HYDROGEN BONDING

1. a) From HCl to HBr to HI, the halogen atom is getting bigger with more electrons. That increases the size of the temporary fluctuating dipoles which cause van der Waals dispersion forces. That makes the attractions between neighbouring molecules stronger, and so more heat is needed to separate them.

(Note: If you are really wide-awake, you will also have considered the effect of the change of halogen on the dipole-dipole interactions which will also be present. In fact, the permanent polarity of these molecules is falling, because the halogens get less electronegative from Cl to Br to I, and so there is less electronegativity difference between the halogen and the hydrogen. The permanent dipole-dipole attractions therefore fall – but not enough to counteract the effect of the increasing dispersion forces. Well done if you thought about that!)

b) Fluorine is a very electronegative element, and so the bonding electrons will be attracted strongly towards the fluorine, away from the hydrogen. That leaves the hydrogen with quite a lot of positive charge, and the fluorine quite negative.

The fluorine also has small, intense, 2-level lone pairs which will be very strongly attracted towards anything positive.

The fairly positive hydrogen on one HF molecule will be attracted to one of these lone pairs on a nearby HF molecule. This is a hydrogen bond.

Hydrogen bonds are attractions between a δ+ hydrogen on one molecule and a lone pair on a very electronegative atom (N, O or F) on another molecule.

c) In HF, each molecule has one δ+ hydrogen and three active lone pairs. In the liquid as a whole there are therefore three times as many lone pairs are there are δ+ hydrogens. On average, then, each molecule can only form one hydrogen bond using its δ+ hydrogen and one involving one of its lone pairs. The other lone pairs are essentially wasted.

In water, there are two δ+ hydrogens on each molecule and two lone pairs. Because the numbers are equal, each water molecule in the liquid could in principle form four hydrogen bonds, two using the δ+ hydrogens and two using the lone pairs.

d) This time, there are too many δ+ hydrogens and not enough active lone pairs. That means that on average each ammonia molecule can form one hydrogen bond using its lone pair and one involving one of its δ+ hydrogens. The other hydrogens are wasted. So both ammonia and HF can, on average, only form two hydrogen bonds per molecule. So that isn't the reason for the difference!

The difference is that nitrogen isn't anywhere near as electronegative as fluorine. There will be less positive charge on the hydrogens, and less negative charge on the nitrogen. The attractions will therefore be rather weaker between the δ+ hydrogens and the lone pairs on nearby molecules.
2. a) ethanol, CH₃CH₂OH
   van der Waals dispersion forces, dipole-dipole interactions and hydrogen bonding
   (Don't forget that there may be more than one type of intermolecular force operating in any one
   substance. In this case, there is a permanent dipole because of the oxygen, and hydrogen bonding
   as well because of the hydrogen attached directly to the oxygen. All molecules will have dispersion
   forces. If you got this wrong, rethink the whole of this question before you go any further.)

b) ethoxyethane, CH₃CH₂OCH₂CH₃
   van der Waals dispersion forces and dipole-dipole interactions
   (The molecule is V-shaped around the oxygen, and so has a permanent dipole. If everything was in
   a straight line, there wouldn't be any overall polarity, but it isn't like that. If you aren't sure about
   this, re-read the page http://www.chemguide.co.uk/atoms/bonding/electroneg.html There are no
   hydrogens attached directly to the oxygen and so there isn't any hydrogen bonding.)

c) hydrogen sulphide, H₂S
   van der Waals dispersion forces and dipole-dipole interactions
   (Sulphur is more electronegative than hydrogen and the molecule is V-shaped like water, so there
   will be a permanent dipole. Sulphur isn't electronegative enough to allow hydrogen bonding.)

d) ethylamine, CH₃CH₂NH₂
   van der Waals dispersion forces, dipole-dipole interactions and hydrogen bonding
   (The molecule has a permanent dipole because of the nitrogen, which is also electronegative enough
   to allow hydrogen bonding – and there is a hydrogen attached to it, so hydrogen bonding can
   happen.)

e) sulphuric acid, H₂SO₄, bonded as:
   \[
   \begin{array}{c}
   \text{H} \\
   \text{O} \\
   \text{S} \\
   \text{O} \\
   \text{H} \\
   \text{O} \\
   \end{array}
   \]
   van der Waals dispersion forces, dipole-dipole interactions and hydrogen bonding
   (It is an unsymmetrical molecule and so has a permanent dipole, and the hydrogens attached to
   oxygen are obvious candidates for hydrogen bonding.)

f) chloroethane, CH₃CH₂Cl
   van der Waals dispersion forces and dipole-dipole interactions
   (There is a permanent dipole because of the chlorine.)

g) fluoroethane, CH₃CH₂F
   van der Waals dispersion forces and dipole-dipole interactions
   (There is a permanent dipole because of the fluorine. Don't fall into the trap of thinking this must
   be different from the last example. It isn't! Although it has a fluorine which you may associate
   with hydrogen bonding, there isn't a hydrogen attached directly to it.)

h) hexane, CH₃CH₂CH₂CH₃CH₂CH₃
   van der Waals dispersion forces
   (Although each C-H bond has a slight dipole, overall these cancel each other out to give no
   permanent dipole on the molecule as a whole.)
3. a) Propanone has a very electronegative oxygen atom with its active lone pairs, but there isn't a sufficiently positive hydrogen atom. In trichloromethane, the chlorine lone pairs at the 3-level aren't active enough, and the chlorine isn't electronegative enough, to form hydrogen bonds.

b) In trichloromethane, the pull on the electrons from the three chlorines gives the hydrogen atom quite a lot of positive charge. The lone pairs on the chlorines aren't intense enough for the hydrogens to form hydrogen bonds in pure trichloromethane, but they can form hydrogen bonds with the lone pairs on oxygens when it is mixed with propanone.

Well done if you got this right!