Allotropes of sulfur

Sulfur is heated slowly and steadily from room temperature, so that all the changes in colour and consistency as it melts and eventually reaches boiling point, can be observed. A fresh sample of sulfur is heated to just above the melting point, then allowed to cool and crystallise slowly as monoclinic sulfur. A further sample is heated to boiling point, and the liquid rapidly chilled in cold water to form plastic sulfur.

A separate sample of sulfur is dissolved in a warm solvent, and the solution allowed to cool and evaporate, leaving crystals of rhombic sulfur. All the observed changes in properties can be related to the different molecular structures of the three solid forms of sulfur, and to the changes in structure as the temperature of the liquid changes.

Lesson organisation

This practical is described here as a demonstration. However, some teachers may wish to consider whether certain parts could be used as class practicals with appropriately skilful and reliable classes.

A demonstration, without any accompanying discussion about the possible reasons for the changes in properties in terms of structure, would take up to 45 minutes. However, to derive maximum benefit from the experiment, more time needs to be allowed for such discussion.

Apparatus and chemicals

The teacher will require:

- Eye protection
- Heat resistant gloves
- Access to a fume cupboard
- Flexicam or similar camera, digital microscope, digital projector and screen or other method of projecting images of small crystals to the class (as available).
- Test-tubes, 2
- Test-tube holders, 2
- Test-tube rack
- Beaker (250 cm³), 3
- Beaker, 1 dm³
- Thermometer, 0 – 250 °C
- Bunsen burner
- Heat resistant mats, 2
- Filter paper, about 18 - 20 cm diameter
- Spatula
- Paper clips
- Heat resistant gloves
- Damp cloth (to extinguish small sulfur fires)
- Sulfur, powdered roll (100 g)
- Boiling tube
- Watchglass
- Hand lens
- Sulfur, powdered roll (Low hazard), 100 g
- Dimethylbenzene (Flammable, Harmful, Irritant), 5 cm³
**Technical notes**

Sulfur (Low hazard) Refer to CLEAPSS® Hazcard 96A

The sulfur used must be roll sulfur, crushed to a powder. To crush the rolls of sulfur, place in a strong plastic bag on a hard surface. Use a hammer or a vice to break up the roll sulfur into small pieces, then crush to a powder in a mortar and pestle. ‘Flowers of sulfur’ is not suitable because it contains a lot of insoluble amorphous sulfur.

During the experiments sulfur may catch fire, releasing sulfur dioxide (Toxic), which may cause breathing difficulties to some students. If this happens, extinguish quickly by placing a damp cloth over the mouth of the test-tube. If the combustion cannot be extinguished quickly, the test-tube should be placed in fume cupboard, and the fan left running.

The preparation of the saturated solution of powdered roll sulphur in dimethylbenzene at 40 °C must be undertaken using a waterbath of warm water in a fume cupboard.

**Procedure**

**HEALTH & SAFETY:** Wear eye protection. Work in a fume cupboard.

**1. Plastic sulfur**

Work in a fume cupboard

a Half fill the 250 cm³ beaker with cold water.

b Half fill a test-tube with powdered roll sulfur and heat gently. The sulfur will melt to a transparent, amber, mobile liquid.

c Continue to heat the molten sulfur gently over a small Bunsen flame, keeping the contents moving to prevent local overheating. The liquid gets darker and, fairly suddenly, becomes a viscous, gel-like substance. This occurs at about 200 °C.

d The tube can be inverted and the sulfur will remain in it. Show that the mobile liquid reforms on cooling.

e Now heat the sulfur slowly and steadily beyond the gel-like stage. The sulfur liquefies again to a very dark red-brown liquid. Note that during this heating the sulfur may catch fire and sulfur dioxide will be produced. Have a heat resistant mat or damp cloth to hand to place over the mouth of the tube to extinguish the blue flames.

f When the sulfur begins to boil (441 °C), pour the liquid sulfur in a slow stream into a beaker of cold water. A tangled mass of brown plastic sulfur will form.

g Allow this to cool thoroughly. The inside of the plastic sulfur may remain molten after the outside has solidified.

h Remove the plastic sulfur from the water and show that it is rubbery – it can be stretched and will return to its original shape.

i The shiny surface of the plastic sulfur begins to dull and some of the elasticity is lost within 30 minutes, as it begins to turn back to the more stable rhombic sulfur.

**2. Crystals of sulfur**

Work in a fume cupboard

a Prepare a filter paper cone (double layer) held together by a paper clip and supported in a 250 cm³ beaker.

b Half fill a test-tube with powdered roll sulfur and heat gently. The sulfur will melt to a transparent, amber, mobile liquid.

c Pour the molten sulfur into the filter paper cone. Allow the sulfur to cool slowly and solidify, forming a crust.
d Break the crust with a spatula and, handling the filter paper cone with heat resistant
gloves, tilt it so that any remaining liquid flows out of the cone of solidifying sulfur on to
a piece of scrap paper or card (for disposal). Needle-shaped crystals of monoclinic sulfur
will be seen inside the hollow cone.

e When cool, the cone can be passed around. It may be necessary to break the cone open
to see the crystals more easily.

f Over the next day or two, look carefully at the needle crystals from time to time. They will
slowly go cloudy, yet retain their needle shape, as the monoclinic form slowly turns back
to the more stable rhombic sulfur – each needle becomes a mass of tiny rhombic crystals.

3. Rhombic crystals of sulfur

a Working in a fume cupboard measure approximately 5 cm³ of dimethylbenzene into a
boiling tube.

b Place the boiling tube into a 250 cm³ beaker approximately half full of warm water.

c Once the dimethylenzene has reached 40 °C, using a spatula, add the powdered roll
sulfur until a saturated solution is formed (no more will dissolve).

d Decant the solution into a glass watch glass.

e Small rhombic crystals will form as it cools.

f Once the liquid has evaporated the crystals can be examined with a hand lens.

Teaching notes

Very slow heating is essential if all of the changes on heating sulfur are to be seen clearly.
Sulfur is a poor thermal conductor, hence the changes can overlap one another if the
heating is too fast.

Crystalline sulfur consists of puckered $S_8$ rings in the shape of crowns. These can be packed
together in two different ways – to form rhombic crystals and to form needle-shaped
monoclinic crystals, as shown below:
Below about 96 °C, rhombic sulfur is the more stable allotrope. On melting at about 118 °C, sulfur first forms a mobile, amber liquid containing S₈ rings. If this is allowed to cool, monoclinic sulfur forms as crystallisation occurs above 96 °C.

Monoclinic sulfur will turn slowly into the more stable rhombic form on standing below 96 °C.

Further heating of the S₈-containing liquid breaks the rings into S₆ chains. These may join to form longer chains which tangle, causing an increase in viscosity. At higher temperatures, these chains break into shorter ones, perhaps as short as S₂, and the viscosity decreases again.

Rapid cooling of this liquid traps the resulting solid sulfur in the tangled chain state – this is plastic sulfur. On stretching, the chains uncoil and on releasing the tension they return to the partly coiled state.

If solid sulfur is formed below 96 °C by crystallisation from a solution, the stable rhombic form is produced.

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<thead>
<tr>
<th>Chart with Temperature and Composition</th>
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<tbody>
<tr>
<td>445 °C</td>
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<tr>
<td>200 °C</td>
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<tr>
<td>160 °C</td>
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<td>113 °C</td>
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Reference

This experiment was written by Andrew Thompson on behalf of the RSC.