CCIX.—*The Complexity of the Solid State. Part IV. The Behaviour of Pure Sulphur Trioxide. Part III.*

By ANDREAS SMITS and PIETER SCHOENMAKER.

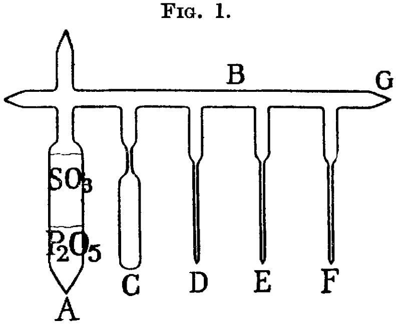
Investigations with X-Rays.

As shown in our last publication (this vol., p. 1120), it is possible by partial distillation to obtain the intensively dried, high-melting, asbestos-like form in a condition having an abnormally low vapour pressure and an initial melting point which is 33° higher than the unary melting point. It appears, indeed, that this form of sulphur trioxide behaves as a mixed crystal; the most volatile pseudo-component can be distilled off, so that the residue is a substance having the above abnormal properties.*

* Only the states of aggregation of a single substance in inner equilibrium will be called "modifications"; the states not in inner equilibrium will be termed "forms" of the substance.

For the X-ray investigation of the different states of the high-melting, asbestos-like form we used the simple apparatus of high-melting Jena glass shown in Fig. 1. The bulb, A, is sealed to B along with a vessel, C, and three very thin-walled capillary tubes, D, E, and F (diameter 0·008 to 0·01 mm.). Bulb A is partly filled with freshly-distilled phosphorus pentoxide and then with intensively dried sulphur trioxide, as described in our first communication (J., 1924, **125**, 2557). The apparatus is then evacuated and the tube B is sealed off at G.

FIG. 1.



The capillary tubes were filled one after another with the high-melting, asbestos-like form by the method of condensation and evaporation. In order to obtain a form with an abnormally low vapour pressure, a part of the contents was distilled off rapidly and the capillaries were subsequently sealed off.

The Röntgenogram was then taken, using CuK_{α}-rays. We obtained a film of 15 lines, the strongest of which are given in the following table :

Distances (mm.)...............	8·9	11·6	13·2	16·4
$10^3 \times \sin^2 \theta/2$	32	54	70	106

(θ is the angle between the incident and refracted beams; the intensities of the lines mentioned here were very strong.)

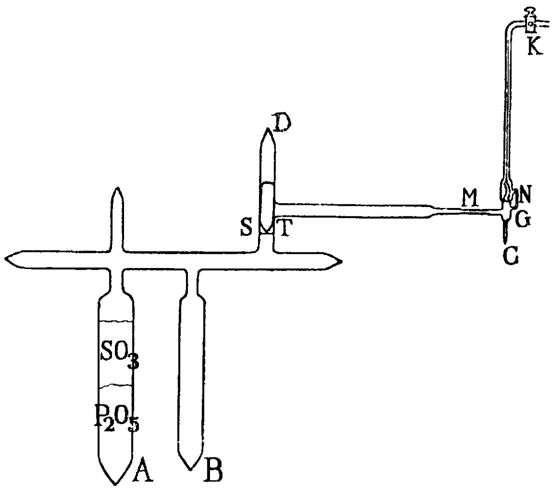
The same capillary was now heated at 50° for 48 hours and, since our experiments had shown that under these conditions the low vapour pressure of the high-melting, asbestos-like form (which had been disturbed by evaporation) increased strongly, it was expected that the Röntgenogram taken after this heating process would show a great difference. *It was, however, unchanged. Hence, either the* X*-ray method was unable to detect the change which had taken place in the solid, or the* X*-rays had already effected the establishment of the inner equilibrium during the first exposure, so that the state of the solid before and after the heating was in reality the same.*

X-Rays effect the Establishment of the Inner Equilibrium.

To decide between the alternatives mentioned above, the following apparatus (Fig. 2) was constructed. As in other cases, pure phosphorus pentoxide was first distilled into vessel A, and then intensively dried sulphur trioxide. A T-piece with septum S was then connected with an exceedingly small glass spring indicator, G, the little vessel of which was provided with a very thin-walled capillary, C, as used in X-ray analysis. The storage apparatus containing the sulphur trioxide was first evacuated and sealed; then the glass spring indicator with its capillary and the T-piece with its breaker were heated to redness in a current of dried air, the breaker-tube was sealed off at D, and this part of the apparatus was evacuated by stopcock K.

Capillary N being sealed off, a part of the sulphur trioxide was distilled into B and this vessel also was sealed off. Septum S was then broken and the capillary C filled with the high-melting, asbestos-like form, by the method of alternate condensation and evaporation.

FIG. 2.



In order to get a highly-disturbed state of this form, a portion was distilled off in the way described above, and then the capillary M was sealed off. The vapour pressure at the ordinary temperature was only 1 cm. Hg, proving that we had indeed a strongly-disturbed state of the high-melting, asbestos-like form.

We now placed the apparatus in front of our X-ray tube, protecting it by asbestos plates from access of heat. The X-rays were allowed to penetrate only the capillary containing the sulphur trioxide. As soon as this capillary was exposed to the X-rays the pressure in the indicator began to rise, showing that X-rays rapidly effect a transformation in the direction of inner equilibrium. In order to determine the final pressure, observations were continued over a period with the following results:

Time of exposure (hrs.)	0	1	4	8	10	13
Vapour pressure (mm. Hg) ...	10·8	22·2	43·1	46·1	46·3	46·3
Temperature	18·0°	18·0°	18·0°	18·8°	19·7°	19·7°

Consequently the final vapour pressure is 46·3 mm. Hg at 19·7°. As shown previously (this vol., p. 1116), the vapour-pressure line for the high-melting, asbestos-like form in inner equilibrium is given by the equation $T\ln P = -Q/R + CT$, where $C = 32{\cdot}0$. Now, giving Q/R the mean, *i.e.*, 8243 cals., of the three values obtained (8246, 8236 and 8246 cals.), we find, for $T = 292{\cdot}7°$ (*i.e.*, 19·7° C.), $P = 46{\cdot}45$ mm. Hg.

The agreement of this figure with the final value shown in the foregoing table proves that X-rays do indeed effect the establishment of inner equilibrium. It appears, therefore, that the X-ray diagrams showed no difference because, on exposure to X-rays, the substance was transformed into the state of inner equilibrium. This very interesting result shows that it is impossible to study the disturbed states of sulphur trioxide more closely by means of X-rays.

X-*Rays bring about the Transformation of the Metastable into the Stable Modification.*

Finally we investigated the X-ray diagrams of the two metastable modifications of sulphur trioxide—the ice-like form and the low-melting, asbestos-like form. Not only were the films obtained identical, but the X-ray diagram in each case was that of the high-melting, asbestos-like form considered above.

Hence X-rays, besides effecting the establishment of the inner equilibrium of sulphur trioxide, transform the metastable states into the stable state, *i.e.*, the high-melting, asbestos-like modification. *The only* X-*ray diagram obtainable is accordingly that of the stable modification in inner equilibrium.*

Summary.

On distillation of a portion of the intensively dried, high-melting, asbestos-like form, different states having abnormally low vapour pressures and abnormally high initial melting points were obtained, thus showing that the intensively dried, high-melting, asbestos-like form behaves as a mixture of pseudo-components which have very different vapour pressures and melting points.

At the ordinary temperature these states do not alter, but at 50° changes take place in the direction of the inner equilibrium. On studying the unchanged state and that changed at 50°, by means of X-rays, a very interesting result was obtained: the Röntgenograms in these two cases were identical.

Using an apparatus which enabled us to determine the vapour pressure during the exposure to X-rays, we found the explanation of the interesting phenomenon mentioned above to lie in the fact

that the X-rays effect a very rapid increase of the vapour pressure, proving that X-rays cause a rapid change in the direction of the inner equilibrium. Calculation showed that the final vapour pressure was exactly that of the high-melting, asbestos-like form in inner equilibrium.

X-Rays bring about not only the establishment of the inner equilibrium, but also the transformation of the metastable modifications into the stable form. The films obtained by exposing the ice-like form and the low-melting, asbestos-like form to X-rays are thus identical with the film of the high-melting, asbestos-like modification.

THE UNIVERSITY, AMSTERDAM. [*Received, March 8th*, 1926.]