They occur in nature in combined state. Their main natures of occurrence are

Fluorine: Fluorspar (CaF_2), cryolite (Na_3AlF_6), fluorapatite $Ca_3(PO_4)_2$. CaF_2

Chlorine: Sea water (NaCl), rocksalt (KCl), carnalite $KCl.MgCl_2 . 6H_2O$

Bromine: sea water and salt lakes (NaBr, KBr, $MgBr_2$),I mpurities in carnallite ($MgBr_2$)

Iodine: Alkali metal iodides in sea weeds, sodium iodate $NaIO_3$ in Chile saltpeter.

ii. With bromine

a. With cold and dilute alkalies

Bromine reacts with cold and dilute alkali solution to give sodium bromide and sodium hypobromite.

$$Br_2 + 2\,NaOH \longrightarrow NaBr + H_2O + NaOBr$$

Cold and dil

Sodium hypobromite

b. With hot and conc. alkalies

Bromine reacts with hot and conc. alkali solution to bromide and bromate.

$$3Br_2 + 6\,NaOH \longrightarrow 5NaBr + 3H_2O + NaBrO_3$$

hot and conc.

Sodium bromate

iii. With iodine

a. With cold and dilute alkalies

$$I_2 + 2\,NaOH \longrightarrow NaI + H_2O + HOI$$

Cold and dil

Hypoiodous acid

b. With hot and conc. alkalies

$$3I_2 + 6\,NaOH \longrightarrow 5NaI + 3H_2O + NaIO_3$$

hot and conc.

Sodium iodate

2. Oxidizing nature of halogen:

All halogens are good oxidizing agents. The oxidizing power is in the order

$$F_2 > Cl_2 > Br_2 > I_2$$

i. Displacement reaction

Fluorine being strong oxidizing agent, it can displace other halogens (Cl_2, Br_2, I_2) from their aqueous salt.

$$F_2 + 2KCl \longrightarrow 2KF + Cl_2$$

Similarly,

Cl_2 displaces Br_2 and I_2 and Br_2 displaces I_2 .

$$Cl_2 + 2KBr \longrightarrow 2KCl + Br_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

And

$$Br_2 + 2KI \longrightarrow 2KBr + I_2$$

Uses of Chlorine

- It is used as disinfectant for sterilization of drinking water.
- Used as bleaching agent for cotton, fabric, paper, rayon, etc.
- Used in the manufacture of bleaching powder, chlorates, hydrochloric acid, chloroform, carbon tetrachloride, PVC (polyvinyl chloride), BHC (benzene hexa chloride), DDT (dichlorodiphenyl trichloroethane) and a number of organic compounds.
- Used in the preparation of poisonous gases like phosgene, mustard gas, tear gas etc.
- Used in the metallurgy of gold and platinum.
- Used as chlorinating agent in organic reactions.

Note:

HBr and HI can not be prepared in the same way as HCl by heating bromide and iodide salt with conc. H_2SO_4 respectively. Because both HBr and HI evolved are strong reducing agent. The order of reducing properties of halogen acids is as HI>HBr > HCl > HF . Therefore, they reduce conc. H_2SO_4 to SO_2 and themselves get oxidized to Br_2 and I_2 respectively.

$$2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr$$

$$2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2$$

Similarly,

$$2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow SO_2 + 2H_2O + I_2$$

Q. Why can not HBr and HI be prepared by treating conc H_2SO_4 with bromide and iodide ?

- HBr and HI are stronger reducing agent and can reduce other compounds besides above reaction shown by HCl.

$$2HX + H_2SO_4 \longrightarrow 2H_2O + SO_2 + X_2$$

(where, HX = HBr and HI)

$$2HNO_3 + 2HX \longrightarrow 2H_2O + X_2 + 2NO_2$$

(where, HX = HBr and HI)

$$2KMnO_4 + 3H_2SO_4 + 10HX \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5X_2$$

(where, HX = HBr and HI) K_2SO_4 +

$$K_2Cr_2O_7 + 4H_2SO_4 + 6HX \longrightarrow Cr_2(SO_4)_3 + 7H_2O + 3X_2$$

(where, HX = HBr and HI)

$$2HIO_3 + 5HX \longrightarrow 6H_2O + I_2 + 5X_2$$

(iodic acid) (where, HX = HBr and HI)

- HI, being the strongest reducing agent among the hydrogen halides, can also reduce $CuSO_4$ and $FeCl_3$ solution.

$$2CuSO_4 + 4HI \longrightarrow Cu_2I_2\downarrow + I_2 + 2H_2SO_4$$

(brown ppt.)

$$2FeCl_3 + HI \xrightarrow{\Delta} FeCl_2 + HCl + I_2$$

(yellow) (light green)