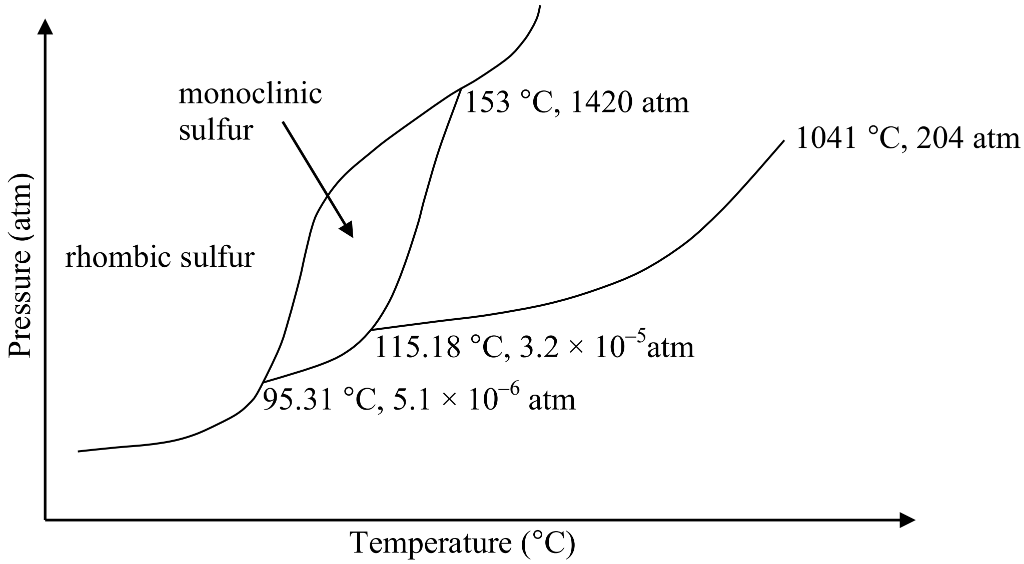
Marks 6

- The diagram below shows the phase diagram of sulfur. Note that 'rhombic' and 'monoclinic' refer to two different crystalline forms of the element.



Determine the number of triple points for sulfur and indicate which species are present at each of the triple points.

There are 3 triple points:

- **rhombic, monoclinic and vapour (at 95.31 °C and 5.1×10^{-6} atm);**
- **monoclinic, liquid and vapour (at 115.18 °C and 3.2×10^{-5} atm);**
- **rhombic, monoclinic and liquid (at 153 °C and 1420 atm);**

Which crystalline form of sulfur is predicted to be more dense? Briefly explain your answer.

The rhombic allotrope is denser. If you start in the monoclinic region and increase the pressure at constant temperature *(i.e.* draw a vertical line upwards) you move into the rhombic region. Rhombic is thus the more stable form at higher pressures, so must be denser.

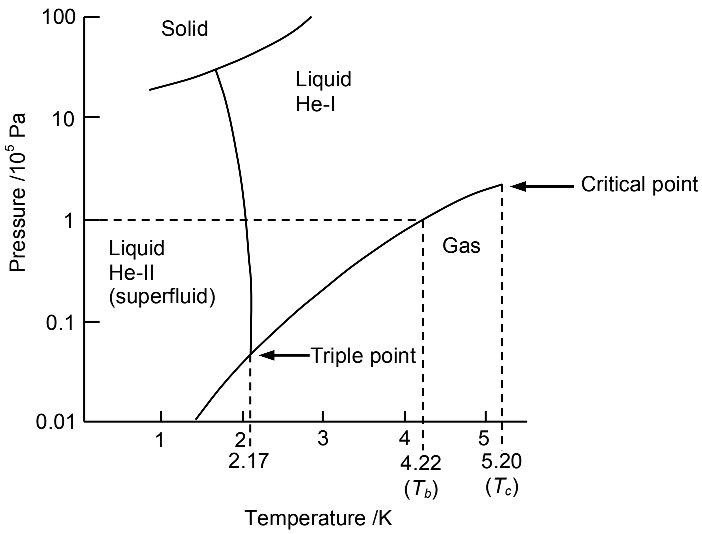
"Plastic" sulfur is a tough elastic substance that is formed when molten sulfur (m.p. = 115.2 °C) is poured into cold water. On standing, it slowly crystallizes. Predict which crystalline form is formed at room temperature and pressure. Also, explain why "plastic" sulfur is not shown on the above phase diagram.

Rhombic sulfur is formed. Plastic sulfur is not shown as it is a metastable state and changes into a more stable state over time. Phase diagrams only show stable states that are in equilibrium with other stable states. There are no conditions of temperature and pressure in which plastic sulfur is in equilibrium with another state of sulfur, so it does not appear on the phase diagram.

Based on the information provided, it is reasonable to assume that plastic sulfur is a compound formed by reaction of water with sulfur or some form of sulfur involving water in its crystal structure. Arguing that, and that the phase diagram for sulfur only shows pure forms of sulfur, was also awarded full marks.

Marks 6

- The diagram below shows a simplified phase diagram of helium.



Describe two unusual properties of helium (other than the "superfluid" He-II phase) that are *not* shared by most substances.

The unusual properties of helium that can be deduced from the phase diagram include:

(i) It has 2 triple points.
(ii) There is no gas/solid equilibrium line (*i.e.* helium does not sublime).
(iii) There is a liquid/liquid equilibrium line.
(iv) The triple points involve 2 liquid phases.
(v) helium cannot exist as a solid at atmospheric pressure.

Is it possible to liquefy helium above 5.20 K? Explain your answer.

No. If $T > 5.2$ K, helium exists as a supercritical fluid above ~2×10^5 Pa and as a gas below this pressure.

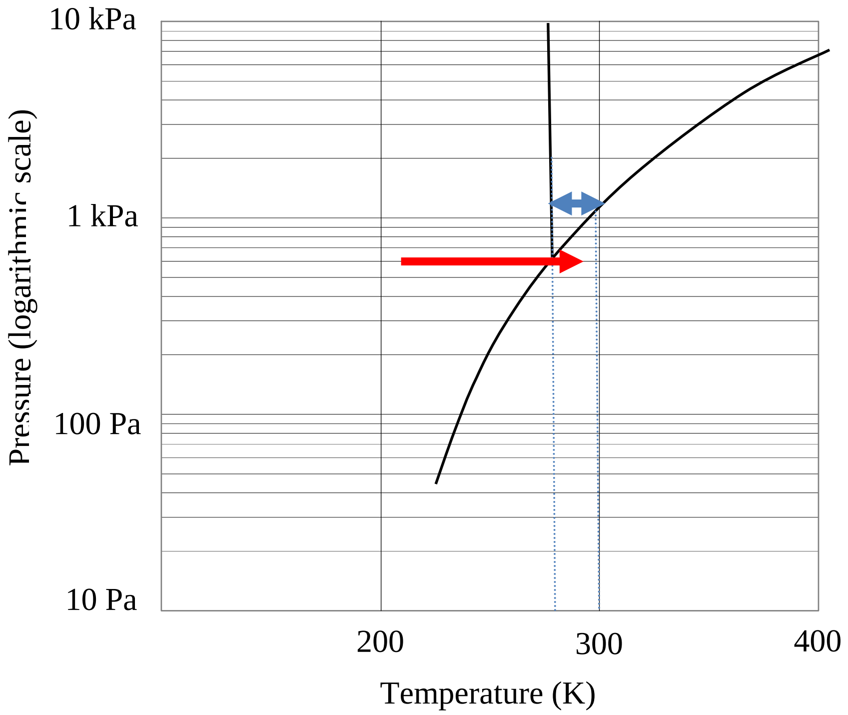
Why is the liquefaction of He very difficult, even at low temperatures?

Intermolecular forces between He atoms are extremely weak.

The electrons are held very tightly in the small 1*s* orbital. The atom is therefore very small and the electron cloud is not very polarisable. As a result, the interatomic dispersion forces required for liquefaction are very weak and they can only sufficient to keep He atoms in a liquid phase at temperatures approaching absolute zero.

Marks
5

- The diagram below shows part of the phase diagram of water.



The average pressure on the surface of Mars is around 0.6 kPa. If the night time temperature is –60 °C and a summer day temperature is 20 °C, describe what happens to any water on the surface of Mars as the sun rises.

This process is illustrated by the red arrow in the phase diagram above. The process occurs just *below* the triple point so the phase changes from solid (at –60 °C) to gas (at 20 °C).

Water sublimes as the sun rises on Mars.

(Note the logarithmic scale on the graph. Each horizontal line between 100 Pa (0.1 kPa) and 1 kPa (1000 Pa) represents an increase of 100 Pa (0.1 kPa).)

The highest surface pressure on Mars is thought to occur at the Hellas Basin, a low-lying area created by the impact of a large asteroid. If the pressure in this region is 1.2 kPa, use the phase diagram to estimate the temperature range in which liquid water will occur. Show your working on the phase diagram.

At 1.2 kPa, water is a liquid in the temperature range covered by the double-headed blue arrow in the phase diagram above.

Within the accuracy possible on the diagram, this corresponds to the temperature range 272 – 305 K.

Marks 2

- The critical point of H_2O is over 250 °C higher than for H_2S, H_2Se and H_2Te. Describe, at the molecular level, what needs to happen to the interactions between the water molecules to reach the critical point and why this requires a higher temperature in water than in the other group 16 hydrides.

At the critical point, the gas and liquid phases are indistinguishable.

As a liquid is heated and undergoes a phase change in a closed container, the density of the liquid decreases and the density of the vapour increases. When these values are the same, there is no longer a phase boundary and a supercritical fluid has been produced.

Water has strong H-bonds, whereas H_2S, H_2Se, H_2Te have much weaker dispersion and dipole-dipole interactions. The stronger H-bonds require a higher temperature to overcome the intermolecular forces, so water has a higher critical temperature than the other Group 16 hydrides.

Marks
4

- F_2 and Cl_2 are gases at room temperature, Br_2 is a liquid, and I_2 is a solid. Explain why the melting points and boiling points of the halogens increase going down the group.

Going down the group, the atoms get bigger - they have more electrons and these occupy orbitals of higher *n* values which are larger and more diffuse.

Hence, they have bigger and more polarisable electron clouds. Dispersion forces depend on the polarizability of the electron cloud and therefore increase going down the group. The melting and boiling points increase accordingly.

- Consider the boiling points of the following monosubstituted benzenes. 3

	C_6H_6	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5OH	C_6H_5I
b.p.	80 °C	85 °C	132 °C	156 °C	182 °C	188 °C

Explain this order of boiling points.

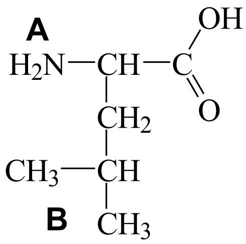
Phenol (C_6H_5OH) has an anomalously high boiling point compared to the other compounds as it forms strong hydrogen bonds.

The boiling points of the other compounds increase in the expected order, as the halogen increases in atomic number, the size and polarisability of its electron cloud increases and the strength of the intermolecular dispersion forces within the liquid increase.

The strengths of the dipole-dipole forces increase in the opposite order (greatest for C_6H_5F as it contains the most electronegative halogen). This shows that dispersion forces are more important than dipole-dipole forces in this series of compounds.

Marks
4

- Shown here is the classical form of the amino acid leucine.



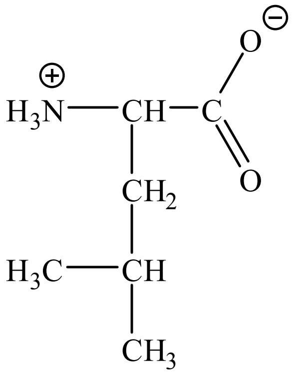
List the types of intermolecular interactions in which the sites **A** and **B** could be involved.

A **Hydrogen bonding and dispersion forces**

B **Dispersion forces**

Leucine has an unusually high melting point for a small molecule. Suggest a reason for this.

All amino acids can undergo an acid-base reaction with themselves. Leucine gives the 'zwitterionic' structure below. Being composed of positive and negative charges, the dominant intermolecular force in the crystal is ionic bonding. Hence the abnormally high melting point for a low molecular weight organic compound.



Marks 2

- Ice is less dense than liquid water. The triple point of water is 0.001 °C, 0.006 atm and its critical point is 374 °C, 218 atm. Sketch the phase diagram for water showing all the main features.