Glass

Horst Scholze

Glass

Nature, Structure, and Properties

With 168 Figures

Translated by Michael J. Lakin

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Preface to the English Edition

When it was learned that Professor Scholze was revising his classic work on the nature, structure, and properties of glass, it was natural to conceive the idea of translating the new edition into English. Professor Scholze enthusiastically endorsed this suggestion and asked for the concurrence of his publisher, Springer-Verlag. Springer-Verlag welcomed the idea and readily agreed to provide support. With the essential agreements in place, Professor Michael Lakin, Professor of German at Alfred University, was asked to do the translation, and I subsequently agreed to work with Professor Lakin to check for technical accuracy. I was happy to accept this task because of my respect for Professor Scholze and because of the value to glass scientists and engineers of having available an English edition of *Glas*.

Professor Scholze died before publication of this English edition of his work. However, he had reviewed the entire English text and had approved it. Professor Lakin and I appreciated the confidence he placed in us, and we were gratified with his acceptance of our efforts. His scientific contributions were numerous and important; they will long serve as guideposts for research in many key areas. We hope this translation of *Glas* will help make his legacy accessible to more people.

Professor Lakin and I have tried to provide a translation that is accurate and true to the original but that has a distinctive English "flavor"; that is, it is not just a literal translation.

Professor Scholze's book *Glas* has long been a valuable reference work for engineers and scientists concerned with making, researching, or using glass. The English-language edition will widen the readership and represents a significant addition to information about glass that is available in English.

The support of Professor Scholze, Professor Pye, the Institute for Glass Science and Engineering at the New York State College of Ceramics at Alfred University, and Springer-Verlag is gratefully acknowledged.

Alfred, New York, July 1990 JAMES R. VARNER

Preface to the Third (German) Edition

The author would like to thank those who have read and utilized his work for their kind reception not only of the first but also of the second (German) edition of this book. He is also grateful that, by and large, the difficult choices he had to make among fundamental principles to be included, as well as applied properties, methods of measurement, and works cited, have been well received. As mentioned in the preface to the first (German) edition, the goal of this book is to contribute to the understanding of glass and its properties through a clear, that is, simple, and thus, in part, simplified description. The presentation of data and the references to methods should facilitate practical work with glass. A relatively complete bibliography points the way to sources providing more depth; special thanks are due to the publisher for allowing this thoroughness. Nonetheless, it was necessary to leave out many citations used in the first two (German) editions. These were replaced principally with those citations that can offer essential results or from which one can learn still more. Appropriate comments and a comprehensive subject index serve to provide cross connections within the book.

In the last 10 years, since the appearance of the second (German) edition, the number of publications about glass has increased considerably, and significant progress has been made in understanding glass and its applications. The author hopes his readership will understand if he has failed to cite or include some of the newer studies; choices had to be made in order to remain within the framework of one volume. As ever, the emphasis is on the behavior of the customary glasses, but an attempt has been made in the section on special glass structures to deal with new types of glass. Modern developments with some optical and chemical properties are also discussed in particular detail. New sections treat the fundamental principles of glass surfaces and nonconventional production using the sol–gel process.

Thus, the author hopes that he has succeeded in accommodating this volume to the current state of knowledge in the area. As far as possible, literature up to the end of 1987 was considered. After consultation with the publisher, the tried and tested units % by wt and mole % were retained.

Finally, the author would like to thank the publisher for consistently being open to his ideas. He would also like to thank the Fraunhofer Society for enabling him to continue to work on this volume in his former workplace. A special word of thanks goes to his wife, without whose critical, competent, and untiring assistance this work would not have been possible.

Würzburg, FRG, July 1988 HORST SCHOLZE

Preface to the First (German) Edition

Glass is a material with a theoretically unlimited variety of possible compositions. Thus, its properties are also very variable, a fact that has opened up many areas of application to glass and that is continually opening up new ones. The number of publications about glass, moreover, is likewise large, and the points of view with regard to certain problems are not always in agreement. For this reason, numerous significant difficulties exist both for the person who would like to acquire a thorough familiarity with this field and for the outsider who desires a brief overview. To help meet these difficulties is the goal of this volume. In the planning stages, however, it soon became clear that a unified picture within the limited framework of this kind of book can be obtained only through restricting ourselves to fundamentals. Thus, it was necessary to deal with only the most important components and, in some sections, when comprehension was an issue, to engage in simplifications, even though our knowledge has brought new complexities. In some other sections, however, the text goes beyond the fundamentals in order to show how interesting glass is and where problems remain unsolved.

With this volume the author would like to speak not only to present and aspiring specialists in glass; he also hopes that it might help scientists and specialists in other areas come in closer contact with glass, its properties and its peculiarities.

Berlin, FRG, December 1964 HORST SCHOLZE

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1
Introduction

Over the course of time, the concept "glass" has had various meanings. It can signify a certain condition of a substance (vitreous), a material (e.g., window glass), or an object (e.g., a wine glass). Thus, it is quite understandable that many definitions are found in print which to some extent differ greatly from one another. (The commonly used terms found in the German language are standardized [1145]. Additional help is provided by a dictionary published by the International Commission on Glass [435].) Practical considerations come into play as well. Scientists are satisfied if they can just obtain trace amounts in vitreous form, while glass makers designate a substance as glass-forming only when they are successful in making larger pieces of it in vitreous form. The next chapter will thus begin with questions of definition arising from such problems.

The art of glassmaking is 5,000 years old, but even before then natural glass, obsidian, was used in the production of tools. The interesting and richly varied history of glass can only be touched on here. Most likely it was by accident that humans first made glass. But soon this new material was being manipulated with great creative skill, resulting in the first glass serving chiefly as valuable decorative jewelry. Then came the use of glass as a vessel, for which the glass was predominantly fritted and then, in a molten, viscous condition, formed around a core. This technique thus had great similarity with that of ceramics. Working the glass in a more liquid condition probably failed because of the lack of a crucible material that was sufficiently durable. The composition of the old Egyptian glasses is known to us not only from analyses, but also from the cuneiform tablets from the library of the Assurbanipal: 70 wt % SiO_2 (with some Al_2O_3), 10 wt % CaO (with some MgO), and 20 wt % Na_2O (with some K_2O). The first glasses were therefore sodium glasses. For the soda that was necessary, the Egyptians had a production monopoly which later went to Venice via the Romans. The first decisive change in glass production was the invention of the glass blower's pipe, which probably occurred in the first century B.C. Better crucible material now allowed the glass to be heated higher and then blown; this created for glass its own technology, a technology which underwent scarcely any change for 2,000 years. The

Romans developed it to a high art and then took it to central Europe, where in the third century A.D., in the area around Cologne, it enjoyed a great flowering. In the time that followed, the production of glass for daily use was emphasized. Instead of sodium carbonate, potash, derived from wood, was used as the alkali raw material, and thus a transition was made to potassium glasses, which were given a greenish hue chiefly through noticeable amounts of iron and which became known as forest glasses. Not until the 15th century was colorless glass produced again. The development of crystal glass emanated from Bohemia, while England was the place of origin of lead crystal glass, which was prized for its high brilliance.

The second turning point in the history of glass was the introduction of machine production of glass at the beginning of this century. For machine processing, no essential change was needed in the composition of the glasses. With about (in percentage by weight) $73SiO_2$, $1Al_2O_3$, $11CaO$ $(+MgO)$, $14Na_2O$, and $1K_2O$, it did not differ greatly from the Egyptian glass. Many new glasses were developed, of which those chemically and thermally resistant glasses containing B_2O_3, as well as vitreous silica, were probably the best known. (Vitreous silica is often called quartz glass, but has only the chemical composition—SiO_2—in common with quartz.) The development of optical glasses contributed numerous other components as ingredients of glass. More recently, theoretical interest led to the production of nonoxide glasses based, for example, on fluoride or sulfide (ZrF_4 or As_2S_3), and of metallic glasses, which likewise have already been put to use in industry. But there are many additional glasses of unusual composition which often have purely scientific interest. Some of these will be discussed later. In the past, the exact composition of the batches was kept strictly secret. Not until about the end of the 19th century, with the rapidly growing development of science and technology, did the fundamentals of glass production become better known. Soon intensive investigations began which aimed to establish the connections between composition and properties of glasses. These were followed by attempts to understand these connections on the basis of the structure of glass.

During the last several decades, much has been accomplished in the area of glass research. The main features of this work will be summarized here. These will generally suffice in order to understand the special behavior and the properties of glasses. Further study can be facilitated by a number of monographs and surveys by, among others, Doremus [196], Eitel [224], Jebsen-Marwedel and Brückner [457], Hinz [406], Jones [463], Navarro [654], Paul [685], Pye et al. [744], Rawson [762], Vogel [1025], Volf [1034], Weyl and Marboe [1061], and Zarzycki [1116]. Moreover, there are book series in which experts have written special chapters, edited, for example, by Tomozawa and Doremus [982] or Uhlmann and Kreidl [1004]. Finally, technical journals and numerous books have been published which contain papers from conferences.

2
Nature and Structure of Glass

It is a goal of science to make conclusions about the structure and properties of a glass from its composition. In this connection, noteworthy successes have been achieved which will be summarized in this chapter. But there are still many unanswered questions, chiefly because with glass there are many additional influences to consider. At times, therefore, not only will the structure of glass be discussed, but also in a more general way its very nature.

2.1 DEFINITION OF GLASS

The different views about the concept of glass have led, unfortunately, to some misunderstandings. Thus, in order to highlight some essential fundamentals, the question of definition will be dealt with here. Later some refinements of these observations will be put forth. Not all the suggestions in the literature can be explored in this chapter; in any case, they differ from each other in part only in nuances. The quest for a general definition is a worldwide activity. It is gratifying that opinions in recent years have been coming into closer agreement.

The general *linguistic usage* of the word *glass* has changed over the course of centuries. Differences are found even in the scientific literature, but these rest more on different ways of looking at things. From this considerable material, only a few typical passages will be mentioned. For example, one of the pioneers of glass research, Tammann [950], begins his book, *Der Glaszustand* (*The Glassy State*) with this sentence:

In the glassy state, there are solid, uncrystallized materials.

This definition, however, is too general, for, according to it, silica gel, for example, would be a glass. Numerous other definitions tend to place most emphasis on *viscosity behavior*. We shall soon return to this point.

These definitions do not limit the *composition* of glass. Another group of definitions comes from authors who are closer to technology. As an example, the definition from 1945 of the American Society for Testing and Materials can be mentioned:

Glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing.

This was accepted into the German Standard [1145], mentioned at the outset, as follows: "Glas ist ein anorganisches Schmelzprodukt, das im wesentlichen ohne Kristallisation erstarrt."

Thus, glass is restricted to inorganic products, which in this general form is questionable. The American definition, however, contains some other remarks which, among other things, also maintain that objects made of glass are designated simply as glass, for example, a wine glass or a magnifying glass.

If the word *glass* is going to be defined, then these concepts should also be included. Within a brief definition, of course—and a definition should be brief—that is not possible; for here very different meanings of the word *glass* are found. In a brief definition, for this reason, one must be able to infer from or to see within the definition just which meaning of glass is meant. The example just given shows that in general usage glass can be understood as a piece to be worked. This definition does not concern us here. However, an essential distinction which occurs with the foregoing definitions (the consideration of the composition) leads back to different meanings of the concept "glass," in which glass is conceived of on the one hand as a physicochemical condition, and on the other as a technical material.

In the context of this book, what distinguishes glass *physicochemically* is of special interest. That can be most easily explained as one follows the technological process of glass production and, in doing so, observes the behavior of a particular property. This should be begun at high temperatures, where a glass melt, that is, a liquid, is present; here the volume should be investigated. In Fig. 1, the relationships are presented schematically. In general, when a liquid or a melt cools, its volume decreases. Normally, crystallization occurs at the melting point T_m, whereby a decrease in volume ensues. As the temperature continues to fall, the volume decreases further, but now with a lower temperature coefficient, that is, the expansion coefficient of the crystal is less than that of the liquid.

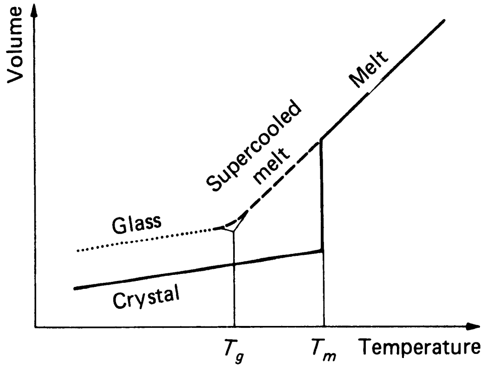


FIGURE 1. Schematic diagram of the temperature dependence of volume.

The complete, solid curve of Fig. 1 corresponds to conditions of thermodynamic equilibrium. When no crystallization occurs at T_m, then the volume continues to decrease continuously along the dashed equilibrium curve. This area of *supercooled melt* or *liquid* is thus still in—albeit metastable—thermodynamic equilibrium.

The metastable equilibrium curve does not proceed with decreasing temperature indefinitely; rather, at a certain temperature one observes that the curve deviates and from that point runs more or less parallel to that of the crystal. From here on, conditions of equilibrium are no longer evident. The cause of the deviation lies in the increasing viscosity of liquids on cooling (see section 2.4.1). In this way, the attainment of equilibrium of the liquid structure corresponding to every temperature occurs increasingly slowly, until finally the viscosity has become so high that with continual cooling the reaching of equilibrium is no longer possible. At this point, the liquid has become a solid. It follows from this consideration that this occurs independent of the composition at a uniform viscosity, namely at about 10^{13} dPa s (= poise).

It has become common to designate the temperature corresponding to this viscosity as the *transformation temperature* T_g. Since, however, the transition continually ensues, it is better to speak of a transformation range. Even more appropriately, Simon [894] calls this phenomenon the *freezing-in process*. If we still want to characterize the intent of the definition, then we have:

In the physicochemical sense, glass is a frozen-in undercooled liquid.

More recent developments of natural science have shown that the boundaries between different areas are increasingly disappearing. That is also true for glass. Thus, it is not justified on the basis of borderline cases to cast doubt on an otherwise valid definition. Rather it is desirable—at least in scientific language—that one clearly distinguishes between glass as a solid (below T_g) and as a melt (above T_g).

2.2 NETWORK HYPOTHESES

The definition introduced above begins to imply conclusions about the structure of glass. If one starts from the principle that liquids have an unordered structure, then this must also be true for glass as a frozen-in liquid. On this basis, several hypotheses—with some variations and amplifications—have been developed about the structure of glass and the conditions for the formation of glass. These are designated as hypotheses because so far it has not been possible to adduce proof. The most productive ideas have been developed by Zachariasen [1107, 1108]. They should be introduced here at the outset in order to provide the foundation for the understanding of the chapters to follow. Additional hypotheses will be explored later (see section 2.5.4).

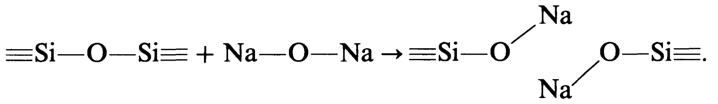
The beginnings of the network hypothesis go back to V.M. Goldschmidt. The point of departure for Zachariasen was the finding that the energy differences between glass and crystal of the same composition are very small, and therefore that in the glass the same states of bonding or units of structure must occur as in the crystal, in silicates for example the $[SiO_y]$-tetrahedron (see section 2.5.3). Whereas in the crystal these tetrahedrons are arranged regularly, in the glass they form a *random network.* On the basis of his reflections about what types of bonding are likewise able to form a network, Zachariasen formulated the following four conditions for the formation of oxide glasses:

(a) The coordination number of the cation must be small.
(b) An oxygen ion may not be linked to more than two cations.
(c) The oxygen polyhedrons may share only corners, not edges or faces.
(d) At least three corners of every oxygen polyhedron must be shared by other polyhedrons.

These conditions are fulfilled by the oxides of the type R_2O_3, RO_2, and R_2O_5, which is confirmed through the occurrence in vitreous form of, for example, B_2O_3, As_2O_3, SiO_2, GeO_2, and P_2O_5.

As will be shown later in more detail (see section 2.5.2), this hypothesis enabled Warren [1043] to interpret his X-ray patterns of glasses quite well, which is why today one often speaks of the network hypothesis of Zachariasen–Warren. With it, it was possible to explain many properties of glasses rather well. Figure 2 shows schematically the structure of an ordered SiO_2 network, which contrasts with the structure of the unordered network of vitreous silica, as seen in Fig. 3.

The foregoing examples involve only glasses made from one oxide. The formation of glass, however, is also possible with systems with several components, for example, in the binary systems $R_2O—SiO_2$ (with R = alkali). The *influence of an alkali oxide* can easily be recognized if the small region $\equiv$Si—O—Si$\equiv$ is extracted and Na_2O is added to it:



$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{Na{-}O{-}Na} \rightarrow \equiv\mathrm{Si{-}O}^{\diagup\mathrm{Na}} \qquad {}_{\mathrm{Na}\diagup}\mathrm{O{-}Si}\equiv .$$

Accordingly, the introduction of Na_2O has as a consequence a significant change in the glass structure. In pure SiO_2 glass, all the O^{2-} ions are bound to two Si^{4+} ions. Since the O^{2-} ions represent bridges between neighboring Si^{4+} ions, they are also called *bridging oxygens.* The incorporation of the Na_2O bursts open the closed connection. Neighboring Si^{4+} ions are formed, for each of which a singly bound O^{2-} ion is found, so that no direct bond among one another is present any longer. Because of the *broken bridges* which thus occur, these singly bound O^{2-} ions are designated as *nonbridging oxygens.* Each Na^+ ion that is introduced produces a nonbridging oxygen.

In the case of these glasses, whenever the condition of the three-dimensional network must be fulfilled, the limit of the formation of glass is reached when

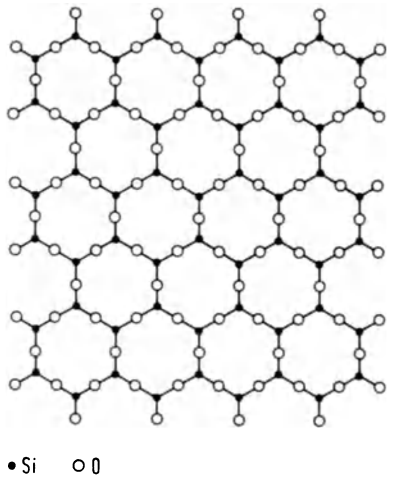


FIGURE 2. Two-dimensional diagram of an ordered SiO_2 network. (The fourth bonds of the Si project upward or downward from the plane of the illustration.)

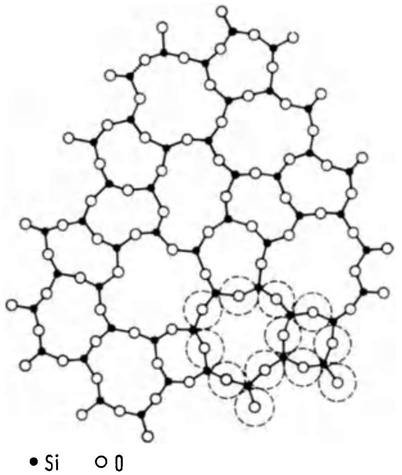


FIGURE 3. Two-dimensional diagram of a random SiO_2 network. (The fourth bonds of the Si project upward or downward from the plane of the illustration; the actual relative surface area requirement of the oxygens is indicated by dashed lines on the lower right.)

every $[SiO_4]$ tetrahedron is shared only at three corners, that is, the composition $R_2O \cdot 2SiO_2$. At even higher R_2O content, the three-dimensional network splits up in order to break down into (theoretically) infinitely long chains at the composition $R_2O \cdot SiO_2$. Since, however, it is unlikely that the connection of the tetrahedrons is perfectly uniform, the chains will also be crosslinked among each other, so that formation of glass is still possible up to the composition $R_2O \cdot SiO_2$, assuming that no other conditions work against it. At still higher alkali content, the chains continue to split up, until finally, at the compound $2R_2O \cdot SiO_2$, isolated tetrahedrons are present which no longer have any connection across Si—O—Si bridges. At this point no more glass formation occurs.

Thus, the basis of glass formation is the network, which in the example just given is formed by the $[SiO_4]$ tetrahedrons. The cations which form this kind of network-building polyhedron are thus called *network formers*, while the cations which break down or transform the network are called *network modifiers*. Network formers include Si, Ge, B, As, and P; network modifiers include the alkalis and alkaline earths. As a supplement to the unordered network, Zachariasen and Warren assume a *random distribution* of network modifiers in glass structure. The limits of this assumption will be discussed in a later section (2.5.5).

Zachariasen's hypothesis has been the foundation of many successful interpretations and experiments. Nonetheless, this hypothesis is quite specific, since it proceeds from the standpoint only of crystal chemistry and thus does not consider—at least not directly—chemical bonding relationships. In addition, since the assertion of this hypothesis, numerous glasses have been found which cannot be explained in this way. We shall return to this topic in a later section (2.5.4). Thus, for example, the $PbO—SiO_2$ glasses with PbO content up to 90% by wt. (corresponds to ca. 70 mole %) assume a special place; for, in order to explain them, one was forced to assign to the Pb^{2+} ion the status of a network former with the coordination number 4. Zachariasen's hypothesis has not been rendered invalid by these new findings; rather, it must be appropriately expanded.

2.3 STRUCTURE OF THE MELT

One can expect further insights concerning the structure of glass when one turns directly to the structure of the melt, from which, through Freezing-in, the glass arises. Thoughts along these lines were first expressed several decades ago by glass researchers who, above all, tried to evaluate the behavior of viscosity of glass melts. Then metallurgists turned to this problem in order to better understand the influence of slags; Turkdogan [993] has summarized these findings. Finally, in more recent years, geophysicists and geochemists have taken an interest in this theme for a better understanding of natural magma and its behavior; surveys on this subject have been done, for example, by Mysen et al. [646] and by Richet and Bottinga [772].

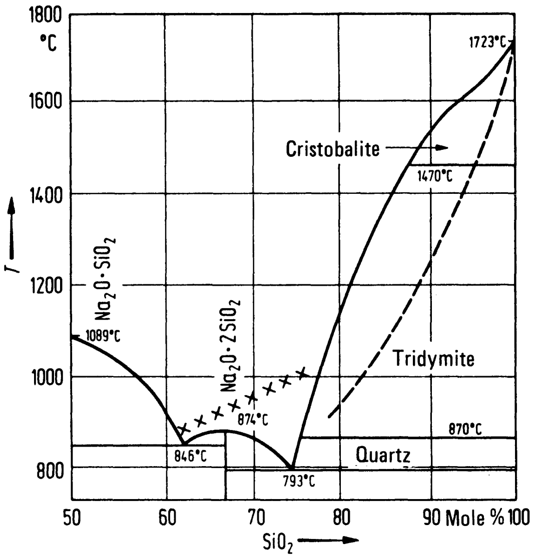
Measurements in or on melts, because of the necessarily high temperatures, usually have met with experimental difficulties, which accounts for the fact that often only a limited precision can be attained. Since, moreover, knowledge about the structure of simple liquids is still relatively meager, it is understandable that so far only a small amount of certain knowledge about the structure of glass melts has appeared. The following sections indicate some results and some unresolved problems.

2.3.1 Evaluation of Phase Diagrams: Activities

Melts are thermodynamically stable only above the melting temperature when there is one compound or above the liquidus temperature in systems with two or more components. It is thus appropriate to turn first of all to the corresponding phase diagrams. It will be assumed here that the fundamentals of phase diagrams as well of thermodynamics are known. In any case, they can be easily looked up in textbooks on the subject. Additional practical information is provided in a series on phase diagrams edited by Alper [74].

Figure 4 offers the SiO_2-rich part of the phase diagram $Na_2O—SiO_2$. It should be clear that in addition to SiO_2 the two crystalline phases sodium disilicate $Na_2O \cdot 2SiO_2$ and sodium metasilicate $Na_2O \cdot SiO_2$ appear, of which

FIGURE 4. The system Na_2O—SiO_2, from Kracek [505, 506] (× = points of equal viscosity $\log \eta = 3.6$).



the latter, at 1089° C, has a significantly higher melting point than the disilicate. Dietzel [177] concludes from this that the presence of structural elements of the metasilicate is especially favored in the melt, because a higher melting point of a compound also indicates a great stability in the melt. This is not correct in all cases, but as yet there is not sufficient information to prove Dietzel s simple and plausible hypothesis.

At this point, the well-known phenomenon of the *depression of the melting point* should be mentioned, according to which the melting point of a substance A is lowered by the addition of another substance B. If in such a mixture the content of A is expressed by the mole fraction x_A, then in ideal solutions its liquidus temperature T_l is expressed thus:

$$\ln x_A = \frac{Q_m}{R}\left(\frac{1}{T_m} - \frac{1}{T_l}\right). \tag{1}$$

(If in the mixture there are n_A moles A and n_B moles B, then the mole fraction x_A is defined as $n_A/(n_A + n_B) = x_A = 1/100$ mole % A.)

In Eq. (1), R represents the gas constant, T_m the melting temperature, and Q_m the heat of melting of the pure substance A, whereby Q_m is assumed to be independent of temperature. Rearranging to solve for T_l gives

$$T_l = \frac{1}{(1/T_m) - (R \cdot \ln x_A/Q_m)}.$$

With the addition of component B, that is, with decreasing x_A, T_l becomes smaller and smaller, and the more decided this is, the smaller Q_m is.

Let Eq. (1) now be applied to the binary system Na_2O—SiO_2. The heat of melting Q_{SiO_2} needed to consider the SiO_2-rich side amounts to about 6 kJ/mole. The melting points calculated with this value are given by Fig. 4 as a dashed curve. It is clear that only in the immediate vicinity of the pure component SiO_2 is there good agreement between the experimental and the calculated liquidus curve; then, however, deviations soon occur.

The reason for the poor agreement between theory and experiment lies first of all in the fact that in the theoretical derivation of Eq. (1) simplifications were introduced and, secondly, in the fact that ideal behavior of the mixture was assumed. One of the simplifications was the assumption that the heat of melting Q_m is independent of temperature. If one considers this temperature dependence, however, which is possible to do relatively simply through the specific heat, one does not arrive at any better agreement. One should therefore turn one's attention to the *deviation from ideal behavior.*

One can take into account the actual behavior by retaining Eq. (1) but, instead of using mole fractions, introducing the *activities a* according to

$$a \equiv \gamma x. \tag{2}$$

Now, the deviations become noticeable in the magnitude γ, the activity coefficient. For ideal behavior, $\gamma = 1$. If $\gamma > 1$, then the interaction between different components (e.g., A–B) is less than that between the pure components (e.g., A–A). That finally proceeds to such an extent that with increasing γ, separation in two liquid phases occurs. $\gamma > 1$ is thus a signal for the tendency to separate, while conversely $\gamma < 1$ is a signal for formation of compounds.

From the new equation resulting from Eqs. (1) and (2),

$$\ln a = \frac{Q_m}{R}\left(\frac{1}{T_m} - \frac{1}{T_l}\right), \tag{3}$$

the corresponding values of a for the different liquidus temperatures can be calculated, from which, with the corresponding x values according to Eq. (2), the values of γ emerge. Table 1 thus shows that in the system Na_2O—SiO_2 a tendency to phase separation is present on the SiO_2-rich side.

TABLE 1. Activity coefficients γ_{SiO_2} in the system Na_2O—SiO_2.

Temperature (° C)	Mole fraction x_{SiO_2}	Activity a_{SiO_2}	Activity coefficient γ_{SiO_2}
1,723	1.00	1.00	1.00
1,627	0.94	0.985	1.05
1,527	0.91	0.965	1.06
1,427	0.88	0.943	1.07
1,327	0.85	0.920	1.08
1,227	0.83	0.893	1.08
1,127	0.805	0.864	1.07
1,027	0.785	0.832	1.06
927	0.770	0.795	1.03

In a somewhat different way, Förland uses phase diagrams in order to make statements about the structure of the melt, as reported by Urnes [1007]. In a phase diagram A–B, with some simplifying assumptions for the partial *mixing entropy* $\overline{\Delta S}$ of the emerging components at the liquidus temperature T_l, the following equation results:

$$\overline{\Delta S} = Q_m\left(\frac{1}{T_m} - \frac{1}{T_l}\right). \tag{4}$$

It should be mentioned here that the melting entropy S_m ($= Q_m/T_m$) of SiO_2 with about 4 J/(mole K) is very small, from which one can conclude that no essential structural changes occur during melting. A small melting entropy is also assumed by Förland when small amounts of alkali are added. The structure of the melt is disturbed the least when the two nonbridging oxygens (which arose through the incorporation of R_2O) along with the cations are arranged together in pairs. This structural unit can then be exchanged in the melt for a Si—O—Si unit, which offers the possibility of calculating the above mixing entropy $\overline{\Delta S}$ for SiO_2. In a mixture made from n_1 mole R_2O and n_2 mole SiO_2, there are $2n_2 - n_1$ bridging oxygens and n_1 pairs of nonbridging oxygens. A statistical mixing of these two units, according to the laws of thermodynamics, leads to $\overline{\Delta S_{SiO_2}} = -2R \ln[2n_2/(2n_2 - n_1)]$ or with the mole fraction x of SiO_2 to $\overline{\Delta S_{SiO_2}} = 2R \ln[(3x - 1)/2x]$. If this structural picture is correct, then the plotting of $\ln[(3x - 1)/2x]$ versus $1/T$ must result in a straight line, as the comparison with Eq. (4) indicates immediately. The heat of melting of SiO_2 can be calculated from its slope. Förland and Urnes found a satisfactory agreement with direct measurements in the systems R_2O—SiO_2, with R = Cs or Rb; but in the series R = K, Na, and Li, they found increasing deviations, which they trace back to the presence of clusters of alkali ions and nonbridging oxygens. Thus, it is not certain whether pairs of cations actually occur in the melt. Nonetheless, this is an interesting approach.

Since these approaches must be further developed, it is appropriate to work more closely with the activities, or activity coefficients. They are especially important because with their help the *free mixing enthalpies* ΔG_M can be calculated. Thermodynamics provides the following equation:

$$\Delta G_M = RT(x_1 \ln a_1 + x_2 \ln a_2), \tag{5}$$

in which R is the gas constant = 8.317 J/(mole K) = 1.987 cal/(mole K) and T is the absolute temperature. For an ideal mixture, in which $\gamma = 1$ or $a = x$, it follows that

$$\Delta G_M^{ideal} = RT(x_1 \ln x_1 + x_2 \ln x_2).$$

The difference ΔG_M^E

$$\Delta G_M - \Delta G_M^{ideal} = \Delta G_M^E$$

is designated as an excess or surplus function and gives information about special processes in the melt.

As a supplementary note, it should be mentioned here that the free enthalpy ΔG derives from the fundamental thermodynamic equation

$$\Delta G = \Delta H - T\,\Delta S,$$

in which ΔH is the difference in enthalpy.

For the *calculation* of Eq. (5), the activities of all the components are needed. For the most part, the experiment yields only the activity or the activity coefficient of one component. If the value of component 1 is known, then that of component 2 can be obtained with the help of the equations of Gibbs–Duhem and Duhem–Margules, from which one can derive

$$\ln \gamma_2 = -\int_0^{x_1} \frac{x_1}{x_2}\, d \ln \gamma_1. \tag{6}$$

The theoretically simplest method for determining the activity of a component in a solution is the determination of activity from *vapor pressure measurements* according to $a = P_A/P_{A,0}$, that is, the activity represents the ratio of the partial pressure of A over the solution to the vapor pressure $P_{A,0}$ over the pure phase at the same temperature.

This method was also employed by Charles [130] with the application of velocities of vaporizations of the systems R_2O—SiO_2 after measurements by other authors. First of all, from the phase diagrams he calculated the activity coefficients of SiO_2 for small R_2O concentrations, as described above (e.g., see Table 1). In so doing, one obtains values for various temperatures. The conversion to equal temperatures ensued according to $\ln \gamma_T = (T_l/T) \ln \gamma_{T_l}$, in which T_l represents the corresponding liquidus temperature. The velocities of vaporization led to γ_{R_2O} values in the range $0.2 < x < 0.5$, with which the corresponding γ_{SiO_2} values could also be calculated using Eq. (6). Figure 5 presents these values for the system Na_2O—SiO_2, while Fig. 6 contains the free mixing enthalpies of the alkali-silicate melts. Certain differences can be recognized from which it can be deduced that the tendency for mixing is greatest in the system K_2O—SiO_2, since the greatest negative values of ΔG occur there. The opposite conclusion for the system Li_2O—SiO_2 will be treated later (see section 2.3.3).

The calculations by Charles have been essentially confirmed by Rego et al. [764] by direct vapor pressure measurements. These authors found, for example, for the composition $Na_2O \cdot 2SiO_2$ at 1400° C $\gamma_{Na_2O} \approx 5 \times 10^{-7}$. Similar measurements by Eliezer et al. [226] for the system K_2O—SiO_2 resulted in $\gamma_{K_2O} \approx 10^{-5}$ for the corresponding composition $K_2O \cdot 2SiO_2$ at 1225° C.

For direct determination of activities, measurments of the *electromotive force* (*EMF*) E have proven themselves well suited. One uses the formula

$$E = E^\circ - \frac{RT}{nF} \ln a,$$

in which E° is the EMF of the pure oxide, n is the valence of the ion to be measured, and F is the Faraday constant = 96,487 C/mole.

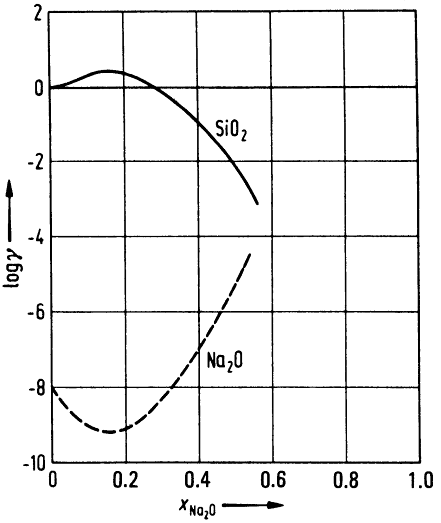


FIGURE 5. Activity coefficients γ of Na_2O and SiO_2 at 1,000° C in $Na_2O—SiO_2$ melts, from Charles [130].

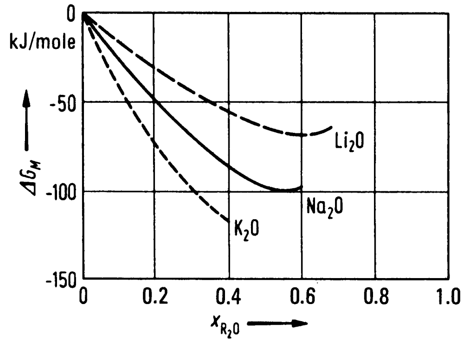


FIGURE 6. Free-mixing enthalpies ΔG_M of binary $R_2O—SiO_2$ melts at 1,000° C, from Charles [130].

The method has been used frequently. Kapoor and Frohberg [472] used it to investigate melts of the system $PbO—B_2O_3$. They use the cell $Pb/PbO + B_2O_3//ZrO_2 + CaO//O_2$, Pt, in which the CaO-stabilized ZrO_2 serves to measure the oxygen-ion activity, which is directly transferable to that of the PbO. The advantage of this system lies in the large accessible region of concentration, which allows the determination of $a_{B_2O_3}$ from a_{PbO} following Eq. (6) to be accomplished quite well. Figure 7 shows these activities; Fig. 8 shows the ΔG_M values determined therefrom. It appears that ΔG_M^E produces negative values, from which a reciprocal action between PbO and B_2O_3 must be concluded. The authors discuss several possibilities, e.g., a change in coordination $[BO_3] \rightleftarrows [BO_4]$ or chain formation, without the data to be able to grasp this in a quantitative way. In the end, it is assumed that the structure of the melt is changing continually with the composition, limited by a breakdown of the network according to $>\!B—O—B\!< + O^{2-} \rightleftarrows (>\!B—O^-)$, without the possibility at this time to express this reaction quantitatively.

Closely connected with the foregoing are similar measurements on molten alkali borates and alkali silicates, e.g., through Shults [883] and his school as well as by Itoh et al. [443]. It is noteworthy that in contrast to the system $PbO—B_2O_3$ the activities of the partner of B_2O_3 again become quite low, namely, according to Itoh et al., for the composition $Na_2O \cdot 2B_2O_3$ at 850° C a_{Na_2O} only $\approx 10^{-10}$. The reason for this has been ascribed to the presence of tetraborate groups in addition to diborate groups.

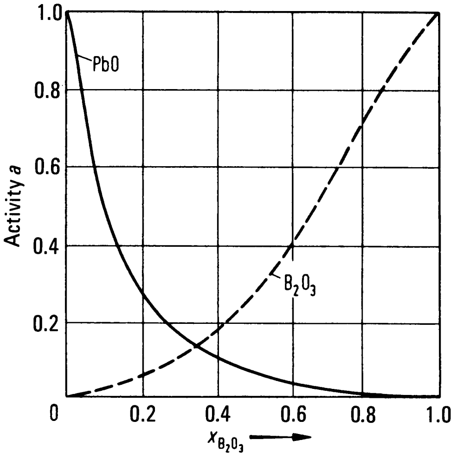


FIGURE 7. Activities of PbO and B_2O_3 at 1,000° C in PbO—B_2O_3 melts, from Kapoor and Frohberg [472].

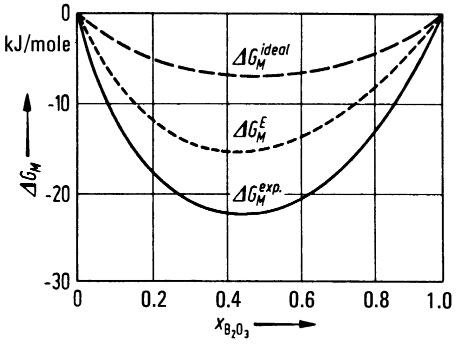


FIGURE 8. Free-mixing enthalpies ΔG_M at 1,000° C in PbO—B_2O_3 melts, from Kapoor and Frohberg [472].

Up to now the systems R_2O— or RO—SiO_2 have been considered binary systems. It is conceivable, however, that in the melt not these oxides but rather *cations* and *anions* will occur. In this way the number of components can change, which likewise causes a change in the mole fraction, which must be calculated using all components present. That can be the cause for the difference between the mole fraction derived from the phase diagram and the calculated activity coefficient. If one assumes ideal behavior of the melt, then deviations occur because other components are present. One can now attempt to vary the type of these components until the calculated and the experimental activity coefficient agree. In this way it might be possible to make assertions from phase diagrams about the components present in the melt.

The point of departure for the consideration that follows is a general derivation of activity according to Temkin [958]. He assumes an ideal mixture of the different cations C and anions A, i.e., the cations C are surrounded in statistical distribution by the anions A, and vice versa. That leads to the following relationship for the activities of the components with the composition $C_i \cdot A_i$, which thus arise from the special cation G_i and the special anion A_i with their mole fractions x_{C_i} and x_{A_i}

$$a_{C_iA_i} = x_{C_i} \cdot x_{A_i}, \tag{7}$$

which can be further solved for the activities of the cations or the anions, for example,

$$a_{A_i} = x_{A_i} = \frac{n_{A_i}}{n_{A_1} + n_{A_2} + n_{A_3} + \cdots + n_{A_n}}. \tag{8}$$

In Eq. (8), the n_{A_i} represent the respective numbers of moles of all the different anions. It is not possible, however, to determine the activities of the ions from thermodynamic measurements, as Förland and Grjotheim [258] clearly point out. They also emphasize that the application of the above relationship always requires the exact definition of the present condition, which one should keep in mind in evaluating the pertinent publications.

With regard to the structures of silicate melts the considerations of Knapp and van Vorst [497] are of some interest. From the system $Na_2O—SiO_2$ (see Fig. 4), they deal with the subsystem $Na_2SiO_3—Na_2Si_2O_5$ and consider it as a new system. If one relates this new system to Na_2SiO_3, then at $x = 1$ (thus, with the pure compound Na_2SiO_3) as well as at $x = 0$ (thus, with $Na_2Si_2O_5$), the slope of the liquidus curve $dT/dx = 0$. This signifies that the compounds in the melt are dissociated. For the simplest case, one can assume the presence of SiO_3^{2-} and $Si_2O_5^{2-}$ anions, so that, following Eq. (8),

$$a_{SiO_3^{2-}} = \frac{n_{SiO_3^{2-}}}{n_{SiO_3^{2-}} + n_{Si_2O_5^{2-}}}.$$

The validity of this relationship can be checked against Eq. (3), which should produce the same values for a. The assumption is that one knows the heat of fusion Q_m. In fact, the agreement of the range $x = 0.3$ to $x = 0.8$ with the known value of $Q_{Na_2SiO_3} = 56$ kJ/mole is very good, which confirms the foregoing assumption of the presence of SiO_3^{2-} and $Si_2O_5^{2-}$ anions.

If this agreement is not reached, then one proceeds as follows: One calculates the a values for different temperatures, using Eq. (3). From the phase diagram one can infer the mole numbers and then insert different anions in Eq. (8), until an agreement of the two a values is obtained. In this way one then obtains information about the type of anions present in the melt.

In the system $PbO—SiO_2$, Richardson and Webb [769] have determined the activities of PbO for different temperatures with another method which is similar to the EMF measurements, namely using the oxygen content of metallic lead, which establishes equilibrium with the melt. These values and those of other authors are shown as zones circles in Fig. 9. In this connection, Flood and Knapp [257] have made further calculations, in which they assumed, starting with pure PbO, that all the added SiO_2 reacts to form the orthosilicate. If n moles PbO and n moles Pb_2SiO_4 are present in the melt, what results is

$$a_{PbO} = \frac{n_{PbO}}{n_{PbO} + n_{Pb_2SiO_4}} = \frac{x_{PbO} - 2x_{SiO_2}}{x_{PbO} - x_{SiO_2}}, \tag{9}$$

whereby the conversion into mole fractions has been performed simultaneously. (The number of moles n_{PbO} on hand results from the mole fraction x_{PbO}, reduced by that portion which is present as orthosilicate Pb_2SiO_4. Since an additional 2 moles PbO are needed per mole SiO_2, it follows that $n_{PbO} = x_{PbO} - 2x_{SiO_2}$. From Fig. 9, it can be inferred that when $x_{PbO} = 0.8$, the value $a_{PbO} = 0.66$, while Eq. (9) yields $a_{PbO} = 0.667$. From the $PbO—SiO_2$ phase

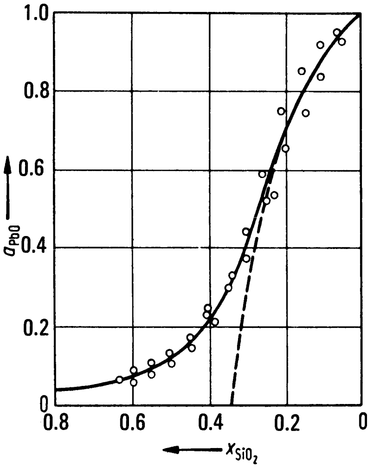


FIGURE 9. Activities a of PbO in PbO—SiO_2 melts at 1,000° C; ○ experimental values of various authors; --- calculated according to Eq. (9); ——— calculated according to Eq. (13) with $k_{11} = 0.196$.

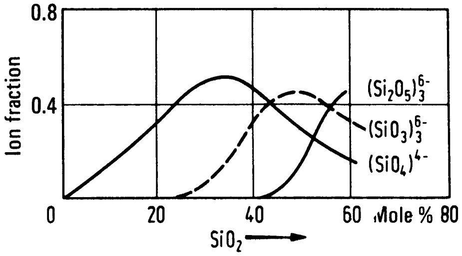


FIGURE 10. Silicate ions present in PbO—SiO_2 melts at 1,100° C, from Flood and Knapp [257].

diagram, one can calculate that with $Q_{m,PbO} = 29$ kJ/mole and $T_{m,PbO} = 1{,}159$ K, for the same composition $a_{PbO} = 0.64$; i.e., in the melt $[SiO_4]$ ions are present, if one considers that this melt is ionically based. The same result would be obtained using the formulation of Temkin with the insertion of the ionic mole fractions.

This good agreement, however, occurs only with SiO_2 content up to 20 mole %. The deviations which then occur show that still other ions are forming at higher SiO_2 content. Flood and Knapp discussed various possibilities and finally obtained the result that is shown in Fig. 10. With increasing SiO_2 content, in addition to the simple $[SiO_4]$ ion, more highly polymerized ions occur in increasing quantities. If, when PbO is introduced, one considers only the O^{2-} ions that are contained therein, then the formation of these other ions may be represented as follows:

$$6SiO_2 + 12O^{2-} \rightarrow 6[SiO_4]^{4-},$$

$$6SiO_2 + 6O^{2-} \rightarrow 2[(SiO_3)_3]^{6-},$$

$$6SiO_2 + 3O^{2-} \rightarrow [(Si_2O_5)_3]^{6-}.$$

The smaller the number of O^{2-} ions on hand, or the lower the basicity of the melt, the greater the *polymerization of the anions*, since, as will be shown later (see section 2.3.4), the concentration of O^{2-} ions is a measure of the basicity of the melt.

Figure 10 also indicates that with higher SiO_2 content several types of ions occur at once. For those compositions for which the compounds corresponding to the anions would be present, i.e., $2PbO \cdot SiO_2$ or $[SiO_4]^{4-}$ with 33.3 mole % SiO_2, with $PbO \cdot SiO_2$ for $[(SiO_3)_3]^{6-}$ with 50 mole % SiO_2, and with $PbO \cdot 2SiO_2$ for $[(Si_2O_5)_3]^{6-}$ with 66.7 mole % SiO_2, only maximums for these anions are present.

The possibility of simultaneous occurrence of anions with different sizes leads to the question of how these are distributed in the melt. The simplest assumption for this is a statistical distribution. Deliberations like these have been made principally by metallurgists on slag systems, which are characterized essentially by a high content of network modifiers, i.e., mostly $x_{SiO_2} < 0.5$. It is assumed in such melts that, in addition to the shared oxygens O° and the nonbridging oxygens O^-, free oxygen ions O^{2-} occur as well, which stand in equilibrium with one another according to the formula

$$2O^- \rightleftarrows O^\circ + O^{2-}.$$

These equilibriums have been looked at from various points of view. Masson [582] has made use of the fundamentals of polymerization of organic molecules. His point of departure is the simple basic equation

$$2[SiO_4]^{4-} \rightleftarrows [Si_2O_7]^{6-} + O^{2-}, \tag{10}$$

which, written differently for the system $PbO—SiO_2$, reads

$$2Pb_2SiO_4 \rightleftarrows Pb_3Si_2O_7 + PbO. \tag{11}$$

The disilicate anion forming according to Eq. (11) can react further according to

$$[SiO_4]^{4-} + [Si_2O_7]^{6-} \rightleftarrows [Si_3O_{10}]^{8-} + O^{2-},$$

or as generally expressed

$$[SiO]^{4-} + [Si_nO_{3n+1}]^{2(n+1)-} \rightleftarrows [Si_{n+1}O_{3n+4}]^{2(n+2)-} + O^{2-}.$$

Equation (11) leads to the equilibrium constant

$$k_{11} = \frac{a_{Pb_3Si_2O_7} \cdot a_{PbO}}{(a_{Pb_2SiO_4})^2}$$

and, with the application of the previously mentioned relationship by Temkin and the assumption that the proportion of the activity coefficients of the anions with the neighboring chain lengths is constant, to the simple relation

$$k_{1n} \cdot \frac{x[SiO_4]^{4-}}{x_{O^{2-}}} = \frac{x[Si_{n+1}O_{3n+4}]^{2(n+2)-}}{x[Si_nO_{3n+1}]^{2(n+1)-}}.$$

Thus, the following dependence of the activity of the network modifier oxide a_{RO} can be derived from the mole fraction:

$$\frac{1}{1 - x_{RO}} = \frac{1}{x_{SiO_2}} = 2 + \frac{1}{1 - a_{RO}} - \frac{1}{1 + a_{RO}[(1/k_{11}) - 1]}. \tag{12}$$

Equation (12) is valid for the assumption that only linear chains develop. If branched chains are also permitted, then Eq. (12) is modified to

$$\frac{1}{1 - x_{\mathrm{RO}}} = \frac{1}{x_{\mathrm{SiO_2}}} = 2 + \frac{1}{1 - a_{\mathrm{RO}}} - \frac{3}{1 + a_{\mathrm{RO}}[(3/k_{11}) - 1]}. \tag{13}$$

Figure 9 shows that with the assumption of branched chains, i.e., with Eq. (13) and with $k_{11} = 0.196$, the various experimentally determined a_{PbO} values can be well understood. In addition, statistics of chain length can be derived whose product for the frequency of $[\mathrm{SiO_4}]^{4-}$ ions corresponds to that in Fig. 10, but which leads to increasingly smaller values with the larger anions. This is easy to understand when one remembers that only three silicate anions were considered in Fig. 10, while Masson considers all *n*. To this extent, Masson's method of consideration has an advantage, but it does not include a possible formation of ring-formed silicate anions, and it cannot be applied for the usual glass melts, since it was derived for an $\mathrm{SiO_2}$ content $x_{\mathrm{SiO_2}} < 0.5$. It is hoped that improved formulas which have since been proposed will also include the range $x_{\mathrm{SiO_2}} > 0.5$.

2.3.2 Interpretation of Other Measurements

The investigations described in the previous section have valuable hints, but produced no proof. Thus, it is necessary to look around for other methods; here, however, only those methods will be treated which are based on measurements on glass melts and which permit more detailed commentary about the structure of the melt. Further data about glass melts can be found in Chapter 3 within most of the treatments of the influence of temperature on properties. In general, it is true here also that because of the necessarily high temperatures, measurements on glass melts are often very difficult, and thus, one cannot make high demands for accuracy in measurement.

Direct methods for ascertaining structures of the melt are not known. One obtains certain information through *X-ray research*. Zarzycki [1110], with such measurements on melts of the network formers $\mathrm{B_2O_3}$, $\mathrm{GeO_2}$, and $\mathrm{SiO_2}$, has been able to show that even in the melt the coordination number known from the glass is present, but that with rising temperature a reduction of the coordination number is observed, which can be explained through formation of fragments. Miyake et al. [617] expand the scope of measurement with their radiographic measurements on a $\mathrm{B_2O_3}$ melt at 650° C. From their interpretation, they infer a structure which exhibits a mixing of $[\mathrm{B_3O_6}]^{3-}$ rings, also called boroxol rings, and independent $[\mathrm{BO_3}]^{3-}$ triangles.

Corresponding measurements on melts of the system $\mathrm{Na_2O}$—$\mathrm{B_2O_3}$ by Titov et al. [971] show great similarity to such measurements on corresponding glasses; thus, the change in coordination number of the boron atom from 3 to 4 can be recognized (see section 2.6.1.1). But, in addition to the thermal fluctuations of the density and of the composition, heterogeneities can be seen on the order of 1 nm in the one case, 20 nm in the other, the cause for which is still unknown, but which have a connection with the tendency for phase separation. It is also interesting to observe that during the cooling, in melts with 6 to 15 mole % Na_2O, while going through the liquidus temperature, the fluctuations change; thus changes in the structure of the melt must also be taking place.

Analogous changes in coordination number in Na_2O—GeO_2 melts are found by Kamiya et al. [468], while melts of the alkali silicates, according to Waseda and Suito [1045], show the simple behavior of these glasses with coordination numbers 4, 6, and 7 for Li, Na, and K with respect to oxygen. Finally, it should be remarked concerning the X-ray research that it shows no evidence for a particular model; rather, it shows only that the measurements are compatible with this model.

The oscillations of individual atoms with or opposed to each other are also sensitive to structure. If the dipolar moment of the grouping in question changes, then the oscillation in question is *infrared* active; if the polarizability changes, then it is *Raman* active. The two spectroscopic techniques complement each other and lie in the wavelength range from about 1 μm or—in the more customary designation with these methods—wave numbers smaller than 10,000 cm^{-1}. There are many corresponding measurements on glasses (see section 2.5.2), but with measurements on melts some technical measuring difficulties must be overcome, e.g., the thermal radiation which lies in the same spectral region. Connected with the general development of measurement technique are recent Raman spectroscopy measurements, etc., which are considered by Seifert et al. [857].

Figure 11 shows such a spectrum of a sodium silicate melt in comparison with the spectrum of the glass. The differences that arise are small, yet unmistakable. The greater intensity of the band at 590 cm^{-1} in the melt is ascribed to a higher defect concentration, most likely open Si—O—Si bridges. From other, smaller differences one can conclude that there are more structural units present that are chain shaped than planar. Further measurements

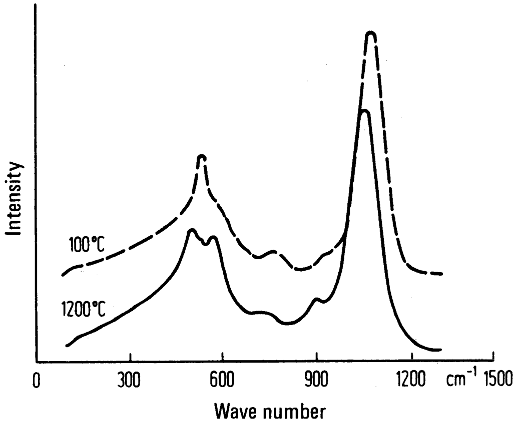


FIGURE 11. Raman spectra of glass (dashed line; curve shifted upward) and melt (solid line) of the composition $Na_2O \cdot 3.25\ SiO_2$, from Seifert et al. [857].

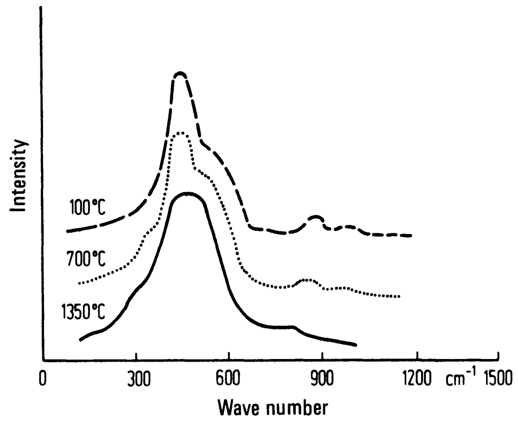


FIGURE 12. Raman spectra of GeO_2 glass (dashed line) and GeO_2 melt (dotted and solid lines), from Seifert et al. [857]; the curves for 100 and 700° C are shifted upward.

yielded the significant result that when an $Na_2O \cdot Al_2O_3 \cdot 10SiO_2$ glass was heated to 1,200° C, the coordination number 4 of the Al does not change (see section 2.6.1.4). Moreover, in the case of GeO_2 glass (see Fig. 12), the coordination number 4 of the Ge remains constant during heating (see section 2.6.1.5), but a strong broadening of the band around 500 cm^{-1} occurs, which is caused chiefly by an increase of the band at 530 cm^{-1}, which is identified as a defect band. As described above, defects thus become detectable in the melts.

Viscosity has a close relationship with the opening and closing of the bonds of the silicate network. The high viscosities of most of the silicate melts are in practice a very important fact, as the typical temperature dependency of viscosity of such melts is also a prerequisite for many forming processes. Thus, there have been numerous attempts to use the viscosities for information about the structures of melts (see also section 2.4.1). Above all, one should mention the classic work of Bockris et al. [80] in the interpreting of physical measurements.

In the analysis of the *measurements of viscosity* in binary systems making use of activaticn energies E_η and the activation entropies, a strong reduction of values up to about 10 mole % R_2O or about 20 mole % RO has been found. To interpret these data, Bockris assumes that at high R_mO_n content discrete anions occur in the melt which are separated by cations and which represent flow units. The size of these anions is obtained when the conditions of electroneutrality and stoichiometry are fulfilled. Because of the Si—O—Si angle of about 145°, rings of three and four tend to form in addition to short chains. The following anions are obtained for some selected compounds:

$R_2O \cdot SiO_2$: simple rings of the form $[(SiO_3)_3]^{6-}$ or $[(SiO_3)_4]^{8-}$.
$R_2O \cdot 2SiO_2$: assemblage of two rings each: $[Si_2O_5)_3]^{6-}$ or $[(Si_2O_5)_4]^{8-}$.
$R_2O \cdot (>2)SiO_2$: at higher SiO_2 content, $(SiO_2)_3$ or $(SiO_2)_4$ rings that are still "neutral" assemble between these two rings, so that oblong anions arise whose general formulas then read: $[(SiO_3 + nSiO_2)_3]^{6-} = [(Si_{n+1}O_{2n+3})_3]^{6-}$ or

$[(SiO_3 + nSiO_2)_4]^{8-} = [(Si_{n+1}O_{2n+3})_4]^{8-}$. Thus, the result, for example, for
$R_2O \cdot 4SiO_2$: $n = 3 \rightarrow [(Si_4O_9)_3]^{6-}$ or $[(Si_4O_9)_4]^{8-}$.

With the supposition of such anions, which form a distinct equilibrium for every composition, the slow decrease (after the rapid decrease previously mentioned) of the E_η values with increasing R_mO_n content can be easily explained. The higher E_η values of the melts of alkali-earth silicates are produced by the stronger bonding of the anions through the alkali-earth ions that lie in between.

Bockris arrives at structure units similar to those which Flood and Knapp [257] inferred through quite different deliberations. Above all stands the agreement in the assumption of $[(SiO_3)_3]^{6-}$ and $[(Si_2O_5)_3]^{6-}$ anions, even if rings of three appear somewhat unusual.

According to Bockris' assumption, *discrete anions* occur in the melt which become increasingly longer with decreasing R_mO_n content, until they finally become unstable, which occurs at an R_2O content of 10 mole % and an RO content of about 20 mole %. The stronger rise of E_η values that follows shows that three-dimensional network formation then takes place. The network formation takes place in alkali-earth melts at higher R_mO_n content, since the alkali-earth ions themselves are producing a lattice effect.

The analysis of *density measurements* using partial molar volumes yields ranges of constant values, which likewise indicate discrete anions in these areas. To be sure, Épel'baum [231] concludes from similar interpretations that in addition to large network fragments only the small SiO_3^{2-} anions occur. The measurements of density at different temperatures were analyzed by Bockris also with respect to the thermal expansion dV/dT. It was found that in binary R_2O—SiO_2 melts the expansion up to about 12 mole % R_2O was practically zero. That can be well accounted for by the foregoing view that up to this alkali content, the cations are confined within the still rigid network and thus cannot contribute to expansion. They can do that only at higher alkali contents, when discrete anions occur.

The views developed by Bockris about the structure of the melt permit an unconstrained interpretation of the results of measurements; these results of measurements, however, do not constitute proof for the structure. Some further experiments, however, can be explained with these views, among others the observation that NaF in that kind of silicate melt dissolves in larger quantities only with R_2O content above 13 mole %; thus, according to Bockris, only when the melts become distinctly ionic.

In order to show that there are also other possibilities of explaining these results of measurements, let the second interpretation, mentioned by Bockris himself, be given as an example: the same structure is assumed up to 12 mole % R_2O. At higher R_2O contents, a microphase $R_2O \cdot 2SiO_2$ is formed which is present as a film between SiO_2-rich islands. As the R_2O content increases, the size of the islands steadily decreases, in order to achieve composition of discrete