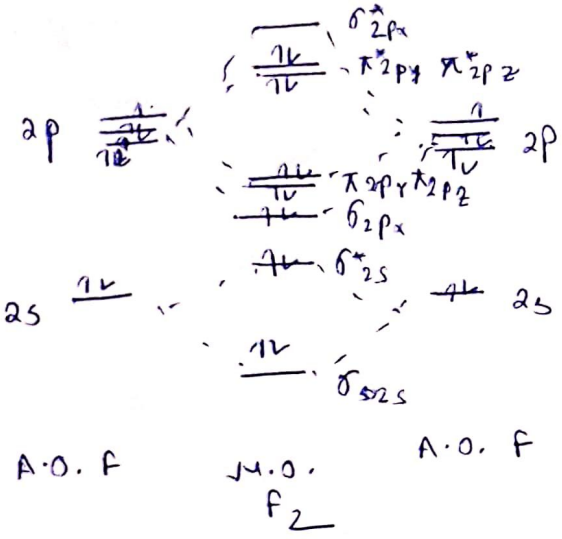
ELEMENTS OF GROUP 17 (VII A): HALOGENS

General properties:

In the vapour state, the halogens normally exist as diatomic molecules. The M.O. description of F_2 is

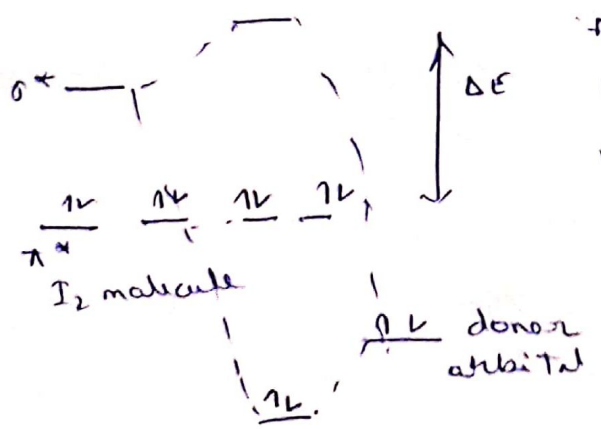


The energy difference between 2s & 2p a.o.s is quite large ($\sim$2500 kJ mol^{-1}), the amount of mixing between the σ_{2s} & σ_{2p} ~~and~~ in F_2 is negligible for practical purposes and is not sufficient to repel the σ_{2p} m.o. above the π_{2p} level. The ns-np separations in other halogens are less than half that of fluorine, their diatomic molecules should then have the m.o. description for their valence shell as $\sigma_{ns}^2\ \sigma_{ns}^{*2}\ \pi_{np}^4\ \sigma_{np}^2\ \pi^{*4}_{np}$. In all cases HOMO is $\pi^*(np)$ & LUMO is $\sigma^*(np)$.

Colours of the halogen :

In the gas phase, the colours of the halogen vary remarkably : fluorine : pale yellow, Cl_2 pale greenish-yellow, Br_2 : deep red-brown, I_2 : deep violet. All these colours may be assigned to transition of an electron from the highest occupied π^* m.o. to the lowest unoccupied σ^* (m.o.. As one moves from F_2 to I_2 the difference between the two energy levels decreases and probability of the transition increases. Hence the absorption maximum gradually shifts from the near ultra violet to the red region, hence we observe the complementary colour.

In case of I_2 it dissolves unchanged in saturated hydrocarbons like CCl_4. But donor solvent molecules may share one of their electron pairs with the empty σ^* m.o. of the I_2 molecule forming weak C.T complexes which vary in colour.



As the separation of HOMO & LUMO increases absorption bands moves towards blue end, the I_2 gives brown soln. in alcohol & ethers.

I_2 produces an intense blue-black colouration with starch in presence of I^-. I_5^- ions ($I_2 + I_3^-$) are trapped in the helical coils of amylose which has absorption at about 600 nm.

Chemical reactivity:

Fluorine is the most electronegative and most chemically reactive of all the elements. It combines directly with metals & almost all non-metals. Reactivity decreases to Cl_2 to Br_2 to I_2: which reacts with H_2 only when heated in presence of a catalyst like Pt.

The exceptionally high reactivity of F_2 may be assigned primarily to the low F-F bond dissociation energy. Also, the bonds in Cl_2, Br_2, I_2 may acquire slight multiple bond character via pd hybridisation.

Few important reactions:

Reaction with	F_2	Cl_2, Br_2, I_2
(i) H_2	$H_2 + F_2 \rightleftharpoons 2HF$	$H_2 + X_2 = 2HX$ X = Cl, Br (sunlight) X = I, Pt cat + heat
(ii) H_2O	(a) $2F_2 + 2H_2O = 4HF + O_2$ (b) $3F_2 + 3H_2O = 6HF + O_3$	(a) $X_2 + H_2O = HX + HOX$ (X = Cl, Br) (b) $2X_2 + 2H_2O = 4HX + O_2$ (X = Cl, Br also)
(iii) aqueous alkali	(a) dil: $2F_2 + 2NaOH = F_2O + 2NaF + H_2O$ (b) conc: $2F_2 + 4NaOH = 4NaF + 2H_2O + O_2$	(a) cold dil: $X_2 + 2OH^- = X^- + OX^- + H_2O$ (b) hot, concentrated: $3X_2 + 6OH^- = 5X^- + XO_3^- + 3H_2O$

	F_2	Cl_2, Br_2, I_2
(iv) Non-metals	O_2, N_2, He - no direct reaction C, S, Br, I etc. burn spontaneously.	C, O_2, N_2, He - No direct reaction S, P etc. combine with decreasing vigour from Cl–I $2S + Cl_2 = S_2Cl_2$ (also Br_2) $S + 2Cl_2 = SCl_4$ $P_4 + 6Cl_2 = 4PCl_3$
(v) metals	Most metals form fluorides, Na, K etc. catch fire. $Ag + F_2 = AgF_2$	Many metals form halides, though less energetically. $2Ag + Cl_2 = 2AgCl$.

oxidising property:

Fluorine is an extremely strong oxidising agent,

$$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-, \quad E^\circ_{F_2/F^-} = +2.65\,V$$

- Cl_2, Br_2 & I_2 are slightly soluble in water, the aq. soln. contains mostly hydrated X_2 together with HOX produced on disproportionation.

Oxidation of water by Cl_2 is extremely slow though thermodynamically feasible. With I_2, the reverse process takes place simultaneously,

$$2H^+ + 2I^- + \frac{1}{2}O_2 \longrightarrow I_2 + H_2O, \quad \Delta G^\circ = -105\ kJ\ mol^{-1}$$

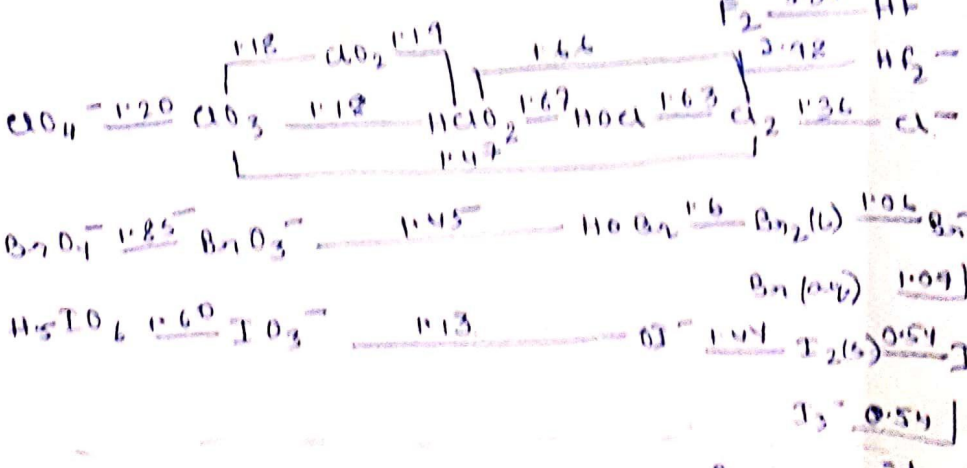
This is why the blue colour of starch-iodine solutions as seen in a solution after titration of I_2 with thiosulphate.

Redox behaviour:

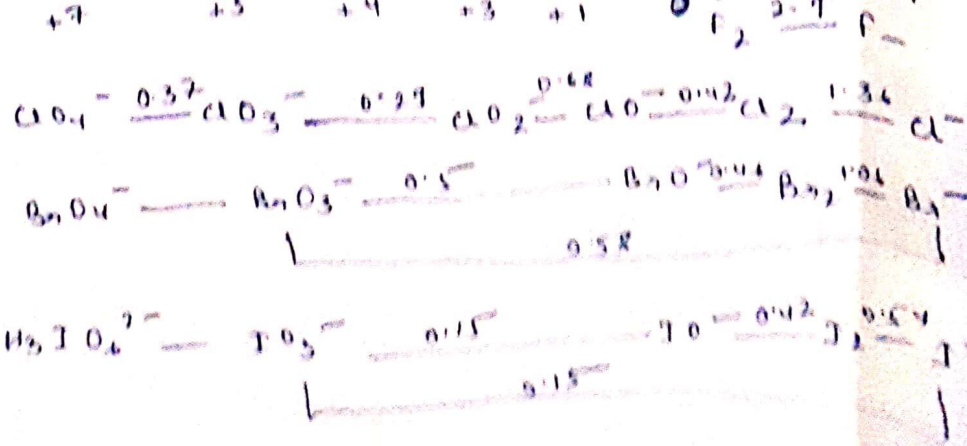
Oxidation state - free energy diagrams for the elements show that the stability of the only negative oxidation state (-1) decreases from F to I, & appears that the positive oxidation states are all fairly stable. I(V) is more stable than I(VII) but Cl(V) than is Cl(V) w.r.t. Cl(VII)

Standard Aqueous reduction potentials:

Acidic solution: +7 +5 +4 +3 +1 0 -1



Basic solution:



Eg:

(i) oxidation states 0, +1, & +3 of the halogens (except F) are supported to disproportionate in both acidic & basic media.

(ii) F_2 & Cl_2 have the thermodynamic potentiality to oxidize water to dioxygen.

Difference of fluorine from other halogens:

Fluorine reacts differently from other halogens due to:

(1) Small size of $F_{(g)}$ atom & F^- ions.

(2) Highest electronegativity among all the elements.

(3) Low bond dissociation energy of F_2.

(4) High bond energy of any element - F bond.

(5) Restriction of the the valence shell to octet.