The Vitreous State

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1. THE GENERAL APPLICABILITY OF MY THEORY FOR THE STRUCTURE OF VITREOUS SOLIDS

IN a recent article Hägg states that my theory for the structure of vitreous solids[1] cannot furnish an explanation of glasses in general, not even for oxide glasses in general. Hägg thinks that my viewpoint is adaptable only to cases where the oxygen polyhedra form three dimensional networks. This statement is due to a serious misunderstanding of my paper. My conception of the atomic arrangement in vitreous solids in general were put forth in Section 2 of my paper. It may be stated briefly: The glasses are built up of extensive three dimensional networks without symmetry or periodicity, these networks being in other respects essentially the same as the ones we find in the corresponding crystals. This picture of the structure of glass certainly has a general enough application. Due to the great variety of glasses it is difficult to give a much more detailed picture for the general case. Indeed, Hägg has been confronted with the same difficulty. Only by applying the general principles on specific types of glasses did I succeed in arriving at a detailed picture of the atomic arrangement, then, of course, applicable to those specific types of glasses only. This is what I did for the oxides in Section 3 of my article. For this class of substances I was able also to take up for discusssion the problem of the conditions under which such vitreous networks could exist. These conditions were in fact derived. Now all the oxides which were known to occur in vitreous forms (and possibly a few other oxides which I enumerated) actually did satisfy these conditions. Similarily I could show that BeF_2 should be the only pure fluoride which could exist in the glassy state. In Section 4 of my article I discuss to some extent general oxide glasses. The conditions for the existence of such glasses were given on page 3848. They do not imply, as Hägg seems

to believe, that the so-called vitreous framework has to have three dimensional extension. That I have not even had this in mind, is clear from the statement on page 3849: "It may be expected quite generally that the glasses would have the most advantageous properties if the tetrahedral or triangular networks had three dimensional extension." It is true, however, that I proceed to give a more detailed picture only for this type of oxide glasses, a fact which probably has been responsible for Hägg's misunderstanding.

It is apparent from my paper that I avoided "explaining" the structure of glass in terms of the conditions in the melt, rather I made correlations to the crystalline state. It is in my opinion no real progress to present a theory for the structure of glass in terms of the equally unknown structure of the liquids.

2. COMPARISON BETWEEN HÄGG'S GENERAL THEORY AND MY OWN

A. The structure of the vitreous solids

It has been known for a long time that the tendency to glass formation was closely connected with the viscosity of the melt. Hence the tendency to glass formation should be related to the size of the molecules or groups present in the melt. This idea Hägg presents in a more definite form: A melt will show tendency to glass formation if it contains large or irregular groups. Provided this criterion is correct (we shall discuss that point in the next section), it gives a general explanation of how glasses can be formed in terms of the structure of the melt. In itself this gives no picture of the atomic arrangement in the vitreous solids. Hägg's idea is now that the glass is built up of the same entities as were present in the melt, i.e., in the case of a melt containing only one type of groups, the glass would be an aggregate of these large or irregular groups. Hägg is rather vague concerning the structure of any one such fragment; it appears that it need not be crystalline, although it would not be in disagreement with his ideas if it were.

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[1] W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

He does not discuss the nature of the aggregate and its bearing on the transparency. Hägg's viewpoint for such glasses (e.g., vitreous oxides, organic glasses, element-glasses) is not identical with mine.

If the melt contains small regular groups or single atoms in addition to the large or irregular groups, Hägg's viewpoint would lead, not to an aggregate of smaller fragments, but to one (or a smaller number) continuous medium, in which the large or irregular groups were cemented together by the remaining constituents. Such a conception would be in formal agreement with my general principles. Indeed, there would be no significant difference of opinion between us. I must admit at this point that I have given a *detailed* picture of the atomic arrangement only for glasses in which the groups are practically unlimited in three dimensions. I did not in my paper present a detailed picture in the case that the groups are unlimited in one or two dimensions. The requirement of non-periodicity would, however, for such glasses lead to Hägg's model, with minor modifications.

B. The conditions for glass formation

According to Hägg the general condition for glass formation is the presence in the melt of large or irregular groups, while according to my viewpoint it depends upon whether extensive networks without symmetry and periodicity are possible. Obviously my condition is considerably more restricted. It is fairly evident that substances satisfying my condition necessarily will satisfy that of Hägg, while the reverse is by no means true.

Let us consider the pure oxides as a concrete example. In order to give a fundamental explanation of the glass-forming tendency of the oxides, Hägg has to prove that large or irregular groups are present only in the melts of those oxides which are known to form glass. Hägg has given no such proof, although he has touched the problem in his article. Thus Hägg seems to believe that a crystal of BeO upon melting would dissociate into very small groups because of a more or less ionic type of binding, whereas larger groups would exist when crystalline silica is melted because of a more homopolar binding. Let us assume that Hägg will be able to furnish the required proof. In view of my results for the oxides it is then likely that the conditions for the existence of large groups (not small irregular ones) in melts of pure oxides will become identical with my conditions for the existence of networks lacking symmetry and periodicity, as given in Section 3 of my original article.

The difference between our viewpoints is perhaps best illustrated by the example of H_3PO_4 mentioned by Hägg. In order that this compound be able to form a glass according to Hägg, larger groups than $(PO_4)^{-3}$ must be formed. According to my viewpoint I must with Hägg explain the formation of larger groups; but *in addition* I have to show that such larger groups can be formed *without symmetry and periodicity*. The cause of the formation of larger groups in H_3PO_4 is the presence of the hydrogen atoms. As in H_3BO_3, KH_2PO_4 or $NaHCO_3$ the individual PO_4 radicals are undoubtedly linked together by hydrogen atoms so as to form a practically unlimited three dimensional network. We know, however, from crystal structure results that the hydrogen atom lies midway between two oxygens belonging to two different radicals. Hence we have the possibility of a random orientation of the PO_4-tetrahedra around a given hydrogen bond, and under those conditions it is possible to have a practically unlimited three dimensional network lacking symmetry and periodicity. (Compare the discussion of SiO_2 in my original article.)

I do believe that Hägg's condition is too general, and that he will find it necessary to impose additional conditions which will reduce his theory to mine of two years ago.

Hägg's statement in the summary: "The glass-forming tendency . . . seems to be especially large when the corresponding crystals contain radicals or molecules unlimited in one or more dimensions" is again too general. It is true, of course, that crystalline SiO_2 contains polymerized molecules unlimited in three dimensions, but so does also crystalline TiO_2 or BeO for example, where there is no tendency to glass formation.