6. GROUP(VII) ELEMENTS

Physical properties

States at room temperature:

- ✓ Fluorine, F_2- yellow gas
- ✓ Chlorine Cl_2 - yellow-green gas
- ✓ Bromine Br_2 - red-brown liquid
- ✓ Iodine I_2 - black (dark purple) solid - sublimes to a purple vapour.

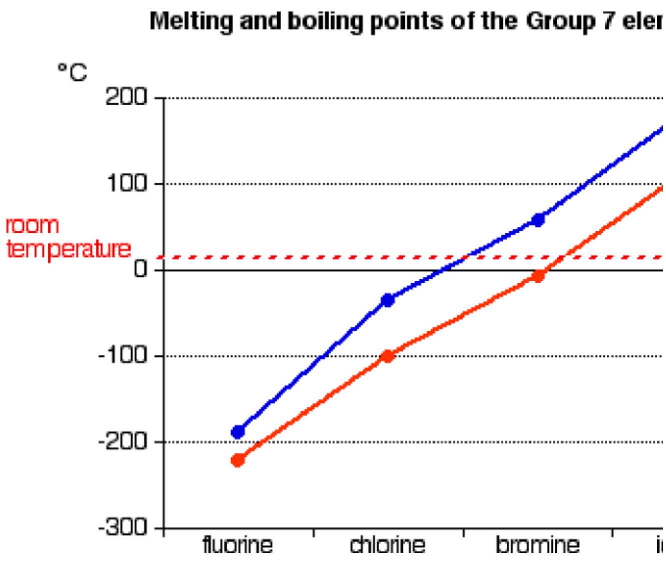
- ❖ Halogens are highly reactive nonmetals. They exist as diatomic molecules X_2 containing a covalent bond. Due to their reactivity the elements do not occur in the free state but are always combined with other elements.
- ❖ All the elements have 7 electrons in their outer most shells with general outer most electronic configuration of ns^2np^5 n= 2,3,4&5
- ❖ They can complete their octet by either gaining an electron to form an ionic bond or sharing electrons with other elements or themselves

  in a covalent bond.
- ❖ The melting and boiling points of the halogens are low but increase down the group.

Explanation

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

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

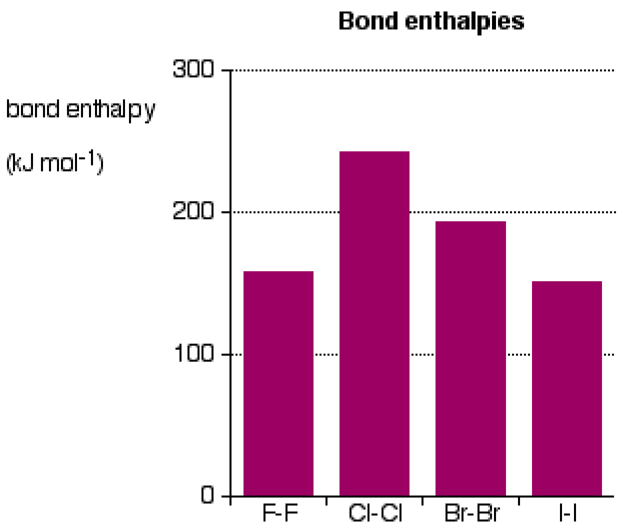


Bond dissociation energy

Bond energy is the energy required to break a bond between two atoms.

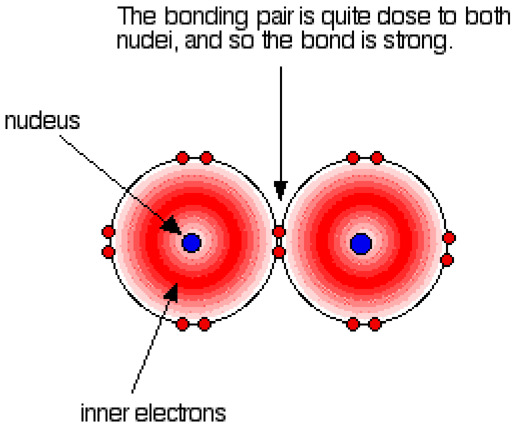
Or its the energy released when a bond is formed between two atoms.

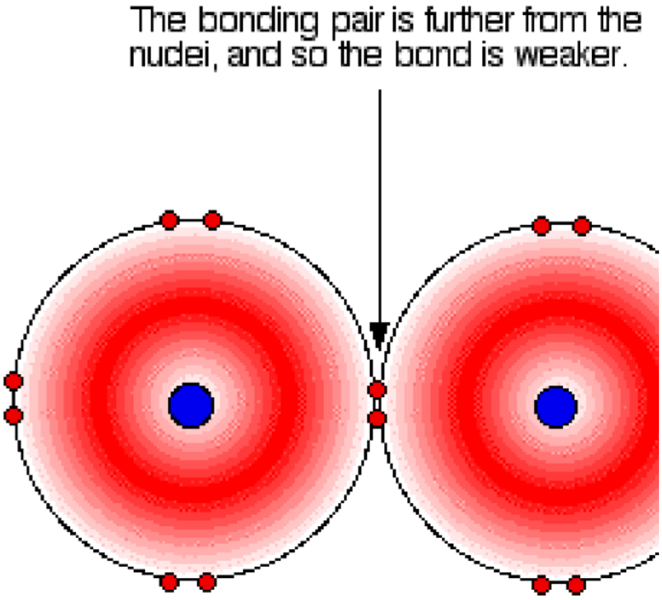
Bond dissociation energy of the diatomic molecules decreases down the group from chlorine to iodine. However ,F_2 has abnormally low bond dissociation energy.



This is due to small atomic radius of fluorine atom, the non bonding p- electrons present in F_2 molecule are closer to one another as such repel @ other strongly thus weakening the F-F bond.

The decrease in B.D.E from Cl_2 to I_2 is attributed to increase in atomic radius as the group is descended, the bonding electrons in the halogen-halogen bond are far from the nuclei of the halogens & are attracted less strongly due to the screening effect of the inner complete shells of electrons thus weakening the bond progressively.





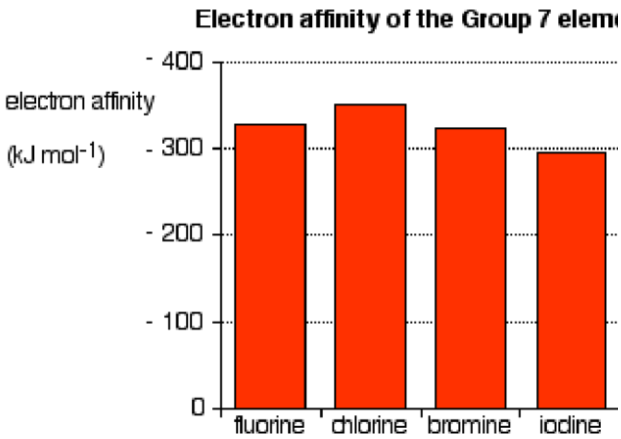
NB: The high reactivity of fluorine may be attributed to its low B.D.E.

Electron affinity of halogens

E.A is the energy change when an extra electron is added to a neutral gaseous atom to form a negatively charged gaseous ion.

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

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



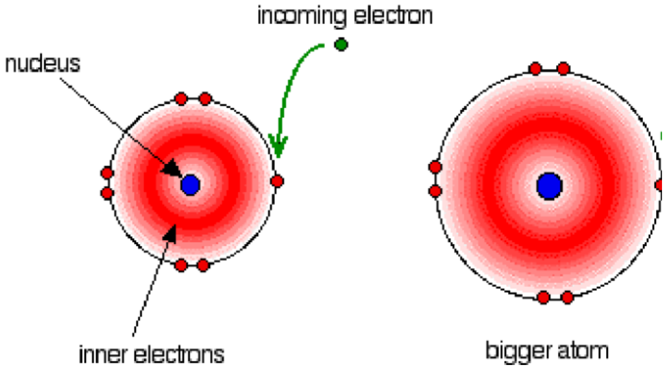
The E.A decreases numerically from Chlorine to Iodine. As the atomic radius increases down the group, the electron being added experiences a greater repulsion from the electrons that are already present than the attraction experienced from the nucleus due to the screening effect of the inner complete shells of electrons.

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

Explanation

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

The electron affinity is a measure of the attraction between the incoming electron and the nucleus. The higher the attraction, the higher the electron affinity.



Oxidizing properties of halogens

- ✓ Halogens are very good oxidizing agents with fluorine being the most oxidizing.
- ✓ This is because fluorine is the most electronegative and has the highest positive value for its standard electrode potential. It oxidises water to oxygen.

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

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

$F_2 > Cl_2 > Br_2 > I_2$

Oxidation states of halogens

They all exhibit oxidation state of 1by gaining an extra electron to complete their octet.

Fluorine is always univalent due to absence of vacant 'd'-orbitals.

Other elements can show higher oxidation states due to availability of vacant 'd'-orbitals which allows them to expand their octet. **Reactions of halogens**

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

1.Reaction with water

a) F_2 oxidises H_2O to O_2 gas in a very exothermic reaction.

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

b) Cl_2 dissolves in H_2O to form 'chlorine water' which is a mixture of two acids. No O_2 is evolved.

$Cl_{2(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HOCl_{(aq)}$ c) Br is only slightly soluble in H_2O .

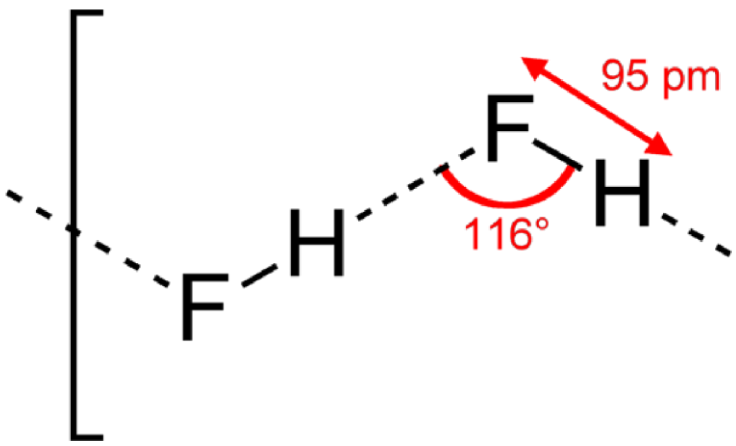
$Br_{2(l)} + H_2O_{(l)} \rightarrow HBr_{(aq)} + HOBr_{(aq)}$ d) I_2 is virtually insoluble in H_2O. It is however soluble in KI solution due to the formation of a soluble complex the tri-iodide anion.

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

I_2 is sparingly soluble in water because the energy involved in disrupting the weak van der Walls forces in molecular iodine crystal lattice and the hydrogen bonds in water exceeds the energy changes involving the weak attraction between iodine and water molecules. Note:

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

2.1



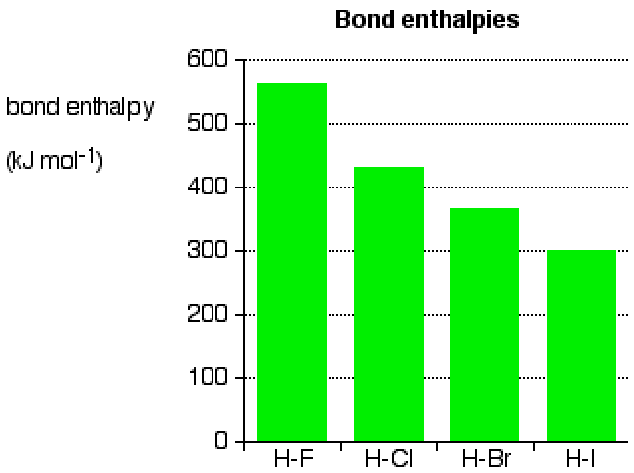
b)The acidity of the hydrides is in the order H-F <H-Cl< H-Br< H-I.

- H-F is the weakest acid because the H-F bond is very strong as a result of small atomic radius and high electronegativity of Fluorine atom. It is weakly dissociated in solution releasing fewer H^+ ions.

- In addition, the presence of hydrogen bonding between HF molecules and water molecules inhibits the ionization of HF in aqueous solution.
- However, as the group is descended, electronegativity decreases whereas atomic radius increases. As such the H- halide bonds become progressively longer and weaker. They dissociate in solution releasing more hydrogen ions.

c) Bond energy/ enthalpy of the hydrides generally decreases in moving from HF to HI ie

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



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

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

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

- Fluorine is always monovalent, others show higher oxidation state. This because fluorine lacks empty d-orbitals but others have.
- H-F is a liquid while other hydrogen halides are gases at room temperature. This is due to the strong hydrogen bonds between H-F molecules as a result of high electronegativity of fluorine atom.
- Fluorine forms the least acidic hydride whereas the hydrides of other members are fairly more acidic in aqueous solution. This is due to the high strength of the H-F bond.
- Fluorine is the most reactive halogen, due to its low bond dissociation energy and high electronegativity.
- Fluorine forms compounds with more ionic character due to its high electronegativity and charge density of the small F^- ion.
- Fluorine forms hydride with the highest boiling point in aqueous solution due to extensive hydrogen bonds .

Why does Fluorine show a difference? ○ Most electronegative in the group. ○ Low bond dissociation energy.

- High positive value of standard electrode potential.
- Smallest atomic radius, F^- ion has very high charge density, high polarising power, high enthalpy of hydration. ○ Absence of a vacant d-orbitals.

Oxy-acids & Oxy-ions

1.Chlorate(i) acid $HClO$

(Chloric(i) acid)

2.Chlorate(iii) acid $HClO_2$ (Chloric(iii) acid)

3. Chlorate(v) acid $HClO_3$

(Chloric(v) acid)

4. Chlorate(Vii) acid $HClO_4$

(Chloric(vii) acid)

The acidity of the oxy-anions of chlorine increases with increase in the number of oxygen atoms attached to chlorine atom. Oxygen being more electronegative than chlorine, withdraws electrons from the O-Cl bond more towards itself.

This weakens the O-H bond in the oxy-acid. The greater the number of oxygen atoms attached the stronger the effect and the stronger the acid.

NB

1. Work out the oxidation state of chlorine in each of oxyacids above

.

2. Draw the molecular structure of each oxyacid .

Qn. Compare the reactivity of Fluorine and Chlorine with the following substances(in each case illustrate your answer with equation)

i) Water