

CXLV.—*The Complexity of the Solid State. Part III.*
The Behaviour of Pure Sulphur Trioxide. Part II.

By ANDREAS SMITS and PIETER SCHOENMAKER.

CONTINUING our earlier publication on the behaviour of pure sulphur trioxide (J., 1924, 125, 2554) we first conclude the description of our investigation of the ice-like form. Tables VIII and IX of that paper contained the vapour pressures of the solid and the liquid phases of the ice-like form when in inner equilibrium up to 49.75°. We have since determined the vapour pressure of the liquid in inner equilibrium up to 90° with the following results :

<i>t</i>	57.1°	65.4°	74.0°	80.9°	90.2°
<i>p</i> (mm. Hg)	1377.2	2041.0	2964.0	3985.5	5794.0

In order to find the point of intersection of the vapour-pressure curves of the solid and the liquid in inner equilibrium we have applied the method already used in the study of phosphorus ("Theory of Allotropy," p. 226; *Z. physikal. Chem.*, 1916, 91, 248). From the equation $T \ln p = -Q/R + CT$, it follows that on plotting $T \ln p$ as a function of T a straight line will be obtained. The values of $T \ln p$ for the temperature range 0—90.2° are in the

second column of Table I, and graphical representation gives two straight lines (see Fig. 5, p. 2565, of the earlier paper).

The two straight lines intersect in the triple point 16.8° and $T \ln p = 1467$, corresponding with $p = 158.5$ mm. (Lighty, Berthoud, and Le Blanc found 16.79° , 16.85° , and 16.8° respectively.) From the slope of the sublimation line, covering the first four temperatures of Table I, it follows that C for this line is 25.84, and hence the values of Q/R for the different observation temperatures may be calculated as shown in the third column of Table I. If the mean value of Q_{SG}/R is taken as 6000, the molecular heat of sublimation, Q_{SG} , is 11900 cal.

Similarly, the value of C for the liquid vapour pressure line is found to be 22.7, and the molecular latent heat of evaporation, Q_{LG} , based on the mean value of Q_{LG}/R (see Table I), is calculated to be 10100 cal. It further follows that the molecular latent heat of fusion, Q_{SL} , is 1800 cal. (Le Blanc calculated 2220 cal. from his determinations.)

From our determinations, it appears that the boiling point under a pressure of 760 mm. is 44.8° (compare Buff, $46-47^\circ$; Schultz-Sellock, 46° ; Weber, 46.2° ; Lighty, 44.88° ; Berthoud, 44.52°), and that the Trouton ratio $Q_{LG}/T_B = 10100/317.8 = 31.8$, as compared with the normal value 22. These results indicate that the liquid is more complex than the vapour, and that the solid and liquid phases differ but slightly in complexity. We shall return later to this phenomenon.

TABLE I.

$t.$	$T \ln p.$	$Q/R.$	$t.$	$T \ln p.$	$Q/R.$
0.15°	1043	6015	35.0°	1889	5102.5
5.0	1164	6019	40.5	2010	5106.5
10.2	1299	6019	45.0	2116	5103
15.5	1434	6021	49.75	2222	5104
17.6	1486	5111	57.1	2386	5107
20.5	1553	5109	65.4	2579	5103
22.5	1602	5100	74.0	2774	5103
25.3	1658	5113.5	80.9	2934	5100
30.65	1786	5106	90.2	3147	5100

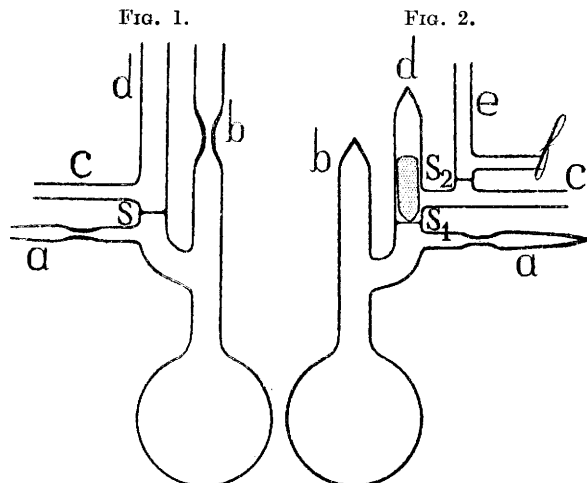
The Insufficiently Dried, Low-melting, Asbestos-like Form.

The region of the pseudo-system, in which the ice-form of sulphur trioxide is situated, is that of a dissociable compound of pseudo-components, related to each other as polymerides or isomerides, these terms being used in the widest possible sense (J., 1924, 125, 2554).

The ice-form of sulphur trioxide is one of the two metastable modifications. The other generally constitutes three-quarters of the pure sulphur trioxide in the bulbs supplied by Kahlbaum; it is

like asbestos in appearance and will be referred to as the low-melting, asbestos-like form.

For our more recent work, several bulbs provided with a septum (Fig. 1) were sent to the firm of Kahlbaum and filled with pure sulphur trioxide, the ends of the tubes *a* and *b* then being sealed. Such a bulb, unevacuated, was joined to a high-vacuum pump at *a* by a very short rubber tube connected with a small steel tube about 5 cm. in length, in such a way that *a* was inside the steel tube; by moving this tube the point *a* (previously scratched) could be broken. (To prevent the mercury in the pump from reacting with the sulphur trioxide, a U-tube cooled in liquid air was placed



in front of the pump.) After evacuation, the capillary tube *a* was sealed off.

A second T-piece with a septum, S_2 , was now sealed to the delivery tube, a breaker of solid glass carefully placed on the septum S_1 (Fig. 2), and the tube *c* sealed to a glass spring indicator, with the bulb *g* and the mantle *w* still connected through a capillary tube, *v*, as shown in Fig. 3. Bulb *g* was connected to a wide horizontal U-tube to which were sealed two or four vertical tubes, provided with capillaries, and a T-piece with septum, S_3 , with breaker and bulb, *m*. The remaining connexion with the vessel *u* is evident from Fig. 3.

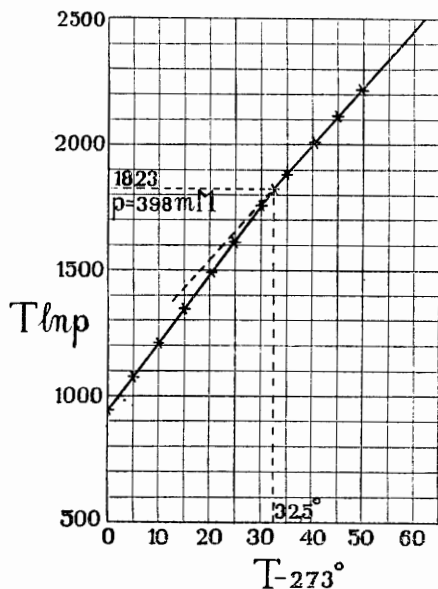
The whole apparatus was heated while a current of dry air was driven through every tube and vessel, and finally the capillary ends of these tubes and vessels were sealed off in succession. The sulphur trioxide bulb being cooled in liquid air, the rest of the apparatus was evacuated by connecting the delivery tube of vessel

The vapour pressures for the not intensively dried, liquid phase were the values employed in Table I.

If $T \ln p$ is plotted against T , Fig. 4 is obtained, in which two straight lines intersect at 32.5° and $T \ln p = 1823$ (i.e., $p = 398$ mm. Hg). This temperature is the melting point of the low-melting, asbestos-like form under this vapour pressure, if it is in inner equilibrium, or, in other words, if it behaves as a unary substance.

The triple point of the low-melting, asbestos-like form is therefore situated at 32.5° and 398 mm. Hg.

FIG. 4.



this form indicates that the value of C in the formula $T \ln p = -Q/R + CT$ is 27.56. The value of Q/R at each observation temperature is in Table II, and the mean value may be taken as 6590, whence $Q_{SG} = 13000$ cal. Since $Q_{LG} = 10100$ cal. (see p. 1109), it follows that $Q_{SL} = 2900$ cal.

The Intensively Dried, Low-melting, Asbestos-like Form.

The method of intensive drying, as applied with the ice form, is very difficult to carry out in this case, since it is an arduous task to prepare the low-melting, asbestos-like form if the sulphur trioxide has been

intensively dried. We have therefore prepared the not intensively dried, low-melting, asbestos-like form and begun to dry it in the *solid* state, an operation which will take a very long time, perhaps several years, for completion.

In a preliminary trial phosphorus pentoxide was distilled into bulb *m* in the way previously described. The bulb was then evacuated, the delivery tube sealed off, the apparatus inverted, and the septum S_3 broken by means of the breaker in tube *l*. The apparatus was again set upright; the large hole in the septum was thus freed, this being necessary for the drying to take place as rapidly as possible in the given circumstances. As we feared, the drying of the solid substance was exceedingly slow, the effect after 3 months being inappreciable. Finally we tried once more to prepare

the intensively dried, low-melting, asbestos-like form from the intensively dried, ice-like form, but obtained the high-melting form.

The High-melting, Asbestos-like Form.

The Intensively Dried, High-melting, Asbestos-like Form (First part).—The apparatus for determining the vapour pressure of this form was filled in the way described in our first publication (*loc. cit.*), a bulb, containing pure sulphur trioxide, of the form shown in Fig. 2 being used. The storing apparatus having been filled with the intensively dried ice form (see Fig. 2, *loc. cit.*), the glass spring indicator was first filled with this form.

By distilling sulphur trioxide alternately from one vessel into another, the distilling vessel being at room temperature or slowly heated and the condensing vessel cooled in liquid air, it is possible to convert the ice form almost completely into the high-melting, asbestos-like form; the last traces of the ice form are removed by distilling into one of the tubes and sealing it off.

As shown in our first publication, the dried ice form of sulphur trioxide, as in the case of a mixture, exhibits a lower vapour pressure after a small portion has been distilled off. This phenomenon, first observed with violet phosphorus ("Theory of Allotropy," pp. 96, 213), is exhibited in a much higher degree by the high-melting, asbestos-like form. The intensively dried, high-melting, asbestos-like form, obtained in the way mentioned above, showed a very low vapour pressure, which remained constant at room temperature. At higher temperatures, however, the vapour pressure rises with a velocity which decreases with the time. The apparatus being kept at constant temperature, this phenomenon has been studied successively with the same filling at 30° and 40°, and with a new filling at 50°; the results are shown in Figs. 5, 6, and 7. In these figures the curves approach asymptotically a final value, indicated by a dotted line.

Calculating $T \ln p$ from the final values of the vapour pressure at the three temperatures, we obtain the results shown in Table III.

TABLE III.

t .	p (mm. Hg).	$T \ln p$.	Q/R .
30°	120	1450	8246
40	290	1780	8236
50	650	2090	8246

The three points obtained by plotting $T \ln p$ against T are collinear as shown in the lower line of Fig. 8.

The behaviour of the high-melting, asbestos-like form agrees completely with that of the ice-like form. There are only quanti-

tative differences, due to the higher temperatures at which the high-melting asbestos-like form had to be studied. The velocity of establishment of inner equilibrium in the intensively dried material being

FIG. 5.

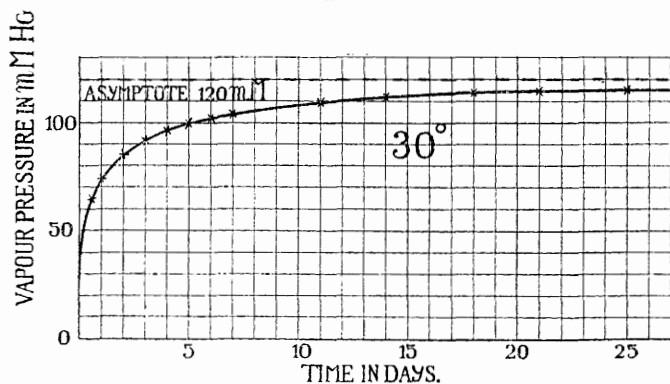


FIG. 6.

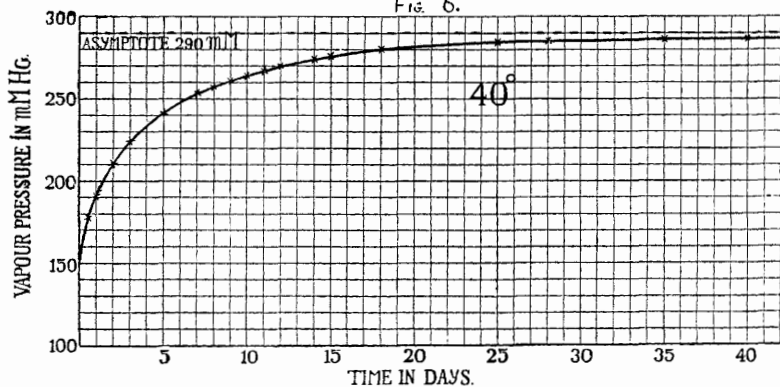
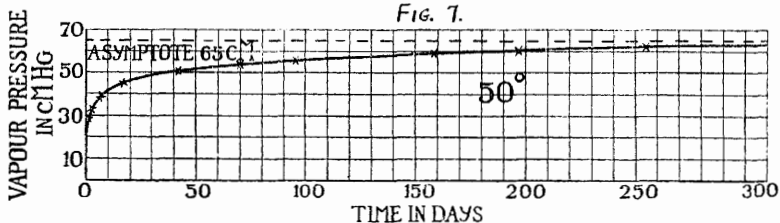


FIG. 7.

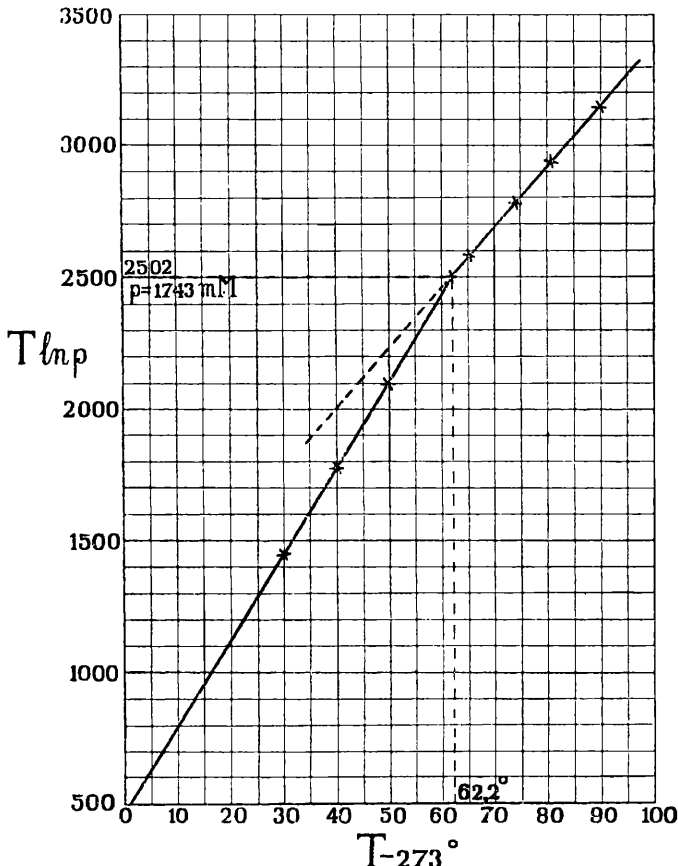


imperceptibly slow at 18°, the initial preparation, highly disturbed by rapid evaporation, showed an abnormally low vapour pressure, which did not change. At higher temperatures, however, the

velocity becomes greater and is manifested in the vapour pressure, which increases until inner equilibrium is reached. Violet phosphorus shows exactly the same interesting behaviour (*Z. physikal. Chem.*, 1916, **91**, 249).

From the vapour-pressure curves of the high-melting form, in inner equilibrium, and of the liquid (Table I), we can find the unary

FIG. 8.



melting point of the high-melting, asbestos-like form under its own vapour pressure, *i.e.*, the triple point $S + L + G$ of this form. The two lines obtained by plotting $T \ln p$ against T for the solid and the liquid form (Fig. 8) intersect at $t = 62.2^\circ$ and $T \ln p = 2502$, or $p = 174.3$ cm. of mercury.

As in the case of the ice-like form and the low-melting, asbestos-like form, we can calculate here the heat quantities. Thus, using

Q Q

the relationship $T \ln p = -Q/R + CT$, we find $C = 32.0$. The mean value of Q/R for the three observation temperatures (see Table III) is 8240, so that $Q_{SG} = 16300$ cal. Now we know that $Q_{LG} = 10100$ cal. Hence $Q_{SL} = 6200$ cal. We see that the molecular heat of sublimation and the molecular latent heat of fusion are greatest with the high-melting, asbestos-like form, which seems to be most complex.

The High-melting, Asbestos-like Form, dried only by Distillation.—Before continuing the description of our experiments with the intensively dried, high-melting, asbestos-like form, we wish to state here that, starting with the not intensively dried, metastable, ice-like form, freshly distilled from a bulb of pure sulphur trioxide, and carrying out the experiment in the way described above, but in an apparatus without phosphorus pentoxide, we have easily obtained the stable, high-melting, asbestos-like form dried only by distillation.

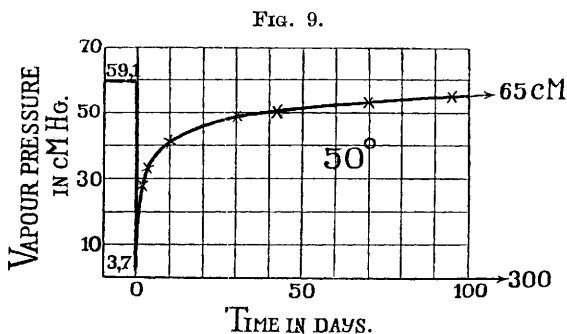
We have examined this form to see if we could determine directly the unary vapour-pressure line of the high-melting, asbestos-like form. This proved to be impossible, for the substance behaved almost exactly like that intensively dried by phosphorus pentoxide. As is mentioned in our first paper on this subject, the literature states that the substance we call the high-melting, asbestos-like form, not intensively dried, shows a very slowly rising vapour pressure. Now, as this substance was of course separated from the ice-like form by distilling off the latter, it was likely that this distillation process was sufficient to lead to the very dry state necessary for the existence of the high-melting, asbestos-like form. Our method of transforming the ice-like form into the high-melting, asbestos-like form is a distillation process repeated several times and therefore it was to be expected that our preparation would be extremely dry.

The Intensively Dried, High-melting, Asbestos-like Form (Second part).—We have already mentioned that in preparing the intensively dried, high-melting, asbestos-like form the last traces of all other forms are distilled off. In this process a part of the high-melting, asbestos-like form is evaporated also and the result is a high-melting, asbestos-like form of very low vapour pressure, constant at the ordinary temperature but rising perceptibly at temperatures above 30° .

We have studied this phenomenon more closely. In an apparatus filled with the intensively dried, high-melting, asbestos-like form which had stood some weeks in a thermostat at 50° the vapour pressure had risen to 591 mm. Hg., and was still rising very slowly. A part of the high-melting, asbestos-like form was now distilled off by cooling one of the condensing tubes in liquid air. After this tube

had been sealed off, and the apparatus replaced in the thermostat, the vapour pressure was found to have decreased enormously, namely, from 591 mm. to 37 mm. Hg. The vapour pressure, however, rose and readings made at intervals gave results which are represented graphically in Fig. 9.

The vapour pressure has risen above the initial pressure, in agreement with the fact that at the start the vapour pressure was still rising, although very slowly. The fact that the vapour pressure decreases so greatly on partial distillation proves that the high-melting asbestos-like form behaves as a mixed crystal consisting of at least two components differing largely in vapour pressure. These components must be pseudo-components, since after partial distillation the vapour pressure is not constant but rises, proving



that a more volatile part is formed from a less volatile part. Consequently the state for which the vapour pressure is abnormally low is a disturbed state of the stable, solid aggregation of the sulphur trioxide system.

As mentioned already, the unary melting point of the high-melting, asbestos-like form under its own vapour pressure is 62.2° , the pressure being 174.3 cm. Hg. Since it is possible to obtain different states of this high-melting asbestos-like form with very low vapour pressure it was important to determine the temperatures at which melting occurred. Since the glass spring is apt to be broken by a sudden rise of vapour pressure, the experiments were carried out very carefully, the temperature of the thermostat being raised slowly and continuously, so that each experiment lasted 2 or 4 days. Although this slow working is not favourable for producing the largest effect, the results in Table IV were obtained.

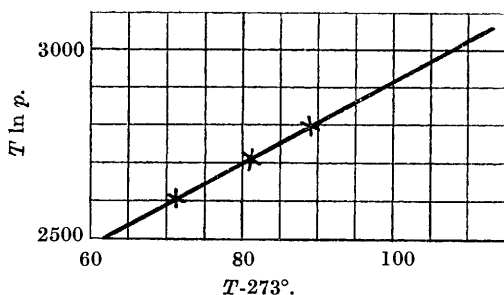
Thus the initial melting points lie respectively 9° , 19° and 26.5° above the unary melting point of the high-melting, asbestos-like form under its own vapour pressure. With more rapid working it should not be difficult to realise still higher initial melting points.

TABLE IV.

Preparation.	Initial m. p.	Vap. press. (cm. Hg) at initial m. p.	$T' \ln p.$	Vap. press. (cm. Hg) of the liquid if in inner equilibrium.
I.	71.0°	192	2601	266.0
II.	81.0	212	2711	400.2
III.	88.8	227	2796	642.7

A very remarkable phenomenon is that as soon as melting begins the vapour pressure rises so rapidly that it is very difficult to prevent the glass spring from being broken. This phenomenon had been expected, for we had already observed that, although the intensively dried liquid phase could behave as a mixture at relative low temperatures, at higher temperatures, *e.g.*, above 50°, the establishment of the inner equilibrium in the liquid took place rapidly. According to the theory of allotropy the liquid initially produced by the melting of a disturbed state of the high-melting, asbestos-like

FIG. 10.



form with a very low vapour pressure, due to the low concentration of the volatile pseudo-components, is a liquid, co-existing with this disturbed solid state, also having an abnormally low vapour pressure, since it contains little of the more volatile pseudo-component. Now, whilst the velocity of establishment of inner equilibrium in the solid, intensively dried, high-melting, asbestos-like form is slow even at, *e.g.*, 81°, inner equilibrium will be established with great rapidity in the liquid. For this state, the vapour pressure at 81° is 400.2 cm. Hg (value calculated by interpolation), so that, when melting begins at 81°, at a vapour pressure of 212 cm. Hg, the vapour pressure must rise considerably at constant temperature.

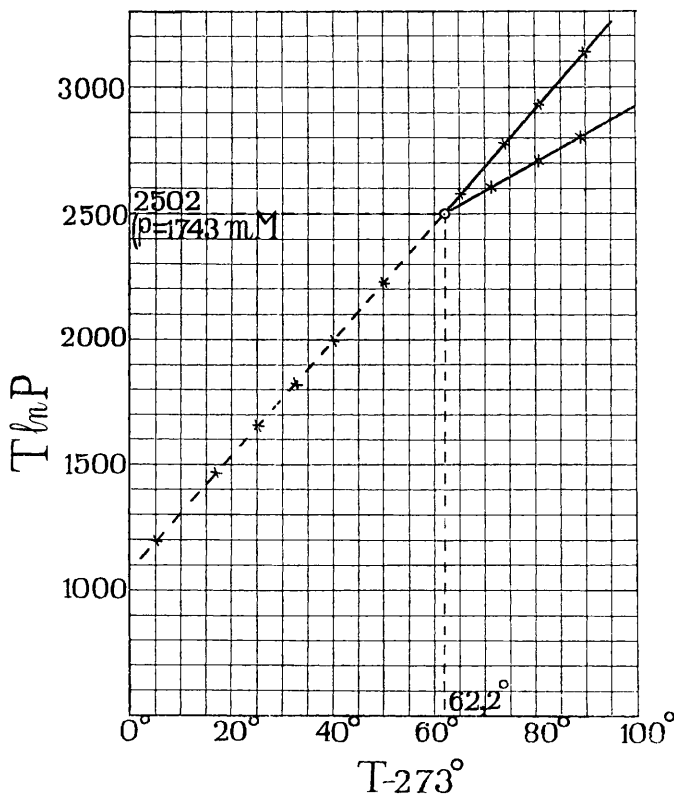
The determination of the temperature and pressure at which the disturbed solid state under consideration begins to melt is very important, for it is evident that these points, where a disturbed solid state co-exists with liquid and vapour (also not in inner equilibrium), are points on a three-phase line in the pseudo-system.

Though the equation $d \ln p/dT = Q/RT^2$ does not hold for a

three-phase equilibrium, the curve of $T \ln p$ plotted against T is a straight line, as Fig. 10 shows.

As is demonstrated in detail in the "Theory of Allotropy" (p. 18, Fig. 24; p. 28, Fig. 41), the unary melting point under vapour pressure is situated where the unary vapour pressure curve, *i.e.*, the vapour pressure curve of the liquid phase in inner equilibrium, meets a three-phase line for the co-existing solid, liquid, and vapour.

FIG. 11.



Plotting $T \ln p$ against T both for the three-phase system and for the unary liquid system we obtain Fig. 11, showing the intersection of these lines at 62.25° and 174.3 cm. Hg . This is in complete agreement with our experiments mentioned on p. 1115.

Initial Melting Points of the Highly Disturbed States of the High-melting, Asbestos-like Form.

In the vapour pressure determinations of the disturbed states of the high-melting, asbestos-like form the rate of heating was very

slow, especially at higher temperatures, in order to prevent the glass spring from being broken. To ascertain at what temperatures melting would occur if the disturbed substance was heated less slowly, some tubes were filled with the intensively dried, high-melting, asbestos-like form, disturbed as much as possible by partial distillation, in the same way as was done in our vapour-pressure apparatus. After being sealed off, these tubes were placed in a stirred oil-bath, the temperature of which was slowly raised. The temperatures at which melting began are in Table V.

TABLE V.

Tube.	Initial m. p.	Vap. press. (cm.) at the moment melting began.	Vap. press. (cm.) of the liquid in inner equilibrium.
I.	65.0°	179.1	198.7
II.	77.0	203.7	344.7
III.	95.0	238.8	703.6

It is seen that initial melting points are realised up to 33° above the melting point of the same substance if in inner equilibrium. These experiments were dangerous, since, as has already been mentioned, the liquid formed establishes inner equilibrium and the pressure rises suddenly to relatively high values.

To demonstrate this we have inserted columns three and four in Table V. The third column shows the pressure at the moment the liquid is formed (the pressure on the three-phase line at the temperature considered here), and the fourth column shows the pressures reached when the liquid formed has established inner equilibrium. In the last case, the pressure rises from 3.14 atm. to 9.24 atm. Obviously the increase of vapour pressure takes place very rapidly and in fact caused a very serious explosion on one occasion.

The Position of the Unary System in the Pseudo-system.

In our first paper on this subject (*loc. cit.*) and in the previous pages of this paper we have described the investigations leading to our knowledge of the P - T diagram of the unary system sulphur trioxide with regard to the equilibria in the vapour phases.

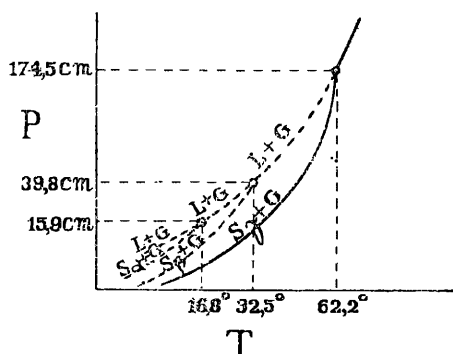
The schematical diagram is shown in Fig. 12.

Further it has proved that the intensively dried phases of sulphur trioxide behave like the phases of a mixture. The continuous change in the vapour pressure of the ice-like form caused by distillation enabled the region of the pseudo-system, to which this form belongs, to be studied. It is the region of a dissociable compound, forming mixed crystals which, if behaving as a unary substance, are a little richer in the more volatile pseudo-component than is the ordinary compound.

As regards the high-melting, asbestos-like form, this stable modification exhibits the phenomenon of falling vapour pressure on partial distillation even more strongly than the ice-like form, and by studying the states of different vapour pressure we found another part of the pseudo-system, namely, that to which the high-melting, asbestos-like form belongs. We realised also a part of a three-phase line for co-existing vapour-liquid-solid, the last phase of which is a mixed crystal of variable composition.

The unary, high-melting, asbestos-like modification is a mixed crystal of the same pseudo-components, with this peculiarity, that the pseudo-components are in inner equilibrium.

FIG. 12.



S_α = ice-like form ; S_β = low-melting, asbestos-like form ; S_γ = high melting, asbestos-like form.

As to the ice-like form, we were fortunate enough to be able to study the larger part of the three-phase line of this form, from which the conclusion could be drawn that the solid co-existing phase was a compound.

The three-phase line of the high-melting, asbestos-like form could only be studied to a small extent, and so far we do not know whether this form is a mixed crystal of a compound or a mixed crystal of the high-melting pseudo-component. For the present, this does not matter, and we will assume here the latter simple case.

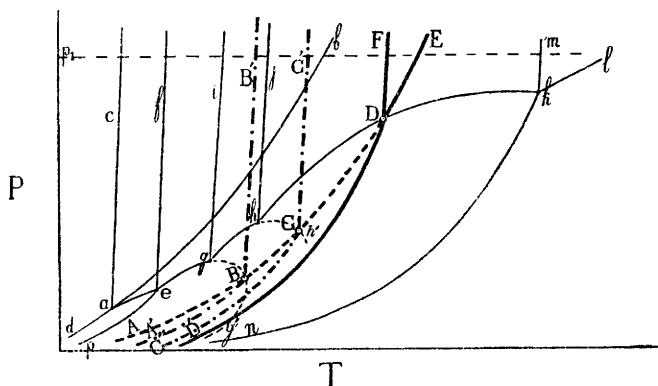
The low-melting, asbestos-like form, which, as already stated, is easily obtained so long as the sulphur trioxide has not been intensively dried, does not appear or appears only in very small quantity if this has been intensively dried. The three-phase line to which the unary melting point under its own vapour pressure, *i.e.*, the triple point, of this form belongs therefore cannot be studied until this form, prepared in the not intensively dried state, is intensively dried. This drying will take several years and therefore we

cannot say whether the low-melting, asbestos-like form is a mixed crystal of a compound or a mixed crystal of a second series of mixed crystals of the highest-melting pseudo-component.

Though the answer to this question will be very interesting, it can have very little influence on the pseudo-system and the situation of the unary system in it which can be deduced from our observations.

In one or two reviews of "The Theory of Allotropy" appears the criticism that the phenomenon of allotropy is regarded as being very complicated. Now it is most remarkable that by chance the first system that could be studied more closely, thanks to the ease of drying, not only gives a strong confirmation of the theory but also shows that the pseudo-system of the so-called simple substance sulphur trioxide is much more complex than the most complicated case dealt with in the theory mentioned above.

FIG. 13.



We will start with the P - T diagram (Fig. 13). It is the diagram of a system of two pseudo-components in which two dissociable compounds appear. The minimum melting points of the compounds, however, are metastable, since the three-phase lines intersect at pressures situated above them.

The case we have to consider here is not one of the simple cases dealt with in the "Theory of Allotropy" (pp. 28, 34), but the much more complicated one following from these cases if compounds are formed.

a is the triple point of the pseudo-component α , and k is the triple point of the pseudo-component β . These points are connected by four three-phase lines, ae representing the three-phase line for the co-existing system α -mixed crystals + liquid + vapour; egg' the three-phase line for the co-existing system $\alpha_x\beta_y$ -mixed crystals + liquid + vapour; ghh' the three-phase line for the co-existing system

$\alpha_u\beta_v$ -mixed crystals + liquid + vapour; and hk the three-phase line for the co-existing system β -mixed crystals + liquid + vapour. We see that the greater part of the three-phase line ghh' represents metastable states.

The position of the unary system in this pseudo-system is given by thick lines. The line ABCDE is the vapour-pressure curve for the liquid in inner equilibrium. Where this curve meets a three-phase line of the pseudo-system a three-phase co-existence of the unary system appears. Every one of the three phases is in inner equilibrium or, in other words, there appears a unary melting point under its own vapour pressure (a unary triple point). The first meeting takes place at D, the stable unary melting point under its own vapour pressure. Further, the metastable part of the unary vapour-pressure line of the liquid still meets two metastable three-phase lines, one at C and the other at B. These points are metastable unary melting points under vapour pressure. At every unary melting point under vapour pressure, or triple point, three two-phase lines meet. The stable sublimation curve, D'D, the stable vapour-pressure curve of the liquid, DE, and the stable melting curve, DF, meet in the stable triple point and the three curves which meet at the two metastable triple points C and B are metastable.

This figure now represents substantially the P - T diagram of the pseudo-system of sulphur trioxide and the position of the unary system in that pseudo-system. ABCDE is the vapour-pressure line of liquid sulphur trioxide in inner equilibrium. A'B is the vapour pressure line of the ice-like form in inner equilibrium, and the three-phase line $egBg'$ that of the pseudo-system, which is a three-phase line for the co-existence of mixed crystals of a compound-liquid-vapour. C'C is the vapour pressure line of the low-melting asbestos-like form in inner equilibrium, and the three-phase line $ghGh'$ that of a mixed crystal of a compound + liquid + vapour, but it is also possible that instead of a mixed crystal of a compound, series of mixed crystals of the β -pseudo-component are existing—which, however, does not change our diagram.

D'D is the vapour pressure line of the high-melting, asbestos-like form in inner equilibrium, and hDk is a three-phase line of the pseudo-system for the co-existing system mixed crystals of the β -pseudo-component + liquid + vapour.

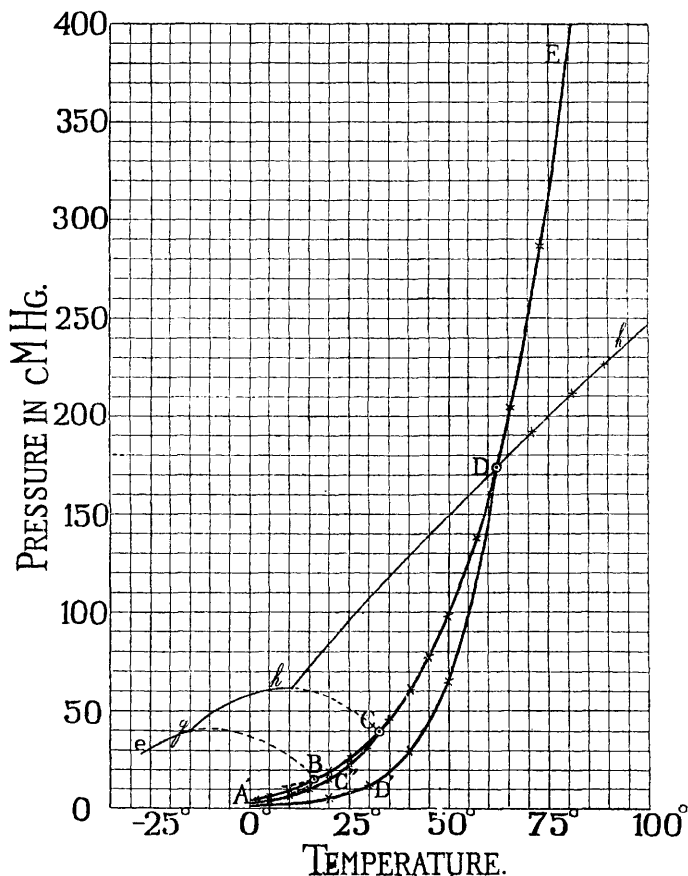
It is possible that here, instead of mixed crystals of the β -pseudo-component, mixed crystals of another compound are co-existing, but as we do not know this, we will assume here the simplest case. Moreover, for an insight into the connexion of the pseudo- and unary systems this question is of little importance.

At two places now we have been able to penetrate the pseudo-
Q Q*

system, (1) in the region to which the ice-like form belongs, and (2) in the region to which the high-melting, asbestos-like form belongs.

By distilling off the intensively dried, ice-like form compositions different from that of the unary ice-like form could be obtained and so it was possible to determine a part of the three-phase line $egBg'$.

FIG. 14.



By distilling off the intensively dried, high-melting, asbestos-like form, enormously high effects were realised and states were obtained the vapour pressures of which were reduced up to 1/15 of the vapour pressure at inner equilibrium at the same temperature. In this connexion vapour-pressure lines could be realised lying far below the unary vapour-pressure line D'D.

This phenomenon enabled us, by continuing these curves, to

stable and of the two metastable solid states at different temperatures, under constant pressure. Our P - T and T - X diagrams do not show a eutectic, which is most probable if β is a polymeride of α .

It appears from our study of sulphur trioxide that the "Theory of Allotropy" has not represented the phenomenon as more complicated than it is. From the experiments of H. B. Baker and Mrs. Baker as well as our own, it was to be expected that a study of substances in an intensively dried state would offer the greatest chance of finding out something about the complexity of the so-called simple substances and we have found that the two first substances which could be obtained easily in an intensively dried state, namely, sulphur trioxide and phosphorus pentoxide, showed the complexity in a most distinct way.

Nature is very complex; and the old theory of allotropy is not satisfactory, for it cannot be assumed that we have studied accidentally the only substances showing complexity. We have studied the substances most easily dried, and we may expect that other substances in the intensively dried state will also show complexity, for there is little doubt that complexity is a general phenomenon.

In the next paper we shall deal with the results of our X -ray investigations.

Summary.

The investigation of the ice-like form of sulphur trioxide has been completed. The unary sublimation curve and the unary vapour-pressure line of the liquid having been determined, the heat quantities can be calculated. The unary triple point is at 16.8° and 158.5 mm. Hg.

The low-melting, asbestos-like form has been studied in the not intensively dried state, in which it is in inner equilibrium, so that here also the heat quantities can be calculated. The unary triple point of this form is at 32.5° and 398 mm. Hg.

The intensively dried, low-melting asbestos-like form cannot be prepared from the intensively dried, ice-like form; instead of the low-, the high-melting form always appears. The intensive drying of the low-melting asbestos-like form must be done with the substance in the solid state, and will take perhaps several years.

The high-melting, asbestos-like form has been studied closely in the intensively dried state. It exhibits more strongly than any other form the property of diminishing vapour pressure on distillation. A decrease from 59.1 to 3.7 cm. Hg has been observed.

The abnormally low vapour pressures remain constant at room temperature. But at higher temperatures the vapour pressure increases with a velocity which decreases with the time. This proves the velocity of the establishment of the inner equilibrium

to be imperceptibly slow at 18° . At higher temperatures, however, this velocity increases, and becomes manifest in the increasing vapour pressure, until inner equilibrium is reached. The vapour tensions asymptotically approach final values, being the values corresponding to inner equilibrium. The unary sublimation curve of this form has thus been found and the heat quantities have been calculated. The unary triple point of this form is at 62.2° and 174.3 cm. Hg.

In a second section the intensively dried, high-melting asbestos-like form has been considered more closely, and the phenomenon of diminishing vapour pressure on distillation studied in detail. The initial melting points (and the corresponding vapour pressures) of states of different low vapour-pressures lie up to 33° above the melting point of the same substance if in inner equilibrium.

The observed phenomena prove that the high-melting asbestos-like form is a mixed crystal of at least two pseudo-components differing widely in volatility and melting point.

Application of the theory of allotropy to these results enables the position of the unary system in the pseudo-system to be deduced. This position is given in a P - T diagram and in a T - X diagram and by its means the observed phenomena can easily be demonstrated.

This study shows most clearly that nature is very complex, and the old simple theory, being unsatisfactory, is to be replaced by the theory of allotropy.

THE UNIVERSITY, AMSTERDAM.

[Received, January 21st, 1926.]
