INTRODUCTION:

F, Cl, Br, I and At constitute the VII A group in periodic table.

- According to IUPAC convention, their group number is 17
- They are p – block elements and their outer shell configuration is $ns^2\ np^5$.
- The list of element is

Element	Period	Symbol	A.t.No	Electronic configuration
Fluorine	2	F	9	$[He]2s^2 2p^5$ (or) 2, 7
Chlorine	3	Cl	17	$[Ne]3s^2\ 3p^5$ (or) 2,8,7
Bromine	4	Br	35	$[Ar]3d^{10}4s^2 4p^5$ (or) 2, 8, 18, 7
Iodine	5	I	53	$[Kr]\ 4d^{10}\ 5s^2\ 5p^5$ (or) 2, 8, 18, 18, 7
Astatine	6	At	85	$[Xe]4f^{14}5d^{10}6s^2\ 6p^5$ (or) 2, 8,18,32,18,7

- Astatine is radioactive element
- F_2, Cl_2, Br_2, I_2 are known as halogens. Halogen means "Produced in the form of sea salt". e.g. Sea water has NaCl, $MgCl_2$, $MgBr_2$, $NaIO_3$.
- All halogens occur only in combined state. Fluorine occurs mostly as fluorspar (CaF_2) and fluorapatite $3Ca_3(PO_4)_2.CaF_2$
- The are the most electro negative elements.

General characteristics and group trends :

- Density, mp, bp, bond length, vander Waal's forces of attractions and intensity of the colour of the halogens increase down the group.
- IP_1, EN, volatility, solubility in water, standard reduction potential value and non-metallic character decrease down the group.

- IP_1 of F is very high because of its small size.
- F is most electro negative element. In Paulig's scale EN of F is 4.0.
- F_2, Cl_2 are gases. Br_2 is liquid. I_2 is solid. The change in physical state is due to the increase in the vander Waal's force between the molecules down the group which is due to increase in molecular weight.
- The order of EA is Cl > F > Br > I.
- The low EA value of F is due to inter electronic repulsions and due to the small size of F atom.

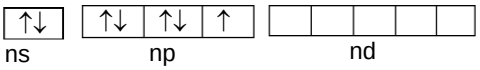
  The incoming electron experience greater repulsions due to high electron density in 2 p sub level.
- The order of bond energies is $Cl_2 > Br_2 > F_2 > I_2$
- F_2 is highly reactive because of its low bond energy.
- Mulliken proposed multiple bonding in Cl_2, Br_2, I_2 with p – d combination. F atom has no d – orbitals. So, multiple bond formation in F_2 is not possible and is the reason for the low BE of F_2.
- Coulson suggested that in F_2, the LP electrons of one atom repel the LP electrons of second F atom because of short F – F distance. High inter nuclear repulsions and inter electronic repulsions are also responsible for its low BE value.
- Of the two explanations, Coulson's view is widely accepted.

  Halogens are coloured.
  - The colour of halogen is due to the absorption and transmission of light in visible region.
  - Transmitted light is the complementary colour of the absorbed light.
  - Absorbed light makes electron to promote from ground state to higher energetic states.
  - As the size of the halogen atom increases, excitation energy of the electron decreases.
  - F absorbs high energetic violet light and transmits low energetic yellow light. Yellow colour is the complementary colour to violet light.
  - I absorbs low energetic yellow light and transmits violet light.
  - F_2 has pale yellow colour
  - Cl_2 is greenish yellow in colour
  - Br_2 has orange red colour
  - I_2 is violet in colour

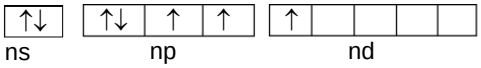
Oxidation States :

- F exhibits only –1 oxidation state in its compounds since it is the most electro – ve atom the valency of F can not be more than one due to the absence of vacant d- orbitals in valence shell.

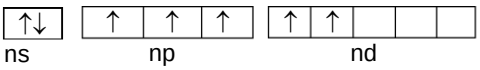
- Cl, Br, I exhibit – 1, + 1, + 3 + 5 + 7 oxidation states because they are less electronegative and contain vacant d –orbitals in their valence shells.
  –1, + 1 oxidation states are possible with ground state configuration.
  + 3, + 5, + 7 oxidation states are possible with excited state configuration.
  +ve oxidation states are seen in only covalent compounds.
- Higher oxidation states are found is interhalogen compounds, oxides and oxo acids.
  (a) Ground state configuration of halogen atom is



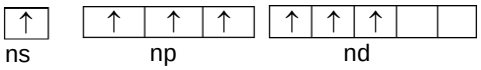
  (b) 1st excited state configuration is



  (c) 2nd excited state configuration is



  (d) 3rd excited state configuration is



- Inter halogen compounds are formed when one halogen combines with another halogen.
- In interhalogen compounds, π bonds are not formed by the halogen atom.

SNO	Interhalogen compound	Configuration	Hybridisation	O.S. of X	No.of bonds	Shape
(i)	XA	(a)	No hybridisation	+ 1	1	Linear
(ii)	XA_3	(b)	sp^3d	+ 3	3	Trigonal bipyramidal with 2 LP (or) trigonal pyramidal (or) T –shape
(iii)	XA_5	(c)	sp^3d^2	+ 5	5	Octahedral with 1 LP (or) square pyramidal
(iv)	XA_7	(d)	sp^3d^3	+ 7	7	Pentagonal bipyramidal

- *Note :* In all above molecules X is the central halogen atom which is less electronegative and A is more electronegative halogen atom.

Oxidising power :

- All the halogens are oxidising agents. Their oxidising power is high due to high EA values.
  The order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$
  The order of S.R.P is $F_2 > Cl_2 > Br_2 > I_2$
- All S.R.P. values are +ve. S.R.P. is a measure of the ability to undergo reduction.
- Oxidising ability of halogens depends on the net energy change of the process, $\frac{1}{2}X_{2(s)} \rightarrow X^-_{(aq)}$
- The net energy change is calculated using Born- Haber cycle (or) Hess law.
  $\Delta H_1 + X_{2(s)} \rightarrow X_{2(l)}$ ΔH_1 =Enthalpy of fusion
  $\Delta H_2 + X_{2(l)} \rightarrow X_{2(g)}$ ΔH_2=Enthalpy of vapourisation
  $\frac{1}{2}D + \frac{1}{2}X_{2(g)} \rightarrow X_{(g)}$? = Enthalpy of dissociation
  $e + X_{(g)} \rightarrow X^-_{(g)} + E$ E = Electron affinity
  $aq + X^-_{(g)} \rightarrow X^-_{(aq)} + \Delta H_3$ ΔH_3=Enthalpy of hydration
- The net energy change of the process, $\frac{1}{2}X_{2(s)} \rightarrow X^-_{(aq)}$ is $\left(E + \Delta H_3 - \frac{\Delta H_1}{2} - \frac{\Delta H_2}{2} - \frac{D}{2}\right)$
- Greater this value, greater is the oxidising capacity of the halogen.
- Higher oxidising capacity of F_2 is due to
  (i) Low enthalpy of dissociation of F – F due to the weakness of F – F bond
  (ii) High enthalpy of hydration of F^- due to its small size.