This page discusses the trends in some atomic and physical properties of the Group 17 elements (the halogens): fluorine, chlorine, bromine and iodine. Sections below describe the trends in atomic radius, electronegativity, electron affinity, melting and boiling points, and solubility. There is also a section on the bond enthalpies (and strengths) of halogen-halogen bonds (for example, the Cl-Cl bond) and of hydrogen-halogen bonds (e.g. the H-Cl bond).

### Trends in Atomic Radius

You can see that the atomic radius increases as you go down the Group.

![Atomic radii of the Group 7 elements](image)

The radius of an atom is governed by

- the number of layers of electrons around the nucleus
- the pull the outer electrons feel from the nucleus.

Compare the electron configurations of fluorine and chlorine:

- F: 1s²2s²2p⁵
- Cl: 1s²2s²2p⁵3s²3p⁵

In each case, the outer electrons feel a net pull of 7+ from the nucleus. The positive charge on the nucleus is cut down by the screening of the inner electrons.
This is equally true for all the other atoms in Group 17. The outer electrons always feel a net pull of 7+ from the center. The only factor which is going to affect the size of the atom is therefore the number of layers of inner electrons which have to be fitted in around the atom. Obviously, the more layers of electrons you have, the more space they will take up - electrons repel each other. That means that the atoms are bound to get bigger as you go down the Group.

### Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.

As shown in the figure above, electronegativity decreases from fluorine to iodine; the atoms become less effective at attracting bonding pairs of electrons as they grow larger. This can be visualized using dots-and-crosses diagrams for hydrogen fluoride and hydrogen chloride.
The bonding electrons between the hydrogen and the halogen experience the same net charge of +7 from either the fluorine or the chlorine. However, in the chlorine case, the nucleus is further away from the bonding pair. Therefore, electrons are not as strongly attracted to the chlorine nucleus as they are to the fluorine nucleus.

The stronger attraction to the closer fluorine nucleus makes fluorine is more electronegative.

Summarizing the trend down the group

As the halogen atoms get larger, any bonding pair is farther and farther away from the halogen nucleus, and so is less strongly attracted towards it. Hence, the elements become less electronegative as you go down the Group.

Trends in First Electron Affinity

The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions. In other words, it is the energy released (per mole of X) when the following reaction takes place:

\[X_{(g)} + e^- \rightarrow X^-_{(g)}\]

First electron affinities have negative values. For example, the first electron affinity of chlorine is -349 kJ mol\(^{-1}\). By convention, a negative sign indicates a release of energy.

The trend down the group is not consistent; the graph above shows a tendency is for the electron affinities to become more positive (less energy is given off), but fluorine does not follow this pattern. The electron affinity is a measure of the
attraction between the incoming electron and the nucleus. The higher the attraction, the higher the electron affinity.

In the larger atom, the attraction from the more positive nucleus is offset by the additional screening electrons, so each incoming electron again experiences the effect of a net $7^+$ charges from each center. An incoming electron is farther from the nucleus of the larger atom, and therefore feels a smaller attraction. The electron affinity therefore decreases down the group.

Fluorine is a very small atom, and an incoming electron is close to the nucleus. However, the new electron enters a region of space already very negatively charged because of the existing electrons. Because the fluorine atom is small, the existing electron density is very high, offsetting some of the attraction from the nucleus. This effect is enough to lower the electron affinity below that of chlorine.

**Trends in Melting Point and Boiling Point**

The figure below shows that the melting and boiling points of the halogens increase down the group. The graph clearly shows that at room temperature, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid.

All halogens exist as diatomic molecules: $\text{F}_2$, $\text{Cl}_2$, etc. The intermolecular attractions between one molecule and its neighbors are van der Waals dispersion forces. As the molecules get larger there are more electrons to move around and form the temporary dipoles that create these attractions. The stronger intermolecular attractions as the molecules get bigger means that you have to supply more heat energy to turn them into either a liquid or a gas - and so their melting and boiling points rise.
Solubility

Because fluorine reacts violently with water to produce hydrogen fluoride gas (or hydrofluoric acid, in solution) and a mixture of oxygen and ozone, analyzing its solubility is fruitless. Chlorine, bromine and iodine are soluble in water, but there is no pattern in their solubilities. The following table shows the solubility of the three elements in water at 25°C.

<table>
<thead>
<tr>
<th>Solubility (mol dm⁻³)</th>
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<tbody>
<tr>
<td>chlorine 0.091</td>
</tr>
<tr>
<td>bromine 0.21</td>
</tr>
<tr>
<td>iodine 0.0013</td>
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</tbody>
</table>

Chlorine dissolved in water is pale green. Bromine solution is yellow or dark orange-red depending the concentration. Iodine in water is pale brown. Chlorine reacts with water to some extent, giving a mixture of hydrochloric acid and chloric(I) acid (also known as hypochlorous acid). The reaction is reversible, and at any time only a third of the chlorine molecules participate in the reaction, shown below:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO} \]

Chloric(I) acid is sometimes denoted HOCl; this format better represents the actual arrangement of the atoms. Bromine and iodine react with water in a similar way, but to a much lesser extent. In both cases, about 99.5% of the halogen remains unreacted.

The solubility of iodine in potassium iodide solution

Although iodine is only slightly soluble in water, it dissolves readily in potassium iodide solution; the resulting solution is dark red-brown. A reversible reaction between iodine molecules and iodide ions produces \( I_3^- \) ions; these ions are responsible for the color. In the laboratory, iodine is often produced by oxidation of a solution containing iodide ions; this reaction should be familiar to many undergraduate students. As long as there are excess iodide ions present, the iodine reacts to form \( I_3^- \). Once the iodide ions have all reacted, iodine is precipitated as a dark grey solid—there is no reactant to keep it in solution.

Solubility in hexane

As nonpolar molecules, the halogens are much more soluble in organic solvents such as hexane than they are in water. Hexane and the halogens are all non-polar molecules whose dominant intermolecular attractions are van der Waals dispersion forces. The attractions broken (between hexane molecules and between halogen molecules) are similar in magnitude to the new attractions formed when the two substances mix.
Bond enthalpies (bond energies or bond strengths)

Bond enthalpy is the heat required to break one mole of a covalent bond to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms. For chlorine, Cl\(_2\)(g), it is the heat energy required to carry out this change per mole:

\[
\text{Cl} - \text{Cl}(g) \rightarrow 2\text{Cl}(g).
\]

Below is the same reaction with bromine:

\[
\text{Br} - \text{Br}(g) \rightarrow 2\text{Br}(g).
\]

Note: GAS not liquid!

Bond enthalpy in the halogens, X\(_2\)(g)

A covalent bond occurs because the bonding electron pair is attracted to both the nuclei at either side of it. It is that attraction which holds the molecule together. The size of the attraction depends, among other things, on the distances from the bonding pair to each of the two nuclei.

As mentioned before, the bonding pair feels a net attraction of 7+ from both ends of the bond. As the atoms get larger
down the group, the bonding pair is progressively farther from the nuclei; it is reasonable to expect the bond strength to decrease. The figure below shows the actual bond enthalpies of the diatomic halogens:

The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decrease as predicted, but the F-F bond enthalpy deviates significantly. Because fluorine atoms are so small, a strong bond is expected; in fact, it is remarkably weak. In addition to the bonding electrons between the two atoms, each atom has 3 non-bonding pairs of electrons in the outer level—lone pairs. If the bond length is very short (as is the case with F-F), the lone pairs on the two atoms close enough together to cause a significant amount of repulsion.

In the case of fluorine, this repulsion is great enough to counteract much of the attraction between the bonding pair and the two nuclei; this weakens the bond.

**Bond enthalpies in the hydrogen halides, HX(g)**

If a halogen atom is attached to a hydrogen atom, this effect is not observed; there are no lone pairs on a hydrogen atom. Bond enthalpies for H-X bonds are given in the figure below:
With larger atoms, the bonding pair is increasingly distant from the nucleus. The attraction is lessened, and the bond weakened—this is perfectly consistent with the data, with no complications.

This is an important factor in the thermal stability of the hydrogen halides because it indicates how easily they are broken into hydrogen and the halogen on heating. Hydrogen fluoride and hydrogen chloride are thermally stable—they do not split into hydrogen and fluorine or chlorine if heated to normal laboratory temperatures. Hydrogen bromide breaks down slightly into hydrogen and bromine on heating, and hydrogen iodide reacts to an even greater extent. Weaker bonds are more easily broken.

*Breaking the hydrogen-halogen bond is only one of the steps in the overall reaction, of course—the end products are not hydrogen atoms and halogen atoms, but the diatomic molecules H$_2$ and X$_2$. It is a useful exercise to use bond enthalpies and atomization enthalpies to calculate the overall enthalpy changes for the decomposition of the hydrogen halides. Remember that bond enthalpies only apply to substances in the gas state, and bromine and iodine would end up as liquid and solid respectively. Using atomization enthalpies for the halogens avoids this problem.*

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