The Absorption of Light by Sulphur at various Temperatures

By

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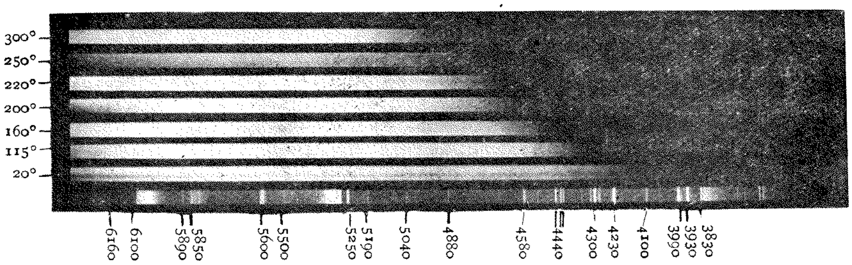
It is well known that sulphur changes its colour when heated. This is due to a shift of the absorption band. Generally, the absorption band of a substance moves toward the less refrangible side as its temperature rises. The writer made an experiment to study how the absorption band of sulphur shifts with the variation of the temperature, and the result obtained is given below.

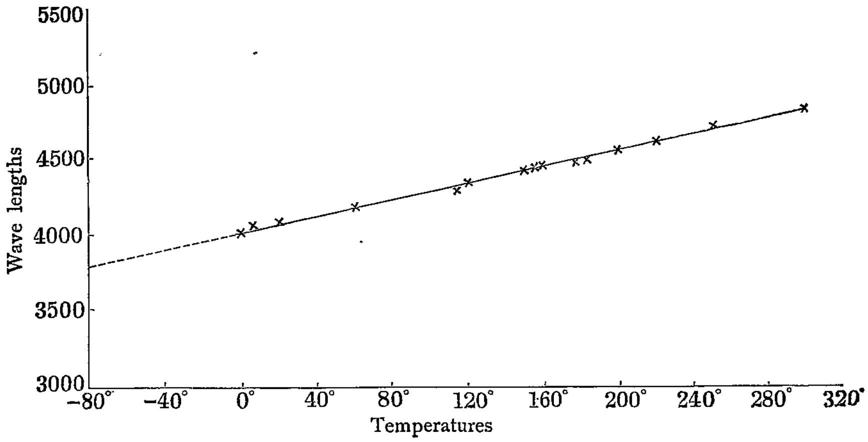
A thin layer of sulphur whose absorption was to be studied was prepared in the following way: a small quantity of the substance was put between two glass plates, and this was slowly heated by a Bunsen-burner until the whole was uniformly melted.

One junction of a thermo-couple consisting of platinum and tungsten was then inserted into the melted sulphur, and the whole was uniformly heated in an air-bath, the temperature of the other junction being kept constant by means of running water. The above thermo-couple consisted of fine wires of platinum (0·02 mm. dia.) and tungsten (0·035 mm. dia.), they being joined together in a flame of a carbon arc. The couple thus made was previously calibrated up to 300°C. in vacuum oil, the temperature of which being determined by a mercury thermometer.

Next, the absorption spectra of the sulphur at various temperatures were examined with a spectrograph having a replica grating. As the source of light, a carbon arc fed with a salt of calcium was used, and wave lengths of an edge of the absorption bands at various temperatures were determined from the reference lines of calcium. The wave lengths of the edge of the absorption bands determined from these photographic plates did not differ more than 3 $\mu\mu$. The wave lengths of one edge of the absorption band at various temperatures are given in the following table, and the relation between them is seen from the accompanying figure.

Temperature of the Sulphur	Absorption
0°C.	From ultra-violet to λ 0·408 μ
20° „	„ λ 0·410 „
60° „	„ λ 0·420 „
115° „	„ λ 0·430 „
120° „	„ λ 0·435 „
160° „	„ λ 0·446 „
180° „	„ λ 0·450 „
200° „	„ λ 0·458 „
210° „	„ λ 0·460 „
250° „	„ λ 0·473 „
300° „	From ultra-violet to λ 0·488 μ
	(Thickness of sulphur: 0·3 mm.)





Thus, the less refrangible edge of the absorption band of sulphur proceeds toward the red as its temperature was raised, and within the range of the experiment, the rise of the temperature by 10°C. produces a shift of about $2\ \mu\mu$.

According to the investigation of Kellas,[1] the molecular complexity of the liquid sulphur between 115°C. and 160°C. was represented by S_6, while polymerization from S_6 to S_{18} occurs at a temperature of about 160°C., the latter remaining stable up to the temperature of the boiling point of the sulphur. Now, if the molecular complexties S_6 and S_{18} would absorb different parts of the spectrum, the absorption band of the sulphur should change suddenly in the neighborhood of 160°C., so that an abrupt bending or discontinuity might be expected in the above line. In the experiment described above, many photographs were taken especially in the neighbourhood of this temperature. No trace of any bending or discontinuity was, however, observed, the edge of the absorption band extending gradually toward the red with the rise of temperature.

Now, if the straight line in the above figure is produced toward the negative side of the temperature axis, it will pass the point ($\lambda=0{\cdot}390\ \mu$, $T=-50$°C.). Since $\lambda 0{\cdot}397\ \mu$ is the violet end of the visible spectrum the above indicates that the sulphur will transmit all the visible part of the spectrum when cooled down below -50C°. This confirms the observation of the previous investigators.

Next, the absorption of light by sulphur in a plastic state was studied.

Temp. of Sulphur		Edge of Absorption Band		
before cooling	after cooling	before cooling	after cooling	untreated one corresp. to temps. given in the second colum
300°C.	100°C.	0.488 μ	0.453 μ	0.418 μ
„	50°C.		0.441 „	0.418 „
„	20°C.		0.435 „	0.410 „
„	10°C.		—	9.405 „
200°C.	100°C.	0.458 „	8.440 „	0.428 „
„	50°C.		0.434 „	0.418 „
„	20°C.		—	0.410 „
„	10°C.		0.430 „	0.405 „

1 J. Chem. Soc. 113. pp 903–922. 1918.

The sulphur was first heated to a high temperature and this was then suddenly put into water at various temperatures. The plastic sulphur thus prepared was squeezed between a pair of glass plates, and this was examined in the way described above. The result is given in the above table.

From this, we see that the absorption of light by the plastic sulphur is not simply determined by its present temperature, but it also depends upon the initial temperature to which the sulphur was previously heated. The higher the initial temperature, the longer is the wave length of the edge of the absorption band.

Now, sulphur has two modifications S_6 and S_{18}, and if the sulphur at 300°C. was gradually cooled down to 100°C. for example, S_{18} would completely transform into S_6, but if it was rapidly cooled, this is not the case, because its absorption spectrum corresponds to that of a higher temperature of about 180°C. Thus, the plastic sulphur will consist of S_6 and S_{18} mixed in a complex way.

In conclusion, the writer wishes to express his thanks to Prof. M. Kimura for his kind guidance.