

AN INVESTIGATION OF SULPHUR TRIOXIDE

WITH REFERENCE TO

ITS SUPPOSED HETEROGENEITY

by

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TO DR. A. N. CAMPBELL

under whose very able direction
this first venture into the field
of research has been undertaken.

To him the writer offers his
most grateful thanks.

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HISTORICAL

Allotropy is the term used to cover the whole complexity of phenomena which substances show in their various forms¹.

Probably the first to observe that substances can exist in different crystalline forms was E. Mitscherlich². He first worked on Sodium Phosphate and later in 1825 he extended this work in other observations on Sulphur, some Sulphates and Mercuric Iodide. At the same time he commented on the influence of temperature on the various forms, especially in the case of mercuric Iodide. Frankenheim² extended the observations of Mitscherlich and compiled the following rules:

1. Isomeric bodies have different melting and boiling points; their vapours have, as a rule, different specific weights.

2. As soon as the warming of an isomeric body A has exceeded a certain temperature (m°), it decomposes and passes into another state B.

3. A can never exist at a higher temperature, but B can not only exist at a lower temperature, but even be produced at a lower temperature.

4. If B is inoculated by A at a temperature lower than m° , it changes into A from the point of contact outwards, but the duration of the change is very variant. Sometimes it is instantaneous over large distances, and sometimes it takes whole hours to pass over one hundredth of a Line.

5. Through contact with foreign substances and more especially through shaking B is transformed into A, if its temperature is below m° , but this is not always the case.

6. The change of B into A is exothermic.

Terwen¹ comments, that with the exception of the third, the above rules are all correct.

The first examples of allotropic organic substances were recorded by Jungfleisch³ in the case of Chlordinitrobenzene 1,2,4, and Zincke⁴ in the case of Benzophenone.

The first attempt to classify allotropic substances was made by O. Lehmann⁵, who in 1868 divided them into:

1. mutually interconvertible, (enantiotropic with transition temperature).
2. those in which the transition is not reversible but can proceed only in one direction, and with evolution of heat, (monotropic without transition temperature).

He was previous to Schaum⁶, Ostwald⁷, and Tamman⁸ in stating that perhaps there was no difference between the two classes, but that in the case of the second class, the transition point of the substances lay above the melting point.

Zincke and Lehmann investigated respectively the alpha and beta forms of dichlorstilbene with the following results.

The alpha modification on rapid heating showed a melting point of 192° but if kept liquid for some time gave a repeated melting point of 160°. The beta modification, on the other hand gave an initial melting point of 97°, but on being kept liquid the melting point sank at first and then rose to 160°. From this melt, on cooling, not the beta but the alpha crystal modifications formed. This behaviour was explained by Bancroft⁹ and Roozeboom¹⁰ on the assumption that an equilibrium existed between the two molecules in the liquid state. According to this method such substances as dichlorstilbene would be conceived as a system of two components, which however, could pass into one another in the liquid state until an equilibrium is reached dependent upon temperature. The name pseudobinary is given to such a system.

Following the researches of Zincke and Lehmann, came others which had a similar explanation. Some of these were, the researches of Carveth¹¹ on acetaldoxime, Soch¹² on Benzil-orthocarbonic acid, Hallmann¹³ on benzaldoxime and de Leeuw¹⁴ on Acetaldehyde.

Aside from the behaviour on melting, the change of other physical properties may point to an equilibrium condition in the liquid. There are numerous examples of molecular association in the gaseous state. The vapour density gives a positive means of identifying it. Ramsay found that in the case of liquefaction of some gases, the vapour pressure does not immediately become constant and he explained this as due to an insufficiently rapid establishment of equilibrium between simple and complex molecules. This points towards the occurrence of associated molecules. Drucker¹⁵ attempted to explain the deviation from Boyles Law for all gases and liquids on the assumption of association of molecules, based on the premise, that in every gas and liquid, different types of molecules are present together.

The establishment of equilibrium of tautomeric substances gives many examples of molecular allotropy, which in turn give rise to phase allotropy. The relation between these two became apparent on the publication by Smits¹⁶ of his theory to explain allotropy.

Smits' Theory of Allotropy¹⁷.

By this theory one can explain quite easily and clearly the relations between enantiotropy and monotropy. The basic reasoning upon which the theory is developed may be tabulated as follows:

1. The velocity of change to establish an equilibrium in a one component system containing m different kinds of molecules determines whether or not the system will behave as a unary or a poly-component system.

2. Since a one component system is made up of a single constituent, we must speak of the different molecular species as pseudo-components.

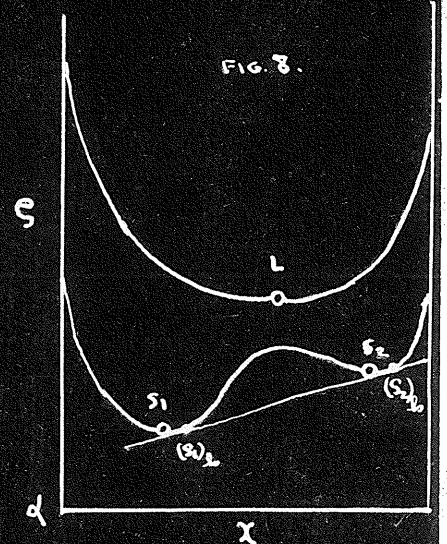
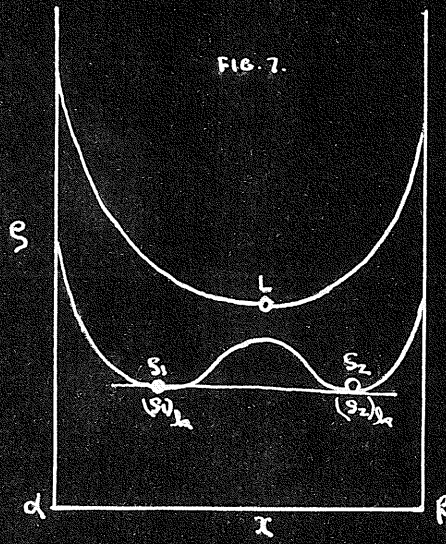
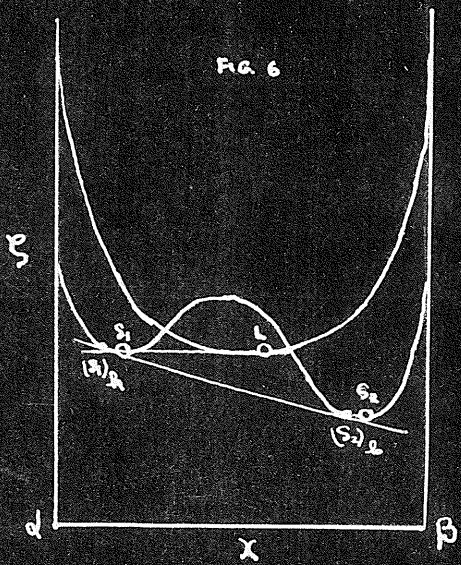
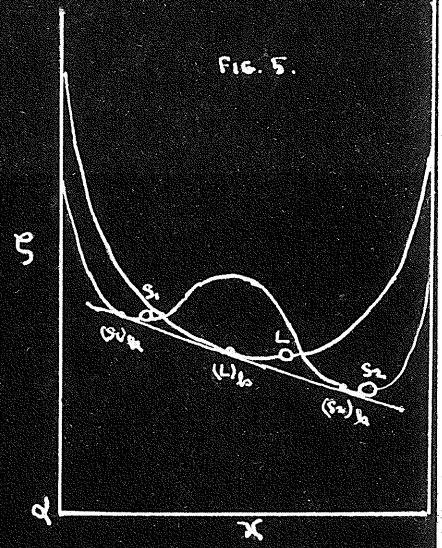
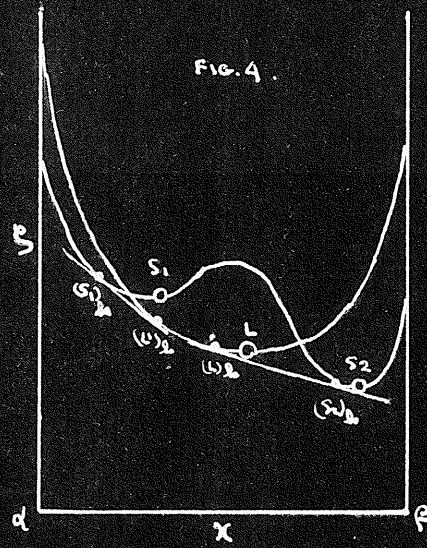
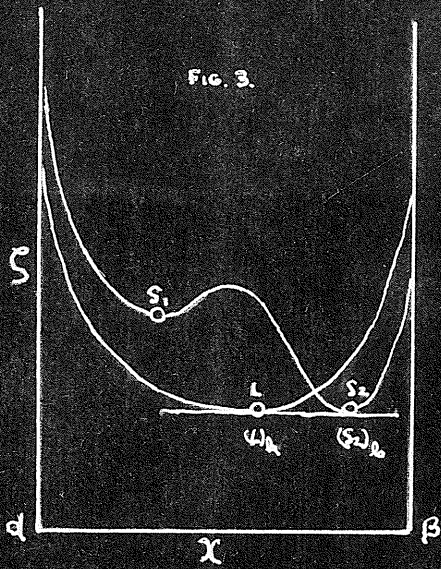
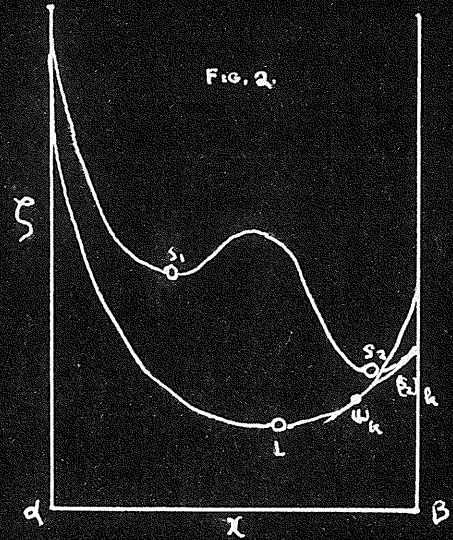
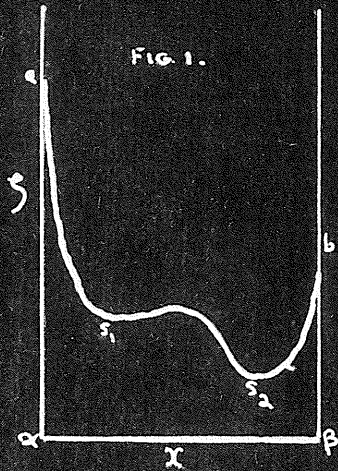
3. The existence of different molecular species of one and the same substance is not exceptional. In liquids we have association, dissociation and tautomerism and we see that liquid phases are complex.

4. Thus from 1. and 3. we must conclude that phase allotropy bears a definite relation to phase complexity. Delimiting molecular species to a narrower sense (e.g., isomers or polymers) we can now say that the origin of phase allotropy is to be found in, or depends on, molecular allotropy.

From these Smits developed the basic hypotheses or assumptions, on which the theory of allotropy is based. The theory states;

1. That every phase, and therefore every crystalline phase of an allotropic substance is a state which, under certain circumstances, can behave as a poly-component phase.
2. On the basis of the analogy between solid, liquid and gaseous states of aggregation he concluded; that the cause of this behaviour must be assumed to be its complexity; i.e., the existence of different molecular species which are in equilibrium when the system behaves as unary.

The deduction of the connection between pseudo and unary systems is facilitated by the derivation of T-X diagrams using the Gibbs Equilibrium Principle. This states that "at a constant temperature and pressure a system tends to change into such a state that the thermodynamic potential (Φ function) becomes a minimum". To illustrate this, the deduction of the T-X diagrams for a pseudo-binary system with that of a unary system situated within it will serve as an example.



The assumption is made that the components are more or less miscible in the solid state, otherwise inner equilibrium is impossible.

The understanding of the T-X diagram will perhaps be made clearer if we first consider its derivation by means of the ξ -X line. In 1891, Roozeboom¹⁶, from the analogy between the behaviour of liquid mixtures and mixed crystals, made the assumption that when the mixed crystal series exhibits a gap, the ξ -X curve has a form represented in Fig. 1 by the line ab. This indicates a continuity, although in the labile region, between the two series of mixed crystals to which the two pseudo-components, α and β , give rise, and which have, in general, different crystalline forms.

If the pseudo-components are miscible in all proportions in the liquid state, the ξ -X curve for the liquid would exhibit no peculiarities, i.e., it would always be convex towards the x axis and show only one minimum. Now if a homogeneous phase of a pseudo-binary system is in equilibrium, where would this equilibrium be found on the corresponding ξ -X curve? At constant temperature and pressure every point on a ξ -X curve represents the smallest value for that mixture. Thus at the minimum point of a ξ -X curve, the ξ value for a corresponding mixture is smaller than that of other neighbouring mixtures and if a reaction is possible between α and β , then this will occur (Gibbs' Equilibrium Principle) and will continue until that composition is reached which corresponds with the minimum point. Here inner equilibrium will be established, and for this, the expression

$$\left(\frac{d\xi}{dx}\right)_{pt} = 0$$

is true. On the mixed crystal line there are two portions outside the labile region where the above expression is true, so that this curve points to the

existence of two equilibria in the solid phase, whilst there is only one in the liquid phase.

If a temperature somewhat lower than the melting point of B is considered, the ζ -X curves for solid and liquid will intersect on the β side (Fig. 2) and under these conditions pure β and mixtures rich in β will be solid. The co-existence between the mixed crystal phase and the liquid phase can be found by drawing the common tangent. If, however, inner equilibrium is established, then the state with the lowest potential appears, i.e. the liquid.

The influence of temperature on the position of the ζ -X curve is given by the equation :

$$\left(\frac{d\zeta}{dt}\right)_p = -\eta$$

Thus when the temperature is lowered the curves rise, but not at the same rate, the liquid curve rising more rapidly than the solid. Thus at a certain temperature we get the co-existence of $(L)_k$ and $(S_2)_k$ with the points L and S_2 (Fig.3). Since both these points are minima of exactly equal value, heterogeneous equilibrium continues to exist unchanged even when inner equilibrium sets in. The temperature is the stable unary melting point.

If the temperature is further lowered, the condition of Figure 4 is reached. In the binary system, two two-phase equilibrium occur between liquid and mixed crystals but in inner equilibrium the most stable state S_2 is formed, i.e. a solid phase.

In Figure 5 we have the three existing phases in the pseudobinary system lying on the same tangent. This is the three phase temperature, but S_2 by nature of inner equilibrium is still its most stable phase.

On still further lowering the temperature the liquid phase in the pseudobinary system will become metastable and at a definite temperature a set of circumstances arises as given by Figure 6. The metastable minimum points S_1

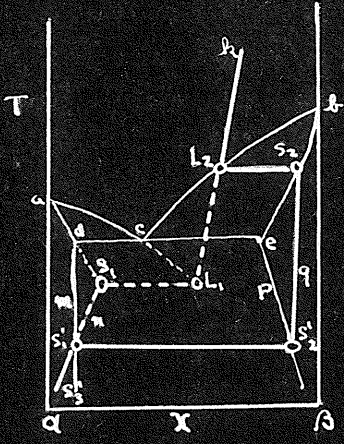


FIG. 9.

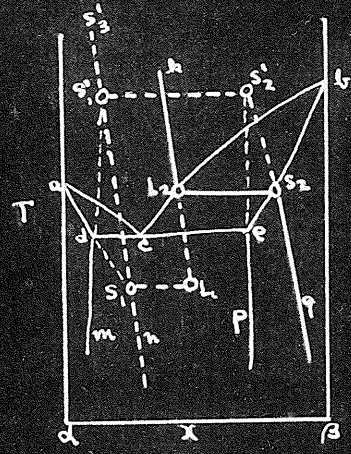


FIG. 10

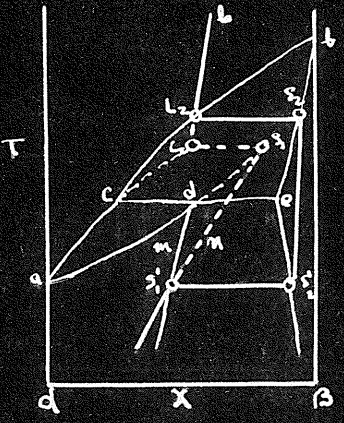


FIG. 11

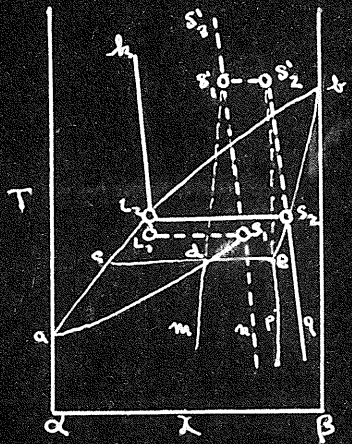


FIG 12

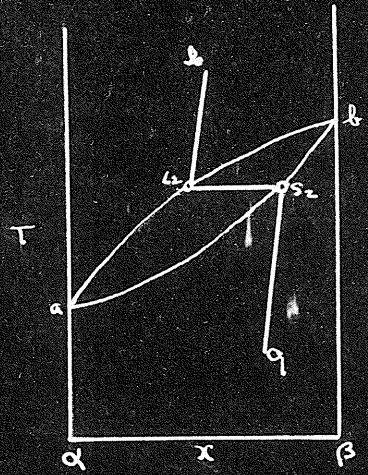


FIG 13

and L have a common tangent which means they can co-exist, i.e. it is the metastable unary melting point. However S_2 is still the most stable phase.

This condition ceases to be very shortly. If the right branches of the ζ curve for the solid phase rises more rapidly than the left, on the reduction of temperature the case occurs where S_1 and S_2 have the same tangent, so that the solid phases $(S_1)_k$ and $(S_2)_k$, which can co-exist in the binary system, can co-exist when inner equilibrium is established. This temperature is the transition point (Figure 7).

If the temperature falls a little more, a reversal occurs (Figure 8), where the minima of S_1 is lower than S_2 and thus S_2 becomes metastable with reference to S_1 .

If this reversal of relationship occurs at a temperature below the stable unary melting point the phenomenon is known as enantiotropy. The case may occur, however, where at high temperatures S_2 is metastable with respect to S_1 and that this relationship is reversed through the more rapid use of the metastable point S_1 than that of the point S_2 . In this case, the transition would occur above the unary melting point and the phenomenon known as monotropy would occur. A third and final case may occur where the minimum on the left hand side of the ζ -X curve for the solid state may be absent.

In this case neither enantiotropy nor monotropy would occur, but only molecular allotropy.

The results of the ζ -X diagrams may be represented by $(TX)_p$ figures. Figure 9 is the T-X diagram for a pseudobinary system with a eutectic. ad and be are co-existing mixed crystal phases together with the melting point curves ac and bc. Below the eutectic temperature dS_1' and eS_2' co-exist. In the liquid phase the change of equilibrium with temperature is given by a point on the line kL_2 . This point corresponds to the ζ -X diagram given by

Figure 2. The point of intersection with the melting curve L_2 , is the unary solidification point (Figure 3). Here the mixed crystal S_2 separates out. At lower temperatures the internal equilibrium for this mixed crystal displaces itself along S_{2q} . The unary melting point curve kL_2 is continued in the metastable region, and would cut the second melting curve in L_1 . This is the metastable unary melting point Figure 6. Here the mixed crystal S_1 would separate and on further lowering of the temperature would displace itself along S_{1n} . The possibility may occur that the inner equilibrium curve of the mixed crystal S_{2q} may cut the mixed crystal curve of the binary system eS_2' . If this happens below the eutectic point, the intersection point S_2' , which itself is in inner equilibrium, is in heterogeneous equilibrium with S_1' (Figure 7). This temperature is the transition temperature. Further cooling would give the stable mixed crystal curve S_1', S_3' , this being the natural continuation of S_{1n} . This represents the case of Enantiotropy.

If the curves S_{2q} and eS_2' do not cut each other below the eutectic point, the transition point is absent and we have the case of Monotropy. (Figure 10) The possibility arises that in this state a separation takes place in the metastable state and as a consequence we have a metastable transition point where S_2' and S_1' are in equilibrium with each other.

In the case where the three-phase temperature in the pseudo-binary system lies between the melting points of the components, the $(T-X)_p$ figures for Enantiotropy and Monotropy would take the forms Figures 11 and 12 respectively. With reference to the ζ -X figures, in these cases the point L (Figure 7) would be to the left of $(S_1)_k$ and not between the two co-existing solid phases.

If the components form a continuous mixed crystal series we have molecular or homogeneous allotropy if, at least, no mixing takes place in the solid state at any temperature. Although we must consider the two molecular species, there

remains but one solid phase, indicated by the inner equilibrium curve S_{2q} (Figure 13).

Lehmann's division of polymorphic substances is not wholly unequivocal according to Tammann¹⁹ because "the conditions of state alone determine whether a phase is to transform reversibly or irreversibly". Citing the behaviour of Ice I and III as an example he concludes that a phase is reversibly transformable into any phase with which it can come into equilibrium upon the equilibrium curve limiting the respective fields and that an irreversible transformation is possible only outside the phase field of the phase concerned. He further concludes that a satisfactory division can only be made upon the basis of the stabilities of the forms concerned. As a measure of stability he utilizes the ζ surface of Gibbs. Dependent upon the positions of the ζ surfaces, two cases present themselves:

1. the ζ surfaces intersect. In this case a change in the stabilities of the two forms occur upon crossing the transition curve, each of the two forms is partly stable and partly unstable.
2. the ζ surfaces do not intersect. In this case one form is stable in the whole phase field and is designated as totally stable whereas the other form is totally unstable.

Whether the ζ surfaces of a substance intersect or not depended, according to Tammann, upon whether the form of the substance belonged to different or the same thermodynamic crystal groups. These groups were according to him atomic in magnitude.

The development of Tammann's theories and a critical analysis of them by the various authorities on the subject of polymorphism is of a very complicated nature. It is the writer's opinion that their inclusion here would only tend to confuse the theoretical considerations incident to the subject of the present investigation.

THE COMPLEXITY OF SULPHUR TRIOXIDE

Historical

The first investigations on Sulphur Trioxide were those of Marignac²⁰, who stated that there were two forms, an ice like or α form (mp. 17°) and a silk like or asbestos form known as the β form. This did not melt under atmospheric pressure but gave a vapour from which the α form condensed.

Schultze and Sellac²¹ found that the liquid obtained from Sulphur Trioxide (mp 16°) sometimes contained white flakes which, below 25° grew into fine white needle like crystals leading ultimately, to the crystallisation of the whole liquid. Melting point determinations in sealed tubes gave a melting range of 50° - 80° and the vapour pressure, which was inappreciable at first, rose in eight days to 30 - 40 mm. of mercury. The work of Weber²² and Rebbs²³ led them to believe that the β form was a hydrate. Reference may be made to the work of Oddo²⁴ and Schenck²⁵ who confirmed Marignac's results as to the formation of the β modification. Schenck²⁵ from dilatometer readings at 35°, concluded that a slow reaction accompanied by a volume change occurred in liquid and assumed the equilibrium.



Lichty's²⁶ experiments did not confirm this view.

Berthoud²⁷ from observations of the melting points and the vapour pressures of the α and β forms concluded that only the α form (mp 16.85°) exists. He found that the β form had a large melting range and that the initial melting point was dependent upon the method of preparation. He regarded the β form as a hydrate and expressed surprise at the extremely small amount of water necessary to cause such a profound change in the properties (estimated at less than 1 molecule per million molecules of Sulphur Trioxide). Le Blanc

and Rühle²⁸ investigated the vapour pressures and melting points of solid Sulphur Trioxide, obtained by various methods, and the vapour pressures of the liquid up to 20°. They came to the conclusion that "Sulphur Trioxide was a chemical chameleon", but nevertheless they managed to separate four groups, each corresponding, according to them, with a definite modification.

These were:

- A, end melting point 95° or 110°
- B, melting point 31°
- C, melting point 16.8°
- D, considered to melt lower than C.

The C modification may be identified with Berthoud's α form.

The Work of Smits and Schoemaker 29, 30, 31,

This work was undertaken in 1922 with a view to testing Smits' Theory. The fact that the β form showed a melting range suggested to Smits and Schoemaker a very slow inner transformation in the solid state. The work of H. B. and Mrs. Baker³² on intensive drying suggested to them that the inner transformation could be further retarded. Accordingly they began work to determine the vapour pressures of the intensively dried forms of Sulphur Trioxide with a view to determine its complexity.

Sulphur Trioxide exists in three forms, the ice like or α form which is unstable, a low melting asbestos like or β form which also is unstable and a stable high melting asbestos like or γ form. These forms obtained by various methods were intensively dried, with the exception of the low melting β form, for a period of thirty days or more, by repeated distillation through phosphorous pentoxide. At the end of this time the vapour pressures were taken and the following very interesting results were found:

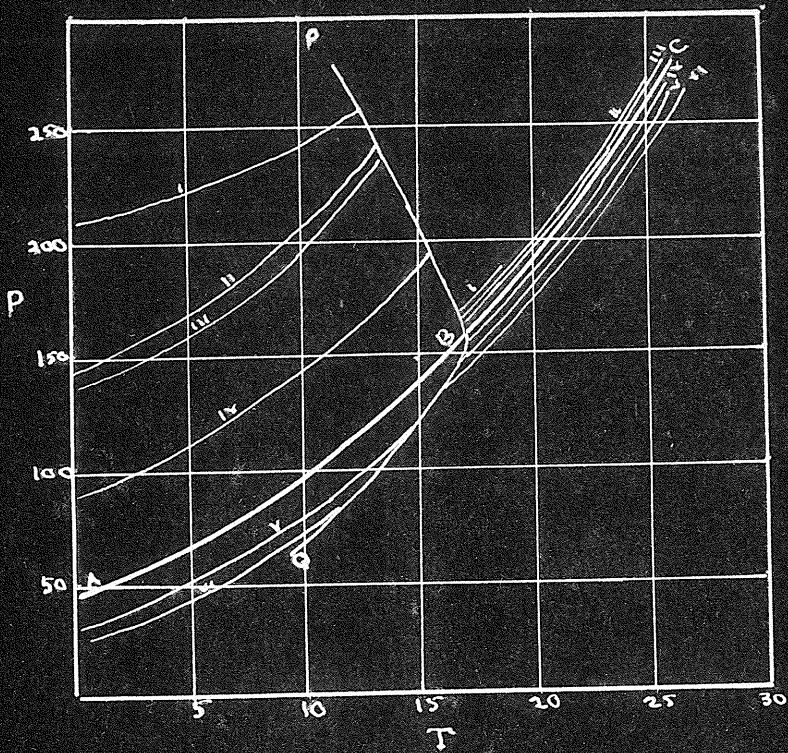
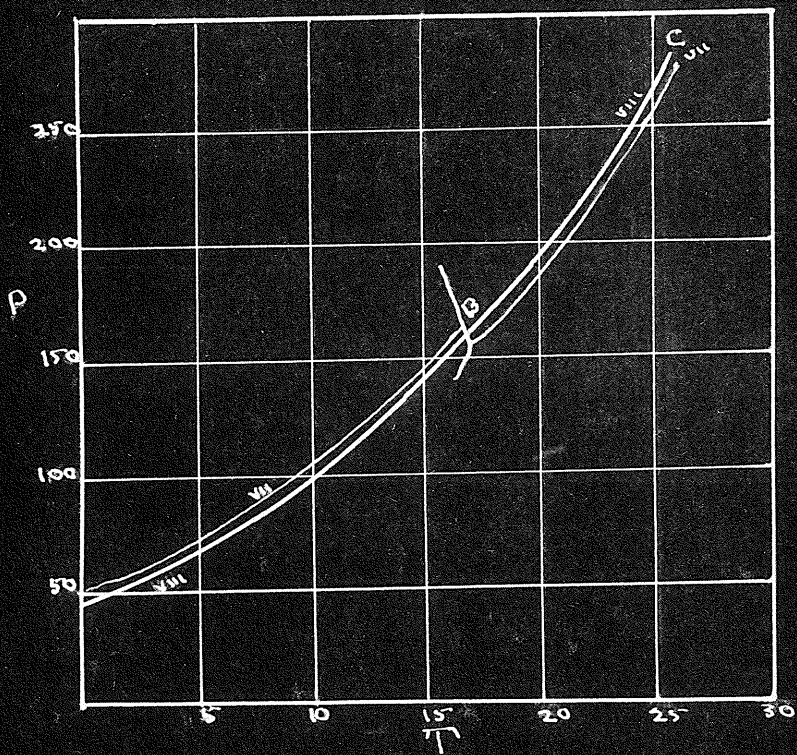


Fig 14

Fig 15



1. The Ice like or d form.

The first determination of the vapour pressure, when plotted, gave curve I in Fig.14. With rising temperature, the vapour pressure in the solid state rose until melting began. Melting took place over a range and during this range the pressure was sinking only to rise again when liquefaction had taken place.

The apparatus was allowed to stand for 18 hours at 18° and the vapour pressure curve was again determined. (Curve II, Fig. 14) It was found that the vapour pressure had fallen considerably in the case of the solid-vapour and liquid-vapour equilibrium, but that the curve for the equilibrium solid-liquid-vapour was in its extent identical with that obtained in the previous case.

The apparatus was again allowed to stand, this time for 40 hours at 18° and the vapour pressure curve was then re-determined. (Curve III, Fig.14) The result was a repetition, to a less degree, of the result obtained in Curve II. Thus for every new series of determinations a lower curve was found for the equilibrium solid-vapour, the same curve for the equilibrium solid-liquid-vapour, and a slightly lower curve for the equilibrium liquid-vapour. Again the decrease of the vapour pressure was more rapid at first but became slower after 40 hours.

By applying the method of partial evaporation, the vapour pressure of the solid state was distinctly reduced and repeated determinations gave the curves IV, V and VI.

Previous to Curve V the vapour pressure of the solid phase was greater than that of the liquid but in Curve V it lay below and a part of the three phase line S-L-G was realised, in which the pressure increased with rise of temperature. Curve VI indicated this to a more marked degree.

That these curves all relate to the same crystal form is indicated by the fact that the vapour pressure lines of the solid state all end in points on the same three phase line PQ.

Smits and Schoenmaker now determined the vapour pressure of a sample of the δ form which had only been intensively dried for a few days. The resultant curve was given in Curve VII, (Fig. 15). The vapour pressure curve of the solid phase was only a little above that of the liquid.

The vapour pressure was very carefully determined after 120 hours had elapsed. The curve is given in Curve VIII, (Fig. 15). The vapour pressure line of the solid phase had fallen and that of the liquid had risen to just the extent that the lines intersected on the three phase line. Melting was complete at one temperature (16.8°), that observed by Berthoud. Thus, in the insufficiently dried preparation, transformation must have taken place leading to the disappearance of the complexity.

The triple point for the δ form was found to be at 16.8° and 158.5 mm. of mercury.

2. The Asbestos like or β form.

The β form was found to consist of two modifications, a low melting metastable β form and a high-melting stable β form.

The low melt β form was studied only in the not intensively dried state and the vapour pressure values were used in determining the triple point data. This was found to be at 32.5° and 398 mm. mercury. Smits and Schoenmaker found that it was very difficult to prepare the intensively dried low melt β form. They prepared it in the not intensively dried state and began to dry it in the solid state. This was a very slow process and the operation would take several years. Since their paper in 1924²⁹, the writer has been unable to find any further data published by them on this form.

FIG. 16.

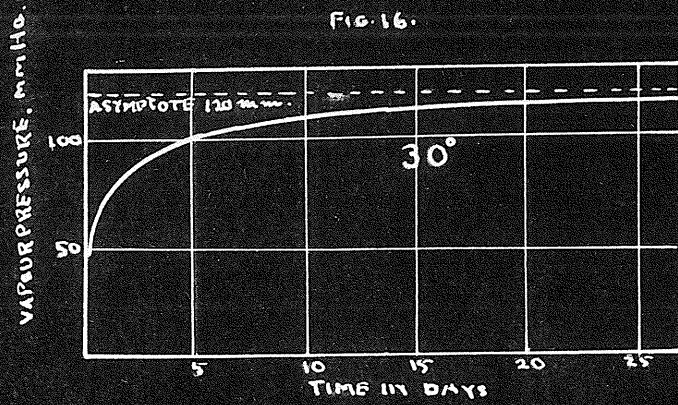


FIG. 17

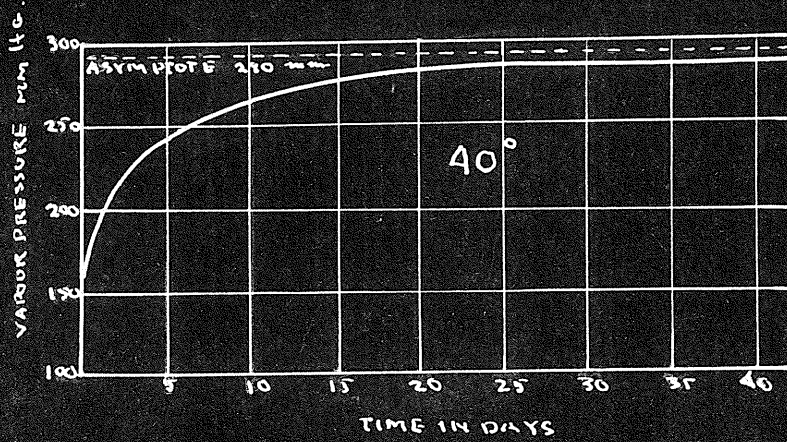


FIG. 18

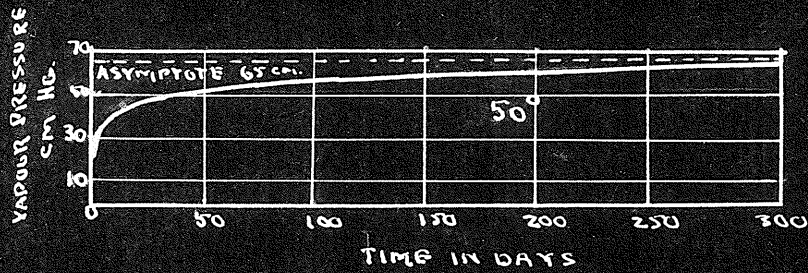
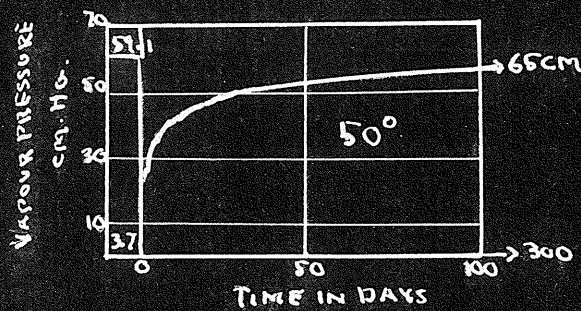


FIG. 19



The intensively dried high melt β form was prepared from a sample of intensively dried α form. The method used was to alternately distil the sulphur trioxide from one vessel to another, the distilling vessel being at room temperature or slowly heated and the receiving vessel cooled in liquid air. By this method the ice like form is practically totally converted to the high melt β form. The residual α form was removed by distillation. The effect of partial distillation on the high melt β form was more marked than in the case of the α form. The intensively dried high melt β form, obtained in the above manner, showed a very low constant vapour pressure at room temperature. At higher temperatures though, the vapour pressure rose with a velocity which decreased with time. This phenomenon was studied at temperatures of 30°, 40° and 50°. The results, given in Fig. 16, 17 and 18, show that the curves approach a final value asymptotically, this value being indicated by the dotted line in the figures.

The behaviour of the high melt β form agrees entirely with that of the α form. Quantitative differences were present due to the higher temperature at which the form was studied. The velocity of establishment of inner equilibrium was found to be imperceptibly slow at 18° but became greater at higher temperatures, as manifested by the vapour pressure, which increases until inner equilibrium is reached.

The triple point data, found from the vapour pressure curves of the high melt β form was found to be at 62.2° and 174.3 cm. of mercury.

In an attempt to determine directly the unary vapour pressure line of the high melt β form, a sample was prepared from not intensively dried α form by simple distillation. This could not be found as it was found that the process of distillation was sufficient to lead to the very dry state.

Smits and Schoenmaker then studied the phenomenon of partial evaporation,

as applied to the high melt form, more closely. The vapour pressure of some intensively dried high melt form, which had stood at 50° for several weeks, was found to be 591 mm. of mercury. This was subjected to partial evaporation. The vapour pressure was found to have decreased to 31 mm. of mercury which later rose as shown graphically in Fig. 19. The fact that the vapour pressure decreased so markedly on partial distillation proved that the high melt β form behaves as a mixed crystal of at least two components differing largely in vapour pressure. These must be pseudo-components as the vapour pressure rises proving the more volatile is formed from the less volatile.

Since it was possible to obtain different states of the high melt β form with very low pressures, the determination of their melting points was of importance as they are points on a three phase line in the pseudo system. Three of these were found to be at 71°, 81° and 88.8°, approximately 9°, 19° and 26.5° above the unary melting point.

An interesting phenomenon was found that whilst the rise of the vapour pressure with temperature rise was slow in the solid state, as soon as melting began, the vapour pressure rose very rapidly, so rapidly in fact as to endanger the mechanism for the determination of the vapour pressure. This was explained on the basis that the liquid first produced on melting of the disturbed state of the high melt β form had an abnormally low vapour pressure due to the low concentration of volatile component. Now while the velocity of establishment of inner equilibrium is slow in the intensively dried solid state, it is by no means so in the liquid and hence inner equilibrium would be established with great rapidity resulting in the sudden rise of the vapour pressure on melting. By determining the melting points of specimens of the highly disturbed high melt β form in sealed tubes, it was found that the initial melting points were up to 33° above that of the form in inner equilibrium.

With this information as to the effects of intensive drying upon the various modifications of Sulphur Trioxide, let us now turn our attention to the theoretical development of its complexity in the light of the Theory of Allotropy.

Theoretical Development

In the case of the intensively dried α form we found that after it stood for 56 hours at 18° , the vapour pressure at 0° had decreased from its initial volume of 207.8 mm. by 71.4 mm. of mercury. Further by distillation the vapour pressure could be changed continuously until a residue with a vapour pressure of 22 mm. at 0° was obtained. That all these different solid phases belonged to the same form, i.e. the α form, was shown by the fact that the melting ranges all fell on the continuous three phase line, corresponding to the equilibrium solid-liquid-vapour for a dissociable compound.

Smits Theory of Allotropy assumes that every state of aggregation of a single substance is complex, and that every crystalline state consists of mixed crystals, built up of molecules of different kinds. These different kinds of molecules can change into one another and the transformation can lead to a chemical equilibrium. Only when this (inner) equilibrium is established does the pure substance behave as a real single one. If the equilibrium is established slowly, or is stopped, e.g. by intensive drying, the pure substance will behave as a mixture.

The rate of establishment of this equilibrium seems to be characteristic for each substance. These substances may be generally classified as "rapid" or "slow". In "rapid" substances, the velocity of establishment of equilibrium is rapid and the substance is simple or unary, whereas in the case of "slow" substances, the substances behaves as a mixture.

To this latter category sulphur trioxide belongs.

The system sulphur trioxide is assumed by Smits and Schoenmaker to be composed of at least two kinds of molecules α and β . These cannot only change into one another but can give a dissociable compound. These

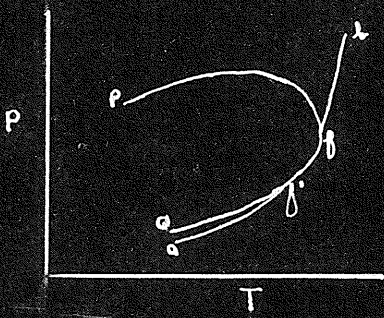


FIG. 20.

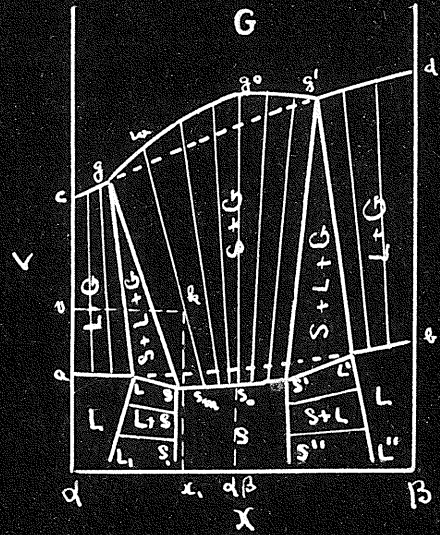


FIG. 21.

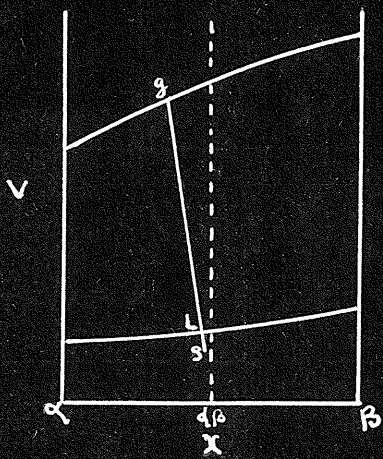


FIG. 22.

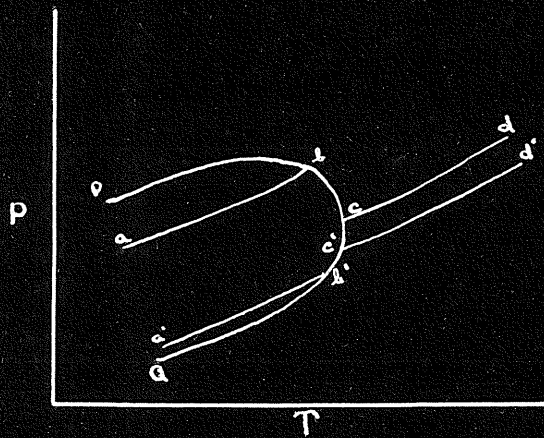
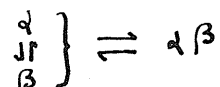


FIG. 23.

transformations can lead to an inner equilibrium thus:



As shown by van der Waals, the three phase line, PQ, of a dissociating compound, composed of a volatile component α and a less volatile component β has the form given in fig. 20. If the compound can exist with the vapour of the same composition there will be a sublimation curve f' tangential to PQ at the maximum sublimation point f' . Similarly, the melting line of the compound will be tangential at the minimum melting point f . The result is that the dissociating compound does not exhibit a single melting point when subject to its own vapour pressure but a melting range ff' , i.e. it realizes a position of the three phase line PQ. With the exception of the maximum temperature, there can exist, at every temperature, two three phase equilibria with different vapour pressures.

Which co-existence can be realised, with a mixture of definite composition, can be deduced by using a V-X diagram, where the molecular volume V is plotted against the composition X. The presence of mixed crystal phases will change the van der Waal diagram slightly.

At the temperature considered it is assumed that the compound alone appears in the solid state, α and β being liquid. The diagram is given in fig.21. At this temperature,

a = molecular volume of liquid α under its own vapour pressure.

c = molecular volume of gaseous α at the same vapour pressure in equilibrium with the liquid phase.

b and d have the same significance with respect to component β . The liquid binodal line ab gives the molecular volumes of the liquid mixtures whilst the vapor binodal cd gives the molecular volumes for the gaseous mixtures. Thus in this diagram every phase is indicated by its V and X

values and corresponding points on the lines ab and cd represent phases in equilibrium. Nodal lines drawn from points on ab to points on cd represent heterogeneous phases in equilibrium. If α is more volatile than β , the vapour will in general, be richer in α than β and therefore the nodal lines from ab will run to the left, except in the case of pure α and β where they will be vertical. A portion of the possible equilibrium liquid-vapour will be metastable because the compound $\alpha\beta$ has been assumed solid at the temperature considered, and thus this stable form will appear in the central part of the V - X diagram. Now the molecular volume of the solid is lower than that of the supercooled liquid, while the volume of the coexisting gas phase is greater than that of the liquid phase in equilibrium with the supercooled liquid. Since the equilibrium of two phases in a system of two components at constant temperature is univariant, ($F = c - p + 2$), there will be a series of equilibria between solid and vapour phases. This series of equilibria is represented by the space $SS_0S'g'g_0g$ in the V - X diagram. SS_0S' represents the compositions and the molecular volumes of mixed crystals of the compound $\alpha\beta$ with either of its components, the line gg_0g' giving the compositions and molecular volumes of the corresponding vapour phases.

The region of mixed crystals and vapour will end abruptly on both sides at the lines Sg and $S'g'$ as we enter into the region of three phase equilibria S - L - G . The vapour line of the system mixed crystal-vapour intersects the vapour lines of the systems liquid-vapour at g and g' giving us the triangles SgL and $S'g'L'$ demarking the regions of three phase equilibria.

With rising temperature the line ab , as well as SS' , rises a little and the vapour lines cd and gg' sink. The nodal lines gL and $g'L'$ move towards the centre, and, as shown by van der Waals, the movement of $g'L'$ is such that it passes through the line of the compound g_0S_0 . At the maximum sublimation pressure g' lies on the line of the compound (at g^0) and subsequently,

at the minimum melting temperature, L' lies on the line (at S_0). Finally the points g and g' , L and L' coincide and the two three phase triangles reduce to one straight line which gives the highest three phase equilibrium in relation to the temperature. (fig. 22.)

From fig. 20 it follows that at any temperature below the maximum three phase temperature, there are two three phase equilibria of different compositions; the composition of the equilibrium with the higher vapour pressure must correspond to a point in the triangle SgL (fig. 21) and that for the system with the lower vapour pressure to a point in the triangle $S'g'L'$.

If we have in our vessel of volume v , a mixture of the composition X_1 , this state is indicated by the point k lying in the two phase region mixed crystal-vapour. From the nodal line we can deduce the quantities of the two coexisting phases, i.e. wk/wS_m gram mols of mixed crystal phase of composition S_m , and S_mk/wS_m gram mols of vapour of composition w .

As before, at higher temperatures the nodal line gS moves to the right. Thus at a definite temperature the point k will enter the shifted triangle SLg which means that we have passed from the two phase equilibrium mixed crystal-vapour to the three phase equilibrium mixed crystal-liquid-vapour. As long as k remains in this three phase triangle we realise points on the three phase line PQ in the P - T diagram. When by movement of the three phase triangle with temperature rise the point k passes the line gL , the solid phase disappears and we get the two phase equilibrium liquid-vapour.

If the composition had lain more to the right, the point k would have entered the triangle $S'L'g'$ and we would have realised points on the lower part of the three phase line PQ in the P - T diagram until the point k had passed the line $g'L'$ when again would be obtained the two phase equilibrium liquid-vapour. By changing the composition from left to right, e.g. by partial distillation of the mixed crystal phase, we would realise with the first

series of compositions, a vapour pressure line for the mixed crystals-vapour, than a portion of the upper three phase line, and finally a vapour pressure line for liquid-vapour.

Since we have a system of two components, the phase rule states that the equilibrium of two phases is bivariant. If, however, the volume is given, the system becomes univariant and the vapour pressure line is fixed.

With the second series of compositions, i.e. where k lies nearer $S'L'g'$ we would realize a vapour pressure for the mixed crystals-vapour, a part of the lower three phase line and finally a vapour pressure line for liquid-vapour.

When k lies on the line which represents the limiting case of the two three phase triangles at the maximum temperature of three phase formation, (fig. 22), we cannot realize a portion of the three phase line PQ but only a point. Consequently, melting would take place at one temperature as with a single substance. i.e. a unary melting point.

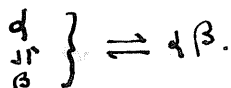
Finally, if the compound has a sublimation line, this line is the lowest curve for the equilibrium mixed crystal-vapour and thus forms the limit attainable by distillation of the mixed crystal.

Let us now draw in a PT diagram, what has been discussed with reference to the vapour pressure lines of mixtures obtained from distillation of the mixed crystal. In fig. 23 we have the vapour pressure lines of (1) a mixture richer in α than the compound α/β and (2) the mixture after distillation, which represents a composition a little poorer in α than the compound α/β . The PT lines of the original mixtures are given by ab , bc and cd , whilst those of the residue after distillation by $a'b'$, $b'c'$ and $c'd'$. Between these two are naturally other mixtures giving intermediate lines. From the vapour pressure lines of the original mixture ab , bc , cd , the mixture on distillation became progressively poorer in α and the portion of the three phase line will shrink

until b and c coincide. This occurs at the maximum temperature of liquefaction. On further distillation b will pass c and the intercept on the three phase line would increase.

In the limiting case, b' will have reached the maximum sublimation point and the line a'b will have fallen below the three phase line with the exception of the maximum sublimation point where the two lines intersect.

From the applications of these above theoretical considerations we can interpret the experimental behaviour of the dried forms of sulphur trioxide. We may conclude that dried sulphur trioxide behaves as a mixture of a system of two components which give a dissociable compound, the initial composition of the mixture lying toward the side of the more volatile component (fig. 14). In the case where inner equilibrium had set in, in the insufficiently dried preparation, the inner equilibrium



must have established itself and the system behaves as unary.

In the case of the low melting asbestos like form, the three phase line, to which the triple point of this form belongs, could not be studied because of the great difficulty of preparing the intensively dried form.

With respect to the high melt asbestos like form, Smits and Schoemaker were able to study part of the three phase line for co-existing vapour-liquid-solid, the last phase of which is a mixed crystal of variable composition. By studying the phenomenon of falling vapour pressure, they found another part of the pseudo-system. They found that the unary high melt asbestos like form is a mixed crystal of the same components, with this peculiarity, that the pseudo-components are in inner equilibrium.

From these results they were able to construct a P-T diagram (fig. 24) which showed that the pseudo system of the so-called single substance sulphur trioxide was much more complex than one would expect.

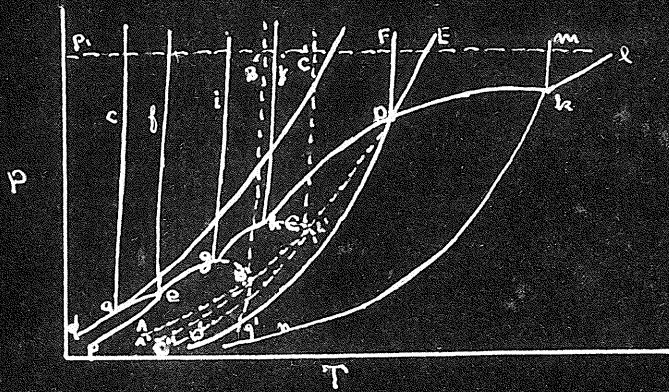


FIG 24.

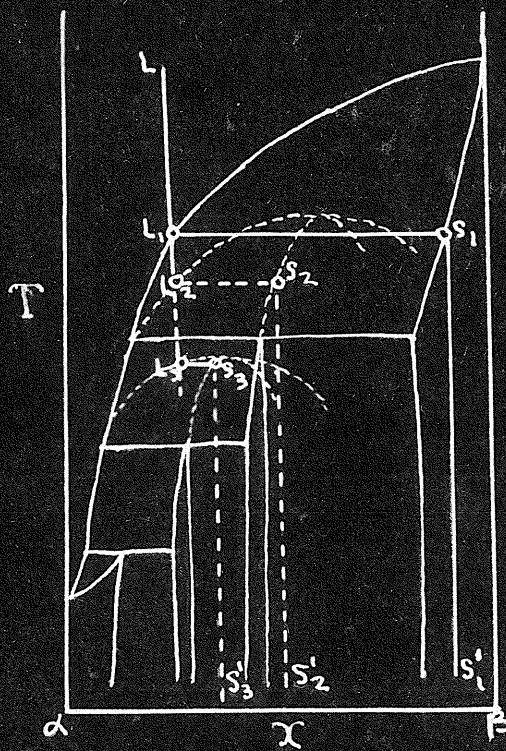


FIG 25.

Fig. 24 is the diagram of a system of two pseudo-components in which two dissociable compounds appear. The minimum melting points of these compounds are metastable, since the three phase lines intersect at pressures situated above them.

a = triple point of pseudo-component, α .

k = triple point of 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, eg g' 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 crystal-liquid-vapour and hk the three phase line for the co-existing system β mixed crystal-liquid-vapour. It will be seen that the greater part of the three phase line ghh' is metastable.

The position of the unary system is given by thick lines. ABCDE is the vapour line for the liquid in inner equilibrium. At the point of intersection with a three phase line of the pseudo system a unary triple point appears. There are three of these intersections, the first at D, the stable unary melting point under its own vapour pressure, and two metastable unary triple points, one at C and the other at B. At every unary triple point three two phase lines meet. Thus at D, the stable sublimation curve D'D meets the stable vapour pressure curve of the liquid DE and the stable melting curve DF. The three curves which meet at the two metastable triple points C and B are metastable.

This figure represents substantially, the P-T diagram of the pseudo system of sulphur trioxide and the position of the unary system in the pseudo system. ABCDE is the vapour pressure line of liquid sulphur trioxide in inner equilibrium. A'B is the vapour pressure line of the α form in inner equilibrium, and the three phase line eg Bg' that of the pseudo system which is a

three phase line for the coexistence of mixed crystals of a compound-liquid-vapour. $C''C$ is the vapour pressure line of the low melt β form in inner equilibrium and the three phase line $ghCh'$ that of a mixed crystal of a compound-liquid-vapour. According to Smits and Schoenmaker, instead of a mixed crystal of a compound, a series of mixed crystals of the β pseudo-component may exist. This, however, does not change the form of the diagram.

$D'D$ is the vapour pressure line of the high melt β form, 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. Here again, instead of mixed crystal of the β pseudo component, mixed crystals of another compound are co-existing, but as they had no knowledge of this they assumed the former simpler case.

As mentioned before, Smits and Schoenmaker were able to penetrate the pseudo system in two places;

1. in the region of the α form where they determined part of the three phase line $egBg'$.
2. in the region of the high melt β form where part of the three phase line hDK was realized.

The PT diagram given in fig. 24 is diagrammatic.

The melting point figure, or T-X diagram, corresponding to the constant pressure, as represented by p_1 in fig. 24, is given in fig. 25. It is that of a pseudo-system which contains two compounds giving mixed crystals. The melting points of these compounds are situated in metastable regions. The line $L L_1 L_2 L_3$ gives the inner equilibrium in the liquid at different temperatures. Where this meets the melting point curve of the pseudo system, a unary melting point occurs. In the figure these appear at L_1 , L_2 and L_3 . The co-existing liquid phase L_1 and the solid phase S_1 at the stable unary melting point, represent the melting equilibrium of the high melt β form. (The term melting equilibrium is used here instead of the melting point, as

the melting phenomenon is expressed in the T-X diagrams by two points, one for the solid and the other for the liquid phase). Similarly L_2 and S_2 are the metastable co-existing phases of the low melt β form at the metastable unary melting equilibrium and L_3 and S_3 , those for the α form. The lines SS_1' , S_2S_2' and S_3S_3' represent the inner equilibria of the stable and the two metastable solids at different temperatures under constant pressure.

Discussion of the Problem.

The problem assigned to the writer was to further investigate the complexity of the substance sulphur trioxide. The foregoing considerations of Smits and Schoenmaker^{29,30} make it evident that sulphur trioxide is composed of at least two molecules α and β , but as to the nature of these pseudo components very little is known. As to whether these forms are isomerides or polymerides, using the terms in the widest possible sense, is still a question. The new ideas on atomic structure show that fine differences are possible between the atoms of the same element. These differences are, for instance, connected with a change in the quantum numbers of the valence electron orbits, and such different atoms can give rise to molecules with finer differences than are commonly exhibited by isomerides. It must be understood, however that in a broad conception of the idea "isomerism", this term will include these different molecular species.

One fact that shows up in the foregoing considerations of Smits and Schoenmaker is that the T-X and P-X diagrams do not show a eutectic (fig. 25, 29) which would probably be the case if α and β were polymerides.

Reference should be made to the works of Smits and Schoenmaker³¹ in their X-ray investigations of the various forms of sulphur trioxide. Briefly, a Roentgenogram was taken of the intensively dried high melt β form, using Cu K α rays. The modification was then heated at 50° for 48 hours. Under those conditions the vapour pressure was found to have increased greatly and it

was expected that the Roentgenogram would have shown a difference. This was not the case. It was unchanged. Thus two alternatives were in order, either the X-ray method was unable to detect the change which had taken place in the solid or the X-rays had effected the establishment of inner equilibrium in the first exposure so that the state of the solid was the same before and after the heating. Accordingly they investigated the effect of X-rays on the establishment of inner equilibrium. It was found that on exposure to X-rays, the vapour pressure of the high melt β form in the disturbed state began to rise showing that X-rays rapidly effect a transformation in the direction of inner equilibrium.

Further, Roentgenograms were taken of the two metastable modifications of sulphur trioxide, the α form and the low melt β form, not only were the diagrams identical, but they were that of the high melt form. Thus, besides effecting an establishment of the inner equilibrium of sulphur trioxide, the X-rays transformed the metastable states into the stable state i.e. the high melting asbestos-like modification.

Since X-ray analysis offered no solution to the investigation of the complexity of sulphur trioxide, it was clear that another channel of investigation must be followed. On consideration, the investigation of the refractive index, or the change in refractive index of the various forms of sulphur trioxide, seemed to be the most promising, and accordingly investigation was begun to determine, if possible, the refractive indices of the various forms of sulphur trioxide, both in inner equilibrium and in the highly disturbed states in the hope that some information might be found to yield a clue to the final nature of the complexity of sulphur trioxide.

Before proceeding to an explanation of the technical difficulties which

were encountered in the problem, it would be profitable to examine some theoretical considerations which have some bearing upon the problem.

The refractive index of one medium with relation to another is given by the formula:

$$n = \frac{\sin i}{\sin r}$$

in which i and r represent respectively the angles of incidence and refraction.

Where V_1 and V_2 represent the respective velocities of light in the two media we get:

$$n = \frac{V_1}{V_2}$$

The refractive index, n , of a liquid, varies with temperature and pressure as the number of molecules in the path of light is changed, but the specific refraction is quite independent of these variables. On the basis of the electro-magnetic theory of light, Lorenz and Lorentz³³ have derived the following formula for the specific refraction:

$$r = \frac{1}{d} \frac{n^2 - 1}{n^2 + 2}$$

Where r = specific refraction.

n = refractive index.

d = density

To compare the refractive powers of different liquids, the specific refractions are multiplied by their respective molecular weights to give the molecular refractions.

This is given by the formula:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

Bruhl's researches on the refractive indices of organic substances

showed that the atomic refraction of an element is dependent upon the ratio of combination with other elements. Nasini³⁴ has investigated the specific refractions of sulphur trioxide, sulphur dioxide and sulphuric acid very thoroughly, and the comparison of the specific refraction of sulphur trioxide obtained, (through the molar refractivity) with these, may shed some light upon its atomic structure. Also, it is said that the molar dispersion, $= R_{\lambda_1} - R_{\lambda_2}$, is more strictly additive than the molar refractivity and this may be of further help.

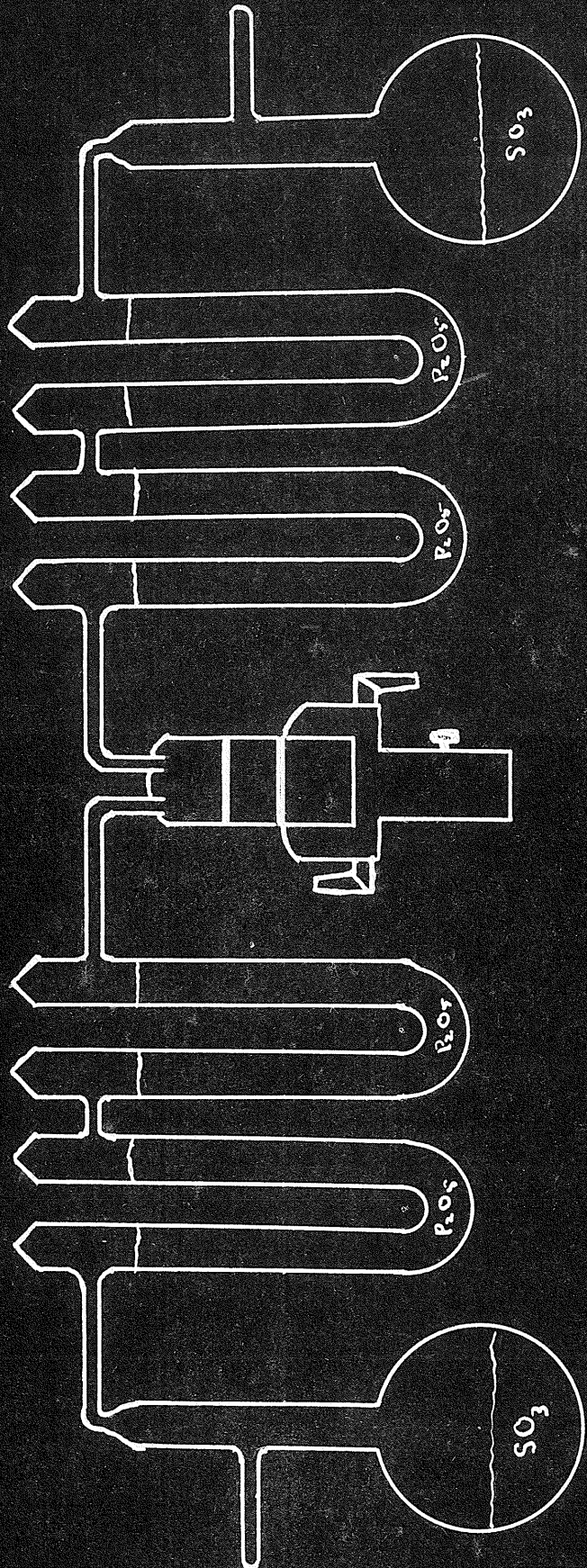


Fig. 26.

Apparatus

The apparatus (fig. 26) consists of Pulfrich refractometer, two double-U drying tubes and two storing vessels. The glass used was Pyrex throughout with the exception of the lowest part of the cell for the determination of the refractive index. This was a part of the equipment which came with the refractometer and as its lower edge was ground to the convexity of the prism surface, it was indispensable to the set up.

The refractometer used was of the Pulfrich type, manufactured by Zeiss. An I^c prism was used of the range 1.31810 - 1.60493. This was calibrated to the instrument for the correction factor. As a source of illumination, a hydrogen tube was used. This gave three lines, the d_{red} , β_{blue} and the γ_{violet} which afforded a good means of checking readings.

The receptacles were converted 125 cc. Pyrex distillation flasks. The tops of these were drawn out in an oxygen flame, and Pyrex tubing of the requisite diameter was sealed in.

The drying tubes consisted of double-U Pyrex tubes which were specially made for the experiment. These were filled with phosphorus pentoxide in a manner which will be described later.

The Cell

The part of the apparatus with which the most trouble was experienced was the cell for holding the liquid sulphur trioxide. The success of the whole experiment depended upon the imperviousness of the cell to moisture. The cell is given diagrammatically in fig. 27.

The first approach to the construction of this cell was made by drilling two holes in a glass plate. Glass tubes were expanded in a flame and then drawn out. These were fitted into the holes and the tube was ground into the

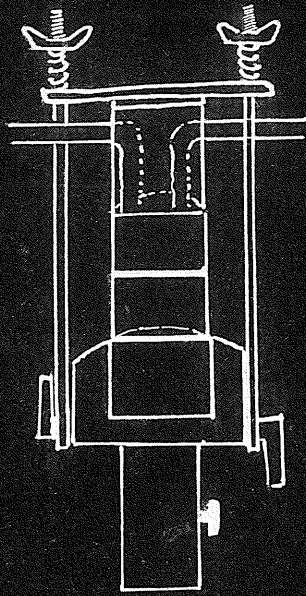


Fig. 27.

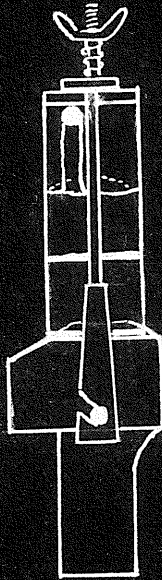


Fig. 28.

hole in the glass plate until a perfect fit was obtained. The tubes were then sealed in and the plate sealed on to the receptacle of the Pulfrich. It was found that the tubes were liable to break rather easily and therefore the adaption was discarded.

The final solution to the construction of the cell is given in figures 27 and 28. A special glass top (Pyrex) was made which was able to withstand any strains or shock to which it might be subject.

The next difficulty was the problem of sealing this top to the Pulfrich receptacle and this unit to the prism. The differences of glass composition between the top and the receptacle precluded any attempt at fusing the two together and so recourse was made to chemical seals.

Chemical Seals

The characteristics of the seal sought for were that it did not contain moisture, that it was impervious to chemical action and that it rendered the join air-tight and was mechanically strong. The construction of the cell was such that two glass to glass seals had to be made and the subject of the proper seal to be used was the subject of much investigation on the part of the writer.

The first seal tried was that of pure sodium silicate or water glass. Whereas this gave a mechanically strong join, on setting it was not entirely air tight due to the development of tiny capillaries which were sufficient to ruin any experimentation with intensive drying. In addition, on setting the silicate showed a bad tendency to crack and scale. This could be overcome by the addition of a small quantity of glycerine but this is too liable to chemical action, the sulphur trioxide abstracting the water from the glycerine and giving a carbon residue. Thus in all refractive index determinations,

aside from discoloration due to carbon, there would be a high percentage of sulphuric acid which would render the determinations useless.

A commercial preparation, Picene, was next tried. It is a wax with a melting point of about 160° and has been found very useful in making vacuum seals in radium work. It was absolutely useless however in the present work. Although temperatures in excess of 60° were rarely used, the wax softened to such an extent as to allow the sulphur trioxide vapour to escape. This was not desirable for two reasons, (1) Sulphur trioxide is very poisonous in small quantities. The maximum safe concentration as given by the International Critical Tables, is 0.002%. (2) On contact with the atmosphere it formed sulphuric acid which reacted on the wax seal and rendered it useless.

A search through various literature brought to light a seal composed of lead oxide and glycerine. This combines to partially form a compound lead glycerate. This made an excellent seal which was air tight even under very reduced pressure (0.03 mm. mercury). It was found, however, that introduction of the sulphur trioxide broke down the lead glycerate. The water was abstracted from the glycerate molecule to form sulphuric acid which then reacted with the lead oxide to form lead sulphate. Thus the receptacle became partially filled with a mixture of sulphur trioxide in sulphuric acid, carbon and lead sulphate, all of which rendered this type of seal useless.

It was then thought that if pressure was brought to bear on the cell, together with a sealing agent, that this would probably serve the purpose. Accordingly two brass strips were cut in such a shape that they would hook under the intake and outlet pipes of the cooling system surrounding the prism.

To the end of these strips were braized brass rods which were then threaded. A brass plate was bored to fit these two bolts and pressure was applied by means of springs and butterfly nuts. The top of the cell was fitted with a brass tube machined to fit, and this was filled with lead glycerate to give stability. The insertion of a rubber disc between the top and the brass plate served to further equalise the pressure. This arrangement is given diagrammatically in fig. 27.

The joins were first filled with sodium silicate as it was thought that with the pressure, only a thin film of sodium silicate would be between the glass to glass joins and that no capillaries would result. The seal proved to be very effective until the introduction of the sulphur trioxide. From then on it began a progressive degeneration which in the end rendered it entirely useless.

A letter to the National Research Council of Canada brought back the suggestion of a seal composed of sodium silicate and calcium fluoride. At ordinary temperatures the calcium fluoride reacts with the sodium silicate to form a fluorsilicate. Accordingly this was tried. It was found that this was the most satisfactory seal. By introducing it between the glass to glass contacts and applying pressure it formed an impervious seal which held a vacuum and further was not subject to chemical action.

The method of procedure was as follows, a little calcium fluoride of less than 100 mesh was placed on the mixing plate. A small quantity of the silicate was poured on the plate and the two intimately mixed. This was then applied to the joining surfaces and pressure was applied by means of the previously described apparatus.

The tendency is for the mixture to set rather rapidly and this may be retarded by adding a drop or two of water.

It requires a matter of several days for the reaction to take place in the seal but this phase cannot be overcome by any means known to the writer. It was found that in sealing the cell, the best method of procedure was to first seal the top to the receptacle. After the reaction had taken place, the seal could be immersed in concentrated alkali to remove the excess silicate and, if necessary, a second coat of the mixture could be applied. On setting the cell could be thoroughly cleaned and dried and finally sealed to the prism.

The size of the calcium fluoride particles and the degree of mixing are two important factors in the success of the seals. As mentioned before, the size of the fluorspar particles was less than 100 mesh but the finer the particles the better, as the closeness of the glass to glass seal depends upon these.

The only disadvantage of this type of seal is that once set up and the fluorsilicate formed, it is permanent. Boiling in concentrated alkali will not loosen the seal, and once the experiment is finished, this part of the apparatus cannot be dismantled. This, however, is not such a great disadvantage as the unit can be used for studying the refractive indices of volatile liquids in the pure state.

The Drying Tubes.

The chemical used for intensive drying was the same used in the previous experiments of Smits and Schoenmaker, i.e. phosphorous pentoxide. The method of introducing this into the drying tubes and its dispersion there constituted another problem in the course of constructing the apparatus. The phosphorous pentoxide could not be introduced wholesale as this would have blocked the tubes and the sulphur trioxide could not have passed through.

Phosphorous pentoxide sublimes at about 500°C and so a small electric

furnace was constructed in an effort to sublime the pentoxide into the tubes. This was not a success due to the fact that the pentoxide would clog the portal of entry and finally this method had to be abandoned.

The method finally evolved was that of using short lengths of glass tubing about 1 cm. in length. These were thoroughly cleaned, dried and introduced along with the pentoxide. Thus the sulphur trioxide could pass through the tubes without obstruction, and further, a larger drying surface was obtained than would probably have been the case if the sublimation method had been successful.

The phosphorus pentoxide was introduced in the open tops of the drying tubes by means of a sheet copper funnel and a copper ladle. The advantage of these two was that after each arm of the tube had been filled and sealed, the utensils could be washed free of phosphoric acid and dried before using again. In this way clogging was prevented and the tubes could be easily filled and sealed.

Method of Assembly

The integral parts of the apparatus were first thoroughly cleaned with a mixture of sulphuric acid and potassium dichromate. They were then rinsed out with numerous rinses of hot water, cold water and finally distilled water to remove all traces of acid. They were then dried on a hot plate and finally placed in an oven at 140° for several days to complete the drying. Upon completion the parts were joined and the apparatus mounted. Smits and Schoenmaker recommended that the apparatus be raised to a dull red heat for some time in order to remove the capillaries but this was impossible with the apparatus concerned, so that drying was employed as much as possible before introducing the sulphur trioxide.

After the apparatus was in place it was dried for several days by passing

air, dried through concentrated sulphuric acid and phosphorus pentoxide, through the whole apparatus. This removed the final traces of moisture. When this was judged complete, the drying tubes were filled with the pentoxide in the manner described. At the same time dried air was passed through the apparatus to make certain that no moisture had gained entrance.

Then the tubes were filled and sealed the whole apparatus was tested under reduced pressure over a period of several days until this was perfect. The apparatus was then dried again for a day and the sulphur trioxide introduced.

This was accomplished by making rubber nipple of pressure tubing and inserting one end over the tube leading from one of the containers of the apparatus. The lead tube from the other container was joined by a similar piece of tubing to a stopcock and a high vacuum pump.

The container of sulphur trioxide was then cooled in a mixture of salt and ice and the end broken. This was quickly inserted into the other end of the nipple and the container gently warmed. The storage bulb of the apparatus was then cooled in a mixture of salt and ice and by this method the sulphur trioxide was transferred.

When it was transferred, the vacuum pump was started and the tube sealed off. When the apparatus was exhausted the tube leading to the vacuum pump was sealed off and the apparatus was ready for experimenting.

Method of Procedure

The object of the investigation was to study the refractive index, or the change of refractive index of those forms of sulphur trioxide which yielded readily to the process of intensive drying. It was planned to distill the sulphur trioxide from one receptacle, through the drying tube and condense it in the cell. Here the refractive index was to be taken and the liquid distilled through the other drying tube into the other storage receptacle.

This was to have been continued until all the sulphur trioxide was transferred. The following day this process was to be reversed. This was to be continued until the results justified the discontinuing of the experiment. When the liquid was in the cell the refractive index was to have been taken at 26°, this being above the temperature at which the low melt β form crystallises from the α . The storage bulbs were to have been left at room temperature in between distillations.

Refractive Index Data.

The only reference to the refractive index of sulphur trioxide was found in the researches of Nasini³⁴ on the atomic refraction of sulphur. He obtained a value, $n_D^{20} = 1.40965$ for the α form. This was obtained using the method of Weber²². Nasini says of this, "in spite of all precautions taken, the substance takes up water, so that the determination resulted more uncertainly than for the other substances", (Sulphur dioxide and sulphuric acid).

The writer was able to take one set of readings with the material in hand. The results given below show that the seals in the cell had degenerated to such an extent as to allow moisture to creep in and the refractive index gradually rose approaching that of sulphuric acid.

$n_{H\alpha}$		$n_{H\beta}$		$n_{H\alpha}^{30^\circ}$	$n_{H\beta}^{30^\circ}$	$n_{H\beta} - n_{H\alpha}$
54°	05'			1.396025		
53	08			1.401688		
52	53	55°	08'	1.403183	1.409486	0.006303
52	51	55	08	1.403381	1.409486	0.006105
52	50	55	06	1.40348	1.409682	0.006202
52	45			1.40438		
52	20	54	37	1.40648	1.412494	0.006014
52	17	54	36	1.406777	1.412592	0.005815
52	16	54	35	1.406876	1.412690	0.005814

Conclusion.

The writer deeply regrets that circumstances, plus lack of material and time, did not permit him to complete the problem. A problem of this nature has never before, to the writer's knowledge, been attempted as shown by printed records of various societies. It was necessary therefore to do all the groundwork on the basis of trial and error and disappointing as the results were, they, nevertheless, cover the groundwork which must be done in a problem of this kind.

Before concluding, the writer would like to make the following criticisms and suggestions to those who may continue this work:

1. The apparatus should be absolutely clean, and perfectly dry before introducing the sulphur trioxide. The cell is particularly liable to contain impurities which will discolor the liquid, which ordinarily is quite colorless, and render the refractive index determinations increasingly difficult.

Even more important is the absolute exclusion of all moisture, both from the cell and the connecting tubes as well as throughout the apparatus. The presence of moisture in either the tubes or the cell will result in the formation of sulphuric acid and therefore the determination will not be that of pure sulphur trioxide but of a mixture of sulphur trioxide and sulphuric acid.

2. In connection with the presence of moisture, exceeding care should be taken to see that the seals of the cell are air tight and moisture proof. The top join should be examined to see whether the fit is perfect or not and care should be taken as to the particle size of the fluorspar. Although the particle size used by the writer was less than 100 mesh, he is of the opinion that better results could be obtained in the seals, if the fluorspar was much finer than this. In the absence of suitable screens the following expedient may be used, that of making a miniature ball mill of the type used in reducing ore to a very small size. This may be accomplished in the laboratory in the

following manner. Place the fluorspar of less than 100 mesh in a bottle and add some glass beads about the size of a small agate or marble, and then screw the top on. By rotating this horizontally with an electric motor at the proper speed, in a matter of twenty-four hours, the fluorspar will be ground to an impalpable powder. With regard to the speed of rotation it should be such that centrifugal force will carry the glass balls to near the top of the bottle, i.e. the top of one side, if placed horizontally, before the action of gravity causes the balls to fall. In this way the reduction of size is accomplished. There will be a certain amount of silica worn off the marbles but this will not affect the efficiency of the completed seal.

As mentioned before, the exposure of sodium silicate to the atmosphere soon covers it with a hardened film and on mixing with the fluorspar it soon becomes unworkable. The presence of a slight amount of water lengthens the time before hardening and care should be taken not to add too much water.

3. On examination of the method of procedure, the following criticism came to mind. As mentioned before, the method was to progressively dry the sulphur trioxide and to take the refractive index as the drying proceeded. Reference to Smits and Schoenmaker²⁹ on the not intensively dried α form brought out the following result; when sulphur trioxide, which was dried for only a few days, was subjected to vapour pressure measurements, the vapour pressure lines of the solid and liquid were respectively slightly above and slightly below the unary vapour pressure lines for liquid and solid in inner equilibrium. After a period of 120 hours rest at 18°, it was found that the vapour pressure line of the solid had fallen and that of the liquid had risen until they coincided with those of the solid and liquid in internal equilibrium. Applying this result to the outlined method procedure, the

following becomes apparent; the time between distillations, when the substance is not in contact with phosphorus pentoxide, would have been sufficient to allow internal equilibrium to set in, so that the effect of drying would be completely nullified at first and partially as the drying proceeds. Thus it would take a much longer time to proceed up the three phase curve than if the form had been intensively dried at first and the refractive index taken as equilibrium conditions set in. In this manner we would be able to proceed down the three phase curve more easily than to proceed up it.

By intensively drying the sulphur trioxide and then transferring to a system, which, although it has been intensively dried, has no drying agent in, one would be able to follow the three phase line without any interruptions from secondary drying effects.

If this method is adopted the most difficult preparation would be the α form. This would require at least a month of distillation through phosphorus pentoxide. The high melting β form could be obtained in the highly disturbed state by fractional distillation of the converted α form. The low melt β form could only be studied in the not intensively dried state but would be of value in the investigation.

With these criticisms and suggestions the writer concludes what has proved to be a thesis on the preliminary work in the investigation of the complexity of sulphur trioxide by the method of refractive index determination. It is his regret that circumstances did not permit him to make a more complete investigation.

For the benefit of those who may carry on this work, a list of additional literature is given after the bibliography.

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