Halogens

Salt-forming elements:

Fluorine (latin: flux)

Chlorine (greek: yellow-green)

Bromine (greek: stink)

Iodine (greek: violet)

Astatine

Halogens

Electronegativity decreasing down the group

X_2 (g)	F_2	Cl_2	Br_2	I_2
E^0 /V	2.87	1.36	1.09	0.54

Preparation of F_2 by chemical means?

(1986): $KMnO_4 + 2KF + 4HF + H_2O_2 \Rightarrow K_2MnF_6 + O_2 + 4H_2O$

$2K_2MnF_6 + 4SbF_5 \Rightarrow 4KSbF_6 + 2MnF_3 + F_2$

Halogens

	H	F	Cl	Br	I
Occurrence	.87%	.07%	1.4%	2.5ppm	.3ppm
Electron configuration	$1s^1$	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$
	[He]-1	[Ne]-1	[Ar]-1	[Kr]-1	[Xe]-1
Ionisation energy/kJmol^{-1}	1312	1681	1254	1143	1009
(cf.)	517(Li)	493(Na)	416(K)	401(Rb)	373(Cs)
Electron affinity/kJmol^{-1}	72	333	349	325	296
Electronegativity	2.2	4	3.2	3.0	2.7
Dissociation energy X_2	436	159	243	193	151
Ionic radius X^- r/Å	1.3-1.5	1.19	1.67	1.82	2.06
E_0/V $(X_2 + 2e^- \rightarrow 2X^-)$	-2.25	2.87	1.36	1.09	.54
Atomic radius/Å X_2	.32	.71	1.0	1.15	1.35
Covalent radius	.32	.54	.97	1.14	1.33
Bp/^{0}C X_2	-253	-188	-34	60	184
Mp/^{0}C X_2	-259	-219	-101	-7.3	113

10.6

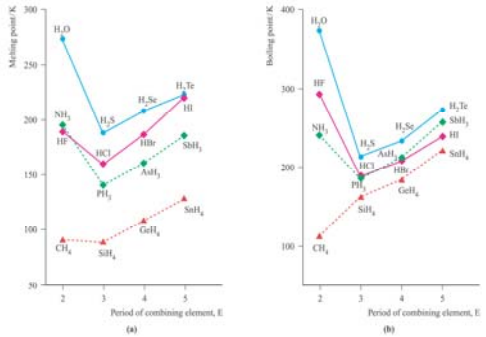


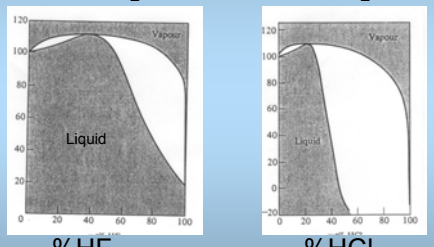
Fig. 10.6 Trends in (a) melting and (b) boiling points for some *p*-block hydrides, EH_n.

Hydrogen halides

	HF	HCl	HBr	HI
Name	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide
Bp/°C HX	19.5	-84	-67	-35
Dipolmoment/μD	1.74	1.07	0.78	0.38
Bond energy	574	428	363	295
Distance H-X /Å	.92	1.27	1.41	1.61
Aqueous solution	Hydrofluoric acid	Hydrochloric acid	Hydrobromic acid	Hydroiodic acid
Solubility of gas liter/liter water	836+	470	600	420
HX "concentrated"	(50%) 29M	(38%) 12M	(48%) 9M	(47%) 5.5M
Azeotrope Bp 1 atm	112	109	124	127
Azeotrope [HX]	(38%) 21.6M	(20%) 6.1M	(48%) 8.7M	(57%) 7.6M
Azeotrope density	1.138	1.096	1.482	1.708

Azeotrope

t °C HF – H_2O HCl – H_2O



Halides

	F^-	Cl^-	Br^-	I^-
Lewis base	hard	fairly soft	soft	soft
hydrogen bond	strong	weak	no	no
K for $X_2+X^- \leftrightarrows X_3^-$		0.2		160
pK for HX	2.9	<0	<0	<0
pL for AgX	soluble	10	12.3	16

Identification

Organic halogenides R-X or other cocalently bound halogens reacts with sodium metal to form NaX. Ionic bound halogens include Cl^-, Br^-, I^-, ClO^-, ClO_2^-, ClO_3^-,and correspondingly BrO_n^- og IO_n^- . ClO_4^- is not included. When a general formula is needed it is XO_n^-

1 $XO_n^- + nSO_2 + nH_2O \rightarrow X^- + nSO_4^{2-} + 2nH^+$

2 $X^- + Ag^+ \rightarrow AgX(s)$ (white, off-white, yellowish)

3a (ammonium carbonate) $2NH_3 + AgX \rightarrow Ag(NH_3)_2^+ + Cl^-$

3b AgBr og AgI

4a (solution from 3a) $2NH_3 + AgBr \leftarrow Ag(NH_3)_2^+ + Br^-$

4b (precipitate from 3b) $2AgX + Zn \rightarrow Ag + Zn^{2+} + 2X^-$

5 (solution from 4b) $2X^- + Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$
Br^- (unchanged)

6 Add toluene, in which I_2 is seen as a violet colour.

7 Heat while bubbling air through the solution to get rid of I_2

8 $10Br^- + 2MnO_4^- + 16H^+ \rightarrow 5Br_2 + 2Mn^{2+} + 8H_2O$

9 Add toluene, in which Br_2 is seen as a brown colour.

Quantification

1. Reduction of X to X^-
2. Insoluble silver salts

Cl^-: Ag^+ ; I: red Ag_2CrO_4

I^-, Br^-: xX Ag^+ ; SCN^- I: red $Fe(SCN)_3$

X^- even all 3 together I: potentiometry

Some fluorides of s and p elements

LiF	BeF_2, xH_2O	BF_3/ BF_4^-	CF_4	NF_3/ NF_4^+	OF_2	F_2	
NaF	MgF_2	AlF_3/ AlF_6^{3-}	SiF_4/ SiF_6^{2-}	PF_5/ PF_6^-	SF_6	ClF_{2n+1}	
KF KHF_2, $2H_2O$	CaF_2 (8:4)			AsF_6^-		BrF_{2n+1}	KrF_2
	SrF_2		$SnF_{2/4}$	SbF_3	TeF_6	IF_7	XeF_{2n}
	BaF_2		$PbF_{2/4}$	BiF_5			
AgF_2 $KAgF_4$					UF_6		

Chloro compounds of p elements

(bp/°C) → reaction with H_2O/HCl

BCl_3 (12.5) →$B(OH)_3$	CCl_4 (76.7)	NCl_3 (71) →HNO_2	ClO_2 (11) →$HClO_2$ + ClO_3^-	FCl (-100)
$AlCl_3$ Al_2Cl_6 (sub 180) →$AlCl_4^-$ $Al(H_2O)_6^{3+}$	$SiCl_4$ (57.6) →$Si(OH)_4$	PCl_5 (subl 160) →$POCl_3$ PCl_3 (76) →H_3PO_3	S_2Cl_2 (14) →H_2S SCl_2 (59) →$H_2S_xO_y$	Cl_2 (-34)
	$GeCl_4$ (83)	$AsCl_3$ (130) →H_3AsO_3 $AsCl_5$ (d) →H_3AsO_4	$SeCl_2$ (130 d)	ClBr (5)
	$SnCl_4$(114) → $SnCl_x(OH)_{6-x}^{2-}$	$SbCl_3$(223) →$SbCl_4^-$ $SbCl_5$ (140 d) →$SbCl_6^-$	Te_4Cl_4 (s)	I_2Cl_6 (s)
	$PbCl_{2\,(s)}$ →$PbCl_3^-$			

Fluorides and fluoro complexes

+1	+2	+3	+4	+5	+6	Oxstate	+1	+2	+3	+4	+5
		ScF_3							ScF_6^{3-}		
		TiF_3	TiF_4						TiF_6^{3-}	TiF_6^{2-}	
	VF_2	VF_3	VF_4	VF_5					VF_6^{3-}	VF_6^{2-}	VF_6^-
	CrF_2	CrF_3	CrF_4	CrF_5	CrF_6				CrF_6^{3-}	CrF_6^{2-}	
	MnF_2	MnF_3	MnF_4						MnF_6^{3-}	MnF_6^{2-}	
	FeF_2	FeF_3							FeF_6^{3-}		
	CoF_2	CoF_3							CoF_6^{3-}		
	NiF_2							NiF_6^{4-}	NiF_6^{3-}		
	CuF_2							CuF_4^{2-}	CuF_6^{3-}		

Chlorides and chloro-complexes

+1	+2	+3	+4	+5	+6	Oxstate	+1	+2	+3	+4	+5
		$ScCl_3$							$ScCl_6^{3-}$		
	$TiCl_2$		$TiCl_4$						$TiCl_6^{3-}$	$TiCl_6^{2-}$	
	VCl_2	VCl_3	VCl_4	VCl_5					VCl_6^{3-}, VCl_4^-		
	$CrCl_2$	$CrCl_3$	$CrCl_4$						$CrCl_6^{3-}$, $CrCl_4^-$		
	$MnCl_2$							$MnCl_4^{2-}$	$MnCl_5^{2-}$		
	$FeCl_2$	$FeCl_3$						$FeCl_4^{2-}$	$FeCl_4^-$		
	$CoCl_2$							$CoCl_4^{2-}$			
	$NiCl_2$							$NiCl_4^{2-}$			
CuCl	$CuCl_2$						$CuCl_2^-$	$CuCl_4^{2-}$			

Oxoacids

- $HOF + H_2O \rightarrow H_2O_2 + HF$
- $HXO_m + H_2O \leftrightarrows H_3O^+ + XO_m^-$

pK for $HOXO_n$ (m=n+1)

pK H_5IO_6: 1.6

Names?

m	1	2	3	4
n	0	1	2	3
Cl	7.5	1.94	-1	-10
Br	8.6		0	
I	10.6		0.8	

ClO_2 - an example

- Yellow gas (bp 11°C; mp -59) red as liquid
- Formation: $3HClO_3 \xrightarrow{H_2SO_4} 2ClO_2 + HClO_4 + H_2O$

  $2ClO_3^- + C_2O_4^{2-} + 4H^+ \rightarrow 2ClO_2 + 2CO_2 + 2H_2O$
- Radical: O–Cl–O, 117.6°, 1.47 Å cf 1.44 Å in ClO_4^-
- Very reactive (may explode) 

ClO_2 - an example