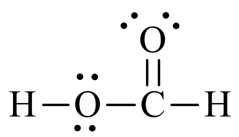
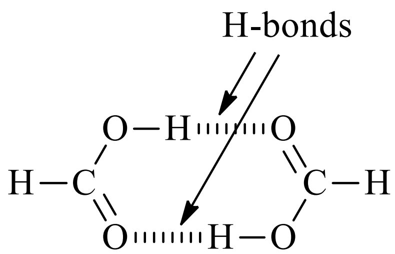
Marks 5

- Complete the Lewis structure of formic acid below by adding double bond(s) and lone pair(s).



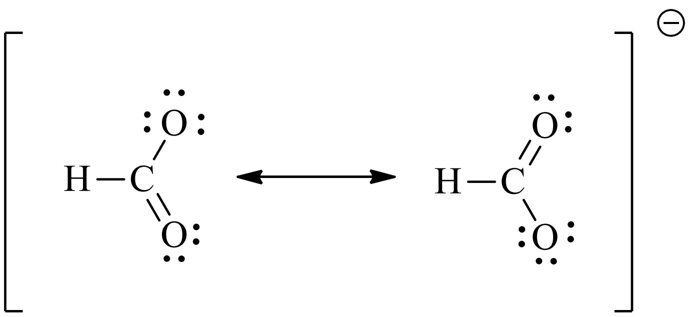
Formic acid can form dimers in which two molecules are paired by mutual hydrogen bonding. Draw a dimer of formic acid, clearly showing the hydrogen bonds between the molecules.



Formic acid may lose H^+ from the oxygen to give a formate ion, shown in Equation 1.

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq) \qquad \text{Equation 1}$$

Draw a Lewis structure of the formate ion and use it to illustrate the concept of resonance.



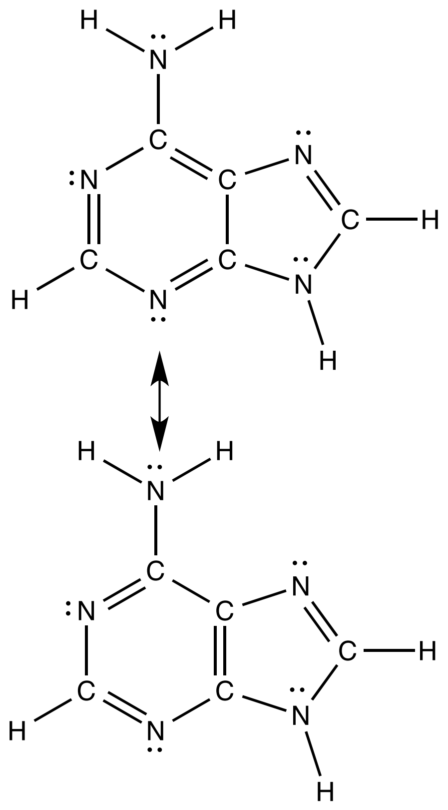
Comment on the carbon-oxygen bond lengths in formic acid and the carbon-oxygen bond lengths in the formate ion.

In formic acid, the C=O double bond is shorter than the C–O bond. In the formate ion, the two C–O bonds are identical because of resonance and hence are the same length.

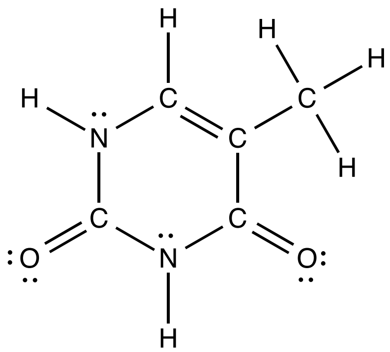
THIS QUESTION IS CONTINUED ON THE NEXT PAGE.

Marks
5

- By adding double bonds and lone pairs, complete the structural formulae of the nitrogen bases adenine and thymine below.

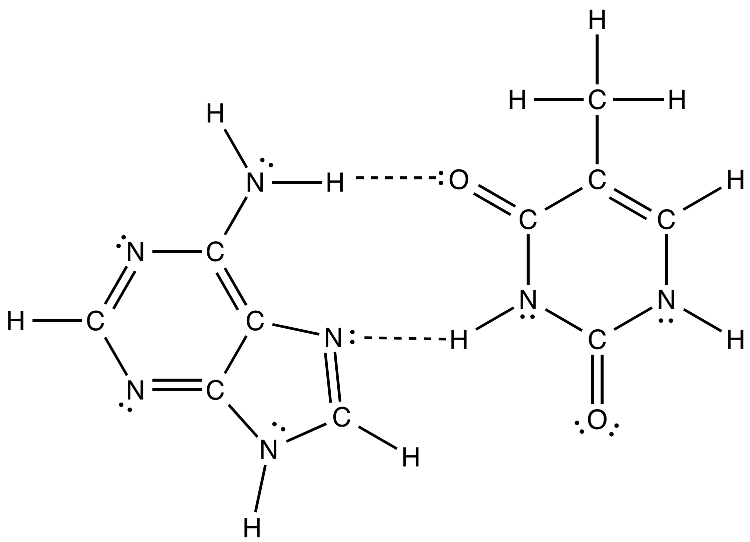


adenine



thymine

In DNA, these two molecules interact through two hydrogen bonds. Redraw the structures below showing the alignment of the two molecules that allows this to occur and clearly show the hydrogen bonds.



Marks
3

- The boiling point of NH_3 is –33 °C and that of HF is +20 °C. Explain this difference in terms of the strengths of the intermolecular forces between these molecules.

The strongest intermolecular force in both comes from hydrogen bonding.

Each HF molecule possesses 3 lone pairs on F and 1 H. HF molecules on average make 2 H-bonds.

Each NH_3 molecule possesses 1 lone pair on N and 3 H. NH_3 molecules on average also make 2 H-bonds.

As fluorine is more electronegative than nitrogen, the H-F bonds are much more polar than the N-H bonds. Due to the higher partial charges on H and F in HF, a hydrogen bond between HF molecules is stronger than that between NH_3 molecules.

The higher boiling point of HF is thus due to stronger H-bonds.

Explain why the boiling point of water (100 °C) is higher than both HF and NH_3.

The polarity of the O-H bonds in H_2O is intermediate between that of H-F and N-H bonds. It is expected that the individual H-bonds between H_2O molecules will also be intermediate in strength.

Each H_2O molecule possesses 2 lone pairs on O and 2 H. H_2O molecules are thus able to form an average of 4 H-bonds.

H_2O has a higher boiling point than NH_3 because (i) the H-bonds are stronger and (ii) it contains twice as many H-bonds.

H_2O has a higher boiling point than HF because it contains twice as many H-bonds, despite these being individually weaker.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- Rank the following compounds in order of increasing boiling point? Justify your answer. **3**

$CH_3CH_2OCH_2CH_3$, CH_3OH, CH_4, CH_3CH_3, CH_3CH_2OH

CH_4 < CH_3CH_3 < $CH_3CH_2OCH_2CH_3$ < CH_3OH < CH_3CH_2OH

Only weak dispersion forces act in CH_4 and CH_3CH_3. The bigger molecule has more interactions and hence the higher b.p. $CH_3CH_2OCH_2CH_3$ is a bigger molecule than CH_4 and CH_3CH_3, so has more dispersion forces. It also has dipole-dipole forces due to the polarised C-O bonds.

CH_3OH and CH_3CH_2OH have hydrogen bonds due to the very electronegative O atom bonded to the H atom. These H-bonds are much stronger than the dispersion and dipole-dipole forces in the other compounds and hence these two compounds have the highest boiling points. CH_3CH_2OH has more dispersion forces than CH_3OH, so it has the highest boiling point.

- Melting points of the hydrogen halides increase in the order HCl < HBr < HF < HI. Explain this trend. **2**

There are two competing intermolecular forces at play:

- **Dipole-dipole forces increase as the halogen becomes more electronegative (I < Br < Cl < F).**
- **Dispersion forces are dependent on the polarisability of the atoms and increase with the size of the halogen.**

Dispersion force dominate in HCl, HBr and HI and determines the order of their melting points.

The dipole-dipole force in HF is so strong (due to the very small and very electronegative F atom) that it is given a special name - a hydrogen bond. This causes HF to have an anomalously high melting point, which just happens to lie between that of HBr and HI.

- Rationalise the order of the boiling points of the following liquids in terms of their intermolecular forces.

3

liquid	F_2	HCl	HBr	Cl_2	HF	Br_2
b.p. (° C)	–188	–85	–67	–34	20	59

The boiling points in F_2, Cl_2 and Br_2 are determined by the size of the dispersion forces between molecules. The bigger the atoms, the more polarisable their electron clouds and the greater the dispersion forces. Hence boiling points are in order $Br_2 > Cl_2 > F_2$.

Dispersion forces also operate in HF, HCl and HBr, but here the dipole formed between the halogen atom and the hydrogen also needs to be considered. F is a very small and very electronegative atom. The H–F bond is therefore highly polarised and strong H-bonds form in this liquid. These are much stronger than dispersion forces and so HF has an anomalously high boiling point. Cl and Br are not as electronegative as F: the dispersion forces in HCl and HBr are more significant than the dipole-dipole forces as can be evidenced by the order of boiling points HF > HBr > HCl.

The values given tell us that the total of the dispersion forces in Br_2 is greater than the H-bonds in HF.

- Sodium chloride is soluble in water, magnesium oxide is not. Using your understanding of the intermolecular forces involved, explain why this is so.

3

Both sodium chloride and magnesim oxide are ionic compounds with strong electrostatic forces between the oppositely charged particles. The energy required to overcome these attractions is called the lattice enthalpy.

When the ions dissolve in water strong bonds are formed between the ions and the polar water molecules. The energy released in this process is called the solvation enthalpy.

If the solvation enthalpy exceeds the lattice enthalpy the compound will be soluble.

Sodium chloride is soluble because the magnitude of ΔH (i) is less than the magnitude of ΔH (ii):

(i) $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

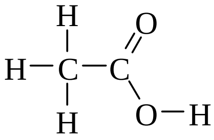
(ii) $Na^+(g) + Cl^-(g) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$

Magnesium oxide is insoluble because the magnitude of ΔH (i) is greater than the magnitude of ΔH (ii):

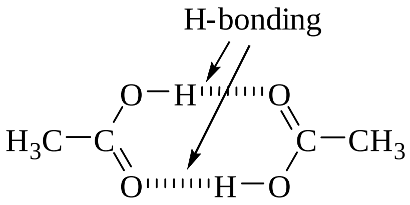
(i) $MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$

(ii) $Mg^{2+}(g) + O^{2-}(g) \xrightarrow{H_2O} Mg^{2+}(aq) + OH^-(aq)$

- The structural formula of acetic acid is shown on the right. Acetic acid forms dimers (*i.e.* pairs of molecules) in the gas phase. Draw the dimer showing the H-bonding that occurs.



1



Marks

- Which of acetone, $(CH_3)_2CO$, and water will have the greater surface tension. Why? **2**

Water will have the greater surface tension. It has much stronger intermolecular forces (H-bonds and dispersion) than acetone (dispersion and dipole-dipole forces).

- Melting points of the hydrogen halides increase in the order HCl < HBr < HF < HI. Explain this trend. **2**

The major intermolecular forces in HCl, HBr and HI are dispersion forces. The heavier the halogen is, the larger is its electron cloud and the more polarisable it is. Higher polarisability leads to stronger dispersion forces therefore leading to melting points which increase in the order HCl < HBr < HI.

F is a very small and very electronegative atom. The H–F bond is therefore highly polarised and H-bonds form. These are much stronger than dispersion forces and so HF has an anomalously high melting point. As seen by the experimental order given, this is enough to raise its melting point above that of HBr, but not above that of HI.

- Why is the solubility of chloroform ($CHCl_3$) in water 10 times greater than that of carbon tetrachloride (CCl_4) in water? **2**

The C–H bond in $CHCl_3$ is quite polarised due to the electron-withdrawing effect of the Cl atoms. $CHCl_3$ has a fairly large dipole moment with ô+ H and ô- Cl.

CCl_4 has no dipole moment. Although each C-Cl bond is fairly polar, the tetrahedral shape of the molecule leads to overall cancellation of these bond dipoles.

The polar water molecules interact better with the polar $CHCl_3$ molecules than with the non-polar CCl_4 molecules so $CHCl_3$ is more soluble.

- Rank the following compounds in order of increasing boiling point? Justify your answer. **3**

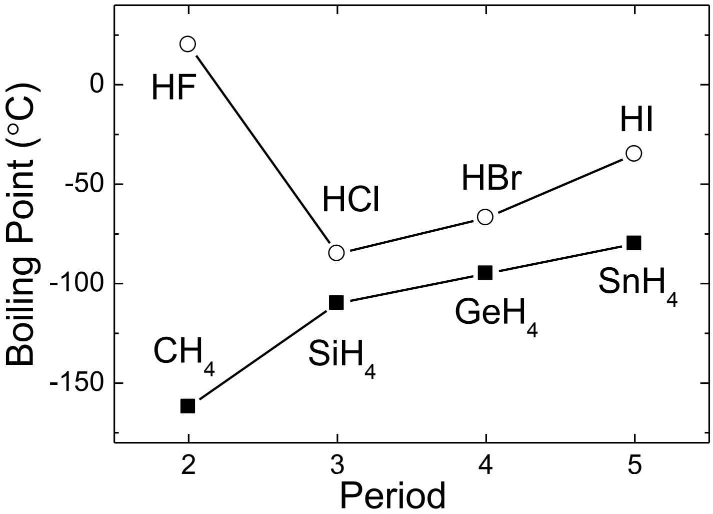
$CH_3CH_2OCH_2CH_3$, CH_3OH, CH_4, CH_3CH_3, CH_3CH_2OH

CH_4 < CH_3CH_3 < $CH_3CH_2OCH_2CH_3$ < CH_3OH < CH_3CH_2OH

- **CH_4 and CH_3CH_3 have only weak dispersion forces; CH_3CH_3 has more electrons so has the dispersion forces are stronger.**
- **$CH_3CH_2OCH_2CH_3$ has dispersion forces and, as the presence of the electronegative oxygen atom leads to a dipole moment, dipole-dipole forces.**
- **CH_3CH_2OH and CH_3OH have H attached to electronegative O atoms and so have relatively strong H-bonds as well as dispersion forces and dipole-dipole forces. CH_3CH_2OH has more electrons so has stronger dispersion forces and hence the higher boiling point.**

Marks
3

- The figure below shows the boiling points of Group 14 and 17 hydrides as a function of the period (row) of the periodic table.



A number of trends are apparent from this figure, including:
- the tetrahydrides have lower boiling points than the monohydrides,
- the boiling point increases with period, with the exception of HF.

Explain these two trends, and the reason that HF is exceptional.

The tetrahydrides are non-polar, so intermolecular attraction is due to dispersion forces only. As the period increases, the central atom gets bigger (more electrons) and its polarisability increases - hence the dispersion forces and boiling points increase.

The monohydrides are polar, so they have dipole - dipole attractions as well as dispersion forces. Hence they have higher boiling points than corresponding tetrahydride from same period.

HF is anomalous as the F atom is very small and very electronegative. HF is therefore able to form strong H-bonds, which are relatively strong intermolecular attractions. This results in an exceptionally high boiling point for HF.