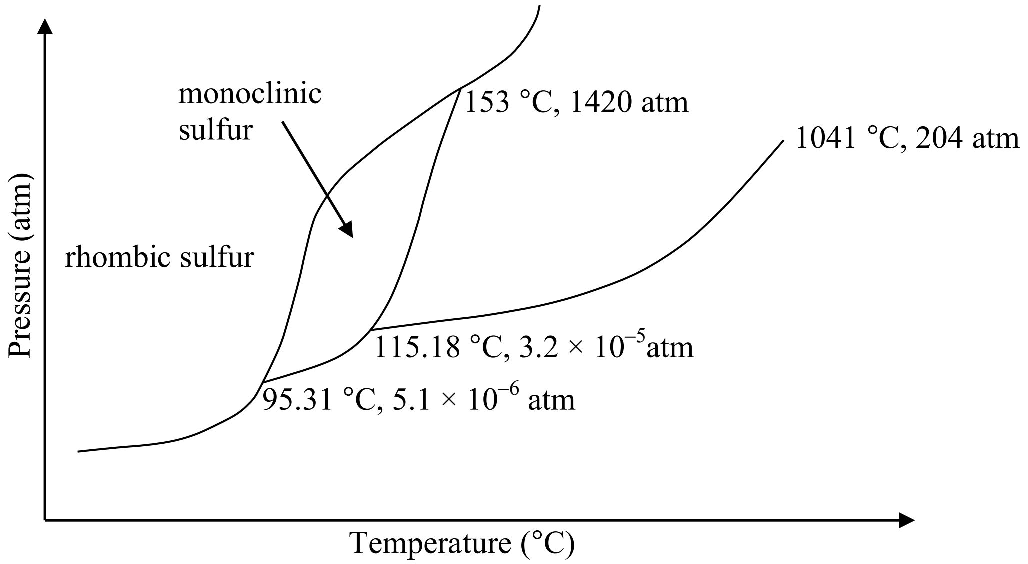
Marks 6

- 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.

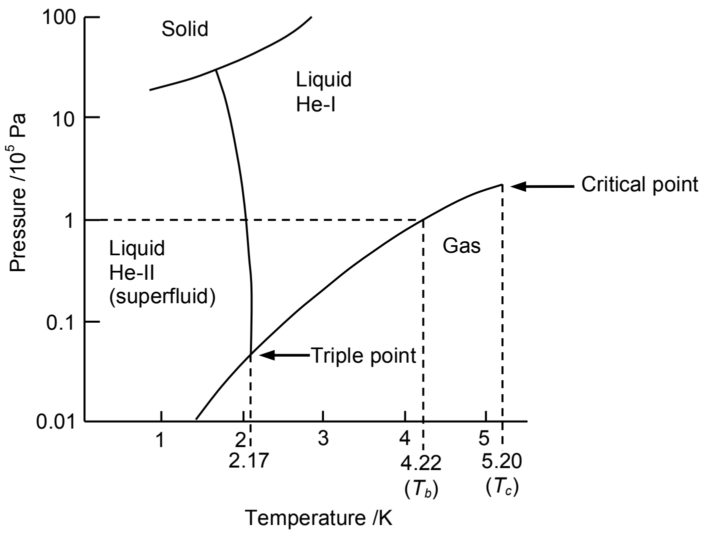
"Plastic" sulfur is a tough elastic substance that is formed when molten sulfur (m.p. = 115.2 °C) is poured into cold water. On standing, it slowly crystallizes. Predict which crystalline form is formed at room temperature and pressure. Also, explain why "plastic" sulfur is not shown on the above phase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

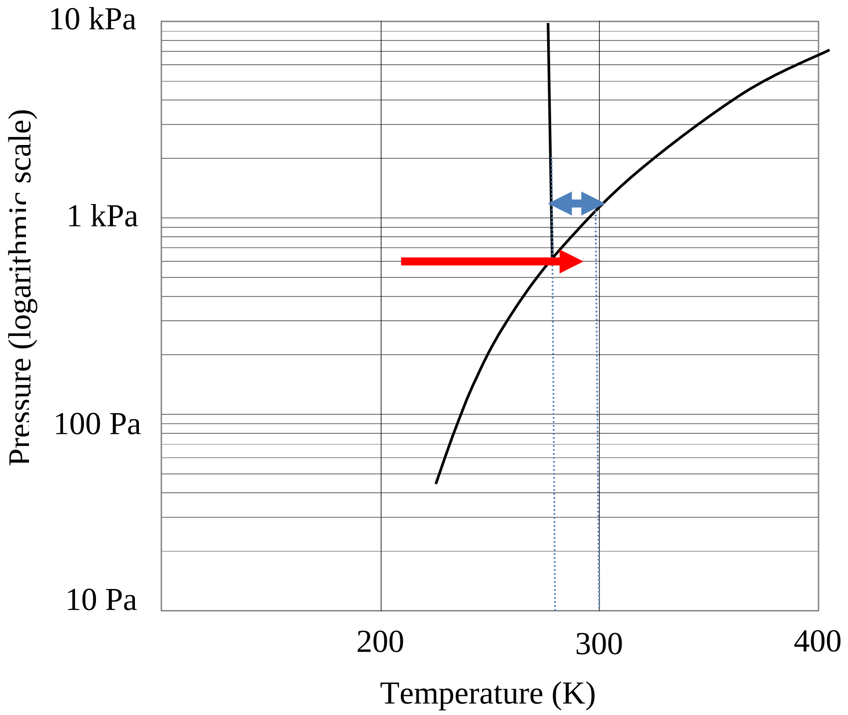
Why is the liquefaction of He very difficult, even at low temperatures?

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.

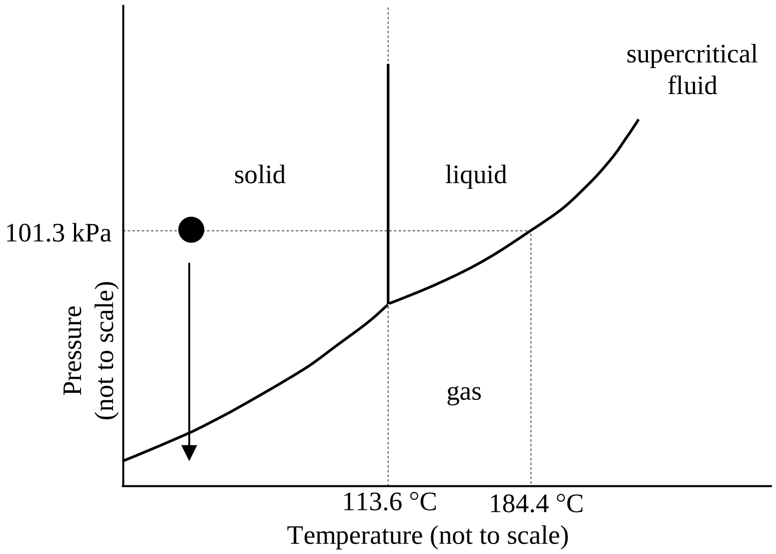
Marks
2

- 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.



Shown above is the phase diagram for iodine. What are the melting and boiling points of iodine at atmospheric pressure?

Atmospheric pressure corresponds to 101.3 kPa. The dotted line corresponding to this pressure crosses the boundary between solid and liquid at 113.6 °C. This is the normal melting point. The dotted line corresponding to this pressure crosses the boundary between liquid and gas at 184.4 °C. This is the normal boiling point.

In what way would you need to change the conditions to make iodine, initially at room temperature and pressure, sublime?

Under these conditions, iodine is a solid (shown by the dot on the phase diagram). To turn it from solid to gas (sublime) requires lowering the pressure (shown by the arrow on the diagram) until it is below that on the solid – gas boundary.

Describe what will happen if pressure is applied to a sample of solid iodine.

At room temperature and pressure, iodine is a solid (shown by the dot on the phase diagram). Increasing the pressure will not do anything to the phase.

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.