SULPHUR

Sulphur has been known for its medicinal value and its germicidal effect since 1000BC. However, its chemical nature remained unknown until 1787 when Lavoisier recognized it is an element.

Sulphur makes up about 0.1% of the earth's crust. It occurs freely as deposits in USA, Poland, Japan, New Zealand, and Silicy. It is also widely found in the combined state as sulphides of iron, zinc, lead, copper and mercury, and as the tetraoxosulphate (VI) salts of calcium, magnesium, and barium. Sulphur is also present in some proteins.

Allotropes of Sulphur

The main allotropes of sulphur are rhombic sulphur (α-sulphur) and monoclinic (or prismatic) sulphur (β-sulphur), which are crystalline. Other allotropes of sulphur are amorphous sulphur (γ-sulphur), and plastic sulphur.

Rhombic Sulphur

Free sulphur exists as rhombic sulphur in nature because it is the only stable allotrope at temperatures below 96°C. Crystals of rhombic sulphur are bright yellow and octahedral. They are made up of S_8 molecules. Rhombic sulphur is prepared by allowing a saturated solution of sulphur in carbon (IV) sulphide to evaporate slowly. Octahedral crystals will gradually be deposited. Caution ought to be taken as carbon (IV) sulphide is poisonous and highly inflammable, thus, this preparation should be done in a fume cupboard.

Monoclinic Sulphur

Monoclinic Sulphur is the only stable allotrope at temperatures ranging between 96°C and 119°C. The crystals are long, thin, and needle-shaped and consist of S_8 molecules. At room temperature, they slowly revert to rhombic sulphur crystals. Monoclinic sulphur is obtained by cooling molten sulphur. Heat some powdered sulphur in a crucible

till it melts. Add more sulphur and continue heat and stirring it at the same time. Repeat this process until the crucible is almost filled with molten sulphur. Then allow the molten sulphur to cool. After some time, a hard crust will be formed at the top. Pierce two holes through the crust and pour off the remaining molten sulphur from inside before removing the crust. Needle-shaped crystals of monoclinic sulphur can be found as deposits on the sides of the crucible. Monoclinic sulphur is less dense than rhombic sulphur. This is because the S_8 molecules are more tightly packed in rhombic sulphur than in monoclinic sulphur.

$$\text{rhombic sulphur} \rightleftharpoons \text{monoclinic sulphur}$$

Amorphous Sulphur

Amorphous sulphur has no regular crystalline shape. It is prepared as a pale yellow, almost white deposit when hydrogen sulphide is bubbled through water for a long time and the saturated solution is exposed to air. It is also deposited in

chemical reactions, e.g. by the action of dilute hydrochloric acid on a trioxothiosulpate (VI) solution.

$$2H_2S_{(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(l)} + 2S_{(s)}$$

$$S_2O_{3\,(aq)} + 2H^+_{(aq)} \rightarrow H_2O_{(l)} + SO_{2\,(g)} + S_{(s)}$$

Plastic Sulphur

Plastic sulphur is a supercooled form of sulphur. If yellow sulphur is heated and poured into cold water, it will roll up into yellow ribbons which look as if they are made of plastic material. It is soft and elastic and will not dissolve in carbon (IV) sulphide. Plastic sulphur is generally not considered to be a true allotrope of sulphur because it is unstable and reverts to rhombic sulphur on standing.

Physical Properties

1. Sulphur is a yellow solid. It exists in two forms: amorphous and crystalline.

2. It is insoluble in water but soluble in carbon (IV) sulphide and methylbenzene (toluene).
3. Being a non-metal, sulphur is a bad conductor of heat and electricity.
4. Density depends on allotropic form.
5. It has a melting point of 119^{o}C and boiling point of 444^{o}C.

Chemical Properties

1. Sulphur combines directly with many metals like Fe, Cu, Na and K to form sulphides when heated in the absence of air.

$$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$$

2. When sulphur is heated in a plentiful supply of air, it forms sulphur (IV) oxide with a bright blue flame.

$$O_{2\ (g)} + S_{(s)} \rightarrow SO_{2\ (g)}$$

3. Sulphur combines slowly with hydrogen at high temperatures to form hydrogen sulphide.

$$H_{2\ (g)} + S_{(s)} \rightarrow H_2S_{(g)}$$

4. Sulphur combines with coke in an electric furnace to form a colourless liquid known as carbon (IV) sulphide, which vaporizes readily, forming poisonous and highly inflammable fumes.

$$C_{(s)} + 2S_{(s)} \rightarrow CS_{2\ (l)}$$

5. Sulphur is readily oxidized when warmed with concentrated tetraoxosulphate (VI) acid to form sulphur (IV) oxide,

$$2H_2SO_{4\ (aq)} + S_{(s)}$$

6. When warmed with concentrated trioxonitrate (V) acid, using bromine as catalyst, sulphur is oxidized to tetraoxosulphate (VI) acide.

$$6HNO_{3\ (aq)} + S_{(s)} \rightarrow H_2SO_{4\ (aq)} + 6NO_{2\ (g)} + 2H_2O_{(l)}$$

Uses of Sulphur

1. Sulphur is used to produce sulphur(IV) oxide for manufacturing tetraoxosulphate (VI) acid.
2. Sulphur is used in the vulcanization of rubber.

3. Sulphur and some of its products are used as fungicide and insecticides for spraying crops.
4. Sulphur is used to manufacture the bleaching agent used in the pulp and paper industry.
5. It is also used for the production of CS_2, skin ointments and dyes and as sulphides in manufacturing matches, fireworks, and gunpowder.