TDC Part I
Inorganic Chemistry

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TOPIC:- Group 17,Oxidation states and Oxidizing power

Oxidation States

Fluorine is the most electronegative element and always shows an oxidation state of -1. This oxidation state is the most common and stable state for all halogens. The other members display positive oxidation states (+1) with oxygen or fluorine. They can also display oxidation states of +3, +5 and +7 by utilizing vacant d orbitals. Positive oxidation states are displayed in halogen oxides and interhalogens. Oxidation states of +4 and +6 are less common and displayed in ClO_2, BrO_2, I_2O_4, Cl_2O_6 and BrO_3.

Oxidizing Power

The halogens are good oxidizing agents. Generally speaking, a higher member displaces a lower from the halide. The following reactions illustrate this point.

$F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X=Cl, Br, I)

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ (X=Br, I)

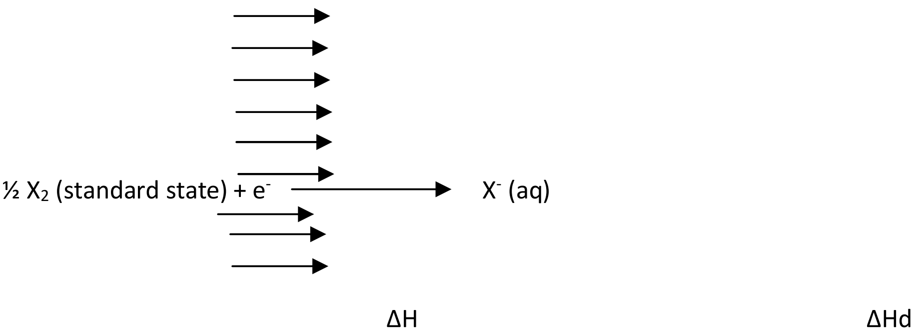
$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

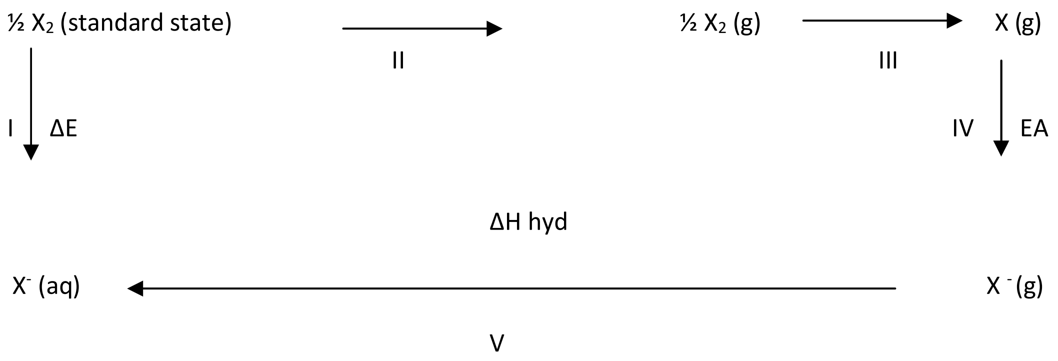
The oxidizing power decreases down the group, which is reflected in their decreasing reduction potential values.

Element	F_2	Cl_2	Br_2	I_2
E^0(V)	2.87	1.40	1.09	0.62

$\frac{1}{2} X_2 \longrightarrow 2X^- (aq)$

The strength of an oxidizing agent depends on several energy terms. The reaction represents the oxidizing action of a halogen and is best represented in the form of a Born - Haber Cycle





If the standard state of the halogen is solid i.e. for I_2, ΔH is the sum of enthalpy of fusion and enthalpy of vaporization. For a liquid halogen, i.e. Br_2, ΔH is enthalpy of vaporization. Energy is absorbed in steps II and III and released in IV and V. From Hess's law ΔE is given by:

$\Delta E = \Delta H + \Delta Hd + EA + \Delta H\ hyd$

Where ΔHd	=	enthalpy of dissociation
EA	=	electron affinity
ΔHhyd	=	enthalpy of hydration

For F_2 and Cl_2which exist as gases, ΔH is omitted. The enthalpy changes associated with the reaction (I) decrease from fluorine to iodine (Table 24). The high oxidizing power of fluorine is attributed to low enthalpy of dissociation and high enthalpy of hydration.

Table 24: Enthalpy Values for ½ X2 $\longrightarrow$ X^- (aq)

Molecule	½ΔHvap (KJmol $^{-1}$)	½ΔHdissoc (KJmol $^{-1}$)	Electron affinity (KJmol^{-1})	½ΔHhyd (KJmol $^{-1}$)	Total ΔH (KJmol $^{-1}$)
F_2	-	+79.4	-333	-460	-713.6
Cl_2	-	+121.3	-349	-348	-575.7
Br_2	+15	+96.4	-325	-318	-531.6
I_2	+30	+75.0	-295	-305	-4950

Some important reactions of halogens are listed in Table 25

Table 25: Some Reactions of Halogens

Reaction	Remarks
$X_2 + H_2 \longrightarrow 2HX$	All halogens
$nX_2 + 2M \longrightarrow 2MX_n$	Most metals form halides, reaction with F_2 vigorous
$3X_2 + 2P \longrightarrow 2PX_3$ $5X_2 + 2P \longrightarrow 2PX_5$	All halogens, similar reaction with As, Sb, Bi F_2, Cl_2 and Br_2
$X_2 + 2S$ S_2X_2 $2Cl_2 + S$ SCl_4 $3F_2 + S$ SF_6	Cl_2 and Br_2
$X_2 + H_2O$ $H^+ + X^- + HOX$ $F_2 + 2H_2O$ $4H^+ + 4F^- + O_2$	Cl_2 and Br_2
$X_2 + SO_2$ $SO_2 X_2$	F_2 and Cl_2
X_2 + Co CoX$_2$	Cl_2 and Br_2
$X_2 + H_2S$ 2HX + S	All halogens

$3X_2 + 8NH_3$ $N_2 + 6NH_4X$	F_2, Cl_2, Br_2