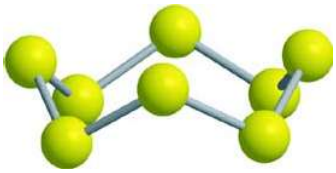
1. This question is about sulfur chemistry

Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is a form of S_8. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.



In the gas phase, the different ring sizes are in equilibrium; the equation for the equilibrium between $S_7(g)$ and $S_8(g)$ is given below:

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

(a) Given that the S–S bond strength in S_7 is 260.0 kJ mol^{-1} and in S_8 is 263.3 kJ mol^{-1}, calculate the enthalpy change for the forward reaction.

When dissolved in an organic solvent, S_6, S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

ring size	S_6	S_7	S_8
% by mass	0.32	0.76	98.92

(b) **i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1.00 dm^3 of solvent.

ii) Give the expression for the equilibrium constant for the reaction between S_7 and S_8 as written above.

iii) Calculate the value of this equilibrium constant.

In the solid phase, S_8 crystallises in two well known forms: orthorhombic and monoclinic. The enthalpy changes of combustion of these two forms are as follows:

$\Delta_c H^\ominus$ ($S_{8,\text{ orthorhombic}}$, 298 K) = −296.8 kJ mol^{-1}, $\Delta_c H^\ominus$ ($S_{8,\text{ monoclinic}}$, 298 K) = −297.1 kJ mol^{-1}

(c) **i)** Determine the enthalpy change at 298 K for the reaction

$$S_8(\text{s, orthorhombic}) \longrightarrow S_8(\text{s, monoclinic}).$$

ii) Which is the more stable form at 298 K?

Sulfur also forms an 8-membered ring in a compound with nitrogen, S_4N_4, which forms gold-coloured crystals.

(d) In S_4N_4, nitrogen and sulfur atoms alternate in the ring. The nitrogen atoms form three bonds; two of the sulfur atoms form two bonds, two form four bonds. Draw the structure of S_4N_4 assuming there are no cross-links within the ring.

(e) An alternative form of the S_4N_4 structure is based on the same arrangement of atoms except there is a bond between both pairs of opposite sulfur atoms. Every sulfur atom has four bonds in this structure; nitrogen atoms again have three bonds. Draw this alternative structure of S_4N_4 (but do not attempt to draw the 3D structure).

(f) If S_4N_4 gas is passed over silver metal it yields a linear polymer, poly(sulfur nitride), that conducts electricity and is a superconductor at very low temperatures. The polymer contains just two types of bond: N−S and N=S. Each N atom has three bonds; each S has two or four. Draw a repeat unit of this polymer.