# GLASS

# SCIENCE AND TECHNOLOGY

Edited by

D. R. UHLMANN AND N. J. KREIDL

VOLUME 1

## Glass-Forming Systems

# GLASS: SCIENCE AND TECHNOLOGY

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# GLASS:
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VOLUME 1

Glass-Forming Systems

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# Preface

This volume of the treatise *Glass: Science and Technology* is focused on glass-forming systems and glass-ceramic materials. In addition to the topics of principal concern, specific attention is directed to glass formation, techniques of forming glasses, and glazes and enamels. Detailed information is given on the glass-forming regions in oxide, fused salt, aqueous, and organic systems, as well as on the newly important classes of metal alloy, fluoride, and chalcogenide glasses.

The present volume, designated Volume 1 of the treatise, is the second to appear. The previous one, designated Volume 5, *Elasticity and Strength in Glasses,* was published in 1980. The next two volumes—*Viscous Flow and Relaxation* and *Glass Processing*—are scheduled for publication within the next year.

The editors are saddened to announce the premature death of one of the contributors to the present volume, Dr. Arnold Bondi. Dr. Bondi was an outstanding scientist in the field of organic glasses; his incisive intellect, breadth of knowledge, and warm personality will be sorely missed. To preserve the flavor of his contribution, the editors have effected only minor changes in the manuscript as originally submitted by Dr. Bondi.

# Contents



* Section X, Ionic Salt and Solution Glasses, is by C. A. Angell.

CHAPTER 1

# The Formation of Glasses

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## I. Introduction

At least some glasses have been formed of materials with all types of bonding. These include covalent ($SiO_2$), ionic [$0.4Ca(NO_3)_2$–$0.6KNO_3$], metallic (0.4Fe–0.4Ni–0.14P–0.06B), van der Waals (toluene), and hydrogen ($H_2O$). As discussed in Chapter 2, glasses can be formed using a variety of techniques, including cooling from the liquid state, condensation from the vapor, pressure quenching, solution hydrolysis, anodization, gel formation, and bombardment of crystals by high-energy particles or by




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shock waves. Of these the technique of cooling from the liquid state is by far the most important and most widely used. As such, it will be the exclusive focus of the present chapter. For treatments of glass formation by other techniques, see Gutzow and Avramov (1977).

The formation of glasses requires cooling to a sufficiently low temperature—below the glass transition—without the occurrence of detectable crystallization. In treating this phenomenon it has been suggested by some authors that specific structural features or properties of the materials will result in glasses being formed. This has led to classifications of materials as glass formers or non–glass formers, where reference is implicitly made to cooling bulk samples at reasonable rates. By others it has been suggested that the critical factor in glass formation is the rate of cooling relative to the kinetics of crystallization. This directs attention to kinetic characteristics of the materials and suggests that nearly all liquids will form glasses if cooled rapidly and will crystallize if cooled slowly.

On this basis the various models that have been advanced to describe glass formation can be grouped into three categories, depending on the factors that are viewed as decisive in the formation of glasses. These categories are (1) structural, (2) thermodynamic, and (3) kinetic. It will be seen, however, that the distinctions among the groups are often rather nebulous, since the structural and thermodynamic models often have related kinetic considerations, and the kinetic models often utilize structural and thermodynamic concepts.

In discussing the principal models for glass formation, kinetic treatments will be considered in greatest detail. Such treatments are preferred because of their potential for providing quantitative predictions of glass-forming behavior and because glass formation is essentially a kinetic phenomenon.

## A. Structural Models

Perhaps the best known model of glass formation is that due to Zachariasen (1932) and Warren (1937, 1941). Speaking of oxides, Zachariasen expressed the "ultimate condition" for the information of glasses as follows: "the substance can form extended three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network." This led to the formulation of his celebrated rules for glass formation, according to which an oxide glass will be formed

> (1) if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles; (2) if these tetrahedra or triangles share only corners with each other, and (3) if

some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations.

The requirement that the network be three-dimensional led to an additional rule:

(4) at least three corners in each oxygen polyhedron must be shared.

The structural implications of this *random network model* led to the classification of cations as network formers, network modifiers, and intermediates; and a sizable literature developed around descriptions of the network-forming or network-modifying character of various cations. This approach is summarized well by Stevels (1957); and the classification of various cations is given in Table I.

The structural model of a random network received support from x-ray diffraction studies of a variety of glasses, although these studies did not establish the model as a unique representation of structure. More recent

TABLE I

CLASSIFICATION OF CATIONS AS NETWORK FORMERS, NETWORK MODIFIERS, AND INTERMEDIATES[a]

| | | | |
|---|---|---|---|
| Glass formers: | B | Modifiers: | Sc |
| | Si | | La |
| | Ge | | Y |
| | Al | | Sn |
| | B | | Ga |
| | P | | In |
| | V | | Th |
| | As | | Pb |
| | Sb | | Mg |
| | Zr | | Li |
| Intermediates: | Ti | | Pb |
| | Zn | | Zn |
| | Pb | | Ba |
| | Al | | Ca |
| | Th | | Sr |
| | Be | | Cd |
| | Zr | | Na |
| | Cd | | Cd |
| | | | K |
| | | | Rb |
| | | | Hg |
| | | | Cs |

[a] After Kingery *et al.* (1976).

diffraction work on a variety of oxide glasses has provided effective support for this model [see Mozzi and Warren (1969), Porai-Koshits (1977), Milner and Wright (1980)]. As noted by Uhlmann (1980), however, the random network may consist of randomly organized structural units larger than the basic oxygen polyhedra (e.g., a random network of boroxyl units rather than $BO_3$ triangles in the case of glassy $B_2O_3$). Further constraints on the use of the random network model to describe glass structure and glass formation have been provided by the widespread occurrence of liquid–liquid phase separation [see reviews by Vogel (1977) and by Uhlmann and Kolbeck (1976)]. Such phase separation results in the glasses consisting of two or more phases and imposes constraints on the use of the random network model that go beyond those recognized by Zachariasen (1932). It seems likely that the structures of the individual amorphous phases in multiphase glasses may be describable by a random network model, although this point remains to be established in detail.

The random network model has also been generalized as a *random array* picture in which the structural elements are randomly arranged and in which no unit of the structure is repeated at regular intervals in three dimensions. In this form it has been used with considerable success in describing the structures of a wide variety of glasses, including metal alloys, chalcogenides, and polymers [see Chaudhari and Turnbull (1978); Uhlmann (1980)].

The utility of the random network or random array models for representing the structures of various glasses will be discussed at length in the volume of this treatise on glass formation. Our present concern, however, is directed not at the structural implications of these models, but at their descriptions of glass formation. In this regard, the original paper of Zachariasen (1932) presented a brief rationale: "Glasses which do not devitrify very rapidly will have an energy only slightly greater than that of the (corresponding) crystal." The justification for the model as an approach to glass formation is then related to a kinetic parameter, the driving force for crystallization. Materials with small differences in energy between liquid and crystal will, at a given undercooling, have smaller driving forces for crystallization than those with large differences in energy. Although Zachariasen also mentioned the mobility ("In melts where there are highly associated groups . . . the viscosity will be high"), no use was made of this factor.

As a general approach to glass formation, the criterion of a small energy difference between liquid and crystal is inadequate. As noted by Morey (1934), the assumption of a small energy difference "is, as far as the writer is aware, without experimental foundation." Examples of good oxide glass formers with large energy differences include $B_2O_3$ and $K_2O \cdot 3SiO_2$. Since there is no simple correlation between energy difference (or heat of

fusion) and glass-forming ability, the model cannot be used to describe the relative ease of forming different materials as glasses.

Other structural models have directed attention to structural units (coordination polyhedra) that are nearly regular but are not space filling. Notable among these are the pentagonal dodecahedral models of Tilton (1957) and Robinson (1965) and the models for simple liquids of Frank (1952), Bernal (1960), and Bagley (1965). All of these models suggest the importance in liquids of structural elements that exhibit fivefold symmetry. Such structural elements are expected to correlate with resistance of the liquids to crystallization, both because of the large number of configurations possible by combining different types of polyhedra and because of the change in topology required for the formation of crystalline arrays. Although such models thus direct attention to important characteristics of liquids and glasses, they provide little insight into the relative ease of forming different materials as glasses.

## B. Thermodynamic Models

The importance of thermodynamic factors in viscous flow and glass formation has been most strongly stated by Gibbs and DiMarzio (1959) and by Adam and Gibbs (1965), who associated the decrease in molecular mobility with falling temperature of liquids with a decrease in their configurational entropy. The configurational entropy was suggested to vanish at a finite temperature, designated $T_2$; and the occurrence of the glass transition at a somewhat higher temperature (about 50°C above $T_2$ for most organic liquids) reflects an approach of the system toward the state of zero configurational entropy, with a limited number of available configurations and large changes in topology required for transitions from one configuration to another.

The relatively small configurational entropy at the glass transition had previously been noted by Kauzmann (1948), who pointed out the paradoxical situation of an amorphous phase with a smaller entropy than its corresponding crystal, which would result if the heat capacity of the equilibrium liquid continues unchanged over a range of temperature below the observed glass transition. A striking example of this paradox is provided by data on lithium acetate (Fig. 1). As shown in the figure, some 90% of the entropy of fusion has been lost from the liquid when the glass transition temperature $T_g$ is reached. If the glass transition did not occur, extrapolation of the equilibrium liquid heat capacity over only 15–20°C would produce an amorphous phase with the same entropy as the crystal. Even if the equilibrium heat capacity begins to decrease at temperatures only a few degrees below the glass transition, the decrease would have to be quite sharp to avoid the paradoxical situation.

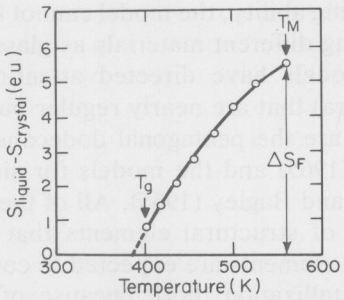


FIG. 1. Entropy difference between liquid and crystal for lithium acetate. (After Wong and Angell, 1977.)

Although the residual entropy difference at the glass transition for most glasses is comparable to the entropy of fusion of metals or $SiO_2$, and hence is by no means insignificant, the problem posed by Kauzmann remains significant. Kauzmann attempted to avoid the problem by suggesting that the amorphous state of zero configurational entropy would never be reached (even with infinitely slow cooling) because transition to a fine-grained crystalline state would become more likely than continued relaxation to amorphous states of progressively lower energy. Cohen and Turnbull (1964) alternatively suggested that the glassy state is metastable rather than unstable, and hence should have zero entropy at 0 K. For this to be true

> each microscopic structural unit of the glass must lie at a position of static equilibrium, the totality of which is randomly distributed. If one such structure exists there must be a large number of similar random structures of equal energy. Nevertheless, the entropy of each is zero, because all these structures are mutually inaccessible.

As a model of glass formation, the views of Gibbs and his co-workers lead to the expectation of the glass transition as a universal feature of liquid behavior, provided crystallization does not occur. It has been used with success to predict the glass transition temperatures of copolymers of varying chain stiffness and leads to predicted viscosity–temperature relations of the Williams–Landel–Ferry (1955) form in the region around the glass transition. The approach provides little insight, however, into the relative glass-forming abilities of different materials; and data on the flow behavior of a variety of liquids indicate a variety of temperature dependences as the glass transition is approached (Cukierman *et al.*, 1973).

A recent extension of the free volume model by Grest and Cohen (1980) considers liquids to be composed of solidlike cells and liquidlike cells,

with the kinetic behavior being dominated by the latter. The model reduces to the familiar free volume form at high temperatures, where it closely describes the flow behavior of a wide variety of liquids; but unlike the simple free volume model, it also describes the observed behavior in the low-temperature region as the glass transition is approached. This model suggests the occurrence of a thermodynamic first-order transition below $T_g$, in contrast to the second-order transition suggested by Gibbs and his co-workers. This aspect of the model remains, however, subject to some question; and the model does not predict the relative ease of forming different materials as glasses.

Energetic bases for the distinction between network-forming and network-modifying cations have been suggested by several authors. Dietzel (1948) proposed that the field strength $z/a^2$ is the critical parameter. Here $z$ is the charge on the cation in electron units and $a$ is the distance in angstroms between the ion centers. On this basis, cations with field strengths greater than 1.3 are regarded as network formers, whereas those with field strengths smaller than 0.5 are considered network modifiers. Exceptions to this classification scheme were suggested for cases where symmetric configurations are formed.

An alternative classification, based on single bond strength (the dissociation energy of the oxide divided by the coordination number), was advanced by Sun and Huggins (1947). On this basis, cations with single bond strengths greater than 80 kcal/mole were suggested to be network formers, whereas those with bond strengths less than 35 kcal/mole were classified as network modifiers. A third approach to classifying cations based on electronegativity was suggested by Stanworth (1946). On this basis, network formers are suggested to have electronegativities between 1.8 eV and 2.2 eV, whereas network modifiers have electronegativities less than 1 eV.

All of these approaches group the important network-forming and network-modifying cations in the appropriate categories. As noted by Stevels (1957), however, the relative rankings within each category differ with the classification scheme employed. Further, all three approaches rank certain ions (e.g., $As^{5+}$ and $Sb^{5+}$) as good glass formers, whose oxides are in fact very difficult to prepare as glasses. The utility of the methods in describing glass formation is restricted to the rather limited class of glasses to which they refer (oxides) and by their lack of reliability in predicting the relative glass-forming abilities of different materials. For detailed criticisms of the three approaches, see Weyl and Marboe (1962).

Other approaches, based primarily on kinetic considerations, have directed attention to thermodynamic quantities such as the melting point and boiling point. These are discussed in Sections III and IV. Since the kinetic models discuss glass formation in terms of the avoidance of