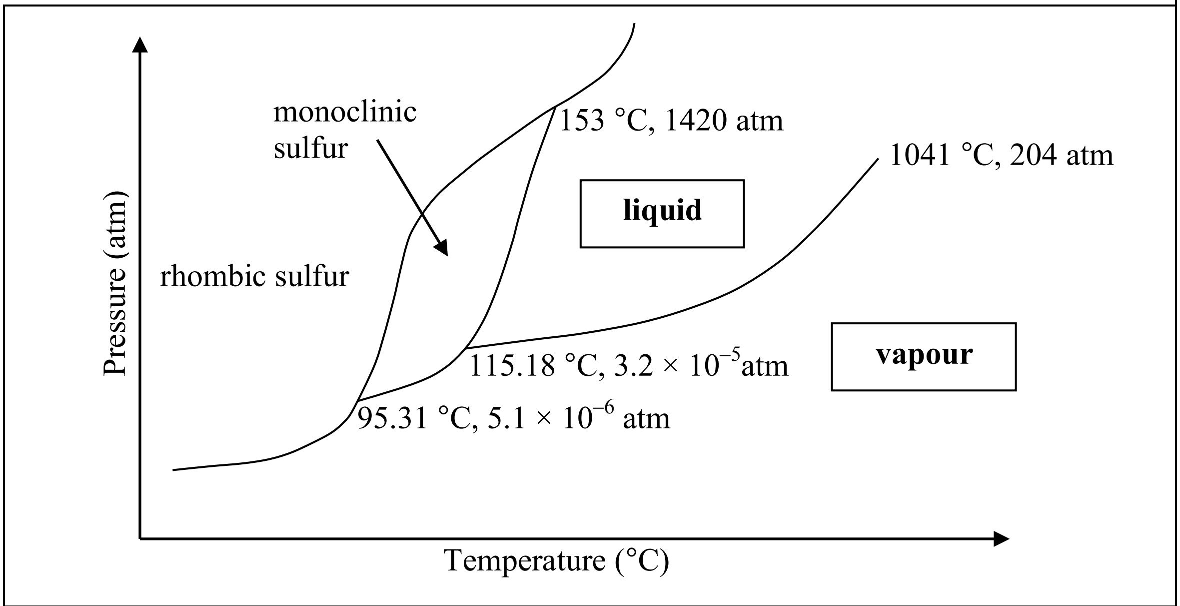
Marks 6

- Solid sulfur can exist in two forms, rhombic sulfur and monoclinic sulfur. A portion of the phase diagram for sulfur is reproduced schematically below. The pressure and temperature axes are not drawn to scale.

  Complete the diagram by adding the labels “vapour” and “liquid” to the appropriate regions.



Which form of solid sulfur is stable at 25 °C and 1 atm? **Rhombic**

Describe what happens when sulfur at 25 °C is slowly heated to 200 °C at a constant pressure of 1 atm.

It changes into the monoclinic form and then it melts.

How many triple points are there in the phase diagram? **3**

What phases are in equilibrium at the triple points?

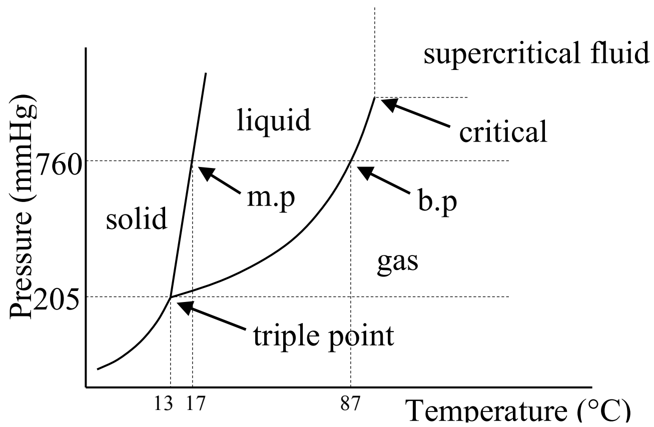
- **rhombic, monoclinic and vapour (at 95.31 °C and 5.1×10^{-6} atm);**
- **monoclinic, liquid and vapour (at 115.18 °C and 3.2×10^{-5} atm);**
- **rhombic, monoclinic and liquid (at 153 °C and 1420 atm);**

Which solid form of sulfur is more dense? Explain your reasoning.

Rhombic 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.

Marks 7

- A phase diagram of a pure compound has a triple point at 13 °C and 205 mmHg, a normal melting point at 17 °C, and a normal boiling point at 87 °C. Draw a phase diagram for this compound. Label all the different regions of the phase diagram.



Indicate whether each of the following statements regarding this compound is true or false.

The density of the solid is greater than that of the liquid.	**True** / False
If the pressure is reduced from 835 mmHg to 85 mmHg at a constant temperature of 11 °C, sublimation occurs.	**True** / False
At a constant pressure of 835 mmHg, evaporation occurs if the temperature is raised from 13 °C to 81 °C.	True / **False**

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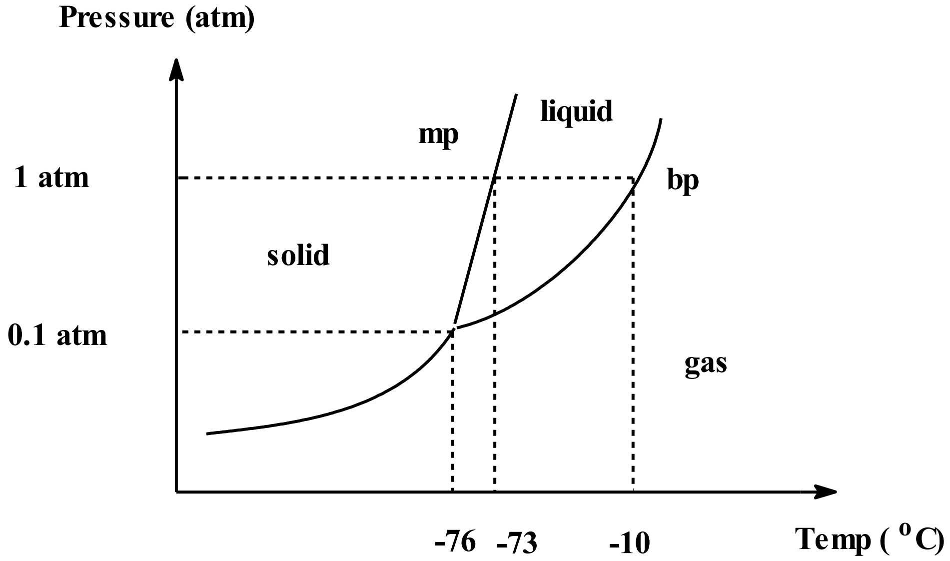
Marks 4

- The phase diagram for sulfur dioxide, SO_2, is shown below.



Io, the innermost of the four Galilean moons orbiting Jupiter, is the most geologically active body in the solar system. Its surface is covered with a frost of solid SO_2. The atmospheric pressure on Io is 10^{-7} atm and the surface temperature is between 90 and 110 K (–183 to –163 °C). As the temperature is raised on Io, does the SO_2 melt or sublime?

It sublimes.

Io has a hot molten magma core. What is the physical state of SO_2 several hundred metres below the surface of Io, where the temperature is –50 °C and the pressure rises to 1 atm?

Liquid

Is it possible to "ice skate" on a surface of solid SO_2? Explain your answer.

No. The increase in pressure can never cause the solid to liquid phase change due to the slope of the solid/liquid equilibrium line.

- Which of the following are allotropes? Explain your answer. **1**

^{16}O, ^{18}O, O_2, O_3, O^-, O^{2-}, O_2^-, O_2^{2-}, H_2O, H_2S, H_2O_2.

Allotropes are different structural forms of an *element*.

The only allotropes in the list are O_2 and O_3.

Marks
1

- The solid-liquid curve in the phase diagram of a particular compound slopes to the left. Can the compound sublime? Explain your answer.

The slope of the solid-liquid curve is irrelevant as sublimation is the phase change from solid to gas.

As long as there is an equilibrium line between these phases then the compound can sublime.

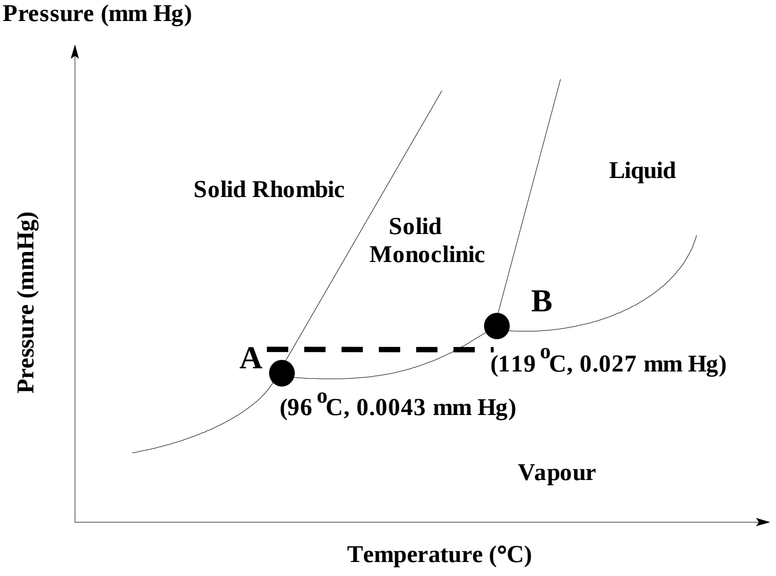
(The sloping of the solid-liquid to the left indicates that the solid is less dense than the solid and applying pressure has the effect of pushing the substance towards the liquid phase.)

- The gas methane, CH_4, has a critical point at –82 °C and 46 atm. Can methane be liquefied at 25 °C? Explain your answer. 2

The critical temperature (T_c) is the temperature above which a substance cannot exist as a liquid. Thus, methane cannot be liquefied above -82 °C and so cannot be liquefied at 25 °C.

Marks 6

- Solid sulfur can exist in both rhombic and monoclinic forms. A portion of the phase diagram for sulfur is reproduced schematically below.



How many triple points are there in the phase diagram?	**2 (marked as dots)**

What phases are in equilibrium at each of the triple points?

(A) rhombic, monoclinic and vapour (at 96 °C and 0.0043 mmHg)
(B) monoclinic, liquid and vapour (at 119 °C and 0.027 mmHg)

What phase is stable at room temperature and 760 mmHg pressure?	**solid rhombic**
Can monoclinic sulfur exist in equilibrium with sulfur vapour at 1.0 atm pressure?	**no**

Which solid form of sulfur is more dense? Explain your reasoning.

Rhombic The equilibrium line between rhombic and monoclinic slopes to the right. Beginning in the monoclinic region close to this line and increasing the pressure, the line is crossed vertically into the rhombic region. As rhombic is more stable at higher pressure, it must be more dense than monoclinic.

Describe the phase changes that occur when sulfur at 0.01 mmHg is slowly warmed from 90 °C to 130 °C.

rhombic → monoclinic → vapour (see dotted line on phase diagram).

- The gas methane, CH_4, has a critical point at –82 °C and 46 atm. Can methane be liquefied at 25 °C? Explain your answer. 2

The critical point is the temperature above which a substance cannot be liquefied by increasing the pressure. The boundaries between the gas and liquid phases disappear.

Thus, above -82 °C, methane cannot be liquefied – it cannot be liquefied at 25 °C.

Marks 3

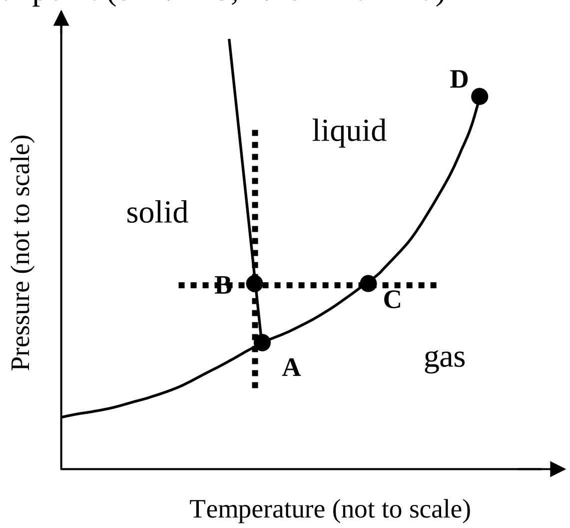
- The figure below illustrates the phase diagram for water. The points on the diagram correspond to:

  A: Triple point (0.0098 °C, 0.610 kPa)

  B: Normal melting point (0 °C, 1.01×10^2 kPa)

  C: Normal boiling point (100 °C, 1.01×10^2 kPa)

  D: Critical point (374.4 °C, 2.18×10^4 kPa)



Describe all of the phase changes that occur when water at 1.01×10^2 kPa is slowly warmed from –20 °C to 200 °C.

The horizontal dotted line on the phase diagram shows the changes. The pressure (1.01×10^2 kPa) corresponds to atmosphere or normal pressure.

The initial temperature of -20 °C is below the normal melting point so the water is initially a solid. As it warms up, it passes through the normal melting point (B, 0 °C) where melting to liquid occurs. After further warming, it passes through the normal boiling point (C, 100 °C). At this point it boils and a gas is formed.

Describe all of the phase changes that occur when water at 0 °C is slowly compressed from 0.500 kPa to 1000 kPa.

The vertical dotted line on the phase diagram shows the changes.

The temperature is below that of the triple point (A) as is the initial pressure (0.500 kPa). The water is initially a gas.

Increasing the pressure leads to water depositing straight from gas to solid. It does not pass through the liquid form or the triple point as the temperature and pressure are lower than at the triple point.

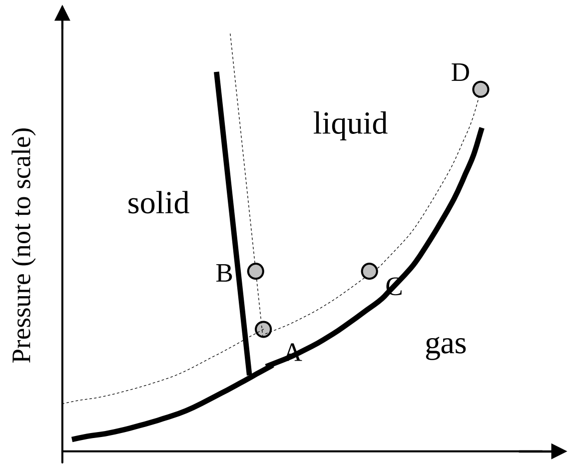
However, increasing the pressure further leads to melting of the solid to form a liquid, through the normal melting point (B).

Marks 3

Addition of salt to water raises its boiling point and lowers its melting point. Sketch the phase diagram for water containing salt, showing how it relates to the phase diagram for water (shown as dotted lines below).

The melting point is lowered so the solid – liquid boundary is shifted to lower temperature.

The boiling point is raised so the liquid – gas boundary is shifted to higher temperature.



In terms of the relative entropies of all relevant species, explain why the boiling point of salt water is higher than that of pure water.

Boiling water leads to a large increase in its entropy: $\Delta_{sys}S > 0$.

Because boiling requires breaking bonds, it is endothermic and requires energy from the surroundings. This lowers the entropy of the surroundings: $\Delta_{surr}S < 0$.

The boiling $\Delta_{univ}S$ to be positive. The boiling point is the temperature at which the gain in the entropy of the water is larger than the loss in the entropy of the surroundings.

When salt water is boiled, the $Na^+(aq)$ and $Cl^-(aq)$ ions form NaCl(s). This greatly reduces their entropy. Hence, when salt water boils the entropy gain is much smaller than when pure water boils.

Because $\Delta_{sys}S$ is less positive for boiling salt water, a *higher* temperature is required before it is larger than the loss in the entropy of the surroundings.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

	Marks
• Define what is meant by an "allotrope". Give an example of a pair of allotropes involving (i) phosphorus and (ii) oxygen.	**2**

Allotropes are different structural forms of the same element. Examples include:

(i) white phosphorus and red phosphorus,

(ii) O_2 and O_3.

Marks

- You may recall from a lecture demonstration or your laboratory work that solid CO_2 sublimes under ambient conditions while ice melts. Define the terms sublimation and melting. **3**

Sublimation is a phase change from solid to gas without passing through the liquid phase.

Melting is a phase change from solid to liquid.

What is a triple point (*e.g.* in the phase diagram of CO_2 or H_2O)?

The triple point is the temperature and pressure at which all three phases (solid, liquid and gas) coexist in equilibrium.

What does the different behaviour of ice and solid CO_2 indicate about the relative positions of their respective triple points?

The triple point of CO_2 is above ambient pressure.

The triple point of H_2O is below ambient pressure.

- Carbon has a number of allotropes, the two major ones being graphite and diamond. The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions? **1**

Graphite is more stable at room temperature and pressure. Diamond has a more compact structure than graphite and becomes more stable than graphite at very high pressures. Under very high pressures, graphite can be converted into diamond.

When the pressure is released, the reverse process is favourable. However, the structural rearrangement required is considerable and the activation energy is very high. Thus, at low temperatures, the diamond → graphite conversion is extremely slow and diamonds can exist for many thousands of years.

Marks 4

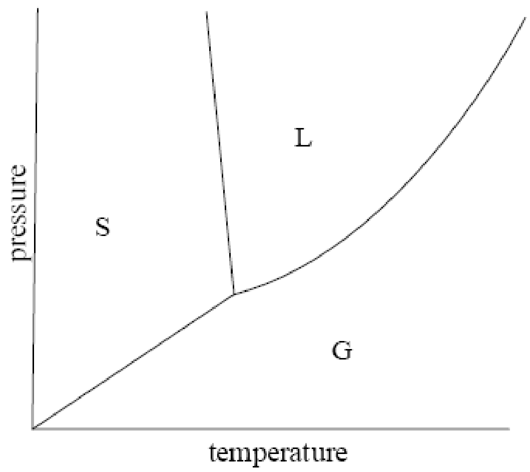
- A lecture demonstration showed that a wire with a weight attached can cut through a block of ice (solid water) without the block falling apart. Explain that phenomenon.

Liquid water is more dense than solid water (ice). When pressure is applied to the ice by the wire, it melts and gravity pulls the wire downwards through the liquid water.

Once the pressure is removed the water refreezes above the wire. The speeds of the two processes are such that the wire slowly cuts through the block without the block falling apart.

Sketch the phase diagram of water and explain how the above phenomenon manifests itself in the phase diagram.

The phase diagram with S = solid, L = liquid and G = gas is shown below:



The negative slope of the S/L equilibrium line means that, increasing the pressure with S ⇆ L moves the system into the liquid region.

Marks
3

- Carbon has a number of allotropes, the two major ones being graphite and diamond. What are allotropes?

Allotropes are different structural forms of the same element.

Give a different example for allotropes.

Examples include red and white phosphorus and O_2 and O_3.

The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?

There is a very high activation energy for the conversion from diamond to graphite as they are structurally dissimilar. This energy is not available under normal conditions.

Marks
3

- Define what is meant by an "allotrope". Give an example of a pair of allotropes involving oxygen and a pair *not* involving oxygen.

Allotropes are different structural forms of the same element.

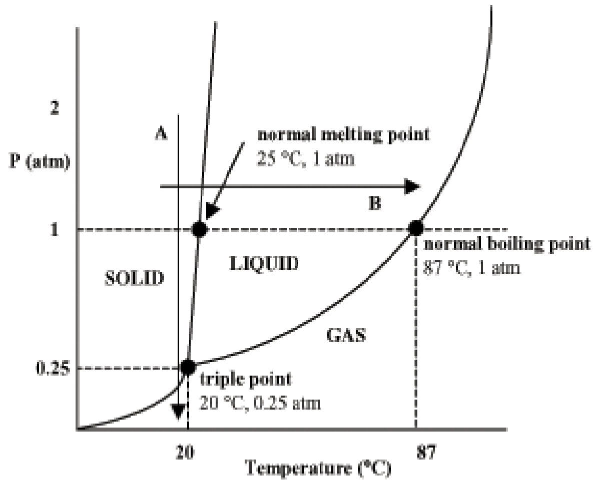
Examples include diamond and graphite for carbon; red and white phosphorus; oxygen O_2 and ozone O_3.

Marks 4

- A phase diagram of a pure compound has a triple point at 20 °C and 0.25 atm, a normal melting point at 25 °C, and a normal boiling point at 87 °C.

  Describe what happens when the pressure is reduced from 2 atm to 0.05 atm at a constant temperature of 15 °C?

The data allows the phase diagram below to be drawn.



Arrow A shows the effect of reducing pressure from 2 atm to 0.05 atm, at 15 °C. The compound passes directly from a solid to a gas: it *sublimes*.

Describe what happens when the temperature is raised from 13 °C to 87 °C at a constant pressure of 1.25 atm?

Arrow B shows the effect of increasing the temperature from 13 °C to 87 °C at *P* = 1.25 atm. The substance passes from solid to liquid: it melts.

Which is more dense, the solid or the liquid? Explain your reasoning.

The solid is more dense. The gradient of the solid/liquid equilibrium line is positive. If the pressure is increased when the compound is on the solid/liquid equilibrium line moves the compound into the solid region. Hence, the solid is more stable than the liquid under increased pressure so it must occupy less volume. It must therefore be more dense than the liquid.