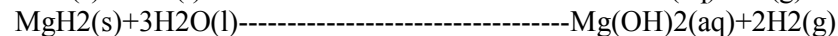
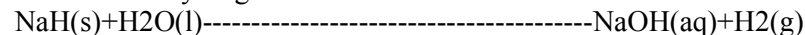


PH₃ is prepared by heating phosphorus with sodium hydroxide solution



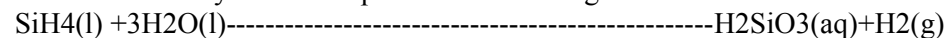
Reaction with water

NaH, MgH₂ and AlH₃ are ionic and react with water forming an alkaline solution and hydrogen.



The reactions indicate that OH⁻ are being removed from solution so the solution becomes less basic. Hence from NaH to AlH₃ via MgH₂ the solution decrease in alkalinity but increases in acidity.

The rest of the hydrides except PH₃ dissolve to give acidic solutions.



Ph₃ is non-polar because P and H are of almost equal electronegative and hence PH₃ does not react with water.



Therefore the nature of hydrides changes from basic to acidic across the period.

CHAPTER SIX

ALUMINIUM

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^1$

Ores

Aluminum naturally is found to exist as

Bauxite	$Al_2O_3 \cdot 2H_2O$
Cryolite	Na_3AlF_6
Kaolin	$Al_2Si_2O_7 \cdot 2H_2O$ in clay

Extraction process

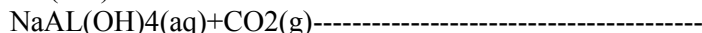
The extraction- of Aluminum can be divided into two major processes as

In the purification process, the impure bauxite which contain silica and iron oxide as impurities, is convert pure Aluminum oxide, Al_2O_3 .

Here the bauxite is first basted at low temperature to convert all the iron ore to the iron (III) state. The roasted product is then crushed to powder form and dissolved in sodium hydroxide solution. The dissolution in NaOH solution is to free the Al_2O_3 from iron (iii) and silica. The Fe_2O_3 remains undissolved and is removed by filtration. The Al_2O_3 dissolves in $NaOH(aq) + 2H_2O \rightarrow 2NaAl(OH)_4(aq)$

Some silica also dissolved but its conc will be aluminium hydroxide is their obtained from the aluminate solution by either:

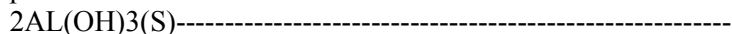
(i) SEEDING ie. little $Al(OH)_3(s)$ is added to the aluminate to precipitate $Al(OH)_3$



(iii) The aluminate solution is treat which a current of carbon dioxide

gas which precipitate $Al(OH)_3$ and not the carbonate.

The hydroxide obtained from either of two methods above is then filtered. Washed and dried. The dry hydroxide obtained is now heated strongly to form pure Al_2O_3

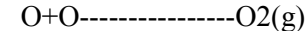
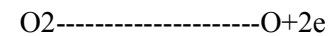


b) Electrolysis of pure Al_2O_3 the pure Al_2O_3

The pure Al_2O_3 obtained in (a) above is electrolysed with mixture of cryolite Na_3AlF_6 . Cryolite is added so as to lower the melting point of the Al_2O_3 . The electrolysis is carried out in a steel tank lined with sheets of carbon which act as the cathode and the anode also made of carbon rods. Aluminium collect at the bottom of the steel tank and is then taped off at intervals. Reactions taking place at the electrodes are

At the cathode

At the anode

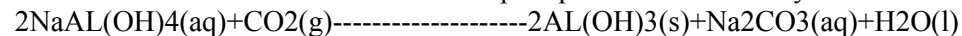


Note The oxygen produced at the anode tends to oxidize the carbon anode and therefore the anode should be renewed at intervals

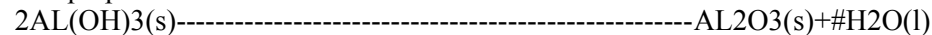
Al_2O_3 and Fe_2O_3 are usually found existing together. Aluminium is extracted from the Al_2O_3 by electrolytic process and not by reduction as in the CASE OF Iron from Fe_2O_3 . This is because Aluminium being more reactive than Iron from more stable oxide which cannot be reduced by carbon.

Aluminium can be separated from the mixture of the Ores ie. Al_2O_3/Fe_2O_3 by dissolution in sodium hydroxide. Aluminium oxide dissolve leaving Fe_2O_3 as a precipitate which can be filtered off. The Al_2O_3 dissolves forming aluminate i.e. $3H_2O(l) + Al_2O_3(s) + 2NaOH(aq) \rightarrow 2NaAl(OH)_4(aq)$

The aluminate is treated with CO_2 to precipitate Aluminium Hydroxide



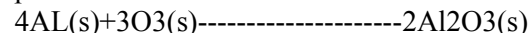
The precipitate is then heated.



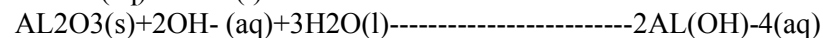
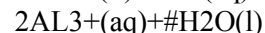
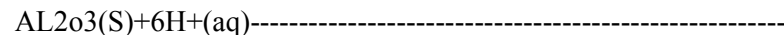
REACTIONS OF ALUMINIUM

Reaction with oxygen

On exposure to air the metal develops very thin layer of aluminium oxide which prevents further reaction.



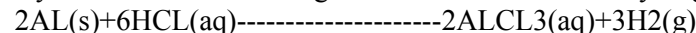
Aluminium oxide is amphoteric dissolving in mineral acids to form aluminium salts and in caustic alkali to form aluminate.



Reaction with acids

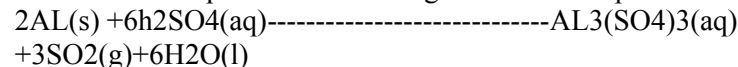
With hydrochloric acid. Aluminium react when warmed with moderately conc.

Hydrochloric acid forming aluminium chloride and hydrogen gas.



With sulphuric

Aluminium does not react with dilute sulphuric acid but reacts with concentrated sulphuric acid forming aluminium sulphate and sulphur dioxide.



With Nitric acid

Aluminium does not react with nitric acid because of the insoluble layer of Al_2O_3 formed which prevents further reaction.

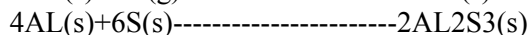
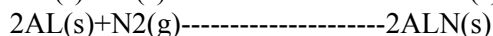
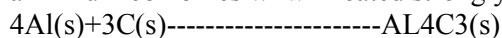
Reaction with Alkali

Aluminium reacts vigorously with sodium hydroxide solution forming sodium aluminate

And hydrogen gas



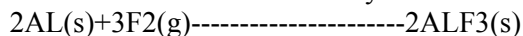
aluminium combines when heated strongly with N_2 , C and S



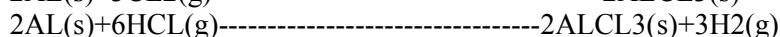
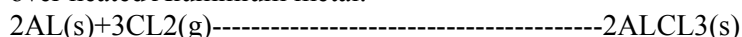
NOTE: Because of this reaction Aluminium saucepans are damaged by alkaline solution.

Reaction with Halogens

Aluminium fluoride is made by direct combination of the metal with fluorine.



Aluminium chloride is made by passing chlorine gas or hydrogen chloride gas over heated Aluminium metal.



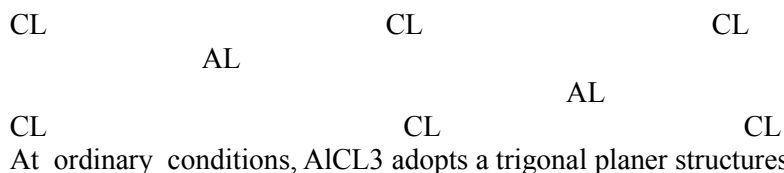
Compounds of Aluminium

Halides e.g. AlF_3 , AlCl_3 , AlBr_3 , AlI_3

Bonding Aluminium shows an oxidation state of +3 in most its compounds. The very high charge (large positive and small ionic radius) of the Al^{3+} causes distortion (polarization) of the electron clouds around the halide ion in contact with it.

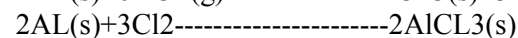
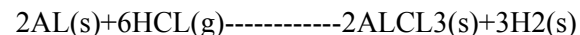
The polarization is greatest as the size of the halide ion increases. Therefore the iodide ion with greatest size is most polarized while the fluoride ion experiences negligible polarization. Therefore AlF_3 is ionic while AlCl_3 is intermediate between ionic and covalent. Aluminium chloride exists as dimer, Al_2Cl_6 in vapour phase and on heating sublimes at 180°C

The structure of chloride in vapour in vapour phase.



Aluminium bromide is typically covalent because of the large Br size. Like Aluminium Chloride, it also exists as dimer Al_2Br_6 and has same structure with Al_2Cl_6 . Al_2Cl_6 is covalent and has also similar properties with Al_2Br_6

Aluminium chloride is prepared by passing dry hydrogen chloride gas over heated aluminium metal.



Properties of halides

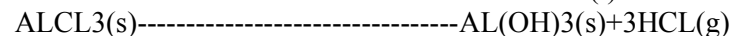
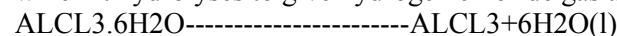
AlF_3	1290	soluble
AlCl_3	Sublimes at 193°C	soluble
AlBr_3	97.5	soluble
AlI_3	180	soluble

Because of high charge and small ionic radius, Al^{3+} exerts polarizing effect on the halide ion in contact with it. This polarizing increases with increase in size of the halide ion.

Because of the small size of F, the F experience negligible polarization and thus remains a typical ionic compound.

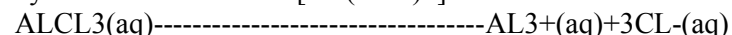
In moving from AlCl_3 to AlH_3 as the halide ion increases, the halide becomes more covalent in character. The very high melting point of AlF_3 is because of its ionic character. Al is intermediate between ionic and covalent. AlBr_3 and AlI_3 are typical covalent compounds. Al_3 has a higher melting point than AlBr_3 because of its larger size due to the bigger I resulting in stronger van der Waals' force

NOTE: Hydrate aluminium chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ on heating forms water in which it hydrolyses to give hydrogen chloride gas according to the equation



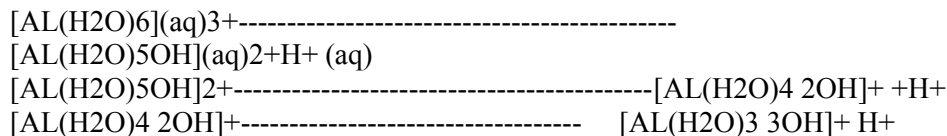
BEHAVIOUR IN WATER

Aluminium chloride solution like other compounds of aluminium contains hydrated aluminium ion $[\text{Al(H}_2\text{O)}_6]^{3+}$

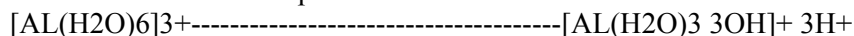


Because of very high charge density Al^{3+} exerts stronger attraction for oxygen

atoms this weakens-H bound of water thus leading to release of a proton' I'e



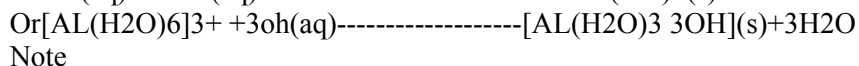
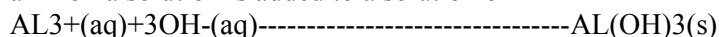
OR the dissociation is represented in short as



The production of H^+ explain why a solution of aluminium chloride is acidic. Beacuse of the same reason, aqueous solutions of FeCl_3 , CuSO_4 , $\text{Cr}(\text{NO}_3)_3$ and $\text{CO}(\text{NO}_3)_3$ and are acidic.

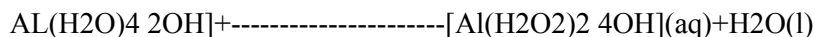
aluminiumhydroxide

Aluminium hydroxide is prepared as a gelatinous white precipitate when ammonia solution is added to a solution of Al^{3+}



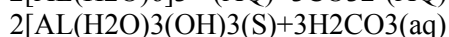
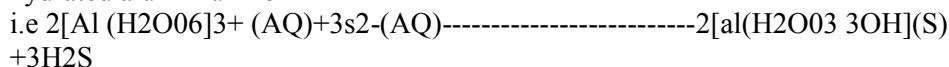
Note

The precipitate dissolve in excess alkali owing to the formation of a solution aluminates.



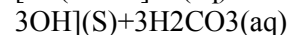
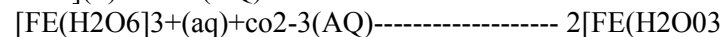
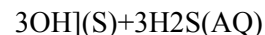
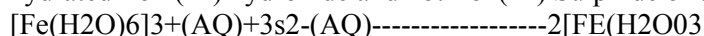
Addition of further NaOH (excess) removes apportion from the insoluble precipitate and the aluminate ion formed is soluble inwater . $\text{Al}(\text{OH})$ is used in sewage treatement and in dyeing.

Addition of strong bases like S^{2-} (from H_2S OR Na_2S) and Co_3^{2-} (e.g from $\text{Na}_2\text{ CO}_2$) form hydroxide and not Al_2S_3 or $\text{Al}_2(\text{CO}_3)_3$. This is because the S^{2-} or CO_3^{2-} being stronger bases than water instead removes H^+ from the hydrated aluminium ion

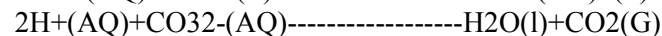
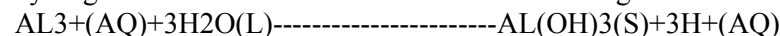


Therefore addition of $\text{CO}_2\text{-3}$ OR S^{2-} ion to a solution of aluminium salts precipitates the hydrated hydroxide and not the carbonate or Sulphide

Similarly, addition of S^{2-} OR Co_3^{2-} to solution of iron (III) salts precipitate hydrated iron (III) hydroxide and not iron(III) Sulphide or carbonate.



Additon of sodium carbonate solution to a solution of aluminium salt (e.g ALCL_3) gives a white precipitate of aluminium hydroxide with evolution of a colourless gas. This is because in solution aluminium salt is rapidly hydrolysed due to high charge density of al^{3+} to give offfff aluminium hydroxide and free hydrogen ions which then combines with Co_3^{2-} to give carbondioxide gas



tThis explains why iron(III) carbonate doesnot exist.

Uses of aluminium

Because of its bright appearance and lightness, it 's used to make cooking utensils

Because of its low density and very good electrical conductivity , it is used as overhead high tension cable for distribution of electricity.

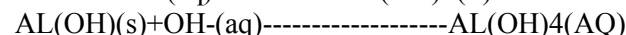
In alloys making e.g maganlium which is an alloys of Al and Mg

Aluminium hydroxide is used as a cnsituent of cement.

Test for AL_3^{+}

Addition of aqueous sodium hydroxide

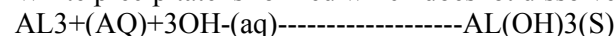
Addition of solution of sodium hydroxide to a solution of a soluble AL_3^{+} salt produces a white precipitate of aluminium hydroxide which dissolves in excess to form a colourless solution of soluble complx called sodium aluminate.



Note By this reaction it resembles Pb^{2+} and Zn^{2+} ions

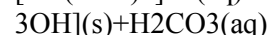
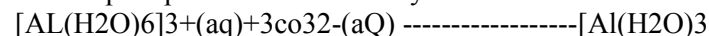
Addion of ammonia solution

White precipitate is formed which doesnot dissolves in excess



Addition of sodium carbonate solution

Awhite precipitateof aluminium hydroxide forms which dissolves in excess



The precipitate of $\text{al}(\text{H}_2\text{O})_3\text{ 3OH}$ then dissolves in h_2co_3 formed

Aaition of aluminium reagent

Here the solution of A_3^{+} is first acidified with dilute HCL and then four drops

of Aluminium reagent added followed by sodium hydroxide solution dropwise
A pink lake is formed.

Chapter 7

TRANSITION ELEMENTS

Transition elements are called d-block elements because of their electronic structure. In the periodic table they are between the S and P block elements and their properties are transitional between the highly reactive metallic elements of the S-block which typically form ionic compounds and the less reactive metallic elements of the P block which form covalent compounds.

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius	0.16	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.13	0.13
Electronegativity	1.2	1.3	1.45	1.55	1.6	1.65	1.7	1.75	1.75	1.6
First I.E /KJ mol ⁻¹	630	660	650	650	720	767	760	740	750	910
Melting point °C	1540	1680	1900	1890	1240	1540	1500	1450	1080	420
Atomic number	21	22	23	24	25	26	27	28	29	30

Electronic configuration of transition elements

	Atomic number	Electronic configuration
Sc	21	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹ 4s ²
Ti	22	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ² 4s ²
V	23	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ³ 4s ²
Cr	24	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ¹
Mn	25	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ²
Fe	26	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶ 4s ²
Co	27	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁷ 4s ²
Ni	28	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁸ 4s ²
Cu	29	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ¹
Zn	30	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ²

After the 2nd energy level, an overlap starts occurring between 3rd and 4th energy levels such that 3d – sub shell is nearer to the nucleus than the 4s sub-shell but at a higher energy level.

After filling the 3s and 3p sub shells, further electrons enter the 4s sub shell and after the 4s sub shell is filled, electrons now enter the 3d subshells. From the electronic configuration a transition element is defined as that having a partially filled 3-d subshell (has between 1 and 9) electrons in 3d-subshell.

Note For chromium and copper an anomalous behaviour occurs because of configuration giving half full e.g. for chromium and filled d-sub shell e.g. for copper are thermodynamically more stable i.e. extra stability is associated with either half or full-d subshell.

For Cr, the configuration is

1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹ and not 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶ 4s²

This also explains why Fe²⁺ with 3d⁶ is easily oxidized to Fe³⁺ with 3d⁵ why Mn²⁺ with 3d⁵ is resistant to oxidation to Mn³⁺ with 3d⁴

Ions of Transition metals

Transition metals form first by losing electrons first from the 4s sub-shell rather than the 3d sub-shell. Hence electronic configuration of Fe²⁺ and Fe³⁺ are Fe (ground state)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
Atomic radius A	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17
Ionic radius (m3+) a	0.81	0.76	0.74	0.69	0.66	0.64	0.63	0.62	

Trend: Atomic radius decreases less rapidly across

Explanation: In transition elements, the electrons are being added to the inner 3d sub-shell.

Therefore the 3d electrons produce greater screening of the 4s electrons which roughly balances the increasing nuclear charge.

General characterising properties of transition metals

Transition elements are metals with high melting and boiling points. This high melting and the boiling points are due to inter atomic bonding which involves the 4s and 3d electrons. i.e. transition metals have higher melting point

because they have both d as well as S electrons for delocalization.

Elements

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Melting point	64	850	1540	1680	1900	1890	1240	1540	1500

Potassium and calcium have lower melting point than transition elements in the same group 4 because they form weaker interatomic bonding due fewer electrons used for bonding. Potassium uses only electron (valence electron) while calcium uses two electrons.

Transition metals have higher melting points than S-block elements in the same period because of stronger interatomic (metallic) bonding formed by use of electrons from both electrons 3d and 4s subshells.

Manganese and copper have abnormally low melting points because of the same period because of the electronic configuration in which for manganese has half filled 3d while copper has full 3d-shell. These configurations for Mn and Cu give a stable lattice which makes the 3d electrons less available for delocalization (bonding).

The increase in melting points from Sc to Cr is due to increasing number of unpaired electrons on the 3d-subshell while the decrease in melting point from Fe to Zn is due to decrease in the number of unpaired electrons on the 3d-subshell. Note Melting point increases with increase in the number of unpaired electrons in the 3d. The very low melting for Zinc is due to stability associated with a full 3d-subshell which makes the electrons less available for bonding.

Ionic Radius

Their ions are smaller compared to those of the alkali metals in the same period. Because of their smaller ionic radius and greater charge, their polarizing powers are greater. Therefore associated anions are greatly polarized and consequently most of their compounds are less ionic than those of the S-block metals e.g. the oxides and hydroxides. Because of greater polarization also. Most salts of transition elements are hydrolysed and are therefore acidic e.g.

$\text{FeCl}_3, \text{NiSO}_4, \text{CuSO}_4$

$\text{FeCl}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{HCl}(\text{aq})$

TRANSITION ELEMENTS HAVE VARIABLE OXIDATION STATES

OXIDATION STATE Is defined as the charge left on the central atom when all the other atoms of the compound have removed as ions e.g. the oxidation state

on the following metals is calculated as

(i) CrO_7^{2-}

The central metal ion = Cr

Overall charge on the ion = -2

Let Y be the charge on each Cr

Overall charge on the 7 oxygen = $7 \times (-2) = -14$

Charge on the 2 Cr + that of 7O = -2 (overall charge)

$$2x + 7 \times (-2) = -2$$

$$2x - 14 = -2$$

$$2x = 12$$

$$x = 6$$

Charge on each Cr ion is +6

Oxidation charge on Cr = +6

(ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]_2\text{Cl} \cdot \text{H}_2\text{O}$

This is a complex ion with Cr the central metal ion.

The salt has two free chloride ions

Overall charge on the complex $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]$ is +2

Let y be the charge on Cr. H_2O is neutral

(charge on Cr) + (charge on 5 H_2O) + (charge on Cl) = +2

$$y + 5 \times 0 + 1 \times (-1) = +2$$

$$y - 1 = +2$$

$$y = 1 + 2 = +3$$

oxidation state on Cr = +3

Transition metals show variable oxidation states because of the availability of 3d electrons. The commonest oxidation states being +2 and +3.

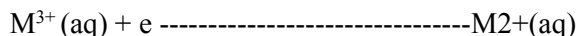
The oxidation states shown by the first transition series are

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

NOTE: The +2 and +3 oxidation states are shown by most elements from Ti and

Cu.

The relative stability of these two oxidation states is governed by the electrode potential for the reaction



	E^0
Ti^{3+}/Ti^{2+}	-0.125
V^{3+}/V^{2+}	-0.25
Cr^{3+}/Cr^{2+}	-0.12
Mn^{3+}/Mn^{2+}	-1.5
Fe^{3+}/Fe^{2+}	+0.25
Co^{3+}/Co^{2+}	+1.75

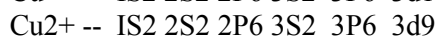
The value for M^{3+}/M^{2+} increases from Ti to Co but M^{3+}/M^{2+} is unexpectedly high and that of Fe^{3+}/Fe^{2+} is unexpectedly low.

The more positive the value of E^0 , the greater the ability for M^{3+} to convert to M^{2+} . Therefore Mn^{3+} is easily converted to Mn^{2+} and Fe^{3+} is not easily converted to Fe^{2+} and hence Fe^{3+} is more stable than Fe^{2+} and Mn^{2+} is more stable than Mn^{3+} . This is because of the electronic configurations of Fe^{3+} and Mn^{2+} in which the 3d sub-shell is half full and stable.

i.e

Fe^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	
Fe^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	stable
Mn^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	stable
Mn^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$	

Note: The Cu^+ is expected to be more than Cu^{2+} because of its electronic configuration.



But Cu^{2+} is more stable because the heat change for $Cu^{+}(aq) \rightarrow Cu$ is less

exothermic

Transition metal ions and their compounds are coloured

Sc^{3+}	colourless	Fe^{2+}	Green
Ti^{3+}	Purple	Fe^{3+}	yellow
V^{3+}	Green	Ni^{2+}	Green
Cr^{3+}	Green	Cu^{2+}	Blue
Mn^{2+}	Pink	Zn^{2+}	colourless
MnO_4^{2-}	purple	Co^{2+}	pink

Scandium and Zn are not regarded as transition metals because their penultimate shell is full for Zn^{2+} (Ar 3d¹⁰) while for Sc^{3+} it is empty (Ar 3d⁰).

Zn^{2+} and Sc^{3+} and their compounds are not coloured (colourless).

Formation of coloured ions

Formation of coloured ions by transition elements is associated with the presence of incompletely filled 3d subshells.

When visible light falls on the metal ion, the 3d subenergy level is split into two. The unpaired electrons in the lower energy level then absorb energy and jump (transition) of electrons; the remaining part of the visible light which is not absorbed is then reflected in the form of electromagnetic radiation.

The colour of a particular transition metal ion depends upon

The nature of the ligand

e.g. the colour of hydrated copper (II)

Chapter 8

SOME INDUSTRIAL PROCESSES

Manufacture Of Cement

Cement is manufactured by two processes

- Dry process and
- Wet process

Dry process

The raw materials used here are limestone ($CaCO_3$), clay, Al_2O_3 , $2SiO_2$ OR Al_2SiO_7 and Gypsum, $CaSO_4$.

Portland cement is a mixture of calcium silicates and aluminium silicate. It is made by strongly heating a mixture of limestone ($CaCO_3$) and

clay($\text{AL}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)

The mixture of finely ground limestone and clay is first mixed with water AND ALLOWED TO PASS DOWN A SLOPPING ROTATING CYLINDER IN WHICH IT IS STRONGLY HEATED.

During the heating, the limestone decomposes to give CaO(quick lime) which then reacts with clay to form small lumps which on cooling and grinding form a smooth fine powder called cement. Gypsum(CaSO_4) is then added so as to slow down the reaction between cement and water(i.e slow setting)

$\text{CaO}(s) \xrightarrow{\hspace{1cm}} \text{CaO}(s) + \text{CO}_2(g)$

The CaO formed then reacts with SiO_2 and present in the clay to give a mixture of calcium silicates and aluminates

$\text{CaO}(s) + \text{SiO}_2 \xrightarrow{\hspace{1cm}} \text{CaSiO}_3(s)$

$\text{CaO}(s) + \text{AL}_2\text{O}_3 \xrightarrow{\hspace{1cm}} \text{CaO} \cdot \text{AL}_2\text{O}_3 \text{ (ca AL}_2\text{O}_4)$

Dicalcium silicates and tricalcium and tricalcium aluminate may also form during the heating process.

$2\text{CaO} + \text{SiO}_2 \xrightarrow{\hspace{1cm}} (\text{CaO})_2\text{SiO}_2$

$3\text{CaO} + \text{SiO}_2 \xrightarrow{\hspace{1cm}} (\text{CaO})_3\text{SiO}_2$

$2\text{AL}_2\text{O}_3 + \text{CaO} \xrightarrow{\hspace{1cm}} (\text{CaO}(\text{AL}_2\text{O}_3)_2$

Cement hence consists of a mixture of calcium silicates and aluminates. It is used in the making of concrete by mixing it with sand and water with gravel. Water reacts with cement particles forming a new substance which expands and binds the unreacted cement particles together. This reaction is slow. In summary cement is manufactured by either wet process and the raw material used are limestone, clay and gypsum.

Manufacture of sulphuric acid(contact process)

The raw materials used in this process are sulphur dioxide and oxygen.

The SO_2 may be obtained by

I) burning sulphur in air

$\text{S}(s) + \text{O}_2(g) \xrightarrow{\hspace{1cm}}$

Burning

temperature effect

The forward reaction is exothermic and therefore theoretically would be favoured by use of low temperatures. However, at low temperature, the rate of reaction is slow but yield of SO_3 is high. At high temperatures, the rate of reaction is high

but the yield of SO_3 is low. A compromise temperature is chosen such that both the rate and yield are high. An optimum temperature of between 400°C - 500°C is used.

Pressure effect

The forward reaction occurs with decrease in volume and theoretically it is favoured by use of high pressure. A high pressure the cost of equipment and running cost are high. Therefore a compromise pressure of about 1-3 atmospheres is used.

catalytic effect

The rate at which equilibrium is attained is increased by use of catalyst. The catalyst used here is vanadium (V) oxide, V_2O_5 .

Concentration effect

The yield of SO_3 may be increased by

Increasing the concentration of either SO_2 or O_2 . Use of excess air is less expensive.

By constantly removing the SO_3 as soon as it is formed

CONVERSION OF SO_3 TO SULPHURIC ACID

The SO_3 obtained is then converted to H_2SO_4 by

Dissolving it directly in water.

$\text{SO}_3(g) + \text{H}_2\text{O}(l) \xrightarrow{\hspace{1cm}} \text{H}_2\text{SO}_4(aq)$

This reaction is so exothermic that it causes sprays of the acid and hence loss of the acid and is not preferred.

Dissolving in Conc. H_2SO_4 and then diluting the oleum formed

$\text{H}_2\text{SO}_4(aq) + \text{SO}_3(g) \xrightarrow{\hspace{1cm}} \text{H}_2\text{S}_2\text{O}_7(l)$ Oleum (fuming H_2SO_4)

$\text{H}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O} \xrightarrow{\hspace{1cm}} 2\text{H}_2\text{SO}_4(aq)$

The H_2SO_4 OBTAINED BY THIS METHOD IS 98 CONC.

Uses of sulphuric acid

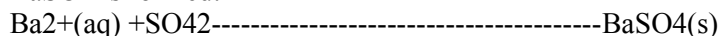
- In the manufacture of fertilizers. e.g. NH_4SO_4 obtained by this method is 98% conc.
- In the manufacture of paints and pigments
- In the manufacture of detergents
- In the manufacture of chemicals
- In the manufacture of synthetic fibres

Test for sulphate ion, SO_4^{2-}

Addition of Barium Chloride or nitrates solution

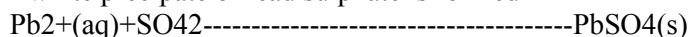
To the solution suspected to contain SO_4^{2-}

Is added to dilute HCL OR HNO_3 followed by the reagent. A white precipitate of BaSO_4 is formed.



Lead elthanate solution or lead nitrate solution

A white precipitate or lead sulphate is formed

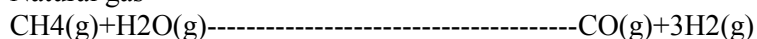


MANUFACTURE OF AMMONIA (HABER PROCESS)

RAW MATERIALS (SOURCE)

The raw materials used in this process are nitrogen and hydrogen. The hydrogen may be obtained from

Natural gas



Water gas i.e. a mixture of CO and H_2 . Nitrogen is from air. The gases obtained are then purified and then passed over heated catalyst.



Temperature effect

The forward reaction is exothermic and hence by Van't Hoff principle, it is favoured by use of low temperature. But at low temperature, the rate at which equilibrium is reached is slow. Therefore an optimum temperature of about 550°C is used where the rate and yield of NH_3 is high.

PRESSURE EFFECT

The forward reaction occurs with decrease in volume and thus theoretically favoured by use of high pressure. Use of high pressure is expensive and therefore a pressure of between 150-350 atmospheres is used.

Catalytic effect

The yield of NH_3 can be increased by:

Increasing the conc. of either H_2 or N_2 . Practically excess air is used since it is cheap.

constantly removing the NH_3 as soon as it is formed.

Note (i) With all the above conditions only 30% of the gases combine. The mixture of unreacted gases are then recycled.

A graph of percentage yield of NH_3 at different temperature and pressure

From the graph, yield of ammonia is favoured by use of low temperature and pressure of between 150-350 atmospheres.

The ammonia obtained above is either liquidified or dissolved in water

Uses of ammonia

In the manufacture of fertilizer for example NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$

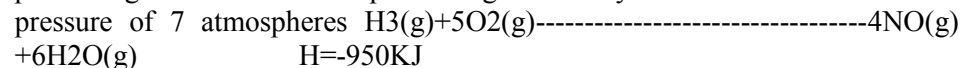
In the manufacture of nitric acid

In the manufacture of nylon

Manufacture of nitric acid

The manufacture of nitric acid involves three stages

Catalytic oxidation of ammonia to nitrogen oxide. Here dry ammonia is passed together with air over platinum gauze catalyst heated to 900°C and at a pressure of 7 atmospheres



Oxidation of nitrogen oxide to nitrogen dioxide

NO formed on cooling rapidly combines with air forming NO_2



Nitric acid is used for making of explosives and dyes

Fertilizers e.g. NH_4NO_3

Properties of Nitric acid

AS AN ACID

HNO_3 REACTS WITH ALKALIS, METAL OXIDE, METAL CARBONATES AND METALS.



$\text{NO}_3(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}(\text{NO}_3)_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 $\text{PbCO}_3(\text{s}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Pb}(\text{NO}_3)_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
 $\text{Mg} + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Mg}(\text{NO}_3)_2(\text{aq}) + \text{H}_2(\text{g})$
Dilute HNO_3 react with Cu forming NO
 $\text{Cu}(\text{s}) + 4\text{HNO}_3(\text{aq}) \rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{NO}(\text{g})$
With concentrated HNO_3 copper forms NO_2
 $\text{Cu}(\text{s}) + 4\text{HNO}_3(\text{aq}) \rightarrow \text{Cu}(\text{NO}_2)_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
As an oxidizing acid
Oxidising green iron(II) sulphate to yellowish brown Iron (III) sulphate
 $\text{HNO}_4(\text{aq}) + 3\text{H}_2\text{SO}_4(\text{aq}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
----- HNO_3 Oxidises C and P to CO_2 and H_3PO_4 respectively.
 $\text{C} + 4\text{HNO}_3(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 4\text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
 $5\text{HNO}_3(\text{aq}) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5\text{NO}_2 + \text{H}_2\text{O}(\text{l})$
Testing for nitrate ion, NO_3^-
a) Brown ring test
b) To the solution of the NO_3^- is added iron (II) sulphate solution followed by conc. H_2SO_4 down the side of the tube.
c) A brown ring forms at the junction of the two liquids
d) Use of copper turning and conc. H_2SO_4

Addition of copper turning and conc. H_2SO_4 to the solid nitrate. Brown fumes and blue solution is formed on heating.

Manufacture of chlorine and sodium hydroxide

Chlorine and sodium hydroxide are manufactured by electrolysis of a concentrated solution of sodium chloride by Castner-Kellner process.

Here a saturated solution of sodium chloride flows through the cell (figure below) in the same direction as stream of mercury which constitutes the cathode. The anode is made of several graphite blocks.

Reactions

$\text{NaCl}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
----- $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

Cathode

$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$

Na^+ is discharged in preference to H^+ because of its concentration.

Anode

$2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

Therefore chlorine is produced at the carbon anodes and is collected and liquified.

At the cathode sodium is produced and it dissolves in the mercury forming sodium amalgam. The sodium amalgam is passed through water where sodium reacts to form sodium hydroxide.

$2\text{Na}(\text{s}) + \text{Hg} + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g}) + 2\text{Hg}(\text{l})$

Note: Sodium Hydroxide is also manufactured on an industrial scale by the electrolysis of brine in a diaphragm cell.

This cell consists of two compartments which are separated by a porous asbestos diaphragm.

Graphite rods act as the anode in one compartment (anode) while the other compartment consists of steel cathode.

Brine is allowed to continuously flow into the cell through an inlet at the top of the cell.

Ions present

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

$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

Reactions

At cathode $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

At cathode $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

Chlorine gas liberated at the anode while hydrogen gas is liberated at the cathode. This leaves Na^+ and OH^- behind which now seep through the porous asbestos and form sodium hydroxide.

The dilute solution of sodium hydroxide contaminated with sodium chloride is first concentrated and then separated from sodium chloride by fractional crystallization.

Note :

Chlorine in the lab can be made by oxidation of conc. HCl with MnO_2 or KMnO_4
 $\text{MnO}_2(\text{s}) + 4\text{HCl}(\text{aq}) \rightarrow \text{MnCl}_2$

$(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{Cl}_2(\text{g})$

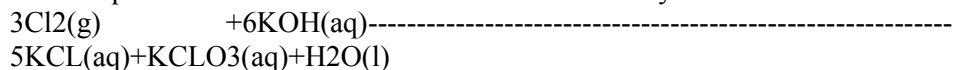
$\text{KMnO}_4(\text{s}) + 16\text{HCl}(\text{aq}) \rightarrow \text{KCl}$

$2\text{KCl}(\text{aq}) + 2\text{MnCl}_2(\text{aq}) + 5\text{Cl}_2 + 8\text{H}_2\text{O}$

Chlorine is used as a bleaching agent, disinfectant for domestic water and

manufacture of chemicals e.g CCL₄

Note: Chlorine can be converted to potassium (v) chlorate by bubbling chlorine gas through a warm concentrated potassium hydroxide solution. The pale yellow solution produced contain KCLO₃ And KCL formed by the reaction



This solution is then allowed to cool where KCLO₃ crystallizes out with some little KCL. The crystal are then dissolved in warm water and the process of crystallization repeated until pure KCLO₃ crystals are formed.

Manufacture of sodium carbonate

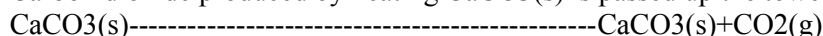
Raw materials are (i) sodium chloride

(ii) Calcium carbonate

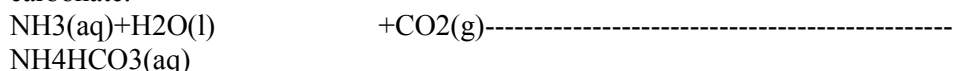
(iii) Ammonia

Sodium carbonate is industrially manufactured by solvay process. In this process, a saturated solution of sodium chloride (brine) saturated with ammonia is allowed to trickle down a tower fitted with perforated mushroom shaped baffles at intervals.

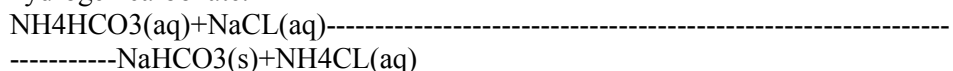
Carbon dioxide produced by heating CaCO₃(s) is passed up the tower



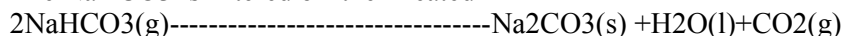
The CO₂ react with ammonia solution producing ammonium hydrogen carbonate.



The NH₄HCO₃(aq) produced then reacts with the brine to precipitate sodium hydrogen carbonate.

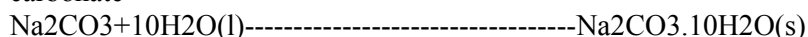


The NaHCO₃ is filtered off then heated



Note

The anhydrous sodium carbonate on crystallization produces hydrated sodium carbonate



Na₂CO₃ · 10H₂O(l) is efflorescent i.e on left standing in air for long it reverts to powdered Na₂CO₃.

Sodium carbonate is used in making of glass and for softening water.

Fertilizers

Fertilizers are compounds that contain plant nutrients and their addition to land increases

Plant nutrients in the soil thus increasing the productive capacity of the land.

There are two types of fertilizers

Natural fertilizer e.g animal and vegetable waste which include dead plants and animals

Artificial fertilizers

Artificial fertilizer mainly provide plants with nitrogen although a balanced diet for plants includes also phosphorous and potassium. The composition of a fertilizer in relation to Nitrogen, Phosphorous and potassium is given by the N.P.K value.

This NPK value shows the amount of N.P.K value. This N P K value shows the amount of N,P,K. Therefore 10-20-20 fertilizer means that it contains 10 % by mass of nitrogen, 20% by mass of P₂O₅ and 20% by mass of K₂O

Good fertilizer should have the following qualities

Should contain a high percentage of the elements required by plants.

Should be cheap and should easily dissolve in rain water.

One disadvantage of very soluble fertilizer (fast acting) is that they are easily washed away by water while a less soluble (slow acting) tends to provide steady and constant supply of nutrients for a long time.

Examples of artificial fertilizers are (NH₄)₂SO₄, NH₄ NO₃, K₂SO₄, Ca₃(PO₄)₂ single super phosphate.

Phosphate.

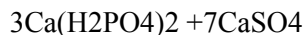
Ammonium sulphate fertilizer is manufactured by passing CO₂ and NH₃ gases through a heated expansion of calcium sulphate. 2NH₃(g) + H₂O(l) + CO₂(g) + CaSO₄(aq) → CaCO₃(s) + (NH₄)₂SO₄(aq)

Ammonia sulphate solution is filtered and then crystallized.

Manufacture of single super phosphate SSP

Stones containing calcium phosphate and calcium fluoride brought from the mine is ground and put in a tank and is then continuously stirred with water to avoid it setting out. This suspension is called slurry. The slurry is then sieved to separate bigger particles from smaller one. Lime is then removed and the resultant product is sent to a floatation tank where sodium C₁₇H₃₃COONa is added as a collecting agent. Here sodium ions adhere to particles containing the calcium salts while the chloride ions go to water.

Air is blown forming a froth where impurities like lime sink to the bottom while particles containing the calcium salts will float where they are removed and treated with sulphuric acid forming Ca(HPO₄)₂ + 7H₂SO₄ →



Disadvantages Of Fertilizers

Large scale use of chemical fertilizers have contributed to environmental degradation and excess fertilizers have contaminated rivers, well and lakes causing death to some water bodies like fish.

Phosphate fertilizers cause growth of planktons and algae which deprive water bodies of air (i.e reduces oxygen content in water) leading to death of aquatic bodies.

CHAPTER 9

APPEARANCE

Always note the physical properties of the substance e.g appearance, colour, smell and solubility in water. The deductions below may be guide as to the substance present but do not constitute proof.

Observation

Inference

Red colour
Orange-red colour
Purple colour
Pink colour
Yellow colour
Green colour
Blue colour
Brown colour
Black colour

Smell of ammonia

Smell of hydrogen Sulphide

Smell of sulphur dioxide

Oxide of metal

Dichromate

Permanganate

Hydrated Salts of Manganese

----- or ferric salt Dilute Hydrochloric (or sulphuric acid)

Ferrous, copper, nickel or chromic salt Add dilute acid to the solid. If there is no reaction always warm gently.

HYDRATED CUPRIC SALTS Identify any gas as evolved. The formation of a clear solution indicates the

Metals oxide

Oxide or Sulphide ABSENCE of insoluble metal chlorides (or sulphate)

Ammonium salt

Sulphide

Sulphate

Heating in a closed tube

Heating a small quantity of the solid in a dry hard glass test tube until no further change occurs. Identify any gases by their smell, colour, action on litmus, action on splint and their usual confirmatory tests. Always observe the residue.

Observation

Influence

Water
Carbon dioxide
Oxygen
Nitrogen dioxide and oxygen
Nitrous oxide (rekindles a glowing splint)
Sulphur dioxide
Ammonia
Hydrogen chloride
Hydrogen Sulphide
Chlorine
Bromine
Iodine
White sublimate
Residue
Yellow hot, white cold
Brownish hot, Yellow brown cold
Black hot reddish brown cold

Hydrated salt
Carbonate, Bicarbonate or
Chlorate, higher oxide or
Nitrate other than of sodium
Ammonium nitrate or nitrite
Normal and acid sulphate.
Ammonia salts
Certain hydrates chloride
Hydrogen Sulphide
Unstable chloride e.g. of
Source similar to chlorine
Free iodine and certain iodides
Ammonium salt.

Zinc oxide
Lead monoxide
Ferric oxide

Observation

Influence

Solids dissolve, no gas evolved
Yellow solid dissolves giving orange solution
White precipitate
Solid dissolves giving smell of acetic acid
Carbon dioxide

BASIC OXIDE
CHROMATE
INSOLUBLE CHLORIDE
ACETATE
CARBONATE OR BICARBONATE

Nitrogen dioxide
Chlorine
Sulphur dioxide
Hydrogen Sulphide

NITRITE
HYPOCHLORITE
SULPHITE
SULPHIDE

On the addition of dilute hydrochloric acid and then heating only BARIUM SULPHATE is

Concentrated sulphuric acid

This Test must be done carefully. If nothing happens, in the cold, warm the mixture carefully. Substances which gave gases with dilute acid will also produce the same gases with this reagents. If hydrogen Sulphide or sulphur dioxide were not given with the dilute acid, these gases must be ignored in this test, as they have probably been produced by a redox reaction, sulphur may also be produced by this reaction.

Observation

Inference

Hydrogen chloride
BROMINE AND HYDROGEN BROMIDE
Iodine and hydrogen Iodide
Nitrogen dioxide and yellow droplets on side of tube
Carbon dioxide and carbon monoxide

CHLORIDE
BROMIDE
IODIDE
NITRATE
OXALATE

BARIUM CHLORIDE SOLUTION

This test gives precipitation of insoluble barium salts.

Observation

Inference

White precipitate

CARBONATE
OXALATES
THIOSULPHATE (from conc. solution)
ORTHOSULPHATE
SULPHITE (on standing oxidised to sulphate)
SULPHATE
CHROMATE

Yellow precipitate

SILVER NITRATE SOLUTION

This test gives precipitate of insoluble silver salts

Observation

Inference

White precipitate

Oxalates
ACETATES (from conc. Solution)
SULPHATES (from conc. Solution)
NITRITES (from conc. solution)
Chloride
SULPHIDE (soluble in excess on boiling gray metallic silver)
CARBONATE (precipitate turns yellow with excess reagent of CO₂)
CHROMATE (OR DICHROMATE BROMIDE
IODIDE or ORTHOPHOSPHATE

Red precipitate

Creamy precipitate

Yellow

N.B On the addition of dilute nitric acid, and then heating, only silver halides are insoluble.

Sodium Hydroxide solution

This reagents precipitate insoluble hydroxides. The amphoteric hydroxides will redissolve in excess of the reagent

Cation

A few drops

NH₄⁺

Ba⁺⁺

Mg⁺⁺

Ca⁺⁺

Mn⁺⁺

Al⁺⁺⁺

Zn⁺⁺

Pb⁺⁺

Excess

No precipitate

No precipitate

White precipitate

White precipitate from conc. Solution

White precipitate H₂O₂

White precipitate

White precipitate

white precipitate

Ammonium

Insoluble

Insoluble

Insoluble

Soluble

Soluble

Soluble

Cr+++	Green precipitate
Fe++	Green precipitate
Ni++	Green precipitate
Fe+++	Brown precipitate
Co++	Blue precipitate
Ag+	Brown precipitate
Cu++	Blue precipitate
Sn2+	White precipitate

AMMONIA SOLUTION

This reagent precipitates hydroxide. In adding excess some cation form soluble MMINE complexes
NH+

Ba++	Milkiness
Ca++	No precipitate
Mg++	White precipitate
Al+++	White precipitate
Pb++	White precipitate
Mn++	White precipitate
Zn++	White precipitate
Fe+++	Brown precipitate
Ag++	Brown precipitate
Fe++	Green precipitate
Ni++	Green precipitate
Cr++	Grey- green ppt
Cu++	blue precipitate
Co++	Blue precipitate
Sn2+	White precipitate

HYROGEN SULPHIDE

Solution of certain metals salts give precipitate of insoluble Sulphide having characteristics colours. Some of these Sulphide are precipitated in acid solution and some in alkaline solution.

Bubble hydrogen Sulphide through a solution of the metal salt which has been acidified or made alkaline in the following way.

1) To the solution ,add dilute hydrochloric acid, and if precipitate forms

Insoluble to give pass H₂S solution

2) To the solution, add solid ammonium chloride, followed by ammonium

Insoluble, turns brown on standing. Then pass H₂S.

Insoluble

Insoluble turn black. Hydrogen sulfide is a very poisonous gas, therefore this test should be carried

Insoluble out in the fume cupboard.

Insoluble, turns black on heating.

Soluble

A few drops

Excess

Fe

No precipitate

Black

Ni++

No precipitate

Black

Zn++

No precipitate

White

Mn++

No precipitate

Pink p

Ag+

Black precipitate

Black

Cu++

Black precipitate

Black

Insoluble

Pb++

Black precipitate

Black

-

Fe+++

Precipitate of sulphur

Insoluble

Mg++

AL++, Ca++, Ba++, Cr+++

Do no

Slightly soluble

Insoluble

PROCEDURE OF CARRYING OUT FLAME TESTS

Soluble ,turns brown on standing

Soluble Some metal ions impart characteristic colour to a flame when their salts are

In Soluble treated in the following manner.

Soluble clean a nichrome (or platinum) wire by dipping it in conc.Hcl and holding it in

In Soluble ,the flame of a Bunsen burner until no additional colour is produced. Then dip the

Soluble, forming pink or violet solution

Slightly soluble forming pink or violet solution

Soluble forming deep blue solution

Soluble turning pink

FLAME COLOUR

Lead

Bluish white

Copper

Greenish white

Barium

Pale green

Sodium

Yellow

Calcium

Orange red

Potassium

Violet (red through blue glass)

N.B In the absence of nichrome wire (or platinum wire), this test may be carried

out using the tip of a lead pencil.

RECOGNITION OF GASES

Gases are often given off either when a substance is heated or when a reagent reacts with a substance. Four easy tests serve to identify most these gases:

The colour of the gas

The smell of the gas

The action of the gas on a lighted splint

The action of the gas on moist red litmus paper

GAS	COLOUR	SMELL	ACTION ON SPLINT	ACTION ON LITMUS
CL ₂	Greenish bleached	Characteristic Irritating	Extinguished	Red, then
HCL	Colourless Red	Irritating	Extinguished	
NO ₂	Reddish- brown	Irritating	Extinguished	Red
HNO ₃	Pale yellow Vapour fumes	Irritating	Extinguished	Red
SO ₃	White fumes Red	Irritating	Extinguished	
SO ₂	None Red, then lbeached	Rusting sulphur	Extinguished	
H ₂ S	None	Rotten eggs	Burns, blue flame deposits Of sulphur on cold surface	Faint Red
NH ₃	None	Characteristic Choking	Extinguished	Blue
H ₂	None	None in pure	Gas burns with blue flame Explodes if mixed with air	None
O ₂	None	None	Relights glowing splint	Faint Red
CO ₂	None	None	Extinguished	None
N ₂	None	None	Extinguished	None

CONFIRMATORY TESTS FOR SOME GASES

HCL Hold the moist stopper of a conc. Ammonia a bottle in the gas forms dense white smoke of ammonium chloride

SO₂ decolourises dilute KMnO₄ S Solution

CO₂ Wwhite ppt with lime water

NH₃ Turns moisture red limus blue

CONFIRMATORY TEST

SECTION A - ACID RADICALS

1. sulphite

a-Acidified potassium permanganate

the purple solution is decolourised when the reagent is added to a solution of sulphate [Acidify with dilute sulphuric acid].

[b]Acidified potassium dichromate solution

The colour of the solution change from orange to green on addition of the reagent to asolution of sulphate

[c] barium chloride.

Addition of barium chloride solution followed by hydrochloric acid gives a white ppt soluble in the acid [distinction from SO₂-4].

[d]stilver nitrae;

Addition of a solution of SO₂-3 slowly to silver nitrate gives awhite ppt soluble in excess.

NB;both reaction [a]and[b] also occur for any other reducing agent.

[e] zinc in dilute hydrochloric acid from which hydrogen is being evolved.if the solution of sulphate is added to this solution,hydrogen Sulphide is produced which can be detected by the black solution it produces in moistened lead acetate paper.

[f] Iodine solution

Decolourised..

[g] lead Acetate solution [CH₃COO]₂pb

White precipitate soluble in cold nitric acid.on boiling white precipitate of lead sulphate appears.[Ditinction from thiosulphate].

2. thiosulphate

[a] silver nitrate solution

Add solution slowly to silver nitrate solution.A white ppt formed which readily trn brown soluble in excess.

[b] lead acetate solution

White precipitate soluble in excess.on boiling black ppt is form.

[c] ferric chloride solution.Dark violet colouration which disappears after ashot time leaving an almost colourless solution.

Nitriter

[a] Acidified ferrous sulphate solution

Dissolve a few crystals of ferrous sulphate in dilute sulphuric acid and add to a solution of the substance. A brown colouration of $\text{FeSO}_4 \cdot \text{NO}$, which disappears on warming, confirms an nitrite. [Note that the colour is produced with dilute acid. Nitrite only give the colour with concentrated sulphuric acid]. [Add fresh FeSO_4 solution in dilute acid. A brown solution is formed].

[b] Acidified potassium iodide solution To a solution of potassium iodide, add dilute sulphuric acid. Add a few drops of this solution to a solution of unknown. If an nitrate is present, iodine is released, which produces blue colour with starch solution.

[c] Devarda's alloy

Heat a solution of the unknown with sodium hydrogen solution and cool. Add Devarda's alloy and warm gently. Ammonia is given off [nitrite is present].

Devarda's alloy consists of 50 percent Al and 5 percent Zn. Hence, addition of any component of the alloy gives same observation.

Acidified potassium permanganate solution

The purple solution is decolourised.

Ammonium chloride

A solution of nitrite when boiled with excess of solid ammonium chloride evolves nitrogen.

[f] Dilute H_2SO_4

Brown fumes of NO_2 gas [Nitrates do not give this positive test].

Bromine water—decolourisation.

4; Chlorite

[a] Dilute hydrochloric acid

Chlorine gas evolved when reagent is added to a solution of the unknown.

[b] Lead acetate or lead nitrate solution

Brown lead dioxide is produced on boiling. To the solution or suspension add a few drops of cobalt [11] nitrate solution, a black ppt is formed and O_2 evolved.

5; chloride

[a] silver nitrate solution.

Acidify the solution with dilute nitric, then add silver nitrate solution. A white ppt of silver chloride is formed which darkens on exposure to light. The ppt is soluble in ammonia solution.

[b] chromyl chloride test

Mix the dry substance with powdered potassium dichromate, place the mixture in a dry test tube and add a few drops of concentrated sulphuric acid. Chlorine is evolved.

[c] lead ethanoate solution; A white ppt of lead chloride is formed. The ppt

is dissolved on heating and reappears on cooling.

6; Bromides;

[a] silver nitrate solution

Bromides give a pale yellow ppt of silver bromide which is insoluble in nitric but is only soluble with difficulty in ammonia.

[b] Chlorine water

To a solution of the substance, add carbon tetrachloride, followed by chlorine water and shake. On standing, a reddish brown colour due to bromine will be observed in the carbon tetrachloride.

[c] Manganese dioxide and concentrated sulphuric acid

When a mixture of solid bromide and conc. sulphuric acid is warmed, a reddish-brown vapour of bromine is evolved.

(e) Lead acetate solution

White crystalline precipitate sparingly soluble in boiling water.

7. Iodines

(a) Silver nitrate solution yellow precipitate of silver iodine insoluble in dilute nitric acid.

(b) Lead acetate solution

A yellow precipitate of lead iodine is produced which is soluble in hot water and is

c) Chlorine water

To solution, add carbon tetrachloride, followed by chlorine, a brown layer confirms an iodine.

Copper sulphate solution

White precipitate of cuprous iodine coloured brown by free iodine.

NITRATES

a) Addition of conc. Sulphuric acid and copper turnings

A blue solution and brown fumes are formed on standing for 5 to 10 mins

b) Brown ring test

To a solution of the substance, add a solution of ferrous sulphate dissolved in dilute sulphuric acid. Then add conc. Sulphuric acid down the side of the tube. A brown ring at the junction of the two liquids confirms a nitrate. (NB: Do not warm the solution).

c) Devarda's alloy (Cu, Al or Zn powder)

Nitrates in sodium hydroxide solution give ammonia when warmed with Devarda's alloy.

SULPHATE

Barium chloride or Nitrate solution

To a solution of the substance, add dilute hydrochloric, followed by the reagent. A white granular precipitate of barium sulphate is formed.

Insoluble (distinction from SO_2 -3)

Silver nitrate solution

From solution of a sulphate, white precipitate of lead sulphate

ORTHOPHOSPHATE

a) silver nitrate solution

From solution a yellow precipitate of normal silver orthophosphate.

b) Barium chloride solution

From solution. White amorphous precipitate of barium phosphate

c) ammonium molybdate reagent

The addition of large excess (2-3ml) of this reagent to a small volume (0.5ml) of a phosphate solution produces a yellow crystalline precipitate. Before using this reagent, it is necessary that it is acidified with nitric acid. The precipitate forms slowly in the cold but rapidly if the mixture is warmed to a temperature not

d) Ferric Chloride Solution

From solution, A yellow precipitate of ferric phosphate, solution in dilute mineral acids but not in acetic acid.

11. CHROMATES

a) Barium chloride solution

Pale yellow precipitate of barium chromate from solution of the unknown.

b) Silver nitrate solution

From solution, a brownish-red precipitate of silver chromate.

C) Lead Acetate solution

From solution of a yellow precipitate of lead chromate.

d) hydrogen peroxide

If an acid solution of a chromate is treated with this reagent a deep blue solution is formed which soon decomposes, yielding oxygen and a green solution. Acidify the solution with dilute sulphuric or nitric acid.

Concentrated Hydrochloric acid

On heating a solid chromate with this reagent chlorine is evolved.

ACETATES

Action of heat

All acetates decomposed upon strong ignition, yielding the highly inflammable acetone and a residue, which consists of the carbonates for the alkali acetates, or the oxides for the acetates of alkaline earth and heavy metals or the metal for the acetates of silver and the noble metals

Dilute sulphuric acid or dilute hydrochloric acid

Warm solid with dilute acid, smell of acetic acid (ethanoic acid)

Ethyl Alcohol and concentrated sulphuric acid

The solid is treated with concentrated sulphuric acid and ethanol in a test tube, and then gently warmed for several minutes. The pleasant fruity odour of ethyl acetate is formed. On cooling and dilution with water on a large glass, the fragrant odour will be more readily detected.

Silver Nitrate solution

From concentrated solution, A white crystalline precipitate of silver acetate

Ferric chloride solution

From neutral solution, a deep red colouration is formed. On diluting and boiling, a red precipitate forms. The red colouration is destroyed by dilute hydrochloric acid.

(ethanedioates)

Action of Heat: All oxalates decompose upon ignition. Those of the alkali metals and of the alkaline earth yield chiefly the carbonates and carbon dioxide.

The oxalates of metals where carbonates are easily decomposed into stable oxides are converted into carbon dioxide each

Concentrated sulphuric acid

Decomposition of all solid oxalates occurs with the evolution of carbon monoxide and carbon dioxide.

Silver Nitrate solution

From solutions. White precipitate of silver oxalate.

Barium chloride or nitrate solution

From solutions, white precipitate of silver oxalate.

Acidified potassium permanganate solution

When warmed to about 60°C , the purple colour of the reagent is discharged and carbon dioxide is evolved. Acidity with dilute sulphuric acid.

Manganous sulphate test

To manganous sulphate solution, add dilute sodium hydroxide solution and warm gently. Add this to a solution of the substance acidified with dilute sulphuric acid. The precipitate dissolves leaving a red colour.

METALLIC RADICALS

SECTION B

Lead

- a) Dilute sulphuric acid

From solution, white precipitate of lead sulphate.

- b) Dilute Hydrochloric acid

from solution, white precipitate, soluble in boiling water.

Potassium Iodide solution

From solutions, a yellow precipitate, soluble in boiling water giving golden yellow plates on cooling.

Potassium chromate solution

From solution, a yellow precipitate of lead chromate.

SILVER

Dilute Hydrochloric acid

From solutions a white curdy precipitate of silver chloride.

Potassium Iodine solution

From solution, a yellow precipitate silver chloride

Potassium chromate solution

from solutions, a red precipitate is produced.

Copper

Potassium ferrocyanide solution

FROM SOLUTIONS, AREDDISH – BROWN PRECIPITATE IS FORMED.

SOLUBLE IN NH_4OH

Potassium Iodide solution

From solutions, a white precipitate, stained brown by free iodine, is formed.

Flame Test- A blue – green flame is produced.

IRON

FERROUS COMPOUNDS

- A) From solution white precipitate, which rapidly becomes green on addition of ammonia solution.
B) Potassium ferric cyanide solution
From solution, a dark blue precipitate, Prussian blue.
C) Potassium thiocyanide solution

FERRIC COMPOUNDS

- a) Potassium Ferrocyanide solution

From solution, a deep blue precipitate

- b) Potassium Ferricyanide solution

From solutions, a brown colouration is formed.

- c) Potassium Thiocyanate solution

From solution, a deep blood red colouration is formed.

- d) Sodium Phosphate solution

From solution, yellowish- white precipitate is formed.

ALUMINIUM

Sodium phosphate solution

From solution, a white precipitate is formed

Sodium carbonate solution

From solutions, a white precipitate of aluminium hydroxide soluble in excess.

Aluminium Reagent

Acidify the solution of the suspected Aluminium salt with dilute hydrochloric acid.

Then add four drops of Aluminium reagent followed by sodium hydroxide solution drop-wise. A pink “Lake” is formed.

Chromium

- a) Sodium phosphate solution

From solution, a green precipitate is formed

- b) Oxidation to chromate Test

- c) To the chromic salt add excess sodium hydroxide solution and a few mls of 20 Volume of hydrogen peroxide and boil the resulting mixture for a few minutes. At this stage, a yellow solution should be produced which is a chromate. The chromate can be identified by the following tests.

- d) Acidify with acetic acid and add barium chloride and solid potassium persulphate and boil the mixture. A reddish violet solution is formed.

- e) The solution is acidified with dilute sulphuric acid and solid potassium periodate is added. The solution is then boiled for 1 minute. A reddish violet solution is formed.

- f) 1-Butanol

- g) The solution is added excess sodium hydroxide followed by 5 cm of H_2O and the mixture boiled and cooled. The 0.5 cm³ of butanol followed by 2-3 drops of dilute H_2SO_4 . The mixture is shaken and left to stand. A blue colour appears in the organic layer.

ZINC

a) SODIUM PHOSPHATE SOLUTION:

Add ammonium chloride followed by the reagent. A white precipitate is produced.

b) potassium ferrocyanide solution

From solution, a white precipitate is formed, soluble in caustic alkalis.

c) Ammonium Sulphide-white ppt soluble in dilute hydrochloric acid.

8; Barium

a) Ammonium carbonate solution

From solution, a white precipitate is formed.

b) Ammonium oxalate solution

From solution, a white precipitate, soluble in hot diluted acetic acid. (Distinction from calcium)

c) Dilute sulphuric acid

From solution, a white precipitate of barium chromate

d) Flame test

A green flame is produced.

9; calcium

a) Ammonium carbonate solution

From solution a white precipitate of calcium carbonate

b) Ammonium Oxalate solution from solution, white precipitate of calcium oxalate. This precipitate is insoluble in hot dilute acetic acid. (distinction from barium)

c) Potassium chromate solution

No precipitate, (Distinction from Barium)

d) Potassium Ferrocyanide solution

Add ammonium chloride followed by the reagent: a white precipitate is formed.

e) Dilute sulphuric acid

From concentrated solution, white precipitate of calcium sulphate.

Magnesium

Ammonium Carbonate solution

From solution, a white precipitate of magnesium carbonate often only on boiling or on long standing.

Sodium carbonate solution

From solution, white precipitate of basic carbonate.

Sodium phosphate solution

To the solution add ammonia solution and ammonium chloride solution. Then add the reagent. A white crystalline solid is formed

Magnesium Reagent

Acidify the solution with dilute hydrochloric acid and then add 4 drops of the reagent. Add sodium hydroxide solution so that the solution becomes alkaline, a blue precipitate is formed.

The Ammonium Radical

a. Sodium Cobaltinitrite solution

A yellow precipitate.

b) Sodium Hydroxide solution

No observable change occurs but on warming ammonia gas is given off.

Cobalt

a) Potassium Cyanide

Reddish brown precipitate soluble in excess.

Potassium thiocyanate

A blue solution formed.

Potassium nitrite

A yellow crystalline ppt of potassium cobalt nitrite formed in the presence of ethanoic acid.

NICKEL

Potassium cyanide

A yellowish-green ppt of $\text{Ni}(\text{CN})_2$ dissolves in excess to form a dark yellow solution of potassium nickel cyanide $\text{K}_2\text{Ni}(\text{CN})_4$.

Dimethylglyoxime

To the solution is added ammonia followed by the reagent. A red ppt is formed.

ANALYSIS OF A SINGLE SALT

Qualitative analysis of a single salt may be divided into 4 parts

Preliminary tests

Identification of the anion

Making a solution of the salt

Identification of the cation.

Preliminary tests

Preliminary tests are used to give general pointers to the analysis of salt.

Appearance- Observe the colour, the nature of the solid (large small crystals or powder) and whether it appears to be deliquescent.

Action of heat- heat a small portion in test tube at first gently, then strongly. Observe colour changes and try to identify the gases or vapours evolved.

iii) 2M sodium hydroxide

- Observe colours change or precipitate.
- Warm the mixture and test for ammonia = gas. It indicates presence of NH_4^+

Making a salt solution

This part of the analysis must be handled carefully. The only solvent used should be water always. If the salt is insoluble in water, try 2 M nitric acid, 2 M hydrochloric or conc. HCl or Conc HNO_3 with warming if necessary.

When a suitable solvent is found, make up a solution for the identification of the cation and anion.

Note: If heating was required for the dissociation of the salt, first cool the solution before starting the group tests.

CONFIRMATORY TESTS

Group Test

CATIONS

- Cu^{2+} -----Add 2M NH_4OH in excess: deep blue solution
- Pb^{2+} ----Add potassium chromate : Yellow precipitate
- Al^{3+} ----Add 1 drop Aluminium reagent (alizarin solution) and 2 M NaOH : pink lake.
- Cr^{3+} ---Add H_2O_2 and 2M NaOH : yellow colour
- Fe^{3+} ----Add potassium hexacyanoferrate (ferrocyanide) dark blue ppt (Turnbull's blue).
- Fe^{2+} ---Add potassium hexacyanoferrate (Ferric cyanide) dark blue ppt (Prussian blue)
- CO_3^{2-} ----conc HCl: blue colour, pink on adding H_2O
- Ni^{2+} ----Add 2 M NH_4OH and dimethylglyoxime solution; pink solution
- Zn^{2+} ---Add 2 M NH_4OH white ppt soluble in excess
- Mn^{2+} ----add HNO_3 and sodium bismuthate: purple solution.
- Ba^{2+} ----add potassium chromate solution: yellow ppt insoluble in ethanoic acid
- Ca^{2+} -add potassium chromate: no precipitate
- Mg^{2+} add magneson and 2M NaOH : sky- blue lake

IDENTIFICATION OF ANIONS

The anions are divided into three categories

- those that involve gases or volatile liquids with 2M HCl E.G HCO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , NO_2^- , CH_3COO^- , CO_3^{2-} .
- THOSE THAT DONOT REACT with 2M HCl but do evolve gases or volatile liquids with conc. H_2SO_4 E.g NO_3^- , HALIDES OXIDES, FORMATES.

- Those that neither react with 2 M HCl nor conc. H_2SO_4 e.g SO_4^{2-} , PO_4^{3-} , CrO_4^{2-} .

Schemes used for analysis of a single salt

a note the physical appearance of the salt.

b heat the solid

c test the solid with dilute HCl

d if no reaction occurs in c, THEN TEST THE SOLID WITH CONC. SULPHURIC ACID.

E if test d is also negative, test now for the presence of SO_3^{2-} , or PO_4^{3-} .

F Proceed from test c, d, e, which was positive to confirm the anion by carrying out further tests.

G Test the solution with sodium hydroxide . this is to give an indication as to which cation is present.

H Carry out further tests to confirm the cation.

APPENDIX

Determination of amount of T in alloy of tin e.g solder

Method

Here a fixed mass of the alloy is dissolved in an excess of hydrochloric acid. The solution is then made up of 250cm³ with distilled water. A aliquot portions of the resultant solution is then titrated with a standard solution of potassium dichromate.

Question;

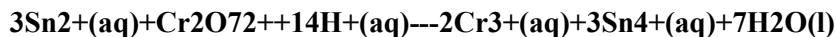
2.8g of solder containing tin was dissolved in excess HCl and the solution made up to 250cm³. if 25.0cm³ of the resultant required 26.2cm³ of 0.01M Potassium dichromate solution, calculate the percentage of tin in the alloy solder.

Solution. Equation of reaction

Reduction half equation is $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

Oxidation half equation is $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$ (ii)

Overall equation is obtained by multiplying equation (ii) by 3 then add to equation I to become



1000 cm³ of Cr₂O₇²⁻ solution has 0.01 moles of Cr₂O₇²⁻

26.2 cm³ Cr₂O₇²⁻ solution has $0.01 \times \frac{26.2}{1000}$ mole of Cr₂O₇²⁻
 $= 0.000262$

Since the mole ratio is 3 moles of Sn²⁺ to 1 MOLE OF Cr₂O₇²⁻
 Number of mole of Sn²⁺ that reacted = 0.000262×3
 $= 0.000786$ moles

25 cm³ of solder solution contain 0.000786 mole of Sn²⁺
 250 cm³ solder solution contain $0.000786 \times \frac{250}{25}$
 $= 0.00786$

Mass of Tin = $0.00786 \times \text{R.F.M of Tin}$
 $= 0.00786 \times 119$
 $= 0.935$ g

Percentage of Tin in the solder = $\frac{0.935}{2.8} \times 100$
 $= 33.4\%$

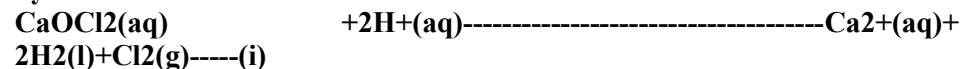
12 Determination of the percentage of available chlorine in the bleaching powder

Method: A fixed mass of bleaching powder is rubbed with water as much as possible and then diluted to 250 cm³. The mixture is then shaken and quickly aliquot portions are pipetted and added to an excess of potassium iodine solution acidified with ethanoic acid. The iodine liberated is now titrated with a standard solution of sodium thiosulphate.

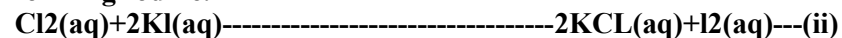
Question 1.2 of bleaching powder was ground up with water and the whole was made up to 250 cm³. 25.0 cm³ of this solution were added to an excess of potassium iodide solution acidified with ethanoic acid and required 22.3 cm³ of 0.05 M sodium thiosulphate solution. Calculate the percentage of available chlorine in bleaching powder.

SOLUTION

In the presence of acid (ethanoic acid), bleaching powder releases chlorine by the reaction.



The chlorine produced by the reaction above now displaces from KI solution forming Iodine.



The iodine produced then reacts with sodium thiosulphate by the equation.
 $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{I}^-$ (aq) (iii)

Note : Amount of chlorine produced by reaction (i) produces the same number of moles of I₂ in equation (ii)

1000 cm³ of S₂O₃²⁻ solution has 0.05 mole of S₂O₃²⁻

22.3 cm³ of S₂O₃²⁻ solution has $0.05 \times \frac{22.3}{1000}$ mole of S₂O₃²⁻
 $= 0.001115$ mole.

Since moles of I₂ that reacted = $\frac{1}{2} \times 0.001115$
 $= 0.0005575$ mole of I₂

25 cm³ of bleaching powder solution contain
0.0005575 mole of I₂

250 cm³ of the solution contain $0.0005575 \times \frac{250}{25}$ mole of I₂
 $= 0.005575$

Of mole of Cl₂ present in 250 cm³ of the solution
0.005575 mole

Mass of chlorine = 0.005575×71
 $= 0.3958$ g

Percentage of available chlorine = $\frac{\text{Mass of Cl}_2}{\text{Mass of bleaching powder}} \times 100$
 $= \frac{0.3958}{1.2} \times 100$
 $= 32.98\%$

1.3 Determination of the percentage of available chlorine in liquid

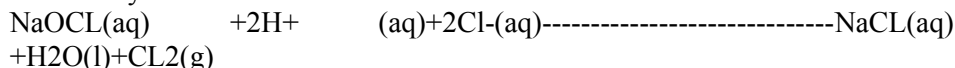
BLEACHES FOREXAMPLEJIK

Method: Here affixed volume of the original liquid bleach (jik) is measured and then diluted to 250cm³ with distilled water. Aliquoot portions of the solution is pipetted and added to an excess of potassium iodide solution acidified with ethanoic acid. The iodine liberated is then titrated with a standard solution of sodium thiosulphate.

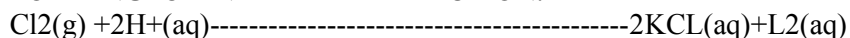
QUESTION: 10CM³ OF JIK was measured and then diluted to 250cm³ in avolumetric flak 25.0cm³ of this solution was pipetted and added to excess of potassium iodine acified with ethanoic acid and required 20.4 cm³ of 0.1M sodium thiosulphate solution.

Calculate the percentage available chlorine

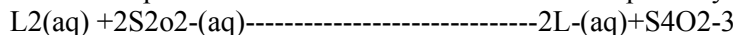
SOLUTION Jik which contains sodium hypochlorite on acidifying produces chlorine by the reaction.



The chlorine produced above then displaces Iodine from KI SOLUTION FORMING IODINE BY THE TREACTION.



The iodine produced then reacts with sodium thiosulphate by the reaction.



1000cm³ of S₂O₃²⁻ solution contain 0.1 mole of S₂O₃²⁻

20.4 cm³ S₂O₃²⁻ solution contain 0.1 X 20.4 mole of S₂O₃²⁻

$$\frac{1000}{0.00004 \text{ mole}}$$

$$0.00004 \text{ mole}$$

Since ratio is 1 mole of L₂ to 2 moles of S₂O₃²⁻

No of moles of L₂ that reacted = 1/2 X 0.00204

25cm³ of solution contain 0.00102 x 250 mole of l₂

$$\frac{25}{0.0102}$$

$$= 0.0102$$

Since 1 mole of Cl₂ produced displaces 1 mole of L₂

No of Cl₂ produced = 0.0102 mole

Mass of chlorine = 0.0102 x 71

$$= 0.724\text{g}$$

Percentage of available chlorine = Mass of Cl₂ X 100

Volume of Jik used.

$$\frac{0.724 \times 100}{0.724 \times 100}$$

$$\frac{10}{= 7.24\%}$$

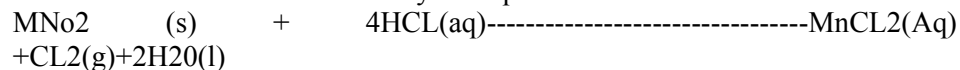
1.4 DETERMINATION OF THE PERCENTAGE OF MNO₂ IN PYROLUSITE

Method: A fixed mass of the impure sample of MnO₂ (pyrolusite) is weighed and then added to an excess of potassium iodide solution. An excess of conc. Hydrochloric acid is added and the mixture heated. The mixture is then diluted to 250cm³. The iodine produced is then titrated with a standard solution of sodium thiosulphate.

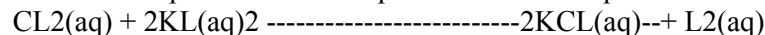
Question 2.30g of an impure sample of manganese (iv) oxide were heated with an excess of potassium iodide and con. Hydrochloric acid. The mixture was the made to 250 cm³ of this solution required 30.6 cm³ of 0.1m sodium thiosulphate solution. Calculate the percentage of MnO₂ in the pure sample.

SOLUTION;

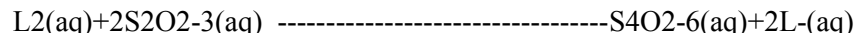
Mno₂ Oxidises warm conc. HCL by the equation.



The chlorine produced then displaces iodine from potassium iodide.



The iodine then reacts with S₂O₃²⁻ as



100cm³ of S₂O₃²⁻ solution contain 0.1 mole of S₂O₃²⁻

30.6 cm³ S₂O₃²⁻ solution contain 0.1 x 30.6 mole of S₂O₃²⁻

$$\frac{1000}{0.00306 \text{ mole}}$$

$$= 0.00306 \text{ mole}$$

===== of mole of L₂ that reacted = 1/2 x 0.00306

$$= 0.00153 \text{ mole of L}_2$$

Cm³ of Mno₂ solution produced 0.00153 mole of l

250cm³ MnO₂ solution produced 0.0153 moles of L₂

Since 1 mole of Cl₂ produces 1 mole of L₂

NO. of mole of Cl₂ = 0.0153 mole

Since 1 mole of MnO₂ produces 1 mole of Cl₂

No of mole MnO₂ = no. of mole of Cl₂

$$= 0.0153 \text{ mole}$$

Mass of MnO₂ = 0.0153 x 87

$$= 1.33\text{g}$$

Percentage of MnO_2 = $\frac{\text{mass of pure MnO}_2 \times 100}{\text{Mass of impure sample}}$

$$\frac{1.33 \times 100}{2.3} = 57.9\%$$

QUESTION

- Outline the steps leading to the formation of concentrated sulphuric acid
- A concentrated solution of sulphuric acid contains 70% H_2SO_4 has a density of 1.6 g cm^{-3}
 - Calculate the molarity of the acid solution
 - What volume of the acid is required to make 1 dm^3 of 0.02 M sulphuric acid.
 - Calculate the volume of the 0.02 M sulphuric acid needed to neutralize 25.0 cm^3 of 0.025 M sodium hydrogen carbonate

(c) 25.0 cm^3 of mixture of two salts containing sodium carbonate and sodium hydrogen carbonate required 11.20 cm^3 of 0.02 M sulphuric acid using phenolphthalein indicator and further 28.6 cm^3 of 0.02 M sulphuric acid using methyl orange indicator. Calculate the concentration in grams per litre of

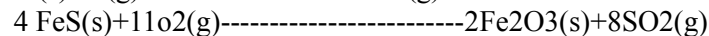
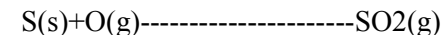
Sodium carbonate

Sodium hydrogen carbonate

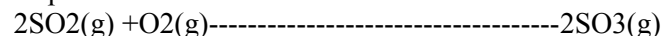
Solution

Sulphuric acid is manufactured industrially by the contact process. The raw materials used are sulphur dioxide and oxygen.

Sulphur dioxide is obtained by either burning sulphur or burning iron pyrite i.e.



The raw materials are then purified and then passed over vanadium pentoxide catalyst heated to about 450°C under pressure where they react to form sulphur trioxide



The sulphur trioxide is then dissolved in concentrated sulphuric acid to form oleum



The oleum is then diluted to give 98% concentrated sulphuric acid
 $\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2\text{SO}_4(\text{aq})$

(i) Density of pure $\text{H}_2\text{SO}_4 = 1.84 \text{ g cm}^{-3}$

1 cm^3 of solution has mass of 1.12 g

1000 cm^3 solution has mass 1.12×1000

Mass concentration = 1120

Molarity = $\frac{\text{Mass concentration}}{\text{Molar mass}} = \frac{1120}{98}$

Molar mass = 98

11.42 M

Or 70% H_2SO_4 by mass means in 100 g of acid the mass of pure H_2SO_4 is 70 g

$$\text{No of moles in } 70 \text{ g} = \frac{70}{98} = 0.714$$

R.F.M = 98

$$\text{Volume of acid} = \frac{\text{Mass of acid}}{\text{density}} = \frac{100}{1.6} = 62.5 \text{ cm}^3$$

$$= 0.0625 \text{ dm}^3$$

Molarity of acid = $\frac{\text{no. of mole of H}_2\text{SO}_4}{\text{Volume}}$

$$\frac{0.714}{0.0625} = 11.42 \text{ M}$$

(II) 11.42 moles are in 1 dm^3 of solution

0.02 mole is in 1×0.02

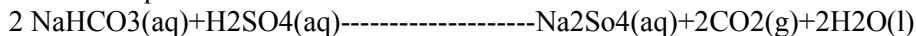
11.42

0.00175 dm^3

0.175 cm^3

$$\text{No. of mole of NaHCO}_3 = \frac{25 \times 0.25}{1000} = 0.00625$$

From the equation



Since ratio is 2:1

$$\text{No of mole H}_2\text{SO}_4 \text{ reacted} = \frac{2}{2} \times 0.00625 = 0.003125$$

0.02 mole of H_2SO_4 is in 1000 cm^3

$$0.003125 \text{ of H}_2\text{SO}_4 \text{ is in } 1000 \times 0.003125 = 9.77 \text{ cm}^3$$

$$= 156.25 \text{ cm}^3$$

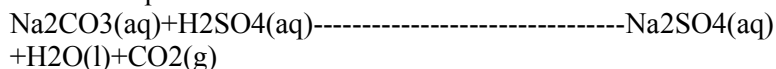
peternelsonsekandi@gmail.com

Volume of H₂SO₄ used for reaction with Na₂CO₃ only = 2 × 11.20 = 22.40 cm³

No of mole of H₂SO₄ that reacted = $\frac{22.40 \times 0.02}{1000}$

0.000448

From the equation



Since mole of Na₂CO₃ that reacted

$0.000448 \times \frac{1}{1} = 0.000448$

25.0 cm³ of solution contain 0.000448 mole

1000 cm³ of solution contain 0.000448×1000

25

= 0.1792

Mass of Na₂CO₃ = 0.1792 × rfm
0.1792 × 106

1.9 g dm⁻³

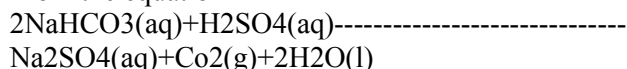
Volume of H₂SO₄ USED IN REACTION WITH NaHCO₃ ALONE

= 28.6 - 11.2 = 17.40 cm³

No of mole of H₂SO₄ that reacted = $\frac{17.40 \times 0.02}{1000}$

= 0.000348

From the equation



Since 2 mole of NaHCO₃ that reacted = 0.000348 × 2
= 0.000696

1000 cm³ of solution contain 0.000696×1000

25

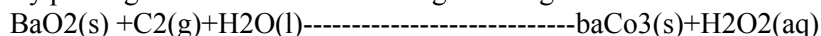
= 0.02784

Conc in g dm⁻³ = 0.02784 × 84
2.34 g

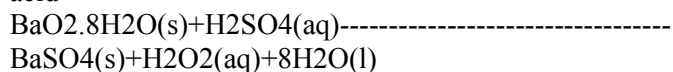
HYDROGEN PEROXIDE

Laboratory

By passing a stream of carbon dioxide gas through BaO₂ stirred with ice cold water



Reaction of a calculated amount of hydrated BaO₂ to ice cold dilute sulphuric acid



Properties of hydrogen peroxide

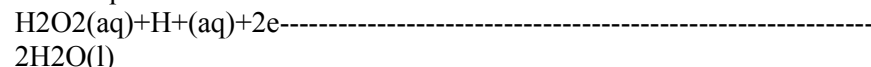
Decomposition

H₂O₂ decomposes rapidly when heated in liberating oxygen gas $2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

NOTE: The decomposition is catalysed by manganese (iv) oxide and kinetically the reaction is first order with respect to the H₂O₂

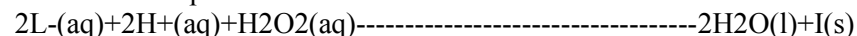
Oxidising reactions

In acidic medium H₂O₂ is powerful oxidizing agent (electron acceptor) according to the equation.

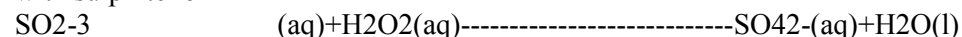


The following are some of the reaction in which H₂O₂ oxidises

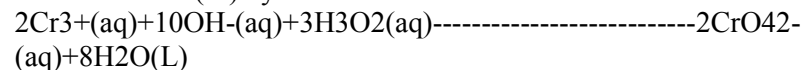
With acidified potassium iodine solution



with sulphite ion

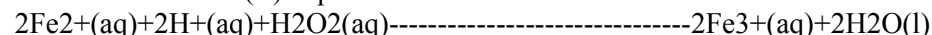


with chromium(III) hydroxide-

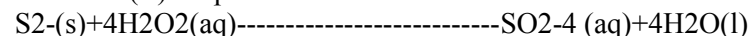


Note: This is done by heating chromium(III)-solution with excess sodium hydroxide to gether with H₂O₂

With acidified iron (II) sulphate solution



With lead(II) Sulphide

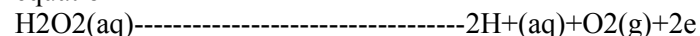


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white

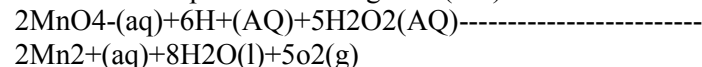
Reducing reactions

Hydrogen peroxide acts as a reducing agent (electron donor) according to the equation

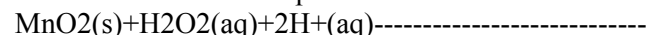


Examples of reactions in which H₂O₂ is a reducing agent

With acidified potassium manganate(VII)



With MnO₂ in dilute sulphuric acid



With lead(IV) oxide

$\text{PbO}_2(\text{s}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{PbO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

$\text{PbO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

Acidic properties

Slightly acidic and ionizes according to the equation

$\text{H}_2\text{O}_2(\text{aq}) \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{O}_2^{2-}(\text{aq})$

In its acidic properties H_2O_2 precipitate barium peroxide from a saturated solution of barium hydroxide

$\text{Ba}(\text{OH})_2(\text{aq}) + \text{H}_2\text{O}_2(\text{l}) \rightarrow \text{BaO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Group vii

Element

First ionization energy in KJ mol ⁻¹	First electron affinity in KJ mol ⁻¹	Electronegativity	Radius A
Flourine	1681	-326	4.0
Chlorine	1255	-364	3.0
Bromine	1138	-320	2.8
Iodine	1002	-295	2.5

Explain what is meant by the following terms

- First ionisation energy
- Electron affinity
- Electronegativity
- Atomic radius

State and explain how each of the terms in (a) above varies across period III and down the group(VII)

Explain why

Magnesium has a higher first ionization than aluminium.

Sulphur has a lower first ionization than phosphorous

Electron affinity of Mg is positive?

Electron affinity of phosphorous is less negative than that of silicon

Electron affinity for fluorine is abnormally low in value?

Discuss the importance of ionization energy in determining the chemistry of an element (use aluminium to illustrate answer)

Lithium, a group 1 element is diagonally related to magnesium a group II element.

Give reasons why Li and Mg are related

State three properties in which Li and Mg resemble.

State also three properties in which beryllium a group II element and Aluminium a group III element are related.

Explain why elements in group II

form less ionic compounds than corresponding compounds of group I.

Do not form many complexes.

Why Na_2CO_3 decomposes at lower temperature than MgCO_3 .

Using water, discuss the difference in reactivity of group I and group II elements.

What reagent can be used to distinguish

CHAMPER 10

Sample questions

The data below show the variation in size, first ionization energy electron affinity and electronegativity across period 3 and down group (vii).

Period iii

Element	Na	Mg	Al	Si	P	S
Element	Na	Mg	Al	Si	P	S
I.E	495	740	580	790	1060	999
	-20	+67	-30	-135	-60	-200
	0.9	1.2	1.5	1.8	2.1	2.5
radius	0.156	0.136	0.125	0.117	0.110	0.104

Mg²⁺ from Ca²⁺

Ca²⁺ from Ba²⁺

Mg²⁺ from Ba²⁺

Explain why aqueous solution of Mg²⁺ has PH less than 7

State and Explain the trend in

Solubilities of hydroxides and sulphates formed by group 11 element

Thermal stability of the carbonates formed by group 11 elements

What is inert pair effect

State two common oxidation states shown by group (IV) Element and Explain how they vary in their stability down the group.

Discuss the reaction of group (iv) elements with

Water

Hydrochloric acid

Sodium hydroxide.

Write equations to show the reaction of tin(ii) oxide and tin (iv) oxide with (i)

Hydrochloric acid(ii) sodium hydroxide.

Discuss the reaction of the group (iv) tetrachloride with water.

How is each of the following prepared(use equations)

Silicon dioxide

Lead(iv) chloride

Silicon hydride

Explain why

PbCl₂ ionic while PbCl₄ has a simple molecular structure.

Germanium(ii) compounds are more stable than germanium may be determined.

The bond energies and boiling point of the elements of group (vii) are indicated in the table below

Element

Na	Mg	Al	Si	P	S
Melting point/°C	97.8	650	660	1410	44

Explain why

Mg has a much higher melting than Na

Si has abnormally higher melting point.

Sulphur has a much higher melting point than phosphorous.

Name the type of bonding that exists in the halides and hydrides of the elements of Na, S and Cl.

Explain why the melting point in the chloride of Na, Mg and Al is in order.

NaCl > MgCl₂ > AlCl₃

Write equation, if any, to show the reaction of water with

The hydrides of Na, S and Cl

The chlorides of Na, Al, P and S

Name any three ores of aluminium

Describe how aluminium may be extracted from one of the ores in (a) above.

State the of cryolite, Na₃AlF₆, in the extraction of Al.

Explain why Al is extracted by electrolysis and not by reduction process.

Using equation, show that Al₂O₃ is amphoteric

Explain why aluminium containers cannot be washed in alkaline solutions.

Discuss the bonding in the halides of aluminium

Explain (i) aqueous solution of aluminium salt are acidic

Why addition of sodium carbonate solution to a solution of Al³⁺ precipitates the hydroxide and not the carbonate.

Name one reagent that can be used to distinguish Al³⁺ from Zn²⁺

Write the electronic configuration of chromium (atomic number = 24)

State all the oxidation states of chromium and in each case write the formula of one compound in which chromium shows the oxidation states in (i)

(iii) Explain why aqueous solutions of Cr³⁺ salts have pH less than 7.

(b) Chromium (III) chloride . 6H₂O, is an example of hydrate isomerism.

(i) Write the formulae and names of three possible isomers of CrCl₃.6H₂O.

(ii) state two tests that can be carried out to identify the isomers

(iii) how can the tests be used to identify them

Write the equation to explain what is observed when to a solution of sodium dichromate is added dilute sodium hydroxide solution.

Write equation to show the behavior of potassium dichromate in acidic medium with

Cl⁻ (i) Sn²⁺(aq) (ii) I⁻ (iii) SO₂

112 State what you would observe if a solution of Cr³⁺ was heated with excess sodium hydroxide solution in the presence of hydrogen peroxide solution.

(i) Write the equation of the reaction.

(ii) State what would be observed if to the product in (i) above was added silver nitrate solution. Write an ionic equation of the reaction that took place.

Manganese, as transition element, has variable oxidation states.

(i) State two common oxidation states and write the formula of one compound in each case in which manganese shows the oxidation states stated.

(ii) Give three other properties of manganese that qualify it as a transition

element.

(i) write equation to show how manganese (iv) oxide is prepared.

(ii) write equation to show how manganese (iv) oxide reacts with concentrated hydrochloric acid (both cold and warm) and acidified solution of sodium ethanedicate.

Potassium manganate (vi), the only stable compound in the +6 oxidation state is unstable in neutral or acidic medium, write equation to show the behaviour of the salt and acidic media.

Potassium manganate (vii) is a powerful oxidizing agent in acidic medium. why is HCl or O_3 not used to acidify $KMnO_4$

(e) write the equation to show the oxidation by $KMnO_4$

(i) of potassium iodine in strongly acidic medium

(ii) of potassium iodine in a neutral medium.

(f) describe a simple experiment that you can carry out to determine the percentage of manganese (IV) oxide in an impure sample of manganese (IV) oxide.

9 (a) name any three ores of iron.

(b) describe how iron may be extracted from one of the ores named above.

(c) (i) what is rust

(ii) briefly illustrate how rust is formed.

(iii) explain how galvanizing of an iron wire may prevent rust formation

(d) give two advantages of ammonium ferrous sulphate over ferrous sulphate salt in volumetric analysis.

(e) explain with aid of equations the following observations

(i) when H_2S gas is bubbled through a solution of Fe^{3+}
A yellowish-brown precipitate of iron (III) Sulphide.

(ii) aqueous solution of iron (III) sulphate has pH less 7.

(f) state what is observed and write ionic equations when

(i) a solution of potassium hexacyano ferrate (III) is added to solution of Fe^{2+}

(ii) a solution of potassium hexacyano ferrate (II) is added to a solution containing Fe^{3+}

10 (a) what would you observe and write a balanced equation for the following reactions.

(i) $Co^{2+}(aq)$ + Excess $NaOH(aq)$

(ii) $Ni(aq)$ + excess $NH_4OH(aq)$

(iii) Co^{2+} + $NaCN(aq)$

(iv) $Co(aq)$ + NH_4OH

(b) Cobalt (III) chloride whose empirical formula is $CoCl_3 \cdot 6NH_3$ just like $CrCl_3 \cdot 6H_2O$ has a number of isomers.

(ii) state two tests that can be carried out to identify the isomers.

11 (a) Name any three ores of copper.

(b) describe how copper metal may be extracted from one of the ores named above.

(c) (i) state the principal oxidation states of copper and write the electronic configuration of the ions (Atomic number = 29).

(ii) which of the oxidation states stated in C(i) above is stable and why

d) explain why the first ionization energy of copper is greater than the second.

e) Copper (I) compounds are non transition

(i) give two reasons why they are not transition.

(ii) give two properties in which copper (I) compound resembles group (I) compounds.

f) state what is observed and write equation of reaction if to a solution of copper (II) sulphate is added.

(i) excess aqueous ammonia

(ii) excess hydrochloric acid and then the resultant mixture diluted.

(iii) A solution of potassium hexacyano ferrate (II)

a) in the extraction of zinc from one of its ores, zinc blende, ZnS , the ore is first concentrated and then roasted in air.

(i) describe briefly how the ore is concentrated.

(ii) describe how pure zinc may be obtained from the concentrated ore.

b) Both zinc and scandium appear in the first series of transition element but some of their properties do not qualify them as transition elements.

i) Mention two properties which do not qualify Sc and Zn as transition elements.

ii) Mention one property in which Zinc behaves as a transition element.

c) Using equations only explain what would happen to a solution of Zn^{2+} is added

i) excess sodium hydroxide solution.

ii) excess ammonia solution.

Cement is a mixture of inorganic compounds and is widely used in the construction industries.

(a) Name

- (i) the two processes by which cement is made
- (ii) the main raw materials used in the manufacture of cement.

(b) describe briefly how cement is manufactured and explain the main physical and chemical changes involved.

(c) Describe what happens when water is added to a mixture of cement and sand

(a) Describe, stating conditions required, the manufacture of

(i) Sulphuric acid by the contact process

(ii) Ammonia by the Haber process

(iii) Sodium carbonate by Solvay process

(b) Describe how ammonia is converted to nitric acid on industrial scale

(c) Write equations to show the reactions of conc. HNO_3 with copper, carbon and sulphur.

15 (a) what is a fertilizer

(b) Briefly describe the manufacture of single super phosphate fertilizer.

(c) What are the features of a good fertilizer?

(d) Give two environmental problems caused by large scale use of fertilizers.

CHAPTER 11

SELECTED WORKED EXAMPLES

The elements Be, Mg, Ca and Ba belong to a group (II) in the periodic table.

(a) (i) State three chemical properties shown by the elements. For each property, write an equation to illustrate your answer.

Explain the trend in the solubilities of the hydroxides and sulphates of the elements in water

(b) Be differs in some of its properties from the rest of the elements in the group

(i) state two properties in which Be differs from the rest of the elements in the group

(ii) Give reasons why Be shows different properties from the rest of the elements

(c) Name one reagent that can be used to distinguish between each of these ions. In each case state what is observed when the reagent is used and write equations for the reactions taking place.

(i) Mg^{2+} and Ba^{2+}

(ii) Ca^{2+} and Ba^{2+}

(iii) Mg^{2+} and Ca^{2+}

(d) Explain

(i) Why MgCl_2 solution has pH less than 7

(ii) Why the tendency to form complexes by group (II) metals decreases down the group

(iii) Group (II) metals form less ionic compounds than group (I) metals.

(e) state 3 properties in which Li and Mg resemble and explain why.

They burn in air to form an oxide of formula MO equation



They react with dilute acids producing hydrogen gas.



They react with halogens



Trend in solubility of hydroxides- _____ Solubility of the hydroxide increases down the group

i.e. solubility of $\text{Ba(OH)}_2 > \text{Be(OH)}_2$

Explanation

Both hydration and lattice energies decrease but the hydration energy decreases more rapidly than lattice energy.

NB;

The solubility of an ionic salt in water is dependent on both hydration and lattice energies

Trend in solubility of sulphates. solubility decreases down the group.

EXPLANATION;

Both hydration and lattice energies decrease but the hydration energy decreases more rapidly than lattice energy.

(b) (i) Be is amphoteric (i.e. it reacts with both acids and alkalis). Be does not react with water at any condition.

(ii) This is because Be being a very small atom forms a very small ion with a very strong charge density (polarizing power) compared to the ions from atoms of the other elements.

(c) (i) Reagent — Ammonium oxalate solution

Observation — A white precipitate is formed with Ba^{2+}

Equation; $\text{COO}^- + (\text{aq}) \quad (\text{Coo})_2\text{Ba}(\text{s})$
 $\text{COO}^- (\text{aq})$

ii) Reagent; potassium chromate solution

Observation; A yellow precipitate only formed with Ba^{2+}

Equation $\text{Ba}^{2+} (\text{aq}) + \text{CrO}_4^{2-} \quad \text{BaCrO}_4 (\text{s})$

(iii) reagent; Ammonium oxalate solution

Observation; A white precipitate is formed with Ca^{2+} only

Equation $\text{Coo}^- + \text{Ca}^{2+} \quad \text{C}_2\text{O}_4\text{Ca} (\text{s})$
 $\text{Coo}^- (\text{aq})$

(d) (i) A solution of MgCl_2 is acidic because of the hydrolysis reaction below which produces H^+ in solution

$\text{MgCl}_2 (\text{aq}) \quad \text{Mg}^{2+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$

Mg^{2+} is hydrated with 6 moles of water and hydrolyses as

$[\text{Mg}(\text{H}_2\text{O})_6]^{2+} \quad [\text{Mg}(\text{H}_2\text{O})_4(\text{OH})_2] + 2\text{H}^+ (\text{aq})$

The hydrolysis is due to small size of Mg^{2+} which gives it very high polarizing power with the result that it exerts very strong attraction for the OH bond of the H_2O molecule setting free H^+ in solution which causes the solution to be acidic.

(ii) the tendency decreases down the group because down the group the size of the ions becomes bigger resulting in decrease in attracting power of the lone pair of electrons by the cations

(iii) group (11) ions are smaller and more highly charged than their corresponding group (1) ions. This gives them very high density (polarizing power) so that any accompanying anion is greatly polarized and thus becoming more covalent than that formed by a corresponding group (1) ion.

Eg NaCl (melting point 80°C) is more ionic than MgCl_2 (melting point 712°C).

(e) Lithium like magnesium readily reacts with oxygen to form an ionic oxide. Lithium like magnesium reacts with carbon to form an ionic carbide.

The similarity in chemistry between Li and Mg is because of them having similar polarizing power.

Carbon, silicon, germanium, tin and lead are elements of group (IV) in the periodic table.

(a) (1) state two important oxidation states exhibited by the elements

(ii) Describe how the stability of the two oxidation states vary down the group

(b) Describe the type of chlorides formed by these elements and show how they react with water

(c) describe the trend in the basicity of the oxide of a group (IV) element and write equations to show how the oxides of C, Si, Ge and Pb react with sodium hydroxide,

(d) when a mixture of carbon and an oxide of group (11) elements was heated to very high temperature, a compound Z was formed. Z reacted with cold water to give a gas Y which decolourised bromine water, write equation for reactions leading to the formation of Y

(e) (i) write the equation to show how lead (II) chloride can be prepared in the laboratory

(1) identify the element in group (11) and the substances in Y and Z

(11).

(ii) the type of bonding in PbCl_2 and also state the physical properties which show that PbCl_2 exhibits the type of bonding stated

(f) Explain why the boiling point of the hydrides of group (IV) is in order

$\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$.

SOLUTION

(i) the two oxidation states are +2 and +4

(ii) the +2 oxidation increases in stability down the group as a result of the inability of s electron in $\text{ns}^2 \text{np}^2$ to participate in bonding (inert pair effect)

The +4 oxidation state decreases in stability down the group

(b) elements of group (IV) form two types of chlorides namely dichloride and tetrachloride.

Dichlorides are formed by Ge, Sn and Pb only.

GeCl_2 is prepared by passing vapor of GeCl_4 over hot Ge

i.e. $\text{GeCl}_4 (\text{s}) + \text{Ge} (\text{s})$

$2 \text{GeCl}_2 (\text{s})$ SnCl_2 is prepared by

passing HCL gas over

heated Sn. $\text{Sn(s)} + 2\text{HCL(g)} \rightarrow \text{SnCL}_2\text{(g)} + \text{H}_2\text{(g)}$

PbCL₂ is formed when lead is heated with CL₂

$\text{Pb(s)} + \text{CL}_2\text{(g)} \rightarrow \text{PbCL}_2\text{(s)}$

GeCL₂ and Sn CL₂ are hidrolysed in water as

$\text{Sn CL}_2\text{(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Sn(OH) CL(aq)} + \text{HCL(aq)}$

PbCL₂ is prepared by passing CL₂ over heated lead

$\text{Pb(s)} + \text{CL}_2\text{(s)} \rightarrow \text{PbCL}_2\text{(s)}$

PbCL₂ is sparingly soluble in water

i.e. $\text{PbCL}_2\text{(s)} \rightleftharpoons \text{Pb}^{2+}\text{(aq)} + 2\text{CL}^{-}\text{(aq)}$

The tetrachlorides are formed by all

The tetrachlorides are covalent liquids which are colourless except form PbCL₄ which is yellow

The tetrachlorides of carbon is formed by the reaction

$\text{CS}_2\text{(l)} + 3\text{CL}_2\text{(g)} \rightarrow \text{CCL}_4\text{(l)} + \text{S}_2\text{CL}_2\text{(l)}$

Those of Si, Ge and Sn are formed by passing CL₂ over heated substance

Heat

$\text{Sn(s)} + 3\text{CL}_2\text{(g)} \xrightarrow{\text{Heat}} \text{SnCL}_4\text{(l)}$

PbCL₄ is prepared by the reaction

$\text{PbO}_2\text{(s)} + 4\text{HCL(aq)} \rightarrow \text{PbCL}_4\text{(l)} + 2\text{H}_2\text{O(l)}$

all the tetrachlorides are hydrolysed except CCL₄

$\text{SiCL}_4\text{(l)} + 2\text{H}_2\text{O(l)} \rightarrow \text{SiO}_2\text{(s)} + 4\text{HCL(g)}$

$\text{PbCL}_4\text{(l)} + 2\text{H}_2\text{O(l)} \rightarrow \text{PbO}_2\text{(s)} + 4\text{HCL(g)}$

(c) the elements form two types of oxides _ Dioxide is formed by all the elements.

The dioxides of CO₂ and SiO₂ are acidic. GeO₂, SnO₂ AND PbO₂ are amphoteric.

Thus basicity of the dioxides increases down the group.

The dioxides react with NaOH as.

$\text{CO}_2\text{(g)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{CO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

$\text{SiO}_2\text{(s)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{SiO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

$\text{GeO}_2\text{(s)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{GeO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

$\text{SnO}_2\text{(s)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{SnO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

PbO

$\text{(s)} + 2\text{Na}_2\text{PbO}_3\text{(aq)} \rightarrow \text{Na}_2\text{PbO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

Monoxides CO and SiO are neutral while the oxides GeO, SnO and PbO ARE AMPHOTERIC

Basicity increase from CO to PbO. CO and SiO do not react with sodium

hydroxide since they are neutral. the GeO, SnO and PbO react with sodium hydroxide as

$\text{GeO(s)} + 2\text{NaOH(aq)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Na}_2\text{Ge(OH)}_2\text{(aq)}$

$\text{Sn(s)} + 2\text{NaOH(aq)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Na}_2\text{Pb(OH)}_2\text{(aq)}$

(d) (i) the element in group (11) is calcium i.e. CaO, Z is calcium dicarbide and Y is ethyne.

(ii) $3\text{C(s)} + \text{CaO(s)} \rightarrow \text{CaC}_2\text{(s)} + \text{CO(g)}$
 $\text{CaC}_2\text{(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{HC}\equiv\text{CH(g)} + \text{Ca(OH)}_2\text{(aq)}$

(e) (i) Lead (11) chloride is prepared in the laboratory by the reaction between lead nitrate solution and dilute hydrochloric acid.

$\text{Pb(NO}_3)_2\text{(aq)} + 2\text{HCL(aq)} \rightarrow \text{PbCL}_2\text{(s)} + 2\text{HNO}_3\text{(aq)}$

(ii) PbCL₂ is ionic and the following properties show that it is ionic

— its molten solution conducts electricity

— Has very high melting and boiling points

(f) the hydrides are all covalent compounds. the boiling points of covalent compounds depend on the sizes of the compound. down the group the sizes of the hydrides increase hence, increase in their boiling points.

3 a) describe one general method for preparing the halogens in the laboratory (excluding fluorine) and write the equation for the reaction.

b) describe the reactivity of fluorine, chlorine and bromine with

(i) sodium hydroxide

(i) water (use equations to illustrate your answer).

c) how would you distinguish between sodium bromide and sodium iodine given chlorine water and tetrachloromethane.

d) state and explain

(i) The trend in the boiling points of the halogens down the group

(ii) the trend in the acidity of the hydrides of group (vii) elements

e) outline one process by which sodium hydroxide is manufactured industrially.

SOLUTION

(a) CL₂, Br₂ and I₂ are generally prepared by heating an alkali metal halide with concentrated sulphuric acid in the presence of manganese (IV) oxide or lead (IV) oxide.

i.e. $\text{NaX(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{HX(g)} + \text{NaHSO}_4\text{(aq)}$

$4\text{HX(g)} + \text{MnO}_2\text{(s)} \rightarrow \text{X}_2\text{(g)} + 2\text{H}_2\text{O(l)} + \text{MnX}_2\text{(aq)}$

Eg. $\text{NaCL(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{HCL(g)} + \text{NaHSO}_4\text{(aq)}$

$4\text{HCL(g)} + \text{MnO}_2\text{(s)} \rightarrow \text{CL}_2\text{(g)} + 2\text{H}_2\text{O(l)} + \text{MnCL}_2\text{(aq)}$

An alternative method of preparation is by heating a concentrated solution of the hydrogen halide with manganese (IV) oxide

ie. $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{X}^-(\text{aq}) \rightarrow \text{X}_2(\text{g}) + \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

eg. $\text{MnO}_2(\text{s}) + 4\text{HCl}(\text{aq}) \rightarrow \text{MnCl}_2(\text{aq}) + \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

$\text{MnO}_2(\text{s}) + 4\text{HI}(\text{aq}) \rightarrow \text{MnI}_2(\text{aq}) + \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

NOTE; potassium manganate(VII) can be used instead of MnO_2

Eg. $2\text{KMnO}_4(\text{aq}) + 16\text{HCl}(\text{aq}) \rightarrow 5\text{Cl}_2(\text{aq}) + 2\text{MnCl}_2(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$

b) fluorine, chlorine and bromine react with sodium hydroxide under two different conditions.

With cold dilute sodium hydroxide, Cl_2 and Br_2 react to form sodium hypohalite and sodium halide.

$\text{NaOH}(\text{aq}) + \text{X}_2(\text{g}) \rightarrow \text{NaOX}(\text{aq}) + \text{NaX}(\text{aq})$

Eg. $\text{NaOH}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow \text{NaOCl}(\text{aq}) + \text{NaCl}(\text{aq})$

$\text{NaOH}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow \text{NaOBr}(\text{aq}) + \text{NaBr}(\text{aq})$

Fluorine reacts with cold very dilute sodium hydroxide to form oxygen difluoride

$2\text{F}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow 2\text{NaF}(\text{aq}) + \text{F}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$

With concentrated and hot sodium hydroxide, fluorine liberates oxygen with formation of sodium fluoride solution.

$2\text{F}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow 2\text{NaF}(\text{aq}) + \text{F}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$

Both chlorine and bromine react with concentrated hot sodium hydroxide to form the corresponding sodium halide and sodium halate

ie. $3\text{Cl}_2(\text{g}) + 6\text{NaOH}(\text{aq}) \rightarrow 5\text{NaCl}(\text{aq}) + \text{NaClO}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

$3\text{Br}_2(\text{g}) + 6\text{NaOH}(\text{aq}) \rightarrow 5\text{NaBr}(\text{aq}) + \text{NaBrO}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

(ii) fluorine reacts with water to form hydrogen fluoride and oxygen

$2\text{F}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HF}(\text{aq}) + \text{O}_2(\text{g})$

Chlorine reacts with water to form hydrochloric and hypochlorous acid

$\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl}(\text{aq}) + \text{HOCl}(\text{aq})$

Bromine reacts with water to form hydrobromic and hypobromous acids

$\text{Br}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HBr}(\text{aq}) + \text{HOBr}(\text{aq})$

c) procedure

Each of the salts is dissolved in water. Then to each solution is added tetrachloromethane followed by chlorine water and the mixture shaken.

OBSERVATIONS

The sodium bromide solution gives a brownish yellow colour in the tetrachloromethane layer

c) (i) trend; boiling point increases down the group.

d)

e)

EXPLANATION; this is because of increasing magnitude of the van der Waals' forces holding the molecules as sizes of the molecules increase down

(ii) aqueous solution of the hydrides of group(VII) elements increases in acidity down the group

EXPLANATION; this is because the bond strength decreases from HF to HI

Therefore the H-F is not easily broken, thus a solution of HI would have the highest concentration of hydrogen ions while that of HF will have the least

e) sodium hydroxide is manufactured industrially by electrolysis of a concentrated solution of sodium chloride (brine) in a mercury cell as the cathode and graphite blocks as the anode.

solu

tions of sodium chloride contain Na^+ , Cl^- , H^+ and OH^- ions produced by reactions

.

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

$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

Because of high concentration, sodium ion is discharged at the cathode and forms an amalgam with the mercury.

ie. $\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$

$\text{Na}(\text{s}) + \text{Hg}(\text{l}) \rightarrow \text{NaHg}(\text{l})$

The amalgam is then removed and treated with water where the sodium present reacts with water forming sodium hydroxide. $\text{Na/Hg}(\text{l}) + \text{H}_2\text{O}(\text{l})$

$\text{NaOH}(\text{aq}) + 1/2\text{H}_2(\text{g}) + \text{Hg}(\text{l})$

The mercury liberated is returned to the cell.

4) The elements Na, Mg, Al, Si, P and Cl are members of the third period of the periodic table.

a), (i) write down the formula of the principal oxides and chlorides of the elements listed above and in each case indicate the types of bonding.

(ii) Explain what happened when each of the above oxides and chlorides is added to water and indicate whether the resultant solution will be acidic, basic or neutral.

Which of the oxides listed above form oxides of the type M_2O_3 ?

Describe briefly how you would prepare each of the oxides and give the equations for the reactions involved.

What would be observed if each of the above oxides in (b) (ii) was reacted with sodium hydroxide. Write equations for the reactions involved in each case.

the melting points of Mg, Si and S are 650°C, 1423°C and 120°C respectively. Explain the differences in the melting points of the elements.

Name the type of the bonding that exists in the hydride of the elements Na, P and S and write equations to show the reaction if any of the hydrides with water.

SOLUTION

- The principal oxides are Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, Cl₂O₇
- The principal chlorides are
- The bonding in Na₂O, MgO and Al₂O₃ is pure ionic bond. SiO₂ is a giant molecular compound with covalent bond linking Si and Oxygen.
- P₂O₅ and Cl₂O are discrete molecules with covalent bonds linking the atoms. NaCl, MgCl₂, and AlCl₃ have ionic bonds. SiCl₄, PCl₅ and Cl₂ are simple molecular compounds with weak van der Waal's force forces holding the molecules while the atoms within the molecules are joined by covalent bonds.
- The reactions of the oxides with water is as follows:
- Na₂O (s) + H₂O (l) ----- 2NaOH (aq)
- MgO (s) + H₂O ----- Mg(OH)₂ (aq)

MISSING NOTES

The force hold a metal together is the attraction between the cations and the delocalised electrons in its charge cloud. Mg contributes two electrons on the charge cloud thus a strong force of attraction exists.

Silicon has the highest melting point because Si forms a giant structure of three dimensional network of covalent bonds which require very high temperature to overcome.

Sulphur has the least melting point because it is a molecular compound with weak van der Waal's forces holding the molecules. These forces are easily overcome.

NaH is ionic and reacts with water to give an alkaline solution.



Phosphorous forms PH₃ which has covalent bonds. Because both P and H almost have same Electronegativity values, PH₃ does not react with water

Sulphur forms H₂S which has covalent bonds and reacts with water to form

an acidic solution.



In the extraction of aluminium, the ore is purified by first treating it with sodium hydroxide solution.

Write the name and formula of one ore from which aluminium is extracted.

Name two impurities in the ore.

Describe what takes place when the ore in (i) above is treated with sodium hydroxide and write equation for the reaction.

Describe how pure aluminium is obtained from the purified ore.

Aluminium chloride whose relative molecular mass in vapour phase is 267 can be obtained from aluminium.

Write an equation to show anhydrous aluminium chloride in vapour phase indicating the bonding

Explain with reference to aluminium oxide, what an amphoteric oxide is. Write the appropriate equations.

Explain giving the necessary equations why

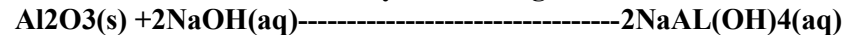
Solutions of simple Al³⁺ salts are acidic.

Aluminium utensils should not be washed in strongly alkaline solutions.

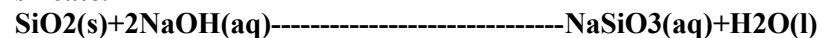
Bauxite, Al₂O₃.2H₂O is the ore from which Al is extracted.

Silica, SiO₂ and Iron Oxide, Fe₂O₃ are impurities

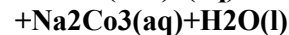
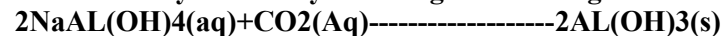
The ore dissolves in sodium hydroxide to give sodium aluminate.



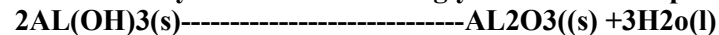
Some of the silica present as an impurity, also dissolves to give sodium silicate.



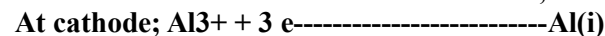
The purified ore which now contains sodium aluminate is then converted to aluminium hydroxide by bubbling CO₂ through it.



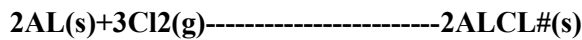
The Aluminium hydroxide is then filtered off washed and dried. The dried aluminium hydroxide is then strongly heated to form pure Al₂O₃



Finally, the pure molten Al₂O₃ is then electrolysed with a mixture of cryolite Na₃AlF₆ in a steel tank lined with sheets of carbon which acts as the cathode. The anode is also made of carbon; The reactions taking place are

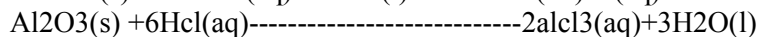


Aluminium collects at the bottom of the steel tank and is then tapped off.



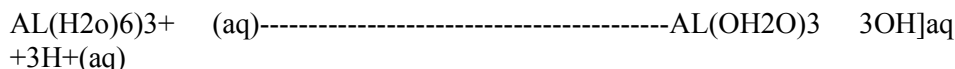
The molecular formula of Aluminium chloride in vapour phase is Al_2Cl_6 diagram

Al_2O_3 as an amphoteric oxide, reacts both as an acid and as a base also.

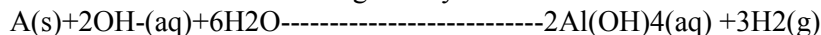


Because of high charge and small size of the Al^{3+} ion, in aqueous solution, it exerts a very strong attraction for O-H bond of water molecules associated with it.

The result is that H^+ is set free which is responsible for the acidity. The hydrolysis reaction is as



This is because aluminium vigorously reacts with alkaline solution.

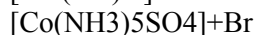
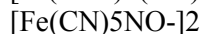
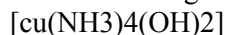


One property of transition elements is that they form complex

What is meant by the term complex

State four other properties exhibited by Transition elements

Determine the oxidation state, co-ordination number of the central ion and name of the following complexes



Solution

A complex ion is an association of two or more species each of which can exist independently of the other.

Four other properties exhibited by transition metals are

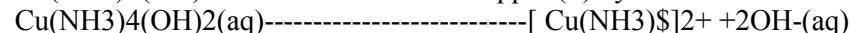
They have variable oxidation state

e.g. Mn has +2, +4, +7 oxidation states

Their ions and compounds are coloured.

Most transition metals are paramagnetic.

$\text{Cu(NH}_3)_4(\text{OH})_2$ is called tetrammine copper (II) hydroxide and ionizes as



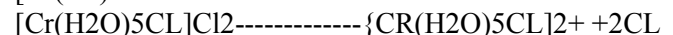
The co-ordination number is 4 and since NH_3 molecules are neutral the charge on the complex $[\text{Cu(NH}_3)_4]^{2+}$ is the oxidation number of the Cu^{2+}

Co-ordination number is $5 + 1 = 6$

Since each cyanide ion has charge of -1 and NO is neutral then the oxidation number = $5 + 1 = 6$

NOTE: Only one Cl^- is bonded to the chromium ion and two Cl^- are free.

$[\text{Cr(H}_2\text{O)}_5\text{Cl}]$ ionises as



since all the H_2O molecules are neutral, the oxidation number of the cobalt ion is +3

$[\text{V(CN)}_6]^{3-}$ is called hexacyanovanadium (III)

Co-ordination number is 6 and oxidation number of the vanadium ion is +3.

Note Co-ordination number is the number of ligands directly bonded to the central metal ion or it is the number of ligands forming co-ordinate bonds to the central metal ion,

Complex ions are named by first naming the ligands followed by the name of the central atom with its oxidation number. If different ligands are present, then the following order of anionic, neutral and cationic ligands should be followed. All anionic ligands should have their names ending in -o e.g. Cl^- and SO_4^{2-} are called chloro and sulphate respectively

7. A solution A contains a divalent metal ion. Addition of excess ethanedioic acid produces a pale pink precipitate B. On heating B in air, it decomposes first to give a green solid C and on further heating to a black solid. C is soluble in acid but D is not.

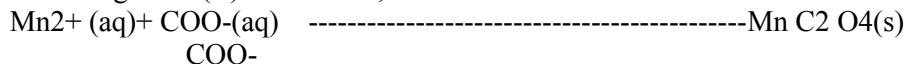
When D is fused with solid potassium hydroxide and potassium chlorate(V) a green solid E is formed which gives a green solution in water. On acidifying the aqueous solution of E, the solution turned purple and a precipitate of D also is formed. The purple solution, F reacts with iron (II) ions in acidic solution to give a solution containing A.

Identify all the species A, B, C, D, E and F and give equations for the reactions

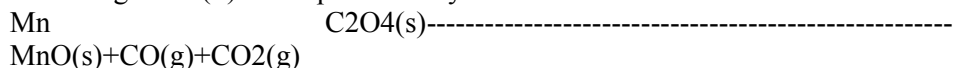
Solution

A is a solution containing Mn^{2+} ion.

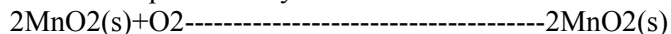
B is manganese (II) ethandioate, $Mn C_2 O_4$



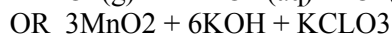
C is manganese (II) oxide produced by the reaction



D is MnO_2 produced by the oxidation of Mn



E is potassium manganate (VI), K_2MnO_4 produced by the reaction



Note; $KClO_3$ decomposes to give O_2 gas used in the reaction above.

F is potassium manganate (VII), $KMnO_4$ produced by the reaction.



8. (a) (i) state two common oxidation states of chromium

(ii) write electronic configuration of the chromium ions in the oxidation states stated in (i)

(iii) write the formula of one compound in each of the oxidation stated in (i)

(b) a dilute solution of chrome alum $K_2Cr_2 (SO_4)_4 \cdot 24H_2O$ was prepared and divided into three portions.

(i) the first portion turned blue litmus red. Explain the observation and write equation to illustrate your answer

(ii) to the second portion was added sodium hydroxide drop-wise until in excess. state and explain what was observed

(iii) to the third portion was added a few drops of hydrogen peroxide and sodium hydroxide. explain the observation made

(c) when 1cm of dilute sulphuric acid was added to about 1cm of potassium chromate, an orange solution was formed.

Addition of an excess dilute sodium hydroxide to the mixture gave a yellow solution. Write equations for the reactions taking place.

(d) briefly describe a test that can be carried out in the laboratory to confirm that potassium chromate contains chromine ion.

(e) Aqueous Sn^{2+} solution was added to a solution containing chromium in the +6 oxidation state

(i) state what was observed

(ii) write half equations for the reactions that took place and the overall equation of reactions

(f) Chromium exhibits structural isomers in some of its complexes. $Cr(H_2O)_6 Cl_3$ has at least three coloured isomers. When one of the isomer, which is violet in colour, reacts with silver nitrate solution, all the chlorine is precipitated as silver chloride

A second, light green isomer also reacts with silver nitrate but only two-thirds of the chloride is precipitated as silver chloride.

The third, dark green isomer precipitates only one-third of its chlorine as silver chloride with silver nitrate solution.

(i) write the structural formula and names of each of the three isomers.

(ii) arrange the isomers in order of their increasing conductivity and explain the order.

(g) give equations of the reaction to show how $Cr^{3+} (aq)$ can be converted to $Cr_2O_3 (s)$

SOLUTION:

(a) (i) the two common oxidation states of chromium are +3 and +6

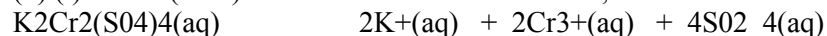
(ii) Cr^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

Cr^{6+} $1s^2 2s^2 2p^6 3s^2 3p^6$

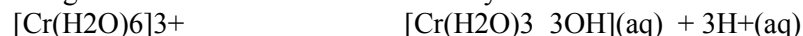
(iii) one compound in the +3 oxidation number is $CrCl_3$

iv) one compound in the +6 oxidation number is CrO_3

(b) (i) $K_2Cr_2 (SO_4)_4$ dissolves in water as follows;



Cr^{3+} in aqueous solution is hydrated as $[Cr(H_2O)_6]^{3+}$ and because of the high charge small size of the chromium ion hydrolysis occurs as



Thus the H^+ set free are responsible for the solution being acidic

iii) Observation here a green precipitate is formed initially which later dissolves in excess of sodium hydroxide to form a green solution.

The green precipitate is due to the insoluble chromium (III) hydroxide formed by the reaction.



The green solution is due to hexa hydroxo chromium(III) which is soluble.

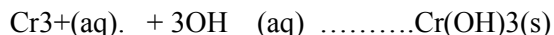


(iii) observation

a yellow solution is formed

EXPLANATION

The yellow solution is due to formation of a chromate by the reaction.



(c) addition of H_2SO_4 to the yellow solution of potassium chromate produced an orange dichromate by the reaction.



When excess sodium hydroxide was added to the orange solution a yellow chromate was formed

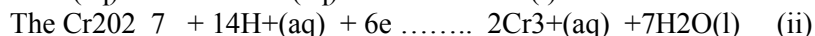
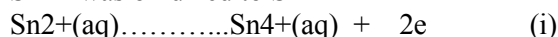


d) Here a solution of potassium chromate is first acidified which converts it to an orange potassium dichromate.

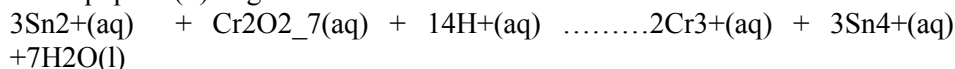
To the green solution produced is added sodium hydroxide solution drop wise until in excess. formation of a green precipitate soluble in excess to give a green solution confirms the presence of Cr^{3+} formed by the reduction of $\text{Cr}_2\text{O}_7^{2-}$ by the ethanol.

e) (i) The orange solution turned green.

Sn^{2+} was oxidized to Sn^{4+}



The overall equation is obtained by multiplying equation (i) by 3 and then adding it to equation (ii) to get

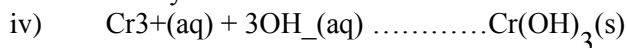


f) (i) the first, violet, isomer is $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^{-}$ Called Hexa aquo chromium(III) Chloride. Here all the chlorine are free and can hence be precipitated.

The second, light green isomer where 2/3 of the chlorine are free is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} 2\text{Cl}^{-}$ CALLED chloropentaaquo chromium (III) chloride.

(ii) the least conducting isomer is $[\text{Cr}(\text{H}_2\text{O})_4 2\text{Cl}]^{+} \text{Cl}^{-}$ followed by $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} 2\text{Cl}^{-}$ and the most conductive is $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^{-}$.

Conductivity here is dependent on the number of ions present in solution. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^{-}$ is the most conducting because it has the highest number of ions (four ions) while $[\text{Cr}(\text{H}_2\text{O})_4 2\text{Cl}]^{+} \text{Cl}^{-}$ is the least conducting because it has only two ions.



When a Pale green solid P was heated, it decomposed to green solid Q and a gas that turned lime water milky was involved. Q dissolves in a nitric acid to give a

green solution R. on adding dilute sodium hydroxide solution to R, a green precipitate S is soluble in excess alkali was obtained. S dissolved in aqueous ammonia to give a purplish blue solution.

(a) identify the compound P, Q, S and solution R.

(b) Write equation for the reaction between

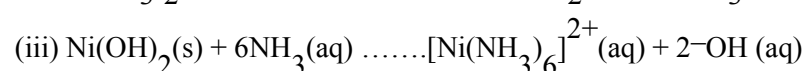
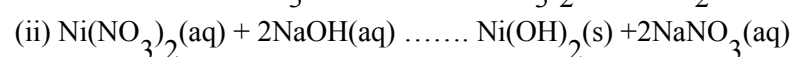
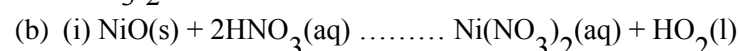
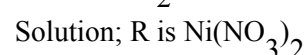
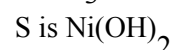
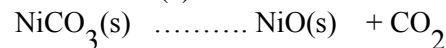
(i) Q and nitric acid.

(ii) R and sodium hydroxide

(iii) S and ammonia.

SOLUTION;

(a) P is nickel carbonate. Solid Q is NiO formed by the reaction.



10. A dilute solution of iron(II) sulfate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ was prepared and divided into three parts

(i) to the first part was added dilute sodium hydroxide drop wise until in excess and warmed. Explain what reactions took place and state any observation made.

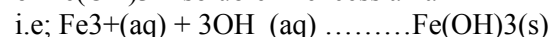
(ii) the second part was added a few drops of potassium thiocyanate. state the observation made and write the equation of reaction taking place.

(iii) to the third part was added a few drops of potassium hexacyanoferrate (II). state any observation made and write an equation for the reaction that took place.

a) Describe an experiment that can be carried out in the laboratory to determine the percentage of iron in the salt above.

SOLUTION;

(a) (i) a solution of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ contains NH_4^{+} and Fe^{3+} . Addition of sodium hydroxide solution produced a yellowish brown precipitate of $\text{Fe}(\text{OH})_3$ insoluble in excess alkali



when the mixture was warmed ammonia gas which turns red litmus blue was also involved

(ii) Observation; a brick red coloration blue was formed.

Equation; $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+} + \text{H}_2\text{O}(\text{l})$

(iii) Observation;

A dark blue precipitate Prussian blue was formed.

Equation; $\text{K}^+(\text{aq}) + [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) + \text{Fe}^{3+}(\text{aq}) \rightarrow \text{K}^+[\text{Fe}(\text{Fe}(\text{CN})_6)](\text{s})$

- b) a fixed mass of salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is dissolved in distilled water and the solution made to 250 cm³ in a volumetric flask. 100 cm³ of this solution is then boiled with some zinc powder until the solution is pale green. This solution is then allowed to cool and let a fixed volume (e.g. 25 cm³) is pipetted and then acidified with about 25 cm³ of 1 M sulphuric acid. The resultant solution is then titrated with a standard solution of potassium dichromate.

The number of moles in 250 cm³ of solution is then calculated from the equation.

$6\text{Fe}^{2+}(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) \rightarrow 6\text{Fe}^{3+}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$

The percentage of iron present is then obtained by expressing the mass of iron present in 250 cm³ of a solution of the mass of the salt used.

11. (a) A metallic element A has atomic number of 29.

(i) write down the electronic configuration of element A.

(ii) To which of the s, p and d blocks of the elements of the periodic table does A belong?

(b) when A was heated with concentrated sulphuric acid, sulphur dioxide gas was given off and a blue solution was formed

(i) Name a reagent used to test for the gas

(ii) write an equation

(c) a small volume of the blue solution from (b) was treated with conc. HCl added dropwise until in excess and then the acid solution diluted about 10 minutes its own volume with water. State and explain what was observed and what species of A were produced.

(i) when the acid was added.

(ii) when the acid solution in (i) was diluted.

(d) describe briefly how you would determine the amount of A present in the blue solution by titration method.

(e) element A exhibits 2 oxidation states of +1 and +2. explain.

SOLUTION;

(a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

(ii) A is a d-block element.

(b) (i) solution of potassium permanganate or acidified potassium dichromate.

(ii) $3\text{SO}_2(\text{g}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 3\text{SO}_4^{2-}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + \text{H}_2\text{O}$
or $5\text{SO}_2(\text{g}) + 2\text{MnO}_4^{2-}(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 5\text{SO}_4^{2-}(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq})$

c) OBSERVATION; addition of conc. HCl to the blue solution produced yellowish brown solution. When the yellowish brown solution was diluted, a pale blue solution is formed.

EXPLANATION; the yellowish brown solution was due to formation of tetrachloro copper (II) ion complex.

$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightarrow [\text{CuCl}_4]^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$

On dilution, the complex $[\text{CuCl}_4]^{2-}$ was broken down to form $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$

$[\text{CuCl}_4]^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Cu}(\text{H}_2\text{O})_4]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$

(i) $[\text{CuCl}_4]^{2-}$ was produced.

(ii) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ was formed

(d) to a fixed volume of the blue solution is added excess potassium iodide solution

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

A is copper so the relevant equations are.

$2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$

$\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$

Combining two equations we obtain

$2\text{Cu}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$

(e) from the electronic configuration

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

The +1 oxidation state is when the single electron on the 4s is removed.

Due to very poor shielding the +2 oxidation state is when one electron is lost from the 3d sub-shell.

12 (a) (i) write the name and formula of one ore of zinc.

(ii) briefly describe how pure zinc can be obtained from the ore you have named

(b) state

(i) two properties that do not qualify Zn as a transition element.

(ii) one property that qualifies Zn as a transition element

© (i) name one reagent that can be used to distinguish Zn^{2+} are treated separately with the reagent. write equations for the reaction

d) explain how zinc protects iron from rusting.

SOLUTION;

(i) Zinc blende, ZnS .

(ii) Zinc extracted from calamine, ZnCO_3 .

The ore is first crushed to powder and then added to mixture of water and an oil which is a frothing agent. The mixture is then agitated by blowing air

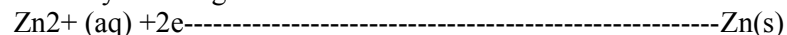
through it. the ore particles are carried to the surface as a froth which are removed, filtered and dried.

The concentrated ore is now then heated strongly in air to convert it to zinc oxide.



The ZnO FORMED IS THEN MIXED WITH COKE AND LIME STONE IN A BLAST FURNACE. HOT AIR IS blown in to furnace through the mixture. the zinc oxide is reduced to zinc metal which distills off. pure zinc is then obtained by redistillation.

NOTE; zinc may also be extracted from its ore called zincate, ZnO in this process, the Zinc ore is located with dilute sulphuric acid. The leached ore is then treated with calcium hydroxide which precipitates any insoluble hydroxide present. The product of this treatment is filtered off. The remaining solution is then treated with Zinc powder and then acidified. It is then electrolysed using aluminium as the cathode where zinc collects.



Note Zinc is also extracted from zinc blende (see notes)

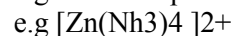
Zn and Zn^{2+} have completely filled 3d sub-shells

Zn^{2+} ion and its compounds are not coloured.

It also has only fixed oxidation state of +2

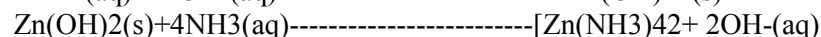
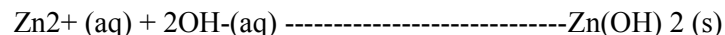
Zn^{2+} form complexes

e.g form complexes



Ammonia solution

With Zn^{2+} a white precipitate initially forms but dissolves in excess to form a colourless solution.



With aluminium a white precipitate initially forms but does not dissolve in excess ammonia



When iron is exposed to moist air, it reacts with oxygen to form (ii) ions which react further to form hydrate iron(III) oxide called rust.

When iron is coated with a layer of zinc metal, the Zinc forms an oxide layer which protects the iron from reacting

If the Zinc layer is scratched, the zinc metal, being higher than iron in the electrochemical series, reacts first to form Zn^{2+} leaving iron unaffected.

Write the name and formula of an ore from which copper is extracted

Explain the following processes as used in the extracting

Flotation

Roasting

Smelting

Refining

Explain what would be observed if to a solution of Cu^{2+} ion was added

A few drops of potassium hexacyanoferrate (II) solution

Magnesium powder.

Solution

Copper pyrite Cu Fe S_2 -

Flotation or selective wetting is a process by which unwanted earthly materials are removed from an ore so as to increase the concentration of copper in the ore.

In this process, the finely ground ore is mixed with water which contains frothing agents like pine oil. This mixture is then agitated by blowing a current of air through it where the ore particles are carried to the surface as a froth which can now be removed and dried. Because of flotation, the amount of copper in the ore increases from 0.6% to about 25%.

In the roasting process, the dried concentrated ore is now heated in air where iron present in pyrite ore is readily oxidized to iron (II) oxide while copper remains as Cu_2S .



In the smelting process, the product of roasting is heated strongly in furnace with silica.

Missing notes

Solution First ionization energy is the minimum potential needed to remove the most loosely held electron from a gaseous atom

Atomic radius is half the distance between two nuclei of two bonded similar atoms

First ionization generally increases across period 3. This is because as electrons are added to the same shell of electrons, nuclear charge increases while screening effect decreases and thus the electron experiences increasing nuclear attraction. Atomic radius decreases across period 3. This is because of increasing effective nuclear charge which pulls the outermost electrons closer to the nucleus.

First ionization energy decreases down group (VII). This is because as the group is descended an extra shell of electron is added from one element to the next. This increases screening effect which thus reduces effective nuclear charge and electrons are less strongly held.

Atomic radius increases on descending group (VII). This is because of increasing screening effect as a result of an extra shell of electrons added and thus electrons are less strongly held hence increase in atomic radius.

Both first ionization energies and atomic radii remain almost constant in moving from Ti to Ni. This is because the increase in effective nuclear charge is roughly balanced by increasing screening effect produced by addition of an electron to inner 3d sub-shell.

The first ionization of Mg is higher than that of Al because the first electron in Mg is being removed from full 3s sub-shell which is very stable and thus requires more energy.

i.e Mg $1s^2 2s^2 2p^6 3s^2$
Al $1s^2 2s^2 2p^6 3s^2 3p^1$

Among Ti, V, Cr, Mn, Fe, Co, Ni,

(c) Explain why

(i) 1st ionization energy is the minimum potential needed to remove the most loosely held electron from a gaseous atom.

(ii) Atomic radius is half the distance between two nuclei of two bonded similar atoms.

(b)(i) first ionization generally increases across period 3. This is because as electrons are added to the same shell of electrons, nuclear charge increases while screening effect decreases and thus the electron experiences increasing nuclear attraction. Atomic radius decreases across period 3. This is because of increasing effective nuclear charge which pulls the outermost electrons closer to the nucleus.

(ii) first ionization energy decreases down group (VII). This is because as the group is descended an extra shell of electrons is added from one element to the next. This increases screening effect which thus reduces effective nuclear charge and electrons are less strongly held.

Atomic radius increases on descending group (VII) this is because of increasing screening effect as a result of an extra shell of electrons added and thus electrons are less strongly held hence increase in atomic radius.

(iii) Both first ionization energies and atomic radii remain almost constant in moving from Ti to Ni. This is because the increase in effective nuclear charge is roughly balanced by increasing screening effect produced by addition of an electron to inner 3d sub-shell.

(c) (i) the first ionization of Mg is higher than that of Al because the first electron in Mg is being removed from full 3s sub-shell which is very stable and thus requires more energy.

i.e Mg $1s^2 2s^2 2p^6 3s^2$

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

(ii) the first ionization energy of P is higher than that of S because the first electron in P is being removed from a half full 3p sub-shell which is thermodynamically stable and thus requires more energy.

i.e P $1s^2 2s^2 2p^6 3s^2 3p^3$

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

(d) atomic number of an element can be obtained from its successive ionization energies

e.g potassium with 19 successive ionization energies has atomic number of 19. The arrangement of successive ionization energies in groups gives the number of electron shell being filled and hence the period to which the element belongs.

e.g successive ionization energies of potassium is arranged in groups of 2:8:8:3 and therefore potassium is period 4 element.

The group to which an element belongs can also be determined e.g in potassium the arrangement of successive ionization energies in groups shows a single electron which is very easily removed and the next 8 with similar ionization energies which are more difficult to remove than the single electron. Therefore potassium is a group 1 element.

The metallic or non-metallic character of an element can be determined from the value of its first ionization energy. Metals have their 1st ionization energy nearly all below 800 kJmol⁻¹ while non-metals have theirs nearly all above 800 kJmol⁻¹.

e.g potassium with its first ionization 419 kJmol⁻¹ is a metal while chlorine with its first ionization 1255 kJmol⁻¹ is a non-metal.

15. Discuss the three main processes involved in obtaining pure metals from their ores.

SOLUTION; the three main processes are

(a) **concentration of the ore.**

Concentration aims at removing unwanted earthy materials like rocks, clay, called gangue to increase the amount of ore containing particles.

(a) physical method

The commonest physical method of concentration is called froth floatation OR differential wetting. This is mainly used for sulphuric ores.

In this method, the ore is ground to powder form and then mixed with water containing special frothing agents e.g pine oil. A current of air is then passed through the mixture where the oil wets the ore while the water wets the gangue.

a froth forms at the surface containing mainly the ore while the gangue because of high density sinks down. The froth is skimmed off, treated with an acid filtered and dried. Floatation is used in the extraction of copper and zinc from copper pyrite and zinc blende respectively. Other physical method that can be used to concentrate ore include separation of the ore by use of a magnet e.g separation of tungsten ore. besides floatation and magnetic method of concentration, washing method is used also where certain ore because of their high density are washed in a stream. the gangue being lighter than the ore are washed away e.g. concentration of galena (PbS).

(ii) chemical method

One of the chemical methods used here is leaching. In this method the ore is dissolved in a suitable aqueous solution so as to extract the metal as a soluble salt. E.g. leaching of sulphides of copper with dilute sulphuric acid in the presence of air to form copper (II) sulphate.

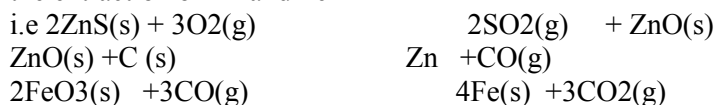
Bauxite ore can be dissolved in sodium hydroxide solution to form sodium aluminate.

(b) Reduction

This method is mainly used in the extraction of metals which are less reactive and which form less stable oxides that are easily reduced by carbon or carbon monoxide.

Reduction process is classified as

(i) high temperature reduction using carbon and carbon monoxide. Here the sulphide or carbonate ores are first converted by heating to the oxide. The oxide is then later reduced to the metal by heating with carbon or carbon monoxide. e.g. here the extraction of Zn and Fe



(ii) cathodic reduction (electrolysis of molten compounds) this is used in the extraction of reactive metals which form stable oxides which cannot be easily reduced by carbon or carbon monoxide.

e.g. electrolysis of molten pure Al_2O_3 in the extraction of aluminium.

this extraction of metal from its ore by a process involving melting is called smelting.

(c) Refining

Refining aims at producing pure metal.

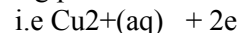
The following are some of the methods used

(i) Electrolysis

Here the electrolyte cell consists of the impure metal to be purified as anode while

the cathode is made of pure metal. The electrolyte is solution of a salt of the metal. During electrolysis metal ions at the anode go into solution and are then later deposited at the cathode.

e.g. purification of copper



Cu(s) (deposited at the cathode)

(ii) Distillation

This is used to purify mainly volatile metals like Zinc. Zinc and calcium are purified by fractional distillation.

16. The data below shows boiling points and bond energies of the halogens.

<u>F</u>	<u>Cl</u>	<u>Br</u>	<u>I</u>
Bond energy (kJ mol ⁻¹)	268	193	151
Boiling points (°C)	-34	59	184

Explain the trend in the variation of

a) Bond energies

b) Boiling points

SOLUTION

a) The strength of the covalent bond between the atoms in the molecule of the halogens decreases from fluorine to iodine.

This is because the increasing size of the molecule down the group causes the bonding pair of electrons to become further away from the two attracting nuclei and thus there is reduced attraction between the bonding pair electrons and the nuclei.

b) Boiling points increase down the group. This is because of the increasing magnitude of the van der Waals forces which hold the molecules down the group.

17. The table below shows the variation of bond lengths and bond energies of hydrides of group VII

<u>H-F</u>	<u>H-Cl</u>	<u>H-Br</u>	<u>H-I</u>
Bond length / nm	0.128	0.244	0.298
Bond energy / kJ mol ⁻¹	431	297	213

Explain the trend in the variation of

a) bond length

b) bond energies

SOLUTIONS

- the bond lengths increases from H_F to I-I. this is because of the increasing sizes of the halogens from fluorine to iodine which results in less attraction for the bonding pair of electrons
- bond energy decreases down the group. this is because the decreasing electronegativity from fluorine to iodine which results in weak attraction between the halogen and hydrogen.

18. (a) Hypochlorite, chlorate (I) is a component of domestic bleaching compounds and undergoes disproportionation reaction.

- state the oxidation state of chlorine in the ion
 - explain what is meant by the terms disproportionation reaction
 - write equation to show the reaction of chlorate (I) ion in (a) above.
- (b) Excess chlorine gas was bubbled through a hot concentrated solution of potassium hydroxide.

Write the equation of the reaction that took place.

(c) 1.6 g of the mixture of the salts in (b) were dissolved to make 250 cm³ of solution.

10.0 cm³ of this solution was then mixed with excess potassium iodine acidified with sulphuric acid

- state what was observed
- write the equation of reaction that took place
- if the product in (c) above required 12.8 cm³ of 0.1 M sodium thiosulphate solution for complete reaction calculate the percentage of potassium chlorate in mixture of the salt.

SOLUTIONS;

a) (i) chlorate (I) ion is ClO₂⁻

Let X = charge on chlorine

Since the charge on each oxygen ion is -2 and the overall charge on the ion is -1

∴ Charge of chlorine + charge of oxygen = -1

$$X + 2(-2) = -1$$

∴ the oxidation state of chlorine on the ClO₂⁻ ion = +1

(ii) Disproportionation reaction is where a reactant is both oxidized and reduced in the same reaction.

(iii) 3ClO₂⁻(aq) → 2Cl⁻(aq) + ClO₃⁻(aq)

Here the oxidation state of chlorine falls to -1 in Cl⁻ (reduction) and then

rises to +7 in ClO₃⁻ (oxidation)

(b) 3Cl₂(g) + 6KOH(aq) → 5KCl(aq) + KClO₃(aq) + 3H₂O(l)

(c) (i) A brown solution was formed (ie brown solution was due to iodine formed).

(ii) ClO₃⁻(aq) + 6H⁺(aq) → 3I₂(aq) + Cl⁻(aq) + 3H₂O(l)

(iii) the iodine produced above reacts with sodium thiosulphate according to the equation

I₂(aq) + 2S₂O₃²⁻(aq) → 2I⁻(aq) + S₄O₆²⁻(aq)

Since reaction in (c) (ii) produces three moles of iodine, equation

I₂(aq) + 2S₂O₃²⁻(aq) → 2I⁻(aq) + S₄O₆²⁻(aq)

is multiplied throughout by three and then later added to equation

ClO₃⁻(aq) + 6H⁺(aq) → 3I₂(aq) + Cl⁻(aq) + 3H₂O(l)

i.e. ClO₃⁻(aq) + 6H⁺(aq) + 6I⁻(aq) → 3I₂(aq) + Cl⁻(aq) + 3H₂O(l)

3I₂(aq) + 6S₂O₃²⁻(aq) → 6I⁻(aq) + 3S₄O₆²⁻(aq)

ClO₃⁻(aq) + 6H⁺(aq) + 6S₂O₃²⁻(aq) → 3S₄O₆²⁻(aq) + Cl⁻(aq) + 3H₂O(l)

Number of moles of S₂O₃²⁻ that reacted = 12.8 × 0.1

$$= \frac{1000}{1000} = 0.00128$$

Since 1 mole of ClO₃⁻ reacts with 6 moles of S₂O₃²⁻

∴ No. of moles of ClO₃⁻ that reacts = 1 × 0.00128

$$= \frac{1}{6} \times 0.00128 = 0.000213$$

∴ 10.0 cm³ of solution of the mixture of the salts contain 0.000213 mole of ClO₃⁻

∴ 250 cm³ solution would contain 0.000213 × 250 mole of ClO₃⁻

$$= \frac{10}{1000} = 0.0053$$

∴ The mixture contains 0.0053 mole of KClO₃

∴ Mass of KClO₃ in the mixture = 0.0053 × 122.5

$$= 0.653 \text{ g}$$

∴ Percentage of KClO₃ in the mixture = 0.653 × 100

$$= \frac{0.653}{1.6} \times 100 = 40.8\%$$

19. Scandium, chromium, copper and zinc are some of the elements of d-block series.

(a) (i) write the electronic configuration of the elements

(ii) explain why the electronic configuration of chromium and copper differ

from those of other elements mentioned above.

(b) using copper and chromium, explain the transitional characteristic of d_block elements

(c) explain why scandium and zinc are not transitional and yet are d_block elements.

SOLUTION

(a) (i) $21\text{Sc } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

$24\text{Cr } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

$26\text{Cu } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

$30\text{Zn } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

(ii) This is because an electronic configuration in which a sub_energy shell is either full or a half is regarded as thermodynamically stable.

Therefore, because chromium and copper have half_full and full 3d respectively, they are regarded as stable in those electronic configurations.

(c) d_block elements are those where the inner 3d sub_shell are being filled. Both chromium and copper are metals with high tensile strength and high melting and boiling points

MISSING NOTES

b) paramagnetism

is the attraction that occurs between transition metal ions and a magnetic field. Paramagnetism among transitional metal ions arises as a result of unpaired electrons in 3d_sub_shell. These unpaired electrons spin about their axes and thus generate a magnetic moment. This magnetic moment increases with the number of unpaired electrons.

Thus Fe^{3+} and Mn^{2+} with highest number of unpaired electrons have the highest magnetic moment

i.e Fe^{3+}

(Mn^{2+} (TABLE))

Cu^+ with only one unpaired electron has the least magnetic moment

i.e (TABLE)

a) Chelation

This is the tendency by some ligands to form ring structures with central metal ions. E.g. Complex ion formed between cobalt (III) ion and ethane 1,2_diamine i.e

STRUCTURE

(c) Monodentate ligand is one with only one donor atom e.g. H_2O , NH_3 etc.

DIAGRAM

Bidentate ligand is one with two donor atoms e.g. ethane 1,2_diamine.

$\text{NH}_2\text{CH}_2\text{NH}_2$ and OOC COO

This is able to donate electrons through the NH_2 groups present.

e.g. $[\text{Cu}(\text{NH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$

DIAGRAM

A multidentate ligand is one with many donor atoms e.g. ethylenediaminetetraacetic acid

EDTA

DIAGRAM

It has six donor atoms

(e) Coordination number is the number of ligands directly bonded with central metal ion.

e.g.	Complex	ion
		Coordination

on number

$\text{Ag}(\text{NH}_3)_2^+$

2

$\text{Ni}(\text{CO})_4$

4

$[\text{Cr}(\text{H}_2\text{O})_4 2\text{OH}]^+$

6

$[\text{Fe}(\text{CN})_6]^{4-}$

6

21. Iron(III) ion in aqueous solution exists as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

(a) state

(i) the oxidation number of ion in the complex

- (ii) the co_ordination number
 (iii) and explain the nature of this solution whether the PH is greater equal or less than 7
 (b) state the characteristics feature present in water molecule which enable it to act as a ligand
 ©(i) name the two possible reactions undergone by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ COMPLEX
 (II) write an equation in each case
 (d) draw a sketch of the hydrated ion (III) ion and name its shape.

SOLUTION

- (a) (i) since water molecules are neutral the charge of +3 on the complex ion is due to the ion i.e. oxidation state of ion is +3.
 (ii) since there are six water molecules bonded to the Fe^{3+} , the coordination number is 6
 (iii) because of the high charge of the Fe^{3+} , and its small size the Fe^{3+} exerts a strong attraction for the water molecules around it so strong that H^+ are set free in reaction.



Because of the H^+ are set free its solution is acidic with PH less than 7

- b) the lone pair of electrons on the oxygen atoms

- c) (i) Types of reactions are

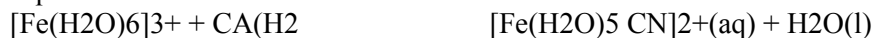
Hydrolysis

Substitution.

- (ii) equation for hydrolysis



Equation for substitution\



DIAGRAM

Shape is called hexagonal

- a) state four features of titanium that are typical of other transition elements
 b) titanium(IV) chloride was dissolved in concentrated hydrochloric acid
 i) write the formula of the product formed.
 (ii) state the oxidation state of titanium in the product.
 (iii) state the coordination number of titanium ion in product
 c) write the equation of the reaction of titanium (IV) chloride with water

SOLUTION

- (a) Has variable oxidation state, +3 and +4.
 The ion and compounds of Ti^{3+} are purple in colour.
 Titanium forms interstitial compounds e.g. TiH_7

Ti^{3+} is paramagnetic due to its single unpaired electron on the 3d

1

i.e.

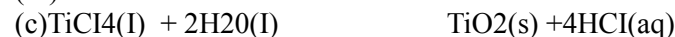
3d

- (b)(i) $[\text{TiCl}_6]^{2-}$. Hence the equation of reaction is



- (ii) +4

- (iii) 6



23.(a) state what would be observed and write equation each if excess potassium cyanide solution was added to aqueous solution containing

- (i) Nickel (II) ion

- (ii) Cobalt (II) ion

- (iii) iron (II) sulphate solution

(b) state what would be observed and write equation of reaction if potassium ferrocyanide potassium hexacyanoferrate (II) was added to solution containing

- (i) Fe^{3+}

- (ii) Zn^{2+}

- (iii) Cu^{2+}

SOLUTION

- (a)(i) observation;

A yellowish green precipitate formed initially which dissolves in excess to form a dark yellow solution.

Equation



- (ii) Observation;

A reddish brown precipitate formed which readily dissolves in excess to give a brown solution.

Equation;



NOTE

On boiling the product in (i) no change occurs but on boiling the product in (ii) the solution immediately turns yellow.

This is used to distinguish Ni^{2+} from Co^{2+}

- (iii) observation

A yellow precipitate of potassium hexacyano ferrate (III)

Equation



(b) (i) Observation

A dark blue precipitate is formed

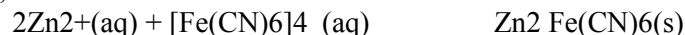
EQUATION



(ii) Observation

A white precipitate is formed

EQUATION;



(iii) OBSERVATION; A reddish brown precipitate is formed



24(a) Discuss the role of the sodium phosphate in the qualitative analysis of the ion

i) Mg^{2+}

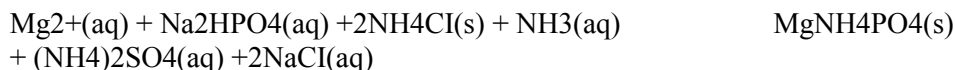
(ii) Ca^{2+}

(iii) Al^{3+}

(b) show how ammonium ethandiolate (oxalate) can be used to distinguish between the following ions Ca^{2+} and Ba^{2+}

SOLUTION

(a) (i) for the white precipitate to appear the disodium hydrogen phosphate solution should be added to the solution of Mg^{2+} to which little ammonia solution and solid ammonium chloride was added.



(ii) with Ca^{2+} the white precipitate is formed when only ammonium chloride (no ammonium solution) is added.

(iii) the white precipitate dissolves in dilute mineral acid or ammonia solutions

(iv) the white precipitate occurs here when the reagent above is added directly to the solution of Al^{3+} .

NOTE; No ammonia chloride and ammonia is required here.



Addition of ammonium ethanediate (

Oxalate) to a solution of Ca^{2+} or Ba^{2+} will produce a white precipitate with both ions .



But on warming each of the precipitate above in the presence of ethanoic acid ,

only the white precipitate of Ba^{2+} dissolves.

Show how you could use chemical test to detect an impurity of

- Nikel sulphate in iron(II) sulphate
- Iron(III) sulphate in iron(II) sulphate
- Ammonium nitrite in ammonium nitrate .
- Sodium sulphite in sodium sulphate.
- Cobalt chloride in nickel chloride
- Ammonium ethanoate in ammonium ethandiolate
- Potassium iodite in potassium iodide

SOLUTION

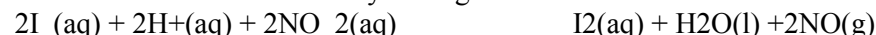
NOTE; For each of the following, an aqueous solution of is prepared

The following reagent then added should identify only impurity.

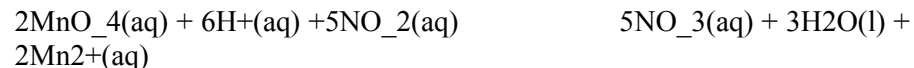
- both anions are the same (sulphate). Therefore we test for the presence of Ni^{2+}

A solution of dimethylglyoxime in the presence of ammonia is added where appears red precipitate confirms the presence of Ni^{2+} and hence NiSO_4 as an impurity.

- addition of a solution of potassium thiocyanate gives a deep blood red coloured product .this confirms the presence of Fe^{3+} of the impurity.
- To the solution add dilute sulphuric acid which produces thick brown fumes of nitrogen dioxide gas from nitrates only OR.A solution of acidified potassium iodide produces brown solution containing iodine which can be confirmed by adding starch solutions.



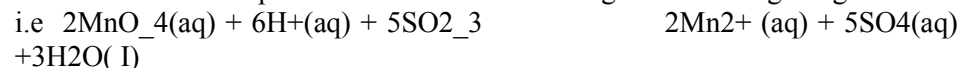
OR Addition of acidified potassium permanganate to a nitrate causes decolouration .



(d) to the solution added dilute sulphuric acid or conc. Sulphuric acid.

Evolution of sulphur dioxide gas which is confirmed using acidified potassium dichromate solution confirms the presence of sulphate ion.

OR addition of acidified solution of potassium permanganate or potassium dichromate . a sulphate di colourises the potassium permanganate while the acidified solution of potassium dichromate is changed from orange to green.



(e) to the solution is added a solution of potassium nitrite.

Formation of a yellow precipitate confirms presence of Co^{2+} as an impurity.

(f) addition of a solution of iron(III) CHLORIDE produces a deep red coloured product which on dilution and boiling produces a red precipitate. This confirms the presence of acetate as an impurity.

9g) to the solution is added excess potassium iodide solution followed by sulphuric acid.

Formation of brown iodine solution which is detected by use of starch solution confirms the presence of an iodite as an impurity



26. describe an industrial manufacture of chlorine

(b) fluorine and fluoride show some properties which are not typical of the rest of the group (VII) members.

(i) state three of these properties

(ii) suggest reason for that

(C) write equation and state the condition for the reaction of the chlorine with

(i) ammonia

(ii) sodium thiosulphate

(iii) calcium hydroxide

d) describe how you can qualitatively distinguish between sodium fluoride and sodium chloride.

e) Describe how you would determine titrimetrically the concentration of a given solution of sodium hypochlorite.

f) State the principal oxidation states shown by chlorine and for each state give one of the compounds formed

g) Give an account of the nature, structure and uses of interhalogens.

h) Briefly describe the manufacture of

i) Potassium chlorate

(ii) potassium iodate

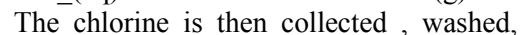
j) state three uses of chlorine gas.

SOLUTION

A) chlorine is manufactured by the electrolysis of concentrated solution of sodium chloride (brine) using the mercury cell process.

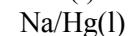
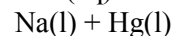
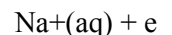
In the same direction is a stream of mercury which is allowed to flow and act as the cathode.

During the electrolysis chlorine gas is produced at the anode by the reaction



The chlorine is then collected, washed, cooled and dried before finally liquefaction.

Cathode sodium is produced and dissolved in the mercury to form sodium amalgam.



The

sodium amalgam is then reacted with a current of water to form sodium hydroxide which is later concentrated by evaporation.



Fluorine is the most reactive member.

Fluorides are more ionic than other halides.

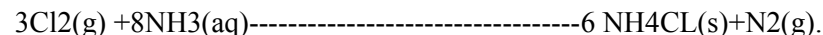
Fluorine forms very strong hydrogen bonds

Because fluorine has the greatest electronegativity value.

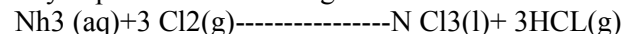
Fluorine has very low bond energy

Fluorine being the smallest in size

Chlorine reacts violently with concentrated ammonia burning with a green flame.

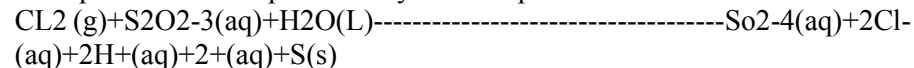


In the presence of excess chlorine, the reaction produces a dangerous yellow oily explosive called nitrogen chloride.



Chlorine reacts with sodium thiosulphate under two different conditions.

In the presence of a moderate amount of chlorine the thiosulphate is oxidized to sulphate with precipitation of yellow sulphur



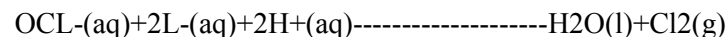
Chlorine reacts with solid calcium hydroxide (slaked lime) to produce bleaching powder $\text{Ca}(\text{OH})_2(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaOCl}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$

Each of these salts is dissolved in water and to the resultant solution formed is added lead ethanoate solution

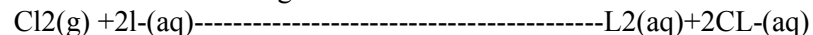
Sodium fluoride solution gives a white precipitate which does not dissolve on heating.

Sodium chloride solution gives white precipitate which dissolves to give a colorless solution on heating.

A fixed volume of the sodium hypochlorite solution is measured e.g. (10 cm³) and then diluted to 250 cm³ of solution with distilled water. Now a fixed volume of the diluted solution is pipetted and to it is added excess potassium iodine solution followed by ethanoic acid. Chlorine gas is formed by the reaction.



The chlorine gas then displaces I^- of the potassium iodine solution forming brown iodine according to the reaction



The iodine produced is then determined by titration with a standard solution of sodium thiosulphate using starch as an indicator and react according to the equation,



Since 1 mole of sodium hypochlorite produces 1 Moles of Cl_2 which then displaces one mole of Iodine, the concentration of the hypochlorite in the 10.0cm³ measured and later 1000cm³ of the original can be determined.

Chlorine shows the following principal oxidation states

+1 e.g $HClO$

+2 e.g Cl_2O

+3 e.g $HClO_2$

+4 e.g ClO_2

+5 e.g $HClO_3$

+7 e.g $HClO_4$

Halogens react with each other to form compounds called interhalogens which are of the type AB , AB_3 , AB_5 , AB_7 where

A is the less electronegative atom (cation) and B the more electronegative halogen (anion).

Under AB example are ClF (g), BrF (g), ICl (l), IBr (s)

AB_3 " are ClF_3 (g), BrF_3 (l), ICl_3 (s)

Under AB_5 examples are BrF_5 (l), IF_5 (l)

AB_7 " are If_7 (g)

The possible structures adopted are AB_3 - T- SHAPED

E.g BF_3 -----T-Shaped

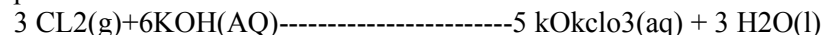
e.g Bf_3 f

F br

F

e.g IF_5

Potassium chlorate may be prepared using excess chlorine gas through hot concentrated solution of potassium hydroxide when slowing reaction takes place.



The resultant solution containing both potassium chlorate and potassium chloride is then concentrated by heating and then allowed to cool.

On cooling the potassium chloride crystals off washed and then

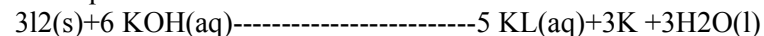
recrystallised to remove any trace of potassium chloride.

A hot concentrated solution of potassium is stirred with excess solid iodine until a permanent brown colour is obtained.

Then carefully more potassium hydroxide just discharge the brown colour.

The mixture is now heated to concentrate it and ---- to cool. During the cooling because potassium iodate(V) has low solubility at room temperature, it will crystallise. The crystals are filtered, washed and then recrystallised to obtain potassium iodate (V)

The equation of reaction is



Use of chlorine

As a bleaching agent and in the measure of bleaching agents e.e bleaching

Power

Sterilizing water for domestic use

Sterilizing water for domestic use

Manufacture of organic chemicals chromethane

Brass is an alloy of which copper is a component

Describe an experiment that can be carried out to determine the percentage of copper in brass.

2.4g of brass was dissolved to make 250cm³ of copper (II) nitrate. To 10.0cm³ of the solution was added excess potassium iodine solution. The iodine liberated required 9.60 cm³ of 0.1M sodium thiosulphate for complete oxidation.

Write the equation of reaction which took place between the potassium iodine and the brass solution. Calculate the percentage of copper in the sample of brass.

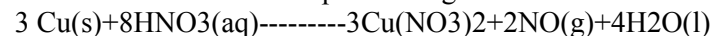
Explain why copper (I) Write the equation of reaction which took place between the potassium iodine and the brass solution.

Calculate the percentage of copper in the sample of brass

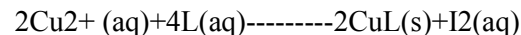
Explain why copper (I) chloride is insoluble in water and dilute hydrochloric acid but dissolves in concentrated hydrochloric acid

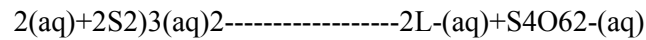
Solution

A known mass of brass is heated with a dilute solution of nitric acid and the resultant solution diluted to 250cm³ of solution with distilled water. A fixed volume of the diluted solution is pipetted and then titrated with a standard solution of sodium thiosulphate using starch solution. Form the reactions



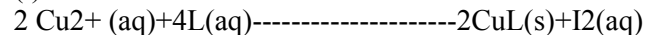
In brass



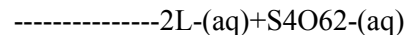


The number of moles of Cu^{2+} and hence copper can be calculated as in (b)

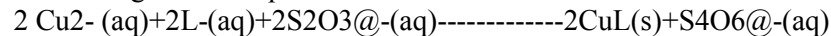
(i) below



Iodine and $\text{S}_2\text{O}_3^{2-}$ react according to the equation $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow$



Combining the two equations above we obtain



No. of mole of $\text{S}_2\text{O}_3^{2-}$ that reacted = $\frac{0.1 \times 0.6}{1000} = 0.00096$

Since SAME NUMBER OF MOLE OF Cu^{2+} AND $\text{S}_2\text{O}_3^{2-}$ REACT,

No of mole of $\text{Cu}^{2+} = 0.0096$

0.0cm³ of the brass solution contain 0.0096 mole of Cu^{2+}

250cm³ of the brass solution contain $\frac{0.0096 \times 250}{10} = 0.024$

Mass of copper in the brass = $0.024 \times 63.5 = 1.524\text{g}$

Percentage of copper in the 2.4 of brass used

$\frac{1.524 \times 100}{2.4} = 63.5\%$

Copper (i) chloride dissolved in concentrated hydrochloric acid because of the formation of a soluble complex called dichlorocupper (i) ion i.3



State the condition by which potassium manganate (iv) oxide

Manganese sulphate

Potassium manganate(VI)

State the oxidation states of chromium in each of the following CrO_3

CrO_2Cl_2

CrO_3

Explain each of the following

When potassium dichromate solution is shaken with sulphur dioxide, a clear dark green solution remains but if hydrogen sulphide is used, however the green solution contain a precipitate.

Addition of an acid to a solution of potassium chromate turns it from yellow to orange. Addition of sodium hydroxide solution, however reverses the change.

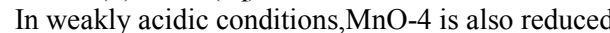
On adding water to anhydrous copper (ii) sulphate it turns blue. When

ammonia solution is added to the blue solution, a pale blue precipitate is first formed which dissolves in excess ammonia forming a deep blue solution. This colour is completely discharged by addition of potassium cyanide solution.

Solutions

On neutral or weakly alkaline condition MnO_4^{-} is reduced to manganese(iv) oxide according to the reaction. $\text{MnO}_4^{-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 3\text{e}^{-} \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^{-}(\text{aq})$

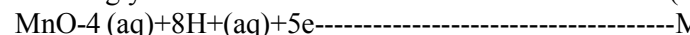
In weakly acidic conditions, MnO_4^{-} is also reduced to MnO_2



In strongly acidic condition MnO_4^{-} is reduced to $\text{Mn}^{2+}(\text{aq})$



In strongly alkaline condition $\text{MnO}_4^{-}(\text{aq})$ IS REDUCED TO MnO_2^{-}



Let m = charge on each chromium since oxygen ion has a charge of -2

Charge on 3 oxygen + charge on 2 chromium = 0

$$3 \times (-2) + 2m = 0$$

$$2m = +6$$

$$m = +3$$

Oxidation state of CR IN $\text{CrO}_3 = +3$

Let y = charge on chromium

Charge on Cr + charge on 2 oxygen on 2 oxygen + charge on 2 chlorine

$$y + 2 \times (-2) + 2 \times (-1) = 0$$

$$y - 4 - 2 = 0$$

$$y = +6$$

The oxidation state of chromium in $\text{CrO}_2\text{Cl}_2 = +6$

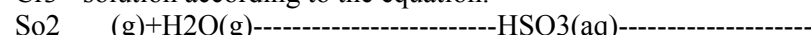
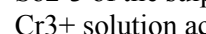
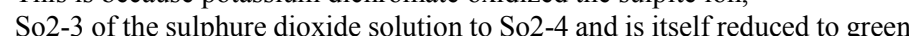
NOTE; The compounds Cr_2O_3 and CrO_2Cl_2 and above are neutral and therefore the charge overall in each of the compound = 0

+6

This is because potassium dichromate oxidized the sulphite ion,

SO_3^{2-} of the sulphur dioxide solution to SO_4^{2-} and is itself reduced to green

Cr^{3+} solution according to the equation:



Orange

green

The solid that appears in the green solution is sulphur formed by the oxidation

of S²⁻ of the hydrogen Sulphide.

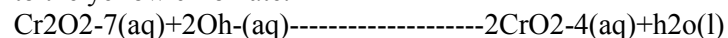
The change in colour from orange to green is because of the reduction of Cr₂O₇²⁻ (orange)

To Cr³⁺ (green)

This because in the presence of H⁺ a chromate (yellow) is converted dichromate according to the reaction.



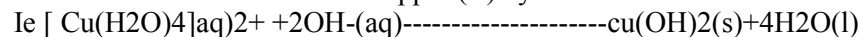
When sodium hydroxide is added the orange dichromate was converted back to the yellow chromate.



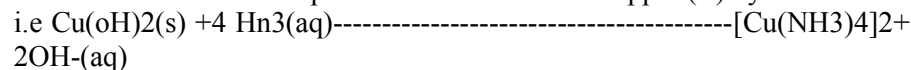
Addition of water to anhydrous copper sulphate produces a blue solution due to formation of hydrated Cu²⁺ in



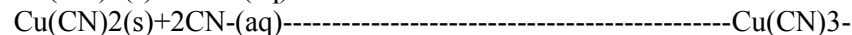
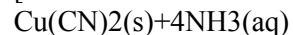
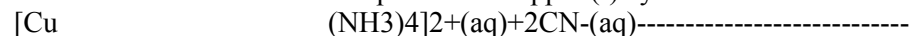
Addition of ammonia to this blue solution produced a pale blue precipitate due to formation of insoluble copper (II) hydroxide.



The deep blue solution formed when excess ammonia was added is due to formation of soluble complex called tetraammine copper (II) hydroxide



The deep blue colour is discharged on addition of potassium cyanide because of the formation of solution of potassium copper (I) cyanide.



4(aq)

Write equation and state the conditions for the reaction of hydrochloric acid with each of the following

Ti

Aluminium

Calcium oxide

Aluminium oxide

Lead (iv) oxide

Barium carbonate

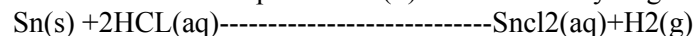
Iron(ii) Sulphide

Sodium thiosulphate

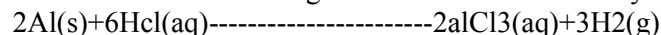
Solution

Tin reacts slowly with hot dilute hydrochloric acid but rapidly with

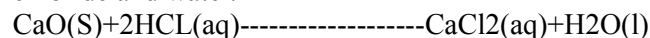
concentrated acid to produce tin (ii) chloride and hydrogen



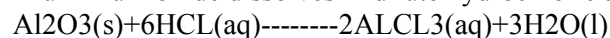
Aluminium reacts slowly with dilute hydrochloric acid but rapidly with concentrated acid forming aluminium chloride and hydrogen gas



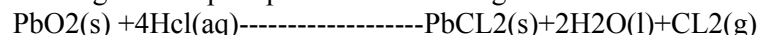
Calcium oxide reacts with hydrochloric acid at all conditions to form calcium chloride and water.



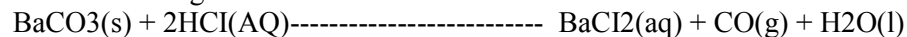
Aluminium oxide dissolves in dilute hydrochloric acid



Lead (iv) oxide reacts when warmed with concentrated hydrochloric acid forming a white precipitate and chlorine gas.



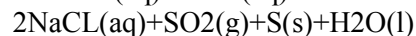
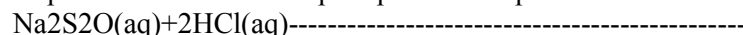
(f) Barium carbonate reacts with dilute hydrochloric acid giving off carbon dioxide gas.



Iron(ii) Sulphide reacts with dilute moderately concentrated hydrochloric acid forming iron(ii) chloride and hydrogen Sulphide gas



Sodium thiosulphate reacts with dilute hydrochloric acid forming sulphur dioxide and white precipitate of sulphur.



write equations FOR THE REACTION OF WATER WITH

Aluminium chloride

Calcium oxide

Tin (IV) chloride

Phosphorus trichloride

How and under what condition tin (II) oxide and tin (IV) oxide react with

Oxygen

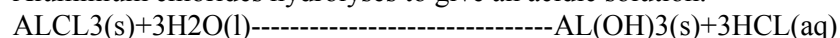
Hydrochloric acid

Sodium hydroxide

State four similarities in the chemistry of Tin and lead.

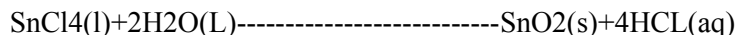
How is tin(IV) oxide prepared from tin.

Aluminium chloride hydrolyses to give an acidic solution.

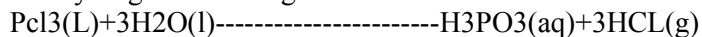


Calcium oxide reacts with cold water with a hissing sound, swells cracks and crumbles to give a white powder of calcium hydroxide (slaked lime)

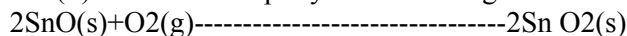
Tin (IV) chloride is rapidly hydrolysed in water forming an acidic solution



Phosphorus trichloride is rapidly hydrolysed to form hypophosphoric acid and hydrogen chloride gas

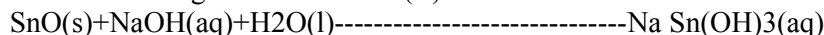


Tin (ii) oxide reacts rapidly with air and glows as the reaction takes place



Tin (ii) oxide dissolves in dilute hydrochloric acid to give tin (II) chloro-chloric acid.

Tin (II) oxide being amphoteric dissolves in aqueous sodium hydroxide solution forming sodium stannate(II)



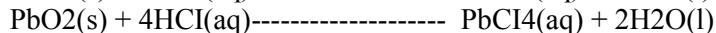
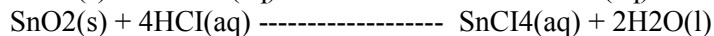
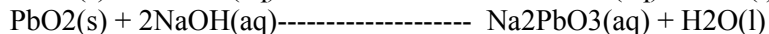
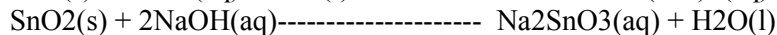
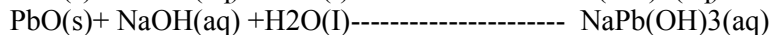
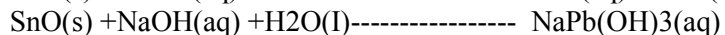
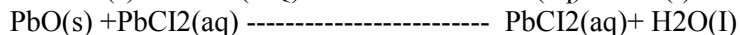
Tin(IV) oxide being acidic does not react with hydrochloric acid

Tin(II) oxide dissolves in sodium hydroxide solution to produce sodium stannate (IV)



(c) Both tin and lead form stable compounds in oxidation states of +2 and +4.

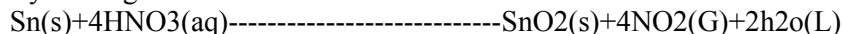
The monoxides and dioxides of both are amphoteric i.e. show both acidic and basic properties.



Both tin and lead can be used in alloying e.g. solder (50% Sn and 50% Pb)

Both Sn^{2+} and Pb^{2+} compounds are ionic

By heating tin metal with excess concentrated nitric acid



Name two reagents which when treated with a solution containing sulphite or a sulphate ion similar observation.

Give equation of reaction for each of the ions.

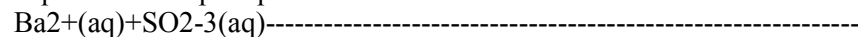
Give one reaction which is undergone by SO_3^{2-} alone and not SO_4^{2-}

Give examples of two reactions which are undergone by both nitrite and nitrate NO_3^- ions

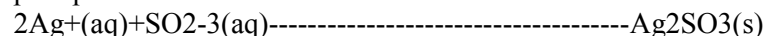
Give three reactions that can be carried out to distinguish NO_2^- from NO_3^- ion.

Solution

Both SO_3^{2-} and SO_4^{2-} react with a solution of barium chloride to deposit a white precipitate



Both SO_3^{2-} and SO_4^{2-} react with silver nitrate solution to give a white precipitate



Sulphite unlike sulphates react with both dilute and concentrated acid to produce sulphur dioxide gas

Both NO_2^- and NO_3^- react with Devarda's alloy (zinc, Aluminum, calcium) to produce ammonia gas

Note:

If any of the three metals above which are components of alloy is used, a similar observation is made.

BOTH NO_2^- and NO_3^- are decomposed to brown fumes of nitrogen dioxide gas on treatment with concentrated sulphuric acid.

Only NO_2^- and not NO_3^- reacts with a solution of acidified potassium iodine to form iodine.

NO_2^- unlike NO_3^- decolorises acidified solution of potassium permanganate.

Describe briefly how

The presence of a chromate CrO_4^{2-} can be determined qualitatively

The amount of a chromate ion in any soluble salt may be determined quantitatively.

3.20 g of an impure salt of potassium chromate was dissolved to make 1 dm³. 25.0 cm³ of this solution was pipetted and to it was added 25 cm³ of potassium iodine solution. The iodine produced required 11.40 cm³ of 0.1M sodium thiosulphate solution.

Write the equation of reaction which took place to produce iodine. Calculate the percentage purity of the salt.

Solutions

A little of the salt is dissolved in water to produce a yellow solution

The following tests are used to confirm the presence of a chromate in the solution.

Addition of lead nitrate or lead ethanoate solution.

OBSERVATION a BRIGHT YELLOW PRECIPITATE OF LEAD

CHROMATE FORMED WHICH DISSOLVE IN NITRIC ACID

Addition of hydrogen peroxide solution to the solution of the chromate containing dilute sulphuric acid.

OBSERVATION;

An intense blue coloration formed.

Addition of silver nitrate solution.

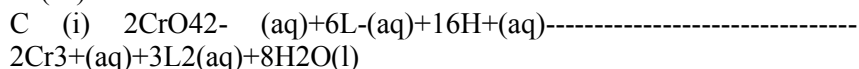
Observation

A red precipitate of silver chromate dissolves in both ammonia and dilute nitric acid.

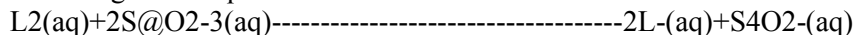
(b) A known mass of the chromate is dissolved to make 250 cm³ of solution. A fixed volume of the resultant solution is pipetted and acidified with sulphuric acid.

To this is then added excess potassium iodide solution. The iodine evolved is then titrated with a standard solution of sodium thiosulphate using starch as an indicator.

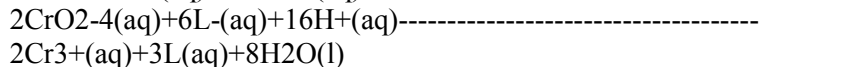
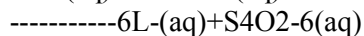
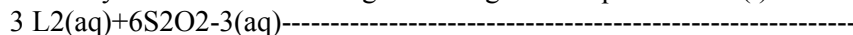
The calculation to determine the amount of the chromate is then done as in (C) below.



The iodine formed in © (i) above then reacts with sodium thiosulphate according to the equation.



The overall equation is now obtained by multiplying throughout equation above by three and then adding according to the equation in © (i)



Overall equation of reaction. 1 mole of CrO₄²⁻ reacts with 3 moles of S₂O₃²⁻

$$\text{No. of moles of S}_2\text{O}_3^{2-} \text{ that reacts} = \frac{11.40 \times 0.1}{1000}$$

$$\text{CrO}_4^{2-} \text{ that reacted} = \frac{1}{3} \times 0.00114 = 0.00038$$

Solution contain 0.00038 mole of CrO₄²⁻

$$\text{Solution contain } \frac{0.00038 \times 1000}{25}$$

$$\text{Sodium chromate} = 0.152 \times \text{r.f.m}$$

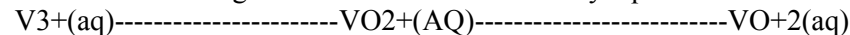
$$= 2.9488 \text{ g}$$

$$\text{purity} = \frac{2.9488 \times 100}{\dots}$$

32

=92%

Slowly show the range of oxidation states shown by aqueous vanadium



OXIDATION REQUIRED TO EFFECT THE FOLLOWING CHANGES. In each case reaction involved.

To Cr₂O₇²⁻(aq)

To Cr³⁺(aq)

To MnO₄²⁻

To MnO₂

Section series was carried out starting with

X(s) → Y(s) → fuse with Z(s)

KOH/KNO₃

Y and Z

Section to show how the following conversions took place

X(s)

Y(s)

Z(s)

Solution b (i) let x = charge on vanadium in VO₂⁺(aq)

Each oxygen as a charge = -2 Overall charge on the VO₂⁺ = +2

Charge on V + charge on O = +2

$$x + 2(-2) = +2$$

$$x = +4$$

Oxidation state on V in VO₂⁺ = +4. In VO₂²⁺: the overall charge on the ion = +1

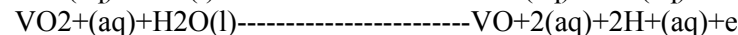
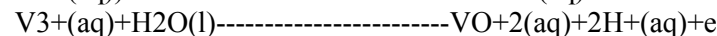
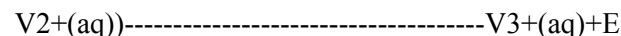
Charge on V + charge on two oxygen = +1

$$x + 2(-2) = +1$$

$$x - 4 = +1$$

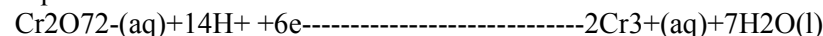
$$x = +5$$

Oxidation state of Vanadium in VO₂⁺ = +5



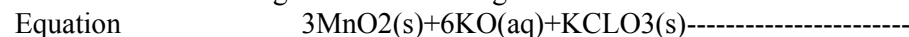
(i) Reagent Acidic medium e.g. H₂SO₄

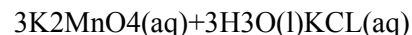
Equation



Reagent with potassium chlorate

The MnO₂ is fused together with the reagents





Reagent Addition of H^+ or dilution with water



MISSING NOTES

Write equation to show the following conversion are effected.

State what would be observed if to L was added

Ammonia solutions dropwise until in excess

A few drop of potassium iodine solution

A few drops of potassium hexacyanoferrate (II)

A few drops of potassium cyanide solution

Write equation in each

Outline the laboratory preparation of copper (I) chloride

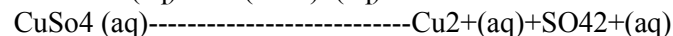
EXPLAIN WHY TRANSITION ELEMENTS

Are suitable as catalyst

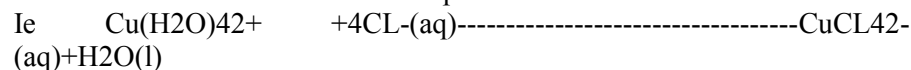
Form complexes

Have high melting points

L is $\text{Cu}^{2+}(\text{aq})$ or $\text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq})$ formed when CuSO_4 dissolves in water.



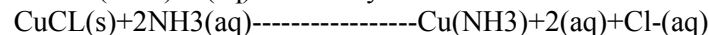
M is CuCl_2 formed when Cl^- are present in excess.



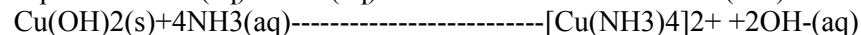
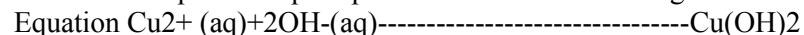
Pale blue green

N is $\text{CuCl}(\text{s})$ formed by reducing of CuCl_2 using excess SO_2 in the presence of water.

P is $\text{Cu}(\text{NH}_3)_2^+(\text{aq})$ formed by the dissolution of CuCl in ammonia

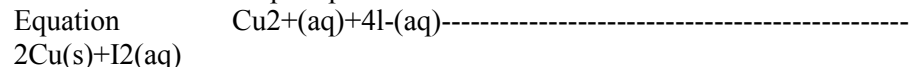


Observation pale blue precipitate solution in excess to give blue solution.



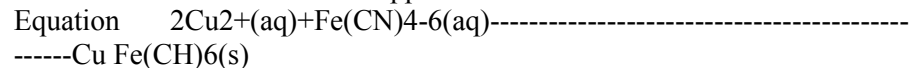
Deep blue solution.

Observation: A white precipitate stained brown with free iodine formed



White ppt brown

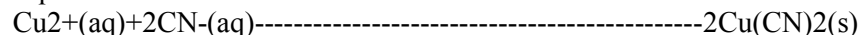
Observation : Reddish- brown ppt



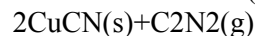
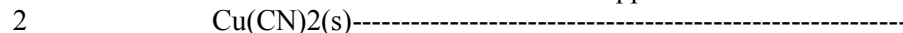
Observation A yellow precipitate which rapidly decomposes giving poisonous cyanogen gas and white ppt of CuCN ,

The precipitate dissolves in excess of KCN

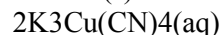
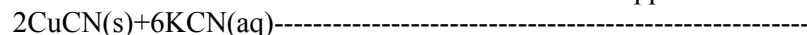
Equation



Yellow ppt



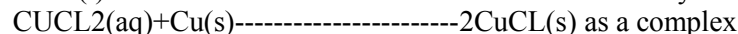
White ppt



Some copper (I) chloride crystals are first dissolved in excess concentrated hydrochloric acid.

The resultant solution is then boiled with some copper turning. The mixture formed here is then poured into boiled water and the mixture stirred. A white precipitate of CuCl forms on cooling. This then filtered and washed with a solution of sulphur dioxide.

Note (i) Excess conc HCl is used so as to hold formed by the reaction



Boiled water is used here because it is free of oxygen which would oxidize the CuCl salt.

The washing also with a solution of SO_2 avoids oxidation

This is because the presence of 3d electrons enable the transition metals to form a temporary bond with the reactant molecules.

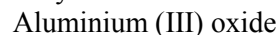
This is because of their small and highly charged ions which strongly attract lone pair of electrons donated and also because of the presence of vacant d-orbitals which can accommodate lone pairs of electrons donated by ligands.

This is because they form strong metallic bonds by involving electrons from both 4s and 3d in delocalization.

Write equation of reactions to show the effect of heat on



Write equation of reaction of each of the following with sodium hydroxide.



Cl_2O_7
 $2\text{PbO}_2(\text{s}) \rightarrow 2\text{PbO}(\text{s}) + \text{O}_2(\text{g})$
 $2\text{Pb}_3\text{O}_4(\text{s}) \rightarrow 6\text{PbO}(\text{s}) + \text{O}_2(\text{g})$
 $\text{Be}(\text{s}) + 2\text{NaOH}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Na}_2\text{Be}(\text{OH})_4(\text{aq})$
 $\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaAl}(\text{OH})_4(\text{aq})$
 $\text{Cr}_2\text{O}_3(\text{s}) + 6\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}_3\text{Cr}(\text{OH})_6(\text{aq})$
Sodium hypochlorite
 $\text{Cl}_2\text{O}(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow$
 $\text{NaClO}_2 + \text{NaClO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Chlorine dioxide sodium chlorite
 $\text{ClO}_6(\text{l}) + 2\text{NaOH}(\text{aq}) \rightarrow$
 $\text{NaClO}_2 + \text{NaClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Chlorine hexoxide sodium chlorate
 $\text{Cl}_2\text{O}_7(\text{l}) + 2\text{NaOH}(\text{aq}) \rightarrow$
 $2\text{NaClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Chlorine heptoxide sodium perchlorate
 Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 are known oxides formed by chlorine in the oxidation states of +1, +4, +6 and +7.
Explain what is meant by the term diagonal relationship
Give two examples of pairs of elements which show diagonal relationship
State three chemical properties for each pair to illustrate the relationship.
Write the formula of the oxides formed by Na, Ca, Al, Si and P.
State the type of bonding and structures adopted by these oxides
Illustrate one trend in the periodic table by considering the properties of these oxides
Explain why
Sodium melts at only 97.8°C and magnesium melts at 665°C and yet both are metals.
Phosphorous has a lower melting point than silicon.
Radius of potassium ion, K^+ (0.13nm) is smaller than that of potassium atom (0.23nm)
Chloride ion Cl^- (radius 0.181nm) is bigger than chlorine atom (radius 0.099nm)
Solution
This is the similarity in the chemistry of two elements and their compounds.
These elements belong to the different adjacent group and are diagonal to each other
Lithium (group I) and magnesium group (II)
Beryllium (group II) and Aluminum (group III)
In the similarity of the chemistry between lithium and magnesium

Both Li_2O and MgO react with carbon dioxide gas.
The hydrogen carbonates of Lithium and magnesium exist only in solution.
The halides of lithium and magnesium dissolve in organic solvents.
The following are some of the properties that make Beryllium and Aluminum to be diagonally related.
The oxide hydroxides of both Beryllium and Aluminum are amphoteric
Both Beryllium and Aluminum dissolve in alkali forming
 $\text{Be}(\text{OH})_4^{2-}$ and $\text{Al}(\text{OH})_4^-$ respectively.
Both Beryllium and Aluminum form complexes with fluoride ion, i.e. BeF_4^{2-} and AlF_6^{3-}
 Na_2O , CaO , Al_2O_3 , SiO_2 and P_2O_5
 Na_2O , CaO and Al_2O_3 have ionic bonding and adopt giant ionic structures
 SiO_2 has covalent bonding and adopts giant molecular structure.
 P_2O_5 has covalent bonding and adopts simple molecular structure.
Across a period in the periodic table, one of the trends is that the elements change from metals via metalloids to non-metals. Metals form ionic oxides which dissolve in water to give solutions which are basic in nature.
Therefore the oxides of metal, Na and Ca dissolve to give basic solutions
e.g. $\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq})$
 $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$
The oxide of non-metal, phosphorous dissolves in water to give an acidic solution.
 $\text{P}_2\text{O}_5(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_3\text{PO}_4(\text{aq})$
Mg has a higher melting point than sodium because it has stronger metallic bonds than sodium. This is due to the greater number of valence electrons which magnesium contributes to its charge cloud than sodium.
Magnesium contributes two electrons while sodium contributes only one.
Sulphur has a higher magnitude of Vander Waal's force due to its greater molecular size than the smaller P_4 molecules formed by sulphur
melting point among metals depends on the number of valence electrons donated by the metal. THE GREATER THE NUMBER OF VALENCE ELECTRONS, THE STRONGER THE IONIC BOND FORMED AND THE HIGHER WILL BE THE MELTING POINT. Among non-metals, melting point depends on the size of the molecule.
THE GREATER MOLECULAR SIZE THE STRONGER IS THE Vander Waal's forces and the higher the melting point.
Potassium ion, K^+ is formed when a potassium atom loses an electron
i.e. $\text{K} \rightarrow \text{K}^+ + \text{e}^-$
This increases the proton-electron ratio so that the remaining few electrons are now more strongly attracted by the constant nuclear charge. This results in

electron being pulled closer to the nucleus hence decrease in radius
Chloride ion is formed when a chlorine atom gains an electron.

I.E $\text{Cl} + e^- \rightarrow \text{Cl}^-$

This results in decrease in the proton-electron ratio with the result that constant nuclear charge will be less attraction for the many electron and hence increase in radius

State the oxidation state of chlorine in

Cl_2

HCl

HClO_4

Name a reagent that can be used to distinguish between each of the following. In each case state what is observed if each member of the pair is treated with reagent

SO_2 and SO_3

CO_3^{2-} and HCO_3^-

SO_3^{2-} and SO_4^{2-}

NO_2 and NO_3^-

Where possible give an equation of reaction.

Solution

Fluorine being more electronegative than chlorine becomes the anion while chlorine the cation. Since each fluoride ion has a charge of -1

Therefore to give an overall charge of Zero the molecule, ClF , the charge on chlorine should be +

i.e. Charge on chlorine + charge on fluorine = 0

$+1 + (-1) = 0$

Here chlorine is more electronegative than iodine.

Therefore the charge on it is -1

Reagent Silver nitrate solution

Observation: A white precipitate of silver sulphate formed insoluble in excess.

$2\text{Ag}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{SO}_4(\text{s})$

With SO_2 , a white precipitate is formed which dissolves in excess and on heating rapidly darkens

Reagent Iron (II) chloride solution

Observation SO_2 - No observable change occurs

SO_2 - 3 - Violet colored product formed which disappears leaving a colorless solution

Or **Reagent** Dilute acids (e.g. Dil HCl)

SO_3^{2-} - Decomposes with evolution of sulphur dioxide and yellow sulphur deposited

Reagent: iodine solution

Observation SO_3^{2-} - No observable change occurs

SO_3^{2-} - The brown colour of iodine is discharged

Reagent: Magnesium sulphate solution.

Observation: No precipitate appears when added to a cold solution of HCO_3^- with CO_3^{2-} ion, white ppt is formed immediately the magnesium sulphate is added to the cold CO_3^{2-}

Boiling with a solution of alkali or ammonium carbonate hydrogencarbonate.

Observation: HCO_3^- - Solution produces bubbles of carbon dioxide gas while with CO_3^{2-} so solution no observable change occurs.

Reagent Dilute sulphuric acid or conc. Sulphuric acid

Observation: Effervescence of sulphur dioxide forms with SO_3^{2-} salt while no observable change occurs with SO_4^{2-} salt

Reagent Barium chloride solution

Observation SO_3^{2-} - A white ppt formed soluble in hydrochloric acid

A white ppt formed insoluble in hydrochloric acid

Reagent: Acidified potassium iodine solution

Observation NO_2 - Brown solution of iodine formed

NO_3^- - No observable change occurs

Reagent Acidified potassium permanganate solution

Observation NO_2 - Purple solution turns colourless

NO_3^- - No observable change occurs

CHAPTER 12

WORKED EXAMPLES ON THE ANALYSIS OF SOME INORGANIC COMPOUNDS

Below is analysis of some inorganic compounds. In the analysis you are expected to record all your observations and deductions in the spaces usually provided

Any gas evolved must be identified by its confirmatory tests

1. Substance A contains one cation and one anion

TEST

OBSERVATION

A spatula end-full of A is melted to give a white sublimate. A must be an ammonium salt. A is first heated gently and then near the mouth of the test tube until no further gas evolves. The gas has a sweet smelling neutral character and changes to a white solid when it meets a glass rod dipped in concentrated sulphuric acid.

DEDUCTION

A must be an ammonium salt. A is first heated gently and then near the mouth of the test tube until no further gas evolves. The gas has a sweet smelling neutral character and changes to a white solid when it meets a glass rod dipped in concentrated sulphuric acid.

(b) To spatula end –full of A dissolves in H_2SO_4 to give product with odour like that of H_2SO_4 and then heated ethanoic acid

(c) A spatula end- full of A is dissolved in about 5cm³ of solution water and the resultant solution divided into three portions

(i) To the first portion is added aqueous sodium hydroxide dropwise until in excess and heated

(ii) To the second portion is added an equal volume of ethanol followed by 3 drops of conc. H_2SO_4 and the mixture heated gently. The mixture is then poured in a small beaker of water

(iii) The third portion was used to carry out a test of one's choice to confirm the anion in A. to the third portion is added a few drops on Iron is chloride solution and water diluted and boiled

Probably A contain an ethanoate (the first portion is added sodium hydroxide solution dropwise until in excess and the mixture warmed smell and which turns red moist red litmus blue is given off

A is a non – transitional element, probably A contains NH_4^+ , Cu^{2+} , Al^{3+} , Ca^{2+} , Mg^{2+} , Ba^{2+} and Pb^{2+}

A white precipitate soluble in excess dilute hydrochloric acid dropwise until in excess

A white precipitate is formed drop of aqueous AgNO_3 and to the mixture is added nitric acid dropwise until in excess

The white ppt dissolves in nitric acid

The purple colour of the mixture is discharged and a colorless gas which turns moist blue litmus red and which turns lime water milky is given off

Presence of ethanoate ion is confirmed

Presence of CH_3COO^- confirmed

On in B = COO^-

Substance C contains one cation and one anion

Non; The cation A = NH_4^+

The anion A = CH_3COO^-

Substance B contain one cation and one anion.

OBSERVATION

DEDUCTION

A spatula end-full of B is heated in a hard glass test tube until no further change takes place.

B decomposes to give off vapour which forms a white sublimate near the mouth of the test. the vapour turns moist red litmus blue

(b) To a spatula end-full of B in a boiling tube is added about 10 cm³ of solution. water. the resultant solution is then divided into four portions

B is probably NH_4^+ , Zn^{2+} , Al^{3+} , Ca^{2+} , Pb^{2+} salt.

TEST

OBSERVATION

A small amount C is heated until there is no further change.

DEDUCTION

C decomposes giving out a neutral gas with sweet smell and which burns. The residue is a whitish solid

To a spatula end-full of C is added a little ethanol and a few drops of conc. H_2SO_4 and the mixture warmed

A sweet fruity smelling product formed

A small amount of C is dissolved in water. The resultant solution is then divided into 5 portions

C dissolves to give a colourless solution

C is a Zn^{2+} ,

The first portion is added sodium hydroxide solution dropwise until is formed

A white precipitate insoluble in excess

in excess		cooled. The resultant solution is then colourless gas which relights a glowing splint.	
To the second portion is added ammonia dropwise until excess	No observable change occurs	Probably Ca^{2+} and Ba^{2+} present	
To the third portion added 3 drop of iron (ii) chloride and the mixture boiled	A deep red product formed which forms a red ppt on boiling	CH_3COO^- presence confirmed	To the first portion added silver nitrate dropwise until further change takes place
To the fourth portion is added 3 drops of potassium chromate	No observable change occurs	Ca^{2+} presence confirmed	To the second portion is added a drop of ammonium thiocyanide solution
To the last portion is added about 0.5 cm ³ of ammonia oxalate solution followed by 2 cm ³ of ethanoic and warmed.	A white ppt formed insoluble on warming with ethanoic acid	Ca^{2+} presence confirmed	To the third portion added a few drops of decolourising acid
The cation in C = Ca^{2+} The anion in C = CH_3COO^- Substance D contains one cation and one anion		To the third part of the solution is (2) above is added a few drops of 2- 3 drops of ethanol followed by 3 drops of dilute H_2SO_4 . To the fourth part was added a few drops of dilute nitrate solution.	
Test		e) To the last part was carried a test of one's own choice.	
Observation		Deduction	
1. A spatula end-full of D is heated strongly in a test tube	Colourless vapour formed which condenses on the collar part of the test tube and turns anhydrous copper (II) sulphate blue. A colourless gas with pungent smell which turns potassium dichromate green is formed. The residue is a dark green solid.	Water of crystallization hydrated salt present. SO_4^{2-} salt presence. D is a transition compound, probably containing Cr^{3+} or Ni^{2+} The cation in D = Cr^{3+} The anion in D = SO_4^{2-} Substance E contains one cation and one anion	A deep blue lake is formed A white precipitate insoluble in nitric acid is formed
2. A spatula end- full of D is dissolved in about 5 cm ³ and the resultant solution divided into four parts.	D dissolves to give green solution	Probably D contains Cu^{2+} , Ni^{2+} , Fe^{2+} or Cr^{3+} ion	
a) To the first part is added ammonium hydroxide solution drop wise until excess		Probably Cr^{3+} presence confirmed.	E dissolves to give off a colourless acidic gas which turns lime water milky. The residue is greenish black solid.
To the second part is added dilute sodium hydroxide solution dropwise until in excess followed by 1 cm ³ of 10% hydrogen peroxide solution and the resultant mixture boiled and later	A green precipitate is formed which slightly dissolves to give a violet solution	H_2O_2 oxidises the mixture to form a yellow solution.	E dissolve with effervescence giving off a colourless gas which turns blue solution is green

To the first portion is added dilute NaOH dropwise until in excess and the mixture heated. A light green precipitate insoluble in excess which does not change on heating is formed. ~~not most likely~~ choice to confirm the anion present in the filtrate.

To the second portion is added aqueous ammonia dropwise until in excess to give a purplish blue solution. A light green precipitate is formed which dissolves in excess to give a purplish blue solution. Presence of Ni^{2+} is confirmed by dilute nitric acid. A white precipitate insoluble in nitric acid is formed. The residue is now washed and dilute HCL added drop wise until there is no effervescence of colourless gas which further change. The resultant solution is acidic and which turns lime water milky. The solution formed is light blue in colour.

Cation in E = Ni^{2+}

Anion in E = CO_3^{2-}

Note most carbonates are powdery.

F contains two cations and two anions. test

Observation: a) A spatula end-full of F is heated strongly in dry test tube. Deduction: Colourless vapour is given off which turns anhydrous CuSO_4 blue. Water of crystallization hydrated salt present.

A colourless gas which turns lime water milky is produced. The residue is a green solid.

The two spatula end-full of F is shaken with about 10 cm³ of water and the mixture filtered. Both the filtrate and the residue are then kept for analysis.

The filtrate is then divided into 5 parts

j) To first part is added dilute

NaOH dropwise until excess. A blue precipitate which is insoluble in excess which later turns pink on standing in air.

To the second part is added aqueous ammonia dropwise until in excess. A blue precipitate slightly soluble in excess. It turns red on standing in air. A blue colouration is formed.

To the 3rd part is added conc. Potassium thiocyanate

(iv) To the fourth part is added 3 drops of lead (ii) nitrate solution. A white precipitate is formed.

v) The fifth portion was used to carry

The gas is CO_2 and hence probably CO_3^{2-} , HCO_3^- or $\text{C}_2\text{O}_4^{2-}$ is present. Residue could be NiO , CuO or Cr_2O_3 .

To the 4th part is added aqueous potassium iodine solution. A white precipitate stained brown with free iodine liberated is formed.

Probably Co^{2+} present. To the last part is added a few drops of potassium thiocyanate. No observable change apparently occurs.

Probably Fe^{2+} , Ni^{2+} , Cu^{2+} or Cr^{3+} salt present. The cation in F are Co^{2+} and Cu^{2+} . The anion in F are Cl^- and CO_3^{2-} .

G contains two cations and two anions

Presence of Co^{2+} is most likely

TEST

Observation: A spatula end- full of G is heated strongly in dry test tube.

Colourless vapour given off which turns anhydrous CuSO_4 blue. Co^{2+} forms a blue complex of tetrahedral shape.

G decomposes to give thick brown gas. The residue is a black solid. MnO_2

Probably Cl^- , SO_4^{2-} or CO_3^{2-} . Two spatula end- full of G is shaken with about 8 cm³ of water. The filtrate is a faint pink solution.

was filtered And both the filtered AndThe residue is a white solid both the filtrate and Residue kept.

The filtrate was divided into four parts.

To the part is added dilute NAOH dropA dirty white precipitate insoluble inPresence of Mn²⁺ most likely.

wise until in excess excess which turns brown is formed

To the second part is added diluteA white precipitate insoluble in excess.Mn²⁺ most CATION is G are Mg²⁺ and Pb²⁺

aqueous ammonia dropwise in excess is formed.The precipitate turns brown

ANION is G are NO₃⁻ and I⁻

To the third part was about someA purple solution is formed

Contains are cation and two anions

lead(IV) oxide followed by about

The Mn²⁺ is oxidized by pbo₂ in the presence of cnc.HNO₃ to purple MnO₄⁻

0.5cm³ of conc.HNO₃ and the

4 Hence presence of Mn²⁺ in the filtrate is confirmed

mixture boiled.

OBSERVATION

Deduction

The last part was used for carrying out a test of one;s choice to confirmed the aion in thje filter.

Aspatula end- full of ---- strongly in aH decomposes to give a colorless gasThe gas dry which turns moist blue litmus red and which turns acidified solution of K₂Cr₂O₇ green

Test: To the last part is added aboutAbrown ring forms at the junction ofNO₃⁻ presence is confirmed

Two spatula end- full H is shaken withThe filtrate is a colorless solution about 10cm³ of water.The resultant

Non- t
Probab
The re

1cm³ of iron the liquids
(ii) sulphate solution.Conc H₂SO₄
uis then slowly added down the side of the test tube.

mixture is filtered and both the filtrate and residue kept

The residue is yellow solid

Probab

The residue is washed and diluteThe residue disssolves to give aProbably Pb²⁺, Zn²⁺, Al³⁺, Mg²⁺ and ca²⁺ present

The filter is then divided into threeAwhite precipitate is formed

HNO₃ added dropwise until no furthercolourless solution

To the part is added a fewcm³ of lead

change occurs.The resultant solution

ethanoate solution

is then divided into 6 parts

To the second oart is added a fewThe colur of the dichromate changespresen

To the first part is added dilute NaOHA white precipitate soluble in excess isEither Pb²⁺ or Al³⁺ present

drops of acidified potassiumfrom orange to green

while

dropwise until in excess formed.

dichromate.

To the second part is added aqueousA white precipitate insoluble in excessEither Pb²⁺ or Al³⁺ present

To the third part is added a few drop ofAwhite put soluble in Hcl is formed toPresen

ammonia is formed

barium chloride followed by littleform a colourless solution

The third was used to carry out a testA thick yellow precipitate is formed

Probably I⁻ present

of on;s change to confirm the cation presnt.

The residue is washed and dried inThe residue dissolves to give an orangeProbab

Test : T o the third part is added a few drops of potassium iodide solution

between filter paper.A spatula end-full-yellow solution

To the fifth part is added dilute

of the residue is dissolved in about

ethanoic and followed by a few drops

5cm³ of dilute HNO₃

of sodium nitrate a carbon

The brown colouration is due to Iodine liberated hence I⁻ present

To the first portion is added diluteAwhite precipitate is formed soluble inProbab

NaOH dropwise until in excess. excess

To the second port-ion is addedA white precipitate is formed in solubleProbab

aqueous ammonia dropwise until in excess.

To the third portion is added aqueous sodium carbonate dropwise until indissolves in excess

The fourth portion was used for a test of one's choice to confirm the cation. observable change occurred

Test: To the fourth portion was added a few drops of potassium iodine solution

To the fifth portion was added little lead ethanoate solution

To the last portion was added a few drops of H_2SO_4 followed by 1 cm³ of hydrogen peroxide.

which relights a glowing splint is formed.

Cation in H = Al^{3+}

Anions present in H are SO_3^{2-} and CrO_4^{2-}

Substance I CONTAINS TWO CATIONS AND TWO ANIONS

TEST

OBSERVATION

DEDUCTION

A spatula end-full of I is heated strongly in dry test tube.

A colourless gas which turns blue litmus red is formed which turns lime water milky

The filtrate is then divided into 5 parts. To the first part is added dilute sodium hydroxide dropwise until in excess

To the second portion is added aqueous ammonia dropwise until in excess

The third part was used for a test of one's choice to confirm the cation

Test To the third part 4 drops of magnesium followed by little sodium hydroxide solution

To the fourth part is added about 1 cm³ of lead ethanoate solution and the mixture warmed

Probably Cl^- and Br^-

To the fifth part is added 1 cm³ of nitric acid followed by few drops of ammonia solution

A white precipitate is formed which dissolves in ammonia solution

The residue is washed and dissolved into three portions. The resultant solution is divided into three portions

To the first portion is added NaOH dropwise until in excess

To the second portion is added 3 drops of acidified potassium dichromate

To the third portion is added a few drops of potassium hexacyano ferrate (III)

The cations present in I are Mg^{2+} and Fe^{2+}

The anions present in I are Br^- and CO_3^{2-}

Substance J contains two cations and two anions

TEST

CO₂ hence CO_3^{2-} probably present

OBSERVATION

DEDUCTION

A spatula end-full of J is heated strongly in an ignition tube

Two spatula ends –full of J is shaken with about 8 cm³ of water.

The filtrate was divided into 6 portions. To the first portion was added aqueous sodium hydroxide until in excess.

To the second portion was added ammonia solution dropwise until indissolved in excess to a blue solution

To the third portion was added aqueous potassium cyanide dropwise until indissolves in excess to form a dark excess

excess	yellow solution	Ni(CN) ₄ ²⁻ mineral acid or ammonia solution with Ca ²⁺ . Ni ²⁺ therefore Disodium hydrogen phosphate reacts with Al ³⁺ to give a white ppt soluble in Ni ²⁺ present in neutral acids
To the forth portion was added about 0.5cm ³ of ammonium chloride solution followed by a few drops of ammonia and then a few drops of dimethylglyoxime	A pink ppt was formed	Substance K contains one cation and ne anion test
To the fifth portion was added lead nitrate solution	A white ppt formed	Probably Cl ⁻ , CO ₃ ²⁻ or SO ₄ ²⁻
To the last portion was added a few drops of barium nitrtte solution followed by some little nitric acid	A white ppt insoluble on dilute nitric acid formed	SO ₄ ²⁻ confirmed present
The resdue was washed in water and later dissolved in about 5cm ³ of dilute nitric acid	The residue dissolved with effervescence of a colourless which turned litmus red and which fiormed a white ppt with limewater. The resultant solution was colourless.	The gas produced was Co ₂ Co ₃ 2- from a carbonate. Probably the solution contained Ca ²⁺ , Mg ²⁺ or Al ³⁺ To spatula end-full of K is added a few drops of conc sulphuric acid then the mixture heated
The residue solution above was then divided into 4 parts	Awhite ppt formed in soluble in excess	Probably Ca ²⁺ or Mg ²⁺ present
To the first part was added aqueous sodium hydroxide dropwise until in excess	White ppt formed insoluble in excess	Mg ²⁺ presence is most likely present
To the second part was added aqueous ammonia solution dropwise until in excess	White ppt formed	Mg ²⁺ present
To the third part was added a few drops of ammonia solution followed by about 1cm ³ of ammonium chloride solution and some little disodium hydrogen phosphate solution.	Awhite ppt crystalline pp is formed	Mg ²⁺ presence confirmed
The cations present in J are Ni ²⁺ and Mg ²⁺ The Anions present in J are SO ₄ ²⁻ and CO ₃ ²⁻ Note Disodium hydrogen phosphate is used to test for the presence of either Mg ²⁺ ,Ca ²⁺ or Al ³⁺ In the presence of little ammonia solution and ammonium chloride solution.In gives a white ppt with Mg ²⁺ Mg ²⁺ (aq)+Na ₂ HPO ₄ (aq)+2NH ₄ CL(aq)----- MgNH ₄ PO ₄ (s)+2NH ₄ +(aq)+2NaCL(aq) In the presence of ammonia chloride solution it gives a white ppt soluble in dilute	References http://www.chemguide.co.uk/inorganic/redox/equations.html#top	