9. Reactions with Oxidizing Agents

It reacts with oxidizing agents like KMnO4 and K2Cr2O7 to liberate oxygen which may oxidize other compounds.

2*KMnO*4 +3*H SO*2 4 →*K SO*2 4 + 2*MnSO*4 +3*H O*2 +5[ ]*O*

10*FeSO*4 +5*H SO*2 4 +5[ ]*O* → 5*Fe SO*2( 4 3) +5*H O*2

4.5.3 Uses of Sulphuric Acid

It is used

1. in the manufacture of fertilizers like ammonium sulphate and calcium superphosphate.
2. in refining of petroleum to remove nitrogen and sulphur compounds.
3. in the manufacture of HCl, H3PO4, HNO3 and sulphates.
4. in the manufacture of many chemicals, dyes, drugs, plastics, disinfectants, paints, explosives, synthetic fibers, etc.
5. in electrical batteries and storage cells.
6. as a dehydrating agent for drying gases.
7. as a laboratory reagent.
8. in textile, iron, steel, leather and paper industries.

###### KEY POINTS

1. In group VA the metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while bismuth is a metal.
2. Phosphorus and other members of VA group can make use of d-orbitals in bonding.
3. Common oxides of nitrogen are N2O, NO, NO2,N2O3 and N2O5.
4. Nitrogen forms two oxyacids, HNO2 and HNO3, HNO2 is an unstable acid and exists only in solution.
5. HNO3 is not only a strong acid but it also acts as a strong oxidising agent.
6. Aqua regia is a mixture of one volume of concentrated HNO3 and three volumes of concentrated HCl.
7. Phosphorus exists in six allotropic forms. White phosphorus is very reactive as compared to red phosphorus.
8. Phosphorus forms two types of chlorides PCl3, PCl5 and two types of oxides P2O3 andP2O5
9. Just like nitrogen, phosphorus also gives two types of oxyacids; phosphorus acid (H3PO3 ) and phosphoric acid (H3PO4).
10. Posphoric acid is a weak tribasic acid and it gives three series of salts with strong base.
11. Group VIA of the periodic table contains only one metal, polonium, the rest of members are non-metals. All these elements show the property of allotropy and they are polymeric in nature
12. Oxygen and sulphur are the most abundant elements of groupVIA. Oxygen is the most widely distributed of all the elements. Sulphur is widely distributed in nature in both free and combined forms
13. Sulphuric acid is commercially prepared by oxidation of SO2 in the presence of a catalyst to SO3 in a process called Contact Process.
14. H2SO4 is a very strong acid. It acts as a dehydrating agent as well as an oxidizing agent.

CHAPTER

5 The Halogens And The Noble Gases

Animation 5.1[: Halogens](https://38.media.tumblr.com/bbd1077dbe598d3ffa21a2db3b3c2fea/tumblr_inline_micp6hWLDB1qz4rgp.gif)

Source & Credit: [Media](https://38.media.tumblr.com/)

|  |
| --- |
| IN THIS CHAPTER YOU WILL LEARN: |
| 1. The electronic configurations and the occurrence of halogens, the peculiar behaviour of fluorine. 2. The volatility of halides and its explanation in terms of van der Waals forces. 3. The relative reactivities of halogens as oxidizing agents. 4. The properties of hydrogen halides, oxides and oxyacids of halogens. 5. The comparison of thermal stability of hydrides in terms of bond energies. 6. Reaction of chlorine with sodium hydroxide (hot/cold). 7. The preparation and reaction of bleaching powder. 8. The commercial uses of halogens and their compounds as bleaches, refrigerants and aerosols. 9. The electronic configurations, physical properties, inertness and isolation of noble gases from air. 10. The properties of oxides, fluorides and oxyfluorides of xenon. |

5.1 Introduction

The elements fluorine (F), chlorine(Cl), bromine(Br), iodine(I) and astatine(At) are called halogens.These elements are called the halogens from Greek hals, “salt” and gennan, “to form or generate”, because they are literally the salt formers.The halogen elements form a group of very reactive nonmetals and are quite similar to each other in their chemical properties. First four elements are the common elements of the halogen family but astatine is a rare halogen. It is radioactive and its most stable isotope has a half life of 8.3 hrs.

Halogens exist as discrete diatomic molecules in all phases (gas, liquid or solid ).Fluorine and chlorine are gases of pale yellow and greenish yellow colours respectively at room temperature and pressure. Bromine is a liquid of red-brown colour and iodine is a metallic-appearing shiny greyish black solid. The halogens have irritating odours, and they attack the skin. Bromine in particular causes burns that heal slowly.The outer shell of halogens have the configuration ns2 np5 (one electron short of the stable octet of the noble gases). The electronic configurations and the important physical properties of the halogens are given in the Table 5.1

The ionization energy data of the halogens show that the fluorine atom holds its electrons tightly whereas the electrons are least tightly bound in iodine. The trend can be correlated with the sizes of the halogen atoms as shown in the Table 5.1. The electron affinity values of halogens are large and negative, that is why halogens gain electrons readily. They have large, positive standard electrode potentials and their electronegatvities are also fairly high.

Animation 5.2: [Halogens](https://38.media.tumblr.com/bbd1077dbe598d3ffa21a2db3b3c2fea/tumblr_inline_micp6hWLDB1qz4rgp.gif)

Source & Credit: [tumblr](https://38.media.tumblr.com/)

The intermolecular attraction is greater in the larger molecules having greater masses. Due to their large size the van der Waal’s forces in iodine molecules are stronger than in the smaller molecules of the other halogens.

Table 5.1 The Electronic Configurations and the Important Physical Properties of the Halogens.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Properties | Fluorine | Chlorine | Bromine | Iodine |
| Atomic number | 9 | 17 | 35 | 53 |
| Electronic configuration | [He]2s22p5 | [Ne]3s2,3p5 | [Ar]3d10,4s2\4p5 | [Kr]4d10,5s2,5p5 |
| Physical appearance | Pale Yellow gas | Greenish yellow gas | Red-brown liquid | Shiny greyish black solid |
| Ionization energy (kJmole-1) | 1681 | 1251 | 1140 | 1008 |
| Electron affinity, (kjmole-1) | -322 | -349 | -325 | -295 |
| Electronegativity | 4.00 | 3.00 | 2.8 | 2.5 |
| Ionic radius (pm) | 136 | 181 | 196 | 216 |
| Covalent radius (pm) | 72 | 99 | 114 | 133 |
| Melting point (°C) | -220 | -101 | -7.2 | 114 |
| Boiling point (°C) | -188 | -34.6 | 58.8 | 184.4 |
| Density (g/cm3) | 0.00181 | 0.00321 | 3.12 | 4.93 |
| Oxidation states | -1 | - l,+ l,+ 3 , + 5 ,+ 7 | -1,1 ,+ 3 ,+ 5 ,+ 7 | -1 ,1 ,+ 3 ,+ 5 ,+ 7 |
| Bond energy (kJmoie-l)(X-X) | 154.80 | 242.67 | 192.46 | 150.6 |

5.2 OCCURRENCE

Elements with the higher values of electronegativity usually exist as negative ions, and those with the lower values of electronegativity exist as positive ions. Elements with intermediate values of electronegativity are often found as ions or molecules or in free (elemental)form.

None of the halogens is found in free form in nature. The halogens exist in nature primarily in the form of compounds. Their most common state is the halide ions F-, Cl-, Br- and I- . These halides are soluble in water and are found in sea, in salt lakes and as underground beds of salt.

|  |
| --- |
| Fluorine Chlorine |
| Fluorospar CaF2 Halite NaCl  Cryolite Na3AIF6 (Salt beds, brine wells, sea water) Fluoroapatite Ca5(PO4)3F Carnallite KCl. MgCl2.6H2O |
| Bromine Iodine |
| Brine wells, sea water, NaBr, KBr, MgBr2 NaIO3, NaIO4, deposits in Chile brine wells. |

Animation 5.3: [Periodic Table](http://www.excelhero.com/blog/images/periodic_table_xml_excelhero.gif)

Source & Credit: excelhero

5.3 PECULIAR BEHAVIOUR OF FLUORINE

The halogens form a homologous series but fluorine differs from the other halogens in many respects which is due to:

1. Small size of F atom and of F- ion.
2. High first ionization energy and electronegativity.
3. Low dissociation energy of F2 molecule as compared to Cl2 and Br2.
4. Restriction of the valence shell to an octet.
5. Direct combination with inert gases.

Due to the small size of the F atom (or F- ion), there will be a better overlap of orbitals and consequently leads to shorter and stronger bonds with elements other than O, N and itself. Ionic fluorides have higher lattice energies than the other halides and these values are responsible for the insolubility of the fluorides of Ca, Mg, Ba,Sr and lanthanides in water. Due to the low dissociation energy of fluorine molecule, it is highly reactive. The other halogens react slowly under similar conditions. The fluorides are, however, more stable with respect to dissociation into elements.

Due to the restriction of valence shell to an octet, many fluoro compounds show inertness, e.g. CF4 and SF6. Also due to this restriction, fluorine remains restricted to -1 oxidation state. Fluorine is the only element that combines directly with noble gases like Kr, Xe, and Rn forming their fluorides.

5.4 OXIDIZING PROPERTIES

Relative Reactivities of the Halogens as Oxidizing Agents

All the free halogens act as oxidizing agents when they react with metals or nonmetals. The reactant elements acquire positive oxidation state in the compounds formed. On forming ionic compounds with metals, the halogens gain electrons and are converted to negative halide ions.

###### 2Na + Cl2 →2Na Cl+ -

The oxidizing power of halogens decreases with increase in atomic number. Fluorine has the highest oxidizing power and iodine the least. The order of decreasing power as an oxidizing agent is F2 > Cl2 > Br2 > I2

The oxidizing power of halogens depends upon the following factors:

1. Energy of dissociation
2. Electron affinity of atoms
3. Hydration energies of ions
4. Heats of vapourization (for Br2 and I2)

If a halogen has a low energy of dissociation, a high electron affinity and a higher hydration energy of its ions, it will have a high oxidizing power.

Oxidizing power of F2 is higher, because it has low energy of dissociation and higher hydration energy of its ions. Due to the relative strength as oxidizing agents, it is possible for each free halogen to oxidize the ions of other halogens next to it in the family. Standard electrode potential measures oxidizing power.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | F2 | CI2 | Br2 | I2 |
| Standard reduction potential. Eo (V)  X +2e- →22X- | +2.87 | +1.36 | +1.07 | +0.54 |

2

Fluorine can oxidize all the halide ions to molecular halogens. (A reaction will occur if the value of E°is positive) Iodine being a weak oxidizing agent cannot oxidize chloride or bromide ion.

F + 2e2 - →2F-  E =2.87Vo

F +2Cl22Cl - →- →Cl +2eCl +2F2 2 - - E = -1.36VE =+1.51Voo

In the similar way, chlorine will oxidize both bromide and iodide ions, while bromine can oxidize only iodide ion. Cl +2Br2 - →Br +2Cl2 -

###### Br +2l2 - →I +2Br2 -

Fluorine and chlorine can oxidize various coloured dyes to colourless substances, e.g. litmus and universal indicator can be decolourized when exposed to fluorine or chlorine. When used for bleaching, chlorine acts as an oxidizing agent.

5.5 COMPOUNDS OF HALOGENS

5.5.1 Hydrides (hydrogen halides, HX)

All halogens react with hydrogen forming hydrides. The reaction of molecular hydrogen and fluorine is very fast and explosive. With chlorine, molecular hydrogen reacts in the presence of sunlight. Bromine and iodine react with molecular hydrogen at a higher temperature. The reaction with iodine is very slow and reversible. Direct combination is used as a preparative method only for HCl and HBr. Hydrogen fluoride and hydrogen chloride can also be obtained by the action of concentrated sulphuric acid on fluorides and chlorides, but analogous reactions with bromides and iodides result in partial oxidation of the hydrogen halide to the free halogen.

2NaCl(s)+H SO (conc.)2 4 →Na SO (aq)+2HCl(g)2 4

2NaBr(s)+2H SO (conc.2 4 )→Na SO (aq)+Br (l)+SO (g)+2H O2 4 2 2 2

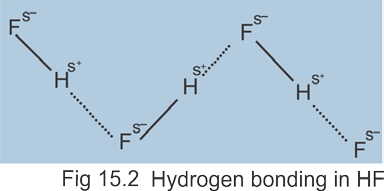
Properties of Hydrogen Halides

HF is a colourless volatile liquid whereas other hydrogen halides (HCI, HBr, HI) are colourless gases at room temperature.

They give fumes in moist air. They are strong irritants.

Hydrogen fluoride attacks glass and has found applications as a nonaqueous solvent. It can be handled in teflon ( polytetrafluoroethylene) containers or if absolutely dry, in copper or stainless- steel vessels kept under vacuum. Pure liquid HF is strongly hydrogen bonded and is a viscous liquid. Its viscosity is less than that of water due to the absence of a three dimensional network of H-bonds which occur in H2O.

Hydrogen bonding is also responsible for the association of HF molecules in the vapour phase. Various test results indicate that gaseous HF consists of an equilibrium mixture of monomers and cyclic hexamers, Fig.5.2.



##### 6HF(HF)6

Chain polymers may also exist under certain conditions. Chains and rings of HF are of various sizes, some of these persist in the vapour phase as well. Some of the physical properties of hydrogen halides are given in Table 5.2.

Table 5.2 Some Physical Properties of Hydrogen Halides

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Property | HF | HCI | HBr | HI |
| Melting points(°C) | -83.8 | -114.2 | -86.9 | -50.8 |
| Boiling points (°C) | 19.5 | -85.0 | -66.7 | -35.3 |
| Heat of fusion at M.P. (kJ/mol) | 4.58 | 1.99 | 2.41 | 2.87 |
| Heat of vaporization at B.P. (kJ/mol) | 30.3 | 16.2 | 17.6 | 19.7 |
| Heat of formation /kJ mol-1(Hf) | -270.0 | -92.0 | -36.0 | +26.0 |
| Bond energy (kJ /mol-1) | 566 | 431 | 366 | 299 |
| H-X Bond length (pm) | 92 | 128 | 141 | 160 |
| Dissociation into elements at 1000°C (%) | 0 | 0.014 | 0.5 | 33 |
| Dipole moment (Debye) | 1.8 | 1.1 | 0.8 | 0.4 |

Melting points, boiling points, heats of fusion and heats of vapourization generally increase regularly from HCl to HI. The HF has much higher values for these properties due to hydrogen bonding. A very high boiling point of hydrogen fluoride is a major evidence of the presence of hydrogen bonding among its molecules.The relative volatility of HCl, HBr and HI reflects the strengthening of the van der Waal’s forces due to increasing size of halogens.

Since the dipole moment of molecules decreases from HCI to HI, probably dipole-induced dipole forces play an important role in the intermolecular binding of the heavier HX molecules.

The strength of the hydrogen halogen bond is very high in HF. It decreases with increasing size of the halogen atom. The bond strength is reflected in the case of dissociation of hydrogen halides at elevated temperatures.

HF, HCl, HBr and HI act as reducing agents in the following order:

#### HF<HCl<HBr<HI

Hydrogen iodide is a strong reducing agent. In redox reactions the hydrogen halides are oxidized to elemental halogens, e.g.

##### 2HI+SI +H S2 2

In water, hydrogen halides give hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. Hydrofluoric acid is a weak acid due to limited ionization. The other three acids are very strong acids. The acidic strength increases in the order. HF<HCl<HBr<HI

5.5.2 Oxides of Halogens

The halogens do not react directly with oxygen. With the help of some indirect methods, following oxides of group VIIA elements have been made.

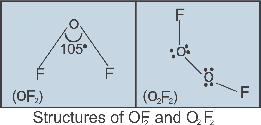
Table 5.3 Oxides of Halogens

|  |  |  |  |
| --- | --- | --- | --- |
| FLUORINE | CHLORINE | BROMINE | IODINE |
| Oxygen difluoride, OF2 | Dichlorine monoxide, CI2O | Brominemonoxide,Br2O | Iodine tetraoxide, I2O4 |
| Dioxygen difluoride,O2F2 | Chlorine dioxide, CIO2 | Bromine dioxide,BrO2 | Iodine iodate, I4O9 |
| Trioxygen difluoride | Chorine hexaoxide, CI2O6  Chlorine heptaoxide.Cl O | Bromine trioxide,  BrO ,(Br O ) | Iodine pentoxide,I2O5 |

2 7 3 3 8

Oxides of Fluorine

Trioxygen Difluoride, O3F2

This oxide can be prepared when a mixture of fluorine and oxygen is subjected to electric discharge. At 363 °C, it is a dark red viscous liquid but turns to reddish brown solid at 350 °C. On decomposition it gives oxygen and other oxide of fluorine.

### 2OF3 2 →2O F+O2 2 2

O3F2 reacts with F2 in the presence of electric discharge to produce O2F2

#### 2OF+F3 2 2 →3O F2 2

OXIDES OF CHLORINE

The oxides of chlorine are generally unstable. It is not possible to synthesize them by direct combination of the elements Cl2 and O2. They have extensive industrial use as commercial bleaching agents for wood, paper- pulp and for water treatment.

1. Chlorine dioxide, CIO2

It is a pale yellow gas. It is prepared by reducing NaCIO3, with NaCl or SO2 or CH3OH in strongly acidic solution.

##### 2CIO-3+2CI +4H- + →2CIO +CI +2H O2 2 2

CIO2 can also be prepared by the action of concentrated H2SO4 on KCIO3,. This reaction is violent. To control the reaction oxalic acid should be added.

2KCIO +H C O +H SO3 2 2 4 2 4 →K SO +2H O+2CO +2CIO2 4 2 2 2

CIO2 explodes into Cl2 and O2 on warming. It is soluble in water and is stable in dark. It decomposes slowly in H2O to HCI and HCIO3. It is a paramagnetic substance. It is used as an antiseptic, for purification of water and to bleach cellulose material.

2. Chlorine Heptaoxide, CI2O7

CI2O7 is an anhydride of perchloric acid (HCIO4). It can be obtained at -10oC by dehydration of HCIO4 with P2O5.

##### 2HCIO +P O -10oC Cl O +2HPO

4 2 5 → 2 7 3

OXIDES OF BROMINE

Oxides of bromine are dark volatile liquids with low thermal stability.

Bromine Monoxide Br2O

It can be prepared by the reaction of bromine vapours with mercuric

oxide. HgO+2Br 50oC HgBr +Br O

2 → 2 2

Br2O can also be prepared by treating the suspension of mercuric oxide in CCI4 with bromine.It is stable in dark in CCI4 at -20°C. It has oxidizing properties.

OXIDES OF IODINE

Out of all the oxides of iodine only iodine pentaoxide (I2O5) is important. The other compounds, I2O4 and I2O9 are salt like and are considered as iodine-iodates.

Iodine Pentoxide I2O5

It can be prepared by heating iodic acid at 240°C.

##### 2HIO3 →240oC I O +H O2 5 2

It is a white crystalline solid, stable up to 300°C. It has a polymeric structure. It is insoluble in organic solvents. It forms iodic acid with water.

I O +H O2 5 2 →2HIO3

It reacts with H2S, HCI and CO as an oxidizing agent. It is used for the quantitative analysis of CO.

##### 5CO+I O2 5 →I 5CO2+ 2

5.5.3 Reactions of Chlorine with Cold and Hot NaOH

The reactions of chlorine with cold and hot NaOH are examples of

“Disproportionation reactions”.

A reaction in which a species (molecule, atom or ion)is simultaneously oxidized and reduced, is called a “disproportionation reaction”. In cold (15°C) state chlorine will react with NaOH (aq) to form hypochlorite and a halide.

2NaOH(aq)+Cl (g2 )→15oC NaCl(aq)+NaClO(aq)+H O(aq)2 (a)

Sod.hypochlorite

The reaction is a disproportionation reaction, because the zero oxidation state of chlorine atom in Cl2, is converted to -1 in chloride and +1 in hypochlorite.

Sodium hypochlorite which is produced in cold state in the above reaction, decomposes forming sodium chloride and sodium chlorate at 70°C.

#### 3NaClO(aq)→70oC 2NaCl(aq)+NaClO (aq3 ) (b)

The reaction (b) involves the disproportionation of hypochlorite ion. To balance overall reaction in hot state, multiply equation (a) with 3 and then add (a) and (b).

6NaOH+3Cl2 →3NaCl+3NaClO+3H O 2

##### 3NaClO→2NaCl+NaClO3 6NaOH(aq)+3Cl (g2 )→5NaCl(aq)+NaClO (aq)+3H O3 2

The above two reactions (a) and (b) show that chlorine atoms are both reduced and oxidized.

5.5.4 Oxyacids

An important class of the compounds of the halogens is the oxygen containing acids and their salts.

No oxygen containing stable acid of fluorine is known (HOF is prepared recently, but it is highly unstable). Other halogens form oxyacids though most of them cannot be isolated in pure form and are stable only in aqueous solutions in the form of their salts.

A system of nomenclature for these acids and their salts is based on the oxidation state of the halogen atom. According to this system, characteristic prefixes and suffixes are attached to a stem that is derived from the name of the central nonmetal (halogen) atom. The system is as follows:-

1. Some common acid is orbitrarily called the \_\_\_\_\_ ic acid (e.g. HCIO3 is designated as chloric acid). The name of a salt of this acid ends in \_\_\_\_\_ ate.
2. An acid whose parent atom has an oxidation state next lower than the \_\_\_\_\_ ic acid (one less oxygen atom) is called ous acid and the name of the salt of this acid ends in \_\_\_\_\_ ite. For example, chlorous acid (HCIO2).
3. The acid in which the oxidation state of the parent atom is higher than it is in the \_\_\_\_\_ ic acid (one more oxygen atom) is called per\_\_\_\_\_ ic acid. A salt of this acid is a per \_\_\_\_\_ ate salt. For example, perchloric acid (HCIO4).
4. An acid in which the oxidation state of the parent atom is lower than it is in the\_\_\_ ous acid is called hypo \_\_\_\_\_ ous acid and a salt of this acid is a hypo \_\_\_\_\_ ite salt. For example, hypochlorous acid (HCIO).
5. The root of the name of the acid or the salt indicates the parent atom.

Table 5.4 shows the oxyacids of halogens (other than fluorine)

###### Table 5.4 Oxyacids of Halogens

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Oxidation state | Formula of the oxyacids of halogens | | | General names of | |
| of halogen | Chlorine | Bromine | Iodine | Oxyacids | Salts of oxyacids |
| +1 | HCIO | HBrO | HIO | Hypohalous acid | Hypo\_\_ite |
| +3 | HCIO2 | ------ | ------ | Halous acid | \_\_\_\_ite |
| +5 | HCIO3 | HBrO3 | HIO3 | Halic acid | \_\_\_\_ ate |
| +7 | HCIO4 |  | HIO4, H5IO6 | Perhalic acid | Per\_\_\_\_ ate |

It is evident from the above given formulas of the oxy acids that the halogen serves as a central atom to which one or more oxygen atoms are covlently bonded. These bonds are polar in character due to the electronegativity difference between halogen and oxygen.

The increase in the oxidation state of the halogen from +1 to + 7 is accompanied by :

1. an increase in the thermal stability of the acid
2. the decrease in oxidizing power of the acid
3. the increase in acidic strength of the acid

The more the number of oxygen atoms in the series of oxyacids of a halogen, the greater is the thermal stability.

The acid strength increases with the increase in the number of oxygen atoms. As the oxidation state of the halogen increases, the bonding electrons are shifted away from the Hatom and the tendency of the molecule to lose a proton increases. This accounts for the change of strength of oxyacids.

The oxyacids of halogens show their strength in the order given below:

HXO >HXO >HXO >HXO4 3 2

An oxyacid molecule contains hydrogen linked to the halogen through an oxygen atom.

The oxyacids of chlorine are stronger than the corresponding oxyacids of bromine which are, in turn, stronger than the corresponding oxyacids of iodine. It is due to decrease in the electronegativity and increase in the size of the halogen.

We will discuss perchloric acid (HClO4) only at this stage.

PERCHLORIC ACID (HCIO4)

Perchloric acid (HClO4)is commonly obtained in aqueous solution. Pure anhydrous compound can by prepared by distilling a mixture of potassium perchlorate (KCIO4) and conc. H2SO4 under reduced pressure.

##### KClO +H SO (conc.)4 2 4 →reduced pressureÄ KHSO (s)+HClO (l)4 4

Perchloric acid is a colourless hygroscopic liquid. At normal pressure it freezes at -112°C and boils with decomposition at 90° C.

In the cold and dilute state,perchloric acid is a very weak oxidizing agent but when hot and concentrated its oxidizing power is enhanced. Dissolving power of perchloric acid is enhanced due to its oxidizing strength. Perchloric acid is the strongest of all the acids in an aqueous medium.

Pure perchloric acid decomposes explosively when heated. That is why it is stored and used as 67% solution in water. Perchloric acid reacts with organic substances violently.

Due to its oxidizing effect, acidic strength and solubility of its salts, it is considered as a valuable analytical reagent.

Animation 5.4: [Perchloric acid](http://bouman.chem.georgetown.edu/S02/lect17/clo4.gif)

Source & Credit: [bouman](http://bouman.chem.georgetown.edu/S02/lect17/clo4.gif)

5.5.5 Bleaching Powder, (Ca(OCl)Cl)

Bleaching powder can be manufactured by the action of chlorine on dry slaked lime using any one of the following methods:

(a) Hasenclever’s method (old method) (b) Beckmann’s method (modern method) The reaction in both the cases will be:

Ca(OH) +Cl2 2 →Ca(OCl)Cl+H O2

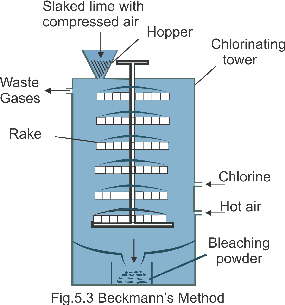
Slaked lime Bleaching powder

1. Hasenclever’s Method

The apparatus used in this method consists of 4 to 8 iron cylinders placed one above the other horizontally. They are interconnected and provided with stirrers. The slaked lime is added in through a hopper in the upper cylinder and is transported from one cylinder to the other with rotating stirrers. Chlorine introduced into the lowest cylinder rises up and reacts with slaked lime to form bleaching powder, which is collected through the outlet in the lowest cylinder.

1. Beckmann’s Method

In this method a cast iron tower with eight horizontal shelves is used. In each shelf there is a rotating rake.Powdered slaked lime is introduced through hopper at the top with compressed air. A mixture of hot air and chlorine are introduced from the base of the tower. The slaked lime is pushed down by the rotating rakes while chlorine rises up. Reaction between slaked lime and chlorine produces bleaching powder which is collected at the bottom of the tower, Fig.5.3



The apparatus works on the countercurrent principle. Thus maximum reaction of slaked lime and chlorine is brought about with very little loss of chorine. Bleaching powder should always be packed in air tight containers to avoid the loss of chlorine.

Bleaching powder is a yellowish white powder with strong smell of chlorine. Some of its chemical properties are given below. 1. It is an oxidizing agent. This property is due to the generation of hypochlorite ion (OCl) in water.

CaOCl2 H O2 Ca +Cl +ClO+2 - -

2. With dilute acid it gives hypochlorous acid.

###### 2CaOCl +dil.H SO2 2 4 →CaSO +CaCl +2HClO4 2

1. If excess of an acid (weak or strong) is added to bleaching powder, chlorine is given out.

CaOCl +H SO2 2 4 →CaSO +H O+Cl4 2 2 ↑

(excess)

The amount of chlorine thus set free is called “available chlorine”. The activity of bleaching powder is measured in terms of available chlorine. The average percentage of available chlorine in bleaching powder is 35-40 percent. The bleaching action of bleaching powder is due to its oxidative character.

1. It oxidizes HC1, HBr and HI giving the corresponding halogens.

###### CaOCl +2HCl2 →CaCl +H O+Cl2 2 2

1. It oxidizes ammonia to nitrogen

3CaOCl +2NH2 3 →3CaCl +3H O+N2 2 2

1. Calcium hypochlorite reacts with carbon dioxide to form calcium carbonate and release chlorine.

CaOCl +CO2 2 →CaCO +Cl3 2

Uses

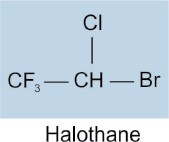
Bleaching powder is used:

1. for the laboratory preparation of chlorine and oxygen. It is also used in the manufacture of chloroform.
2. as a disinfectant and in the sterilization of water.
3. for making unshrinkable wool.
4. for bleaching cotton, linen and paper pulp. (Delicate fabrics like wool, silk etc. cannot bebleached with it as these could be damaged by chlorine).

5.6 COMMERCIAL USES OF HALOGEN AND THEIR

COMPOUNDS

Fluorine is used for the preparation of freons. Freon is the commercial name of low molecular mass fluorochlorocarbons, CCl2F2, CClF3. These are being used as refrigerants and aerosol propellants.

Fluorine is used to prepare Teflon (-CF2— CF2-)n. It is a polymerized tetrafluoro ethylene compound. It is a valuable plastic which resists the action of oxidants, acids and alkalies.Corrosionproof parts of machinery are made of it.It is used for coating the electrical wiring.Teflon is also used as a non-stick coating for cooking pans.Halothane is used as an anaesthetic.

Fluorides in toothpastes build a protective coating on teeth. Chlorine is used in the manufacture of bleaching powder.It is used as a disinfectant in swimming pools and water treatment plants. A number of antiseptics, insecticides, weedkillers and herbicides are manufactured from chlorine.It is also used in the manufacture of hydrochloric acid, which is the cheapest industrial acid.Chlorine is also used in the manufacture of polyvinyl chloride (PVC) plastics. Chloroform and carbon tetrachloride are prepared from chlorine which are used as solvents.

Ethylene dibromide (C2H4Br2) is added to leaded gasoline to save the engine from lead oxide and lead sulphate deposits. Bromine is also used as fungicide. Silver bromide is used in photography. The major applications of iodine are in pharmaceutical industry.It is used as disinfectant and germicide.Tincture of iodine and iodex are popular preparations of iodine.

Diet with insufficient iodide ions leads to an enlargement of the thyroid (Goiter). To ensure the presence of iodide ion in the diet, sodium or potassium iodide is added to the common salt which is known as iodized salt.

5.7 NOBLE GASES

5.7.1 Introduction

The elements helium(He), neon (Ne), argon(Ar), krypton (Kr), xenon (Xe) and radon (Rn) are placed in the zero group or group VIIIA of the periodic table. All the elements of this group are colourless and odourless monoatomic gases which can be liquefied and solidified. These are called noble gases or sometime known as rare gases. The noble gases occur as minor constituents of the atmosphere (about 1%). The electronic configurations and some physical properties of noble gases are given in the Table 5.5.

Table 5.5 Electronic Configurations and Physical Properties of Noble Gases

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Property | He | Ne | Ar | Kr | Xe | Rn |
| Atomic number | 2 | 10 | 18 | 36 | 54 | 86 |
| Electronic configurations | Is2 | (He)2s2 2p6 | (Ne)3s2 3p6 | (Ar)3d10 4s2 4p6 | (Kr)4d10 5s2 5p6 | (Xe)5d10 6s2 6p6 |
| Ionization energy (kJmol-1) | 2372 | 2081 | 1521 | 1351 | 1170 | 1037 |
| Atomic radius (pm) | 40 | 70 | 94 | 109 | 130 | 140 |
| Melting points (oC) | -272 | -249 | -189 | -157 | -112 | -71 |
| Boiling points (oC) | -269 | -246 | -186 | -153 | -108 | -61 |
| Water solubility (ml/lit) at 20oC | 13.8 | 14.7 | 37.9 | 73.00 | 110.9 | ---- |
| Heat of vapourisation (kJmol-1) | 0.08 | 1.77 | 6.5 | 9.7 | 13.7 | 18.0 |

The noble gases are isolated from air, either by fractional distillation or by some chemical method. The principal commercial source of Ne, Ar, Kr and Xe is air. Helium is present on earth as a result of radioactive decay. After hydrogen, it is the second most abundant element in the universe. a-Particles are doubly ionized helium atoms He2+. It is simple and economical to isolate the helium gas from certain natural gases by liquefaction method.

Argon is a colourless and odourless gas. It is very inert and not known to form any true chemical compound. It is obtained as a by-product during the lique faction of air.

Neon is 1/65000th part of the atmosphere and it is also isolated during liquefaction of air. In a discharge tube, neon glows reddish (of all the noble gases, the discharge of neon is the most intense at ordinary voltage and current). Liquid neon has over 40 times more refrigeration capacity than liquid helium.

Traces of krypton are present in air. It is a colourless, odourless and fairly expensive gas. It is characterized by its brilliant green and orange spectral lines. Its compound krypton difluoride (KrF2) can be prepared by various methods.

Xenon is present in the atmosphere to a very small extent (0.08 ppm). It is obtained as a by-product during the fractional liquefaction of air. Xenon is available commercially in cylinders at high pressure. It reacts with fluorine but not with water. However it is slightly soluble in water to the extent of about

110 ml/lit at 20°C.

Radon is the a-decay product of the radium. Radon is present to a very small extent in the atmosphere and it could be obtained as a by-product from the liquefaction of air. However, the small quantities of this gas which are usually needed can be collected from the radioactive decay of radium isotopes.

##### 226 Ra 222 Rn+ He4

88 →86 X

The noble gases have valence shells which are closed octets (except He). Due to closed shells their ionization energy values are very high. They have low boiling points. The boiling point of helium is the lowest of any known substance. Their boiling points increase with increasing atomic number down the group.

The very low values of melting and boiling points and low heats of vapourization show that noble gases have weak forces of attraction between their atoms. As there are no ordinary electron pair interaction, these weak forces must be of the van derWaals type.

The solubility of the noble gases in water increases with increasing atomic number. This is because the bigger atoms are more readily polarized by water molecules.

###### 5.7.2 Compounds of Xenon

Xenon reacts directly with fluorine only. The known oxidation state of Xenon in its compounds range from +2 to +8. These compounds are stable and can be obtained in large quantities.

Some important compounds of Xenon are give in the Table 5.6

Table 5.6 Compounds of Xenon

|  |  |  |  |
| --- | --- | --- | --- |
| Oxidation state of xenon | Compound | Physical form | Melting Point (°C) |
| +2 | XeF2 | Colourless crystals | 140 |
| +4 | Xe F4  XeOF2 | Colourless crystals  Colourless crystals | 114  90 |
| +6 | XeF6 XeOF4 | Colourless crystals Colourless liquid | 48 -28 |
| +8 | XeO3  XeO4 | Colourless crystals Colourless gas | 25 (Explodes)  -39.9 (Explodes on warming) |

Animation 5.5: [flroride](http://waterus.com/images/under_sink_graphic_3.gif)

Source & Credit: [waterus](http://waterus.com/)

5.7.3 Fluorides of Xenon

Three known fluorides of Xenon are XeF2, XeF4 and XeF6.

XeF2 can be prepared by direct interaction of the elements.The compound formed should be removed immediately from the reaction zone, otherwise further reaction with F2 will give XeF4. The reaction is completed in about 8 hours. XeF2 is a crystalline solid. It is stored in nickel vessels. XeF2 is a mild fluorinating agent.

XeF4 can be prepared by heating a mixture of Xe and F2 in 1:5 ratio in a nickel container under 6 atmospheric pressure for a few hours. It can be stored in nickel vessels. Its properties are similar to that of XeF2 but it is a strong fluorinating agent.

XeF6 requires more severe conditions. Xe and F2 are taken in 3:20 ratio in a stainless steel vessel and heated to 300°C at 50 atmospheric pressure. More than 95% conversion to XeF6 takes place. XeF6 is a crystalline solid.

It is colourless in the solid state but yellow in liquid and gaseous forms.

Xe+F2 →XeF2

XeF+F2 2 →XeF4

XeF+F4 2 →XeF6

Animation 5.6[: flroride1](http://waterus.com/images/counter_top_graphic_3.gif)

Source & Credit: [waterus](http://waterus.com/)

Chemical Reactions

Fluorides of xenon can be reduced with hydrogen at 400°C, giving xenon and hydrofluoric acid.

XeF+H2 2 →Xe+2HF

XeF+2H4 2 →Xe+4HF

XeF+3H6 2 →Xe+6HF

Xenon tetra-fluoride is a good fluorinating agent and can be used to prepare metal fluorides as follows:

##### XeF+2Hg4 →Xe+2HgF2

Reaction occurs with explosion when XeF4 is brought in contact with liquid ammonia.

3XeF+4NH4 3 →3Xe+12HF+2N2

Hydrolysis of XeF6 with small amount of water gives XeOF4

###### XeF +H O6 2 →XeOF +2HF4

5.7.4 Xenon Oxyfluorides

Xenon oxytetrafluoride, XeOF4 is also formed by a rapid reaction of XeF6 with silica (quartz).

##### 2XeF +SiO6 2 →2XeOF +SiF4 4

XeOF4 is a colourless volatile liquid. It can be kept in nickel vessel.It reacts with water to give XeO3.

##### XeOF+2H O4 2 →XeO +4HF3

Xenon oxydifluoride, XeOF2 is obtained when xenon reacts with oxygen difluoride in an electric discharge.

##### Xe+FO2 →XeOF2

5.7.5 Oxides of Xenon

There are two oxides of xenon

1. Xenon trioxide
2. Xenon tetraoxide

Animation 5.7: [Oxidized](http://1.bp.blogspot.com/-AZQ64-s3EqU/U4dRLIHMhyI/AAAAAAAAAWM/vMZLqHfwonA/s1600/chemical_physical_reactions_12.gif)

1. Xenon Trioxide XeO3 Source & Credit: [bp.blogspot](http://1.bp.blogspot.com/)

Xenon trioxide can be obtained when XeF6 is hydrolysed slowly.

###### XeF+3H O6 2 →XeO +6HF3

It is a crystalline solid. It explodes at very low temperature. It is weakly acidic and its aqueous solution is almost non-conductor.

2. Xenon Tetraoxide XeO4

It is obtained by the addition of barium or sodium perxenate to conc.H2SO4

Ba XeO +2H SO2 6 2 4 →XeO +2BaSO +2H O4 4 2

Na XeO +2H O4 6 2 4 →XeO +2Na SO +2H O4 2 4 2

5.7.6 Applications of the Noble Gases

1. Helium is used in weather balloons, in welding and in traffic signal light.
2. A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.
3. Helium is used as a cooling medium for nuclear reactors.
4. Neon is largely used in making neon advertising signs, in high voltage indicators and TV tubes.
5. Neon and helium arc is used in making glass lasers.
6. Argon is used in electric light bulbs, in fluorescent tubes, in radio tubes, and in Geiger counters (used to detect radioactivity).
7. Argon is also used for arc welding and cutting.
8. Krypton is used to fill fluorescent tubes and in flash lamps for high speed photography.
9. Xenon is used in bactericidal lamps.
10. Radon being radioactive is used in radiotherapy for cancer and for earth quake prediction.

KEY POINTS

1. The halogens are very reactive. Intermolecular forces in halogens increase down the group, fluorine is a gas but iodine is solid.
2. They form ionic compounds with s-block metals, covalent compounds with p-block elements and complex ions with d-block metals. Fluorides are usually ionic.
3. They show oxidation states -1, +1, +3, +5, + 7 but fluorine shows the oxidation state of -1 only.
4. Oxidizing power of halogens decreases down the group in the following order:

F2 Cl2 Br2 I2

V

V

V

1. Reducing power of halide ions decreases from I- to Br- Chloride and fluoride ions are not reductants.
2. Chlorine, bromine and iodine form their respective oxides and oxyacids.
3. Halogens and their compounds are used for bleaching, refrigeration and as aerosols, etc.
4. Noble gases are placed in zero (VIIIA) group of periodic table.
5. They have valence shells which are closed octets (except helium).
6. Very low values of melting and boiling points show that there are very weak forces of attraction between their atoms.
7. Oxides, fluorides and oxyfluorides of xenon can be prepared.
8. Noble gases have multi-dimensional uses.

EXERCISE

Q.l Fill in the blanks.

1. The halogen with the highest electronegativity is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.
2. HI is \_\_\_\_\_\_\_\_\_ agent.
3. The only halogen acid which is not a strong acid is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ .
4. Tincture of\_\_\_\_\_\_\_\_\_\_\_\_\_\_ is a common antiseptic.
5. The halogen with the lowest melting and boiling points is \_\_\_\_\_\_\_\_\_\_.
6. Bleaching powder is prepared from \_\_\_\_\_\_\_\_\_ and \_\_\_\_\_\_\_\_\_\_\_\_.
7. \_\_\_\_\_\_\_\_\_\_\_\_\_ is the halogen which causes burns on the skin which heal slowly.
8. \_\_\_\_\_\_\_\_\_\_\_\_\_is used for making unshrinkable wool.
9. A mixture of \_\_\_\_\_\_\_\_\_\_\_and \_\_\_\_\_\_\_\_\_\_\_\_ is used for breathing by the sea divers.
10. Noble gas used to fill fluorescent tubes is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

Q.2 Indicate True or False.

1. HF is used for etching glass.
2. HI is weaker reducing agent as compared to HF(iii) Bleaching powder is completely soluble in water.
3. The formula of perchloric acid is HCIO2.
4. On warming, aqueous KOCl disproportionates as follows.
5. a-particles emitted by radioactive elements are ions of radon.
6. Radon is the only one of the noble gases that is radioactive.
7. The molecules of the noble gases are all monoatomic.
8. Argon is used to fill electric bulbs.
9. The noble gas which is present in the largest amount in atmosphere is krypton.

Q 3. Multiple choice questions. Encircle the correct answer.

1. Which of the following hydrogen halide is the weakest acid in solution?
   1. HF (b) HBr (c) HI (d) HCI
2. Chlorine heptaoxide (Cl2O7) reacts with water to form:
   1. Hypochlorous acid (b) Chloric acid

(c) Perchloric acid (d) Chlorine and oxygen

1. Hydrogen bond is the strongest between the molecules of:
   1. HF (b) HCl (c) HBr (d) HI
2. Which halogen will react spontaneously with Au(s) to produce Au3+?
   1. Br2 (b)F2 (c) I2 (d) Cl2
3. The anhydride of HCIO4 is :
   1. CIO3 (b) ClO2 (c) Cl2O5 (d) CI2O7
4. Bleaching powder may be poduced by passing chlorine over:
   1. calcium carbonate (b) hydrated calcium sulphate

(c) anhydrous calcium sulphate (d) calcium hydroxide

(e) magnesium hydroxide

(vii)Which is the strongest acid?

(a) HCIO (b) HClO2 ( c ) HClO3 (d) HClO4

1. Which halogen occurs naturally in a positive oxidation state?

(a) Fluorine (b) Chlorine (c) Bromine (d) Iodine

1. An element that has a high ionization energy and tends to be chemically inactive would most likely to be:

(a) an alkali metal (b) a transition element

(c) a noble gas (d) a halogen

1. Which of the following represents the correct electronic configuration of the outermost energy level of an element of zero (VIIIA) group in the ground state.

(a) s2p2 (b) s2p4 (c) s2p5 (d) s2p6

* 1. What is bleaching powder? How it is prepared commercially? Give its uses.
  2. (a) Discuss the oxides of chlorine.

(b) What are disproportionation reactions? Explain your answer with an example.

Q.6 Discuss the system of nomenclature used for oxyacid of halogens. Support your answer with examples.

Q.7 (a) How the halogen acids are ionized in water?

(b) Why HF is weaker acid than HCl?

Q.8 In the following sets, arrange the substances in order of the property indicated. Give reasons. (a) Increasing acidic character

HCIO, HCIO2, HClO3, HClO4

(b) Increasing oxidizing power

F2, Cl2, Br2, I2

Q.9 What happens when bleaching powder reacts with the following reagents dil. H2SO4,excess of conc. H2SO4, NH3, HI and CO2.

Q.10 Discuss the various commercial uses of halogens and their compounds.

1. .11 What are noble gases? Explain their inertness on the basis of their electronic configuration.

Q.12 Write notes on the followings. (i) Oxyfluorides of xenon.

(ii) Applications of noble gases.

Q.13 Short questions.

1. What is “Iodized Salt”?
2. What are Freons and Teflon?
3. Arrange the following ions in order of increasing size:

F-, CI-, I-, Br-

1. Why iodine has metallic luster?
2. Which halogen sublimes to violet vapours?
3. Which halogen is used as an antiseptic?
4. Which halogen is used in water treatment to kill becteria ?
5. Name the gas, which is used for earthquake prediction.
6. Name the gas, which is used in bactericidal lamps.

# CHAPTER 6 Transition Elements

[Animation 6.1 : Complexanima](http://www.ciceco.ua.pt/index.php?tabela=pessoaldetail&menu=218&user=478)

Source and credit : [Ciceco](http://www.ciceco.ua.pt/)

In This Chapter You Will Learn:

1. The definition and classification of transition elements.
2. The electronic configurations and the general characteristics like colour binding energies, etc.
3. The definition of a complex compound and the related terms like ligand, coordination number etc.
4. The nomenclature and the geometrical shapes of simple complex compounds.
5. A brief description of the manufacture of wrought iron and steel from iron ore.
6. How corrosion is caused and the ways to prevent it.
7. The important methods of preparation of potassium chromate, potassium dichromate, potassium permanganate and their properties.

## 6.1 INTRODUCTION

Transition elements may be defined as those elements which have partially filled d or f-subshells in atomic state or in any of their commonly occurring oxidation states.

Table 6.1 Electronic configuratios of three series of d-block elements

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 3d-block elements | | 4d-block elements | | 5d-block elements | |
| Elements | Electronic configuration | Elements | Electronic configuration | Elements | Electronic configuration |
| Sc (21) | [Ar] 3d1 4s2 | Y (39) | [Kr]4d1 5s2 | La (57) | [Xe] 5d1 6s2 |
| Ti (22) | [Ar] 3d2 4s2 | Zr (40) | [Kr]4d2 5s2 | Hf (72) | [Xe] 4f14 5d2 6s2 |
| V (23) | [Ar] 3d3 4s2 | Nb (41) | [Kr]4d4 5s1 | Ta (73) | [Xe] 4f14 5d3 6s2 |
| Cr (24) | [Ar] 3d5 4s1 | Mo (42) | [Kr]4d5 5s1 | W (74) | [Xe] 4f14 5d4 6s2 |
| Mn (25) | [Ar] 3d5 4s2 | Te (43) | [Kr]4d5 5s2 | Re (75) | [Xe] 4f14 5d5 6s2 |
| Fe (26) | [Ar] 3d6 4s2 | Ru (44) | [Kr]4d7 5s1 | Os (76) | [Xe] 4f14 5d6 6s2 |
| Co (27) | [Ar] 3d7 4s2 | Rh (45) | [Kr]4d8 5s1 | Ir (77) | [Xe] 4f14 5d7 6s2 |
| Ni (28) | [Ar] 3d8 4s2 | Pd (46) | [Kr]4d10 | Pt (78) | [Xe] 4f14 5d9 6s1 |
| Cu (29) | [Ar] 3d10 4s1 | Ag (47) | [Kr]4d10 5s1 | Au (79) | [Xe] 4f14 5d10 6s1 |
| Zn (30) | [Ar] 3d10 4s2 | Cd (48) | [Kr]4d10 5s2 | Hg (80) | [Xe] 4f14 5d10 6s2 |

The d-block and the f-block elements are called transition elements because they are located between the s and p-block elements and their properties are in transition between the metallic elements of the s-block and nonmetallic elements of the p-block.The electronic configurations of three series of d-block elements are given in Table 6.1.

Table 6.2 Detailed electronic configurations of the valence shell of first series of transition elements

|  |  |  |
| --- | --- | --- |
|  | 3d | 4s |
| Sc(Ar) | |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | |  | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | | |
| Ti (Ar) |
| V (Ar) |
| Cr (Ar) |
| Mn (Ar) |
| Fe (Ar) |
| Co (Ar) |
| Ni (Ar) |
| Cu (Ar) |
| Zn (Ar) |

The detailed electronic configurations of the valence shell of the first transition series is shown in Table 6.2. You will notice that in chromium one electron from s-subshell has been used to half fill d-subshell. Similarly, in copper, one electron from s-subshell has gone to d-subshell to fill it completely. This appears to be due to a certain measure of stability associated with a half-filled d5 shell and a full d10 shell.

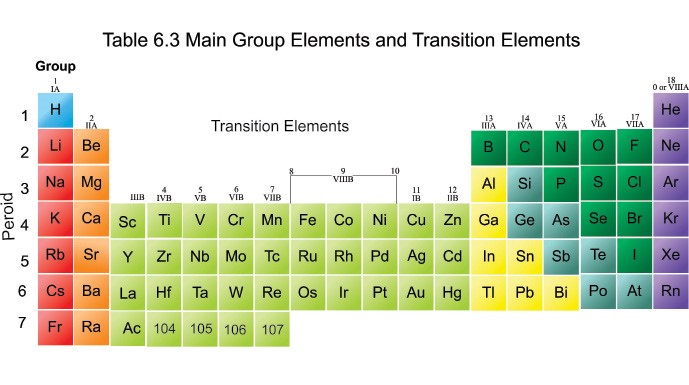
6.1.1 Typical And Non-Typical Transition Elements

Group IIB elements (Zn, Cd and Hg) do not have a partially filled d-subshell either as elements or in any of their ionic state. Neither do they show typical properties of transition elements to any appreciable extent (except complex formation). Similarly, IIIB (Sc, Y and La) is another group of elements which do not show many of the properties associated with typical transition elements.

They are transition elements by definition, as there is one electron in the d-subshell of each atom. In compounds they mostly occur as the tripositive ions, having no d-electron (the atom having lost its only one d-electron), hence they do not exhibit properties of transition elements and behave like main group elements.

In order to maintain a rational classification, the elements of group IIB and group IIIB are referred to as non-typical transition elements and the elements in the remaining transition series are called typical transition elements, Table 6.3.

We treat the coinage metals Cu, Ag and Au as transition metals, since Cu2+ has a 3d9 configuration, Ag2+a 4d9 and Au3+ a 5d8configuration. f- Block elements i.e. Lanthanides and Actinides are also called inner transition metals, whereas d-block elements are called outer transition metals.



## 6.2 PROPERTIES OF TRANSITION ELEMENTS

Because of a similar electronic configuration, the d-block elements closely resemble one another in their physical and chemical properties. Some of the points of their resemblance are given below.

1. They are all metals in true sense, some of which play important role in industry, e.g. Ti, Fe, Cr, Ni, Cu, Mo, W, Zr, Nb, Ta, Th, etc.
2. They are all hard and strong metals with high melting and boiling points. They are also good conductors of heat and electricity.
3. They form alloys with one another and also with other elements.
4. With few exceptions, they show variable valency or oxidation state.
5. Their ions and compounds are coloured in solid state as well as in solution form at least in one if not all the oxidation states.

6.2.1 General charactetistics

(a) Binding energies

Transition metals show good mechanical properties. They are tough, malleable and ductile. The toughness of these metals indicate strong metallic binding. This is because, apart from s-electrons of the outer most shell, the electrons of underlying half-filled d-orbitals also participate in binding.

In moving from left to right in any transition series, the number of unpaired electrons increases up to groups VB and VIB, after that pairing takes place and number of unpaired electrons goes on decreasing until it becomes zero at group IIB, Table 6.3

Therefore, binding is stronger upto group VIB and weakens progressively upto group IIB. This trend of variation in binding energies is shown in Fig. 6.1. In the first transition series the general increase in binding energy ends at vanadium. This is due to changes in metallic structure, e.g. Mn. In the third transition series, the increase in binding energy ends at tungsten when all the 5d electrons contribute to binding.

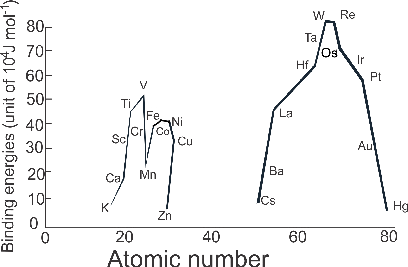


Fig. 6.1 Binding energies of the elements of the first and third transition series

1. Melting and Boiling Points

Transition metals have very high melting and boiling points due to strong binding forces present between their atoms. Melting points increase up to the middle of the series and then decrease to a minimum level at the end of the series.

This trend in melting points correlates well with the strength of binding forces as is clear from the Figs. 6.1 and 6.2.

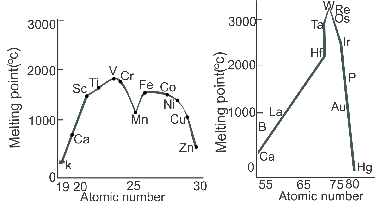


Fig.6.2 Melting points of the elements of the first and the third transition series

Animation 6.2 : [Binding energies](http://www.esrf.eu/news/spotlight/spotlight154/index_html)

Source and credit[:ERSF](http://www.esrf.eu/)

1. Covalent Radii and Ionic Radii

The covalent radii decrease rapidly at the start of the series, then become almost constant and finally begin to increase at the end of the series. The increase in covalent radii is possibly due to the fact that the filled 3d orbitals have contracted into the electron core and so shield the outer 4s electrons more effectively from the nucleus, Fig. 6.3.

Changes in the ionic radii along the series are much less regular, so that periodic trends in the properties of these ions are difficult to rationalize.

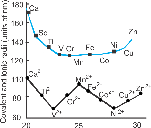


Fig. 6.3 Covalent radii (— } and ionic radii (for M2+) (— ) of first transition series elements.

1. Paramagnetism

Substances which are weakly attracted by a strong magnetic field are called paramagnetic substances.Those substances which- are weakly repelled by a strong magnetic field are called diamagnetic substances.

Paramagnetic behaviour is caused by the presence of unpaired electrons in an atom, molecule or ion because there is a magnetic moment associated with the spinning electron. It increases with increase in the number of unpaired electrons.

When the electrons are paired in an orbital, then magnetic moments are cancelled out and the substances become diamagnetic.

Table 6.4 No. of Unpaired electrons in the First Series of Transition Elements.

|  |  |  |
| --- | --- | --- |
| ION | 3d orbital electronic structure | No. of unpaired  electrons |
| Sc3+ | |  |  | | --- | --- | |  |  | |  |  |  | |  |  |  |  | |  |  |  |  |  | |  |  |  |  |  | |  |  |  |  |  | |  |  |  |  |  | |  |  |  |  |  | | 0  1  2  3  4  5  4  3  2  1 |
| Ti3+ |
| V3+ |
| Cr3+ |
| Mn3+ |
| Mn2+,Fe3+ |
| Fe2+ |
| Co2+ |
| Ni2+ |
| Cu2+ |
| Zn2+ | |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | 0 |

The paramagnetic behaviour is the strongest for Fe3+ and Mn2+ and decreases on both sides of the first transition series. The reason is that both Mn2+ and Fe3+ have 5 unpaired electrons each. The number of unpaired electrons decreases gradually to zero on both sides, as it is clear from the Table 6.4. Fig.6.4 shows the variation in the paramagnetic effect of the ions belonging to the first transition series.

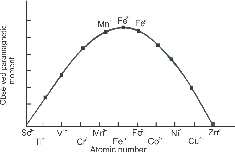


Fig 6.4 Variation in the paramagnetic effect shown by the selected ions across the first transition series

(e ) Oxidation State

One of the most important properties of the transition elements is the fact that they exhibit variable valency or oxidation state. They show variable valencies because of the involvement of the unpaired d electrons in addition to s electrons in bond formation. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states. +2 oxidation state is shown when only the 2s electrons are involved in bonding. In the highest oxidation states of the first five elements all the s and d electrons are used for bonding. After Mn, the number of oxidation states decreases as the d-subshells fill up and fewer unpaired electrons are available for bond formation as shown in Table 6.5.

Table 6.5 Commonly Occurring Oxidation States of the 1st

Series of Transition Elments

Oxidation states



Sc (Ar)

d

3

1

s

4

2

3

2

Ti (Ar)

3

d

2

4

s

2

2

3

4

V (Ar)

3

d

3

4

s

2

2

3

4

5

Cr (Ar)

3

d

5

s

4

1

5

6

4

3

2

Mn (Ar)

3

d

5

s

4

2

2

7

5

6

3

1

4

Fe (Ar)

d

3

6

4

s

2

3

4

5

6

2

1

Co (Ar)

3

d

7

s

4

2

2

3

4

5

Ni (Ar)

3

d

8

4

s

2

2

3

4

Cu (Ar)

3

d

10

4

s

1

3

1

2

Zn (Ar)

3

d

10

4

s

2

2

1. Colour

In transition elements, the d orbitals are responsible for the colour development in their compounds. When these orbitals are involved in bonding, they split up into two energy levels, one set has a higher energy than the other. The electrons residing in low energy d-orbitals absorb a part of the visible light and jump to high energy d orbitals. The process is called d-d transition, Fig. 6.5. The energy difference of d-orbitals varies from ion to ion. Thus, every ion absorbs a different wavelength and transmits the remaining set of wavelengths that gives different colours to the ions.

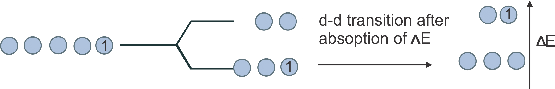


Fig. 6.5 Absorption of yellow light by [Ti(H2O)6]3+ ion.

In [Ti(H2O)6]3+, yellow light is absorbed, while most of the blue and red lights are transmitted, therefore the solution of [Ti(H20)6]3+ ions looks violet in colour.

1. Interstitial Compounds

When small non-metal atoms like H, B, C, N enter the interstices of transition metals and impart useful features to them, they are called Interstitial compounds.These are non-stoichiometric compounds.Sometime they are also termed as interstitial alloys.

1. Alloy Formation

Owing to the similarity in their sizes, some transition metal atoms are able to replace one another in the metallic lattice and form substitutional alloys among themselves. Alloy steels are an important example of this type of material in which iron atoms are substituted by chromium, manganese and nickel atoms, etc. to give the steel more useful properties. Other examples are brass, bronze, coinage alloys, etc.

## 6.3 COMPLEX COMPOUNDS

It has been observed that when the aqueous solutions of Fe (CN)2 and KCN are mixed together and evaporated a new compound is obtained, which in aqueous solution does not ionize as Fe2+ and CN ions but ionizes as K+ ion and [Fe (CN)6]4- ion (Ferrocyanide ion). On this basis it has been given a formula

K4 [Fe (CN)6].

## *Fe CN*( )2 +4*KCN*→*K Fe CN*4[ ( ) ]6 →*ionization* 4*K*+ +[*Fe CN*( ) ]6 4−

Here [Fe (CN)6]-4 is called a complex ion.

Such compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds or complexes. A complex compound may contain

1. a simple cation and a complex anion
2. a complex cation and a simple anion

6.3.1 Components of Complex Compounds

It is necessary to understand different terms used in the study of the complex compounds.These are as follows:

(a) Central Metal Ion

A metal atom or ion (usually a transition element) surrounded by a number of ligands is called a central metal atom or ion, e.g. K4 [Fe(CN)6], [Ag(NH3)2]Cl In the above examples, Fe2+ and Ag1+ are the central metal ions, respectively.

(b) Ligand

The atoms or ions or neutral molecules, which surround the central metal ion and donate electron pairs to it,are called ligands.They may be anions or neutral molecules,

e.g. K4 [Fe(CN)6], [Ag(NH3)2]Cl.

In the above examples, CN- and NH3 are the anionic and neutral ligands, respectively. Ligands having two donor atoms are called bidentate ligands, e.g.

COO-

Oxalate ion | is a bidentate ligand and its coordination with the metal

### COO-

ion occur through its both negatively charged oxygen atoms. (c) Coordination Number

The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called the coordination number of the central metal atom or ion, e.g.

K4 [Fe(CN)6] , [Cu(NH3)4]SO4

In the above examples, coordination number of iron is 6 and that of copper is 4.

1. Coordination Sphere

The central metal atom or ion alongwith ligands is called the coordination sphere.It is usually placed in square brackets. It may be anionic, cationic or neutral, e.g.

K4 [Fe(CN)6] , [Cu(NH3)4]SO4 , [Ni(CO)4]

In the above examples, [Fe(CN)6]4- , [Cu(NH3)4]2+ and [Ni(CO)4]0 are anionic, cationic and neutral coordination spheres, respectively.

Animation 6.3 [:Coordination compounds](http://www.ciceco.ua.pt/index.php?tabela=pessoaldetail&menu=218&user=478) Source and credit: [ciceco](http://www.ciceco.ua.pt/)

1. Charge on the Coordination Sphere

It is the algebric sum of the charges present on the central metal ion and the total charge on the ligands, e.g;

[Fe(CN)6]4-

Charge on iron = + 2

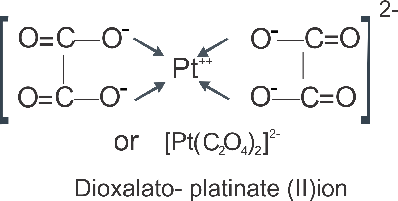
Total charge on six CN- ions = - 6

Charge on the coordination sphere = -6 + 2 = - 4

6.3.2 Chelates

When all the donor atoms of a polydentate ligand get coordinated with the same metal ion, a complex compound is formed which contains one or more rings in its structure and hence is called a Chelate. Metal chelates are more stable metal complexes.

When two oxalato ligands C2O42- (bidentate ligand) get coordinated with Pt2+ ion, dioxalato platinate (II) ion is obtained. Each oxalate ligand forms a five membered ring with the cation.



|  |  |  |  |
| --- | --- | --- | --- |
| |  | | --- | | Animation 6.4 : [Chelate test page](http://soils.wisc.edu/facstaff/barak/images/chelate.htm) Source and credit: [Soil Science](http://soils.wisc.edu/) | | |  | | --- | | Animation 6.5 : [Chelate test page](http://soils.wisc.edu/facstaff/barak/images/chelate.htm) Source and credit: [Soil Science](http://soils.wisc.edu/) | |

6.3.3 Nomenclature

The nomenclature of complex compounds is based upon the recommendations by the Inorganic Nomenclature Committee of IUPAC.

The rules for naming the complex compounds are as follows.

1. Cations are named before anions.
2. In naming the coordination sphere, ligands are named in alphabetical order regradless of the nature and number of each, followed by the name of central metal ion.
3. The prefixes di, tri, tetra, penta, hexa, etc, are used to specify the number of coordinated ligands.
4. The names of anionic ligands end in suffix O, e.g, hydroxo, (OH-) carbonato

(CO32-).

1. The names of neutral ligands are usually unchanged, e.g. for NH3, ammine and for H2O, aqua. and for CO, carbonyl.
2. The suffix ‘ate’ comes at the end of the name of metal if the complex represents an anion, otherwise it remains unchanged.
3. The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal.

Examples : K4 [Fe(CN)6] Potassium hexacayno ferrate (II)

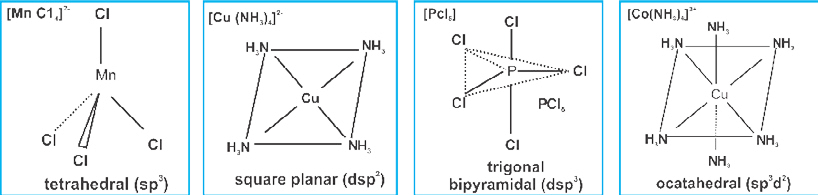
[PtC1(NO2)(NH3)4]SO4 Tetraammine chloronitro-platinum (IV ) sulphate

[CO (NO2)3(NH3)3] Triammine trinitrocobalt (III)

In writing the formula of a complex ion, the usual practice is to place the symbol of the central metal atom first, followed by the formulas of the anionic ligands in alphabatical order, then neutral ligands in alphabatic order and the formula of the whole complex ion is enclosed in square brackets as is clear from the above examples.

6.3.4 Geometry of Complexes

The geometry of complexes depend upon the type of hybridization taking place in the valence shell of the central metal atom.



Animation 6.6 [:Shapes of complex compounds](http://oscar.iitb.ac.in/onsiteDocumentsDirectory/complex_structures/complex_structures/shell.swf) Source and credit[:Oscar](http://oscar.iitb.ac.in/oscarHome.do;jsessionid=50801202E123383EAD276B3DCA008658)

### 6.4 IRON

The important ores of iron are magnetite (Fe3O4), haematite (Fe2O3)and limonite Fe2O3.3H2O etc. Iron has been known since prehistoric days. It was used in Egypt in 1500 B.C. It is known that the Chinese also used iron as early as 2500 B.C. In the subcontinent, iron was produced around 600B.C.

6.4.1 Commercial Forms of Iron

Iron is available commercially in the following three forms. They differ in carbon contents as follows:

1. Pig iron or cast iron 2.5 to 4.5% carbon
2. Wrought iron 0.12 to 0.25% carbon
3. Steel 0.25 to 2.5% carbon

6.4.2 Wrought Iron

Composition

It is the purest form of commercial iron and contains the lowest percentage of carbon and upto 0.3% of impurities like S,P,Si and Mn, etc.

S = 0.2 to 0.15%, Mn = upto 0.25 %, P = 0.04 to 0.2%