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Structural Defect Equilibria in Vitreous Silica and Dilute Silicates

ROBERT A. HUGGINS*

Advanced Research Projects Agency, Washington, D.C. 20301

AND

MAURICE L. HUGGINS

Arcadia Institute for Scientific Research, 135 Northridge Lane, Woodside, California 94062

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The principles developed for the description of defect equilibria in crystalline solids are applied to the structon model of the structure of vitreous silica and a dilute solid solution of the oxide of a monovalent cation in vitreous silica.

Introduction

During the past few years a considerable degree of success has accompanied the use of the defect model of the structure of crystalline solids. The basic approach taken in applying this model is to focus attention upon the description and behavior of structural perturbations; that is, upon deviations from the "ideal" regularly repeating structure of a "perfect crystal." This has been a very useful viewpoint, leading to an understanding of many of the structure-sensitive properties of crystalline solids.

Furthermore, it has been found that defects in such materials can be treated as quasichemical species and that many of the standard techniques for handling chemical equilibrium and kinetics can be applied to them. A considerable body of knowledge has been accumulated concerning defect chemistry, pointing the way toward control of the defect structure and, hence, of many of the important defect-dependent properties of crystalline solids.

In this paper, these concepts are applied to vitreous oxides, specifically silica (commonly represented by the stoichiometric formula SiO_2), in order to establish a framework for treatment of the interaction between the various structural configurations in this and other similar "amorphous" materials under conditions in which local equilibrium can be assumed (generally, above the glass transition temperature).

The application of the techniques developed by study of the defect chemistry of crystalline solids to vitreous systems depends upon the proper identification of the normal structural units, as well as those which can be treated as defects or deviations.

Although it is recognized that the state of understanding of the structure of glassy or vitreous oxides is presently well behind that of the structure of crystalline solids, a considerable amount of information is nevertheless at hand. The general concept of the microscopic structure of vitreous materials has gone through a gradual transition. A completely random and disordered model has been replaced by various less disordered types of network models, and more recently, by one in which the network structure is determined by the preference for some types of local structural arrangements over others. This last approach has been greatly strengthened in recent years by results obtained using modern experimental tools, such as optical spectroscopy, electron and nuclear spin resonance, and x-ray diffraction [especially that using fluorescence X-radiation (*1*).

The local structural units found in vitreous materials are usually the same as, or very similar to, those in chemically similar crystalline solids (*1–3*).

There are various ways in which these local arrangements can be described. In silicon dioxide,

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* On leave from Stanford University, Stanford, California 94305.

for example, one can consider the structure to be composed of silicon cations and oxygen anions. This approach has a certain attractiveness because of its inherent simplicity and the fact that it leads to the correct prediction of some structural features in related materials that depend primarily on coulombic forces. On the other hand, this extreme viewpoint leads (*3*) to the incorrect prediction of an Si–O–Si bond angle of 180°, as well as incorrect predictions of the structure in a number of other substances. Furthermore, it is definitely known that the silicon and oxygen atoms in silica and silicates are held together by bonds that, although quite polar, possess a considerable amount of electronpair sharing character.

For present purposes, as well as others, it is preferable to focus attention upon local structural groupings as the basic structural units. The label "structon" was introduced some time ago (*4–7*) for this purpose, each type of structon signifying a specific type of atom, with specified kinds and numbers of close neighbors. A considerable body of evidence has been accumulated that demonstrates the relationship of many of the important properties of vitreous solids to the predominant, and in some cases to the minority, types of structons (local structural arrangements) present.

It is useful to have a simple, easily understandable way of symbolically representing each structon type. In the system adopted for doing this, the normal chemical symbol for the central atom in the structon is given first; then, in parentheses, symbols for the numbers and types of its neighboring atoms. In the case neighboring oxygen atoms, it is desirable also to indicate whether they also "bridge" to other silicon atoms. The convention that is used here is to represent the preponderant bridging oxygens that are closely adjacent to two silicon atoms by the symbol O''. A "nonbridging" oxygen (close to only one silicon) is represented by the symbol O'; one that is close to three silicons is signified by O'''. To avoid confusion between these oxygen symbols and zero, a centered dot is used between a number and an oxygen symbol following it in a structon formula.

To help avoid confusion with the ordinary formulas for molecules and ions, the structon formula is enclosed in angle brackets: $\langle\ \rangle$. Also, if a structon has a "formal charge," it is indicated by a plus or minus. The formal charge is defined (*8*) as the number of electron charge units related to the presence of the structon, computed on the assumption that one electron of each shared electronpair associated with the structon "belongs" to it. A number of examples of structon formulas are given in Table I, as well as Eqs. (2)–(4).

The local configurations around both electropositive atoms, such as silicon, and electronegative atoms, such as oxygen, are important. It should be pointed out, however, that the close neighbor structure is completely determined by either the set of electropositive atom-centered (Si) structons alone or the set of electronegative atom-centered (O) structons alone. Either set can be reproduced from the other by using the requirement that for each *B*-type neighbor around an *A*-type atom there must be an *A*-type neighbor around a *B*-type atom.

Before considering structural defects, one should obviously have knowledge of the background or "normal" structure. Deviations from this normal structure then constitute the defects (defect structons). They may or may not be electrostatically charged relative to the normal structure. At present we are interested in those which are charged, and are concerned with the differences between the defect structons and the related normal structons, as regards the numbers and kinds of neighbors, the structon charge (as indicated by the formal charge), and stability.

We shall discuss the relationships between the numbers of charged defect structons of different types, the numbers of (extra) electrons and holes, certain equilibrium constants, and experimentally variable factors, such as the partial pressure or chemical activity of gaseous oxygen in equilibrium with the solid.

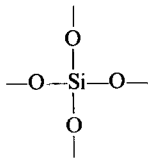
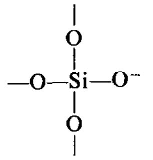
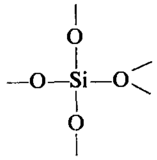
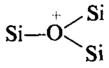
Intrinsic Defects in Vitreous Silica

Although it is not really very realistic in many practical cases because of the presence of alkali ions and other "foreign" species, let us first consider the structural species in the vitreous pure silicon oxide system. In both quartz (*3*, *9*) and vitreous silica (*1*) the normal structons are of just two types: a silicon surrounded tetrahedrally by four oxygens, and an oxygen bridging between two silicon neighbors. Both silicon and oxygen atoms in these structons have formal charges of zero, so we consider these normal structons to be uncharged. (See Table I.)

Considering possible types of oxygen-centered defect structons in pure silica, the only reasonable ones are those in which the oxygen atom has either one (a nonbridging oxygen) or three close silicon neighbors. In these the formal charges of the oxygen atoms (and so the structon charges) are −1 and +1, respectively. Nonbridging oxygens are found in many silicate crystals, but experimental evidence for

TABLE I

STRUCTURAL UNITS IN VITREOUS SILICA AND DILUTE VITREOUS SILICATES CONTAINING OXIDES OF MONOVALENT CATIONS

Structural species	Structon formula	Structural diagram	Formal charge	Simplified notation
Normal structons				
1. Predominant Si-centered structon	⟨Si(4·O″)⟩	 $-\mathrm{O}-\overset{\overset{\vert}{\mathrm{O}}}{\underset{\underset{\vert}{\mathrm{O}}}{\mathrm{Si}}}-\mathrm{O}-$	0	
2. Predominant oxygen-centered structon (bridging oxygen)	⟨O″(2Si)⟩	Si—O—Si	0	
Defect structons				
1. Silicon-centered structon with one oxygen neighbor nonbridging	⟨Si(O′, 3·O″)⟩	 $-\mathrm{O}-\overset{\overset{\vert}{\mathrm{O}}}{\underset{\underset{\vert}{\mathrm{O}}}{\mathrm{Si}}}-\mathrm{O}^-$	0	
2. Silicon-centered structon with one oxygen neighbor forming a three-way bridge	⟨Si(3·O″, O‴)⟩		0	
3. Nonbridging oxygen structon	⟨O′(Si)⁻⟩	$\mathrm{Si—O^-}$	−1	⟨S⁻⟩
4. Most probable oxygen-centered structon with positive charge (three-way bridging oxygen)	⟨O‴(3Si)⁺⟩		+1	⟨S⁺⟩
5. Monovalent cation (eg., Na, K)	⟨M⁺⟩		+1	⟨M⁺⟩
Electronic defects				
1. Electron			−1	e^-
2. Hole			+1	h^+

oxygens with three silicon neighbors has not yet been reported.

The existence of small concentrations of defect structons of the nonbridging oxygen type in vitreous silica has been shown by the observation (*12*) of a structure-sensitive band in the 900–950 cm^{-1} region of the infrared spectrum, apparently the same band as is observed (*13*) in binary silicate glasses which are known to contain nonbridging oxygens. This and other experimental observations have been supported by recent theoretical calculations (*14*).

The lack of experimental evidence for defect structons consisting of oxygens with three close silicon neighbors is not surprising. The concentration of such structons is subject to the equilibrium related to their reaction with nonbridging oxygen structons to form normal bridging oxygen structons. In pure vitreous silica these concentrations are expected to be quite low. Furthermore, as will be shown later, this equilibrium is displaced in favor of nonbridging oxygen defect structons when monovalent cations such as hydrogen or sodium are present. From a practical standpoint, it is very difficult to avoid the existence of small but significant concentrations of such ions. It may be noted, however, that oxygen atoms are known to have three boron neighbors in a high temperature form of boric oxide and in a few crystalline borates (*11*). On the other hand, oxygen atoms with no silicon neighbors (oxide ions) and oxygen atoms with four or more silicon neighbors are relatively very unlikely. Their formal charges would be -2 and $+2$, respectively, and they would not conform to the principle that structures tend to deviate as little as possible from local charge neutrality (*3*, *10*). Such structons are unknown (as normal components) in silicates.

In the crystalline and amorphous forms of silica as well as in all silicates of known structure, the silicon atoms always have four oxygen neighbors (*1*, *9*, *15–17*). One apparent exception to this rule, however, is silicon pyrophosphate, in which the silicons each have six oxygen neighbors (*18*), but the situation there is very different from that in the systems we are now considering. For one thing, the phosphorus atoms hold oxygens even more tightly than do silicon atoms. It seems safe to assume that all of the silicon atoms in pure silica and in silica containing small amounts of a metal oxide such as Na_2O as impurity have just four oxygen neighbors. If some of the oxygens have either one or three silicon neighbors, then some of the silicon-centered structons must be of the $\langle \mathrm{Si}(\mathrm{O}', 3\cdot\mathrm{O}'')\rangle$ or $\langle \mathrm{Si}(3\cdot\mathrm{O}'', \mathrm{O}''')\rangle$ types. In these, as in the normal $\langle \mathrm{Si}(4\cdot\mathrm{O}'')\rangle$ structons, the formal charge on the silicon atoms, and so the structon charge, is zero.

By analogy to the situation in crystalline solids, it is reasonable, because of the entropy term in the Gibbs free energy, to expect the structure of vitreous silica to contain finite concentrations of defect structons under conditions in which local equilibrium can be attained. Furthermore, the concentrations of the various defect structons should depend on temperature, component activities at interfaces, and the presence of foreign species.

General Methodology Used in Treatment of Defect Equilibrium

By analogy to the procedure normally followed in the defect chemistry of simple nonmetallic crystals, defect equilibrium in vitreous oxides can be expressed in terms of quasichemical reactions involving the pertinent defect structon species. Straightforward thermodynamic treatment results in the use of the law of mass action formalism, written in terms of the chemical activities of these species.

If care is exercised in writing such quasichemical reactions with regard to electrostatic charge and mass balances, a perfectly rigorous result is obtained in terms of the activities of the pertinent species. Assumptions must be introduced, however, if one wishes to translate from activities to concentrations, as in the case of crystalline materials.

The usual method of treatment of intrinsic defect equilibrium in chemically pure but not necessarily stoichiometric binary solids in which crystallographic (ionic) disorder predominates over electronic disorder involves an assumption (often based upon experimental observation) of the identities of the two most probable ionic defect species. They contribute opposite electrostatic charges and cause opposite compositional changes by their presence. Differences in their concentrations result in a net electrostatic charge, which must be balanced by small concentrations of other charged species, such as electrons or holes. The total number of defect species which are involved in the pertinent equilibrium in such binary systems within any given compositional range is thus usually four. Their concentrations can be found by the solution of four simultaneous independent relations, the condition for electroneutrality and the law of mass action expressions relating to three independent quasichemical reactions. If other defect species are also assumed to exist (such as defects with different ionization states) further independent reactions are obviously required.

The selection of the appropriate quasichemical reactions to consider to solve defect equilibrium problems is quite straightforward. The Gibbs phase rule indicates that at specified pressure and temperature an equilibrium system is completely determined if the number of compositional variables which are specified is one less than the number of chemical components. Therefore, in a binary system such as nonstoichiometric silica, one composition-determining relation is needed. In a ternary system, two are required. These compositional relations can be of various types. The concentration (or activity) of one of the species may be known, the ratio of species concentrations (or activities) may be known, or the concentration (or activity) of one species may be determined by equilibrium with an adjacent phase of known properties, this equilibrium being expressed by a quasichemical reaction across the phase boundary.

Another type of independent relation is obtained from the reaction to form a defect pair such as an electron and a hole. In addition, a structural defect pair formation reaction is needed. The selection of the specific defects to be involved in this latter relation depends, of course, upon the disorder model and resultant defect species assumed to be dominant.

When dealing with simple binary systems at a given temperature it is quite common to use this method to calculate the concentrations of all pertinent defect species as functions of either the overall chemical composition or, preferably, the activity of one component. This is facilitated by approximating the electroneutrality condition by assuming equality between the concentrations of the two dominant defects in any given compositional range (*19*). If both this approximate electroneutrality condition and the law of mass action expressions for the appropriate quasichemical reactions are written in logarithmic form, a simple set of simultaneous linear equations results which can be easily solved. A number of examples of the use of this method have been discussed elsewhere (*20–22*).

Application to Defect Equilibria in Pure Vitreous Silica

One can make the reasonable assumption that there are only four important defect species in the pure binary vitreous silica system, two defect structons, and electrons and holes. The four independent relations to be solved simultaneously involve two defect pair formation reactions, one composition relation, and the appropriate electroneutrality expression.

As in other solids that are poor electronic conductors, we assume that small numbers of electrons can be removed from atoms in the silica. These unattached electrons and the sites from which they have come ("holes") will be designated by the symbols e^- and h^+, respectively. Furthermore, we expect that such electronic defects will be sufficiently mobile that their concentrations can be described in terms of a standard electron-hole pair formation reaction. This results in a law of mass action expression which can be written in the form

$$K_i = [e^-][h^+] \tag{1}$$

in which the square brackets designate concentrations in number per cubic centimeter and K_i is an equilibrium constant. The distinction between itinerant and trapped electronic species is not important at this juncture.

The other defect pair formation reaction of importance for our purposes involves the formation of small numbers of defect structons from a structure consisting of normal structons. A reasonable reaction of this type in pure silicon dioxide would be represented by the following two equations, one written for silicon-centered structons, and the other for oxygen-centered structons:

$$4\langle \mathrm{Si}(4\cdot \mathrm{O}'')\rangle \rightleftarrows \langle \mathrm{Si}(\mathrm{O}', 3\cdot \mathrm{O}'')\rangle + 3\langle \mathrm{Si}(3\cdot \mathrm{O}'', \mathrm{O}''')\rangle \tag{2a}$$

and

$$2\langle \mathrm{O}''(4\mathrm{Si})\rangle \rightleftarrows \langle \mathrm{O}'(\mathrm{Si})^-\rangle + \langle \mathrm{O}'''(3\mathrm{Si})^+\rangle. \tag{2b}$$

These equations are not independent, but are coupled together because each silicon–oxygen contact is also an oxygen–silicon contact, as discussed earlier. Because of this redundant relationship, the equilibrium for the overall structural change occurring need not be expressed in terms of the sum of Eqs. (2a) and (2b). Instead, only Eq. (2b) will be used. Since the normal $\langle \mathrm{O}''(4\mathrm{Si})\rangle$ structons are present in an overwhelmingly large and essentially constant concentration relative to the others, the law of mass action expression for this reaction, written in terms of the defect structon concentrations, becomes

$$K_d = [\langle \mathrm{O}'(\mathrm{Si})^-\rangle][\langle \mathrm{O}'''(3\mathrm{Si})^+\rangle]. \tag{3a}$$

The value of the equilibrium constant K_d is, of course, determined by the free energy change resulting from the formation of the defect structons from normal structons.

For simplicity and to make the resulting equations more readily applicable to other systems, the two defect structon types in Eq. (3a) will be represented by the abbreviated symbols $\langle \mathrm{S}^-\rangle$ and $\langle \mathrm{S}^+\rangle$. Hence, Eq. (3a) becomes

$$K_d = [\langle \mathrm{S}^-\rangle][\langle \mathrm{S}^+\rangle]. \tag{3b}$$

Since a change in the ratio of the concentrations of the two types of defect structons in Eq. (3) produces a change in the overall silicon–oxygen ratio, it is to be expected that the concentration of the negative structons can be increased by reaction of oxygen gas from the environment with the normal structons in the silica. In order to maintain charge balance, this must be accompanied by concurrent removal of electrons from (unspecified) atoms to form holes. The two coupled equilibria are

$$\tfrac{1}{2}\mathrm{O}_2 + \langle \mathrm{O}''(2\mathrm{Si})\rangle \rightleftarrows 2\langle \mathrm{O}'(\mathrm{Si})^-\rangle + 2\mathrm{h}^+ \tag{4a}$$

and

$$2\langle \mathrm{Si}(4\cdot \mathrm{O}'')\rangle \rightleftarrows 2\langle \mathrm{Si}(\mathrm{O}', 3\cdot \mathrm{O}'')\rangle. \tag{4b}$$

As explained in the discussion of Eq. (3), we need consider only one of these two equations and can neglect changes in the concentrations of the normal structons. We therefore write for the equilibrium constant:

$$K_0 = [\langle \mathrm{O}'(\mathrm{Si})^- \rangle]^2 [h^+]^2 p^{-1/2}, \tag{5a}$$

or more simply

$$K_0 = [\langle \mathrm{S}^- \rangle]^2 [h^+]^2 p^{-1/2}. \tag{5b}$$

Here p represents the partial pressure of oxygen gas assumed to be in equilibrium with the solid.

For electroneutrality,

$$[\langle \mathrm{S}^- \rangle] + [e^-] = [\langle \mathrm{S}^+ \rangle] + [h^+]. \tag{6}$$

The concentrations of the four defect species presumed to be dominant in pure vitreous silica can now be determined, as functions of K_i, K_d, K_0 and p, by solution of the simultaneous Eqs. (1), (3), (5), and (6). The following results, expressed in logarithmic form, are obtained.

$$\ln [e^-] = \ln K_i - \tfrac{1}{2} \ln [1 + K_i(K_0 p^{1/2})^{-1/2}] + \tfrac{1}{2} \ln [K_d + (K_0 p^{1/2})^{1/2}] - \tfrac{1}{2} \ln [K_0 p^{1/2}], \tag{7}$$

$$\ln [h^+] = \tfrac{1}{2} \ln [1 + K_i(K_0 p^{1/2})^{-1/2}] - \tfrac{1}{2} \ln [K_d + (K_0 p^{1/2})^{1/2}] + \tfrac{1}{2} \ln [K_0 p^{1/2}], \tag{8}$$

$$\ln [\langle \mathrm{S}^- \rangle] = -\tfrac{1}{2} \ln [1 + K_i(K_0 p^{1/2})^{-1/2}] + \tfrac{1}{2} \ln [K_d + (K_0 p^{1/2})^{1/2}], \tag{9}$$

and

$$\ln [\langle \mathrm{S}^+ \rangle] = \ln K_d + \tfrac{1}{2} \ln [1 + K_i(K_0 p^{1/2})^{-1/2}] - \tfrac{1}{2} \ln [K_d + (K_0 p^{1/2})^{1/2}]. \tag{10}$$

These rather complicated equations can be simplified considerably for certain special cases. For example, at intermediate values of oxygen partial pressure, when the concentrations of the two types of defect structons can be assumed to be much greater than those of electrons or holes, the electroneutrality Eq. (6) can be approximated by

$$[\langle \mathrm{S}^- \rangle] = [\langle \mathrm{S}^+ \rangle]. \tag{11}$$

Solution of the simultaneous Eqs. (1), (3), (5), and (11) then yields the following:

$$\ln [e^-] = \ln K_i + \tfrac{1}{2} \ln K_d - \tfrac{1}{2} \ln (K_0 p^{1/2}), \tag{12}$$

$$\ln [h^+] = -\tfrac{1}{2} \ln K_d + \tfrac{1}{2} \ln (K_0 p^{1/2}), \tag{13}$$

$$\ln [\langle \mathrm{S}^- \rangle] = \tfrac{1}{2} \ln K_d, \tag{14}$$

and

$$\ln [\langle \mathrm{S}^+ \rangle] = \tfrac{1}{2} \ln K_d. \tag{15}$$

Thus we see that in this region of oxygen partial pressure the concentrations of both minority defects (electrons and holes) vary with the magnitude of the partial pressure of oxygen in equilibrium with the silica, while the concentrations of the dominant structon defects are essentially constant. The latter concentrations, however, will be temperature-dependent, for the equilibrium constant K_d should vary with temperature according to the relation

$$K_d = \exp(-\Delta G_d / RT), \tag{16}$$

where ΔG_d is the free energy change for the reaction in which one mole of each of the defect structons is formed. See Eq. (2b).

Because of the dependence of the concentrations of electrons and holes on the oxygen partial pressure [Eqs. (12) and (13)], it follows that when p is small enough, the electron concentration becomes greater than the concentration of the negatively charged structon. Then the electroneutrality condition [Eq. (6)] can no longer be approximated by Eq. (11). As $[e^-]/[\langle \mathrm{S}^- \rangle]$ approaches infinity, the relationship

$$[e^-] = [\langle \mathrm{S}^+ \rangle], \tag{17}$$

is approached.

Solution of the simultaneous Eqs. (1), (3), (5), and (17) yields the following equations for the defect concentrations at very low values of oxygen partial pressure:

$$\ln [e^-] = \tfrac{1}{2} \ln K_i + \tfrac{1}{2} \ln K_d - \tfrac{1}{4} \ln (K_0 p^{1/2}), \tag{18}$$

$$\ln [\mathrm{h}^+] = \tfrac{1}{2} \ln K_i - \tfrac{1}{2} \ln K_d + \tfrac{1}{4} \ln (K_0 p^{1/2}), \tag{19}$$

$$\ln [\langle \mathrm{S}^- \rangle] = -\tfrac{1}{2} \ln K_i + \tfrac{1}{2} \ln K_d + \tfrac{1}{4} \ln (K_0 p^{1/2}), \tag{20}$$

and

$$\ln [\langle \mathrm{S}^+ \rangle] = \tfrac{1}{2} \ln K_i + \tfrac{1}{2} \ln K_d - \tfrac{1}{4} \ln (K_0 p^{1/2}). \tag{21}$$

The transition from the regime of intermediate oxygen partial pressures, in which Eqs. (12)–(15) are good approximations, to that in which Eqs. (18)–(21) are approximately valid is, of course, gradual. The location of the transition region on the oxygen partial pressure scale can be determined by assuming a sharp transition from one set of approximations [Eqs. (11)–(15)] to the other [Eqs. (17)–(21)] and calculating the value of the "critical partial pressure" p_{c1}, at which it occurs. If Eqs. (11) and (17) simultaneously hold in such a hypothetical system,

$$[e^-] = [\langle \mathrm{S}^- \rangle]. \tag{22}$$

Setting the right sides of Eqs. (12) and (14) equal, we see that

$$\ln p_{c1} = 4 \ln K_i - 2 \ln K_0. \tag{23}$$

Considering now the situation at very high oxygen partial pressures, comparison of Eqs. (13) and (15) shows that the hole concentration then dominates over the positive structon concentration. Likewise, from Eqs. (12) and (14), the negative structon concentration dominates the electron concentration. Hence the electroneutrality relation, Eq. (6), reduces to

$$[\langle S^- \rangle] = [h^+]. \tag{24}$$

Simultaneous solution of Eqs. (1), (3), (5), and (24) yields, for very high oxygen partial pressures,

$$\ln [e^-] = \ln K_i - \tfrac{1}{4} \ln (K_0 p^{1/2}), \tag{25}$$

$$\ln [h^+] = \tfrac{1}{4} \ln (K_0 p^{1/2}), \tag{26}$$

$$\ln [\langle S^- \rangle] = \tfrac{1}{4} \ln (K_0 p^{1/2}), \tag{27}$$

and

$$\ln [\langle S_i^+ \rangle] = \ln K_d - \tfrac{1}{4} \ln (K_0 p^{1/2}). \tag{28}$$

The second "critical partial pressure" p_{c2}, for the transition between the intermediate and very high oxygen partial pressure regimes can be calculated in the same manner as p_{c1} with the result,

$$\ln p_{c2} = 4 \ln K_d - 2 \ln K_0. \tag{29}$$

In accordance with normal practice in dealing with defects in crystalline solids, one can construct a "defect equilibrium diagram" in which the logarithms of the various defect concentrations are plotted versus the logarithm of the oxygen partial pressure. From such a diagram one can quickly see both the relative magnitudes of the defect concentrations at a given oxygen partial pressure (or activity) and the way that these magnitudes change as the oxygen partial pressure is varied. Such a defect equilibrium diagram, for arbitrarily chosen values of the equilibrium constants, is shown for the case of vitreous silica in Fig. 1.

It is seen that (with the chosen constants) there is a broad central region of oxygen partial pressure over which the concentrations of the defect structons are essentially constant, dominating the electron and hole concentrations. For equilibrium with very low values of oxygen partial pressure, however, the electron concentration becomes significant, and at very high oxygen partial pressures, the hole concentration becomes important.

Influence of a Third Element

Silicates have at least one other element present in addition to silicon and oxygen. It may be hydrogen, a monovalent element such as sodium, a bivalent element such as calcium, or an element of higher valence, such as aluminum. These additional atoms are invariably surrounded by oxygens, the forces holding them there being largely coulombic, at least in the monovalent and bivalent cases. For our purposes, it is a good approximation, in such

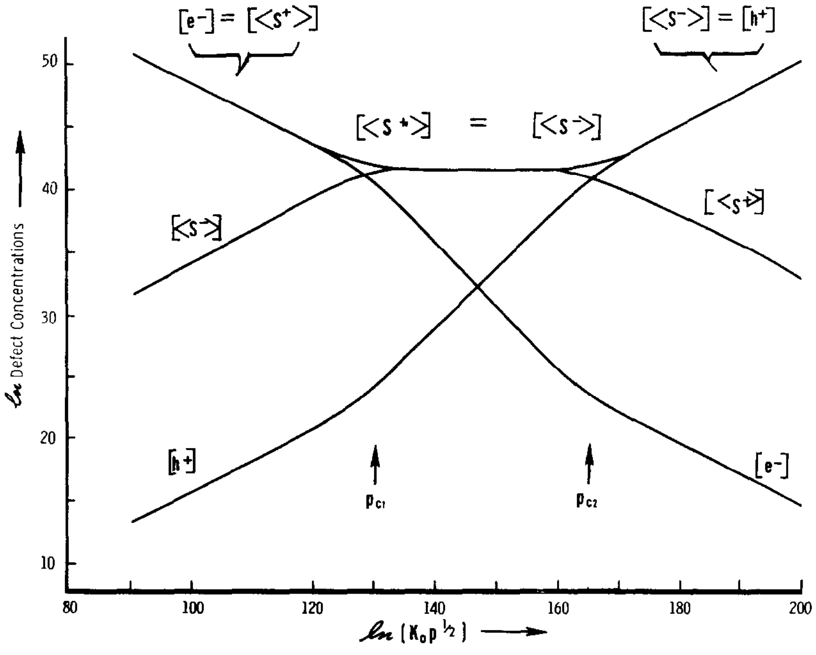


FIG. 1. Defect equilibrium diagram for vitreous silica, illustrating the influence of oxygen partial pressure on the concentrations of the pertinent structon and electronic defects. Assumed values: $K_i = 10^{28}$, $K_d = 10^{36}$, $K_0 = 10^{64}$.

cases, to consider the added atoms as cations, neglecting any electronpair bonding that may exist. Consideration of silicates containing elements of higher valence, such as boron, aluminum, or phosphorus, introduces complications that we do not wish to contend with here, but hope to deal with in future papers, For the present we shall limit our discussion to silicates containing relatively small amounts of a monovalent cation, such as sodium. For short, we call these "dilute silicates."

Sodium (or other) cations cannot, of course, be added to silicon dioxide without the simultaneous addition of anions, such as O^{-2}, to maintain electrostatic charge balance. The representation of the compositions of sodium silicates by use of formulas such as $Na_2O\cdot SiO_2$, $Na_2O\cdot xSiO_2$, etc., may give the correct relative numbers of atoms, but is somewhat misleading since the actual structures do not contain discrete Na_2O or SiO_2 units.

The addition of cations and oxide anions causes changes in the normal silicon dioxide structure, primarily by reducing the number of oxygen bridges. In the resulting structure, more of the oxygen-centered structons are thus of the O′ type, with only one close silicon neighbor. The structon changes occurring when an oxide ion (from sodium oxide, for instance) is added to silicon dioxide can be represented by the reaction

$$2\langle \mathrm{Si}(4\cdot \mathrm{O}'')\rangle + \langle \mathrm{O}''(2\mathrm{Si})\rangle + \mathrm{O}^{-2} \rightleftarrows 2\langle \mathrm{Si}(\mathrm{O}', 3\cdot \mathrm{O}'')\rangle + 2\langle \mathrm{O}'(\mathrm{Si})^{-}\rangle. \tag{30}$$

The addition of two monovalent cations and one oxide ion from a metal oxide thus adds two positive $\langle M^+\rangle$ structons and two negative $\langle O'(Si)^-\rangle$ structons to the structure. Since the latter type is the same as one of the two types of defect structons that we have considered to be present in pure silica, the equilibrium involving these intrinsic defect structons, holes, and electrons must be affected.

The electroneutrality relation is now

$$[\langle \mathrm{O}'(\mathrm{Si})^{-}\rangle] + [e^{-}] = [\langle \mathrm{O}'''(3\mathrm{Si})^{+}\rangle] + [h^{+}] + [\langle \mathrm{M}^{+}\rangle] \tag{31a}$$

or

$$[\langle \mathrm{S}^{-}\rangle] + [e^{-}] = [\langle \mathrm{S}^{+}\rangle] + [h^{+}] + [\langle \mathrm{M}^{+}\rangle]. \tag{31b}$$

Simultaneous solution of this equation with Eqs. (1), (3), and (5) leads to the following equations for the concentrations of the defects (other than the M cations) as functions of the equilibrium constants, M cation concentration, and oxygen partial pressure.

$$\ln [e^{-}] = \ln K_i - \ln (K_i + f_p) + \ln Y, \tag{32}$$

$$\ln [h^{+}] = \ln (K_i + f_p) - \ln Y, \tag{33}$$

$$\ln [\langle \mathrm{S}^{-}\rangle] = \ln f_p - \ln (K_i + f_p) + \ln Y \tag{34}$$

$$\ln [\langle \mathrm{S}^{+}\rangle] = -\ln f_p + \ln (K_i + f_p) + \ln K_d \ln Y \tag{35}$$

where

$$Y = \tfrac{1}{2} [\langle \mathrm{M}^{+}\rangle] + \{\tfrac{1}{4}[\langle \mathrm{M}^{+}\rangle]^2 + (K_d + f_p)(K_i + f_p)/\mathrm{F}\}^{1/2} \tag{36}$$

and

$$f_p = (K_0 p^{1/2})^{1/2}. \tag{37}$$

If the concentration of the M cations is sufficiently less than that of either of the other two positively charged species on the right side of Eq. (31), the presence of these cations has but little influence on the defect equilibria. This becomes obvious on comparison of this equation with Eq. (6).

On the other hand, when the right side of Eq. (31) becomes dominated by the concentration of the cations, variations in the defect concentrations must occur. It can be seen from Fig. 1 that the importance or lack of importance of the cations will depend primarily on the concentration of the positively charged defect structons. From Eqs. (6) and (15) we can conclude that, for intermediate values of oxygen partial pressure, the defect concentrations will be appreciably affected whenever

$$\ln [\langle \mathrm{M}^{+}\rangle] \geqq \tfrac{1}{2} \ln K_d. \tag{38}$$

The critical parameter is thus the equilibrium constant K_d.

Although the details will be omitted here, it can be shown that at larger values of cation concentration the defect equilibria are modified as depicted in the schematic diagram of Fig. 2.

It is seen that the major effect of the presence of the cations is to expand the range of oxygen partial pressure over which the defect structons dominate the electronic defects.

In the extremely low-oxygen partial pressure regime, in which the electron concentration is significant and the monovalent cation concentration is overwhelmed by the concentration of positively charged oxygen-centered structons, the defect concentrations are given by Eqs. (18)–(21).

When the oxygen partial pressure becomes so great that the concentration of the positive defect structons falls below the monovalent cation concentration, the appropriate approximation for the electroneutrality relation, Eq. (31), becomes

$$[e^{-}] = [\langle \mathrm{M}^{+}\rangle]. \tag{39}$$

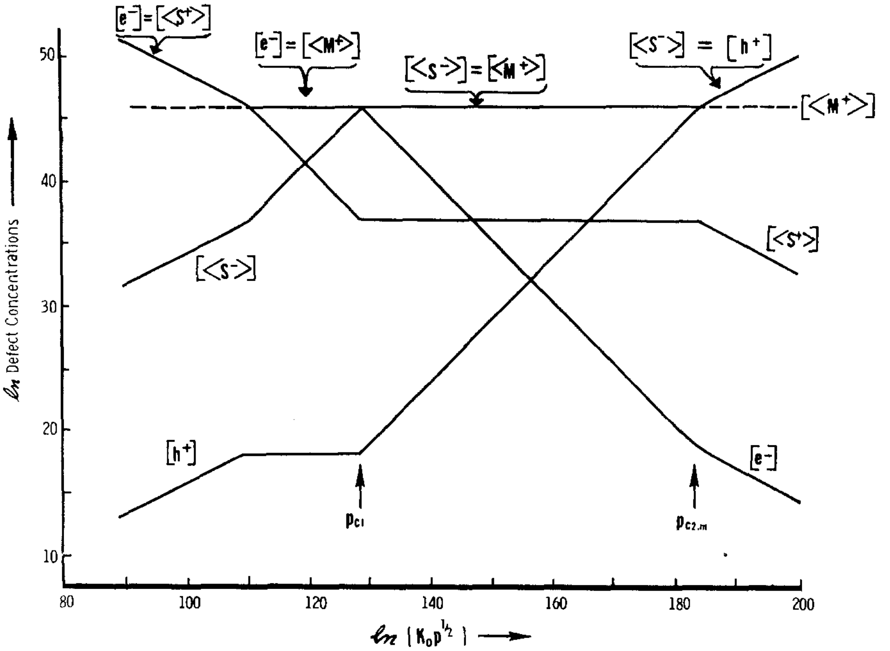


FIG. 2. Defect equilibrium diagram for vitreous silica containing a small amount of the oxide of a monovalent cation. Cation concentration assumed to be $10^{20}/\text{cm}^3$; constants the same as for Fig. 1. For simplification, the curvature of the concentration curves near the critical values of oxygen partial pressure has been neglected.

This can be solved simultaneously with Eqs. (1), (3), and (5) to give the defect concentrations:

$$\ln[e^-] = \ln[\langle M^+\rangle], \tag{40}$$

$$\ln[h^+] = \ln K_i - \ln[\langle M^+\rangle], \tag{41}$$

$$\ln[\langle S^-\rangle] = \ln[\langle M^+\rangle] - \ln K_i + \tfrac{1}{2}\ln(K_0 p^{1/2}), \tag{42}$$

and

$$\ln[\langle S^+\rangle] = \ln K_d - \ln[\langle M^+\rangle] + \ln K_i - \tfrac{1}{2}\ln(K_0 p^{1/2}). \tag{43}$$

Comparison with Eqs. (18)–(21) shows that the dependence of the defect concentrations on the oxygen partial pressure has been changed. Most importantly, the concentration of the negatively charged defect structons, containing nonbridging oxygens, increases more rapidly with oxygen partial pressure than is the case when M cations do not influence the charge balance. It can be shown that this results in the concentration of this species replacing the electron concentration as the dominant member of the negative side of the electroneutrality Eq. (31), at the same critical value of oxygen pressure as that with no M ions present [Eq. (23)].

The concentrations of the defect species at increasing values of oxygen partial pressure are then found by simultaneous solution of

$$[\langle M^+\rangle] = [\langle S^-\rangle] \tag{44}$$

and Eqs. (1), (3), and (5). The results are as follows:

$$\ln[e^-] = \ln K_i + \ln[\langle M^+\rangle] - \tfrac{1}{2}\ln(K_0 p^{1/2}), \tag{45}$$

$$\ln[h^+] = -\ln[\langle M^+\rangle] + \tfrac{1}{2}\ln(K_0 p^{1/2}), \tag{46}$$

$$\ln[\langle S^-\rangle] = \ln[\langle M^+\rangle], \tag{47}$$

and

$$\ln[\langle S^+\rangle] = \ln K_d - \ln[\langle M^+\rangle]. \tag{48}$$

The oxygen partial pressure range over which these relations hold will be terminated when the hole concentration becomes equal to the M ion concentration, so that the former begins to dominate the positive side of Eq. (31). At still greater values of oxygen partial pressure the presence of M ions will not significantly influence the concentrations of the other defects. As before, they will be given by Eqs. (25)–(28).

The upper oxygen pressure limit for appreciable influence of the M ions on the concentrations of the other defects can be found from

$$[\langle M^+\rangle] = [h^+] \tag{49}$$

and Eq. (46) to be

$$\ln p_{c2,m} = 8\ln[\langle M^+\rangle] - 2\ln K_0. \tag{50}$$

Thus we see that the presence of M ions in a vitreous silicate has a very substantial influence on the equilibrium concentrations of the defect species.

Specifically, it causes the number of negative defect structons, containing nonbridging oxygens, to increase and extends the range of oxygen partial pressure over which ionic disorder predominates over electronic disorder.

Discussion

The purpose of this paper has been to establish a framework upon which a more detailed understanding of the structure of vitreous solids can be constructed. Attention has been focused on the identification of important minority structural species in such materials, and upon their thermodynamic interaction under conditions of local equilibrium. It has been shown how this can be done by the use of methods analogous to those that have been developed for the quantitative description of defect equilibria in crystalline materials.

Only the very simple isothermal cases of pure silica and a dilute solution of the oxide of a monovalent cation in silica have been treated here. Further elaboration can be done in a straightforward manner, following the crystalline analogy. A reasonably detailed review of various applications of these techniques to semiconductors and other nonmetallic crystalline solids is given in Ref. (*22*).

This discussion has been focused on parametric relationships, without attention being given to actual values of the pertinent constants in real systems. Some of these are presently unknown.

The present approach has been based on the assumption that many structure-sensitive properties in solids such as those dealt with here can be related to the types and concentrations of minority close neighbor arrangements (structons). With regard to properties dependent upon majority species, there is a considerable body of evidence supporting the structon point of view. For example, it was shown some time ago (*6*, *7*) that the density of simple silicate glasses can be directly related to the types and numbers of structons present. Since the refractive index, n, is related (*23*, *24*) to the molal refraction, R, and the molal volume, V, by

$$n = 1 + R/V, \tag{51}$$

it is therefore also closely related to the structon concentrations.

Furthermore, the viscosity of vitreous materials is strongly affected by changes in the overall composition and hence in the types and numbers of structons. It is to be expected that the temperature dependence of the viscosity, as well as the thermal expansion coefficient (*25*) and compressibility (*26–28*) of vitreous materials can also be explained in terms of the temperature dependence of their structon compositions. In dealing with such properties, especially the viscosity, it is to be expected that defect structon species will sometimes play a major role, as is the case in metals.

The relationship between the presence and concentration of nonbridging oxygens and phase separation phenomena in glasses has been discussed by a number of authors (*29*). Further investigations of this and related problems in terms of structon equilibria should prove fruitful.

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