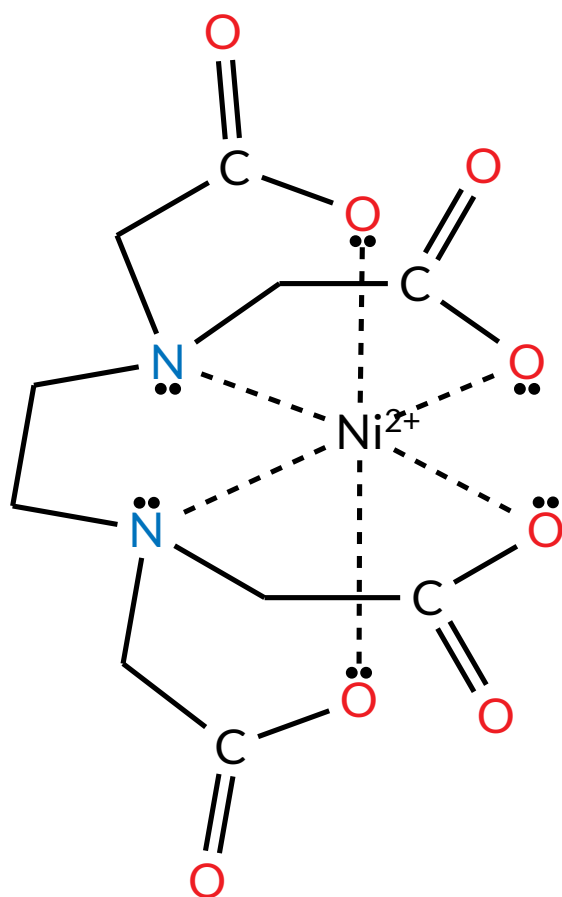


# Inorganic Chemistry



Chapters 20 to 23



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## PART I

# Group VII

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## 1 Overview

As should be familiar by now, group VII elements are the *halogens*, and are the most reactive group of non-metals. They are reactive to the point of not occurring as free elements ( $\text{Cl}_2$ ,  $\text{F}_2$ ) in nature, almost always being found as part of other compounds in an ionic state.

## 2 Physical Properties

### 2.1 Electronic Configuration

Halogens have a  $np^5$  valence shell, and so tend to form  $X^-$  ions.

F:  $1s^2 2s^2 2p^5$   
Cl:  $1s^2 2s^2 2p^6 3s^2 3p^5$   
Br:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^5$   
I:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 5p^5$

### 2.2 Various Radii

All the halogens exist as diatomic molecules with a covalent bond between the two atoms. Both the ionic radii, and the covalent radii, which is half the distance between the two atomic centres in  $X_2$ , increase down the group as expected.

The ionic radius for any halogen is always greater than its corresponding covalent radius, since the anion has one more electron, leading to greater interelectronic repulsion and hence a larger radius.

## 2.3 Bond Energy

Generally speaking the bond energies of the halogens decrease down the group, as the atomic radius increases and hence the orbital overlap decreases; this leads to a lengthening of the covalent bond, which makes it weaker.

Element	X–X bond energy $\text{kJ mol}^{-1}$
F	159
Cl	242
Br	193
I	151

The discrepancy in the F–F bond energy is due to electrostatic repulsion between the lone pairs on each F atom, which naturally would weaken the bond. This repulsion is due to the length of the bond and the size of the atoms.

## 2.4 Electron Things

### 2.4.1 First Ionisation Energy

Although the ionisation energy for halogens is typically not of great interest, it is still useful to know their trend. The trend is completely regular, with the ionisation energy decreasing down the group.

This is due to the increasing distance between the valence shell and the nucleus, increasing the shielding effect and thus reducing the energy needed to remove one valence electron.

### 2.4.2 First Electron Affinity

Of more interest is the first electron affinity, which measures the enthalpy change when adding one mole of electrons to one mole of gaseous atoms, forming one mole of singly-charged anions (if you do not recall).

In short, it is the enthalpy change to in creating  $\text{X}^-$  from X by adding  $\text{e}^-$ .

Element	First Electron Affinity $\text{kJ mol}^{-1}$
F	–328
Cl	–349
Br	–325
I	–295

The general trend is that the electron affinity decreases down the group (becomes less exothermic) since the electrostatic attraction between the new electron to be added and the nucleus decreases with increasing atomic radius.

Again, the anomaly for fluorine is due to its small size, and electron lone pairs — it takes slightly more energy to fit a new electron into the already crowded area around the fluorine atom.

### 2.4.3 Electronegativity

The trend for electronegativity is fairly regular in decreasing down the group; fluorine is the most electronegative element (ever), and iodine is the least electronegative in the group.

The decrease in electronegativity is explained by the increasing distance between the bond pair of electrons and the nucleus, which reduces the electrostatic force attracting the electrons to the nucleus.

## 2.5 Melting and Boiling Points

The melting and boiling points of the halogens are largely determined by their atomic size, and hence number of electrons. Since they exist as covalent diatomic molecules, the only intermolecular attractions are instantaneous dipole-induced dipole interactions.

Naturally, as non-polar molecules the polarisability depends only on the number of electrons. As the number of electrons increase, then so does the intermolecular force, and hence so does the melting and boiling point.

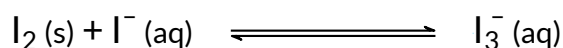
TL;DR: melting and boiling points increase down the group.  $F_2$  and  $Cl_2$  are gasses at room temperature,  $Br_2$  is a liquid, and  $I_2$  is a solid.

## 2.6 Solubility

### 2.6.1 In Polar Solvents (Water)

Generally, all the halogens except fluorine dissolve in water to *some* extent. Fluorine reacts explosively due to its high reduction potential, and oxidises water.

Chlorine and bromine react to form a number of ionic products in water in a disproportionation equilibrium, which will be discussed later. Iodine neither dissolves in water nor disproportionates (due to its low reduction potential), but can form a soluble complex  $I_3^-$  in the presence of  $I^-$  ions:



## 2.6.2 In Non-polar Solvents

It should be no surprise that the solubility of the halogens in non-polar solvents is simply a function of their polarisability, and as with their melting and boiling points, said solubility increases down the group.

## 2.7 Colours

Generally speaking the colour of the halogens increase in intensity down the group.

Element	Gaseous	Liquid/Solid	Aqueous	Non-polar
F	pale yellow	-	- goes boom -	very pale yellow
Cl	yellow-green	-	very pale yellow	very pale green
Br	reddish-brown	reddish-brown	yellow/orange	orange/reddish-brown
I	dark purple	shiny black	pale yellow	violet

Note that when concentrated in aqueous solution, the colour intensity naturally increases. Also, the  $I_3^-$  complex is brown in colour when aqueous.

### 3 Chemical Properties of the Elements

#### 3.1 Oxidation State

The most stable oxidation state for the halogens is of course -1, due to having a filled valence shell. However, chlorine, bromine and iodine have *low-lying* d-orbitals (in the number 3, 4, and 5 quantum shells respectively) that can accommodate more electrons and form more bonds. Thus, they can exist in the +1, +3, +5 and +7 oxidation states.

Examples of compounds with the halogen in positive oxidation states include  $\text{HClO}$ ,  $\text{ClF}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ , and  $\text{HClO}_4$ .

#### 3.2 Oxidising Power

As explained above, the electronegativity of the elements decrease down the group, and since they describe basically the same fundamental electron behaviour, it is no surprise that the reduction potential of the halogens decrease down the group as well.

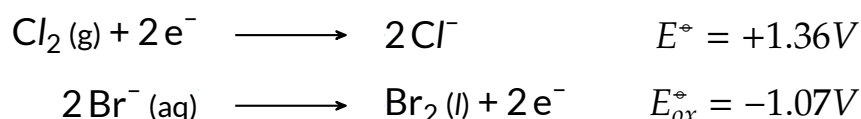
Reaction	$E^\circ/\text{V}$
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.80
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.07
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54

This means that oxidising power decreases down the group as well.

#### 3.3 Halogen Displacement

A halogen that is more reactive (ie. has a higher reduction potential) can oxidise a less reactive halogen and itself get reduced, thereby *displacing* the less reactive halogen.

For example, with  $\text{Cl}_2$  displacing  $\text{Br}^-$ :

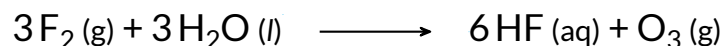
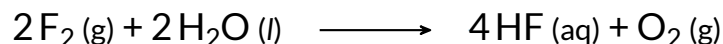


Since the  $E_{\text{cell}}^\circ$  value ( $1.36 + (-1.07) = +0.29\text{V}$ ) is positive, the reaction is feasible. Naturally were the conditions reversed, nothing would happen; bromine would not displace chloride.

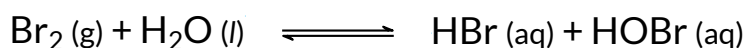
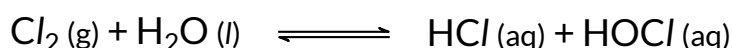


### 3.4 Reaction with Water

Fluorine reacts with water to form hydrogen fluoride and a mixture of oxygen and ozone, explosively – even when cold.



Chlorine and bromine, on the other hand, undergo a disproportionation reaction in water, in an equilibrium reaction:



Of note is that HOCl is the primary agent responsible for the bleaching mechanism in chlorine water. Also, the position of equilibrium for bromine's disproportionation is further to the left than chlorine, aka. disproportionation occurs to a *smaller* extent.

Iodine does not react with pure water.

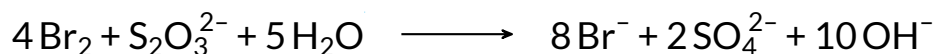
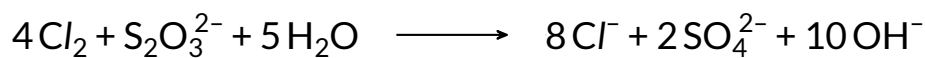
### 3.5 Reaction with Aqueous $\text{Fe}^{2+}$ Ions

A simple calculation of the  $E_{\text{cell}}^\circ$  values for the reaction would show that only chlorine and bromine are able to oxidise  $\text{Fe}^{2+}(\text{aq})$  to  $\text{Fe}^{3+}(\text{aq})$  (producing the relevant colour change). Iodine does not oxidise  $\text{Fe}^{2+}$ .

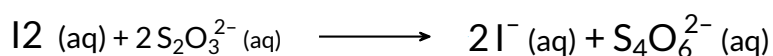
Fluorine would first explode, so it cannot react with the *aqueous* solution.

### 3.6 Reaction with Thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ) Ions

Thiosulphate ions can be oxidised by chlorine and bromine to give sulphate ions:

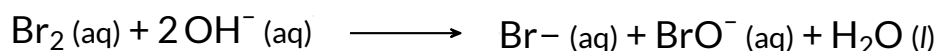
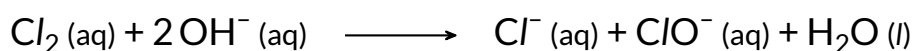


Above, sulphur is oxidised from a +2 oxidation state in thiosulphate to a +6 state in sulphate. However, iodine, given its weaker oxidation strength, can only oxidise thiosulphate to a +2.5 (yes, that's right) oxidation state, forming  $\text{S}_4\text{O}_6^{2-}$ .

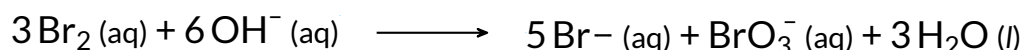
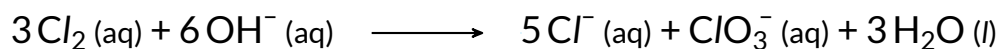


### 3.7 Disproportionation in Alkaline Solutions

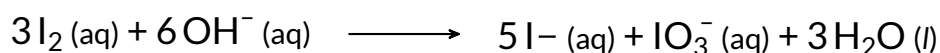
Chlorine, bromine and iodine disproportionate readily and non-reversibly in alkaline solutions to give various ions. Under cold conditions, both  $\text{Cl}_2$  and  $\text{Br}_2$  disproportionate to form the halogen in the +1 oxidation state.



The maximum temperature for the formation of  $\text{ClO}^-$  is around room temperature, while that for  $\text{BrO}^-$  is around  $0^\circ\text{C}$ . When heated, the halogen enters the +5 oxidation state instead of the +1 oxidation state.



Iodine being iodine, it enters the +5 oxidation state to form  $\text{IO}_3^-$  regardless of temperature.



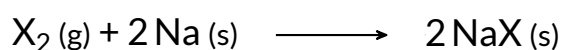
## 3.8 Reaction with Metals

Given that the halogens are oxidising agents, they can easily oxidise most reactive metals to give ionic compounds. Fluorine exceptionally can react directly with all metals, including traditionally unreactive ones such as gold and silver.

Unsurprisingly the vigour of the reaction reduces down the group.

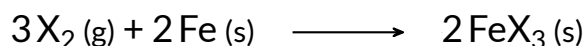
### 3.8.1 Reaction with Sodium

All 4 halogens can react with sodium, which results in the metal burning with a *bright orange* flame, forming a solid ionic product NaX.

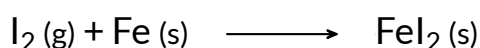


### 3.8.2 Reaction with Iron

The first 3 halogens, fluorine, chlorine, and bromine, can oxidise iron metal from the 0 oxidation state directly to the +3 oxidation state.

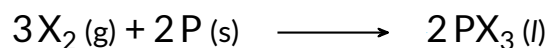


Naturally, iodine being what it is, can only oxidise iron to the +2 oxidation state.

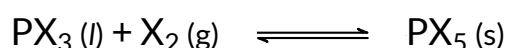


### 3.9 Reaction with Phosphorus

All of the halogens can react vigorously and irreversibly with solid phosphorus at room temperature to give phosphorus trihalides.



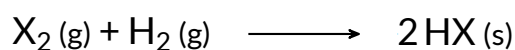
In the case of chlorine and bromine, there exists an equilibrium in excess halogen that results in the formation of  $\text{PX}_5$ .



These compound should be familiar as chlorinating and brominating agents in the nucleophilic substitution of OH groups in organic chemistry.

### 3.10 Reaction with Hydrogen

The halogens react with hydrogen gas with *decreasing vigour* down the group to form the respective hydrogen halide.



As usual, the reaction with fluorine is explosive even at  $-200\text{ }^\circ\text{C}$  and in the dark, while chlorine reacts explosively in sunlight and rapidly otherwise. Bromine reacts slowly, and typically requires heating at  $300\text{ }^\circ\text{C}$  with a Pt catalyst.

As usual, iodine's reaction is reversible and occurs slowly; the reaction is typically incomplete and a mixture of HX and  $\text{I}_2$  is obtained; this is due to the positive enthalpy change of formation.

## 4 Chemical Properties of Hydrogen Halides

### 4.1 Physical Properties

The hydrogen halides are polar, diatomic molecules. The melting and boiling points generally increase down the group, due to the larger electron cloud, which at larger sizes is the main determinant of the intermolecular attraction force.

Thing	Melting Point °C	Boiling Point °C
HF	-80	20
HCl	-115	-85
HBr	-89	-67
HI	-51	-35

The large discrepancy with HF is due to its ability to form *hydrogen bonds*, which are stronger than the *pd-pd* interactions and of course *id-id* interactions of the other halogens.

Note that other than electronegativity, the size of the negative atom also contributes to the ability to form hydrogen bonds, which is why HCl is not considered to be able to form them even though it has similar electronegativity to nitrogen and oxygen.

### 4.2 Thermal Stability

The weaker hydrogen halides can be decomposed back into  $X_2$  and  $H_2$  when heated. Naturally the temperature that is required for this decomposition decreases down the group, due to the decreasing strength of the  $H-X$  bond. HF and HCl cannot even be decomposed when heated strongly.

- HF and HCl do not decompose
- HBr decomposes on strong heating, yielding reddish-brown fumes of  $Br_2(g)$
- HI decomposes simply by contact with a hot metal rod, yielding violet fumes of  $I_2(g)$ .

### 4.3 Acid Strength

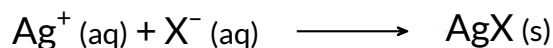
HCl, HBr and HI are strong acids that dissociate fully in water to give  $H^+(aq)$  ions.

The acid strength *increases* down the group, since the  $H-X$  bond becomes weaker, which allows for easier dissociation. However, HF notably behaves as a weak acid due to incomplete dissociation which can be attributed to the high strength of the  $H-F$  bond.

## 5 Chemical Properties of Halide Ions

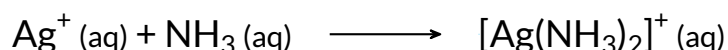
### 5.1 Precipitation Reactions

Silver ions react with halide ions in an equilibrium reaction to form insoluble AgX.



As discussed in previous chapters, the solubility of the AgX salt depends on the concentration of  $\text{Ag}^+$  and  $\text{X}^-$  ions in the solution; recall that ionic product =  $[\text{Ag}^+][\text{X}^-]$ . If IP is less than  $K_{sp}$ , then the salt will dissolve. Otherwise, the salt will precipitate out of the solution.

Upon adding  $\text{NH}_3 (\text{aq})$ , a complex ion is formed with the silver ions.



The formation of this complex reduces the concentration of  $\text{Ag}^+$  in the solution, thus decreasing the value of IP in the original reaction. When the ionic product becomes smaller than the  $K_{sp}$ , the precipitate will dissolve.

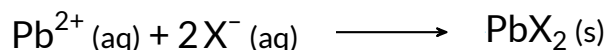
For AgCl, dilute  $\text{NH}_3 (\text{aq})$  is enough to lower the ionic product below  $K_{sp}$ , and allow the salt to dissolve. For AgBr, concentrated  $\text{NH}_3 (\text{aq})$  must be used to lower the concentration of  $\text{Ag}^+$  enough such that the ionic product becomes smaller than the  $K_{sp}$  of AgBr.

For AgI, the  $K_{sp}$  value is so small that no amount of  $\text{NH}_3 (\text{aq})$  will lower the concentration of  $\text{Ag}^+$  enough for the salt to dissolve.

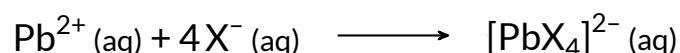
Ion	Colour of AgX	Required $\text{NH}_3 (\text{aq})$	$K_{sp}/\text{mol}^2 \text{ dm}^{-6}$
$\text{Cl}^-$	white	dilute	$1.6 \times 10^{-10}$
$\text{Br}^-$	cream	concentrated	$7.7 \times 10^{-13}$
$\text{I}^-$	yellow	nothing works	$8.3 \times 10^{-17}$

## 5.2 Reaction with Lead (II) Ions

As you might know, lead halides are insoluble. Only lead iodide ( $\text{PbI}_2$ ) is yellow, while the precipitates of the other halides are white.

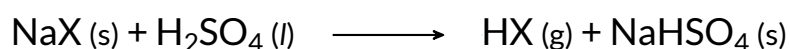


Addition of excess  $\text{X}^{-}$  will cause the precipitate to re-dissolve, since a soluble complex ion,  $[\text{PbX}_4]^{2-}$  is formed.

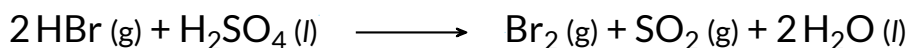
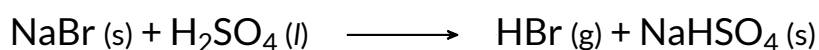


## 5.3 Reaction with Concentrated $\text{H}_2\text{SO}_4$

Generally speaking,  $\text{X}^{-}$  ions can act as a Brønsted base, accepting  $\text{H}^{+}$  ions from acids. When concentrated sulphuric acid is added to solid halide salts, this indeed occurs.

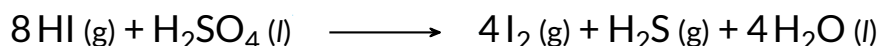
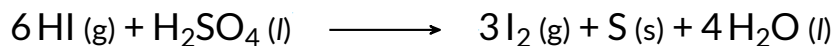
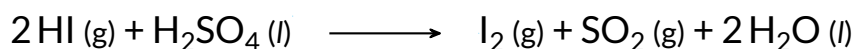
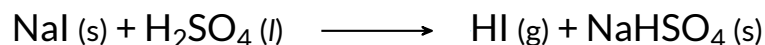


However,  $\text{H}_2\text{SO}_4$  is also a strong oxidising agent; thus, it is able to oxidise the  $\text{HBr}$  and  $\text{HI}$  formed in the acid-base reaction above. Note that it is insufficiently strong to oxidise  $\text{HF}$  and  $\text{HCl}$ .



In this reaction, most of the  $\text{HBr}$  remains untouched, and some  $\text{Br}_2(\text{g})$  is produced, leading to the observation of slight reddish-brown fumes.

Below,  $\text{H}_2\text{SO}_4$  continues to oxidise HI in a complex and frankly ridiculous manner.

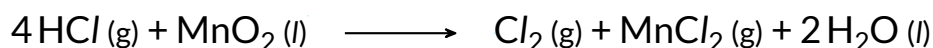
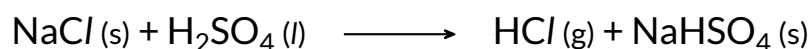


Due to the ease of oxidising HI,  $\text{H}_2\text{SO}_4$  is itself reduced, with sulphur going from a +6 oxidation state to a -2 state in  $\text{H}_2\text{S}$ . As a sidenote, it is  $\text{H}_2\text{S}$  that smells like rotten eggs. Furthermore,  $\text{SO}_2$  is also a pungent gas. This is a smelly reaction.

Most of the HI is oxidised, thus there will be a large output of violet fumes, with some white fumes of HI.

### 5.3.1 Reaction in the Presence of $\text{MnO}_2$

Manganese dioxide is a stronger oxidising agent than  $\text{H}_2\text{SO}_4$ , and thus it can serve to oxidise the HCl that sulphuric acid cannot.



### 5.3.2 $\text{H}_3\text{PO}_4$ as a Weaker Oxidising Agent

Given that sulphuric acid will obliterate HBr and HI, a less powerful oxidising agent can be used to obtain these instead of getting  $\text{Br}_2$  and  $\text{I}_2$  – concentrated phosphoric acid is such an acid.

