INORGANIC CHEMISTRY

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For

2nd Students

Physical and Chemistry group

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INORGANIC CHEMISTRY

THE MAIN GROUP ELEMENTS

Introduction:

Inorganic chemistry has often been said to comprise a vast collection of untreatable facts. It deals with many compounds formed by many elements. It involves the study of the chemistry of more liquids or solids whose reactions may be or may have to be studied at very low or very high temperatures.

Although various concepts help to bring order and system into inorganic chemistry, the oldest and still the most meaningful relies on the periodic table of the elements. It depends on the electron structures of the gaseous atoms of different elements, where a pattern of electronic structures of the elements was built by successively adding electrons to the available energy levels. However, the periodic table can also be based entirely on the chemical properties of the elements and so it gives us a good knowledge for chemical facts.

The nature and types of the elements :

It is self evident that the chemical properties of an element must depend on the electronic structure of the atom.

This determines not only how the elements can bind to other elements but also to their selves thus hydrogen (l s) can

clearly only from a diatomic molecule. Briefly, elements divided into:

<u>Monatomic elements</u> : e.g. , noble gases (He , Ne, Ar,Kre, Xe ,Rn) and vapor mercury.

<u>Diatomic molecules</u>: H_2, N_2, O_2, F_2, Cl_2, Br_2 , I_2 for single electron-pair bond in a diatomic molecule completes the octet. For nitrogen $2S^2$ $2P^2$ $2P^3$ and oxygen $2S^2$ $2P^4$ multiple bonding can give simple diatomic molecule. Also P_2 and S_2 are stable at elevated temperatures, but not at $25C^o$.

<u>Polyatomic molecules</u>: P_4, Sn,Se_8, in which the P-P bonding of the type found in N_2 and O_2 is less effective. White phosphorus has tetrahedral molecules. Sulfur has a profusion of allotropes; these contain multy atom sulfur rings. The largest ring known is S_{20}, but the most stable form is orthorhombic sulfur.

With respect to certain properties elements are divided into metals and nonmetals.

<u>Metals</u>:

The majority of the elements are metals. These have many physical properties different from other solids: notably

1- high reflectivity.

2- high electrical conductance decrease with increasing temperature.

3- high thermal conductance.

4- mechanical properties such as strength and ductility.

There are three basic metal structures: cubic hexagonal close packed and body-centered cubic

With respect to chemical properties we see that metals are highly electropositive (giving positive ions), consequently they have basic character and can be used as reducing agents.

<u>Nonmetals</u> :

Elements have tendency to accept electrons and form negative ions are known as nonmetals. They have acidic character and can be used as oxidizing agents.

Elements which have properties between those of metals and nonmetals are known as semimetals or metalloids.

According to the electronic configuration of the atoms of the elements, they are divided into:

(a)<u>Non-transition elements</u>: which form the main group elements and we will discuss in details.

(b)<u>Transition elements</u>: which may be strictly defined as elements have partly filled d or f shells. We adopt a broader definition and include also elements that have partly filled d or f shells in compounds. So we treat the metals Cu, Ag and

Au as transition metals. Since Cu (II) has a $3d^9$ configuration, Ag (II) has a $4d^9$ configuration, and Au (III) has a $5d^8$ configuration. This group of elements will be discussed in details in separate course.

<u>The chemistry of the main group elements in relation to their position in the periodic table:</u>

Now we can proceed to more detailed commentary on the chemical reactivity and types of compounds formed by the elements. The periodic table forms the basic for the discussion, starting with the simplest chemistry, namely that of hydrogen, and proceeding to the heaviest elements.

<u>Hydrogen $1S^1$</u>

Its chemistry depends on three electronic processes:

(1) Loss of the 1S valence electron to form the Proton H^+. The proton never exists as such except in gaseous ion beams. It is associated with other atoms or molecules and it found in water as H_3O^+ or $H(H_2O)_n^+$.

(2) Acquisition of an electron: The H atom can acquire an electron forming the hydride ion H^+ with the He; $1S^2$ structure. This on exists only in hydrides (The compounds produced as a result of combination of H^+ ion with electropositive metals are called hydrides, e.g. NaH, CaH_2).

(3) Formation of covalent bonds with nonmetals and even many metals, e.g. NH_3 , BH_3.

Helium $1S^2$ and the noble gases $nS^2\ np^6$

It has the closed 1S shell. The physical properties of the other noble gases very systematically with size. Although the first ionization energies are high because of their inert character; the values decrease as the size of the atom increases and consequently the ability to inter into chemical combination with other atoms should increase.

Elements of the first short period :

The seven elements Li to F constitute the first members of the groups of elements. Li (z=3) has the structure $1S^2$,2S. With increasing z, electrons enter the 2S and 2P levels until the closed shell configuration $1S^2\ 2S^2\ 2P^6$ on neon is reached. These elements are in common with the elements of their respective groups in view of the similarity in the outer electronic structures of the gaseous atoms. The increase in nuclear charge and consequent changes in the extranculear structure result in extremes of physical and chemical properties: Li has low ionization enthalpy according to the facile loss of an electron to form Li^+ ion. This leads to high reactivity of Lithium toward oxygen nitrogen, water and many other elements. For Be, the first and second ionization enthalpies are high and so the Be^{+2} ion does not occur, (in BeF^2 the Be-F bonds have covalent character) B ($2S^2$, $2P^1$) is bound covalently in all its compounds.

Anion formation first appears for carbon, which forms C^{2-}_2 and some other polyatomic ions. The existence of C^{4-} is uncertain. Carbon is a true nonmetal It can form single, double and triple bounds, and also it is able to form chains of carbon-carbon bonds.

Nitrogen compounds are covalent. With electro-repetitive elements, ionic nitrides containing N^{3-} may be formed .

Oxygen molecule has two unpaired electrons, and so it is very reactive. It forms covalent bond with many compounds (CO, SO_3,). Oxygenated ions O^{2-}, O_2^- , O^{2-}_2 are also exist.

Fluorine is extremely reactive due largely to the low bond energy in F_2. It forms ionic compounds containing F^- ions and covalent compounds, owing to the high electron negativity of fluorine.

The second short period

The elements Na, Mg, Al and Si ,P, S and Cl constitute the second short period. Their outer most shells are similar to those of the first short period, but the chemistries differ. In particular, the chemistries of Si , P , S and Cl. The main reason for this is; the heavier atoms would encounter large repulsive forces due to overlapping of their filled inner shells, whereas the small compact inner shell of the first-row elements, that is, just $1S^2$, does not produc this repulsion.

However, the second row elements give a better guide to the chemistries of the heavier elements in their respective groups than do the first row members.

<u>Remainder of no transition elements</u>

Group I : (Li , Na , K , Rb , Cs and Fr).

All the elements are highly electropositive giving +1 ions. These metals show most clearly the effect of increasing size ad mass on chemical properties. Thus as examples , the following decrease from Li to Cs:

(a) melting points and heat of sublimation of the metals.

(b) hydration energies.

(c) strength of covalent bonds in M_2 molecules.

<u>Group II</u> : Be, Mg, Ca, Sr, Ba and Ra

Calcium, Sr, Ba and Ra are also highly electropositive forming +2 ions. Systematic group trends are shown, for example, by increasing:

(a) hydration tendencies.

(b) insolubilities of sulfates.

(c) thermal stabilities of carbonates and nitrates.

<u>Group III</u>: B, Al, Ca, In and T1

Al has a considerable tendency to covalent bond formation, and the mainly ionic nature of the heavier elements. Gallium, In and T1 like Al are borderline between ionic and covalent in compounds, even thought the metals are quite electropositive and they form M^{+3} ions.

<u>Group IV</u>: C, Si, Ge, Sn and Pb

Carbon is nonmetallic; silicon is also nonmetallic but little of the chemistry of Si can be inferred from that of C. Germanium is much like silicon, although it shows more metallic-type behavior in its chemistry. Tin and lead are metals, and both have some metal lime chemistry especially in the divalent state.

The main chemistry in the IV oxidation state for all the elements is essentially one that involves covalent bonds and molecular compounds (e.g. Ge Cl_4 and Pb Et_4). There is a decrease in he tendency to catenation in the order C> S1 > Ge~ Sn ~ Pb. The strengths of covalent bonds to other atoms decrease in going from C to Pb. The divalent state is also found in compounds like carbines (e.g., : CF_2) and those for the other group IV elements can be regarded as carbon like.

<u>Group V</u>: P, As, Sb and Bi

Like nitrogen, phosphorus is essentially covalent in all its chemistry but arsenic, antimony and bismuth show increasing tendencies to cationic behavior. Although electron gain to achieve the electronic structure of the next noble gas is conceivable (as in N^{-3}) considerable energies are involved so that the anionic compounds are rare. Similarly, loss of valence electrons is difficult because of high ionization energies. There are no + 5 ions and even the + 3 ions are not simple, being SbO^+ and BiO^+, BiF_3 seems

predominantly ionic. The increasing metallic character is shown by the oxides that changes from acidic for phosphorus to basic for bismuth, and by halides that have increasing ionic character.

Group VI: S, Se, Te and Po

These atoms can achieve the configuration of the noble gas by forming :

(1) The M^{-2} ions, in salts of highly electropositive elements.

(2) Two electron pair bonds as in H_2S or $SeCl_2$.

(3) Anionic species with one bond as in HS^-.

(4) Three bonds and one positive charge as in Sulfonium ions R_3S^+

There are also compounds in formal oxidation states IV and VI with 4,5, or 6 covalent bonds, (e.g., $SeCl_4$, SeF_5^-, and TeF_6).

Except Po there is no cationic behavior. There are gradual changes in properties with increasing size and decreasing electro negativity.

a) Decreasing stability of the hydrides H_2X.

b) Increasing metallic character.

c) Increasing tendency toward forming anionic complexes, such as $(SeBr_6)^{-2}$, $(TeBr_6)^{-2}$, $(PoI_6)^{-2}$

<u>Group VII</u>:

The halogen atoms are only one electron short of the noble gas configuration and the elements form the anion X^- or a single covalent bond.

Their chemistries are completely nonmetallic. The change in behavior with increasing size are progressive, and there are closer similarities within the group.

The halogens can form compounds in higher formal oxidation states, mainly in halogen fluorides such as ClF_3, ClF_5.

HYDROGEN

Hydrogen, the first element in the periodic table. It has the simplest atomic structure of all elements, and consists of a nucleus of charge +1 and one orbital electron. Hydrogen has little tendency to lose this electron and great tendency to pair the electron and form covalent bond. Also hydrogen can gain an electron and form negative ions in reactions with highly electropositive metals. Since its properties differ from those of both group I and group VII elements, it could well be put in a group of its own.

Isotopes of hydrogen:

If atoms of the same element have different mass numbers, they are called isotopes. Three isotopes of hydrogen are known: 'H hydrogen "H", ^{2}H deuterium (D) and ^{3}H tritium (T).

Since these isotopes have the same electronic configuration, they have the same chemical properties, but the difference in mass makes them show much greater differences in physical properties. The only differences in chemical properties are equilibrium constants and the rates of reactions.

Deuterium is found in the ordinary hydrogen, and it can be separated by electrolysis. D_2O may be obtained by repeating electrolysis of H_2O several times. Tritium is radioactive and has a half life time of 12.26 years.

$$^{3}_{1}T \longrightarrow {}^{3}_{2}He + B^{-}$$

It is produced in nuclear transformations.

$$^{14}_{7}N + {}^{1}_{o}n \longrightarrow {}^{12}_{6}C + {}^{3}_{1}T$$

<u>Ortho and Para hydrogen:</u>

The hydrogen molecule H_2 exists in two different forms known as ortho and para hydrogen. If the nuclear spins of the two atoms in the molecule are in the same direction, it gives ortho hydrogen, and if the nuclear spins of the two atoms in the molecule are in opposite directions, it gives para hydrogen.

(ortho) (para)

At absolute zero, hydrogen is 100% in the para form, but as temperature is raised, the proportion of ortho hydrogen increases up to a limiting mixture containing 75 % ortho hydrogen .

<u>Properties of molecular hydrogen</u>

Hydrogen is the lightest gas known, and is colorless, and almost insoluble in water. It is found in many compounds such as water, carbohydrates and organic compounds, ammonia and acids, but as molecular hydrogen's , its abundance is very small .

It can be prepared according to the following methods :

(1) Electrolysis of water or sodium hydroxide.

(2) From hydrocarbons.

$$CH_4 + H_2O \xrightarrow[\text{Ni catalyst}]{\text{high temp.}} Co + H_2$$

(3) From coal also, but this method is too expensive

$$C + H_2O \xrightarrow{\text{red hot}} CO + H_2 \xrightarrow[450^{o}C/Fe_2O_3]{+H_2O} 2H_2 + CO_2$$

CO_2 is removed by dissolving in water under pressure, or reacting with K_2CO_3 solution, giving $KHCO_3$.

(4) Hydrogen can be prepared by the reaction of salt like hydrides with water.

$$LiH + H_2O \longrightarrow LiOH + H_2$$

(5) In the laboratory, the usual method is the reaction of dilute acids on metals.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

1- Hydrogen burns in air, but it is not very reactive and under certain conditions, it explodes with oxygen and halogens.

2- It is used in the production of ammonia.

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$

and this reaction is favored by high pressure, low temperature and the presence of suitable catalyst.

3- Hydrogen is also used to reduce metal oxides to meals.

4- It is useful in hydrogenation processes. Hydrogen molecule is very stable.

$$H_2 \longrightarrow 2\ H \qquad \Delta H = 431\ kg\ mol^{-1}$$

S-Block Elements

Group I- Alkali Metals

Table (1) :

Element	Symbol	Electronic structure
Lilthium	Li	(Ne) $2S^1$
Sodium	Na	(Ne) $3S^1$
Potassium	K	(Ar) $4S^1$
Rubidium	Rb	(Kr) $5S^1$
Caesium	Cs	(Xe) $6S^1$
Francium	Fr	(Rn) $7S^1$

Electronic structure:

As we mentioned in the last chapter, the elements of group I all have one electron in their outer orbital an S-electron in a spherical orbital. There are similarities in the electronic structures of the outer most shells of these elements (Table1); accordingly, many similarities in chemical behavior would be expected. The elements are typically soft, highly reactive, univalent metals, and form colorless ionic compounds Li shows considerable differences from the rest of the group.

General properties:

The atoms are the largest in their corresponding period in the periodic table, and when the outer electron is removed to give a positive ion, the positive charge on the nucleus is greater than the number of electrons so that the

electrons are attracted towards the nucleus, and the ion is smaller than the corresponding atom. Even so, the ions are very large, and increase in size from Li to Fr where shells of electrons are added.

These elements have low density because of their large size.

They have low ionization energies, because the outer orbital electrons are a long way from the nucleus and they are relatively easy to remove, and as the size of the atom increases, the electrons are further away from the nucleus and are less strongly held, so the ionization energy decreases. (Table 2).

Electro negativity values for this group elements are very low. Thus when they react with other elements to form compounds, ionic bonds are formed.

$$Na + 1/2\ Cl_2 \longrightarrow Na^+\ Cl^-$$

Table (2)

Element	atomic radius (A^o)	ionic radius (A^o)	density (g/cc)	ionization energy kJ mol^{-1}	Electro-negativity	M.p. C^o
Li	1.23	0.60	0.54	520	1.0	181
Na	1.57	0.95	0.97	496	0.9	99
K	2.03	1.33	0.86	419	0.8	63
Rb	2.16	1.48	1.53	403	0.8	39
Cs	2.35	1.69	1.87	373	0.7	29

Since there is only one valiancy electron in this group have a low cohesive energy and are soft. The cohesive energy decreases and softness increase (Li → Cs), because the increase in size of atoms in this direction is followed by increasing repulsion from the nonbonding electrons. According to the low values of cohesive energy and its decrease (Li → Cs), the values of melting and boiling points are low and decrease as size increases.

The melting point of lithium is different from the other element of the group .

Sodium is found in NaCl, and potassium occurs as KCl in sea water. Francium is radioactive and has a short half-life period of 21 minutes.

The metal ions all have inert gas configuration, thus all electrons are paired and consequently they are diamagnetic and colorless.

<u>Chemical properties:</u>

(1) Chemically these elements are very reactive, and tarn rapidly in air to form the oxide; and the nitride in the case of lithium (Li_3N) but not other elements.

(2) These elements react with water and liberating hydrogen to form hydroxides, which are the strongest bases.

$$2\ Na + 2\ H_2O \longrightarrow 2\ Na\ OH + H_2$$

The reaction increase from Li to Cs.

(3) Mono oxides, peroxides, and super oxides are formed when metals are burnt in air (e.g., Li_2O, Na_2O_2, and KO_2). They are prepared by dissolving the metal in liquid ammonia and casing it to react with the appropriate amount of oxygen. M_2O oxides are basic oxides because they react with water and forming strong bases. They are all very soluble in water (except for LiOH). M_2O_2 and NO_2 oxides are oxidizing agents because they react with water and acid giving H_2O_2 and O_2.

$$Li_2O + H_2O \longrightarrow 2\ LiOH$$

$$Na_2O_2 + 2H_2O \longrightarrow 2\ NaOH + H_2O_2$$

$$KO_2 + 2H_2O \longrightarrow KOH + H_2O_2 + 1/2\ O_2$$

(4) The metals all react with sulphur forming sulphides and polysulphides.

$$2\ Na + S \longrightarrow Na_2S$$

$$2\ Na + nS \longrightarrow Na_2S_n \quad (n=2,3,4,5,\text{ or }6)$$

The reaction takes place in ammonia solution as solvent.

(5) The metals react with hydrogen forming hydrides, which contain the H-ion (as indicated from electrolysis, where the hydrogen liberated at the anode). These hydrides react with water liberating hydrogen.

$$Li + 1/2\ H_2 \longrightarrow LiH$$

$$LiH + H_2O \longrightarrow LiOH + H_2$$

$Li(AlH_4)$ is a useful reducing agent in organic chemistry. It is prepared as shown in the following equation:

$$4\,LiH + Al\,Cl_3 \xrightarrow{ether} Li\,(Al\,H_4) + 3LiCl$$

As the size of atoms increase (Li → Cs), reaction with hydrogen becomes less easy.

Solubility and hydration :

All the simple salts are soluble in water, and conductivity measurements give results in the order, $Cs^+ > Rb^+ > K^+ > Na^+ >$ Li+ in aqueous solution. This is due to the ions being hydrated in water or in solution. Li^+ is heavily hydrated, hence it moves slowly, and Cs^+, the least hydrated moves faster. (Table 3).

The primary shell of water molecules which hydrate a metal ion is forming a complex. A secondary layer of water molecules further hydrates the ions, though these are only held by weak ion dipole attractive forces. The strength of such forces is inversely proportional to the distance, that is to the size of the metal ion. Thus the secondary hydration decreases from Li → Cs. The size of the hydrated ions affect the passage of these ions through water and this explains why hydrated Li^+ are attached less strongly, and hence eluted first from action exchange columns.

Table (3)

Element	atomic radius (A^{o})	ionicmobility at infinite dilution	Approx. radius of hydrated ion (A^{o})	Approx. hydration number
Li^+	0.60	33.5	3.40	25.3
Na^+	0.95	43.5	2.76	16.6
K^+	1.33	64.5	2.32	10.5
Rb^+	1.45	67.5	2.28	10.0
Cs^+	1.69	68.0	2.28	9.9

As we said before, simple salts of group I elements are all soluble in water. The solubility of most of the salts in water decrease on descending the group. For a substance to dissolve, the hydration energy must exceed the lattice energy.

All the metals of Group I dissolve directly in very high concentration in liquid ammonia, and these solutions conduct electricity better than any salt in any liquid. The metals are also soluble in other amines and act as powerful reducing agents.

<u>Oxy salts (carbonate, bicarbonate and nitrate) of Group I metals:</u>

Because of the highly electropositive or basic nature of these metals, their oxy salts are uite stable. The carbonates are remarkably stable, and decompose into oxides at temperatures over 1000^{o}C Li_2CO_3 is less stable and decomposes more readily.

Group I metals also form solid bicarbonates. Except NH_4HCO_3, these are the only solid bicarbonates known. They decompose to carbonates on gently heating liberating CO_2

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Note that Li does not form a solid bicarbonate but it can exist in solution.

All carbonates, and bicarbonates are soluble in water, and Na_2CO_3 is used as washing soda but Na_2HCO_3 is used as baking powder.

The nitrates are all very soluble in water, and $LiNO_3$ and $NaNO_3$ are deliquescent. KNO_3 is used in gun powder. The solid nitrates are very stable, but decompose on strong heating into nitrites.

$$Na\ NO_3 \longrightarrow Na\ NO_2 + 1/2\ O_2$$

$LiNO_3$ decomposes forming the oxide:

$$2Li\ NO_3 \longrightarrow Li_2O + 2\ NO_2 + 1/2\ O_2$$

<u>Halides of Group I elements</u>:

Li form hydrated halides of the type $LiX._3H_2O$ (X = Cl or Br or I) because of the small size of its ion. The other alkali metal halides form anhydrous crystals, which have NaCl structure with coordination number 8.

Alkali metal halides react with halogens and inter halogen compounds forming ionic plyhalide compounds.

$$KI + I_2 \longrightarrow KI_3$$

$$KBr + ICl \longrightarrow K(BrICl)$$

$$KF + BrF_3 \longrightarrow K(BrF_4)$$

Extraction of the metals:

Sodium is obtained by the Downs process i.e. electrolysis of NaCl with $CaCl_2$ added to lower the operating temp. from 803°C (m.p. of NaCl) to 505°C (m.p. of $NaCl/CaCl_2$ mixture).

Also sodium may be obtained by Castner process in which fused NaOH is electrolyzed .

$$4\ NaOH \longrightarrow 4Na + 2\ H_2O + O_2$$

But that method has low current efficiency and is absolete.

The modern method to obtain potassium is to pass sodium vapor over molten KCl in a large fractionating tower.

$$Na + KCl \longrightarrow K + NaCl$$

Compounds with carbon:

Metals of group I elements react with acetylene forming carbides.

$$Na + C_2H_2 \longrightarrow NaHO_2 \longrightarrow Na_2C_2$$

which on hydrolysis give acetylene.

$$Na_2C_2 + H_2O \longrightarrow 2\ NaOH + C_2H_2$$

Li forms carbide by direct reaction with carbon

$2Li + 2C \longrightarrow Li_2C_2$. Also these metals replace hydrogen in organic acids forming salts.

$$Na + CH_3COOH \longrightarrow CH_3COONa + H$$

$$K + C_6H_5COOH \longrightarrow C_6H_5COOK + H$$

<u>Differences between Li and the other group I elements</u>:

Lithium is a typical of group I elements, but shows slight similarity with group. II elements, particularly Mg. This is due to the polarizing power $\frac{\text{(ionic charge)}}{\text{(ionic radius)}^2}$ being similar.

The following points illustrate the common properties of lithium and the diagonal relationship.

(1) The melting point and boiling point of Li are comparatively high.

(2) Lithium is much harder than the other group I metals.

(3) Lithium reacts the least readily with oxygen forming the normal oxide, but the higher oxides being unstable.

(4) Li is much less electropositive, and therefore many of its compounds are less stable (Li_2CO, $LiNO_3$ and LiOH) all form oxide on gentle heating, and no solid bicarbonate is known.

(5) The ion and its compounds are more heavily hydrated than those of the rest of the group.

(6) Unlike the other group I elements, Li reacts directly with C to form carbide.

(7) Li has a greater tendency to form complexes because of the small size of its ion.

Group II

Alkaline Earth Metals

Table (4)

Element	Symbol	Electronic	Structure
Beryllium	Be	(He)	$2S^2$
Magnesium	Mg	(NE)	$3S^2$
Calcium	Ca	(Ar)	$4S^2$
Strontium	Sr	(Kr)	$52S^2$
Barium	Ba	(Xe)	$6S^2$
Radium	Ra	(Rn)	$7S^2$

Electronic structure:

All group I elements have two S electrons in their outer orbital as shown in the above table. They are typically divalent. These metals are highly reactive, but less basic than group I. Beryllium shows some differences from the rest of the group.

General properties:

The size of atoms is large, but is smaller than the corresponding group I elements, since the extra charge on the nucleus draws the orbital electrons in. Similarly, the size of ions is large, but is smaller than the corresponding group I elements, since the removal of two outer electrons increases the effective unclear charge.

The number of bonding electrons in the metals is now two, so that these have higher melting and boiling points and

densities than group I metals. Also the two valence electrons participate in metallic bonding, make these elements harder than group I.

The metals of group II are electropositive with high chemical reactivates.

The ionization energies are higher than those of group I atoms. The total energy required to produce divalent ions for group II elements is over four times greater than the amount needed to ionize group I metals; also the hydration energies of group II ions are greater than for group I elements, because of the small size and increased charge of nucleus of group II ions. As the size of ions increase down the group I, the hydration energy decrease. (Table 5).

Since the divalent ions have the inert gas structure with no unpaired electrons, the compounds of group II element are always divalent, ionic, diamagnetic and odorless, unless the acid radical is colored.

Table (5)

Element	atomic radius (A^o)	ionic radius M^{+2} (A^o)	Ionization energy Kg mol^{-1} 1st	2nd	Melting point C^o	Electro negativity
Be	0.89	0.31	899	1757	1277	1.5
Mg	1.37	0.65	737	1450	650	1.2
Ca	1.74	0.99	590	1145	838	1.0
Sr	1.91	1.13	549	1064	768	1.0
Ba	1.98	1.35	503	965	714	0.9
Ra	-	1.50	509	979	700	-

Behavior of Beryllium:

Beryllium differs from the rest of the group partly because it is extremely small and partly because of its comparatively high electro negativity; so that it forms two covalent bonds in its anhydrous compounds. Its ions in solution have the form $(Be(H_2O)_4)^{2+}$. This increases the effective size of the beryllium ion, and stable ionic salts $((Be(H_2O)_4))\ SO_4$, $(Be(H_2O)_4)\ (NO_3)_2$.)) are known.

In pure water beryllium salts are acidic. This is due to the strength of Be-O bond which weakens the O-H bonds, hence there is a tendency to lose protons.

H

$(H2O)_3\ Be^{+2} \longrightarrow$ O $\longrightarrow$ $(H_2O)_3Be^{+} \longleftarrow$ O + H^+

H H

Solubility and hydration energy:

The solubility of most salts decreases with increased atomic weight. The hydration energy also decreases as the metal ions become larger.

Fluorides and hydroxides increase in solubility on desc-ending the group. This is because the lattice energy decreases more rapidly than the hydration energy, and this favors increased solubility since a substance to dissolve, the hydration energy must exceed the lattice energy.

Chemical properties:

(1) The electro positively of the metals is less than that in group I.

(2) The metals still react with water to form hydrogen and metal hydroxides.

$$M + 2\ H_2O \longrightarrow M(OH)_2 + H_2$$

Beryllium is not typical. It reacts with steam to form the oxide BeO or fails to react at all. Magnesium reacts slowly with hot water. The other metals react with cold water.

(3) The basic strength of group II hydroxides increase with increasing the atomic weight of metals. Beryllium hydroxide $Be(OH)_2$ is amphoteric.

$$Be(OH)_2 + 2\ HCl \longrightarrow BeCl_2 + 2H_2O$$

$$H_2BeO + KOH \longrightarrow K\ H\ BeO_2 + H_2O$$

$Mg(OH)_2$ is weakly base, $Ca(OH)_2$ is moderately strong base, while $Sr(OH)_2$ and $Ba(OH)_2$ strong base. Calcium hydroxide

is used as lime water to detect CO_2. The effect of excess CO_2 on these is to produce soluble bicarbonates, thus removing the turbidity.

$$Ca(OH)_2 + CO_2 \rightarrow H_2O + CaCO_3 \text{ (insoluble white ppt.)}$$

$$CaCO + CO_2\text{(excess)} \rightleftharpoons Ca(HCO_3)_2 \quad \text{(soluble).}$$

These bicarbonates are stable in solution only, and decompose to carbonates.

(4) Oxides of group II elements have the form MO. They are usually prepared by thermal decomposition Of MCO_3, $N(NO_3)_2$, MSO_4 and $M(OH)_2$. Also when this group elements burin in oxygen, MO oxides are produced. Beryllium oxide is covalent, but all the other oxides are ionic. Beryllium oxide is insoluble in water. It dissolves in acids to give salts, and in alkalis to give beryllates. That means, this oxide is amphoteric. Magnesium oxide reacts with water forming magnesium hydroxide.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

CaO reacts very readily with water, and $Ca(OH)_2$ is produced, and also but more readily the reaction of Sr and Ba with water.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 1500 \text{ Cal}$$

Calcium oxide is prepared on a large scale by heating $CaCO_3$ in lime kilns. It is used in the manufacture of Na_2CO_3, NaOH, CaC_2, bleaching powder, glass and cement.

Also group II elements form peroxides and the case with which the peroxides are formed increases with increasing size. No peroxide of beryllium is known. Crude magnesium peroxide has been made using hydrogen peroxide. Calcium peroxide can be made as the hydrate by treating $Ca(OH)_2$ with H_2O_2 and then dehydrating the product. Strontium peroxide can be formed by passing air over SrO at high pressure and temperature. Barium peroxide BaO_2 is formed by passing air over BaO at 500°C.

The peroxides are white ionic solids containing, $(O\text{-}O)^{-2}$ ion. On treatment with acid, H_2O_2 is formed .

(5) The sulphates are soluble in water but the solubility decreases down the group, Be > Mg>>Ca > Sr>Ba and $CaSO_4$ is almost insoluble. Sulphates decompose on heating, giving oxides.

$$Mg\ SO_4 \xrightarrow{heat} MgO + SO_3$$

With respect to carbonates, the stability of the salt increases with increasing basicity. For nitrates; all nitrates can be prepared in solution and as hydrated salts by the reaction of HNO_3 on carbonates, oxides, or hydroxides to the oxides. Anhydrous nitrates can be prepared using liquid dinitrogen tetroxide.

$$Mg\ Cl_2 + N_2O_4 \longrightarrow Mg(NO_3)_2 + 2\ N_2O_4$$

$$Mg\ (NO3)_2\ 2N_2O_4 \xrightarrow[\text{Under vacuum}]{\text{warm } 50^oC} Mg(NO_3)_2$$

Beryllium is unusual in that it forms a basic nitrated in addition to the normal salt.

$Be(NO_3)_2 \xrightarrow{120^oC} Be_4O(NO_3)_6$ basic beryllium nitrate.

(6) All the elements except beryllium form hydrides of type MH_2 by direct combination, and impure beryllium hydride has been made by reducing $BeCl_2$ with $LiAlH_4$. All group II hydrides are reducing agents, which react with water and liberate hydrogen. Calcium, strontium and barium hydrides are ionic, and contain the hydride ion H^-. Beryllium and magnesium hydrides are covalent and polymeric $(BeH_2)n$.

H H H

Be Be Be Be

H H H

(7) All metals are forming halides (MX_2) by direct combination with the halogen or by the action of acid halogen on the metal or carbonate. Beryllium halide are covalent, hygroscopic and fume in air due to hydrolysis. They sublime, and they do not conduct electricity. Anhydrous beryllium halides are polymeric $(BeX_2)_n$ and like $(Be\ H_2)_n$

Cl Cl Cl

Be Be Be Be

Cl Cl Cl

The fluorides MF_2 are almost insoluble. The other metal halides are ionic and readily soluble in water. The

halides are hygroscopic and form hydrates. $CaCl_2$ is a well known drying agent.

(8) By contrast with elements in group I the alkaline earth elements burn in nitrogen and form nitrides M_3N_2. The beryllium nitride is rather volatile, the others are not. All nitrides are colorless crystalline solids. They decompose on heating and react with water to liberate ammonia and form metal oxide or hydroxide .

$$Mg_2\ N_3 + 3H_2O \longrightarrow 2NH_3 + 3MgO$$

(9) Group II elements form ionic carbides MC_2 by heating the metals Mg to Ba or by heating their oxides with carbon. Calcium carbide is the best known; it reacts with water, liberates acetylene and is thus called an acetylide.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

(10) All the metals react with acids and liberate hydrogen, although beryllium reacts slowly. Sodium hydroxide also gives hydrogen when treated with beryllium, but has no effect on the other metals. This illustrates the increase in basic properties from amphoteric to basic on descending the group.

(11) By treating magnesium with an alkyl or aryl halide (Cl^-, Br^- or I^-) in an absolutely dry organic solvent such as diethyl ether, magnesium forms Grignard reagents, which are probably the most versatile reagents in organic chemistry.

$$Mg + RBr \longrightarrow RMgBr \quad \text{(Grignard reagent)}$$

$$RMgBr + CO_2 \xrightarrow{acid} RCOOH$$

$$RMgBr + I_2 \longrightarrow RI$$

(12) Group II metals are not noted for their ability to form complexes, since complex formation is favored by small highly charged ion with suitable empty orbital's. Thus Be form many $M_2\,(BeF_4)^{-2}$ complexes and Ba very few.

Extraction of the metals :

The metals of this group are not easy to produce by chemical reaction because they are strong reducing agents and they form carbides. They are strongly electropositive and so aqueous solutions cannot be used for displacing one metal by another, or for electrolysis because of the reaction of the metal with water.

All the metals can be obtained by electrolysis of the fused chloride, with the addition of NaCl to lower the m. point, although Sr and Ba tend to form colloida suspension.

Beryllium is obtained by reducing BeF_2 with Mg. Magnesium is now prepared commercially by the Pigeon process by reduction of magnesium oxide with ferrosilicon and aluminum. The MgO is obtained by treating sea water, which contains Mg^{+2} ions, with $MgCa(CO_3)_2$. $Mg(OH)_2$ is obtained, and can filtered off and heated to give the oxide.

Calcium is obtained by heating $CaCO_3$ to give the oxide CaO, treating with NH_4Cl and water to give $CaCl_2$, followed by electrolysis of the fused chloride.

Strontium and Barium are obtained from their oxides by reduction with aluminum.

<u>Differences between Beryllium and the other Group II Elements:</u>

Beryllium is anomalous in many of its properties and show a diagonal relationship to aluminum in group III:

(1) Be is very small and has a high charge density, so it should have a strong tendency to covalence. The melting point of its compounds is lower.

(2) Be forms many complexes–not typical of group I and II.

(3) Be like Al is rendered passive by nitric acid.

(4) Be is amphoteric, liberating M_2 with NaOH and forming beryllates. Al forms aluminates.

(5) Be $(OH)_2$ like $Al(OH)_3$ is amphoteric.

(6) Be salts are among the most soluble known.

P - BLOCK ELEMENTS

Group III The Boron Group

Table (6)

Element		Electronic Configuration	Oxidation state
Boron	B (He)	$2S^2 2P^1$	III
Aluminium	Al (Ne)	$3S^2 3P^1$	(1) III
Gallium	Ga (Ar)	$3d^{10} 4S^2 4P^1$	1 III
Indium	In (Kr)	$4d^{10} 5S^2 5P^1$	1 III
Thallium	Tl (Xw)	$4F^{14} 5d^{10} 6S^2 6P^1$	1 III

General properties :

In this group the first element boron is nonmetal, but the other elements are fairly reactive metals.

The most important are of aluminum is bauxite $AL_2O_3.H_2O$. Boron occurs in earth's crust as borax $Na_2B_4O_7.10.H_2O$. Gallium, indium and thallium are found as traces in zinc and lead sulphides ores.

All the elements show oxidation state, III, unlike the S block elements, some of the elements of this group show lower valence states in addition to the group. Valence the heavier elements show an increased tendency to form univalent compounds, and in fact univalent thallium, compounds are the most stable. Mono valence is explained by the S electrons in the outer shell remaining paired, and not participating in bonding because the energy to unpair them is too great. This occurs particularly among heavy elements in the p-block and is called the inert pair effect. Gallium is apparently divalent in a few compounds such as $GaCl_2$, but the structure has been shown to be $Ga^+(GaCl_4)^-$ which contains Ga(+1) and Ga(+III) (Table 6).

The small size of the ions, their high charge and the large values for the sum of the first the ionization energies suggest that the elements are largely covalent.

In solution, the large amount of hydration energy evolved off sets the high ionization energy an all metal ions exist in a hydrated state. The hydrated metal ions have six molecules of water which are held strongly giving an octahedral structure. The strength of the metal oxygen bond weakens the O-H bonds. Some hydrolysis occurs, and protons are released thus giving acidic solutions.

$$(HO)_5\ M \longleftarrow \underset{H}{\overset{H}{O}} \longrightarrow ((H_2O)_5\ M \longleftarrow \underset{H}{O}\ ) + H^+$$

The covalent radial of the atoms (Table 7) do not increase in a completely regular way from B to Ti as was found on descending Group I and II.

This is because the inner electronic configuration of Ga In and Ti contains ten d-electrons. These shield the nuclear charge less efficiently than the S and P electrons, so the outer electrons are more firmly held by the nucleus.

(Shielding decreases S > P > d > f). Thus atoms with a d^{10} inner shell are smaller and consequently have higher ionization energies than would other wise be expected. In a similar way the inclusion of fourteen even more poorly shielding f electrons further affects the size and ionization energy of T1.

Table (7)

Element	covalent radius	Ionic radius	Ionization Energy $M \longrightarrow M^{+3}$	electro-negativity
B	0.50	0.20	6764	2.0
Al	1.25	0.52	5114	1.5
Ga	1.25	0.60	5500	1.6
In	1.50	0.81	5066	1.7
Th	1.55	0.91	5413	1.8

The finely divided amorphous boron is usually impure and burns in air to form the oxide and nitride, and in the halogens to form tri-halides. It reduces nitric and sulphuric acids and liberates hydrogen with NaOH.

Pure crystalline boron is, in contrast, un-reactive except at very high temperatures or with reagents such as hot concentrated ulphuric acid or Na_2O_2.

Aluminum is stable in air because it develops an oxide film which protects the metal from further attack.

Gallium and indium are stable in air and are not attacked by water except when free oxygen is present.

Thallium is a little more reactive and is superficially oxidized in air.

The electropositive or metallic nature of the elements increases from B to Al according to the increase in size and because they follow immediately after the S block elements. From Al to T1 the electropositive deceases because these elements follow after the d-block elements. These extra d-electrons do not shield the nuclear charge very effectively, so that the orbital electrons are more firmly held and the metals are less electropositive. This is illustrated by the increase in ionization energy between Al and Ga even though the larger atom would be expected to have a lower values. (Table 7).

Group III oxides:

(a) Boron sesquioxide and the borates :

Sesquioxide M_2O_3 of all the elements can be made by heating the elements in oxygen. B_2O_3 is more usually made by dehydrating boric acid.

$$\underset{\text{Ortho boric acid}}{H_3BO_3} \xrightarrow{100^{o}C} \underset{\text{metal boric acid}}{HBO_2} \xrightarrow{\text{red heat}} B_2O_2$$

B_2O_3 is acidic in its properties ad is the anhydride of ortho boric acid.

On heating with metal oxides it gives meta borates which indicate its acidic properties.

$$COO + B_2O_3 \longrightarrow CO(BO_7)_2$$

Boron sesquioxide can react with very strongly acidic oxides such as phosphorus pent oxide, and forming a phosphate. In these reactions it is being forced to behave as a base.

$$B_2O_3 + P_2O_5 \longrightarrow 2\ BPO_4$$

Ortho boric acid H_3BO_3 behaves as a weak mono basic acid.

$$H_3BO_3 + H_2O \rightleftharpoons H^+ + (B(OH_4)^- \qquad pK=9$$

OH   OH   OH

B   B

HO   OH   HO   OH

On titration with NaOH:

$$H_3BO_3 + NaOH \longrightarrow \begin{matrix} Na(B(OH)_4) \\ NaBO_2 + 2\,H_2O \end{matrix}$$

The ortho boric acid can be converted into a strong mono basic acid by the addition of certain organic polyhydroxy compounds such as glycerol, manitol or sugars. The added compound must have OH groups on adjacent atoms in the cis configuration. The increase in acid strength

occurs because the cis diol forms complexes and effectively removes $(B(OH)_4)^-$ from solution, thus upsetting the balance of the reversible reaction, hence all the H_3BO_3 ionizes and the maximum number of H^+ are produced.

C – OH	HO	OH		C – O	OH		C – O	O - C
		B	⟶		B	⟶	B	
C – OH	HO	OH		C – O	OH		C – O	O – C

The most important metoborat is borax

$Na_2 B_4O_7 . 10H_2O + 2 HCl \longrightarrow 2NaCl + 4 H_3BO_3 + 5 H_2O$

Sodium per borate is produced in a large amounts. It is used as a brightener in washing powders.

$$NaBO_2 + H_2O_2 \longrightarrow NaBO_3 . 4 H_2O$$

(b) <u>The other group III oxides</u>:

Alumina Al_2O_3 can be made by dehydrating $AL(OH)_3$. Aluminum has a very strong affinity for oxygen, and this is used in the thermite reduction of metal oxides.

$$3 Mn_3O_4 + 8 Al \longrightarrow 4 Al_2O_3 + 9 Mn$$

Aluminum hydroxide is amphoteric, thought it acts as a base principally, giving salts that contain the $(Al(H_2O)_6)^{+3}$ ion.

$$Al(OH)_3 \longrightarrow Al^{+3} + 3 OH^-$$

Aluminum hydroxide exhibits acidic properties when it reacts with NaOH forming sodium aluminates which is often formulated Na $AlO_2 . 2H_2O$.

Gallium, like aluminum, forms an amphoteric oxide and hydroxide. Indium sesquioxide is completely basic. Thallous hydroxide TlOH is a strong base, and is soluble in water, thus differing from the trivalent hydroxides. If an element can exist in more than one valence state there is a general tendency for the lower valence state to be the most basic.

Hydrides of group III elements:

None of the group III elements react directly with hydrogen, but a number of interesting hydrides are known.

Boron hydrides are called boranes. There are seven well characterized boranes.

$B_n H_{n+4}$		$B_n H_{n+6}$	
B_2H_6	diborane	B_4H_{10}	tetraborane
B_5H_9	pentaborane-9	B_5H_{11}	pentaborane - 11
$B_{10}H_{14}$	decaborane-14	B_9H_{15}	nomaborane
		$B_{10}H_{16}$	decaborane - 16

==

Diborane has been studied more than the other boranes. It may be prepared by a variety of methods.

1- $Mg_3B_2 + H_3PO_4 \longrightarrow$ mix. of boranes $\xrightarrow{\text{heat}}$ B_2H_6

2- $2BCl_4 + 6H_2 \xrightarrow[\text{electric charge}]{\text{silent}} B_2H_6 + 6HCl$

3- $4BCl + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$

In diborane there are twelve valence electrons, three from each boron atom and six from the hydrogen's. Electron diffraction results indicate the structure.

H H H

B B

H H H

All the boranes react with ammonia, but the products depend on the condition

$$B_2H_6 + NH_3 \xrightarrow[\text{Low. temp.}]{\text{excess } NH_3} B_2 H_6 . 2NH_3$$

$$\xrightarrow[\text{Higher temp.}]{\text{Excess } NH_3} (BN)_x \text{ boron nitride}$$

$$\xrightarrow[\text{high temp.}]{\text{ration } 2NH_3:1B_2H_6} B_3N_3H_6 \text{ borazole.}$$

In addition to the boranes, rather more stable complex borohydrides containing the group $(BH_4)^-$ are known. Sodium borohydride can be made.

$$4\ NaH + B\ (OCH_3)_3 \longrightarrow Na(BH_4)\ \ 3\ NaOCH_3$$

Methyl borate

The borohydride ion is tetrahedral and reacts with water with varying ease. Li (BH_4) reacts violently with water.

$$Li(BH_4) + H_2O \longrightarrow Li\,BO_2 + 4\,H_2$$

$Na(BH_4)$ may be re crystallized from cold water.

$K(BH_4)$ is quite stable.

The stability of $Na(BH_4)$ in alcoholic and aqueous solutions makes it a useful reagent in the reduction of aldehydes to primary alcohol, and ketones to secondary alcohols.

$$R.CHO \quad Na(BH_4) \quad R.CH_2OH$$

$$\begin{matrix} R_1 & & & R_1 \\ & C = O & \xrightarrow{Na(BH_4)} & CHOH \\ R_1 & & & R_2 \end{matrix}$$

The other elements in the group also form electron deficient hydrides.

$(AlH_3)_n$ can be made from LiH and $AlCl_3$

$$LiH + AlCl_3 \longrightarrow (Al\,H_3)_n$$

with excess LiH, $Li(AlH_4)$ is formed

$$\text{excess } LiH + AlCl_3 \longrightarrow Li(Al\,H_4)$$

$Li(AlH_4)$ is a most useful organic reducing agent.

Gallium forms $Li(GaH_4)$

Indium forms $(In\,H_3)_n$

There is a doubt the existence of a hydride of thallium.

<u>Hydroboration</u>:

An important reaction occurs between B_2H_6 and olefins and acetylene.

$$B_2H_6 + RCH = CHR \longrightarrow B(CH_2\text{-}CH_2R)_3$$

$$B_2H_6 + RC = CHR \longrightarrow B(RC = CHR)_3$$

The reactions are carried out in dry ether and under an atmosphere of nitrogen because H_2H_6 and the products are very reactive. The alkyl borane products are not usually isolated, but may be converted to hydrocarbons by treatment with carboxylic acids, to alcohols by reaction with alkaline H_2O_2 and to ketones or carboxylic acids by oxidation with chromic acid.

$$BR_3 + 3\ CH_3COOH \longrightarrow 3RH + B(CH_3COO)_3$$

Hydrocarbon

$$B(CH_2 - CH_2R)_3 + 3H_2O_2 \longrightarrow 3RCH_2CH_2OH + H_3BO_3$$

$$\left(\begin{array}{c} R \\ \quad CH \\ R \end{array}\right)_3 B + H_2\,CrO_4 \longrightarrow \begin{array}{c} R \\ \quad C = O \\ R \end{array} \quad \text{ketone}$$

$$(CH_3 - CH_2)_3\ B + H_2\,CrO_4 \longrightarrow CH_3COOH$$

Carboxylic acid

Hydroboration is a simple and useful process because of the mild conditions required for the initial hydride addition and the variety of products which can be produced using different reagent to break to B-C bond.

Halides of Group III elements:

a) Tri halides

All the elements from tri halides. The boron halides BX3 are covalent and gaseous. They are all hydrolyzed by water, the fluoride forming fluoro borates and the other halides giving boric acid.

$$BF_3 + H_2O \longrightarrow H_3BO_3 + HF$$

$$BF_3 + HF \longrightarrow H^+ + (BF_4)^-$$

The B atom in the BX_3 molecule can accept alone pair of electrons from a donor atom such as

F NH$_3$

O , N , P , or S ; B

F F

This makes BF_3 a useful organic catalyst for Friedel - Crafts reactions such as alkylations, acylation and esterifications. BF_3 is produced in the U.S.A by the reaction.

$$B_2O_3 + 6HF + 3H_2SO_4 \longrightarrow 2BF_3 + 3H_2SO_4.H_2O$$

Fluorides of Al, Ga In and Tl are ionic and have high melting points. The other halides are largely covalent when anhydrous. $AlCl_3$, $AlBr_3$ and $GaCl_3$ exists as dimmers, thus attaining an octet of electrons.

Cl Cl Cl

Al Al

Cl Cl Cl

A group III element has only three valence electrons, and when it forms three covalent bonds it has a share in only six electrons and is therefore electron deficient. The BX_3 halides attain an octet by bonding, but the other elements are larger, and cannot get effective overlap, so they polymerize to remedy the electron deficiency.

```
      F              F              F
      B              B              B
   F     F        F     F        F     F
```

(b) Di halides:

In addition to the tri halides, boron forms halides of formula B_2X_4. These decompose slowly at room temperature. B_2Cl_4 can be made:

$$2\ BCl_3 + 2Hg \xrightarrow[\text{Low pressure}]{\text{electric discharge}} B_2Cl_4 + Hg_2Cl_2$$

The structure is:

```
   Cl            Cl
       B ------ B
   Cl            Cl
```

Gallium and indium form di halides:

$$GaCl_3 + Ga \longrightarrow GaCl$$

$$In + HCl\ \text{gas} \longrightarrow InCl_2$$

These are more properly written $Ga^{+}(GaCl_4)^{-}$ and contain M(I) and M(III) rather than divalent Ga and In.

Thallium forms univalent thallous halides which are more stable than the tri halides.

<u>(c) Mono halides:</u>

All group III elements form mono halides M in the gas phase at elevated temperature

$$\mathbf{Al\ Cl_3 + 2\ Al \xrightarrow[\text{temp.}]{\text{high}} 3\ AlCl}$$

These compounds are not very stable. They are covalent except for Tl^+F^- which is ionic. Boron form a number of stable polymeric mono halides $(Bx)_n$

$$\mathbf{H_2Cl_4 \xrightarrow{\text{mercury discharge}} B_4Cl_4}$$

Slow

Decomposition $\searrow$ $\mathbf{B_8Cl_8, B_9Cl_9, B_{10}Cl_{10}, B_1Cl_{11}, B_{12}Cl_{12}}$

<u>Complexes:</u>

Group III elements form complexes much more readily than the S block elements on account of their smaller size and increased charge. Many complexes are known such as tetrahedral hydride and halide complexes $Li(AlH_4)$ and $H(B F_4)$. Also octahedral complexes are important, for example, $(GaCl_6)^{-3}$, $(In\ Cl_6)^{-3}$ and $(TlCl_6)^{-3}$. Complexes with chelate groups are useful in gravimetric determination such as 8 hydroxy quinoline complex.

8- hydroxy quinoline complex

Organometallic compounds:

In addition to carboranes and the alkylboranes, all the Group III tri halides will react with Grignard reagents and organo lithium reagents forming tri alkyl or tri aryl compound.

$$FB_3 + 3\ C_2H_5MgI \longrightarrow B(C_2H_5)_3$$

$$AlCl + 3\ CH_3MHI \longrightarrow Al(CH_3)_3$$

$$GaCl_3 + 3C_2H_5Li \longrightarrow Ga(C_2H_5)_3$$

$$InBr_3 + 3C_6H_5Li \longrightarrow In(C_6H_5)_3$$

The use of aluminum alkyls in producing poly thene alcohols and isoprene is of considerable industrial importance.

Extraction of the elements :

Boron is obtained by the reduction of B_2O_3 with magnesium or sodium.

$$Na_2B_4O_7.10H_2 \xrightarrow{acid} H_3BO_3 \xrightarrow{heat} B_2O_3 \xrightarrow{Na\ or\ Mg} B$$

Boron obtained in this way is amorphous, and may contain 5 % impurities. Pure crystalline boron may be obtained in small quantities by the reduction of BCl_3 with H_2, or the pyrolysis of BI_3.

$$2BCl_3 + 3H_2 \xrightarrow{\text{red hot filament}} B_2 + 3HCl$$

$$3BI_3 \xrightarrow[\text{W or Ta}]{\text{red hot filament}} 2\ B + 3\ I_2$$

Boron is used to increase the harden ability of steels.

Aluminum is obtained from the ore , bauxite $Al_2O_3.H_2O$ by the addition of NaOH, forming sodium aluminate which dissolves, thus separating Al from iron oxide. Aluminum is produced on a large scale and is used widely in alloys, paint and coking utensils.

Gallium, indium and thallium occur only in minute quantities and are usually obtained by electrolyzing aqueous solution of their salts.

The large differences between boron (non metal always covalent, acidic, high melting point) and aluminum are to be expected since Al^{3+} is 2.5 times the size of B^{+3}.

Group IV The Carbon Group

Table (8)

Element			Electronic Configuration	Oxidn number	
Carbon	**C**	**(He)**	**$2S^22P^2$**		**IV**
Silicon	**Si**	**(Ne)**	**$3S^23P^1$**	**II**	**IV**
Germanium	**Ga**	**(Ar)**	**$3d^{10}4S^24P^2$**	**II**	**IV**
Sn	**Sn**	**(Kr)**	**$4d^{10}5S^25P^2$**	**II**	**IV**
Lead	**Pb**	**(Xe)**	**$4F^{14}5d^{10}6S^26P^2$**	**II**	**IV**

<u>Metallic and nonmetallic character</u>:

The change from nonmetal to metal with increase atomic number is well illustrated in group IV. Carbon and silicon are nonmetals, germanium he some metallic properties, and tin and lead are metal. This can be illustrated from the structures (Table 8).

<u>Differences between carbon silicon and the remaining elements:</u>

Carbon differs from the other elements in its limitation to a coordination number of four (because there are no orbital's in the second shell), its unique ability to form multiple bonds such as C=C, C=C , C=O and C=N and in its ability to form chains (catenation). The tendency to catenation is related to the strength of the bond.

Carbon and silicon have only S and P electrons, but the other elements follow a completed transition series with ten

d electrons. Thus some differences are expected, and carbon and silicon differ both from one another and from the rest of the group, while germanium, tin and lead form a graded series.

General properties:

The covalent radial increase down the group, but the difference in size between Si land Ge is less than might be otherwise expected because the filling of the 3d shell increase the nuclear charge and provides only poorly shielding d electrons. In a similar way the small difference in size between Sn and Pb is because of the filling of the 4f shell.

The ionization energies decrease from C to Si, but then change in an irregular way because of l the effects of filling the d and f shells. The large amount of energy required to form M^{4+} ions suggests that simple ionic compounds will be very rare, and occur only with highly electronegative elements such as F and O. The compounds SnF_4, SnO_2, PbF_4 and PbO_2 are ionic.

The elements of this group form covalent compounds with four covalent bonds, by promotion of electrons from the ground state to an excited state; and SP^3 hybridization of the orbital's, results in a tetrahedral structure.

<u>Electronic structure of carbon atom :</u>

Ground state : **1S** **2S** **2P**

Two unpaired electrons from two covalent bonds

excited state:

four unpaired electrons from four covalent bonds and SP^3 hybridization results in a tetrahedral structure .

The elements in this group are relatively un reactive, but reactivity increases down the group. They are generally attacked by acid alkalis, and the halogens: graphite by F, Si by HF, Ge by H_2SO_4 and HNO_3 and Sn and Pb by a number of acids.

<u>Inert pair effect</u>:

The inert pair effect shows itself increasingly in the heavier members of the group. On descending the group, there is a decrease in stability of + IV oxidation and an increase in stability of (+II) state.

<u>Formation of complexes</u>:

The ability to form complex is favored by a high charge, small size, and availability of empty orbital's of the right energy. Carbon has a maximum of eight electrons in its outer shell. In four covalent compounds of carbon, the second shell contains the maximum of eight electrons.

Because this structure resembles that of an inert gas, these compounds are stable, and carbon does not form complexes. Four covalent compounds of the subsequent elements can form complexes due to the availability of d orbital's, with coordination number six.

<u>Formation of hydrides:</u>

Al the elements form covalent hydrides, but differ in the number of formed and the ease with which they formed. Carbon forms a vast number of chain and ring compounds including the alkenes, alkenes, alkenes (C_nH_{2n+2}) C_nH_{2n}, and C_nH_{2n-2}, respectively), and aromatic compounds. The strong tendency to catenation has been related to the strenergth of C-C bond.

Silicon forms a limited number of saturated hydrides Si_nH_{2n+2}, called silanes and exist as straight chains or branched chains.

Germanium hydrides are similar to silanes, but are less inflammable, and less readily hydrolyzed. SnH_4 is less stable and more difficult to prepare. pbH_4 is even less stable and even more difficult to prepare.

<u>Formation of halides:</u>

All the tetra halides are known except PbI_4. They are all very volatile and covalent, except SnF_4 and PbF_4 which are ionic. CF_4 is un reactive and very stable, and used solvent and insulator. Mixed chloro fluro hydro-carbons

such as $CFCl_3$ and CF_2Cl_2 are known as freons, and used as refrigeration fluids. SiF_4 is readily hydrolyzed by alkali

$$SiF_4 + 8\ OH^- \longrightarrow SiO_4^{-4} + 4F^- + 4H_2O$$

Silicon halides are rapidly hydrolyzed by water to give silicic acid.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

$CeCl_4$ and $GeBr_4$ are hydrolyzed less readily. $SnCl_4$ and $PbCl_4$ hydrolyze in dilute solutions, but hydrolysis can be repressed by the addition of halogen acid.

$$Sn(OH)_4 \underset{H_2O}{\overset{HCl}{\rightleftarrows}} Sn\ Cl_4 \underset{H_2O}{\overset{HCl}{\rightleftarrows}} (Sn\ Cl_6)^{-2}$$

<u>Oxides formation</u>:

Five oxides of carbon are known, CO, CO_2,C_3O_2 , C_5C_2, and $C_{12}O_9$, though only the first two are known. CO is a poisonous gas, sparingly soluble in ater. It is formed when carbon is burned in a limited amount of air. It is prepared by dehydrating formic acid with concentrated sulphuric acid.

$$H.COOH + H_2SO_4 \longrightarrow CO + H_2O$$

It is an important fuel because it burns in air and a considerable amount of heat evolves.

$$2CO + O_2 \longrightarrow 2CO_2 + 565\ Kg\ mol^{-1}$$

CO is a good reducing agent and can reduce many metal oxides.

$$Fe_2O_3 + 3\,CO \xrightarrow{\text{blast furnace}} 2\,Fe + 3CO_2$$

$$Cu + CO \rightarrow Cu + 2CO_2$$

Also carbon monoxide is an important ligand which can donate a share in a lone pair of electrons, and can form a coordinate bond with many transition metals and form carbonyl compounds (e.g. $Ni(CO)_4$).

C O or : C : O : (electronic structure of (CO)).

CO_2 is obtained by the action of dilute acid on carbonate, by burring carbon in excess of air and on an industrial scale by heating $CaCO_3$. Solid CO_2 sublimes directly to the vapor state. The gas is detected by its action on lime water.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$CaCO_3 \xrightarrow{+\,CO_2} Ca(HCO_3)_2$$

CO_2 is acidic oxide and it is the anhydride of H_2CO_3 acid .

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

The acid is unstable and has never been isolated, but it gives arise to two series of salts, carbonates and bicarbonates .

$$NaOH + H_2CO_3 \longrightarrow NaHCO_3 \quad \text{(acid salt)}$$

$$NaOH + H_2CO_3 \longrightarrow Na_2CO_3 \quad \text{(normal salt)}$$

The structure of CO_2 is :

$$O = C = O \longleftrightarrow O^{+}\ C - O \longleftrightarrow O - C\ O^{+}$$

and the structure of carbonic acid:

H - O

C = O

H - O

Silicon have the oxides SiO and SiO_2. Germanium, tin and lead have the dioxides: GeO SnO_2 and PbO_2, and mono oxides GeO, SnO and PbO. Monoxides are slightly more basic and ionic than the corresponding higher oxides.

Lead forms also a mixed oxide Pb_3O_4 (red Iead) which may be represented as $2PbO.PbO_2$ and used in paint.

<u>Occurrence and extraction of the elements</u>:

Carbon occurs mainly as coal and in crude oil and also as carbonates in rocks such as $CaCO_3$ and $MgCO_3$.

Germanium is found as traces in some silver and zinc ores, and in some coals.

Tin is mined as SnO_2, and lead is found as the ore galena PbS.

SiO_2, GeO_2 and SnO_2 may be reduced by carbon to the element. PbS may be roasted in air to give PbO

$$3\,PbS \xrightarrow{heat/air} PbS + PbO \longrightarrow Pb + SO_4$$

Group V The Nitrogen Group

Table (9)

Element		Electronic structure	Oxidation state
Nitrogen	N)	$2S^22P^3$	- III – II – I O
			I II III IV V
Phosphorus	P	$3S^23P^3$	III V
Arsenic	As	$3d^{10}4S^24P^3$	III V
Antimony	Sb	$4d^{10}5S^25P^3$	III V
Bismuth	Bi	$4F^{14}5d^{10}6S^26P^3$	III V

Electronic structure and oxidation states:

All the elements of the group have five electrons in their outer shell. They exhibit a maximum oxidation state of five towards oxygen by using all five outer electrons in forming bonds. Valencies of 3 and 5 are shown according to the inert pair effect of 5 electrons Table (9).

In case of nitrogen, a very wide range of oxidation states exists:

(-III) in ammonia NH_3

(-II) in hydrazine N_2H_4

(-I) in hydroxylamine NH_2OH .

(O) in nitrogen N_2 .

(+ I) in nitrouns oxide N_2O .

(+ II) in nitric oxide NO .

(+III) in nitrous acid HNO_2 .

(+IV) in nitrogen dioxide NO_2 .

(+V) in nitric acid HNO_3 .

<u>Metallicl and nonmetallic character</u>:

Within the group there is an increase in electro-positive (metallic) character. M and P are nonmetals. As and Sb are metalloids which show many metallic proporties, and Bi is a true metal. This is shown in the properties of their oxides. Normal oxides of N and P are strongly acidic, whilst As and Sb are amphoteric and Bi is largly basic.

<u>Bond type</u>:

The ionization energy required to produce M^{+5} is so high that it never occurs .

The sum of the first three ionization energies for Sb and Bi are just low enough for them to form M^{+3} ions, such as SbF and BiF_3. The M^{+3} ions are rapidly hydrolyzed in water to SbO^+ and BiO^+, but this change is reversed by adding 5M HCl .

$$Bi^{3+} \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} BiO^+$$

Nitrogen can gain three electrons and form N^{-3} ion.This require higher energy. Generally in these elements, the bonds l are convalent.

Hydrides:

Elements of this group form volatile hydrides of formula MH_3. The ease of replacing the hydrigens by other grops decreases from MH_3 to BiH_3.

Ammonia is prepared in the labortory by heating an ammonium salt with sodium hydroxide.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2$$

As the stability of hydrides decreases on descending the group, the hydrides of the other elements may be obtained in small amounts only.

The ammonia forms ammonium NH_4 salts very readily and utilizes the lone pair of electrons to form a coordinate bond as shown.

Electronic structure of nitrogen atom-ground state	**1S**	**2S**	**2P**
Nitrogen having gaind a share in three electrons from three hydrogen atoms in NH_3 molecule			

SP^3 hybridization tetrah dral with one position occupied by a lone pair.

The structure of ammonia is tetrahydral with one position occupied by a lone pair.

Thus ammonia forms coordination complexes with metal ions from the Co, Ni, Cu and Zn groups which accords with its strong donor properties.

Ammonia is a weak base, and is hydrogen bonded in the liquid state. Hydrides of other elements are much weaker and not form hydrogen bonds. Hydrides of Nitrogen are:

Ammonia	NH_3	**(-III)**
Hydrazine	N_2H_4	**(- II)**
Hydroxylamine	NH_2OH	**(- I)**

Hydrazine is manufactured by oxidizing ammonia by sodium hypochlorite in dilute aqueous solution .

$$NH_3 + NaCl \rightleftharpoons NH_2Cl + NaOH$$

$$2NH_3 + Na_2Cl \rightleftharpoons NH_2 - NH_2 + NH_4Cl$$

Side reactions may occur are

$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl$$

$$2NH_3 + 3NH_2 \longrightarrow N_2 + NH_4Cl$$

These side reactions are inhibited by using dilute solution and adding gelatin.

Hydrazine is covalent liquid and have strong reducing properties. It is basic and form two series of salts.

$$N_2H_4 + HX \longrightarrow N_2H_5^+ + X^-$$

$$N_2H_4 + 2HX \longrightarrow N_2H_6^{2+} + 2X^-$$

The structure of hydrazine is similar to that of hydrogen peroxide.

H H

N N H – O – O – H

H H

Hydrazine is powerful reducing agent only in alkaline solution but in acidic or neutral is only mild agent.

$$N_2H_4 + 2\ I_2 \longrightarrow 4\ HI + N_2$$

$$N_2H_4 + 2O_2 \longrightarrow 2H_2O_2 + N_2$$

When there are powerful reducing agent in acidic solution it is forced to react as an oxidizing agent .

$$N_2H_4 + Z_n + 2HCl \longrightarrow 2NH_3 + Z_n\,Cl_Z$$

The nitrogen atoms of hydrazine have a lone pair of electrons, which can form coordinate bonds to metal ions such as Ni^{+2} and Co^{2+}.

Hydroxyl amine, like hydrazine, is a weaker base than ammonia.

$$NH_2\,OH + HCl \longrightarrow (NH_3OH)\ Cl$$

$$NH_2\,HO + H_2SO_4 \longrightarrow (NH_3OH)\ HSO_4$$

Hydroxyl amine is mild reducing agent, but it can as an oxidizing agent. It can form coordinate bonds and complexes with metals.

<u>Hydrazoic acid and azides:</u>

Hydrazoic acid HN_3 is exploxidve when pure, but stable in aqueous solution.

It reacts with metals forming salts called azides, and nitrogen is evolved.

$$6\ HN_3 = 4\ Li \longrightarrow 4LiN_3 + 2NH_3 + 2N_2$$

Lithium azide

Sodium azide can be made by reaction between nitrous oxide and sodamid under anhydrous condition.

$$N_2O + NaNH_2 \longrightarrow NaN_3$$

For the N_3^- ion three resonance structures may be drawn .

$$\overset{..}{:N} = \overset{+}{N} = N: \qquad {}^{2-}\overset{..}{:N} \leftarrow \overset{+}{N} = N: \qquad :N = N \rightarrow N:^{-2}$$

For the acid MH$_3$, the resoaance structures allowed are:

$$\underset{H}{N} = N^{+} \rightleftarrows N:^{-} \qquad \underset{H}{N} \leftarrow N^{+} = N:$$

<u>Halides</u>:

<u>For nitrogen</u>; halides derived from HN_3 acid are: FN_3, ClN_3, BrN_3 and IN_3. They are extremely unstable and explosive.

Trihalides: NF_3 is stable, but NCl_3 is explosive NBr_3 and NI_3 are unstable.

All trihalides are hydrolyzed with water;

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3\ HOCl$$

But NF_3 is stable towards towards hydrolysis, unless sparked with water vapour:

$$NF_3 + 3H_2O \longrightarrow 6HF + N_2O_3$$

For the other elements of group V, all the possible trihalides are known, (phosphine PH_3 form salts with HCl while the other not).

<u>Oxides and oxyacids of nitrogen</u>:

Nitrogen forms a very wide range of oxides :

N_2O	**Nitrous oxide**
NO	**Nitric oxide**
N_2O_2	**Nitrogen sesqui oxide**
NO_2 , N_2O_4	**Nitrogen dioxide**
N_2O_5	**Dinitrogen pentaoxide**
NO_3 , N_2O_6	**Nitrogen trioxide**

(very unstable)

<u>Nitrous oxide</u>: It is stablel and relatively, unreactive gas. It prepared by heating NH_4NO_3 gently.

$$NH_4\,NO_3 \longrightarrow N_2O + 2\,H_2O$$

It is used in the preparation of azides.

$$N_2O + NaNH_2 \longrightarrow NaN_3 + H_2O$$

The N_2O molecules is linear, and there is resonance between two extreme structures:

$$:N \quad N \quad O: \longrightarrow \quad :N \quad N \rightarrow \quad O:$$

Nlitrous oxide is anutral oxide and does not form hyponitrous acid with water ($H_2N_2O_2$).

<u>Nitric oxide</u>: it is colourless gas. It is used in preparing nitric acid by oxiding ammonia.

It is prepared in laboratory by the reduction of dilute nitric acid with copper, or nitrous acid with iodide ions.

$$3Cu + 8HNO_3 \longrightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

$$2HNO_2 + I^- + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O$$

NO gas is paramagnetic since there is an odd electron in molecule. However, the liquid and solid states are diama-gnetic because dimers are formed and unpaired electrons cancels out.

N O

O . . . . N

<u>Nitrogen sesquioxide</u>: It is unstable gas and can be obtained by condensing NO and NO_2 together.

$$NO + NO_2 \xrightarrow{\text{condensation}} N_2O_3$$

It is an acdic oxide and is the anhydride of mitrous acid.

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

The structure of N_2O_3 is not known, but the nitrite ion NO_2^- has a plane triangular structure, in which one position is occupoied by a lone pair.

O O⁻

:N ⟷ N

O⁻ O

Nitrous acid is unstable, and both HNO_2 and nitrites act as oxidizing agents with formation of N_2O or NO. But in the

presence of powerful oxidizing agent they acts as reducing agents.

<u>Nitrogen dioxide:</u> is a red brown poisonous gas. It is produced by oxidizing NO in manufacture of nitric acid.

In laboratory, it prepared by heating lead nitrate.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

The gas becomes dimers on condensation to the colorless dinitrogen tetra oxide .

$$2NO_2 \rightleftarrows N_2O_4$$

NO_2 is an odd electron molecule, but the resonance energy is unsufficient to prevent dimerization. The dimer has no unpaired electrons, and the solid has been shown to have a planar structure.

O O

N N

O O

N_2O_4 reacts with water to give nitric and nitrous acids.

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$

and HNO_2 decomposes into NO and NO_2

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O$$

The NO_2 -N_2O_4 system is an oxidizing agent .

<u>Dinitrogen pentaoxide :</u>

It is the anhydride of HNO_3. It is prepared by dehydrating HNO_3 with P_2O_5.

$$2H\,NO_3 \xrightarrow{P_2O_5} H_2O + N_2O_5$$

It has the structure :

O   O

N -- O -- N

O   O

HNO_3 is an exellent oxidizing agent when not and concentrated.

It is produced by the Haber-Bosch process.

$$N_2 + 3H_2 \xrightarrow{\text{200 atoms } 500^{o}C} 2\,NH_3$$

Haber – Bosch

$$2NH_3 + O_2 \xrightarrow[\text{catamust,5-10 atmosphere}]{\text{Platinumlohdium}} NO \quad NO_2 \quad HNO_3$$

$$N_2 + O_2 \rightarrow NO$$

The nitrate ion is planar and may be represented as a resonance hybrid.

O   O   O   O   O   O

$N \leftrightarrow N \leftrightarrow N \leftrightarrow N \leftrightarrow N \leftrightarrow N$

O O O O O O O O O O O O

Reduction of nitrates in acid solution gives either NO_2 or NO, but in alkaline solutions ammonia is produced.

$$3Cu + HNO_3 \xrightarrow{\text{cold dilute } (<lM)} NO + Cu(NO_3)_2 + 4HO$$

$$Cu + 3HNO_3 \xrightarrow{\text{stronger acid}} NO_2 + Cu(NO_3)_2 + H_2O$$

$$Cu/Al/Zn \text{ (alloy)} + NaOH \longrightarrow H$$

$$NO_3^- + H \longrightarrow NH_3$$

Oxides of Phosphorus , Arsenic and Bismuth

The oxides of the rest of the group are listed in the following table:

P_4O_6III	As_4O_6III	Sb_4O_6 III	BI_2O_3III
P_4O_7III V		$(SbO2)_n$III V	
P_4O_8			
P_4O_9			
P_4O_{10}	As_4O_{10} V	SbO_{10} V	

===

Fewer oxides are formed than are with nitrogen because of the inability of these elements to form double bonds.

Oxyacids of phosphorous :

1)Phosphoric acids: (p is (+v) oxidation state, and compounds have oxidizing properties).

Ortho phosphoric acid : H_3PO_4

O

OH --- O --- OH

OH

A very large number of phosphoric acids and their slats the phosphates arise by sharing oxygen atoms at 1 or 2 corners f PO_4, such as:

O O

HO --- P --- O --- P --- OH **Pyro phosphoric acid**

HO OH $H_4P_2O_7$

O O

HO --- P --- O --- P --- O --- P --- OH **tripoly phosphoric acid**

OH OH $H_5P_3O_{10}$

$H_3\ PO_4$ **is prepared from phosphate rock.**

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 2H_3\ PO_4 + 3CaSO_4$$

Also, by hydrolysis of P_4O_{10} or by the action of HNO_3 on phosphorous.

$P_4O_{10}+H_2O$

$$H_3PO_4 \xrightarrow[\text{heat}]{\text{gentle}} H_4P_2O_7 \xrightarrow[\text{heat}]{\text{strong}} (HPO_3)_n$$

$P + HNO_3$

Pyrophosphoric acid **meta phosphoric acid**

2)Phosphorous Acids:(P is (+III) oxidation state and have reducing properties).

They are less well known and are basic:

H H

HO --- P --- O --- P --- OH **Pyro phosphorous acid**

O O $H_4\ P_2\ O_5$

O

HO --- P --- OH **ortho phosphoric acid**

O $H_3\ PO_3$

Phosphates are used as fertilizers (ammonium phosphate) super phosphate, and triple super phosphate.

$$Ca_3(PO_4)_2 + H_2SO_4 \qquad [Ca_2H_2(PO_4)_2 + CaSO_4]$$

Super phosphate

$$Ca_3(PO_4)_2 + H_3SO_4 \qquad [Ca_2H_2(PO_4)_2] \text{ triple}$$

Super phosphate

<u>Occurrence and extraction :</u>

Nitrogen comprises 78% of the earth's atmosphere and it also occurs as Nitrates ($NaNO_3$ is the most common).

It is obtained commercially by the fractional distillation of liquid air (N_2 b.pt.- 196°C).

In laboratory it is made by warming ammonium nitrite or by oxidizing ammonia with sodium or calcium hypo chlorite.

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + NH_4NO_2 \longrightarrow N_2 + H_2O$$

$$4NH_3 + 3Ca(OCl)_2 \longrightarrow 3CaCl_2 + 6H_2O + 2N_2$$

Phosphorous is obtained by reduction of calcium phosphate with C or SiO_2 at 1300°C.

$$Ca_3PO_4 + SiO_2 \longrightarrow CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + C \longrightarrow P + CO$$

As Sb and Bi are obtained as metallurgical byproducts.

Group VI The Oxygen Group

Table (10)

Element		Electronic structure	Oxidation state	
Oxygen	**O**	$2S^2 2P^3$		**(- III),(– I)**
Sulphur	**S**	$3S^2 3P^3$	**(-II)**	**(II),(IV),(VI)**
Selenium	**Se**	$3d^{10} 4S^2 4P^3$	**(-II)**	**(II),(IV),(VI)**
Tellurium	**Te**	$4d^{10} 5S^2 5P^3$		**(II),(IV),(VI)**
Polonium	**Po**	$4F^{14} 5d^{10} 6S^2 6P^3$		**(II),(IV)**

Metallic and Nonmetallic Character:

The first four elements are nonmetallic in character and the nonmetallic character is strongest in O and S, weaker in Se and Te, whilst Po, which is radioactive is markedly metallic.

Electronic structure and oxidations states:

The elements all have the electronic structure S^2P^4 and tend to attain an inert gas configuration by gaining two electrons forming M^{-2} ions, or by sharing two electrons thus forming two covalent bonds Table (10).

Most metal oxides are ionic and contain O^{2-} ions because oxygen is highly electronegative. S^{-2}, Se^{-2}, and T^{2-} ions are less probable and compounds formed with S, Se and Te are 50 % ionic.

Also the elements form covalent compounds such as H_2O, Cl_2O, H_2S. Cl_2S .

Oxygen is never more than divalent because the second shell is limited to eight electrons and it requires too much energy to excite an electron into a higher shell.

Other elements S, Se, Te and Po have empty d orbital's which may be used for bonding and they can form four or six bonds by unpairing electrons.

S P d

Ground state

two unpaired electrons can form two bonds

Excited state

four unpaired electrons can form four bonds

Further
Excited state

six unpaired electrons can form six bonds

<u>Differences between oxygen and other element</u> :

1-Oxygen is more electronegative and more ionic in its compounds.

2-Hydrogen bonding is very important for oxygen compounds.

3-There is no higher valence states for oxygen because of the limitation of the second shell to eight electrons, whereas the

other elements can use d orbital's and have higher valence states.

Abundance and extraction:

Oxygen is manufactured by the fractional distillation of liquid air.

It is prepared in the laboratory:

(1) by thermal decomposition of $KClO_4$ (with MO_2 as catalyst) .

$$KClO_4 \xrightarrow[MnO_2\ \text{catalyst}]{\text{heat}} KCl + O_2$$

(2) by the catalytic decomposition of hypo chlorites

$$2\,HOCl \xrightarrow{Co^{2+}} 2\ HCl \quad O_2$$

(3) by electrolysis of water acidified with trace of H_2SO_4

Large amounts of sulpher are obtained from oil refineries and natural gas plants.

H_2S is oxidized in air to give SO_2 which is subsequently reacted with H_2S giving S.

$$2H_2S \quad 3O_2 \longrightarrow 2SO_2 \quad 2H_2O$$

$$SO_2 \quad 2H_2S \longrightarrow 2H_2O \quad 3S$$

Se and Te occur among sulphide ore .

Molecular structure:

Oxygen is gas stable as a diatomic molecule, S, Se, Te and Po are solids at normal temperature and have complex structure. If oxygen molecule had two covalent bonds:

O = O **: O : : O :**

then all electrons would be paired and the molecule should be diamagnetic. Oxygen is paramagnetic and there for contains unpaired electrons.

The other form of oxygen is ozone O_3. Ozone decomposes slowly to oxygen. Pure liquid O_3 may be explosive because its decomposition into oxygen is exothermic.

$$2O_3 \longrightarrow 3O_2 \qquad H = 284 \ \text{Kg/mole.}$$

Therefore oxygen needs energy to be changed to ozone. This energy could be obtained in many forms:

(i)Thermal energy: by heating oxygen to high temperatures in the electric are oven.

(ii)Photo energy: by the action of ultraviolet rays.

(iii)Electricenergy: by passing a silent electric discharge through oxygen gas.

(iv)Chemical energy: by decomposition of water with fluorine.

$$F_2 \ \ H_2O \longrightarrow H_2F_2 + O + \text{heat}$$

$$3 \ O \ \ \text{heat} \longrightarrow O_3$$

The ozone molecule is diamagnetic and has an angular structure. Both O to O bonds have the same length (1.27A^o) which is intermediate between the double bond distance(1.1 A^o) and the single bond distance (1.4 A^o). The molecule may be represented as a resonance hybrid

O + ↔ O +

$^-$ O :O: O :O: $^-$

Ozone is highly reactive. Its higher reactive in compare-ison to oxygen is consistent with the higher energy content of ozone. It is a powerful oxidizing agent ($O_3 \rightarrow O_2 + O$)

$$2\,KIO_3\ \ H_2O \longrightarrow 2KOH + I_2 + O_2 \text{ (detection Ozone).}$$

Ozone reacts with unsaturated organic compounds to form explosive compounds called ozonides; the latter are broken up with water giving interesting compounds H_2O_2 is evolved in most of the cases.

$$CH_2 = CH_2 + O_3 \longrightarrow \begin{array}{c} CH_2 - O \\ O \\ CH_2 - O \end{array} \xrightarrow{H2O} H_2O_2 + 2HCHO$$

Hydrides:

The elements all form volatile bivalent hydrides H_2O, H_2S, H_2Se, H_2Te and H_2Po. These can be made from the elements, but normally H_2S and H_2Te are obtained by the action of acids on metal sulphides selenides and telluride's.

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

Hydrogen polonide has only been obtained in trace amounts from a mixture of Mg, Po and dilute acid.

The hydrides decrease in stability from H_2O to H_2Te, because the overlap with hydrogen become less favorably.

The H-O-H bond angle of 105 in water is in accordance with SP^3 hybridization of the oxygen atom, with slight distortion due to the two lone pairs of electrons.

In H_2Se and H_2Te the bond angles becomes close to 90^o suggesting that almost pure p orbital's on Se and Te are used for bonding to hydrogen.

Volatility usually decreases as the atoms become larger and heavier. This trend is shown by the boiling points of H_2Se, H_2Te and H_2Po.

	Bond angle	Boiling point
H_2O	H-O-H = 105o	100
H_2S	H-S-H = 92o	-60
H_2Se	H-Se-H = 191o	-42
H_2Te		-2.3

==

Water has an abnormally low volatility because it is associated by means of hydrogen bonds in the solid and liquid states.

Oxygen and hydrogen also react to form hydrogen peroxide, H_2O_2, which is also obtained by the addition of an acid to a peroxide salt.

$$BaO_2 + H_2SO_4 \qquad\qquad BaSO_4 + H_2O_2$$

H_2O_2 can be commercially obtained by electrolysis of H_2SO_4 here by the resulted peroxy sulfuric acid reacts with water to give H_2O_2

$$2H_2SOP_4 \rightleftharpoons 2H^+ + 2HSO_4^-$$

$$2H^+ + 2e^- \xrightarrow{\text{cathode}} H_2$$

$$2HSO_4 \xrightarrow{\text{anode}} H_2S_2O_8 + 2e^-$$

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H2O_2$$

H_2O_2 is a colorless liquid. It is a weak diprotic acid in water solution; one or two hydrogen's can be neutralized by NaOH to give sodium hydro peroxide $NaHO_2$ or sodium peroxide NaO_2 respectively. H_2O_2 could function either as oxidizing agent ($H_2O_2 \rightarrow H_2O + O$).

$$pbS + 4H_2O_2 \longrightarrow pbSO_4 + 4H_2O$$

$2KI + H_2O_2 + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + I_2$ (detection of H_2O_2) or as a reducing agent ($H_2O_2 + O \rightarrow H_2O + O_2$), $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$ and this reaction is used for quantitative determination of H_2O_2. H_2O_2 is sold under the name "perhydrol" and is used as a bleaching agent (soda bleach, NaOH + H_2O_2) for bleaching silk, wool and hair. It is also used as antiseptic in medicine for washing wounds, ears and teeth, as oxidizing agent, for restoring color of black-ened lead paintings, as a preservative, as a fuel or propellant in submarine and rockets and as a source of oxygen for the combustion of liquid fuel.

<u>Strength of H_2O_2 solution</u>:

The strength of H_2O_2 solution is stated in terms of the volume of oxygen evolved on heating

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

The commercial preparations are "10,20,30 or 100 volumes" according as it gives off 10.,20,.30 or 100 times its volume of oxygen respectively. A" 10 volume "Solution would be or ugly 3% in strength. Exact calculation may be done as follows:

A"10volume"solution should give oxygen=10x 10 =100 ml.

As per equation: $2H_2O_2 \longrightarrow 2H_2O + O_2$, 68 g. H_2O_2 gives 22,400 ml of oxygen at N.T.P.

Wt of H_2O_2 that giving 100 ml oxygen at N.T.P.

would be $\frac{68}{22400} \times 100 = 0.03$ g i.e. the solution

would be 3.03 % .

Also we could find out that a "10 volume" H_2O_2 is 1.786 N H_2O_2. Also in H_2O_2 solution is "5.6 volume H_2O_2" solution.

<u>Halides:</u>

Compounds of oxygen and halogens will be described in group VII under halogen oxides.

Fluorine forms SF_6, SeF_6, and TeF_6. They are all colorless gases. SF_6 is inert and SeF_6 is slightly more reactive and TeF_6 is hydrolyzed by water.

$$TeF_6 + 6H_2O \longrightarrow 6HF + H_6TeO_6$$

Many tetra halides are known. In contrast to the relatively stable hexa fluorides, the tetra halides are very water sensitive.

$$SF_4 + H_2O \longrightarrow SOF_2 + 2HF$$

SCl_2 is the best known di halide.

Dimeric mono halides such as S_2F_2, Se_2Cl_2 and Se_2Br_2 are known.

<u>Oxides</u>:

Element	MO2	MO3	other	oxides	
S	SO_2	SO_3	S_2O		S_2O_3
Se	SeO_2	SeO_3		TeO	
Te	TeO_2	TeO_3		PoO	
Po	PoO_2				

<u>Dioxides MO_2 :</u>

O:

So_2 is gas and its structure is :S

O:

SeO_2 is solid at room temperature. The gas has the same structure as SO_2, but solid forms infinite chains which are not planar.

O O O O

Se

Se Se

SO_2 dissolves in water and H_2SO_3 acid cannot be isolated SO_2 is important in the manufacture of sulphuric acid and for bleaching. It also acts as a mild reducing agent in acidic solution and as a strong reducing agent in alkaline solution. It has also been used as a non-aqueous solvent, but there is considerable doubt its postulated self ionization.

$$2\ SO_2 \rightarrow SO^{2+} + SO_3^{2-}$$

Trioxides MO_3:

SO_3 is the only important trioxide. It is manufactured by direct reaction of O_2 on SO_2. SO_3 reacts with water and forms H_2SO_4. Also SO_3 dissolves in H_2SO_4 to give fuming sulphuric acid. SO_3 gas has the structure:

:O:

S

:O   :O

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

Other oxides :

S_2O it very reactive. It attacks metals and KOH It is formed when S and SO_2 are subjected to a silent electric discharge.

Oxy acids of sulphur:

The oxy acids of sulphur are more numerous and important than those of Se and Te. Many of them are not exist as free acids, but are known as salts. These acids have S

in the oxidation state (IV) or (VI). The acids are listed in five groups according to structural similarities.

(1) Sulphoxylic acid :

H_2SO_2 sulphoxylic acid

(2) Sulphurous acid series

OH

H_2SO_3 sulphurous acid S=O

OH

OH

$H_2S_2O_2$ sulphurous acid S=S

OH

O O

$H_2S_2O_5$ dior pyrosulporous acid OH – S – S - OH

O

O O

$H_2O_2O_4$ dithionous acid HO – S – S - OH

(3) <u>Sulphuric acid series</u>:

O

H_2SO_4 sulphuric acid OH – S – OH

O

S

$H_2S_2O_3$ thio sulphuric acid OH – S – OH

O

O O

$H_2S_2O_7$ dior pyro sulphoric acid OH – S – O – S -OH

O O

(4) <u>Thionic acid series</u>:

O O

$H_2S_2O_6$ dithionic acid OH – S – S - OH

O O

O O

$H_2S_nO_6$ poly thionic acid OH – S – $(S)_n$ – S - OH

(n=1 – 12) O O

(5) Paroxo acid series:

O

H_2SO_5 peroxomono sulphuric acid HO – O - S - OH

O

O O

$H_2S_2O_6$ peroxodisulphuric HO – S - O – O – S - OH

O O

<u>Oxidation-Reduction Reactions:</u>

The term oxidation was originally applied to reactions in which substances combined with oxygen, and reduction was defined as the removal of oxygen from an oxygen-containing compound. Now oxidation and reduction are the processes in which an atom undergoes an algebraic increase or decrease in oxidation number respectively. On this bases, oxidation-reduction is involved in thereaction ,

$$S^o + O_2^o \longrightarrow SO^{2-}_2$$

i.e. sulfur is oxidized and oxygen is reduced. It is clear that neither oxidation nor reduction can occur alone; each process must occur to the same extent in a given reaction; and again, the sum of the oxidation numbers of any chemical

species equals the charges on that species (zero if the entire compound is considered). In any reaction, the sum of the reactant species must equal the sum of the charges of the product species (zero for reactions involving only molecules).

Since one substance cannot be reduced unless another is simultaneously oxidized, the material that is reduced is responsible for the oxidation; therefore it is called the oxidizing agent or oxidant. The material that is itself oxidized is called the reducing agent or reluctant. Therefore,

S^o (oxidized, reducing agent)+O^o_2 (reduced, oxidizing agent)

$$\longrightarrow \quad S^{4+}O^{2-}_2$$

There are two methods, commonly used to balance oxidation-reduction equations:

(a) <u>The oxidation-number method</u>:

The unbalanced expression for the reaction of HNO_3 with H_2S is :

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

1- Oxidation numbers of the atoms in the equation are determined, thus:

$$H\overset{+5}{N}O_3 \quad H_2S^{2-} \longrightarrow \overset{2+}{N}O + S^o + H_2O$$

2- Coefficients are placed before the appropriate formulas so that the total decrease in oxidation number equals the total increase in that number, i.e. Nitrogen is reduced (5+ to 2+ , a decreases of 3) and sulfur is oxidized (2- to O, an increase of

2). Thus it is necessary that 2 molecules of HNO_3 and 2 molecules of NO, as well as 3 molecules of H_2S and 3 atoms of S , be indicated. Thus the total increase in oxidation number will be 6 and will equal the total decrease of 6.

$$2\,HNO_3 + 3H_2S \longrightarrow 2\,NO + 3S + H_2O$$

3- Balancing is completed by inspection. Now 8 hydrogen atoms on the left, therefore $4H_2O$ molecules must be indicated on the right.

$$2\,HNO_3 + 3\,H_2S \longrightarrow 2\,NO + 3S + 4H_2O$$

Finally, balanced equation should be checked to ensure that there are as many atoms of each element on the left as there are on the right.

The method may be used to balance Net Ionic Equations, in which only ions and molecules that actually take past in the reaction are shown. e.g. K^+ ion does not take part in the reaction of $KClO_3$ with I_2 and is not shown in the equation. The steps in balancing are:

$$\text{1- } H_2O + \overset{0+}{I_2} + \overset{5+}{Cl}O_3^- \longrightarrow \overset{+5}{I}0_3^- + \overset{-1}{Cl} + H^+$$

2- Each iodine atom undergoes an increase of 5 (from 0 to 5). The increase in oxidation number is 10 (two iodine atoms). Chlorine undergoes a decease of 6 (from 5 to -1).

The lowest common multiple of 6 and 10 is 30. Therefore $3I_2$, molecules must be indicated (a Total increase of 30) and $5ClO_3^-$ ions are needed (a total decrease of 30). The

coefficients of the products, 10^{-3} and Cl^-, fellow from this assignment.

$$H_2O + 3I_2 + 5ClO_3^- \longrightarrow 6\,IO^-_3 + 5Cl^- + H^+$$

If H_2O is ignored, there are now 15 oxygen atoms on the left and 18 oxygen atoms on the right. To make up 3 oxygen atoms on the left, we must indicate $3H_2O$ molecules, thus the coefficients of H^+ must be 6 to balance the hydrogen's of the H_2O molecules.

$$3H_2 + 3I_2 + 5ClO^-_3 \longrightarrow 6lO_3^- + 5Cl^- + 6H^+$$

An ionic equation must indicate charge balance as well as mass balance. Since the algebraic sum right (5-), the equation is balanced. Electron transfer reactions are examples of oxidation-reduction e.g. the reaction of Na and Cl_2, a Na atom loses it valence electron to a Cl^-atom.

$$\overset{o}{2\,Na} + \overset{o}{Cl_2} \longrightarrow 2\,\overset{I+}{Na} + 2\,\overset{-1}{Cl^-}$$

Hence, electron loss represents a type of oxidation and electron gain a type of reduction. This equation can be divided into two partial equations that represent half reaction.

Oxidation : $2\,Na \longrightarrow 2\,Na + 2e^-$

Reduction : $2e^- + Cl_2 \longrightarrow 2Cl^-$

(b)The ion-electron method of balancing oxidation Reduction Equations :

These employ partial equations and only ions that are involved in the reaction are shown: Unionized (or slightly ionized) species and insoluble substances that take parting the reaction are written in molecular form. The steps of the method can be illustrated using the reaction between $Cr_2O_7^-$ ion and Cl^- ion.

1- Two skeleton partial equations for the half reactions are written with the central element of each partial equation balanced.

$$Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} \quad \& \quad 2Cl \longrightarrow Cl_2$$

2- The hydrogen and oxygen atoms are then balanced. Since this reaction occurs in acid medium, H^+ and H_2O can be added where needed. For each O-atom that is needed, one H_2O molecules is added to the side of the partial equation that is deficient. The hydrogen is then brought into balance by the addition of $2H^+$ to the opposite side. Thus 7 oxygen must be added to the right side of the partial equation, the second partial equation is already in material balance.

$$Cr_2O^{2-}{}_7 + 14\,H^+ \longrightarrow 2Cr^{3+} + 7H_2O \;\&\; 2Cl^- \longrightarrow Cl_2$$

3- The partial equations are then electrically balanced. In the first equation the net charge is 12+ on the left side of the equation (14+ and 2-) and 6+ on the right side. Six electrons

must be added to the left. The second equation is balanced electrically be the addition of 2 electrons to the right.

$Cr_2O^{2-}_7 + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ & $2Cl^- \longrightarrow Cl_2 + 2e^-$

4- The number of electrons lost must equal the number of electrons gained, therefore, the oxidation equation is multiplied by 3.

$Cr_2O^{2-}_7 + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ & $6Cl^- \longrightarrow Cl_2 + 6e^-$

5- Addition of the two partial equations gives the final equation.

$$Cr_2O^{2-}_7 + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 3C^- + 7H_2O$$

These steps are illustrated for the reaction in which As_4O_6 reacts with MnO^-_4 to produce H_3AsO_4 and Mn^{2+}.

1- $MnO^-_4 \longrightarrow Mn^{2+}$ & $As_4O_6 \longrightarrow 4H_3AsO_4$

2- To the first equation $4H_2O$ are added to the right side and $8H^+$ to the left side. In the second equation, 10 H_2O must be added to the left side to make up the needed 10 oxygen (16-6=10)., In the second equation we have now 20 hydrogen atoms on the left (10 x 2 = 20) and 12 (4 x 3 = 12) on the right, therefore $8H^+$ must be added to the right side of equation 2.

$$MnO^-_4 + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

$$As_4O_6 + 10H_2O \longrightarrow 4H_3AsO_4 + 8H^+$$

3- To balance the net charges, electrons are added.

$$MnO^-_4 + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$As_4O_6 + 10H_2O \longrightarrow 4H_3AsO_4 + 8H^+ + 8e^-$$

4- Now the first equation must be multiplied through by 8 and the second by 5.

$$8\,MnO_4^- + 64H^+ + 40e^- \longrightarrow 8Mn^{2+} + 32H_2O$$

$$As_4O_6 + 50H_2O \longrightarrow 20H_3AsO_4 + 40H^+ + 40e^-$$

5- When these two partial equations are added, water molecules and hydrogen ions must be cancelled as well as electrons.

$$8\,MnO_4^- + 5As_4O_6 + 24H^+ + 18H_2O \longrightarrow 9Mn^{2+} + 20H_3AsO_4$$

In alkaline medium, equations are balanced in a manner slightly different from those that occur in acidic solution. All the steps are the same except the second one; H^+ cannot be used to balance equations for alkaline reactions. e.g., the reaction between MnO_4^- and N_2H_4 in alkaline solution.

1- $MnO_4^- \longrightarrow MnO_2$ **&** $N_2H_4 \longrightarrow N_2$

2- For reactions occurring in alkaline solution, OH^- and H_2O are used to balance oxygen and hydrogen added to the side of the equation that is deficient and one H_2O molecule is added to the opposite side. For each hydrogen that is needed, one H_2O molecule is added to the side that is deficient, and one OH^- ion is added to the opposite side.

In the first equation, the right side is deficient by 2 oxygen atoms, we add, therefore, 4 OH^- to the right side and $2H_2O$ to the left.

$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

In the second equation, we must add 4 hydrogen atoms to the right side. For each H-atom needed we add one H_2O to the side deficient in hydrogen and one OH^- to the opposite side. In the present case, we add $4H_2O$ to the right side and $4OH^-$ to the left side to make up the 4 hydrogen atoms needed on the right.

$$N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O$$

3- Electrons are added to effect charge balance.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

$$N_2O_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^-$$

The lowest common multiple of 3 and 4 is 2. Therefore,

4- The first equation is multiplied by through by 4 and the second by 3 so that the number of electrons gained equals the number lost.

$$MnO_4^- + SH_2O + 12e^- \longrightarrow 4MnO_2 + 16OH^-$$

$$3N_2H_4 + 12OH^- \longrightarrow 3N_2 + 12H_2O + 12e^-$$

5- Addition of partial equations, with cancellation of OH^- ions and H_2O molecules as well as electrons, gives the final equation.

$$4MNO_4^- + 3N_2H_4 \longrightarrow MnO_2 + 4H_2O + 4OH^- + 3N_2$$

As a final example, consider the following skeleton equation for a reaction in alkaline solution .

$$Br_2 \longrightarrow BrO^-_3 + Br^-$$

In this reaction the same substance, Br_2 is both oxidized and reduced. Such reactions are called disproportionateness or auto-oxidation-reduction reactions.

1- $Br_2 \longrightarrow 2\,BrO_3^-$

$Br_2 \longrightarrow 2Br^-$

2- $Br_2 + 12\ OH^- \longrightarrow 2BrO_3^- + 6H_2O$

$Br_2 \longrightarrow 2Br^-$

3- $Br_2 + 12\ OH^- \longrightarrow 2BrO_3^- + 6H_2O + 10e^-$

$Br_2 + 2e^- \longrightarrow 2\,Br^-$

4- $Br_2 + 12\ OH^- \longrightarrow 2BrO_3^- + 6H_2O + 10e^-$

$5Br_2 + 10e^- \longrightarrow 10\,Br^-$

5- $6Br_2 + 12\,OH^- \longrightarrow 2BrO_3^- + 10Br^- + 6H_2O$

However most oxidation–reduction reactions may be balanced by the ion electron method which is especially convenient for electrochemical reactions and reactions of ions in water solution. Half reactions cannot occur alone and partial equations do not represent complete chemical changes. Even ion the electrochemical cells, where the two half reactions take place at different electrodes, the two half reactions always occur simultaneously.

Group VII The Halogens

Table (11):

Element		Electronic configuration	Oxidation states
Fluorine	F	$2S^22P^5$	-I
Chlorine	Cl	$3S^23P^5$	-I,+I,III,+IV,+V,VI,+VII
Bromine	Br	$3d^{10}4S^24P^5$	-I,+I,+III,IV,+V,IV
Iodine	I	$4d^{10}5S^25P^5$	-I,+I,III,+IV,+V,VI,+VII
Astatine	At	$4F^{14}5d^{10}6S^26P^5$	

Electronic structure and oxidation states:

The halogens show very close group similarities. The elements all have seven electrons in their outer shell, and they either gain an electron and form (X^- ion) or form covalent bond in order to complete their octet.

Fluorine is always univalent and has the oxidation number (-1). It is the most electronegative element. Other elements have oxidation number (+I), (+III), (+V) and (+VII). Table (11).

General properties:

*** The melting and boiling points are increased with increased atomic number for these elements.**

*** Fluorine and chlorine are gases, bromine is liquid and iodine is solid.**

*** The elements all form diatomic molecules.**

*** The ionization energies of the halogens are all very high, because of the little tendency to lose the electrons. The value for F is the highest, and for I is the lowest.**

*** The halogen molecules are all colored. F_2 gas is yellow, and I_2 gas is violet.**

*** Halogens act as oxidizing agents, since they have tendency to gain electrons. The oxidizing power decreases on descending the group. F_2 is so strong as an oxidizing agent that it oxidizes water to oxygen.**

$$F_2 + H_2O \longrightarrow 2H^+ + 2F^- + 1/2\ O_2$$

The reaction is exothermic and spontaneous. For Cl_2 the following reaction occurs.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

I_2 is very weak oxidizing agent

$$I_2 + H_2O \rightleftharpoons 2H^+ + 2I^- + 1/2\ O_2$$

The reaction is endothermic and the reverse process occurs and oxygen oxidizes iodide ions to iodine.

<u>Reactivity of the elements :</u>

Fluorine is the most reactive of the elements in the periodic table. It reacts with all elements except the noble gases He, Ne, and Ar.

The reactivity of the halogens decrease with increasing atomic number.

Chlorine and bromine react with most of the elements, though less vigorously. Iodine is less reactive and does not combine with some elements such as S and Se.

The great reactivity of fluorine is due to the low energy of the F-F bond, (the extremely high oxidizing power, the small size of the atoms or ions and the high electro negativity).

Hydrogen halides:

The halogens all react with hydrogen and form HX hydrides. Whilst the reaction of hydrogen with fluorine is quite violent, the reaction with iodine is slow at room temperature.

HF and HCl are usually prepared by treatment of salts with strong sulphuric acid.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

In the gaseous state, the hydrides are essentially covalent, but in aqueous solutions they ionize and HCl, HBr and HI function as strong acids.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Liquid HF has been used as a non-aqueous solvent It undergoes self ionization.

$$2HF \rightleftharpoons H_2F^+ + F^-$$

Halogen oxides:

Most of the halogen oxides are unstable. The iodine oxides are the most stable, then chlorine oxides and the

bromine oxides all decompose below room temperature. The higher oxidation states are more stable than the lower states. The bonds are largely covalent because of the small difference in electro negativity between the halogens and oxygen fluorine form binary compounds (fluorides of oxygen) because fluorine is more electronegative than oxygen. Compounds of the halogens with oxygen are shown in the following table.

	MX_2	M_2X_2	M_2X	Others
Fluorides	OF_2	O_2F_2		O_4F_2
	Cl_2O		ClO_2	Cl_2O_6 , Cl_2O_7
Oxides	Br_2O		BrO_2	BrO_3
				I_2O_4 , I_4O_9 , I_2O_5

==

<u>Oxyacids</u>:

Chlorine, bromine and iodine form four series with formulae :

formulae :	**HOX**	**hypohalous acids**
	HXO_2	**halous acids**
	HXO_3	**halic acids**
	HXO_4	**perhalic acids**

<u>Hlous acids: HOX</u>

The hypogalous cids HOCl, HOBr and HOI are all weak acids and only exist in aqueous solutions. Hypochlorous acid is the most stable and its sodium salt

NaOCl (sodium hypochlorite) is used for bleaching cotton fabric.

<u>Halous acids :</u> HXO_2

The only halous acid known is $HCLO_2$ (chlorous acid). It exists only in solution. It is a strong acid than HOCl.

<u>Halic acids: HX</u>O_3

$HClO_3$ and $HBrO_3$ are known in solution, but HIO_3 exists as white solid. The acids all are strong oxidizing agents and strong acids.

Chlorates may be made by the action of Cl_2 on NaOH

$$6HaOH + 3Cl_2 \xrightarrow{heat} NaClO_3 + 5NaCl + 3H_2O$$

<u>Perhalic acids</u>: HXO_4

$HClO_4$ and HIO_4 and their salts are well known; perbromates (BrO_4^-) have only recently been prepared.

$HClO_4$ is one of the strongest acids, and is a powerful oxidizing agent. It can be made from NH_4ClO_4 and dilute nitric acid or from $NaClO_4$ and concentrated hydrochloric acid.

$NaClO_4$ is made by electrolysing aqueous $NaClO_3$, using smooth platinum electrodes to give a high oxygen over potential to prevent the electrolysis of water.

$$NaClO_3 + H_2O \xrightarrow{electrolysis} NaClO_4 + H_2O$$

Group VIII The Noble Gases

The outstanding characteristics of the noble gases is their low order of chemical reactivity. Until 1962, no true compounds of these elements were known and hence they were called "inert gases". Since 1962, approximately 25 compounds of the heavier elements of this group have been prepared.

The noble gases or zero group of the periodic table consists of six elements, helium, neon, argon exception of radon, which is obtained from radioactive disintegration, are contained in atmosphere, thought only in very minute quantities, and therefore called the rare gases of the atmosphere.

Table (12) : Some properties of Noble gases :

Element	Symbol	Electronic structure	First I.P. v.	M.P °C	B.P. °C
Helium	He		24.6		-268.9
Neon	Ne	$[He]2S^2 2P^6$	21.6	-248.6	-246.0
Argon	Ar	$[Ne]3S^2 3P^6$	15.7	-189.4	-185.9
Krypton	Kr	$[Ar]3d^{10} 4S^2 4P^6$	14.0	-157.2	-153.2
Xenon	Xe	$[Kre]4d^{10} 5S_2 5P^6$	1201	-111.9	-108.1
Radon	Rn	$[Xe]4f^{14} 5d^{10} 6S^2 2P^6$	10.8	- 71.0	- 62.0

<u>Electronic structure and general properties</u> :

The two electrons of He form a complete shell, and all the other inert gases have an octet of electrons in their outer shell. The electronic configuration is related to their chemical in activity. These atoms have an electron affinity near to zero and have ionization potentials than any other elements. Consequently they do not gain or lose electrons under normal conditions and do not form many bonds. Thus they exist as single atoms (mono atomic molecules. The only forces between these atoms are very weak Van der Waals forces and so the melting points and boiling points are very low, (table 12). With increasing atomic number, the atomic size increase and the outer electrons become slightly less tightly held. Therefore, the ionization potential decreases regularly from He to Rn. This factor (i.e. increasing size of electron cloud), also accounts for increasing strength of Van der Waals forces, and consequently the increasing melting point and boiling point from He to Rn. However, He, has the lowest boiling point of any known substance, this is because there are no strong interatomic forces; only the weakest Van der Waals forces operate which hold atoms together.

<u>Compounds of the Noble Gases</u>:

Considerable efforts have been made to find evidence for compounds formation by the noble gases.

(1) Under excited conditions:

$$\text{He-ground state } (1S^2) \quad (\text{ 460 Kcal }) \rightarrow \text{ He-excited state } (1S^1\ 2S^1)$$

These high energy conditions are only realized spectra-scopically under conditions of electrical discharge, or electron bombardment. In a discharge tube He^{+2} , HeH and HeH^{2+} have been observed, but only survive momentarily. Metal electrodes in discharge tubes absorb inert gases to form Pt_3 He, FeHe and FeAr, perhaps as interstitial compounds.

(2) By coordination:

Noble gas atoms may donate an electron pair to suitable acceptor. Thermal analysis of Ar with BF_3 was said to give peaks in the freezing point curves corresponding to 1Ar: 1, 2,3,6,8 and16 BF_3 (i.e. Ar: → BF_3), but this work was not repeatable by other workers.

(3) By dipole/induced dipole attractions :

The noble gas atoms may be polarized by a strong dipole on other molecules and thus possess a weak induced dipole of their own. The solubility of the noble gases in water is high and increases with increased size. This is probably because the larger atoms are more easily polarized by the surrounding water molecules. Certain derivatives of phenol, Kr $(phenol)_2$, Xe $(phenol)_2$ and Rn $(phenol)_2$ may have this sort of attraction.

(4) Clathrate compounds:

Until recently, the only well-established "compounds" of the noble gases were those in which the gases are trapped in cavities in the crystal lattice of other compounds. If quinol (1,4 di hydroxy benzene, HO OH) is crystallized in the presence of the heavier noble gases under a pressure of 10-40 atmospheres, the gas becomes trapped in cavities of about $4A^o$ diameter in the ß-quinol structure. When the clatherate is dissolved, e.g. in ethanol, the hydrogen bonded arrangement of ß-quinol breaks down and the inert gas escapes. Other small molecules such as O_2, SO_2, MeCN and CH_3OH form clathrates as well as Ar, Kr and Ke. The absence of He and Ne compounds occurs because they are too small and can escape from the cavities. The composition of these compounds corresponds to 3 quinol trapped molecule, though normally all the cavities are not filled.

The gases Ar, Kr and Xe may be trapped in cavities in a similar way when water solidifies in the presence of these noble gases. The So-called inert gas hydrates have formula approximating to $6H_2O$: a gas atom.

Clathrates are useful in the separation of noble gases, e.g. Ne can be separated from Ar, Kr and Xe, because Ne is the only gases that doest from a clathcate with quinol. Kr-85 chathrate provides a safe and useful source of ß-radiations while Xe-133 clathrates provides a compact source for ß-

radiations. In addition, clathrates are a convenient from of handling, processing and shipping of rare gas isotopes.

However, the first chemical reaction of a noble gas to be observed, the reaction of Xe with PtF_6 was reported by Bartlett in 1962. P_tF_6 is a powerful oxidizing agent, it reacts with oxygen to give oxygen to give oxygen hexafloroplatinate (V)$[O^+_2]$ $[P_tF_6]^-$. Since the first ionization potential of molecular O_2 is 12.2eV is close to that of Xe (12.1 eV), Bartlett, reasoned that Xe should react with PtF_6 giving the red crystalline solid consisting of xenon haxafluroplatinate (V) $[Xe^+]$ $[P_tF_6^-]$ and other compounds.

The best characterized noble-gas compounds are the xenon fluorides, XeF_2, XeF_4 and XeF_4 with oxidation states +2, +4, and +6 respectively. These are prepared by direct reaction of Xe and Fe using suitable proportion of Xe and F_2.

$$Xe + F_2 \longrightarrow XeF_2$$

$$XeF_2 + F_2 \longrightarrow XeF_4$$

$$XeF_4 + F_2 \longrightarrow XeF_6$$

There are unconfirmed reports of XeF_8. The fluorides react quantitatively with hydrogen:

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$

Oxygen-containing compounds of Xe are produced by reactions of xenon fluorides with water. Partial hydrolysis of XeF_6 yields xenon oxytetrafluride $XeOF_4$, a colorless liquid.

$$XeF_{6(S)} + H_2O \longrightarrow XeOF_{4(L)} + 2HF_{(g)}$$

Complete hydrolysis of XeF_6 or hydrolysis of $XeOF_4$ produces a solution that yields XeO_3 upon evaporation.

$$XeF_{O(S)} + 3H_2O \longrightarrow XeO_{3(aq)} + 6HF_{(g)}$$

$$XeOF_{4(L)} + 2H_2O \longrightarrow XeO_{3(aq)} + 4HF_{(aq)}$$

Also, XeO_4 and also sodium xenate $Na_4\,XeO_6.8H_2O$ with oxidation number of Xe as 8 are known.

The order of decreasing reactivity of the group elements (increasing I.P.) is Rn > Xe > Kr > Ar > Ne > He. Thus, Rn should be the most reactive noble gas and He is the least. There is evidence that Rn reacts with F_2; however, the radioactive disintegration of Rn-isotopes makes the chemistry of Rn difficult to assess.

Uses of noble gases:

Helium is used in lighter than air crafts, and in low temperature work. Being noninflammable and less diffusible over hydrogen, it is used for filling airships and balloons. A mixture of (O_2 + He) is used for respiration in deep sea diving in preference to air. The reason is that Nitrogen of air is highly soluble in blood under high pressure below, and on release of pressure, as the diver comes to the top, it

evaporates suddenly causing great pain. The above mixture being less soluble does not cause this trouble.

Neon signs (sign advertising are made from discharge tubes containing. Neon gas at low pressure.

Argon is used to fill electric light bulbs, the gas does not react with the hot filament but rather conducts heat away from its, thus prolonging its life.

Argon is also used as an inert atmosphere in welding and high temperature metallurgical processes; the gas protects the hot metals from air oxidation. Radon has been used as a source of α-particles in cancer therapy.