

THE SURFACE TENSION
OF
INTENSIVELY DRIED
SULPHUR TRIOXIDE

by

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TO DR. A. N. CAMPBELL

under whose excellent supervision
this first venture into the field
of research has been undertaken.

To him the writer tenders
his deepest appreciation.

CONTENTS

- Theoretical -

	<u>Page</u>
I. Allotropy.	
1. Historical Survey	1
2. Smits' Theory of Allotropy	4
3. Intensive Drying and Physical Properties	10
4. The Mechanism of Intensive Drying	15
II. Sulphur Trioxide.	
1. Historical Survey	18
2. Work of Smits and Schoemaker	19
3. Theoretical Development	24
4. The Constitution of Sulphur Trioxide	27
5. Discussion of the Problem	31
III. Surface Tension	34

- Experimental -

I. Measurement of Refractive Index.	
1. Introduction	36
2. The Drying Apparatus	36
3. The Drying Tubes	37
4. Charging with Sulphur Trioxide	38
5. The Intensive Drying	40
6. The Refractometer	41
7. The Measuring Apparatus	41
8. The Seal	42

II. Measurement of Surface Tension.

1. Introduction	45
2. The Measuring Apparatus	45
3. The Cathetometer and Travelling Microscope	45
4. Fusion of the Two Units	46
5. The Intensive Drying (continued)	46
6. Measurements	48
(1) Capillary rise	48
(2) Radius of the capillaries	50
(3) Densities	51
(4) Surface tension values	53
(5) Melting-points	57
III. Discussion of Results	60
IV. Conclusions	62
V. Bibliography	63

- THEORETICAL -

I. ALLOTROPY

1. Historical Survey.

The term allotropy was first introduced by Berzelius¹ in 1841 to mean the existence of one and the same element in different forms, to distinguish the phenomenon from that of isomerism, applied to compounds². This was because isomerism in this sense of the word was thought to be due to different arrangements of atoms in molecules, and as elements were believed to consist of single atoms, this theory could not be applied to elements. With the advent of Avogadro's doctrine, however, this distinction in terminology was weakened, and at present the word allotropy is equally applicable to elements and compounds.

Allotropy includes isomerism, polymerism and polymorphism, and also the different physical states of matter. Lowry³ states that it would be dangerous to exclude polymorphism from the category of allotropy, for what appear to be "mere" polymorphic changes are really reversible isomeric or polymeric changes, when studied more closely. The term polymorphism, however, does not usually infer the chemical differences that other kinds of allotropy exhibit⁴.

We now distinguish between two classes of allotropy, that of elements and that of compounds. The former embodies all the different forms of an element differing both in chemical and physical properties. The allotropes of a compound, on the other hand, differ chiefly in physical properties, their chemical dissimilarities being slight, but there is no sharp difference between the two classes.

Allotropy among elements, which incidentally appears to be favoured by smallness of atomic weight, was probably first observed in the case of diamond and graphite by Smithson Tennant in 1796. Mitscherlich in

1821 studied the modifications of sulphur and other substances. Later examples are those of yellow and red phosphorus, and in the case of compounds, mercuric sulphide and iodide. Numerous examples are known today.

Copisarow⁵ in discussing the allotropy of elements in particular, claims that the causes of allotropy are due to (1) the intermolecular association or aggregation of elements (according to the laws of crystallography), and (2) the intramolecular structure of the elements. Polymorphism is considered to be accounted for by the first, and the remaining types of allotropy by the second. According to his valence theory, Copisarow defines allotropy as not only a function of valence, but also the capacity of an element to exist in forms differing in the mode of their intramolecular linkage. He shows that elements of zero valence will not exhibit allotropy, that those with a valence of one, two or three, will have at the most, two allotropes, one with saturated valences and one with free valences, and that those of higher valence will exist in three forms.

As examples of allotropic compounds that have been studied we may mention chlordinitrobenzene, benzophenone, benzaldoxime and acetaldehyde.

With regard to the earlier theoretical aspects of the subject, Frankenheim prepared a set of rules governing the general behaviour of allotropes, referring to their relative stabilities and their heat relations. In 1888 Lehmann made the following division of allotropic substances:

- (1) Those whose allotropes are mutually interconvertible.
- (2) Those in which the conversion of one form into the other is irreversible, the one form being always metastable with respect to the other.

He considered that the two types were essentially the same, the only difference being that in the second type, the transition temperature of the first type lay above the melting-point. The occurrence of the first is termed enantiotropy, and of the second, monotropy.

Dichlorstilbene occurs in an α and a β form. Zincke and Lehmann studied these forms and observed, among other things, that their melting-points depended on the rate at which the solids were heated. Such behaviour was explained by Bancroft⁶ and Roozeboom⁷ on the assumption that an equilibrium could exist between the two forms in the liquid state to give a unary system, which however could become binary with rapid working.

Soch⁸ found that the freezing-point of benzil-orthocarbonic acid determined by rapid cooling depended on the temperature to which the liquid had previously been heated. This investigation led Smits⁹ to his conception of the phenomenon of allotropy, in which he introduced the new idea which had not occurred to Bancroft or Roozeboom, that the internal equilibrium which prevailed in the liquid state was continued in the solid state.

In contrast to Lehmann's ideas, Tammann¹⁰ regards enantiotropy and monotropy as fundamentally different phenomena, treating the subject from the standpoint of thermodynamics. If a solid figure showing the relation between the temperature, pressure and thermodynamic potential of a substance is constructed, the surfaces so formed are termed the

ζ -surfaces, and are bounded by equilibrium curves. These ζ -surfaces may or may not intersect. If they do, then a change in the stabilities of the two forms occurs upon crossing the equilibrium curve of intersection. If they do not intersect, then the one form is totally stable and the other totally unstable, and the equilibrium curve of the unstable form always has its course within the phase field of the stable form. On this basis,

Tammann divides the forms of a substance into thermodynamic crystal groups such that the forms of different groups can come into equilibrium with each other, but not with members of the same group.

In short, according to Tammann we are not in a position to state that a given form is unstable until its complete stability relations are known: cases of monotropy at low pressures, for example, become cases of enantiotropy at higher pressures.

Mention should be made of E. Cohen whose researches on allotropy have been quite extensive. He stresses the fact¹¹ that a good deal of our physical constants are erroneous because the measurements were not made on physically pure substances. Cohen is outstanding for his work on the allotropy of metals.

2. Smits' Theory of Allotropy. ^{9, 12}

The most important theory to explain the causes of the phenomenon of allotropy, and the relation between enantiotropy and monotropy is that advanced by Smits in 1910.

Smits assumes that Phase Allotropy is due to Phase Complexity, i. e., the existence in every phase of a substance of two or more different molecular species. If there are m different species in a one-component system, in which as a result of reversible changes an equilibrium may be established, then the velocities of these changes determine whether the system will behave as a unary system or a system of m components according as the reversible transformations take place with high or low velocities. The occurrence of different molecular species is not exceptional: association, dissociation and tautomerism are very common.

Fig. 1.

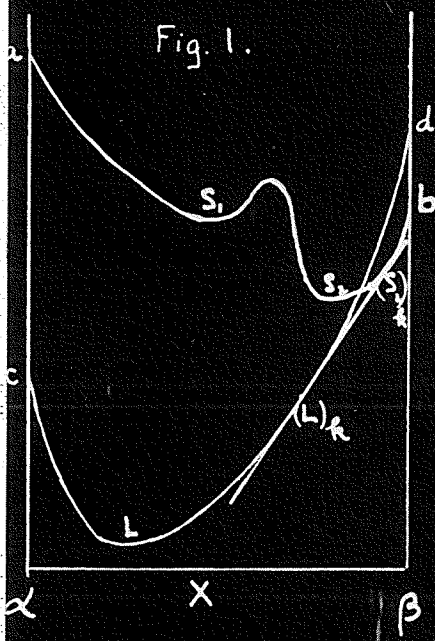


Fig. 2.

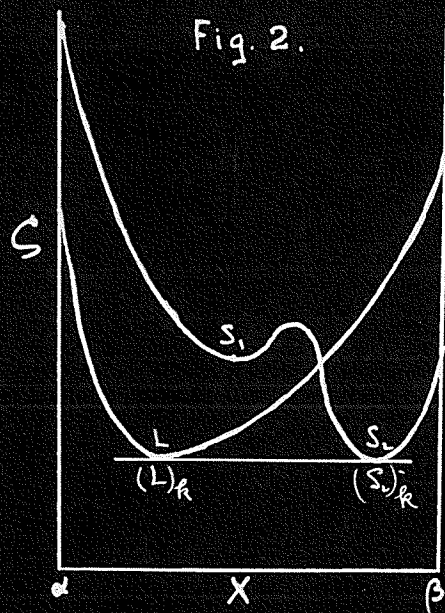


Fig. 3.

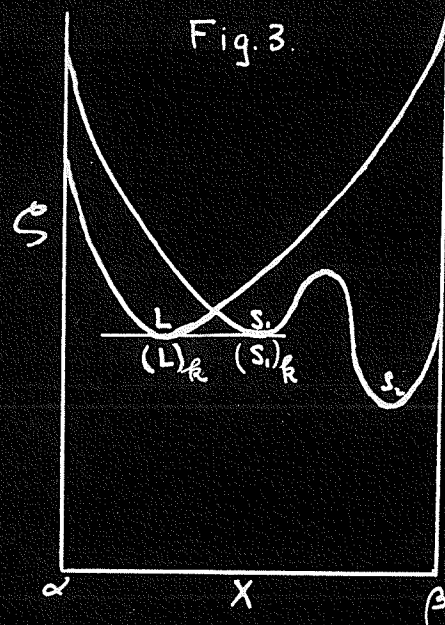


Fig. 4.

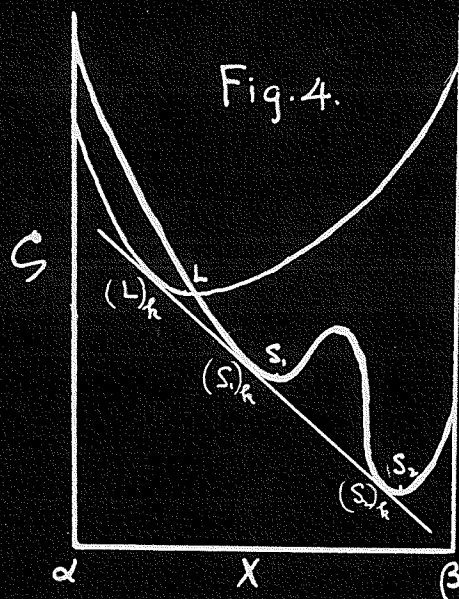


Fig. 5.

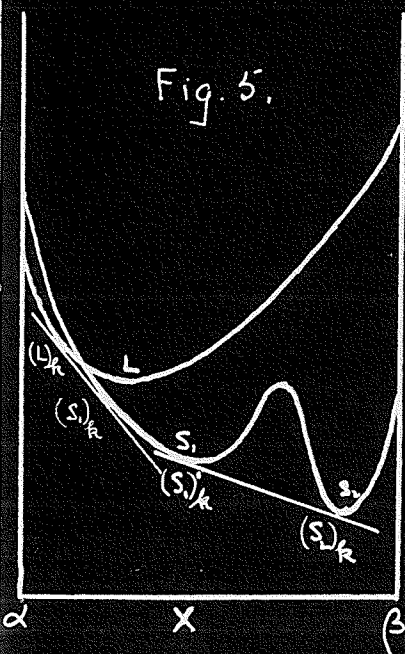


Fig. 6.

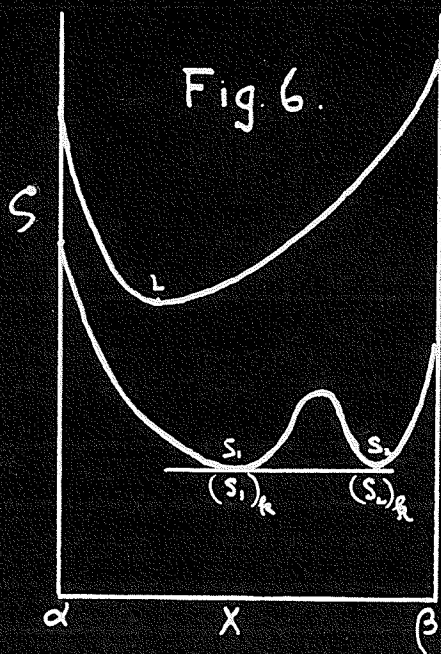
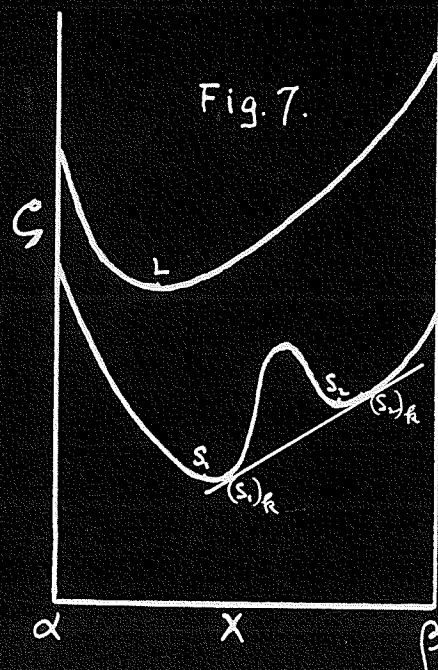


Fig. 7.



Accordingly, Smits builds his Theory of Allotropy upon the following two hypotheses:

(1) Every phase and therefore also every crystalline phase of an allotropic substance is a state which, under certain circumstances, can behave as a poly-component phase.

(2) The cause of this behaviour must be assumed to be the complexity of the phase, i. e., the existence of different molecular species, which are in inner equilibrium when the system is unary.

These different molecular species of a substance are termed its pseudo-components, and will be represented by α , β , γ , etc.

We shall now derive the T-X diagram for a single allotropic substance, showing how a unary system may be situated within a pseudo-binary system, and also the close relation between enantiotropy and monotropy. For simplicity, let us consider a pseudo-binary system only.

Use is made of the ζ -X diagram, showing the relation between the thermodynamic potential (ζ) of a substance, and its composition (X). The thermodynamic potential is defined by the relation

$$\zeta = E - T\phi + PV$$

where E is the internal energy of the system and ϕ is its entropy.

According to Gibbs' Equilibrium Principle a system at constant temperature and pressure tends to change to such a state that its ζ function becomes a minimum. In the ζ -X diagram this will correspond to the condition

$$\left(\frac{\partial \zeta}{\partial X}\right)_{PT} = 0$$

The ζ -X curves for the liquid will exhibit the form shown by cd in Fig. 1, and the point L representing a minimum potential will correspond to the composition of the stable liquid to which liquids of all

other compositions will tend by adjustment of the inner equilibrium.

Similarly, by assuming that two separate mixed crystal series of the substance can exist, the ζ -X curve for the solid phase may have the form of ab (Fig. 1), the two minima representing the two solid states in which inner equilibrium exists. Roozeboom was the first to make this assumption. It is probable that for many substances the central portion of this curve does not exist, but for the present purpose, this would make no difference, as long as the minima were present.

The following thermodynamic derivation is interpreted by the T-X diagram of Fig. 17, in which thick lines represent the unary system, and thin lines the pseudo-system.

Referring again to Fig. 1, we have the ζ -X curves for solid and liquid at a temperature slightly lower than the melting-point of β . Now the coexistence between a mixed crystal phase and a liquid phase is given by drawing the common tangent to the two curves. Moreover, the lowest point of the ζ -X diagram gives the composition of the most stable state of the system. Hence, at the temperature and pressure of the diagram, $(L)_k$ and $(S_2)_k$ are coexisting liquid and solid phases, and L is the stable liquid phase in inner equilibrium.

Fig. 2 shows the state of affairs at a slightly lower temperature. Both curves have risen, for

$$\left(\frac{\partial \zeta}{\partial T}\right)_p = -\phi,$$

showing that with decrease of temperature, there is increase of thermodynamic potential. The liquid line, however, rises more rapidly than the solid line. L and S_2 are not only on the common tangent but are also minima on the curves. This temperature is thus the stable unary melting-point, indicated by

l_2S_2 in Fig. 17.

Fig. 8.

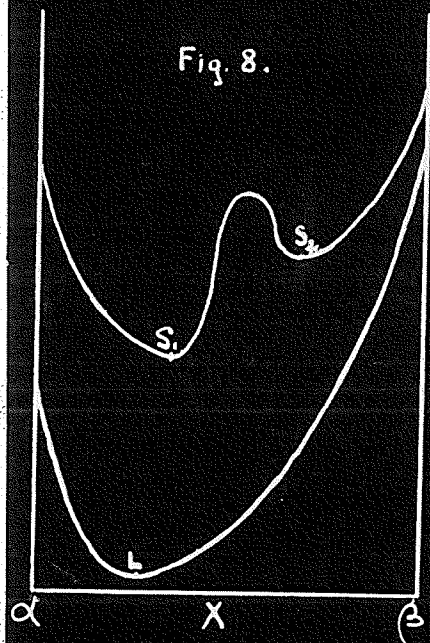


Fig. 9.

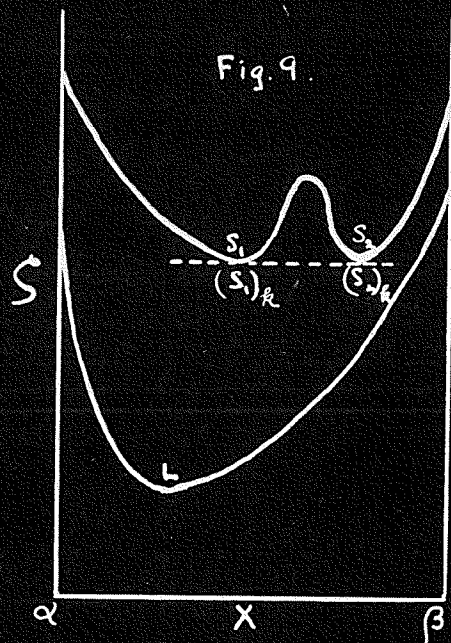


Fig. 10.

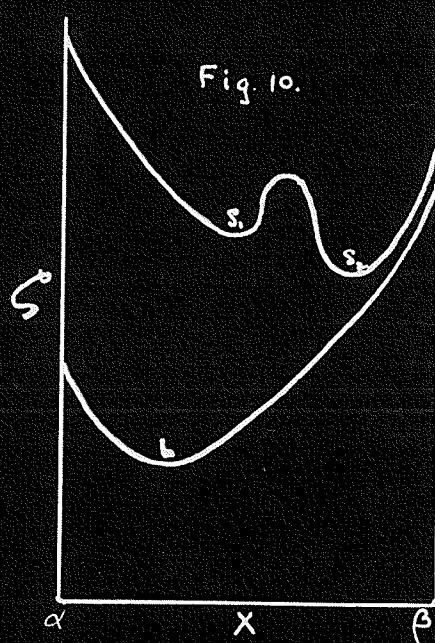


Fig. 11.

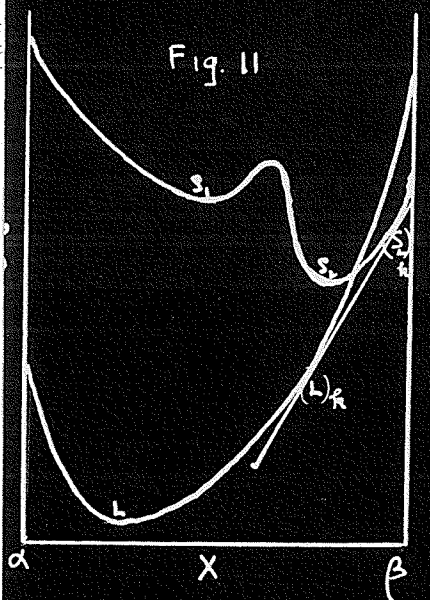


Fig. 12.

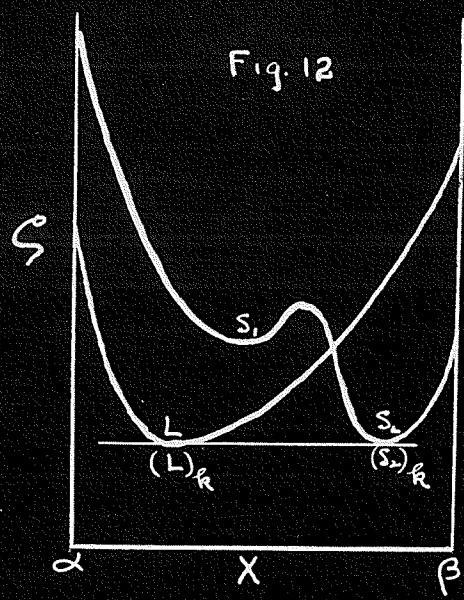


Fig. 13.

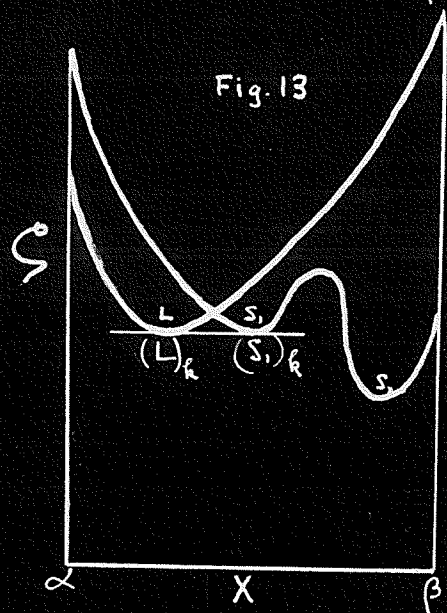


Fig. 14.

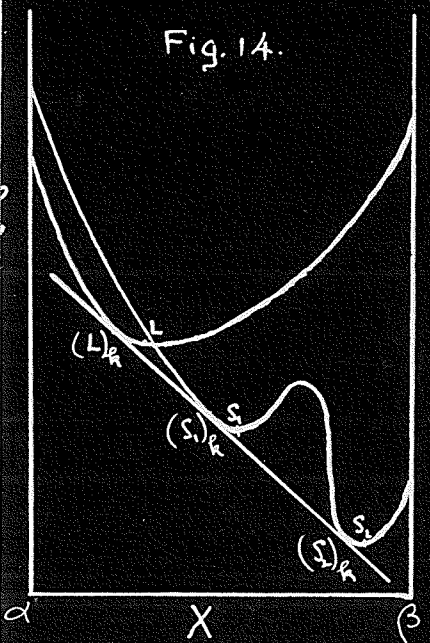


Fig. 15.

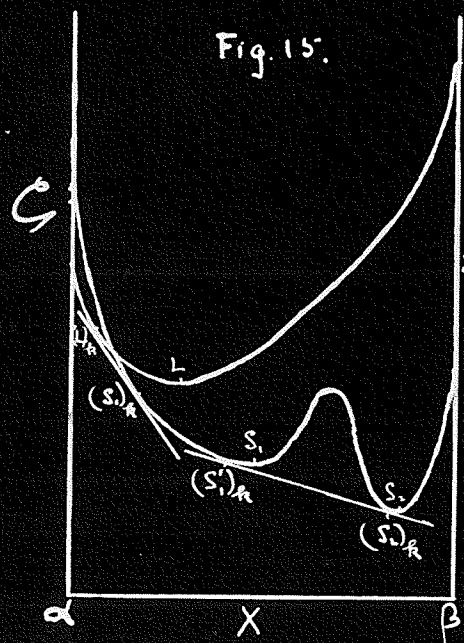
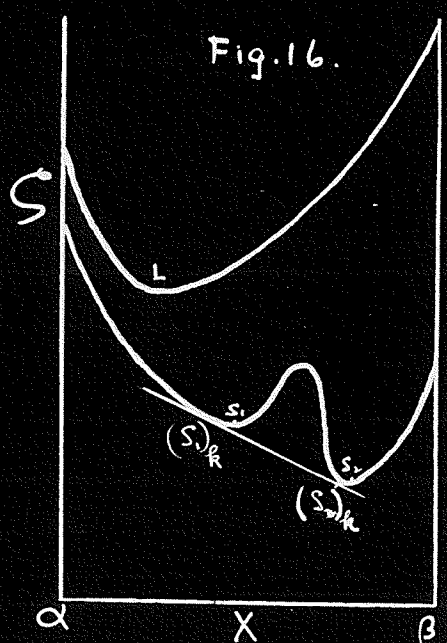


Fig. 16.



As the temperature falls, we obtain in succession Figs. 3, 4, 5, 6 and 7. In Fig. 3, S_1 and L are the solid and liquid phases in heterogeneous equilibrium and also in inner equilibrium. This is accordingly a second unary melting-point ($\mu_1 S_1$ in Fig. 17). It is, however, metastable, the phase S_2 being the only stable one.

Fig. 4 represents a three-phase equilibrium of the pseudo-system, the three phases being $(L)_K$, $(S_1)_K$ and $(S_2)_K$, (c, d, e, in Fig. 17). S_2 is still the stable phase.

At the temperature represented by Fig. 5, two heterogeneous equilibria are possible, but none of these phases represents inner equilibrium. S_2 is still the stable phase.

We now suppose that a change in the form of the solid phase takes place, causing the right hand side to rise more than the left. At a certain temperature, that of Fig. 6, S_1 and S_2 are in stable unary equilibrium, and this is termed the transition temperature, ($S_1'S_2'$ in Fig. 17).

At still lower temperatures S_1 now becomes the stable solid phase, and Fig. 7 is obtained.

In this way the phenomenon of enantiotropy is explained.

Now it may happen that instead of the reversal of the relationship of the two solid phases taking place below the stable unary melting-point it may take place above it. This represents the phenomenon of monotropy, and is illustrated in the series of conditions given by Figs. 8 to 16, the T-X counterpart being given in Fig. 18. In this case at the outset (Fig. 8) S_2 is metastable with respect to S_1 , but after passing the metastable transition point (Fig. 9) S_1 has become metastable with respect to S_2 .

It is to be observed that the above examples are illustrative

Fig. 17.

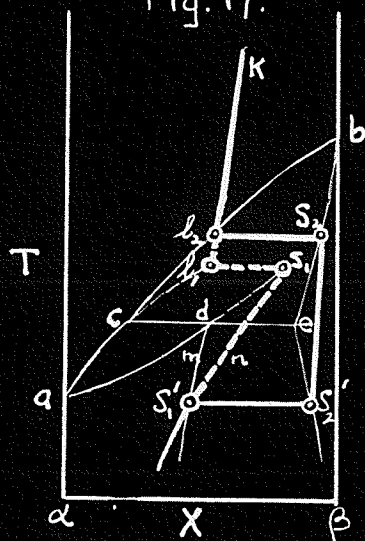


Fig. 18.

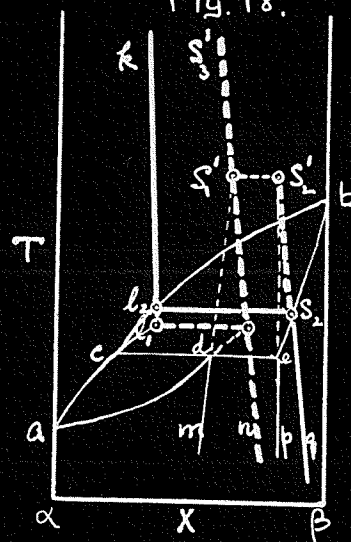


Fig. 19.

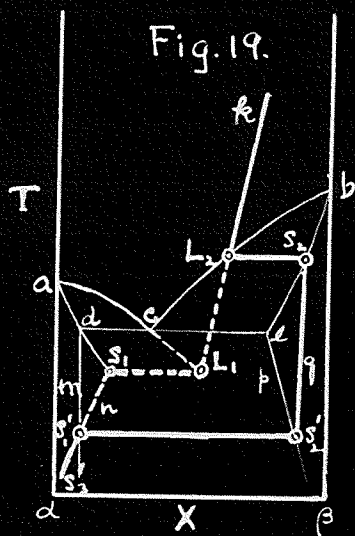


Fig. 20.

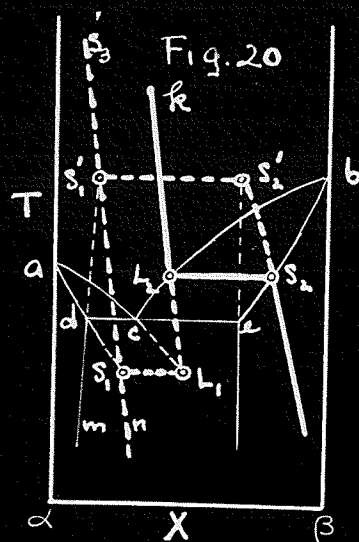


Fig. 21

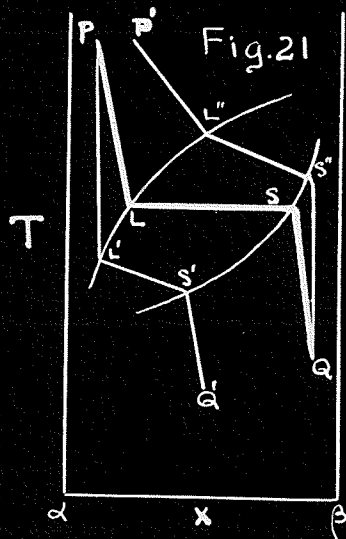
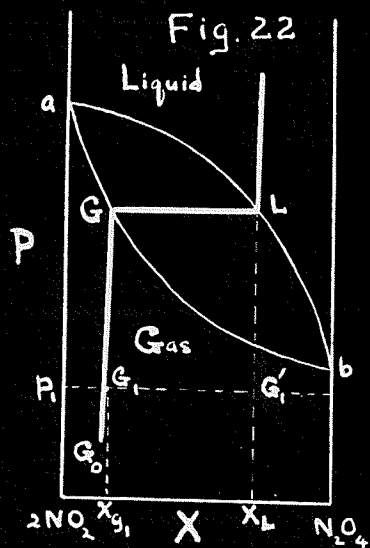


Fig. 22



of pseudo-binary systems with no eutectic. This was done purposely because of the applicability of the discussion to the pseudo-system of sulphur trioxide - the subject of the present investigation. A similar derivation may be applied to a pseudo-system containing a eutectic, the chief difference being that the composition of the minimum of the liquid S -X curve lies between those of the minima of the solid curve. Figs. 19 and 20 represent this case for enantiotropy and monotropy respectively. There is also the possibility that the line for inner equilibrium in the liquid may meet the melting line ac instead of bc .

It should be mentioned here that compound formation between the two pseudo-components is also considered possible. A T-X diagram illustrating this state of affairs will be discussed later (see Fig. 34).

If the pseudo-system is a ternary one, the complete behaviour at constant pressure is indicated diagrammatically by a triangular prism, but should equilibrium between two of the three pseudo-components be reached comparatively rapidly, the ternary diagram reduces to a binary one.

Generally speaking, the pseudo-components may be isomers or polymers, and there will be a heat effect in the formation of one pseudo-component from the other. Now in T-X diagrams, the slope of the lines for inner equilibrium in the phases indicate the sign of this heat effect, for according to van't Hoff's Law of Mobile Equilibrium, a rise in temperature will favour an endothermic change, so that these inner equilibrium lines will slope towards the side of the component the formation of which involves an endothermic effect. Hence in the case

where the pseudo-components are polymers, the inner equilibrium lines will slope towards the side of the less complex form, for polymerization is an exothermic reaction. Also it is highly probable that at the transition temperature, the heat of polymerization will predominate over the heats of mixing and unmixing of the solid phases, so that the allotropic change will also be in the direction of formation of the less complex form.

Smits' Theory of Allotropy is very complicated, and the above account only touches on the most essential features. As yet of course, it is only a theory, but the experiments to which it has led certainly seem to point to the correctness of Smits' fundamental assumptions.

Methods of investigating the truth of Smits' theory may be broadly grouped into two divisions, viz., those involving rapid working, and those involving the effects of intensive drying.

To illustrate the first, let us consider Fig. 21, which represents a portion of an inner equilibrium line with the related liquid and mixed crystal lines. By slowly cooling the unary liquid, the system will follow the lines PL, LS, SQ. Sudden chilling of the unary liquid, however, should have the effect of freezing without complete adjustment of the inner equilibrium, with the result that the system should follow some such course as indicated by the lines PL', L'S', S'G'. The freezing-point would accordingly be changed. Similarly, sudden heating should alter the melting-point (QS", S"L", L"P").

Investigation by means of the effects of intensive drying on physical properties is of more importance in the present problem. It is necessary therefore, to give a brief account of this very important and interesting subject which has developed only in comparatively recent years.

3. Intensive Drying and Physical Properties.

As mentioned before, Smits postulates that a single substance will exhibit binary behaviour when the interaction between the pseudo-components is retarded by some anti-catalyst. This anti-catalytic effect may be obtained, for instance, by removing the very last traces of water from the substance. Incidentally, the drying effect probably occurs in the early stages of the usual long intensive drying process¹³.

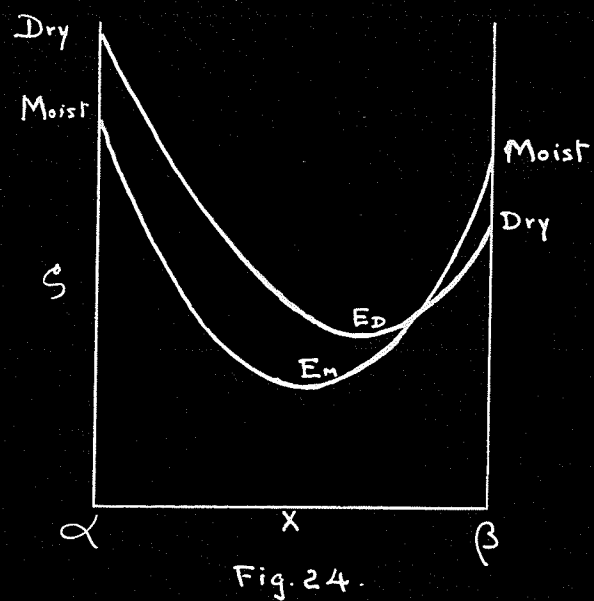
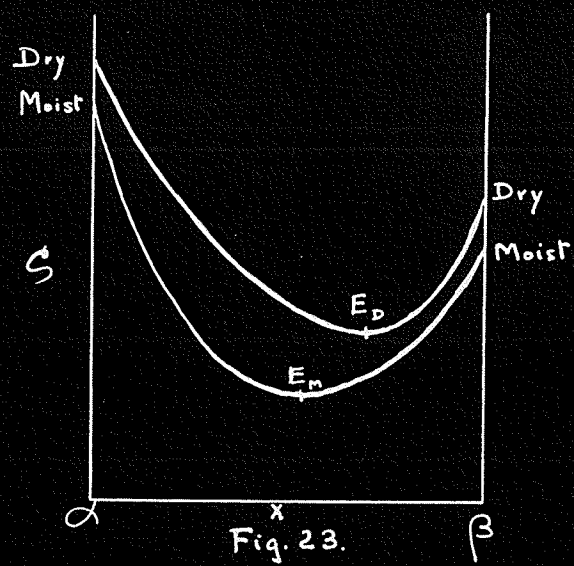
H. B. Baker and Mrs. Baker¹⁴ were the first to study the effects of intensive drying on physical properties. They observed, for example, that drying over phosphorus pentoxide increased the vapour density and raised the boiling point of nitrogen trioxide^{14, 15}. In 1922, they found that liquids which had been sealed for eight or nine years in vessels containing phosphorus pentoxide had abnormally high boiling-points^{16, 17}. They were also able to produce slight changes in the melting-points of solids by intensively drying them. Though Baker was unable to detect any change in the density of liquids during the drying process he found that the surface tensions by the method of capillary rise, and also the vapour densities of several liquids measured by the Victor Meyer method, had changed considerably. Similarly, the latent heat of evaporation of benzene changed with drying¹⁸. We shall refer to these results shortly.

Returning to the theoretical aspect, there is considerable controversy as to whether intensive drying fixes the equilibrium, or displaces it first and then fixes it. G. N. Lewis¹⁹ holds to the former theory, while Smits²⁰, though he originally held the same view, inclined toward the latter in 1922. Their arguments in brief are as follows:

Lewis cannot believe that the removal of small traces of water can effect such profound changes as occur in an equilibrium shift. Little besides the laws of thermodynamics is required to prove Raoult's law for infinitely dilute solutions, and yet a shift of the inner equilibrium would imply changes in the activity of the solvent which are very many times as great as those demanded by Raoult's law. The elevation of the boiling-points of liquids, observed by Baker, is explained on this theory by assuming that the more volatile pseudo-component, being prevented from conversion into the less volatile, has already evaporated, thus leaving a residue of abnormally high boiling-point. Again, it is predicted that no change in a static property such as density should be observed - which is in agreement with the aforementioned results of Baker. Surface tension, however, is a static property, and yet Baker observed a change in this case. Lewis accounts for this by assuming that we have here a process analogous to the formation of a new phase.

A. Smits²¹ on the other hand, though he had argued along the same lines as Lewis two years previous to him, assumes that in the reaction $\alpha \rightleftharpoons \beta$ between the pseudo-components, it is possible that the reaction $\alpha \rightarrow \beta$ could be stopped before the reverse reaction. It follows from this that a trace of moisture can displace the inner equilibrium to a very considerable extent, the thermodynamic significance of which is that a very large amount of work is necessary to withdraw the last traces of water - which is not improbable, according to Smits.

Which of the two theories is correct should be shown by measurements of say, vapour pressure, during the process of drying. If the pressures show a constant value, but a decrease on distillation, then the



equilibrium cannot have been displaced. If however, the vapour pressure changes with drying, then displacement must have taken place. With this object in view, Smits²¹ experimented with benzene, and found the boiling-point to rise as much as 7° . He did not, however, consider these results as conclusive. Additional experimental evidence in favour of an equilibrium shift was produced by Mali²² in 1925 and Smits, who found a continuous change in the vapour pressures of several liquids with intensive drying.

To support his arguments, Smits²⁰ refers again to the $S-X$ curves of pseudo-binary systems in both the moist and dried states. Three possibilities arise:

(1) Pure α and pure β are more stable in the moist than in the dry state (Fig. 23). It would be fortuitous if the two minima (points of inner equilibrium) corresponded to the same value of X .

(2) The moist α is more stable than the dry α , but the dry β is more stable than the moist β (Fig. 24).

(3) The dry and moist α and the dry and moist β have identical stability.

Hence, if intensive drying affects the stability of the pseudo-components at all, we may expect a displacement of equilibrium by drying, but the direction of the displacement cannot be predicted.

Briscoe, Peel and Robinson²³ distilled a sample of benzene, intensively dried for sixteen months, and measured the density and surface tension of the head and tail fractions. They observed that slight density differences between the fractions were only temporary, so were considered negligible. In this respect they confirmed Baker's results. With regard

to surface tension, the head and tail fractions showed only very slight changes, but for the liquid as a whole a fall of only .30 units was observed occurring almost entirely within the first few days. This is in distinct contradiction to the experiments of Baker who observed a considerable rise in surface tension with drying. Briscoe, Peel and Robinson conclude from their own experiments that there was neither appreciable fractional separation nor association of the pseudo-components, it being assumed that any movement in equilibrium would produce a measurable change in density or surface tension.

Manley²⁴ found the refractivity of benzene to change with time of drying. Such a change could be explained on Lewis' theory by assuming a change to a more stable state, but on Smits' theory, by assuming a change of the inner equilibrium.

An interpretation of Baker's observations on the boiling-points, vapour densities, vapour pressures and latent heats of intensively dried substances as indications of complexity in the liquid state was made by Smits in 1928²⁵. He considered that the abnormalities noted by Baker were very large in comparison with the small changes in vapour pressure observed by himself and others. In seeking an explanation of this, he distinguished between two classes of phenomena, viz., "velocity" phenomena such as rapid distillation and rapid evaporation, and "equilibrium" phenomena, such as vapour pressure. By the following argument Smits was able to show that Baker's experiments on the vapour density of nitrogen tetroxide were indications of a "velocity" phenomenon. In Fig. 22, L and G are the coexisting liquid and gaseous phases within the bulb used in Victor Meyer's method and p_1 represents one atmosphere.

When the bulb is broken, in the moist substance the reaction $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ takes place upon evaporation, and the liquid of composition x_L now gives a vapour of composition x_{g_1} . If however, the nitrogen tetroxide is so intensively dried that the attainment of inner equilibrium is retarded, the liquid will behave as a mixture and will give a gas phase G_1' . In the first case, vapour density determination will correspond to a composition x_{g_1} and in the second case to a composition x_L . In this way the nitrogen tetroxide behaves as a mixture with regard to "velocity" phenomena. A similar argument shows that abnormal latent heats and vapour pressures are also "velocity" phenomena.

In 1928 Smits²⁵, (also Lenher²⁶) by applying an electric field to benzene, succeeded in raising its boiling-point 15° . This benzene, however, boiled normally when heated with a small flame. He concluded that since the electric field probably removed charged dust particles, Baker's abnormal boiling points were largely superheating phenomena. Similarly, by assuming that prolonged standing in a sealed tube can remove the dust particles from a liquid, Smits thinks it possible that this would cause a change in the surface tension, hence Baker's abnormal values for the surface tensions of dried liquids.

A survey of all the work on intensive drying, brings one to the conclusion that the most definite data we have at present illustrating changes in physical properties due to drying, are those of vapour pressure.

Smits²⁵ concludes that in some cases, relatively small displacements of the inner equilibrium have been found with liquids, and large displacements with gases.

4. The Mechanism of Intensive Drying.

As explained above, Smits prefers to assume that intensive drying shifts and then freezes the equilibrium between the pseudo-components. His most recent supposition is that each pseudo-component exists in an active and an inactive form, there being an equilibrium between the two forms. The interaction between the pseudo-components is supposed to take place only between the active forms. Thus if and are two pseudo-components we have the equilibria



where the subscripts a and i represent active and inactive forms respectively. The nature of the activation is not described. It may resemble the process of the removal of electrons to outer orbits in Bohr's theory of the atom. Now it is supposed that the removal of water will shift the horizontal equilibria to the right (how, we do not know) and thus prevent interaction between the pseudo-components. These shifts may or may not keep step. If they do not, the resulting mixture will have a composition different from the composition in bulk of the original substance, and a vapour pressure change may accordingly take place.

The very small quantity of water necessary to produce activation is explained by assuming that the fraction of the total number of molecules existing in the active state is only of the order of magnitude of 10^{-10} so that probably the fraction of water molecules necessary for activation is of the same order of magnitude.

Smits however, does not offer any explanation as to the actual mechanism of the catalytic action of the water.

Several theories have been offered to explain the action of moisture in catalyzing ordinary chemical reactions, but their applicability to pseudo-systems is limited. Obviously, a sound knowledge of the mechanism underlying the attainment of equilibrium awaits information concerning the actual nature of the pseudo-components. Two theories will be mentioned here which may, with modification, be applicable to pseudo-equilibria. Both are of an electrical nature.

Sir J. J. Thomson supposed that the electrical forces binding the atoms of molecules together are lessened when the molecule is close to a conductor with a very large specific inductive capacity, water, for example. This is due to the fact that a charged atom close to the conductor induces in it a charge of opposite sign which tends to neutralize the electrical effects of the atom, thus weakening its affinity for other atoms in the molecule.

Rather similar is the theory of S. B. Mali²⁷ who assumes that a compound possesses residual affinities which give it the power to combine with other substances. These residual affinities (all types of unsaturation) produce in the surrounding ether, a field of force depending of course upon the amount of residual affinity present. Molecules then, will tend to form into groups producing closed systems of lines of force, and be more or less inactive chemically. These closed systems can only be opened when they receive suitable energies. If water is present, Mali postulates that it absorbs radiations selectively (probably in an excited state) and then emits them, these emitted radiations energizing the molecules and enabling them to exist independently. The quantity of radiation from the water is supposed to increase with rising temperature. Mali believes that it is the ions of the water that are responsible for

the catalytic behaviour.

Let us now turn from these general considerations to a study of the particular substance, sulphur trioxide.

II. SULPHUR TRIOXIDE

1. Historical Survey.

Probably the first to investigate sulphur trioxide was Marignac²⁸, who, in 1853, observed two forms of it, an ice-like (α) form which melted at 17° , and an asbestos-like (β) form which sublimed under atmospheric pressure to give a vapour from which the ice-like form condensed.

Weber and Rebs thought that the asbestos-like form was a hydrate because they were unable to prepare it in the absence of moisture. Oddo showed that the β form is the polymer S_2O_6 but Lichty²⁹ found that the molecular weights of both α and β in solution in phosphorus oxychloride were the same. The melting-point of the α form varies with different authors: Marignac 18° , Schultz-Sellac 16° , Weber 14.8° , Berthoud 16.85° and Lichty 16.79° . Schultz-Sellac found the melting-point of the β in sealed tubes to be $50-60^{\circ}$. Schenck³⁰ found an abnormally large coefficient of expansion for liquid sulphur trioxide, made density and surface tension measurements, and determined the critical temperature (216°). He also got a volume change in the liquid at 35° , due to polymerization. The rate of change was increased by the addition of small quantities of concentrated sulphuric acid.

Oddo found the β form to be less active chemically than the α .

Berthoud³¹ reported that to distil the β under constant pressure it was necessary to raise the temperature as the amount of solid diminished. He made measurements of the surface tension and critical point of the liquid and determined the liquid and vapour densities. He emphatically agreed with Weber and Rebs in regarding the β as a hydrate, for he kept tubes containing the two forms in contact for four years without any

further formation of β , which he explained by assuming that only enough water was present to convert a part of the α into a hydrate. He expressed surprise at the extremely small amount of water necessary to produce the hydrate.

Le Blanc and Rühle³² investigated the melting-points of solid sulphur trioxide and the vapour pressures of solid and liquid sulphur trioxide. Their measurements were chaotic, but they concluded that four allotropic modifications of the substance existed.

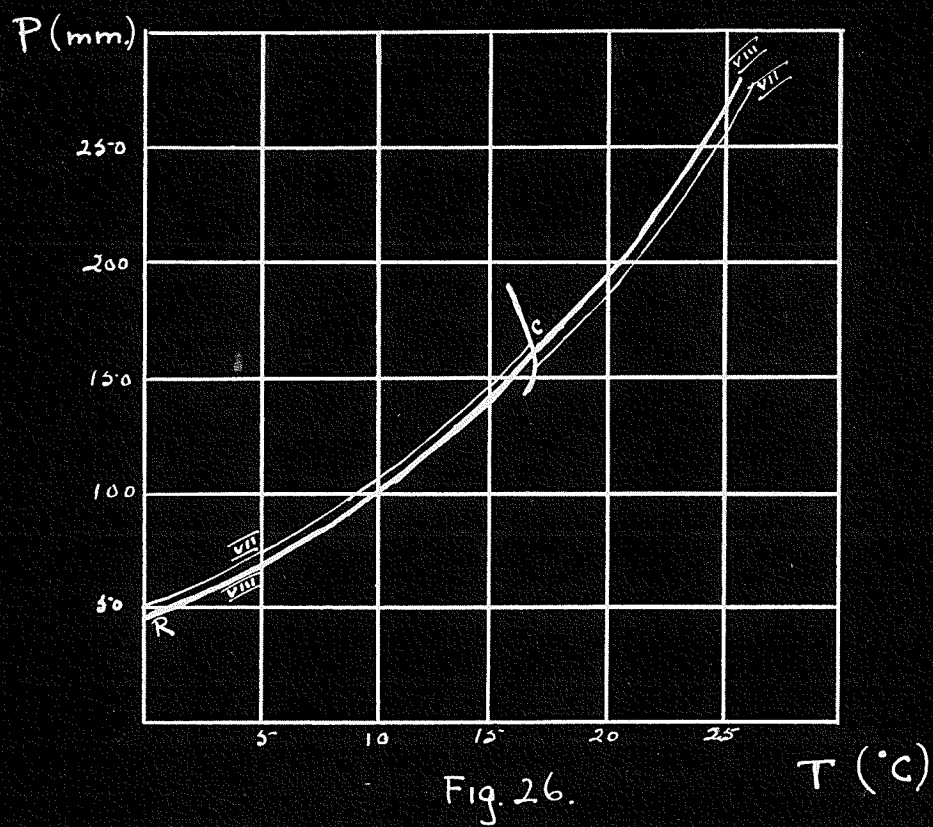
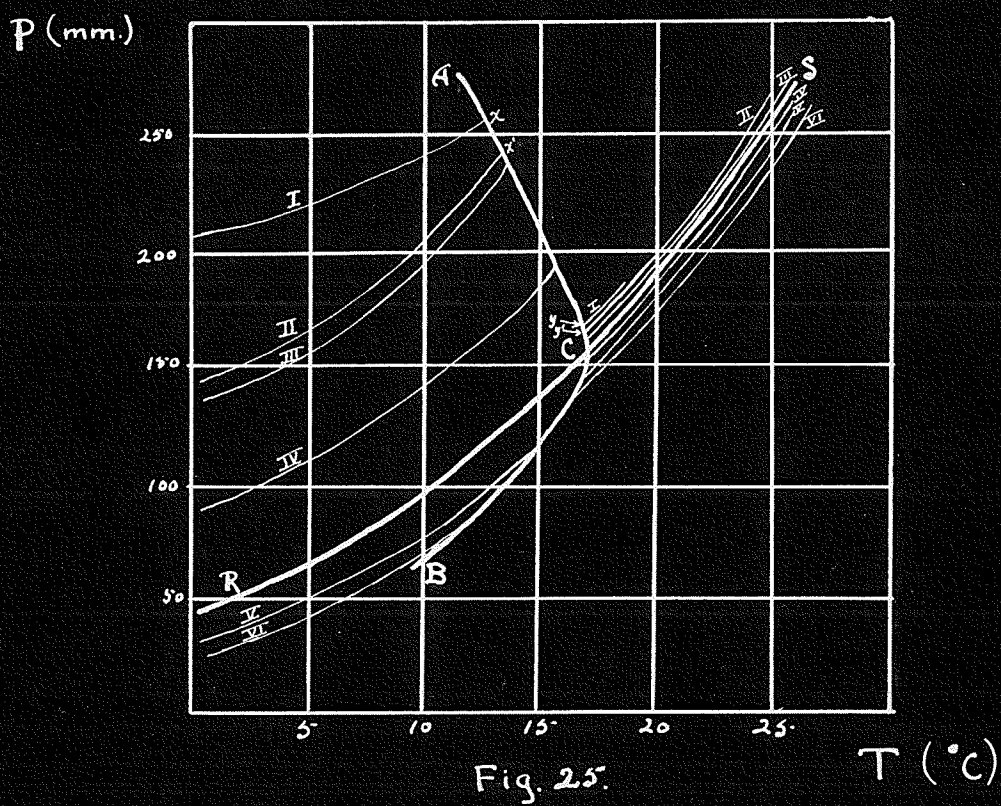
2. Work of Smits and Schoenmaker.^{33, 34, 35, 36}

By far the most accurate and thorough investigation of sulphur trioxide has been accomplished by Smits and Schoenmaker. Accordingly their work merits special reference.

In the remarkable results of H. B. Baker on the effects of intensive drying on physical properties Smits saw a surprising confirmation of his Theory of Allotropy. Seeking for a substance with which to continue the study, he chose sulphur trioxide, which, since it had the special property of being self-drying, would in all probability reach an intensively dried state far sooner than say, benzene.

Sulphur trioxide is now known to exist in three forms, to which we shall refer throughout this discussion as the α , β and γ forms respectively, according to Smits' latest paper³⁶ on the subject.

The α or ice-like form is unstable and has a low melting-point. The β or low-melting asbestos-like form is also unstable, and the γ or high-melting asbestos-like form is stable. By measurements of the vapour pressure Smits and Schoenmaker were able to draw the P-T curves for all three forms in the undried state. Furthermore, by distillation over phosphorus pentoxide, they were able to get the α and γ forms in the intensively dried



state and so examine their pseudo-systems to some degree.

It may be remarked here that the moisture present in the majority of substances studied in relation to the effects of intensive drying is not in chemical combination with them, whereas in the case of sulphur trioxide it must be in the form of sulphuric acid. The writer is not aware of any literature in which a distinction is made between the two cases, but undoubtedly they represent two distinct effects.

(1) The α form.

The α form was produced by distillation at 18° to a receiver at -80° . Having intensively dried it by repeated distillation through phosphorus pentoxide, its vapour pressure was measured at different temperatures, using the glass indicator method. The first determinations when plotted gave the solid-vapour and liquid-vapour curves denoted by I in Fig. 25, separated by the line xy representing a melting range or three-phase equilibrium.

After standing for 18 hours at 18° , the vapour pressure curve was redetermined, giving curve II. It is seen that the sublimation curve had sunk considerably and the liquid-vapour curve slightly, whereas the three-phase line, $x'y'$, though shorter, coincided with the previous determination.

Similarly, after standing for 40 hours at 18° , the vapour pressures denoted by curve III were determined. Again is seen the same lowering of the two-phase curves and the coincidence and shortening of the three-phase curve.

To continue this process still further, partial evaporation was resorted to, i. e., a more volatile portion of the ice-like form was removed by condensation into a side tube of the apparatus, which was then sealed off. Measurements of the vapour pressure following each partial evaporation gave curves IV, V and VI, and it is to be noted that in the last two, the three-phase equilibrium line rises with increase of temperature.

On repeating the experiment with α sulphur trioxide, which had been dried for only a few days, curve VII (Fig. 26) was obtained. After 120 hours, measurements gave curve VIII.

It is seen that the longer the period of standing, the shorter the three-phase line becomes, till the limiting case corresponding to curve VIII is reached, in which melting takes place at a single temperature and pressure. Though we shall examine these results in more detail later, it may be stated that this limiting case is interpreted by Smits as representing the behaviour of the α form in inner equilibrium and also that the three-phase line represents a part of the pseudo-system of the α form.

By plotting the absolute temperature T against $T \log P$ (P = vapour pressure) for the solid-vapour and liquid-vapour equilibria, according to the method of Young, two straight lines were obtained, the intersection of which represented the unary triple point of the α form, which was found to be at 16.8° and 158.5 mm. of mercury.

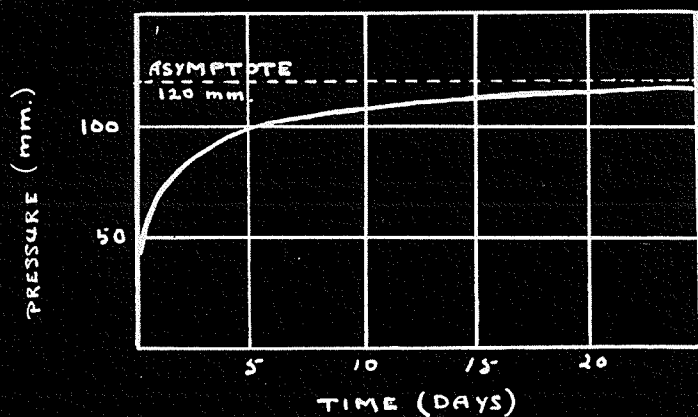
By applying the Clausius-Clapeyron equation in the form

$$T \log P = \frac{-Q}{R} + CT$$

to the liquid and solid P - T curves, the heat absorbed (Q) in the change from solid to vapour, and from liquid to vapour was calculated.

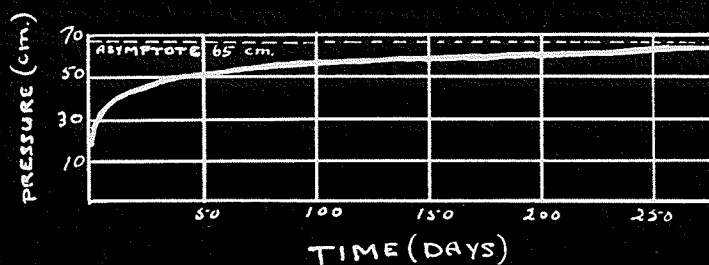
(2) The β form³⁴.

The β form usually constitutes three-quarters of the bulbs of sulphur trioxide supplied by Kahlbaum. It was transferred to the apparatus from the bulb by distilling at room temperature into a receiver at -80° (solid carbon dioxide and alcohol). Attempts to intensively dry the β form by distillation resulted in the formation of the γ form, so that only the unary behaviour of the not-intensively-dried β could be examined. As in the case of the α form, vapour pressure measurements were carried out



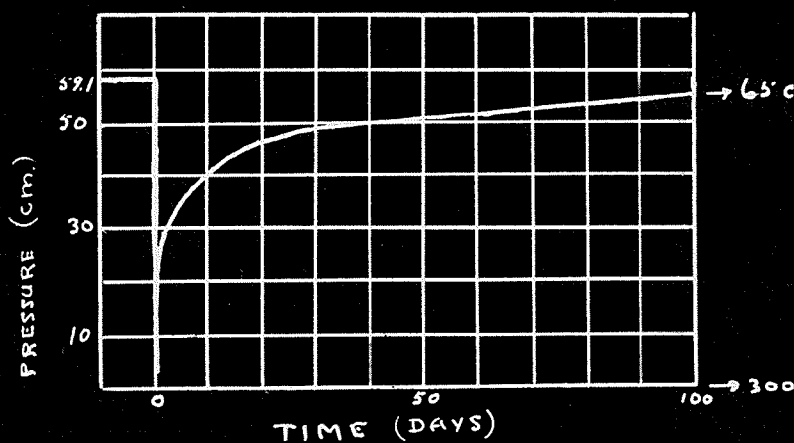
30°

Fig. 27.



50°

Fig. 28.



50°

Fig. 29.

for both solid and liquid β . Plotting T against $T \log P$ gave two straight lines intersecting at the point corresponding to 32.5° and 398 mm. of mercury - the triple point of the β form. Also the heat quantities involved in the processes of sublimation and vaporization were calculated as for the α form.

To surmount the abovementioned difficulty of drying the β form, it was planned to dry it in a solid state, a process which would require several years. With the exception of their work with X-rays to be mentioned later, no further work has been published by Smits and Schoenmaker on this form.

(3) The γ form³⁴.

The γ form was prepared by repeated distillation at room temperature over phosphorus pentoxide into a receiver at the temperature of liquid air, any residual α sulphur trioxide being removed by slight partial evaporation into a side tube of the apparatus which was then sealed off.

Measurements of the vapour pressure of this intensively dried form at room temperature gave constant values, but at higher temperatures the pressure was found to rise to an asymptotic value on standing, representing a slow transformation in the solid state (corresponding to the similar effect observed with the α form). A reproduction of the results at 30° and 50° is given in Figs. 27 and 28.

As with the α form Smits and Schoenmaker conducted a partial evaporation of some of the high-melt form which had stood at 50° for several weeks. The diminution of vapour pressure resulting therefrom was found to be even more remarkable than with the α . Fig. 29 shows the drop in pressure and the subsequent rise to the usual asymptotic value accompanying the readjustment of the inner equilibrium by the formation of the more volatile component from the less volatile.

From the preceding it is evident that different disturbed states of the high-melt solid having very low pressures could be obtained. Smits and Schoenmaker determined the melting-points of several of these solid forms, and as in the case of the α , were able to determine points on the three-phase line of the γ form. Fig. 32 shows these results combined with part of the unary diagram. Part of the pseudo-system of the γ form was thus penetrated. Due to the fact that inner transformation takes place with much more rapidity in the liquid than in the solid state, the fusion of the highly disturbed forms gave rise to sudden increases of vapour pressure, which endangered the apparatus.

It was observed that mere distillation of the sulphur trioxide without passing the vapour over phosphorus pentoxide was sufficient to convert it to the intensively dried state.

Plotting T against $T \log P$ for the γ form in inner equilibrium gave as before two straight lines intersecting at the unary triple point: 62.2° and 174.3 cm. of mercury. The heat quantities involved in sublimation and vaporization were also calculated.

Besides their measurements of vapour pressure, Smits and Schoenmaker³⁵ studied the effect of X-rays on sulphur trioxide. They took a Roentgenogram of the intensively dried γ form, using Cu K_α rays and found it to consist of fifteen lines. After heating at 50° for 48 hours another Roentgenogram was taken. Under these conditions inner transformation had previously been shown to take place to a considerable extent, as shown by vapour pressure measurements. The two films were identical, showing that either the X-rays were unable to detect the inner change, or that the radiation itself had effected the change. It was proved that the latter of these two possibilities is the correct one for further investiga-

tion showed the vapour pressure of the intensively dried high-melt form to rise with exposure to the X-radiation.

Further, Roentgenograms of both the α and β forms were taken. They were not only identical, but were that of the γ form. It follows that exposure to X-rays not only effects the establishment of the inner equilibrium, but also causes the transformation of the metastable (α and β) modifications, into the stable modification (γ).

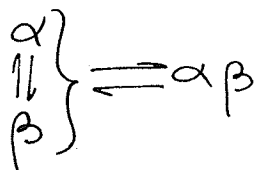
We have now to interpret this experimental evidence in terms of Smits' Theory of Allotropy.

3. Theoretical Development.

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.

Now the rate of establishment of equilibrium for different substances may be either "rapid" or "slow". A "rapid" substance will exhibit unary behaviour, and a "slow" one will behave as a mixture, sulphur trioxide being an example of the latter type.

Sulphur trioxide is assumed by Smits to be composed of at least two kinds of molecules, α and β , which can not only change into one another, but can give a dissociable compound. We have then, the equilibria



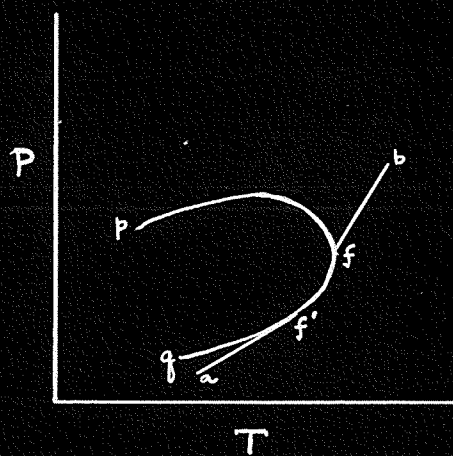


Fig. 30.

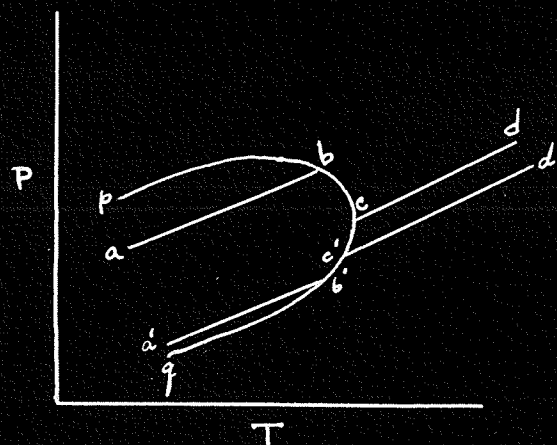


Fig. 31.

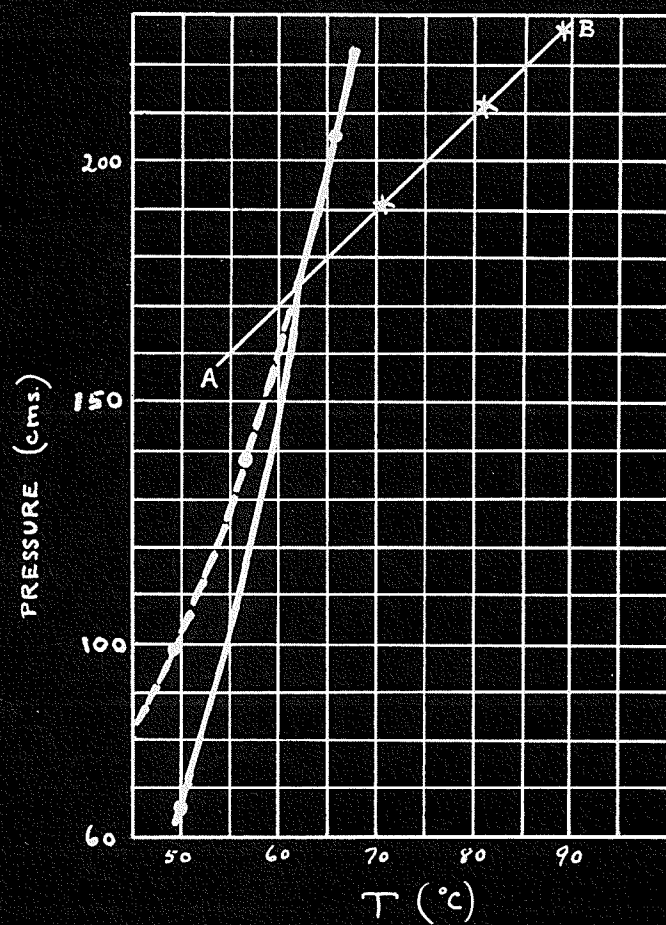


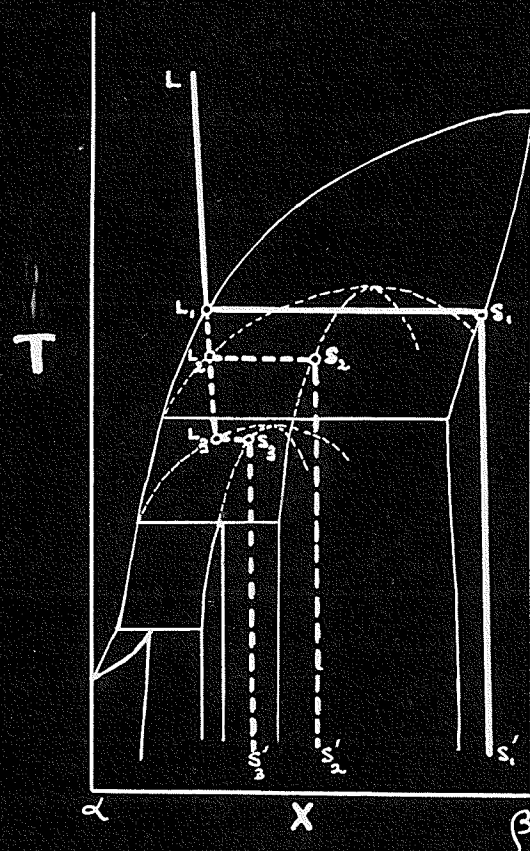
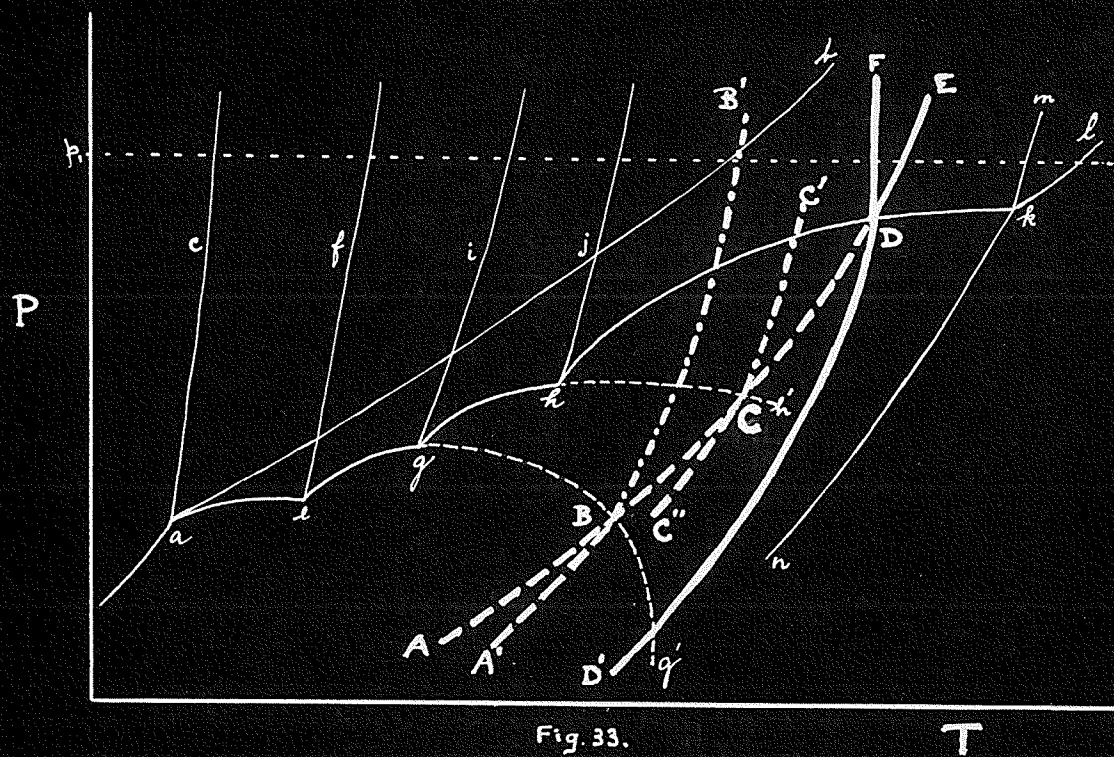
Fig. 32.

Now van der Waals has shown that the three-phase line of a dissociating compound composed of a volatile component α , and a less volatile component β , has the form shown in Fig. 30 by the line pq. We should expect this univariant behaviour from the Phase Rule alone. If the compound can exist with vapour of the same composition there will be a sublimation curve tangential to pq at the maximum sublimation point f' and a melting line tangential to it at the minimum melting-point f . Accordingly, the compound exhibits the melting range ff' , and with the exception of the maximum temperature, there can exist at every temperature, two three-phase equilibria with different vapour pressures.

Smits and Schoemaker have been able to show that intensively dried sulphur trioxide behaves in accordance with the theoretical predictions for binary systems. Curve pq of Fig. 30 corresponds to ACB of Fig. 25. The fact that all the melting ranges for the determinations shown in Fig. 25 fell on the same three-phase line for a dissociating compound showed that the forms all belonged to the same allotropic variety. Fig. 31 represents Fig. 30 diagrammatically to correspond with Fig. 25.

By means of a V-X diagram showing the relations between molecular volumes and compositions, Smits and Schoemaker³⁴ are able to demonstrate that it is the original total composition of the system that determines which of the two possible three-phase equilibria will be formed on raising the temperature to the beginning of melting.

In Fig. 31, ab, bc, cd represent the P-T lines of the original mixtures, and a'b', b'c', c'd', represent those of the residue after evaporation, which residue will contain less of the more volatile component. Intermediate lines are given by mixtures of intermediate composition. In the limiting case, b' will have reached the maximum sublimation point.



It may be concluded that intensively dried α sulphur trioxide behaves as a mixed crystal of two components which give a dissociable compound, the initial composition of the mixture lying toward the side of the more volatile component. In the undried form, inner equilibrium has set in, and the unary behaviour of melting at a single temperature is observed.

As mentioned in a preceding section, a study of a part of the three-phase line for the γ form was also accomplished (AB, Fig. 32). It was found that the γ form is also a mixed crystal of the same pseudo-components as the α .

From the results of their experiments, Smits and Schoenmaker were able to construct a tentative P-T projection (Fig. 33) of the P-T-X space model for the complex system of sulphur trioxide, assuming it to consist of two pseudo-components which form two dissociable compounds. Thick lines represent the unary system, thin lines the pseudo-system, and dotted lines metastability.

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 coexisting system α mixed crystals-liquid-vapour, egg' the three-phase line for the coexisting system $\alpha_x \beta_y$ mixed crystals-liquid-vapour, ghh' the three-phase line for the coexisting system $\alpha_u \beta_v$ mixed crystals-liquid-vapour and hk the three-phase line for the coexisting system β mixed crystals-liquid-vapour.

In the unary system, 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.

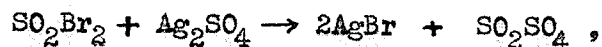
The interpretation of this in terms of the various forms of sulphur trioxide is as follows: ABCDE is the vapour pressure line of liquid sulphur trioxide in inner equilibrium, A'B the sublimation curve of the α form in inner equilibrium, egBg' the three-phase line of the pseudo-system representing the equilibrium α sulphur trioxide mixed crystals-liquid-vapour, and ghCh' the three-phase line of the pseudo-system representing the equilibrium β sulphur trioxide mixed crystals-liquid-vapour. D'D is the vapour pressure line of the γ form, and hDk is a three-phase line of the pseudo-system for the equilibrium γ sulphur trioxide mixed crystals-liquid-vapour.

Fig. 34 is a diagrammatic representation of the T-X diagram for sulphur trioxide at constant pressure (that of p_1 , Fig. 33). The line LL₁L₂L₃ gives the inner equilibrium in the liquid at different temperatures, L₁, L₂ and L₃ being unary melting-points of the γ , β and α sulphur trioxide respectively and S₁, S₂ and S₃ the unary coexisting mixed crystal phases. Of these three equilibria only the first is stable. S₁S₁', S₁S₂' and S₂S₃' represent the inner equilibria in the solid phases.

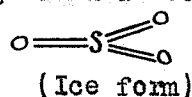
4. The Constitution of Sulphur Trioxide.

Problems in molecular constitution may be attacked through both the chemical and physical properties of the substance in question.

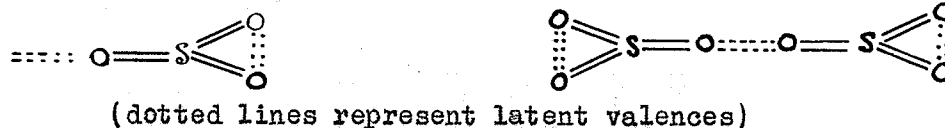
With our growing knowledge of valence, the structure assigned to the sulphur trioxide molecule has altered with time³⁷. Since sulphur trioxide is formed by the reaction



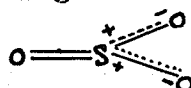
Odling and Abel regarded the trioxide as sulphuryl sulphate. Oddo gave the following formulae to the ice and asbestos forms:



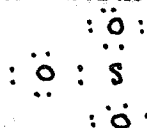
In accordance with the theory of latent valences, J. A. N. Friend³⁸ modified these formulae thus:



E. B. R. Prideaux however assigns the formula

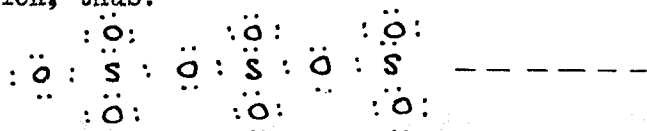


Hagg³⁹ suggests that the formation of sulphur trioxide by oxidation of sulphur dioxide indicates the structure



in which the three oxygen atoms form an equilateral triangle with the sulphur atom at its centre. There is no experimental proof of this.

Hagg explains polymerization of sulphur trioxide in the crystallized form as the result of a tendency on the part of the sulphur to form a figure-of-eight configuration, thus:



Of all physical properties probably the most useful in problems of constitution are those of molecular refraction and parachor (a refinement of molecular volume).

Let us now consider the first of these. In 1880, Lorenz and Lorentz deduced theoretically that for any substance

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

where r is its specific refraction, a constant independent of temperature,

d is its density and n its refractive index. Multiplying by M , the molecular weight of the compound, gives

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

known as the molecular refractive power, or refraction, or refractivity.

This property is primarily additive but also constitutive in character.

A knowledge of the refractive index of sulphur trioxide could lead then, to a knowledge of its constitution by comparing the observed value of the refractivity with the sum of the constituent atomic refractivities. With regard to the vapour state, Guthbertson and Metcalfe⁴⁰ have already worked along these lines. They remark that the refractivities of sulphur dioxide and sulphur trioxide "are very interesting in that they depart widely from the additive values". For example, experimentally, the refractivity of sulphur trioxide vapour was found by them to be 1.000661 whereas the calculated value is 1.000825, a decrease of 23.2%!

The writer has been unable to find any further reference to the application of molecular refraction to the constitution of sulphur trioxide. Swientoslawski⁴¹ who has investigated many organic compounds, makes no reference to inorganic structures.

H. Hunter⁴² has observed that the general discrepancy between the calculated and theoretical values of molecular refraction is too great to be an error in experiment. He attributes this to the fact that the D line of sodium is always used in measuring the refractive indices, and in this way the effects of dispersion are neglected. Accordingly he suggests the use of wave-lengths for which, say, the slope of the refractive-dispersion curves are equal, and also suggests a comparison of values on the basis of the constants in Sellmeier's formula.

Of still more importance in shedding light on structural problems, is the parachor discovered by Samuel Sugden⁴³ in 1924. It is designated by P, and defined by

$$P = \frac{M}{(D-d)} \gamma^{\frac{1}{4}}$$

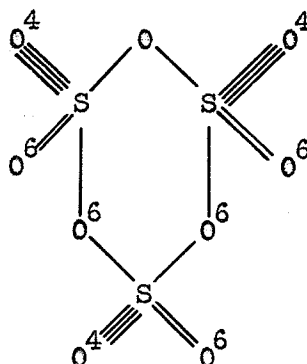
where M is the molecular weight, D and d are the densities of the liquid and vapour respectively and γ the surface tension, all measured at the same temperature. We may neglect d when the vapour pressure is low. He was led to this relation by the empirical equation

$$C (D-d)^4 = \gamma \quad \text{or} \quad C' (D-d) = \gamma^{\frac{1}{4}}$$

discovered by Macleod⁴⁴ in which C is a constant for a given non-associated liquid.

Comparison of parachors of different substances gives a comparison of molecular volume under conditions of equal surface tension. The significance of this is apparent when one considers the relation of surface tension to internal pressure, and of internal pressure to volume.

The parachor is an additive and a constitutive property and calculated and observed parachors agree remarkably well, both in organic and inorganic compounds. Sugden⁴⁵ has already applied it to sulphur trioxide, and gives the electronic formula in the liquid state as



(the numerals indicate unshared electrons)

In other words, he shows the existence of the S_3O_9 molecule at the temperature at which he took his values of surface tension and density.

5. Discussion of the Problem.

The problem assigned to the writer was to further investigate the behaviour of intensively dried sulphur trioxide, and thus provide additional experimental evidence relevant to Smits' theory.

The question arises: What is the nature of the pseudo-components of sulphur trioxide? Are they isomers or polymers, using the terms in their widest sense to include even electrically charged dissociation products and different atomic structures, e. g., atoms differing in the quantum numbers of their valence electrons. When the T-X diagram for an ordinary binary system exhibits a eutectic, we seem justified in concluding that the components are not polymers, for this would mean that over a certain range of composition, liquids could exist which contain more of the polymer than the mixed crystal phases in equilibrium with them, which is highly improbable. However, when there is no eutectic in the T-X diagram, it does not follow that the components are polymers. Applying this to the pseudo-system of sulphur trioxide, Fig. 34 indicates no eutectic, hence we cannot conclude from this whether the pseudo-components of sulphur trioxide are polymers or isomers.

It was thought that further information regarding the nature of the pseudo-components could be obtained by using the following principle:

Intensive drying of the sulphur trioxide by passing its vapour repeatedly over phosphorus pentoxide would freeze the equilibrium, thus causing the substance to exhibit binary behaviour. The sulphur trioxide would then be distilled in fractions and some physical property of each successive fraction measured. The magnitude of this property would either remain constant or show a change with fractionation, but the interpretation of the result would depend upon the particular property concerned.

What physical property would be best suited to the purpose? H. L. Fanshaw in 1934-1935 had attacked the problem from the standpoint of refractive index. Previous to him, Guthbertson and Metcalfe⁴⁰ had measured the refractivity of the vapour, and Nasini⁴⁶ and others had measured the refractivity of the liquid, though finding it impossible to exclude moisture, thus introducing an error. These measurements are not specifically those of the intensively dried substance, nor have they any reference to pseudo-components.

Fanshaw had surmounted many of the technical difficulties connected with such an investigation, and it was the writer's privilege to continue with the problem, namely, the determination of the refractive index of intensively dried sulphur trioxide. However, the same difficulty that brought Fanshaw's work to a close was encountered, and the experiment was finally abandoned. In this case, since refractive index is what we may call an "atomic" property, had a change in the refractive index been found with fractionation we should have been led to conclude that the pseudo-components were isomers, whereas a constant value would have indicated the possibility of them being polymers, if pseudo-components exist at all.

It was now decided to attempt a similar investigation measuring surface tension instead of refractive index. A knowledge of the former would probably be even more instructive than a knowledge of the latter (see preceding section on The Constitution of Sulphur Trioxide). In this case, however, since surface tension appears to be related to molecular association, a change in the value of surface tension with fractionation would not necessarily point to the isomeric nature of the pseudo-components, but rather to their polymeric nature.

Schenck³⁰ made the first reliable measurement of the surface tension of sulphur trioxide, which had been dried by phosphorus pentoxide to a considerable extent. Twenty years later, Berthoud³¹ repeated the determination under similar conditions. It is seen then that the writer's chief claim to originality lay in the effect of fractionating on the surface tension and density, since density measurements would also have to be made.

III. SURFACE TENSION

Molecules in the body of a liquid are acted on by the intermolecular attractive forces equally in all directions. At the surface of a liquid, or any interface, the molecules are subjected to an unbalanced force at right angles to the surface, which gives the surface of the liquid a tendency to contract. The force acting perpendicularly to a section of the surface 1 cm. long is called the surface tension, usually expressed in dynes per cm., and represented by γ .

There are three methods of measuring γ : (1) the capillary rise method, (2) the drop method, (3) the torsion balance method. The theory of the first is far simpler than that of the second, but its technique is difficult. The second is more correct experimentally, though the theory has not been completely worked out. For our purpose, the latter two were not available.

If a capillary tube is held vertically with its lower end dipping into a liquid which wets the glass, the liquid will rise in the tube, due to its surface tension. The force of gravity acting on the column of liquid is exactly balanced by the surface tension forces, and we have the relation

$$\gamma 2\pi r = \pi r^2 h d g$$

$$\text{or } \gamma = \frac{1}{2} r h d g$$

where r is the radius of the capillary, d the density of the liquid, h the height of the column and g the acceleration due to gravity. The height of the column is usually measured by a cathetometer, and the radius of the capillary by weighing a mercury thread which occupies a known length of the capillary. Considerable attention has been given in recent years to refinements of the methods for measuring surface tension. For example, Harkins⁴⁷ eliminates any error in measuring r due to difference of curvature of menisci by using a "two-thread" method. Mills and Robinson⁴⁸ avoid the

difficulty of placing the lower meniscus accurately by using two or three capillaries.

The surface tension of a liquid decreases with rising temperature. Ramsay and Shields' modification of the original equation of Eotvos is

$$\gamma (Mv)^{2/3} = k (t_c - t - 6)$$

where t_c is the critical temperature, M the molecular weight, v the specific volume, t the temperature of the liquid at which the surface tension is measured, and k is termed the Ramsay and Shields constant.

For normal liquids k usually has the value 2.12, and formerly the deviation of k from this value was taken as indicating molecular association in the liquid. On this assumption the associated molecular weight of the liquid was calculated. At the present time, however, it is generally believed that there is little quantitative significance attached to the Ramsay and Shields constant.

A more popular application of surface tension lies in its relation to the parachor, and this has been referred to in the previous section.

- EXPERIMENTAL -

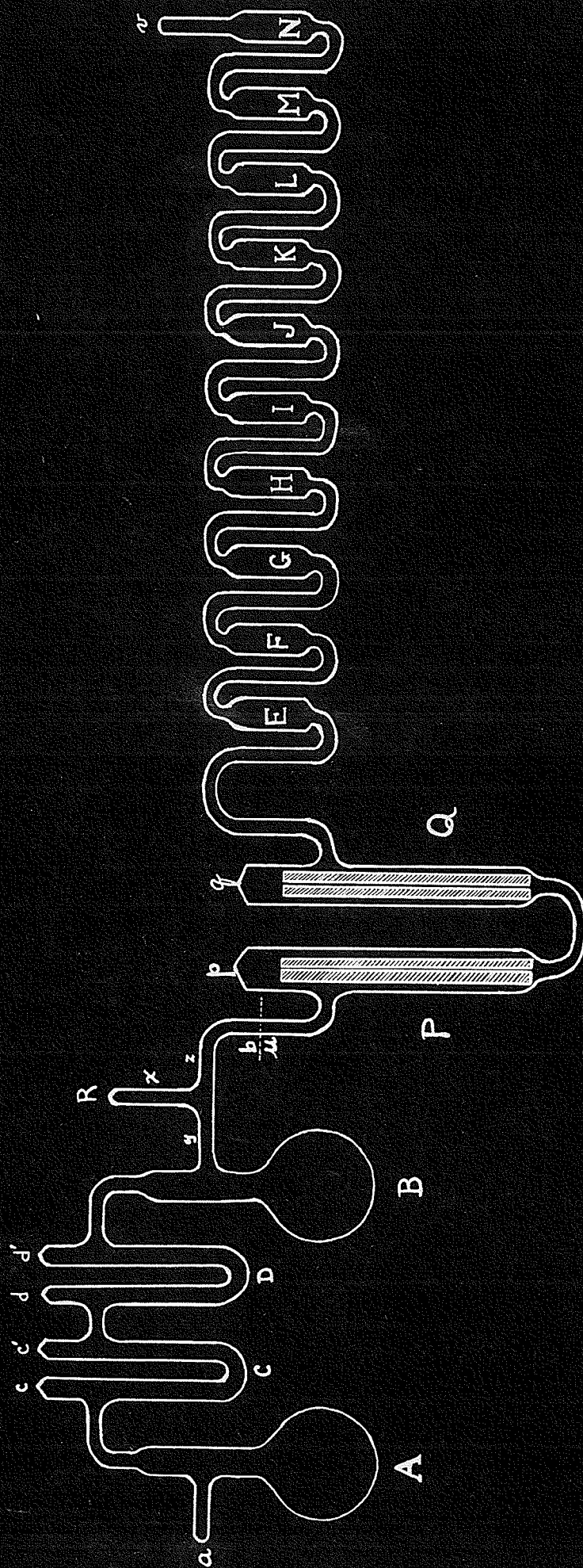


Fig. 35.

I. MEASUREMENT OF REFRACTIVE INDEX

1. Introduction.

Reference has already been made to the work of Fanshaw. His method consisted of distilling sulphur trioxide back and forth over phosphorus pentoxide and measuring the refractive index of the fractions by means of a Pulfrich refractometer. The cell of this instrument was made an integral part of the drying apparatus so that the freedom of the sulphur trioxide from moisture depended on the reliability of the cement used to seal the cell to the prism. This was a source of weakness in his experiment and it was decided to avoid contact of the sulphur trioxide with the cell as far as possible by carrying out the drying operation in an apparatus entirely apart from the refractometer and then transferring it to another apparatus involving the refractometer.

2. The Drying Apparatus.

This is shown diagrammatically in the left hand portion (a to b) of Fig. 35. Hard glass was used throughout as with all other glass apparatus. Flasks A and B were ordinary new 125 c.c. distilling flasks to act as receptacles for the sulphur trioxide. C and D were U-tubes to contain the drying agent - phosphorus pentoxide. The charging of the apparatus with the sulphur trioxide and phosphorus pentoxide will be described later.

In order to remove from the glass tiny capillaries which might occlude moisture we adopted a method similar to that employed by Smits and his co-workers⁴⁹ who heated their glass apparatus just to the softening point. The whole apparatus with the exception of the flasks was wound with Nichrome resistance wire which was to carry an electric current.

Between the wire and the glass was a layer of thin sheet asbestos to prevent the glass from cracking and to distribute the heat more evenly. To prevent loss of heat another layer of asbestos was placed on top of the resistance wire and held in place by pieces of copper wire. In order to get sufficient current through the wire it was found necessary to use two separate electrical circuits in parallel. The flasks were heated by placing them in cans wound on the outside with resistance wire and placed in larger cans, asbestos sheeting being used as an electric and thermal insulator, and asbestos fibre filling the space between the inner can and the flask. Each can had its own electric heating circuit and each circuit a resistor in series. The 110 volt A.C. was used. Whilst a current of air, intensively dried by passage through a calcium chloride tube, two sulphuric acid bubblers and two phosphorus pentoxide towers, entered the apparatus at a and b, leaving it at cc'dd' (R being sealed temporarily), the heating current was gradually turned on till the temperature within the apparatus, indicated by a platinum-iridium thermocouple and milliammeter, exceeded 500°C . The current was now gradually reduced till the apparatus regained room temperature (the dried air being continually passed through it), and the asbestos and resistance wire were removed. It was noticed that in several places the wires had left an impression on the glass, thus proving that it had been heated to softening temperature.

3. The Drying Tubes.

A fresh specimen of phosphorus pentoxide, manufactured by Mallinckrodt, was used for the drying agent. It was introduced into the U-tube by means of a funnel of copper foil and a spatula. Following the plan adopted by Fanshaw, pieces of narrow glass tubing about 1 cm. long

were placed in the U-tubes along with the phosphorus pentoxide. Their purpose was to permit freer passage of the sulphur trioxide vapour through the pentoxide, and also incidentally to present a greater drying surface. These small lengths of tubing were first heated in a metal crucible with a Meker burner to over 500° in order to remove capillaries from the glass. It was found advisable to fill the bottoms of the U's with the glass tubes before adding any phosphorus pentoxide. This helped to prevent the latter from settling to the bottoms of the U's.

Approximately 5 grams of the pentoxide was put in the apparatus in the final attempt (See below).

During this filling process, dried air was passing through the apparatus continually. The outlets cc'dd' were now drawn out and sealed after wiping the necks with filter paper to remove any pentoxide adhering to them. The phosphorus pentoxide would have tended to make the glass brittle, it was learned. The outlet a was sealed and b was temporarily stoppered. The apparatus was now ready for charging with the sulphur trioxide.

4. Charging with Sulphur Trioxide.

Considerable difficulty was experienced at this stage of the experiment, and three attempts were necessary before the apparatus was finally sealed.

The first attempt - The apparatus used in the first attempt had stop-cocks at x, y and z. The sulphur trioxide used was manufactured by Grasselli and contained in a rather thick-walled glass bottle with a glass stopper. It was cooled in ice and salt and the stopper removed. All stop-cocks being open, end b was inserted in its place through a rubber stopper, R was connected to the Hyvac pump and mercury manometer (through a soda-lime

tube to protect the pump from acid fumes) and flasks A and B cooled in ice and salt. The apparatus was exhausted, and cock x closed. The sulphur trioxide bottle was now slowly heated in a glycerol bath and the trioxide slowly distilled into B. Finally, when it was judged that sufficient had distilled, the apparatus was sealed at y.

It was noticed that a brown discolouration had contaminated the sulphur trioxide in the drying apparatus, due to the action of the trioxide on the stop-cock lubricant. Moreover, as the condensed solid in B was very porous, there was actually less trioxide in the flask than there first appeared to be. Also, it was decided that too much phosphorus pentoxide had been put into the U-tubes, thus blocking them. For these reasons the apparatus was discarded.

The second attempt - Another drying apparatus was built, dried, and filled with phosphorus pentoxide, exactly as described above, except that the stop-cocks were omitted and less pentoxide used. As in the above procedure, the bottle containing the sulphur trioxide, having been cooled in ice and salt, was removed from this freezing mixture, and placed in glycerol at room temperature. At this point, it was noticed that a crack had developed near the neck of the bottle, apparently due to the small change in temperature it had undergone. The bottle was bound with wire, and the experiment continued, but before long the crack grew and the glycerol from the bath entered the bottle. This caused a vigorous reaction (dehydration and charring of the glycerol) which destroyed all the sulphur trioxide and filled the apparatus with a charred mass.

The third attempt - A new apparatus (no stop-cocks) was again constructed, raised to a temperature of 500° before charging, and filled with phosphorus

pentoxide (5 grams) all in the manner previously described. The sulphur trioxide was a 100-gram 25-year-old preparation of Kahlbaum and was contained in a round soft glass bulb with a short neck drawn to a tip. Having cooled it in ice and salt, the tip was broken, and the bulb joined to the end b by a piece of pressure tubing. The apparatus was exhausted, and sealed at R. The distillation was now begun, using a glycerol bath to heat the bulb, and cooling A and B in ice and salt. When the temperature of the bath reached 35-40° however, the internal pressure blew off the rubber connection at b.

An attempt was made to seal a piece of tubing on to the neck of the bulb, but without success. Also, a crack had appeared in the neck of the flask. Finally, with considerable difficulty in manipulation, the bulb was broken, and its contents placed in a glass jar provided with a rubber stopper, through which b was passed. The end a was opened, and suction applied there by means of a water suction pump to hasten distillation, and prevent explosion. On raising the temperature of the jar very slowly, the sulphur trioxide was finally distilled into B where it condensed as a white frost-like solid. The apparatus was exhausted and sealed at a and b. It now contained 40 to 50 grams of sulphur trioxide, which when fused, occupied about 26 c.c.

5. The Intensive Drying.

The sulphur trioxide was distilled over the phosphorus pentoxide from B to A and from A to B alternately. The receiver flask was cooled in ice and salt, and the flask containing the sulphur trioxide and the phosphorus pentoxide tubes heated in separate glycerol baths provided with thermometers and stirring rods. The temperature of the U-tube bath was usually kept 5-10° lower than that of the other bath. The maximum temperatures which the two baths reached were usually in the neighborhood

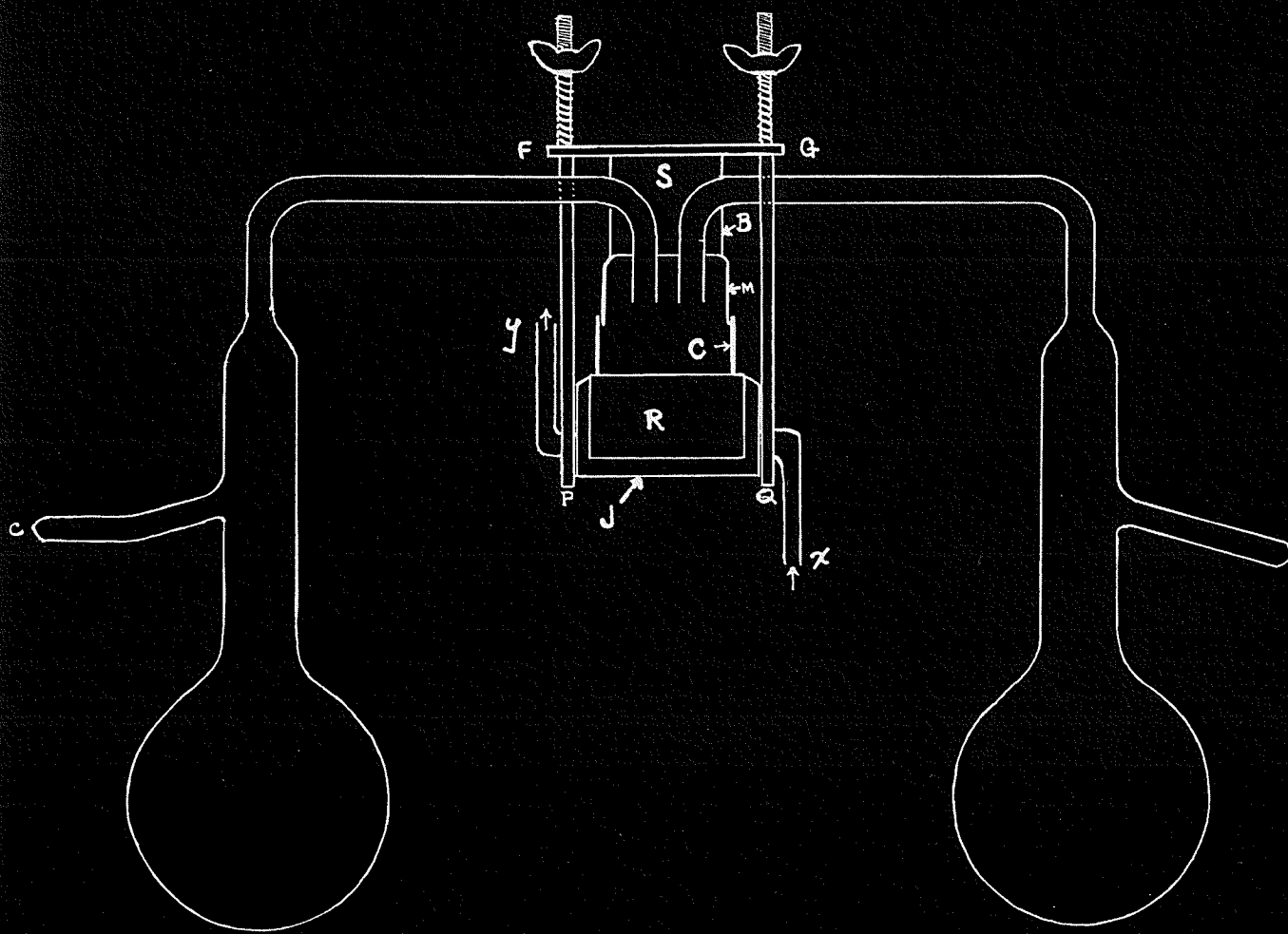


Fig. 36.



Fig. 37.

of 70° and 80° respectively, such temperatures being attained gradually, and distillation lasting from one to two hours.

It should be mentioned that later an attempt was made to shake the phosphorus pentoxide nearer to the tops of the U-tubes, but with no success. The pentoxide had become quite compact, due probably to liquid sulphur trioxide which it had absorbed.

Part of the drying process was carried out with refractive index, and part with surface tension measurements in view. As it was thought advisable to keep all the observations associated with the drying under one heading, a description of them will be found under "Measurement of Surface Tension".

6. The Refractometer.

A Pulfrich refractometer, manufactured by Zeiss, was to be used to measure the refractive indices of the fractions of sulphur trioxide in the liquid form. The source of monochromatic light was a Plucker hydrogen tube, and prism No. 1c was used, as its range of values was most suited to liquid sulphur trioxide. Readings were to be taken for the C (red) and F (blue-green) lines, (the violet line being invisible), and water from a thermostat circulated through the prism jacket.

7. The Measuring Apparatus.

The apparatus into which the sulphur trioxide was to be transferred for measurement is indicated in Fig. 36. With the exception of the prism R and the cell C of the instrument, all the glass apparatus was intensively dried by heating to 500° with resistance wire using cans for the flasks exactly as described under "The Drying Apparatus". A special glass unit M was used to fit onto the cell. B was a brass cylinder and

the space S was filled with lead glycerate. As it was impossible to avoid using a cement to seal the cell to the unit and the prism to the cell, great pains were taken to find a satisfactory cement - one which would resist the action of chemicals, be mechanically strong, and make a gas-tight seal. This investigation will be described later.

Though it was not accomplished, the transferring of the intensively dried sulphur trioxide into this apparatus was to have been as follows:

Having raised the drying apparatus to the temperature at which the vapour pressure of the sulphur trioxide becomes approximately one atmosphere, end b (Fig. 35) was to have been drawn to a tapering tip. A short piece of pressure tubing was to have connected b Fig. 35 to c Fig. 36 as shown in Fig. 37. The measuring apparatus having been exhausted, the tip b could have been broken off and the sulphur trioxide distilled from one apparatus to the other.

In order to add strength to the seal a device was used consisting of two brass hooks, P and Q, threaded at one end for butterfly nuts, the hooks passing under the water inlet and outlet, x and y, of the prism jacket J. The threaded ends passed through holes at the ends of a bar FG pressing on the cylinder B.

8. The Seal.

Fanshaw had experimented with sodium silicate, picene, litharge and glycerol, and finally with a mixture of sodium silicate and fluorite. Only the last mentioned gave him any satisfaction; accordingly work was commenced to see what proportions of the silicate and fluorite gave the best seal.

To test any cement prepared, a piece of a microscope slide was

sealed across the end of a wide, thick glass tube, similar in size to the cell, though tapered at one end for insertion into pressure tubing. The surfaces to be cemented had previously been ground with coarse and fine emery powder, so as to produce conditions similar to those of the cell and prism. The cement was applied to the joint while the test-piece was under suction. Considerable investigation showed the most efficient seal to consist of two parts fluorite and one part silicate, with no cement between the ground glass surfaces. After drying for one day on a hot plate, the test pieces showed only a slight leak with an internal pressure of three atmospheres, such pressures being measured by a closed mercury manometer. However, with further drying (formation of a fluosilicate) the cement became so porous as to be useless for the purpose.

The writer on hearing of a cement prepared by GENCO, called "Insa-lute" decided to test its suitability. The results were encouraging, for when dry (a matter of a day), and under reduced pressure, fifteen hours were required for the pressure to rise from 0 mm. to 140 mm. As this was the best seal that could be found, it was decided to use it. The ground glass surfaces of the cell and prism were carefully rubbed with fine emery and then cleaned. Placing the joint under suction, a small coating of "Insa-lute" was applied, the smooth surfaces of the prism being covered with gummed labels for protection. Four layers were applied, time being given for each one to dry. The seal still leaked slightly however. Fanshaw had found a lead oxide-glycerol seal satisfactory for holding reduced pressures, though attacked by sulphur trioxide. Accordingly a layer of the composition $\text{PbO} : 5 \text{ gm.}, \text{ glycerol} : 0.6 \text{ c.c.}$ was added. Improvement was noticed, so two more applications were made, followed by a layer of Canada balsam. The seal was now found to be gas-tight. Apart

from this, however, it was discovered that the "Insa-lute" which formed the foundation of the seal had softened to such an extent as to make the joint mechanically weak, and therefore useless.

Another possibility suggested was that of silvering the ground glass surfaces and joining them by some low-melting alloy, but this was not attempted. Other means of measuring refractive index, such as the "real and apparent depth" method, were considered, but found impracticable, and investigation in this direction was abandoned.

The sulphur trioxide, by this time reasonably well dried, was still available, however, and preparation of an apparatus to measure its surface tension was begun immediately.

II. MEASUREMENT OF SURFACE TENSION

1. Introduction.

The only suitable method of measuring surface tension was that of capillary rise, and this required a knowledge of density. Accordingly, an apparatus consisting of capillary tubes and density bulbs was built, and is shown diagrammatically in the right hand portion (u to v) of Fig. 35. It was thought that by making a single glass system of the two units (a to b and u to v), any doubt as to the admissibility of a procedure such as that connected with Fig. 37 would be avoided. As before, the method consisted of (further) intensive drying, followed by measurements of the surface tension and density of successive liquid fractions.

2. The Measuring Apparatus.

The limbs of the U-tube P and Q (Fig. 35) contained two hard glass capillary tubes, resting loosely in them. E, F.....N were ten bulbs for density measurements. Before inserting the capillaries, scratches were made outside of the capillaries at intervals of about 1 cm. for points of reference. The whole apparatus was gone over with a Meker burner to heat it to a dull redness whilst intensively dried air was passed through it. The hard glass capillaries, having been very carefully cleaned, were intensively dried by imbedding in a pile of parallel carbon rods in a can through which dried air was passing, and heating with a Meker burner.

3. The Cathetometer and Travelling Microscope.

Two cathetometers were used, one for measuring the rise in the capillary, and the other for measuring levels in the density bulbs. The latter, used also to calibrate the former, was manufactured by W. G. Pye & Co., Cambridge. It was fitted with a vernier and a micrometer screw, the

vernier being used for the density measurements and the micrometer for calibration purposes where higher accuracy was required.

The travelling microscope used in calibrating the capillaries was a comparometer manufactured by Hilger. The movement was by a rotating drum and micrometer screw giving an accuracy of 0.001 mm.

4. Fusion of the Two Units.

The sulphur trioxide having been distilled into flask A (Fig. 35), and A and B cooled in ice and salt, the drying apparatus was joined to the surface tension apparatus as follows: A scratch was made near the tip at b. Over this tip was slipped a piece of rubber tubing leading to a drying train (calcium chloride, sulphuric acid, phosphorus pentoxide). The tip was broken off, and dried air allowed to enter till the pressures were equalized. Openings q and v being temporarily closed, u was sealed onto b, blowing at p through two phosphorus pentoxide towers. The capillaries were inserted and p and q sealed. The apparatus was exhausted at v with the Hyvac pump and sealed off at v.

5. The Intensive Drying. (Continued)

Prior to the addition of the surface tension apparatus, the sulphur trioxide had been distilled thirteen times, extending over a period of two months, and now the drying was recommenced, using ice and water instead of a freezing mixture, for the receiving flask. Each density bulb was provided with an oil bath, and the surface tension apparatus with a glycerol bath.

The following phenomena were observed during the course of the drying:

(1) In flask B there always remained a small quantity of white solid which even at a temperature of 170° did not distil. There is the possibility

that this was phosphorus pentoxide.

(2) The distillate from the first distillation remained solid on warming to room temperature, whereas each succeeding distillate, which at the temperature of the freezing mixture had the appearance of snow, melted in A to a clear colorless liquid on attaining room temperature, but usually only partly melted in B.

(3) The fourteenth distillation (that immediately succeeding the procedure described in Section 4) gave the asbestos-like form in flask B. As this process had unavoidably admitted traces of moisture, we see that this fact, together with (2) confirms Weber's observation that the drying of sulphur trioxide hinders the formation of the asbestos-like form. It is remarkable that Smits and Schoenmaker³⁴ use continued distillation over phosphorus pentoxide in order to obtain the asbestos form from the ice form.

(4) Whereas liquid in B always boiled at low temperatures (20° to 30°), usually liquid in A did not boil till high temperatures were reached. This was probably due to superheating in A caused by the absence of solid - cf. (2).

(5) If the boiling was maintained at a constant temperature, it would cease boiling after a time and would continue only on raising the temperature. This would indicate the presence of components differing in volatility.

(6) Slow condensation at room temperature gave the asbestos-like form in many parts of the apparatus in contrast to the α form by condensation at 0° .

(7) Fast condensation at temperatures from 17° to 21° in the surface tension apparatus, gave liquid sulphur trioxide, which however spontaneously crystallized at varying rates from nuclei formed either in the vapour or the liquid. An attempt to remove these nuclei by raising the surface

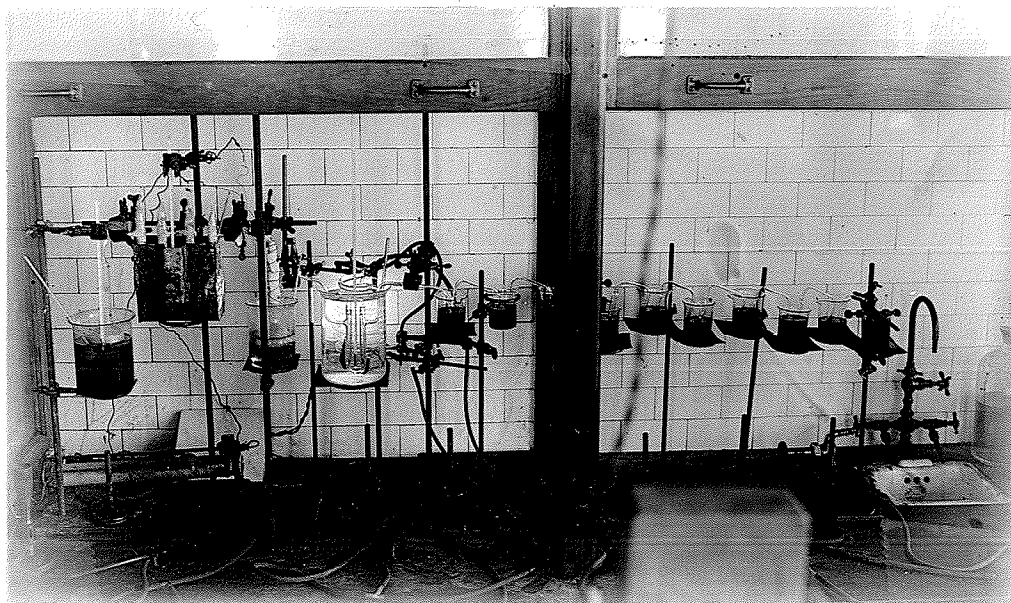


Fig.38.

tension apparatus and density bulbs to over 100° was unsuccessful.

(8) There was usually a small quantity of white membranous solid in A which sublimed only at a high temperature.

(9) Once, a perfectly clear liquid was obtained in B when two distillations were carried out within less than two hours, involving unusually quick melting of the distillate in B.

Since the addition of the surface tension unit, the sulphur trioxide had been passed over the phosphorus pentoxide some thirty times over a period of forty days, and so could be assumed to be in the intensively dried condition. The next step was the fractional distillation, and the measurements of the capillary rise and density of each fraction.

The complete apparatus is shown in the accompanying photograph (Fig. 38).

6. Measurements.

(1) Capillary Rise

Preliminary approximate measurements of capillary rise were made during the course of the drying as well as after it. In order to obtain liquid sulphur trioxide in the surface tension apparatus, it was found necessary to make this the coldest part of the whole system. For this purpose, the U-tube containing the capillaries was placed in a water bath kept at 20° . At the same time, the density bulbs were heated to about 70° by means of individual oil baths, and the temperature of the flasks containing the sulphur trioxide was slowly raised till sufficient liquid had condensed. During the majority of these preliminary measurements, the liquid, on standing for an hour or so at 20° , spontaneously crystallized, as mentioned before to give a solid which appeared partly to melt and partly to sublime, the latter chiefly in the region of 60° - evidently

not the α form. To obtain a stable liquid, the effect of condensation at 0° in the U-tube, followed by melting, was tried, since the solid condensed at 0° in the flasks usually melted to give a stable liquid. This was unsuccessful however, so that readings had to be made before crystallization set in.

With the period of intensive drying completed, the final measurements were commenced. The liquid sulphur trioxide was condensed in the surface tension apparatus as described above, and the capillary rise measured at 20° and 50° by means of the calibrated cathetometer. A frosted electric bulb placed behind the apparatus aided in placing the menisci. Temperature control was by means of a water bath kept at 20° by immersing in it a spiral of glass tubing through which flowed water from a thermostat, and at 50° by a regulated flame. At 50° it was necessary to heat the remainder of the apparatus to above 50° , and difficulty was experienced in preventing the liquid from boiling, and in keeping the menisci steady, due to unequal pressures in the two limbs of the U. For this reason measurements of the capillary rise at 50° could not be made directly as at 20° . An indirect method was used which consisted of placing the graduated scale of a thermometer beside the capillary and observing the point on this scale that the upper meniscus lay opposite, at the same instant placing the cross-hair of the cathetometer on the lower meniscus. The distance between the two menisci could thus be measured, though with less accuracy than at 20° . Where possible both capillaries were used for the determinations, and the position in the capillary of the upper meniscus noted by reference to the scratches on the tube. This precaution was observed in case the bore of the tube was found to be irregular in the calibration.

The capillary rise of the most volatile fraction present having been measured at the two temperatures, the same fraction was distilled to the density bulb at the extreme end of the apparatus, and the bulb sealed off. In order that the internal pressure of the sulphur trioxide be less than atmospheric, at the moment of sealing most of the heating baths were removed. In this way, nine different fractions were measured and sealed off. The surface tension of the tenth fraction remaining in the apparatus was also measured. Difficulty was experienced in filling the first density bulb (N, Fig. 35) due to the fact that what air remained in the apparatus collected in N and prevented filling it with sulphur trioxide. Only the bulb M could be filled, so that both M and N had to be removed together. No further trouble was caused by air in the apparatus.

All nine fractions were measured and sealed off within ten days. (One day separated the treatments of the fifth and sixth fractions).

The results of the above measurements are given in Section (4).

(2) Radius of the Capillaries

The mercury used for calibration purposes was purified by spraying in nitric acid. A short thread was drawn into the capillary the radius of which was to be measured, and the length of this thread, when placed with each of the reference marks at its centre, determined by means of the travelling microscope. The thread was then weighed. Assuming the bore to be circular, the radius of each capillary was then calculated, with the following results. The density of mercury at the temperature of measurement, 19.3° , is 13.5474 . No correction was made for the curvature of the menisci of the mercury thread.

Table I

Reference mark No.	Radius (cms.)	
	Capillary I	Capillary II
1	.03592	.03563
2	.03594	.03561
3	.03594	.03561
4	.03595	.03565
5	.03597	.03564
6	.03595	.03569
7	.03598	.03567
8	.03597	.03572
9	.03594	.03573
10		.03595
11		.03596
	Mean: .03595	Mean: .03571

(3) Densities

Within one hour of the sealing off, the sulphur trioxide in each bulb was poured into the narrow limb of the bulb (where possible), and the whole inserted in a water bath at 20°. The inside diameter of the narrow limbs was about 4 mm. The vertical distance between the level of the meniscus and the scratch made on the glass above or below it was measured by a cathetometer with an accuracy of at least 0.01 cm. The temperature of the bath was now raised to 50° and the level of the meniscus again noted. Each bulb was then weighed.

As mentioned before, it was necessary to remove both M and N (Fig. 35) in a single operation. M and N were immediately separated by fusion, but the heat of the blowpipe caused the vapour to blow a hole in the glass allowing air and a slight amount of moisture to enter. It is significant that this accident resulted in the immediate solidification of the liquid in M and N. This solid however, melted on placing immediately in a bath at 50° . Only in the case of this first fraction, were the 50° levels measured prior to those at 20° .

The next step was the fracture of the bulbs and the removal of the sulphur trioxide. They were then filled with distilled water to the same level and again weighed. Finally, the empty bulbs were weighed. The resulting densities referred to water at 4° are given below, together with the successive means.

Table II

Fraction No.	Density at 20°		Density at 50°	
		Successive mean		Successive mean
1	1.919	1.919	1.781	1.781
2	1.934	1.927	1.780	1.781
3	1.889	1.914	1.782	1.781
4	1.933	1.919	1.782	1.781
5	1.897	1.918	1.781	1.781
6 (#)	1.889	1.910	1.793	1.783
7	1.948	1.916	1.783	1.783
8	1.937	1.918	1.781	1.783
9	1.932	1.920	1.783	1.783

(#) Large unavoidable experimental error.

Table III compares our mean values with those of previous observers.

Table III

Observer	Density	
	20°	50°
Schenck ³⁰	1.909 (#)	1.773 (#)
Lichty ²⁹	1.9229	1.782 (#)
Berthoud ³¹	1.9255	1.7812
Campbell & Smith	1.920	1.783

(#) By interpolation.

Using the values of the present experiment, we obtain for the coefficient of expansion of liquid sulphur trioxide the value 0.00256.

It will be observed that the densities at 20° show considerable variation but not gradation, whilst those at 50° (neglecting the sixth fraction) are practically constant. Also, the density of the first fraction, the one into which moisture had entered, has a value very close to the mean value. These results will be referred to later.

(4) Surface Tension Values

By means of the formula

$$\gamma = \frac{1}{2} h d g r$$

the surface tension of each fraction was calculated. The value of g was taken as 980.6 cms. per sec. per sec.

In the following table h represents the average of a set of several readings. The values of r were taken from table I corresponding to the position of the upper meniscus in the capillary, and the densities used were the mean values for 20° and 50°.

Table IV

Fraction No.	20°			50°		
	h (cms.)	r (cms.)	γ (dynes/cm.)	h (cms.)	r (cms.)	γ (dynes/cm.)
1	0.919	.03594	31.11 (I)	0.828	.03595	26.02 (I)
2	0.936	.03565	31.43 (II)	0.832	.03595	26.16 (I)
	0.935	.03564	31.38 (II)			
3	0.880	.03595	29.77 (I)	0.816	.03595	25.65 (I)
	0.880	.03597	29.82 (I)			
	0.875	.03595	29.61 (I)			
4	0.902	.03595	30.53 (I)	0.819	.03595	25.74 (I)
	0.903	.03594	30.54 (I)			
	0.895	.03597	30.31 (I)			
5	0.858	.03597	29.08 (I)	no readings		
	0.924	.03567	31.01 (II)			
	0.933	.03572	31.37 (II)			
6	0.882	.03595	29.85 (I)	0.795	.03595	24.99 (I)
	0.935	.03572	31.45 (II)			
	0.933	.03573	31.39 (II)			
7	0.905	.03594	30.62 (I)	0.811	.03595	25.50 (I)
	0.910	.03594	30.78 (I)			
	0.941	.03595	31.84 (II)			
8	0.916	.03594	30.98 (I)	0.811	.03595	25.48 (I)
	0.922	.03595	31.25 (I)			
	0.931	.03572	31.34 (II)			
9	0.908	.03594	30.74 (I)	0.809	.03595	25.41 (I)
	0.907	.03595	30.71 (I)			
	0.899	.03597	30.44 (I)			
	0.940	.03596	31.82 (II)			

Table IV (Continued)

Fraction No.	20°			50°		
	h (cms.)	r (cms.)	γ (dynes/cm.)	h (cms.)	r (cms.)	γ (dynes/cm.)
10 (#)	0.879	.03597	29.76 (I)	no readings		
	0.937	.03573	31.53 (II)			

(#) Using density of ninth fraction.

The Roman numerals in brackets indicate the capillary used.

The values for capillary II give consistently higher values for surface tension than those for capillary I. This may be due to a consistent error in placing the lower menisci of one or other of the capillaries.

In table V are given the surface tension and the successive means at the two temperatures. For reasons which will appear later only the highest values for each fraction have been selected.

Table V

Fraction No.	Surface tension (dynes per cm.)			
	20°		50°	
		Successive mean		Successive mean
1	31.11	31.11	26.02	26.02
2	31.41	31.26	26.16	26.09
3	29.73	30.75	25.65	25.94
4	30.46	30.68	25.74	25.89
	31.19	30.78	no readings	
6	31.42	30.89	24.99	25.71
7	31.84	31.02	25.50	25.68
8	31.34	31.06	25.48	25.65
9	31.82	31.15	25.41	25.62
10	31.53	31.19	no readings	

The maximum deviations from the mean at 20° are $+2.08\%$ and -4.66% , and at 50° , $+2.1\%$ and -2.36% .

Table VI compares the mean values with those of previous observers. Though neither Schenck's nor Berthoud's measurements are specifically those of the intensively dried substance, no doubt these experimenters reached a fairly dry condition of the liquid, for both used phosphorus pentoxide as a drying agent. Schenck used sulphur trioxide which had been repeatedly distilled in a knee-shaped tube containing phosphorus pentoxide.

Table VI

Observer	Surface tension	
	20°	50°
Schenck (#)	32.70	27.61
Berthoud (#)	33.99	28.55
Campbell & Smith	31.19	25.62

(#) By interpolation.

At 20° the values of the present experiment differ from Schenck's by 4.6% whereas Schenck's differ from Berthoud's by only 3.6% . At 50° our values differ from Schenck's by 7.2% whereas Schenck's differ from Berthoud's by only 3.3% . The present values are therefore definitely quite low.

Using the final mean values of table V gives for the molecular surface energy at 20° the value 374.9 ergs, and at 50° the value 323.5 ergs. It follows that over the temperature range $20-50^{\circ}$ the mean value of the Ramsay and Shields constant is 1.71 for the intensively dried liquid,

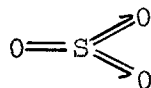
probably indicating association in the liquid. Substituting this value in the Ramsay-Shields-Eotvos equation gives a value of 245.2° for the critical temperature, but, since the molecular surface energy is not a linear function of temperature for an associated liquid such as sulphur trioxide, this value deviates considerably from the experimental value of Schenck (216°).

The parachors at 20° and 50° , calculated from the final mean values of tables II and V, and neglecting the density of the saturated vapour, have the following values:

$$P_{20^{\circ}} = 98.5$$

$$P_{50^{\circ}} = 101$$

Sugden⁴⁵ quotes the calculated parachor of the simple unassociated molecule as 128.2, presumably from the formula



In other words, anomalies of -29.7 and -27.2 are exhibited at the two temperatures. This is explained by assuming association in the liquid. Now the formula given on page 30 gives a parachor of 107 per SO_2 molecule, but undoubtedly there are present in the liquid other types of molecules besides this one (S_2O_6 , for example), giving parachor values differing from 107 by amounts depending on the number of other types of molecules present. In this way our values of 98.5 and 101 may be accounted for.

(5) Melting-Points

Determinations of the melting ranges of each fraction were made from one to two weeks after they had been sealed off. All fractions except the first and third had remained liquid. In the first the whole had solidified but in the third there still remained a small quantity of liquid which

solidified when placed in a bath at 12°.

Prior to the melting, the liquids were solidified by chilling in ice and salt, and the melting range observed by slow heating in a water bath. It should be emphasized that the beginning and ending of melting was not sharp so that the temperatures given are in many cases only approximate, particularly those of the first fractions.

Table VII

Fraction No.	Beginning of melting	Melting essentially complete	Melting not yet complete	On cooling to room temperature
0 (#)	35.1°	?	61°	solidification
1	26.9	52°	62.5	solidification
2	14	49	62	largely solidified
3	13.1 (##) 32	17.1 48 (###)	60	only partly solidified
4	9.5 (####)	20	45	remained liquid
5	11	20	60	" "
6	16.9	21	48	" "
7	16.9	25	?	" "
8	16.7	21.3	?	" "
9	16.9	25	66.5	" "
10	16.9	35	65	" "

(#) The fraction referred to as the zero fraction was the one sealed off at the same time as No. 1. Both contained moist air.

(##) The first of the two values for No. 3 indicates the initial melting-point of the liquid that had just been frozen, and the second, that of the remainder.

(###) Appearance of turbidity.

(####) The initial temperature of the melting bath was 9.5° and at this temperature the sulphur trioxide had already partly melted.

III. DISCUSSION OF RESULTS

The agreement in the density values at 50° indicates the accuracy of the experimental method. Experimental error, then, cannot account for the variation in density found at 20°. We conclude that these variations at 20° actually do exist, indicating that the density of the liquid at 20° represents a disturbed state of equilibrium, the attainment of the stable equilibrium having been retarded. The values of density at 20° are therefore chance values depending probably on the rate of cooling to 20°, and the original condition of the liquid. In this respect Schenck's volume changes at low temperatures are confirmed.

The successive means at both temperatures show no definite trend so that fractionation has evidently not affected the density. This is in agreement with Briscoe, Peel and Robinson's²³ results for benzene.

Table III indicates close agreement with previous authors. The fact that the density of the first fraction which accidentally contained moist air agrees with the mean value and also with those of Lichty and Berthoud could be explained on Smits' theory by assuming that the moisture caused the return to the not-intensively-dried state.

Table V shows a considerable difference from other observers. There is the possibility that either their or our results are in error. Now microscopic examination of the capillaries showed a slight departure from circular cross-section but we believe that this would introduce only a slight error. For example, enlarged cross-section area would be compensated by a correspondingly enlarged perimeter. Moreover, as the difference between Schenck's and Berthoud's values is considerably less than the difference between Schenck's and our values, and also greater than our maximum experimental error, we feel justified in concluding that intensive drying has definitely lowered the surface tension. Our highest values were given

in table V in order to load this argument against us. These results agree with those of Briscoe, Peel and Robinson, who found the intensive drying of benzene to cause a slight lowering of the surface tension.

Again, our maximum deviations at 50° , where a higher experimental error would be expected, are no larger than our maximum deviations at 20° . From this it might be concluded that the deviations at 20° are real.

With regard to the effect of fractionation on the surface tension, a very slight trend in the successive means exists. This cannot be regarded as significant, however.

The only definite conclusions that can be drawn from the melting-point determinations is evidence of heterogeneity. This of course, does not constitute a proof of Smits' theory.

IV. CONCLUSIONS

1. Sulphur trioxide is a heterogeneous compound.
2. The density and surface tension of successive distilled fractions of intensively dried liquid sulphur trioxide have been measured.
3. The values of density and surface tension show no definite gradation with fractionation.
4. Density values for intensively dried liquid sulphur trioxide at 20° indicate that various disturbed states can exist in the liquid at that temperature. These disturbed states were not found at 50° .
5. The intensive drying of sulphur trioxide lowers its surface tension.

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