

Chemguide – answers

GROUP 7: PROPERTIES OF THE ELEMENTS

1. Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It falls as you go down Group 7.

In any covalent bond involving a halogen, the bonding pair feels a net pull of 7+ from the halogen nucleus – the charge on the nucleus minus the number of inner, screening electrons. But because of the extra layers of electrons, the bonding pair gets further from the nucleus as you go down the group, and so the effect of the attraction gets less. So by definition, the electronegativity falls.

2. a) The electron affinity is a measure of the attraction between an incoming electron (to form a negative ion) and the nucleus. The higher the attraction, the higher the electron affinity. As you go down the group, the incoming electron ends up in a level further and further from the nucleus, still feeling the same 7+ net attraction (as above), but now further away. Because the overall attraction gets less, electron affinity falls.

b) Fluorine is a very small atom, and so the incoming electron is going into a region which already has a high electron density. Repulsions between the incoming electron and those already present weaken the overall attraction to the nucleus so much that the electron affinity is less than it would otherwise be.

3. Melting points and boiling points are both governed by the strength of the intermolecular attractions. In the halogens, these are simple van der Waals dispersion forces. These depend on the number of electrons in the molecules – as the molecules get bigger, movements of the greater number of electrons present lead to greater temporary dipoles and therefore greater dispersion forces. As you go down the group, more energy is needed to break these attractions, and so melting and boiling points increase.

4. a) $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$

The products are hydrochloric acid and chloric(I) acid (also known as hypochlorous acid). (Calling HCl “hydrogen chloride” is wrong! The HCl is formed in solution in water and is therefore called hydrochloric acid. “Hydrogen chloride” refers exclusively to the gas.)

You could also write HClO as HOCl.

b) Iodine molecules, I_2 , react with iodide ions to form the soluble ion I_3^- , which has a red-brown colour.

c) Hexane also only has van der Waals dispersion forces between its molecules. That means that the attractions that need to be broken in the halogen and in the hexane can be replaced by similarly sized attractions between halogen and hexane molecules. That isn't true in water, where stronger hydrogen bonds in the water have to be broken as well, but no similar attractions can be set up between halogen and water molecules.

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5. a) Apart from the fluorine case, bond enthalpies fall as you go down the group. The strength of a covalent bond is governed by the strength of the attractions between the bonding pair of electrons and the two nuclei. As the atoms get bigger, the bonding pair is getting further from the nuclei. It still feels a net charge of $7+$ from the two nuclei – but more distantly. The attraction gets less as you go down the group, and so the bond enthalpies fall.

In the fluorine case, because the atoms are so small, and the bond so short, lone pairs on the two fluorine atoms are brought close together, and this causes repulsions which weaken the bond compared with what you would otherwise expect.

b) The trend is exactly as before without the complication in the fluorine case. The halogen atoms are getting bigger, and so the bonding electrons are further from the halogen nucleus, and experience less attraction towards it. The bond is therefore more easily broken. There is no complication in the HF case, because hydrogen doesn't have any lone pairs of electrons.

c) Thermal stability falls as you go down the group. HF and HCl are very stable to heat because the bonds are very strong. HBr does decompose to an extent on heating, and HI more easily still. This is an effect of the decreasing hydrogen-halogen bond strength as you go down the group.