

Element

At. No.

Group 17 elements

F

9

[He] 2s² 2p⁵

Cl

17

[Ne] 3s² 3p⁵

Br

35

[Ar] 3d¹⁰ 4s² 4p⁵

I

53

[Kr] 3d¹⁰ 4s² 4p⁵

At

85

[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p⁵

Te

117

[Rn] 7s² 7p⁵

First four elements - Halogen (sea salt producer)

At - Radioactive + I+ (I-NaCl) I₂ NaIO₃

F₂ - superhalogen Br-MgBr₂

Abundance order F₂ > Cl₂ > Br₂ > I₂

C+ Fluoropao - CaF₂

Fluorapatite - 3Ca₃(PO₄)₂ · CaF₂

C+ Ceyolite - Na₃AlF₆

Rock salt - NaCl

F+ Sylvite - KCl

Hemihydrate - AgCl

Carnalite - KCl · MgCl₂ · 6H₂O

Atomicity is 2

F₂, Br₂, Cl₂, I₂

Physical state

F₂, Cl₂ - gases

Br₂ - liquid

I₂ - solid

Atomic Radius F₂ to I₂ ↑

I.P value - high I.P

I.P F₂ to I₂ ↓

I₂ easily form the ion

E. Negativity $F_2 > Cl_2 > Br_2 > I_2$

Electron affinity $Cl_2 > F_2 > Br_2 > I_2$

F-small size $(Cl_2) \text{ F}_2 \text{ Br}_2$
 $349 \text{ kJ} - 333 \text{ kJ} - 325 \text{ kJ}$

There will some repulsions

but added e^- and electrons present in fluorine atom.

Oxidation state $Cl^+ 2F^- [Ar] \text{ FII}$

"F" always exhibit "1" O.state

Cl, Br, I $100\% +1, +1, +3, +5, +7$ O.state

$Cl - 3s^2 3p^5$

1st E state $- 3s^2 3p^4 3d^1$

$\boxed{1s} \boxed{2s} \boxed{2p} \boxed{3s} \boxed{3p} \boxed{3d} \boxed{4s} +3$

2nd E state $- 3s^2 3p^3 3d^2$

$\boxed{1s} \boxed{2s} \boxed{2p} \boxed{3s} \boxed{3p} \boxed{3d} \boxed{4s} +5$

3rd E state $- 3s^1 3p^3 3d^3$

$\boxed{1s} \boxed{2s} \boxed{2p} \boxed{3s} \boxed{3p} \boxed{3d} \boxed{4s} +7$

25/4/23

Colour $Cl_2 - \text{yellow} \quad F_2 - \text{yellow}$

Halogen exhibit colours $Br_2 - \text{reddish brown} \quad I_2 - \text{violet}$

F_2 - yellow

$3s^2 3p^5$

Cl_2 - Greenish yellow

$3s^2 3p^5$

Br_2 - Reddish brown

$3s^2 3p^5$

I_2 - violet

$3s^2 3p^5$

Halogens exhibit colours due to excitation and de excitation.

Bond energy

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ mixed mottled

Cl_2 - high B.E

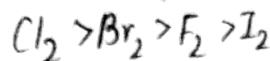
9.I dipole \rightarrow auto. 9.I

F_2 - has abnormally low B.E

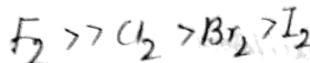
out of place $1s^2$

F - small size : $\ddot{\text{F}}-\ddot{\text{F}}$: The repulsions b/w the lone pairs of F atoms weakens the bond b/w F & F.

B.E order

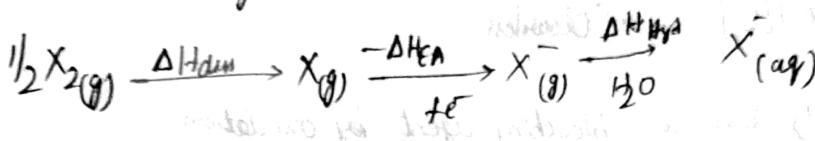


Oxidizing power



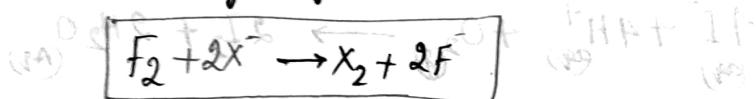
F_2 - strong oxidizing agent

- High S.R.P value

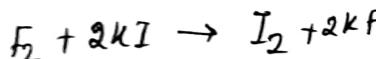
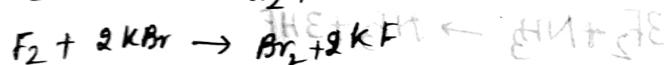


F_2 - low B.E, low E.A

has high hydration enthalpy for dissolution



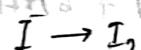
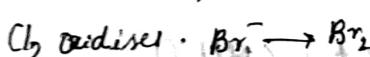
$$\text{X} = \text{Cl}, \text{Br}, \text{I}$$



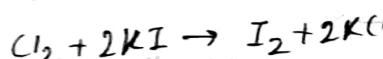
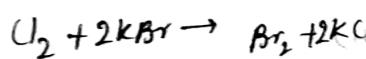
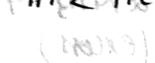
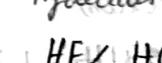
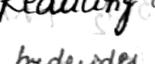
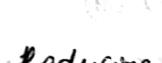
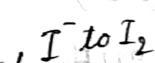
F_2 oxidizes Cl^- to Cl_2 , Br^- to Br_2 , I^- to I_2



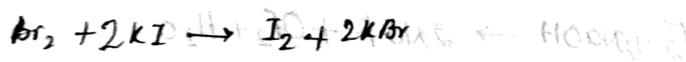
$$\text{X} = \text{Br}, \text{I}$$



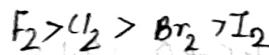
Hydrolysis



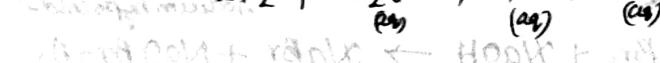
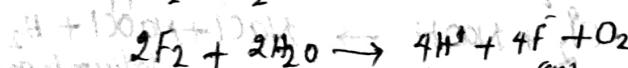
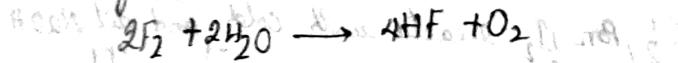
Br_2 oxidizes I^- to I_2 then I_2

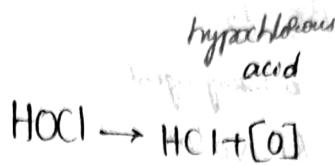
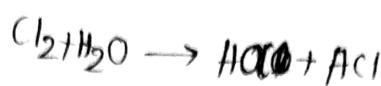
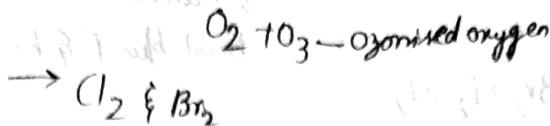


Reactivity:



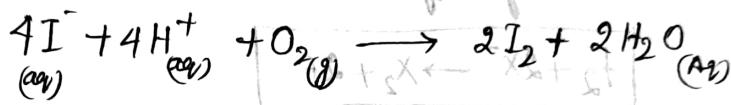
Solubility in water



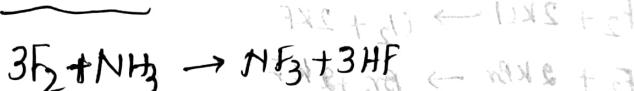


Cl_2 acts as bleaching agent by oxidation

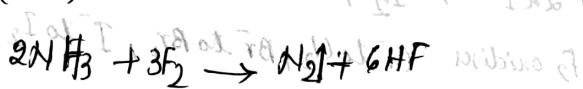
→ Solubility of I_2 in water non spontaneous



→ with NH_3



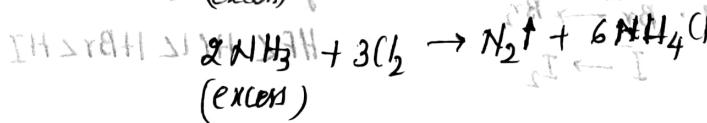
(excess)



(excess)



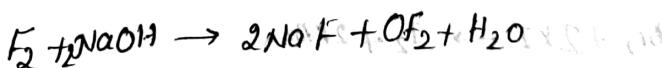
(excess)



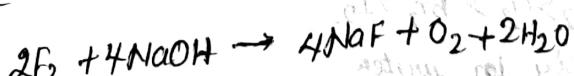
(excess)

→ with alkalis ($NaOH$)

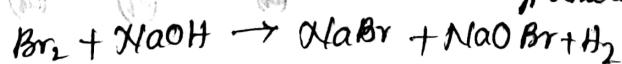
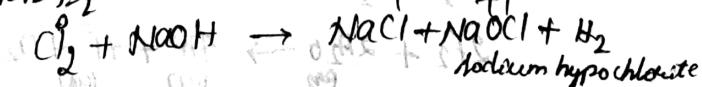
F_2 reacts with cold and dil $NaOH$

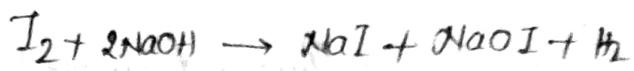


F_2 reacts with hot and conc. $NaOH$



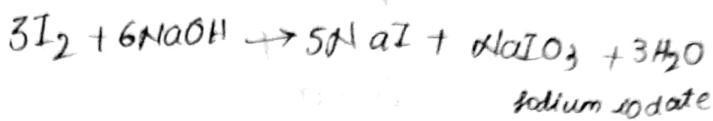
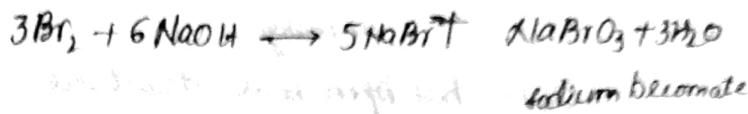
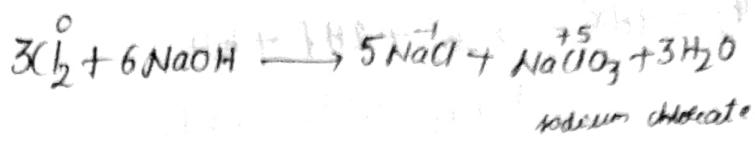
Cl_2, Br_2, I_2 reacts with cold and dil $NaOH$





above are due to disproportionation reaction.

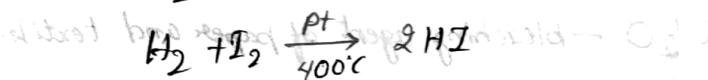
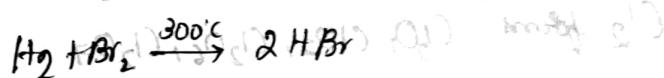
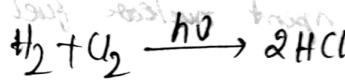
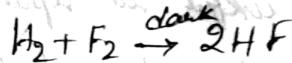
I_2, Br_2, Cl_2 reacts with hot and conc. $NaOH$



with H_2

Hydrides

Reactivity $F_2 > Cl_2 > Br_2 > I_2$



Thermal stability : $HF > HCl > HBr > HI$

A.Poeder : $HCl < HBr < HI < HF$

M.Poeder : $HI > HF > HBr > HCl$

HF has intermolecular H-bonds



Acidic nature

$HF < HCl < HBr < HI$

Conjugate base (or) Basic nature of halogen ions :

$F^- > Cl^- > Br^- > I^-$

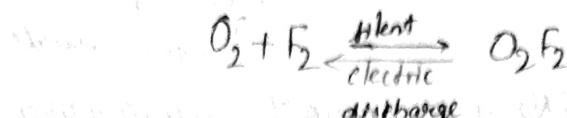
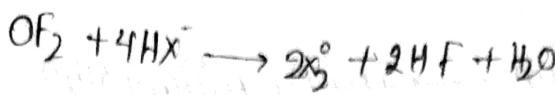
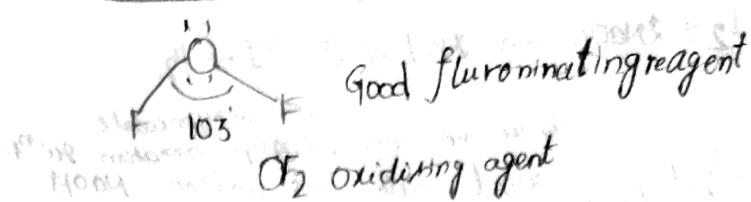
Oxides

F_2 forms O_2F_2 and OF_2 (oxygen fluorides)

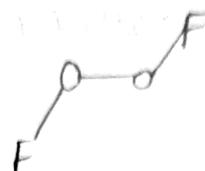
OF_2 stable at $298K$

Room temp.

$2F_2 + 2NaOH \xrightarrow{\text{dil}} NaOF + OF_2 + H_2O$



O_2F_2 has open book structure



O_2F_2 oxidises "Pu" into PuF_6

Reaction is useful to separate "Pu" from "Pu" from spent nuclear fuel.

Cl_2 forms $ClO, ClO_2, Cl_2O_6, Cl_2O_7$

Cl_2O - bleaching agent of paper and textile.

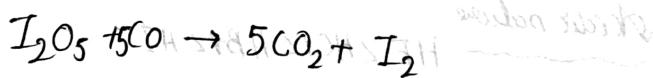
Br_2 forms unstable oxides

Br_2O, BrO_2, Br_2O_6

Stable oxide is Br_3O_6

I_2 forms I_2O_4, I_2O_5, I_2O_7

I_2O_5 - Oxidising agent



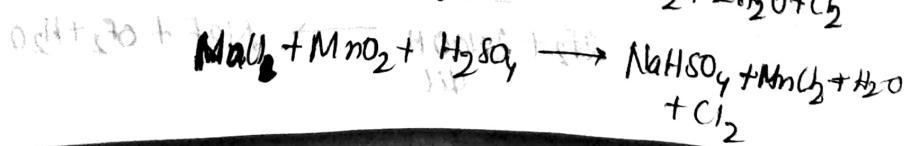
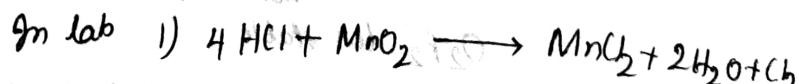
For estimation of " O " and chlorine

Stability order is $I > Cl > Br$
of oxides

27/4/23

(1) Chlorine (Cl_2) \rightarrow $Cl + Cl$ \rightarrow Cl_2

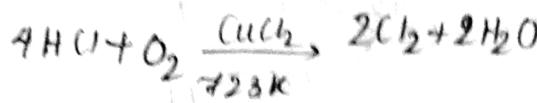
"Scheele's
method"



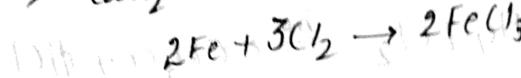
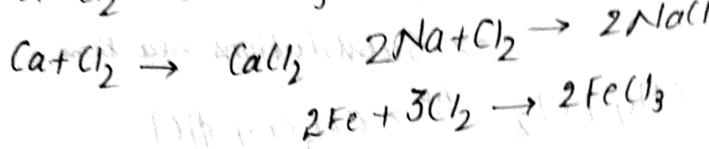
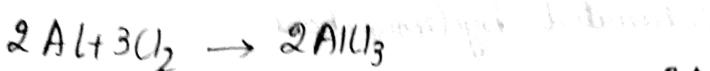
2) HCl is oxidised with KMnO₄



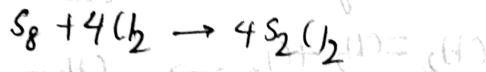
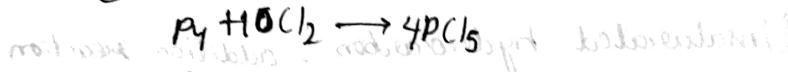
Deacon's process



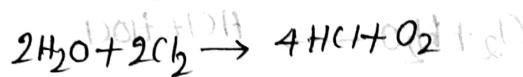
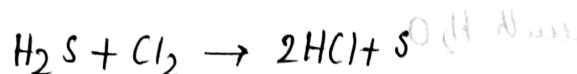
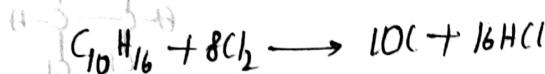
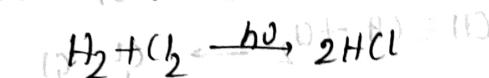
Cl_2 - greenish yellow gas, pungent smell, 2.5 heavier than air
with metals



Non-metals



Cl_2 has greater affinity towards hydrogen



\rightarrow with NH_3 $[\text{O}] + \text{H} \leftarrow \text{HOA}$

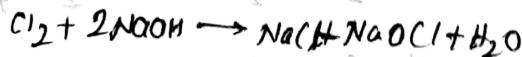
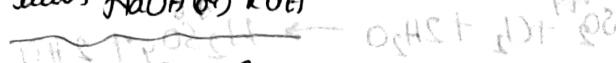


Excess NH_3 $\text{NCl}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{Cl}$

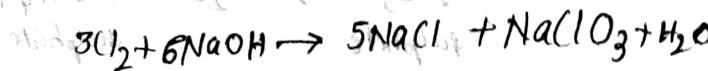


Excess $2\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH}$

with NaOH or KOH

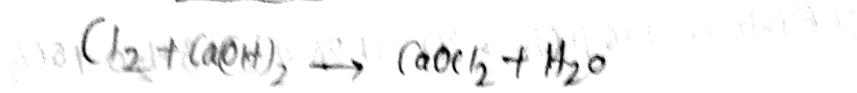


Excess $\text{NaOH} \rightarrow \text{NaOCl} + \text{H}_2\text{O}$

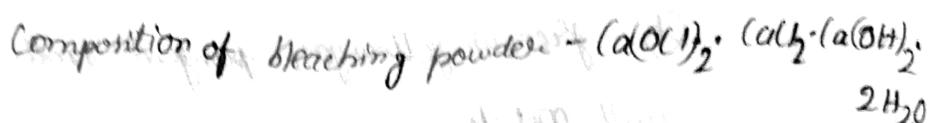
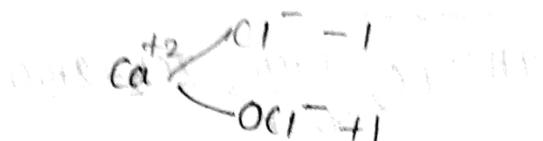


not conc

with Ca(OH)_2

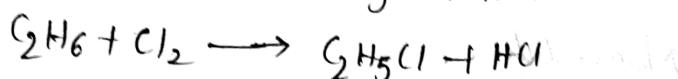


bleaching powder

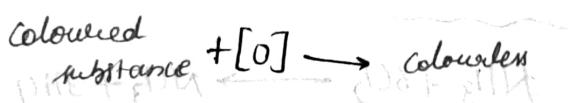
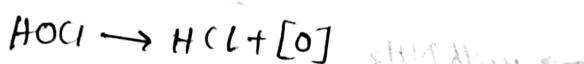
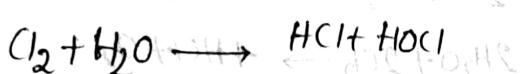
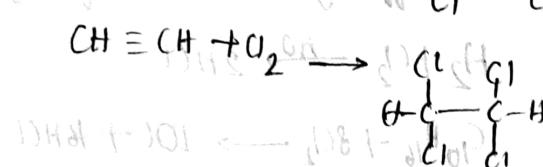
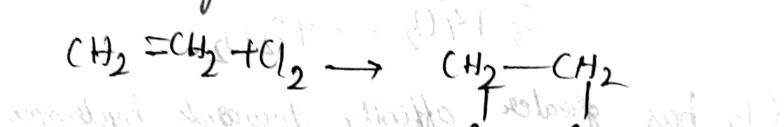


Saturated hydrocarbons

\rightarrow Substitution reactions

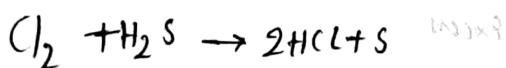


Unsaturated hydrocarbons - addition reaction



Cl_2 acts as bleaching agent by oxidation.

$\text{O} + \text{Cl}_2$ - oxidising agent + H_2O

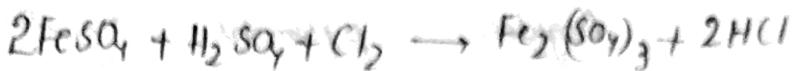


with SO_3^{2-} sulphite $\leftarrow \text{H}_2\text{O}$ sulphate

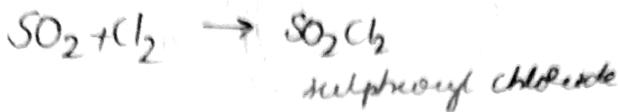
200 p 104



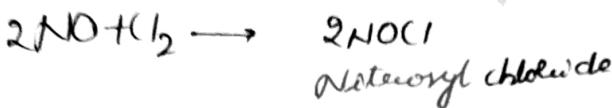
Sodium thionylphate



Addition reactions

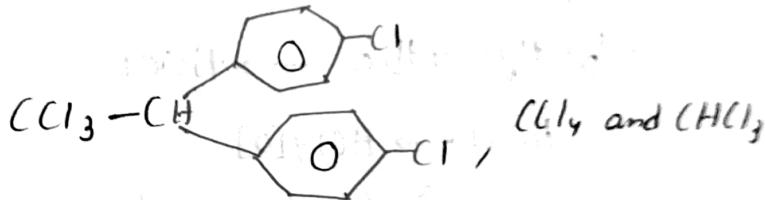


phosgene



Uses:

→ DDT



C₆H₄ and CHCl₃

→ Bleaching agent of wood, paper, cotton and textile.

→ Extraction of Au & Pt.

→ Preparation of phosgene, tear gas, mustard gas.

Oxoacids

F₂

Cl₂

Br₂

I₂

^{sp³} hybridisation

Hypohalous acid

HOF

HOCl

HOBr

HOI

(I) hypofluorous acid

hypochlorous acid

hypobromous acid

hypoiodous acid

Halogen acid

HOClO

-

Halic acid

ClO₃

-

Pearhalic acid

HClO₄

-

Acidic Nature

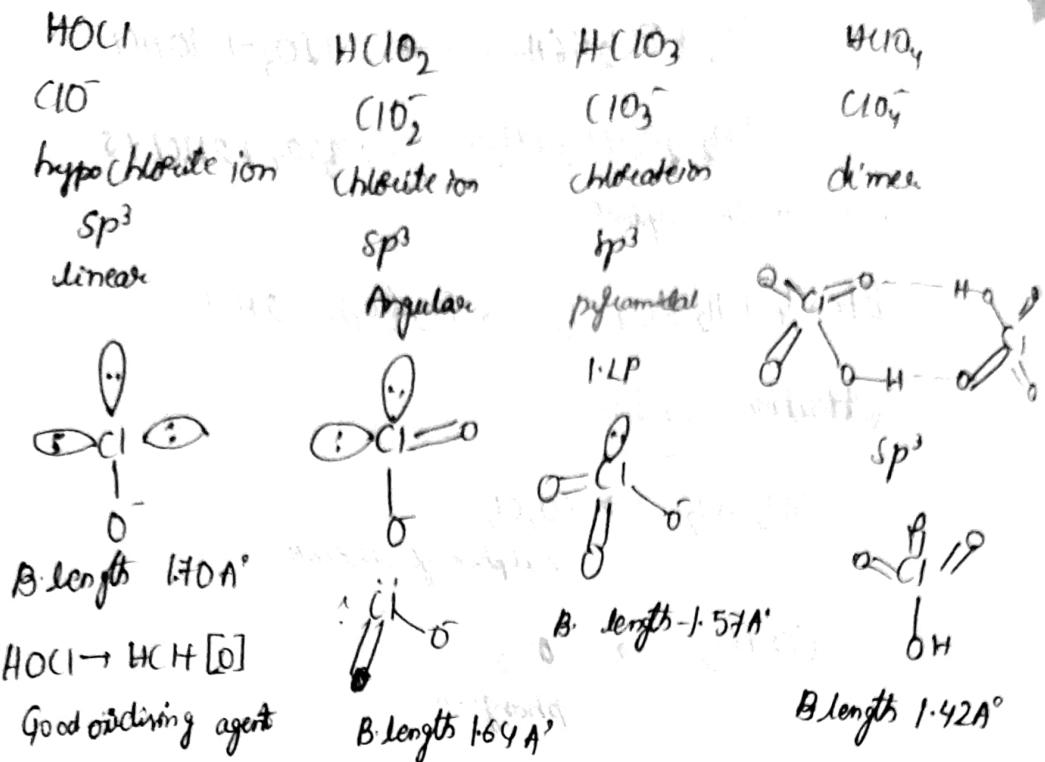
HClO₃ > HBrO₃ > HIO₃

-

HClO₄ > HClO₃ > HClO₂ > HClO

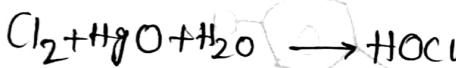
HIO₄

periodic acid

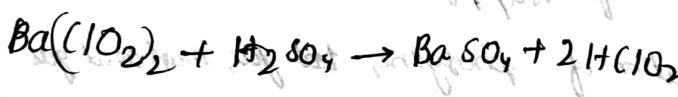
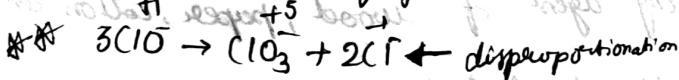


28/9/23

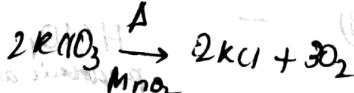
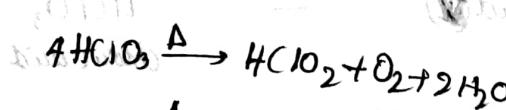
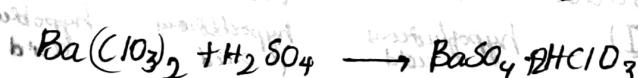
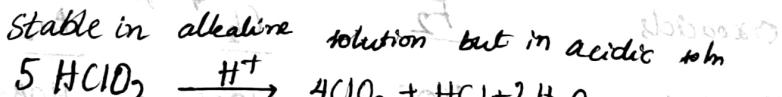
Preparation

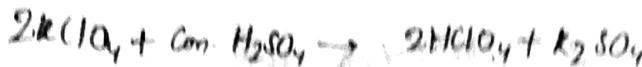


Good oxidising agent



Barium chlorite





HClO_4 - strong acid

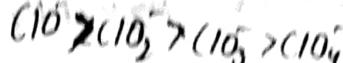
Acidity nature $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$

Thermal stability $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$

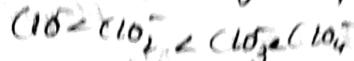
B. Order:



B. length



B.E.



Oxidising power



HCl Hydrochloric acid

"Glauber"

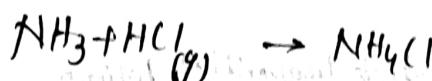
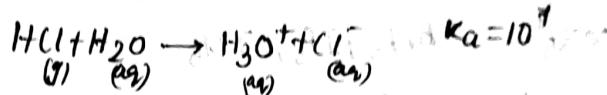


coloured gas

it can be denied by H_2SO_4

F.P - 159 K B.P - 189 K, colourless liquid

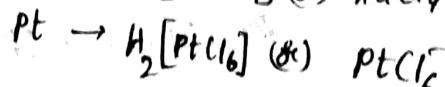
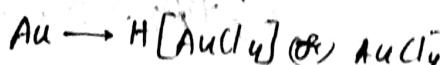
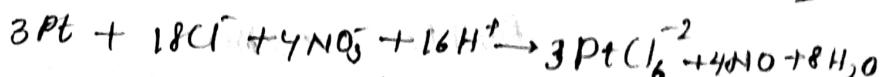
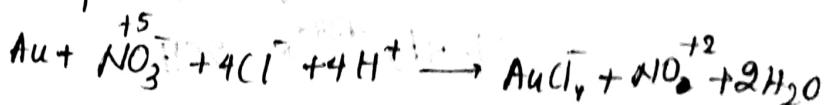
HCl - S. acid

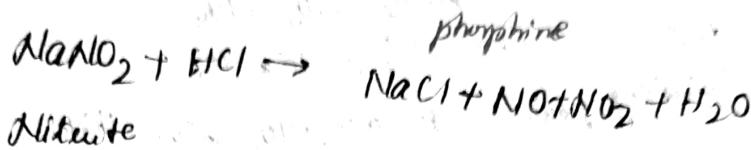
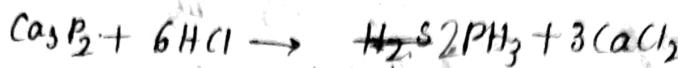
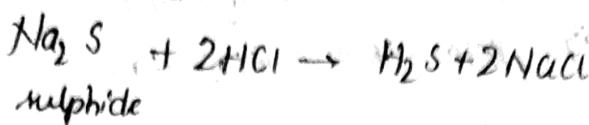
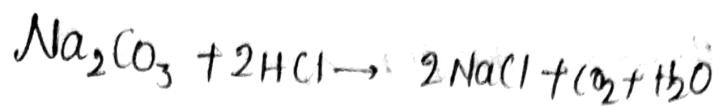


nitrate fumes

Aqua regia 3 parts of HCl + 1 part of HNO_3

Au, Pt noble metals

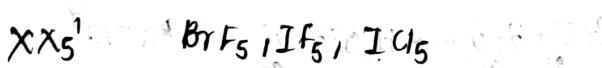
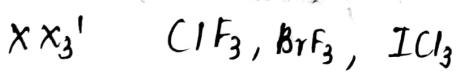
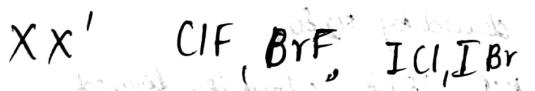




Uses:

1. Extraction of glue from bones.
2. HCl is used for the purification of bone black.
3. Preparation of Cl_2 .

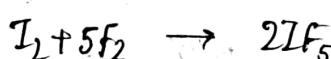
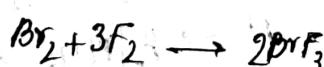
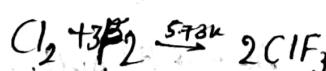
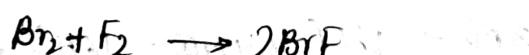
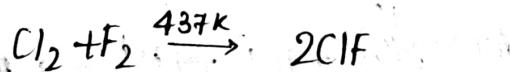
Interhalogen compounds

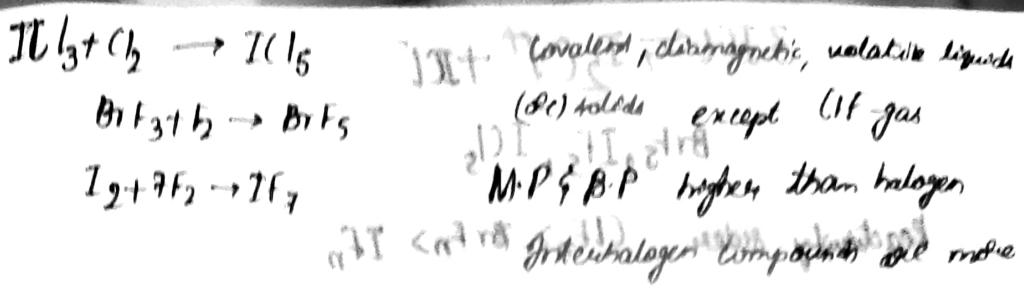


X - high electropositive halogen

X' - lower halogen

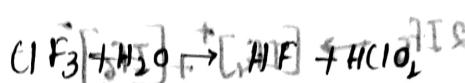
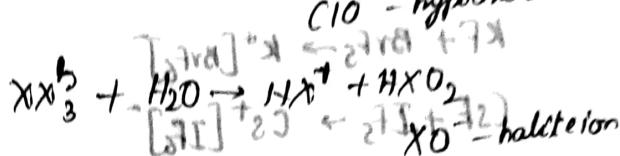
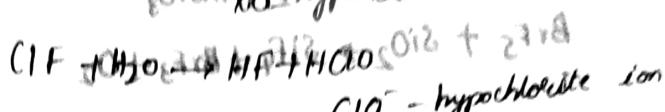
No. of atoms in interhalogen depends on Radium ratio



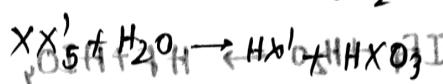


~~Hydrolysis~~ $H_2O \rightarrow HX + HXO$

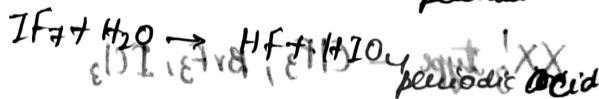
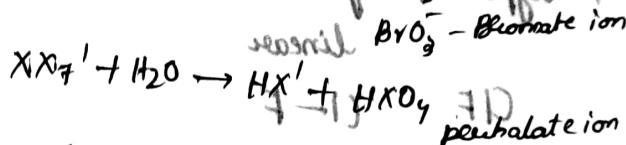
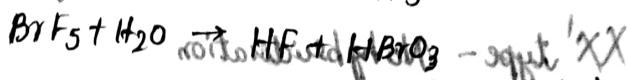
for all XO_2^- hypohalite ion



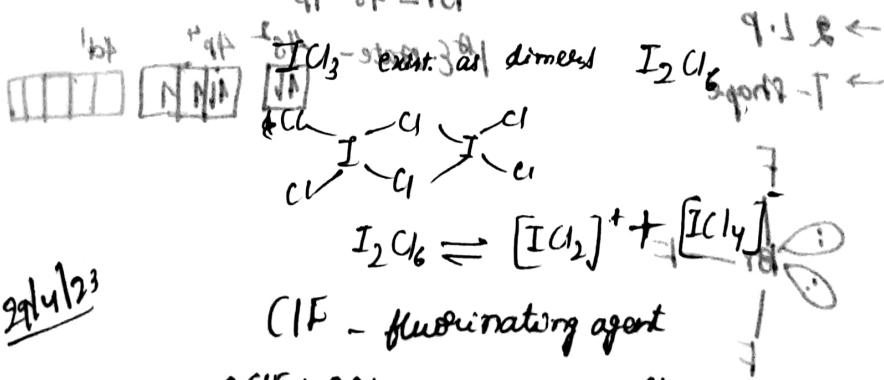
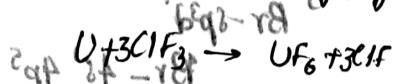
ClO_2^- - chlorite ion



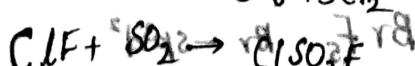
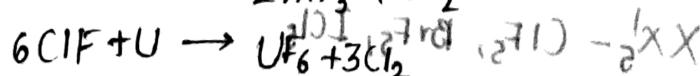
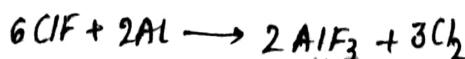
ClO_3^- \leftarrow ClO_2^- halate ion

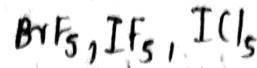
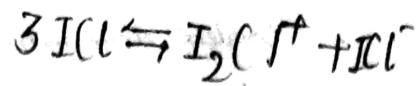


ClF₃ - good fluorinating agent

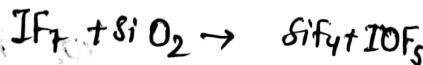
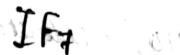
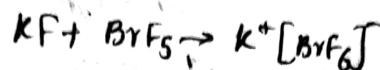
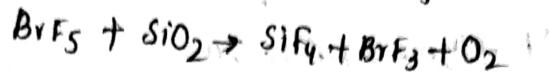
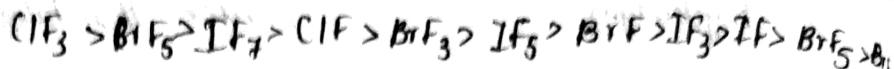


ClF - fluorinating agent





Reactivity order $\text{ClF}_n > \text{BrF}_n > \text{IF}_n$

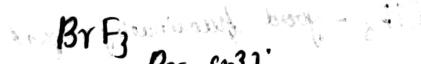


XX' type - No hybridization

linear



XX'_3 type - $\text{ClF}_3, \text{BrF}_3, \text{ICl}_3$



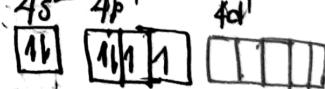
Br-sp^3d

$\text{Br} - 4s^2 4p^5$

$\rightarrow 2 \text{L.P}$

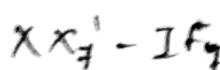
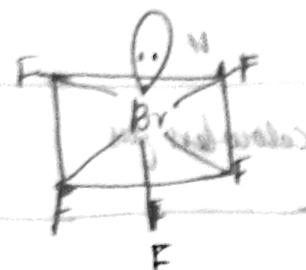
$\rightarrow \text{T-shape}$

AO E-state - $4s^2 \quad 4p^4 \quad 4d^1$





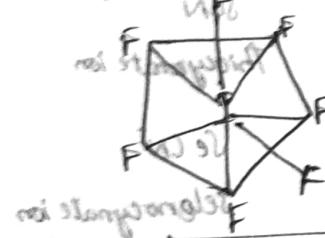
Square pyramidal



sp^3d^3 state

3d² E-state

No 2-plane
Pentagonal bipyramidal



neglect absent

neglect absent

s(N)

neglect

f(N)

neglect

(N32)

neglect angle

Type	Formula	Physical state and colour	Structure
XX'	ClF	colourless gas	Linear
	BF	pale blue/green gas	CD
	IF	detected spectroscopically gas	"
	BrCl	gas	CD
	ICl	smoky green solid (or form)	"
	IBr	black solid O-O	"
XX'_3	ClF_3	colourless gas	Bent-T shape
	BrF_3	yellow green liquid	Bent-T shape
	IF_3	yellow powder	"
	ICl_3	orange solid	"

Type	Formula	Physical State and colour	Structure
XX_5'	$NaCl$	Colourless gas	square pyramidal
	IF_5	colourless liquid	square pyramidal
	ClF_5	"	"
XX_7'	IF_7	colourless gas	pentagonal bipyramidal

Pseudo halogens



pseudo halogens



Cyanogen



Thiocyanogen



Selenocyanogen

pseudo halides & ions

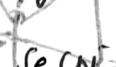


Cyanate ion

labile ligand borofuge



Thiocyanate ion

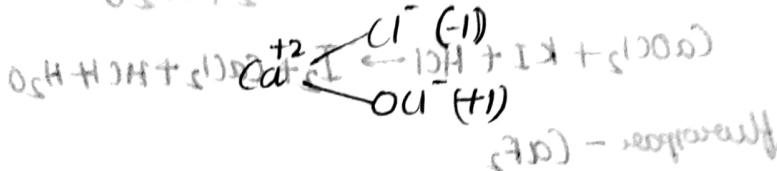
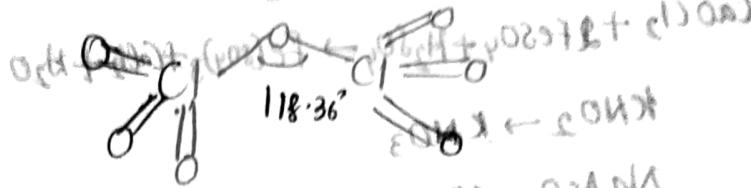
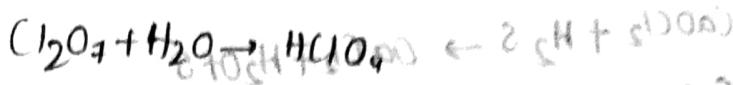


Selenocyanate ion

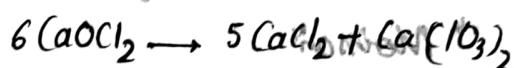
metastable	NCN^2 or brostoff borofug	N^-3 aluwot	soft
stable	cyanamide ion	azide ion + 1)	soft
"	Cl_2O	soft	soft
"	angular	soft	soft
"	ClO_2	soft	soft
"	(soft) $Cl-O-Cl$ (soft)	soft	soft
"	(soft) $Cl-O-Cl$ (soft)	soft	soft
"	(soft) $Cl-O-Cl$ (soft)	soft	soft
"	$Cl-O$ (Bd length 1.47 Å)	soft	soft
equil T - two	$2ClO_3 \rightarrow Cl_2O_6$ (soft)	soft	soft
equil T - two	bipolar weak walle	soft	soft
"	O=O	soft	soft
"	weak walle	soft	soft
"	strong walle	soft	soft
"	strong walle	soft	soft
"	strong walle	soft	soft
"	strong walle	soft	soft



trigonal pyramidal shape - Cl_2O_7



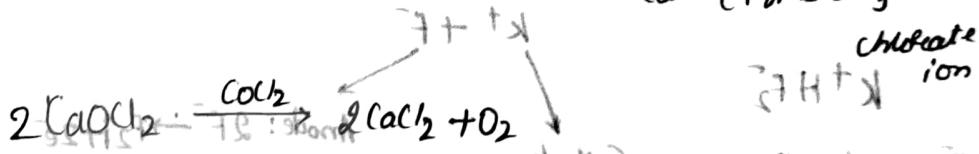
coloured amorphous powder



bottled (green) water of calcium chloride

In cold water - solution consists Ca^{+2} , Cl^- and ClO_4^- hypochlorite ion

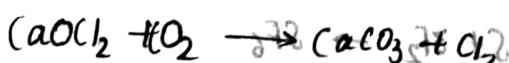
In hot water - solution consists Ca^{+2} , Cl^- and ClO_3^-



in sufficient amount $\text{H}^+ + \text{Cl}^- \leftarrow \text{K}^+ + \text{ClO}_4^-$



sufficient water then there is available gas

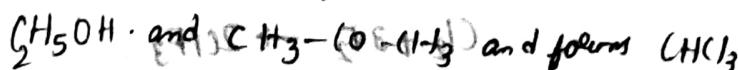


Good sample of bleaching powder

35-38% available chlorine

% of Cl_2 - 56% regulated

CaOCl_2 - bleaching agent

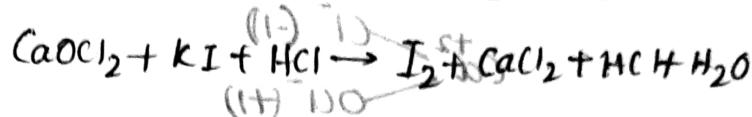
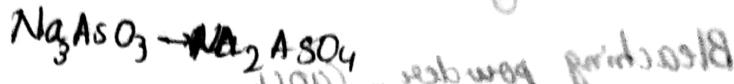
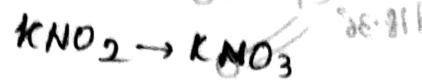
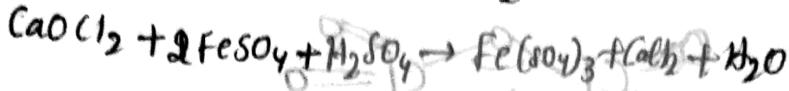
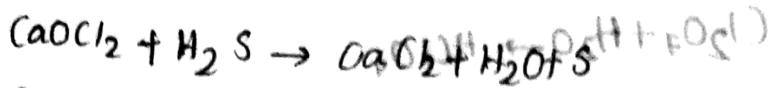


$\text{HCl} \leftarrow \text{H}^+ + \text{Cl}^-$

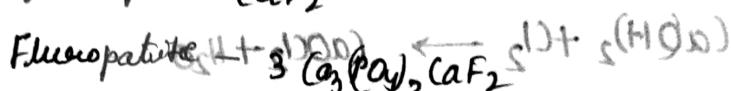
chloroform

CaOCl_2 - Good oxidizing agent

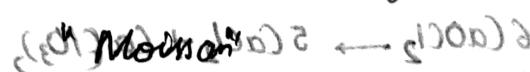
$\text{FO}_5(\text{I})$



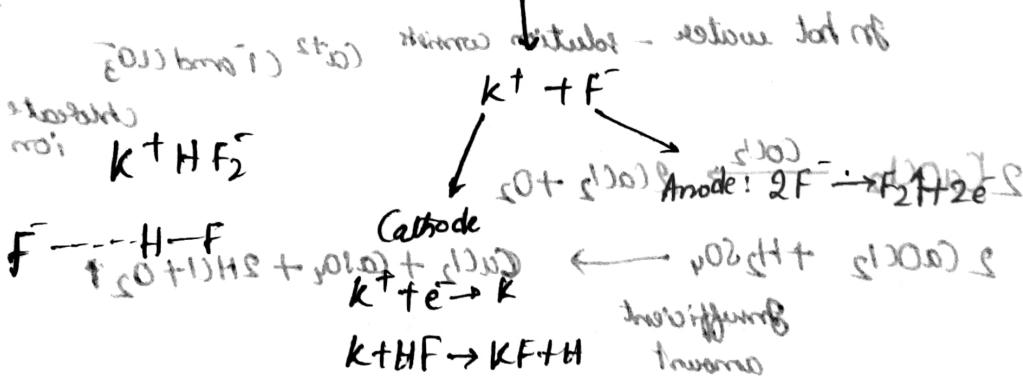
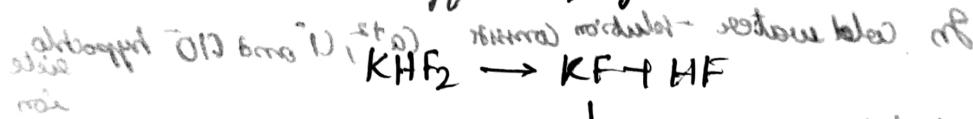
F_2 : fluoroperoxide - (CaF_2)



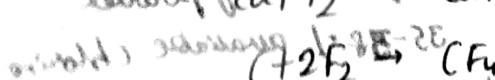
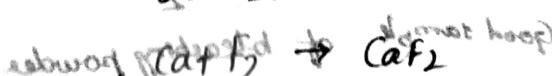
(cyclotactic Na_3AlF_6 non-polar structure)



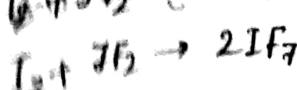
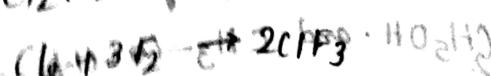
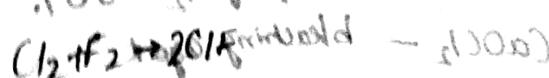
Why draw Greevy's method

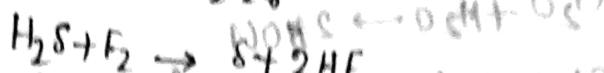
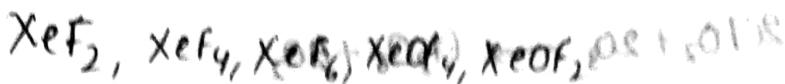


so F_2 reacts with nonmetals

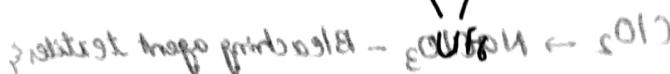
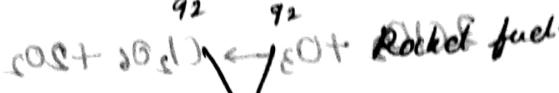
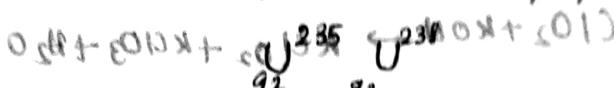
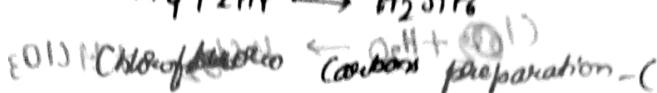


\rightarrow Interhalogen XF_2

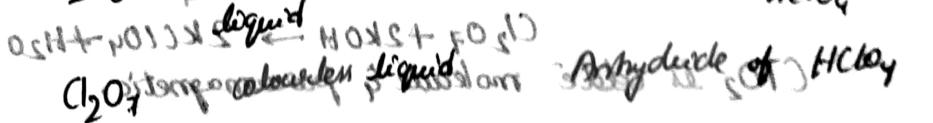
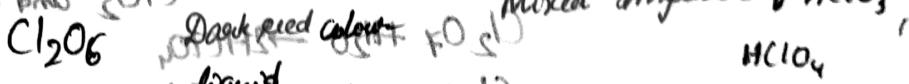
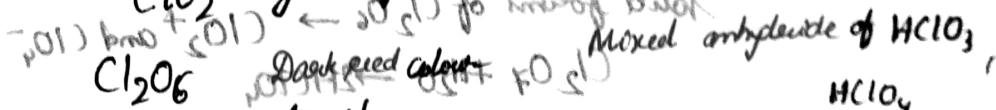
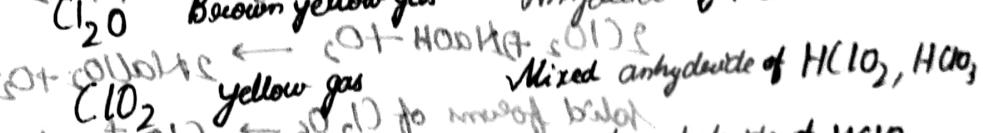
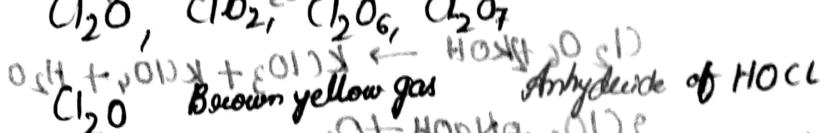
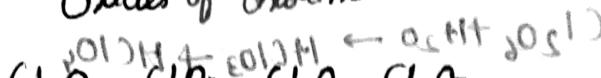




principle products to form all in halides $O_2 + O_3$
Silica in HF

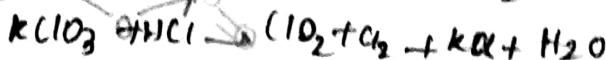
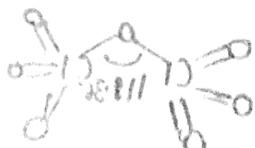
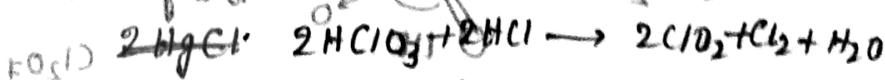
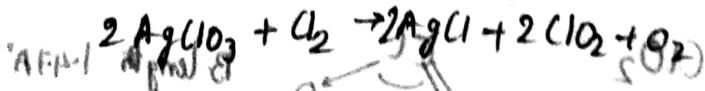
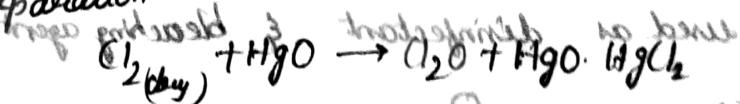


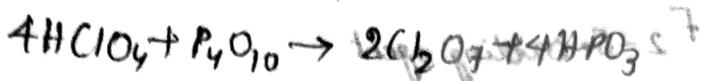
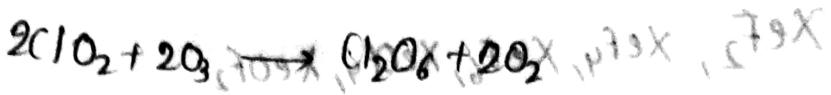
Oxides of chlorine



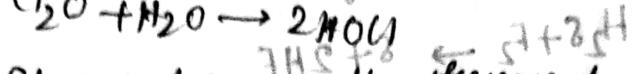
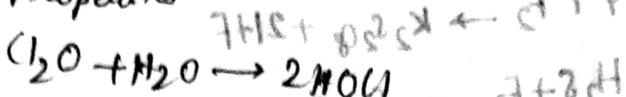
reaction involving $O_2 + O_3$ (both O_2 reactants)

Preparation

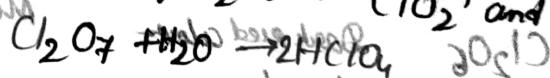
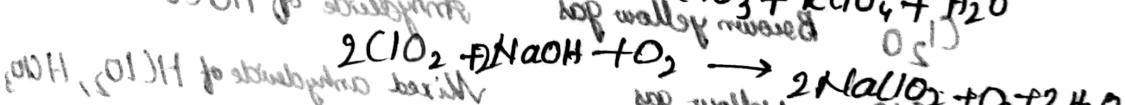
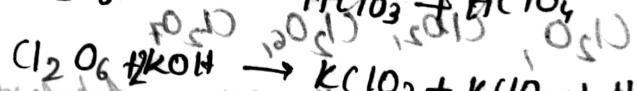
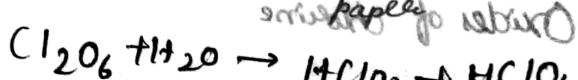
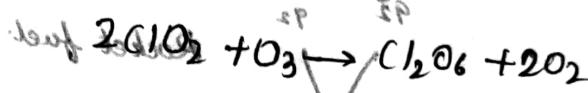
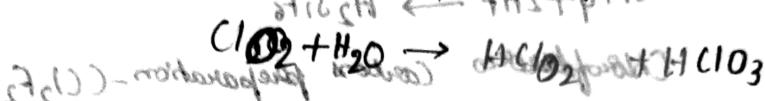
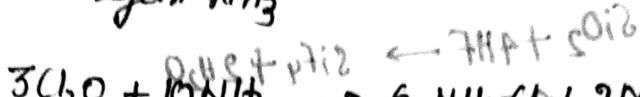




Properties



Cl_2O exploded in the presence of strong reducing agent NH_3



ClO_2 is odd molecule & paramagnetic

Mixture ClO_2 and Cl_2 in chlorine mixture, used as disinfectant & bleaching agent.

