الهالوجينات Halogen

- The group that contains, ^{9}F,^{17}Cl, ^{35}Br, ^{53}I, and ^{85}As (Astatine) elements is called halogen element group. This name means in Greek salts, the electronic configuration of the outer shell (covalence) is $ns^2\ np^5$, so we call it as group VII. Astatine is produced in very few amounts from the radiation degradation processes as an intermediate element with short life, no details are know about.

- General properties of the group elements:-
- The electronic configuration of the ... their extreme tendency to gain an e forming ionic halides as NaCl or their contribution by es forming covalent halides, e. g. HCl, also their presence as diatomic molecules can be explained from ns^2np^5.
- These elements (except fluorine) show positive oxidation no. in their compounds with O2 as in the following examples:-

Element	$^{9}F_2$	$^{17}C_{12}$	$^{35}Br_2$	$^{53}I_2$
Color	Pale yellow (g)	Green (g)	Reddish brown (l)	Violet (s)
M. P. °C	-288	-101	-7	113
B. P. °C	-188	-35	59	184
Ionization pot (eV)	17.4	13	11.8	10.4
E.N.	4	3	2.8	2.5
Energy of bond KJ/ mol	154.8	242.7	192.5	150.2
Radius of atom (pm)	72	99	114	113

- It is very clear that the properties are systematically ranging among the group (from F to I) e. g. Ionization potential . Decomposition while the radius increases. These element have a high ionization potential coming directly after that of the nobal gases, the metallic character increase through the group (from F to I).
- Halogens are present in the normal conditions as diatomic molecules bonded by a covalent bond (single), also there are van der walls forces bonding the molecules in the liquid and solid state.
- Iodine molecule is the largest molecule of the group VII elements in size, it has the largest no. of electrons which make its polarization easy, so it has large van der walls forces that explain why Iodine is a solid in normal conditions and has a high m. p. compared to the other elements in the group.

- The elements of the 2nd period, where the F is found [illegible] their group [illegible] properties because of the [illegible] of their [illegible] ms, higher EN, they doesn't have d orbitals [illegible] they [illegible] covalency shell, e. g. [illegible] no. of electron [illegible]

- [illegible] bond in (F_2) because of the decomposition energy of the molecule which is due to the repulsion between the two atoms of the molecule and their non-bonding electrons.
- Chlorine has higher decomposition energy that the other elements because the non-bonding electrons form with (d) orbitals (vacant) in the neighboring atom what called (pπ-dπ) bond which increases the strength of Cl-Cl bond, while the large size of Br and I decrease the possibility of (pπ-dπ) bonds formation, so that the decomposition energy of their molecule is less than that of chlorine.

Methods of preparation

1- **F_2**:- The more active element and the stronger oxidizing agent, cannot be prepared in aqueous solution because it oxidizes water.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

Fluorine can be prepared by electronic analysis of the fluorides melts inside Cu-containers or alloys of Cu- Ni, because it forms an isolating layer of fluoride when react with them prevent the reaction to continue and then protect the containers.

a- $2K[HF_2] \longrightarrow H_2 + 2KF + F_2$

Also we can get fluorine from the fluorides decomposition by heat:-

b- $AuF_3 \longrightarrow AuF + F_2$

2- Cl_2:- Is prepared by the electronic analysis of NaCl

$$2NaCl + H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$$

also by oxidation of HCl (conc.) by one of the strong oxidizing agent e. g. $KMnO_4$, $K_2Cr_2O_7$, PbO_2, MnO_2:

$MnO_2 + 4HCl \longrightarrow [MnCl_4] + [illegible]H_2O$

[illegible] $\longrightarrow MnCl_2$ [illegible]

3- Br_2:- Prepared by oxidation of bromide [illegible]

$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$ or in Lab. A[illegible]

[illegible] $2KBr$ [illegible] $2H_2SO_4$ [illegible] SO_4 [illegible] Br_2 [illegible] H_2SO_4 [illegible] $2H_2O$

4- I_2:-By oxidizing of iodide by Cl2

$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$

Industrially by reducing iodides present in chilli salt using sodium bisulfite:-

$$2IO_3 + 5HSO_3^- \longrightarrow I_2 + 5SO_4^{-2} + 3H^+ + H_2O$$

Laboratory prepared in a similar way as in Cl_2 and Br_2 by oxidation iodide using $Cr_2O_7^{-2}$:

$$Cr_2O_7^{-2} + 14H^+ + 6I^- \longrightarrow 2Cr^{+3} + 3I_2 + 7H_2O$$

Compounds of halogens with hydrogen :-

Halogens give hydrogen halides when react with hydrogen ,the strength of reaction decomposition from (F to I). e. g. hydrogen chloride HCl and HF in industry are prepared from hot conc. H_2SO_4 with NaCl, CaF_2

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$CaF_2 + H_2SO4 \longrightarrow CaSO_4 + 2HF$

The products HCl and HF are easily separated from the reaction liquid, because

Hydrogen halides are similar in their physical properties and to a large extent in their chemical properties, they are colorless gases have a sharp and bad smell HF, m. p. =19.5°c which is considered high due to the tendency of F to form hydrogen bonds because of its high EN.

Hydrofluoric acid reacts with glass forming tetra fluoro silicon (SiF_4), this is because of the presence of SiO_2 in glass structure.

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

For this reason HF is kept in plastic containers.

Preparation Methods

1- Direct reaction between halogens and elements:-

3- Fluorides are prepared from HF or ZnF_2 with chlorides:-

$$CrCl_3 + 3HF \longrightarrow CrF_3 + 3HCl$$

$$PCl_3 + 3ZnF_2 \longrightarrow 2PF_3 + 3ZnCl_2$$

Compounds of oxygen and halogens:-

Compounds of F_2 with O_2 are called oxygen fluorides because the EN of (F) is larger than that of oxygen, while others are called halogen oxides.

a- Oxygen fluorides OF_2:- prepared by passing F_2 in 2% NaOH solution

$$2F_2 + 2^{-}OH \longrightarrow F_2O + 2F^{-} + H_2O$$

It is a pale yellow gas, toxic, relatively unactive, its structure like water.

b- Chlorine oxides: very active, unstable, tends to explode under different conditions e. g. Cl_2O is prepared:-

$$2Cl_2 + 2HgO \longrightarrow HgCl_2\text{-}Hg + Cl_2O$$

Reddish yellow gas at room temperature, dissolve in water forming HOCl which forms with molecular chlorides oxohalides:-

$$TiCl_4 + Cl_2O \longrightarrow TiOCl_2 + 2Cl_2$$

ClO_2 :- Highly explosive and active, oxidizing agent, it's structure is angular.

Other oxides are like Cl_2O_6, Cl_2O_7 .

c- Bromine oxides:- unstable, prepared by O_2 with Br_2 reaction under electricity discharging at low temperature e. g. Br_2O white solid, thermally unstable above 80°c, keep in ozone atmosphere.

d- Iodine oxides:- e. g. I_2O_5 white crystalline, it is an oxidizing agents.

Iodine doesn't form such acids. The most important example are oxochloro acids, HOCl, HOBr, HOI (oxidation no. +1), $HClO_2$(+3).

Negative ions of such acid, e. g. (ClO^-) from by losing protons. Negative ions are more stable than acids due to their gaining (accepting) resonance energy, e. g. ClO^-_2:-

Inter halogen cpds.

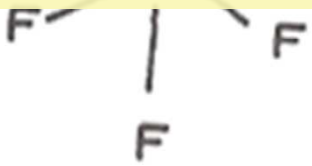
These can be produced by the reaction of halogens themselves xx-n, where (n) is an odd no., e. g. ICl, ICl_3, IBr, BrF, ...etc.

Fluorides are very active, react strongly with water and organic cpds. Sometimes the activity causes explosion.

The activity is following the order:-

$ClF_3 > BrF_3 > IF_7 > ClF > BrF_3 > IF_5 > BrF$

The structure of these cpds can be deduced by help of (VSEPR) theory, the tetra cpds. e. g. XF_4 have the structure



Three bonding pairs and two non-bonding pairs of es.

Pseudo halogens:-

They are molecules formed from elements of high (EN), like halogen in their properties, from ions called pseudo ions which like halides ions in behavior : example:- cyanogene $(CN)_2$, Thiocyanogene $(SCN)_2$, .(OCN^-) etc.

The common properties with halogens are:-

1- Volatile materials form from two radicals combination:-

6- Pseudo ions form complexes as halides ions:-
e. g. $[Zn(NCS)_4]^{-2}$

7- They form covalent pseudo halides like covalent halides when hydrolyze in water e. g. $Si(OCN)_4$, $SiBr_4$.

All halocyanogenes are known and can be prepared by the reaction of halogen and cyanide, they are volatile cpds. Their structure is linear:-

X-C-N