

THE SURFACE TENSION
OF
INTENSIVELY DRIED
SULPHUR TRIOXIDE

by

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Being a Thesis

submitted to the Committee on
Post-Graduate Studies of the
University of Manitoba in par-
tial fulfilment of the require-
ments for the Degree of
Master of Science.

March, 1936.

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.

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- 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.

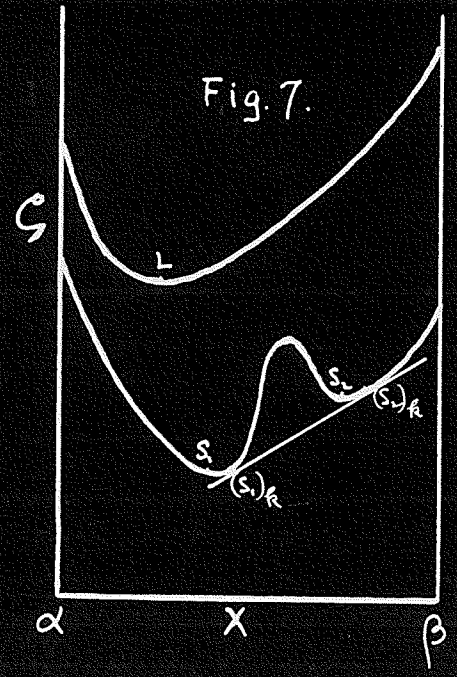
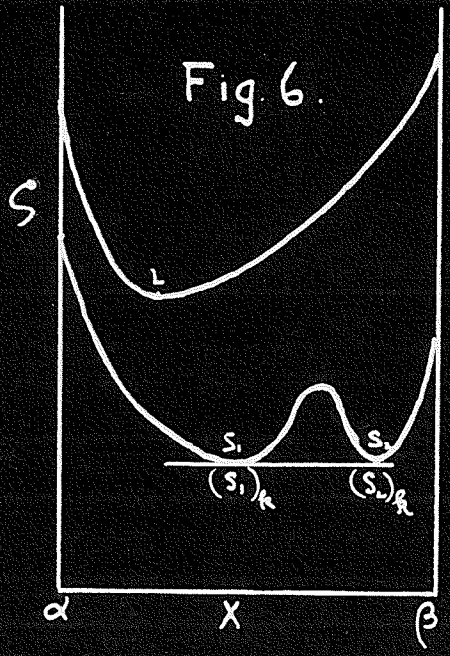
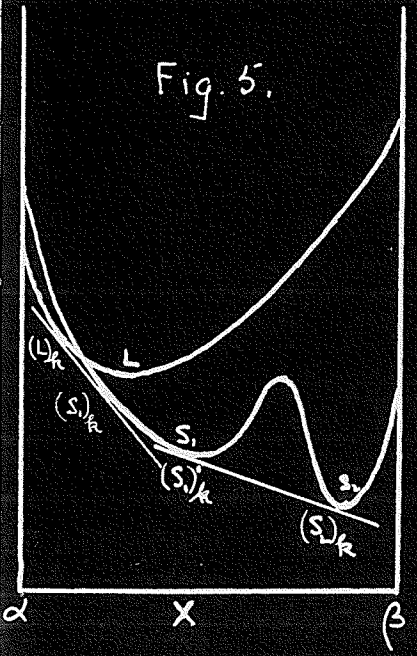
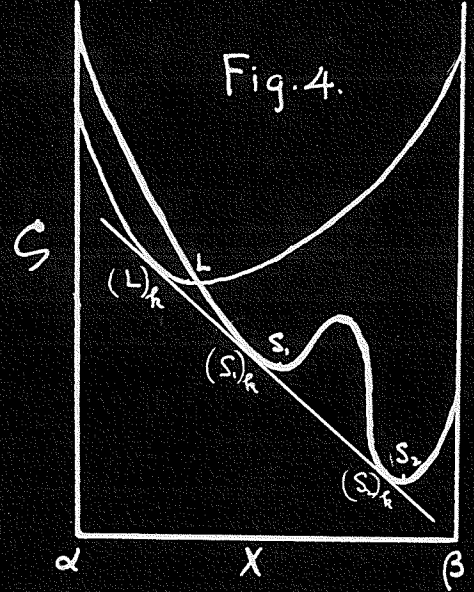
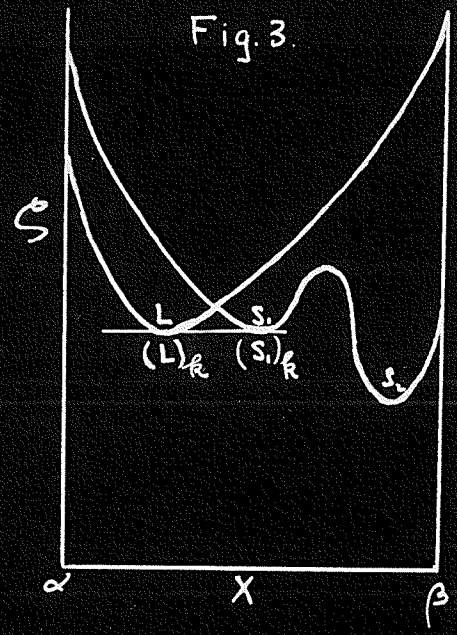
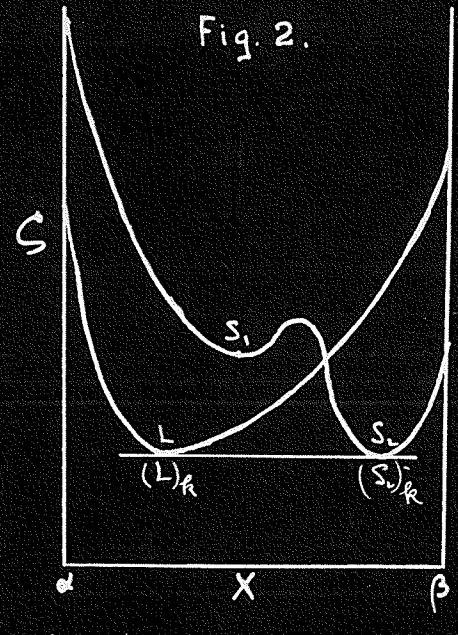
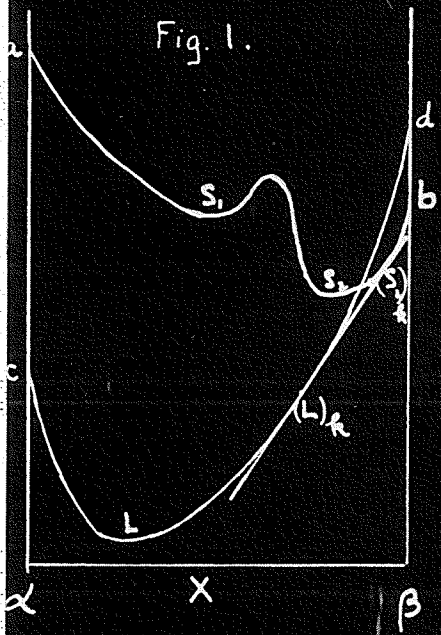
In short, according to Tammann we are not in a position to state that a given form is unstable until its complete stability relations are known: cases of monotropy at low pressures, for example, become cases of enantiotropy at higher pressures.

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.



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