OXIDE MELTS

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I. Introduction

Inorganic chemistry is generally concerned with the preparation, structures, and properties of crystalline solids. Relatively little attention is directed towards the fusion products, or melts, of these solids. Studies of liquids, too, have been confined mostly to room temperature work on the molecular liquids such as carbon tetrachloride or the hydroxylic liquids like water and the alcohols. This is not too surprising since most metals and their oxides or halides have high melting temperatures which present additional experimental difficulty in any physicochemical measurements. From an industrial standpoint, it is well-known that an understanding of the nature of oxide melts is of importance in extractive metallurgy and glass technology. Scientifically, however, it is perhaps less widely appreciated that the fusion of oxides can give liquids with structures and properties not only grossly different from one another but from the commonly encountered "room temperature" liquids as well. The quantitative investigation of such high temperature liquids thus represents a new and challenging field in the study of liquids.

Until recently, most of the physicochemical data on molten oxides have been directly obtained from the industrial slags and glasses. These are mainly based on highly complex polycomponent systems and hence not usually amenable to basic interpretation. In the last two decades, however, the increasing interest in high temperature chemistry and the advances in experimental techniques have resulted in a large increase of quantitative studies on simpler melts. These results on the pure oxides, their binary melts, and to a lesser extent, the polycomponent systems are discussed in this review. The experimental aspects, though equally important, are not included since these are readily available elsewhere (*10*).

The emphasis of the present chapter is on the correlation of the physical properties and structures of oxide melts. Since long-range order is destroyed in the process of fusion, the meaning of "structure" is necessarily different for the crystalline solid and its melt. For the latter, structural information is often only obtainable at the present by indirect means such as the comparison of certain properties at a particular temperature. Here, a meaningful interpretation may become doubtful because of the lack of a "corresponding temperature." For instance, if the melting points of two oxides differ by 1000°C, on what basis can a property of their respective melts be compared? For such reasons, some of the conclusions regarding structure discussed below must be considered as qualitative and treated with reservations.

II. Pure Oxides

Instead of adhering to the sequence of the periodic table, the pure oxide melts discussed in this section are being broadly divided into three main liquid *types*. These are the network liquids, the electrically conducting melts and the molecular liquids. It is emphasized that this distinction is not definitive in every case and serves only to illustrate the wide range of liquid properties and structures encountered.

A. NETWORK LIQUIDS

The crystalline oxides, SiO_2, GeO_2, B_2O_3, P_2O_5, and As_2O_3 are commonly known as "glass-formers." On fusion, highly viscous melts of low electrical conductance are obtained which may be easily supercooled to give glasses (*37*). In fact, the crystallization of supercooled liquid B_2O_3 is extremely difficult and can be achieved only under special conditions such as the application of high pressure (*38*). Available information on the glassy and crystalline solids together with that on the liquids indicate that the melts are polymeric. On the average, each cation such as Si or B is surrounded by 3 or 4 oxygens and each oxygen is in turn bonded to two cations to give three or two dimensional networks. The physicochemical data from which this general conclusion is drawn are described below.

1. Viscosity

Although the viscosity values of a particular liquid alone may not furnish much insight into its structure, a comparison between a large number of different liquids can be informative. In Table I, it is seen that for most liquids at the melting temperature, the viscosity is seldom in excess of 0.1 poise. The viscosities of the network liquid oxides are 10^5–10^7 poise. The so-called energy of activation for flow E_η, given by the empirical equation

TABLE I
VISCOSITY AND ENERGY OF ACTIVATION FOR FLOW OF DIFFERENT LIQUIDS AT MELTING TEMPERATURE
[after Mackenzie (*37*)]

Substance	Liquid type	T_m (°C)	Viscosity (poise)	E_η (kcal/mole)
Benzene	molecular	5.5	0.01	2.3
Naphthalene	molecular	80	0.01	—
Octadecane	molecular	28	0.04	4.0
Sulfur	molecular	120	0.1	7.0
Water	hydroxylic	0	0.02	5.1
Methanol	hydroxylic	−98	0.1	2.5
Glycerol	hydroxylic	18	15	13
Stearic acid	hydroxylic	69	0.1	—
Sodium	metallic	98	0.01	1.5
Zinc	metallic	420	0.03	3.1
Iron	metallic	1535	0.07	6.8
LiCl	ionic	613	0.02	8.8
$CdBr_2$	ionic	567	0.03	4.5
Al_2O_3	ionic	2050	0.6	30
As_2O_3	network	309	10^6	23
B_2O_3	network	450	10^5	40
GeO_2	network	1115	10^7	180
SiO_2	network	1710	10^7	180
BeF_2	network	540	$>10^6$	>100

$$\eta = A_\eta \exp (E_\eta/RT) \tag{1}$$

where η is the viscosity and A_η is a constant, is also much larger for the network melts. In the high temperature forms of crystalline SiO_2 and GeO_2, MO_4 groups are linked together by strong M—O bonds (about 100 kcal) to give continuous three-dimensional networks. The very high values of η and E_η for these liquids at the melting temperature thus suggests that much of this three-dimensional network is retained on fusion (*37*).

Although no viscosity measurements have been reported for P_2O_5, some important qualitative information is available (*58*). On fusion of the hexagonal modification of P_2O_5, which is a molecular solid consisting of P_4O_{10} units, a liquid of high vapor pressure is obtained from which no glass has been prepared. However, when either of the orthorhombic forms, both of infinite sheet-type structures, is melted, viscous liquids of lower vapor pressures are obtained which can be supercooled to the vitreous state. In the case of As_2O_3 too, the highly viscous melt is structurally related to claudetite which has a corrugated sheet-type structure and not to arsenolite, the lattice of which is made up of As_4O_6 molecules (*23*). This suggests that the polymeric units in liquid P_2O_5 and As_2O_3 are probably of a two-dimensional nature and differ from those in SiO_2 and GeO_2.

There is considerable controversy regarding the structure of liquid B_2O_3. The magnitudes of η and E_η in Table I correspond to those of the other network melts and are not compatible with a structure involving, for instance, B_4O_6 molecular units, held together by weak Van der Waals forces (*29, 31, 34*). Although the B—O, Si—O and Ge—O bond energies are similar, both η and E_η for liquid B_2O_3 are markedly less than those of SiO_2 and GeO_2 at the melting temperature. The similarity of the flow parameters of B_2O_3 and As_2O_3 in Table I and a consideration of the crystal structures of SiO_2, GeO_2, and As_2O_3 would suggest that the structure of molten B_2O_3 is probably of a layer-type similar to P_2O_5 and As_2O_3 (*37*).

The viscosity-temperature relationships for the network liquids are highly complex and, over an extended temperature range, are not described by Eq. (1) (*40*). Similar to the associated liquids such as water and the alcohols, the energy of activation for flow decreases with increasing temperature. In water, for instance, this has been attributed to a decrease of the degree of association (or the number of H-bonds) with increasing temperature (*19*). Similarly, liquid oxides such as SiO_2 or B_2O_3 have been considered as a special type of associated liquid in which the network is maintained by the Si—O or B—O bonds (*37*). For liquid B_2O_3, E_η decreases from 40 kcal/mole at the melting point (450°C) to about 12 kcal/mole at 1300°C (*40*). For liquid SiO_2 and GeO_2 comparable decreases of E_η have also been observed although the form of the variation of E_η with temperature is grossly different between B_2O_3 and SiO_2 (*37, 40*). By the treatment of viscous flow as a rate process, the entropy of activation for flow, ΔS^*, can be evaluated (*19*). For the network oxides, ΔS^* decreases with increasing temperature and this has been interpreted as further evidence for the decreasing of association (*33, 37*).

2. Electric Conductance

If the fusion of the network oxides does give rise to highly associated liquids held together by strong covalent bonds, the ionic conductivity is expected to be small. In Table II, it is seen that the specific conductivity K of SiO_2, GeO_2, and B_2O_3 at the melting temperature is less than 10^{-5} ohm^{-1} cm^{-1}. For most ionic halides and oxides, K is in the order of unity (*vide infra*). For liquid B_2O_3, it has been demonstrated that the measured conductance is extremely sensitive to small amounts of residual water and other impurities such as alkali oxides (*34*). Dissociation of B_2O_3 itself to yield conducting ions is considered negligible up to at least 1350°C (*34*). From the magnitudes of the energy of activation for conduction, similar conclusions have been drawn for liquid GeO_2 and SiO_2 (*37*, *40*). No measurements are reported for As_2O_3 and P_2O_5 but the present author has suggested that, by analogy, these liquids are expected to exhibit low electric conductivity (*37*).

TABLE II

ELECTRIC CONDUCTIVITY OF SOME NETWORK LIQUIDS AT MELTING TEMPERATURE

Oxide	T_m (°C)	Specific conductivity ($\text{ohm}^{-1}\ \text{cm}^{-1}$)	Reference
B_2O_3	450	$<10^{-6}$	(*34*)
GeO_2	1115	$<10^{-5}$	(*33*)
SiO_2	1710	10^{-5}	(*44*)

3. *Expansivity*

The expansivity α defined as $(1/v)(\partial v/\partial T)_p$, of supercooled liquid SiO_2 is approximately 10^{-6} per degree compared to 10^{-3} per degree for ordinary liquids (*13*). Between 1935° and 2165°C α has increased to approximately 1×10^{-4} per degree (*2*).

The small magnitude of α and its increase with increasing temperature are compatible with those of a network liquid in which the degree of association decreases with rising temperatures. Values of α for liquid B_2O_3 are also in the order of 1×10^{-4} per degree. However, unlike SiO_2, α decreases with increasing temperature (*34*). Thus at 900°C and 1100°C, the respective values of α are 1.06×10^{-4} and 0.60×10^{-4} per degree. To explain this anomalous behavior, a number of plausible models which also satisfy the viscosity and electric conductance data have been postulated. These include (1) the sharing of two oxygens by adjacent borons (*30*), (2) the variation of coordination from three to four (*31*), and (3) the formation of $—B{=}O$ groups, all as a function of temperature (*34*). Unfortunately, direct information to confirm these hypotheses is at present lacking.

4. *Surface Tension*

Unlike most liquids, perhaps with the exception of some liquid metals, the temperature coefficients of the surface tension of B_2O_3, GeO_2, and SiO_2 are positive (*24*, *50*). Some possible causes of this anomaly are (1) a preferred orientation occurring in the surface layer, and (2) dissociation or changes in coordination number with increasing temperature. Kingery (*24*) has indicated that (1) can only be a minor contribution to the observed positive coefficients which are primarily the result of (2). In Table III, it is seen that liquid P_2O_5 has a negative coefficient. The present author has suggested that this may be due to the contribution arising from the molecular modification of liquid P_2O_5 (*37*). It is emphasized that although $d\gamma/dT$ for network liquids may be positive, the reverse is not necessarily true. Thus liquid PbO which is an ionic melt also exhibits a positive coefficient of 0.03 dyne cm^{-1} deg^{-1} (*51*).

TABLE III
SURFACE TENSION OF NETWORK LIQUIDS[a]

Oxide	T (°C)	γ (dyne cm^{-1})	$d\gamma/dT$ (dyne cm^{-1} $°C^{-1}$)
B_2O_3	1000	83	+0.055
GeO_2	1150	250	+0.056
SiO_2	1800 ± 50	307	+0.031
P_2O_5	300	55	−0.021

[a] After Kingery (*24*).

5. X-Ray Diffraction

Although structural information on crystalline oxides has been obtained primarily from X-ray diffraction studies, similar approach with the oxide melts has met with little success. For the solid glasses obtained from the network liquids, it has been demonstrated that coordination numbers calculated from peak areas of radial distribution curves are subjected to serious uncertainty (*56*). Thus Borgen *et al.* (*11*) have shown that for B_2O_3 glass, published values of the coordination number of 3 for boron can be as much as 30% in error. However, interatomic distances can be determined with less uncertainty. Even then, this technique will provide reliable information only on nearest neighbor interactions. For instance, if it is certain that BO_3 triangles are the basic "building" units in liquid B_2O_3, it is presently not possible by X-ray diffraction alone to show how these units are linked together (*36*). Some of the controversial results on the network liquids are examined below.

Herre and Richter (*20*) studied liquid B_2O_3 at 450°C and 600°C. At these temperatures, only two distinct maxima corresponding to interatomic separations $r = 1.38$ Å (B—O) and 2.40 Å (O—O) are found. These values are identical to those found for the solid glass and indicate that at least up to 600°C, the basic structural unit, probably BO_3, is still unchanged. The other maxima at larger values of r observable at room temperature have become diffuse. This was interpreted as an increasing disorder in the melt with increasing temperature. As the solid glass was postulated to have a layer-like structure, this picture was extrapolated for liquid B_2O_3.

Diffraction studies at much higher temperatures have been carried out by Zarcycki (*64*) on liquid B_2O_3 and GeO_2 and supercooled liquid SiO_2. For glassy and liquid B_2O_3, the coordination of oxygen around boron was estimated to be 3.3, 2.3, and 2.2 at 20°, 1200°, and 1600°C respectively. In the case of GeO_2, the coordination number also decreases from 4.4 at room temperature to 3.4 at 1200°C. This decrease of the average coordination was attributed to increasing ionic dissociation with increasing temperature giving rise to free O^{2-} ions. At 1200°C, 30% of the B—O bonds and 23% of the Ge—O bonds are ruptured. If this is correct, the concentration of O^{2-} ions in these network liquids would be 15 and 12% respectively. Besides the experimental uncertainty mentioned above, it has been shown that the presence of such a high concentration of O^{2-} ions in the melt is not compatible with the observed electrical conductivity of these liquids (*29, 37*). For supercooled SiO_2 at 1600°C, the diffraction pattern was similar to that of the glass at room temperature (*64*).

6. *Infrared and Raman Spectra*

The infrared reflection spectrum of liquid B_2O_3 has been studied by Markin and Sobolev (*42*) up to 1000°C. The only effect of temperature is to shift one of the two bands at 1316 cm^{-1} to 1276 cm^{-1}. The other principal band at 720 cm^{-1} appears unchanged even up to 1000°C. It was concluded that the structure of the melt was essentially similar to that of the glass. Since earlier work (*17, 41*) had suggested that B_4O_6 units exist in the glass, liquid B_2O_3 was pictured to be a molecular liquid made up of such dimeric units held together by Van der Waals forces. This has been shown to be incompatible with viscous flow observations (*vide supra*). The infrared absorption spectrum has been examined by the present author up to 1000°C (*35, 39*). In agreement with Markin and Sobolev, the 1265 cm^{-1} band (corresponding to 1316 cm^{-1} by reflection) is shifted to lower frequencies with increasing temperature. However, the 723 cm^{-1} band was not stationary but showed a pronounced shift towards higher frequency at higher temperatures. Attempts to confirm the presence of —B=O groups by studying the absorption between 2000–2800 cm^{-1} was unsuccessful (*39*).

The Raman spectra of liquid B_2O_3 have been examined by Young and Westerdahl (*62*) up to 800°C. The intensity of the 808 cm^{-1} line was found to decrease rapidly with increasing temperature. These authors have also concluded that a major structural change has occurred in the network-like melt which is compatible with a model postulated by the present author (*30*).

The infrared reflection spectra of liquid SiO_2 has also been studied up to 2000°C (*42*). The room temperature 1120 cm^{-1} band of vitreous SiO_2 was found to have shifted to 1054 cm^{-1} at 2000°C and with greatly reduced intensity. No direct interpretation was made.

7. *Nuclear Magnetic Resonance Absorption*

Recently, Silver and Bray (*52*) were able to differentiate and to estimate the relative proportions of three- and four-coordinated borons in binary borate glasses. This technique was thus adopted by the present author in order to ascertain the presence or absence of four-coordinated boron in liquid B_2O_3 (*35*). Glassy samples were quenched in liquid mercury from temperatures up to 1400°C but no four-coordinated boron was detected. (The lower limit of detectability was estimated to be about 2%.) Experiments were also carried out on liquid B_2O_3 up to 500°C but again no four-coordinated boron was found. It thus appeared that at least up to 500 or 600°C, the structural variation of liquid B_2O_3 with temperature is not primarily the result of a boron coordination change of from three to four.

B. ELECTRICAL CONDUCTORS

A large number of oxides which are commonly solid insulators at room temperature (e.g., Al_2O_3) yield highly conducting (specific conductance > 10 ohm^{-1} cm^{-1}) melts on fusion. Some of these melts are undoubtedly ionic conductors whereas others are electronic conductors. It is, however, not always possible to differentiate between these two general types since both mechanisms may be operative to comparable extents at a particular temperature. Relatively few experiments have been reported in which reliable estimates of the transport numbers of either ions or electrons could be made. The subdivision in this section into the two general types of conductors is thus not to be interpreted as rigid.

With few exceptions, these liquid oxides are relatively fluid (10^{-1} to 10^{-2} poise) at the melting temperature. The viscosity of liquid Al_2O_3, for example, at 2050°C is only 0.6 poise (*25*). Geach and Harper (*18*) reported that at the melting temperatures, Cr_2O_3, TiO_2, and V_2O_5 are highly fluid. Because of the similarity of their physical properties, the structures of electrically conducting oxide melts are considered to be not greatly different from that of the fused metal halides (*57*). For the molten halides, X-ray and neutron diffraction studies indicate that in general, the average coordination numbers of the cations are slightly less than that in the corresponding solids (*27*). This together with the volume increase on fusion suggest the presence of "ionic clusters" in a melt with considerable "unoccupied volume" (*27*). No such experiments are reported on corresponding oxide melts to permit comparison.

A summary of most of the early work on conducting oxide melts has been prepared by Van Arkel *et al.* (*57*). These results were based primarily on the fusibility of an oxide in an electric arc furnace. Values of the specific conductance of some of these melts at the fusion temperature, with an uncertainty of ±50%, estimated by these authors are shown in Table IV.

TABLE IV
SPECIFIC CONDUCTIVITY OF SOME OXIDES AT THEIR MELTING TEMPERATURE (*57*)

Oxide	T_m (°C)	Specific conductivity, (ohm^{-1} cm^{-1})
MgO	2800	35
CaO	2580	40
ZrO_2	2600	15
ThO_2	3050	8
Cr_2O_3	2275	65
Al_2O_3	2050	15
TiO_2	1650	10

Other "conductors" for which no quantitative data are available include K_2O, BeO, SrO, BaO, ZnO, SnO_2, MnO_2, CeO_2, and MoO_3 (*57*). At the fusion temperature of 196°C, the specific conductivity of liquid CrO_3 is less than 10^{-6} ohm^{-1} cm^{-1} and the melt is viscous (*57*); it is difficult to classify this as either a network or a conducting melt.

1. *Electronic Conductors*

The specific conductivity of a large number of oxide melts is in excess of 1 ohm^{-1} cm^{-1} and the temperature coefficient of conductance is positive. Two types of experiments from which conclusions are drawn regarding the mechanism of conduction are to be found in the literature. In one, the applicability of Faraday's laws is directly tested. In the second case, the conductivity of both the crystalline solid up to the melting point and that of the melt is measured; if the change in specific conductivity on fusion is negligible, and if the so-called activation energy E_K defined by

$$\mathrm{K} = A_K \exp(-E_K/RT) \tag{2}$$

is similar for both solid and liquid, then the material is considered to be a semiconductor. Unfortunately, the disparity of the results of many workers for both solids and melts, the possibility of superheating and supercooling and the inapplicability of Eq. (2) often create uncertainty over conclusions based solely on the latter approach.

The conductivity of liquid FeO has been measured by Inouye *et al.* (*21*) up to 1500°C. Solid FeO is known to be a *p*-type semiconductor deficient in Fe. The high specific conductivity of about 120 ohm^{-1} cm^{-1} at the melting temperature of 1370°C, the absence of a marked change of conductance on fusion, and the positive temperature coefficient indicate that a similar mechanism is operative in the melt. Supporting evidence was obtained by

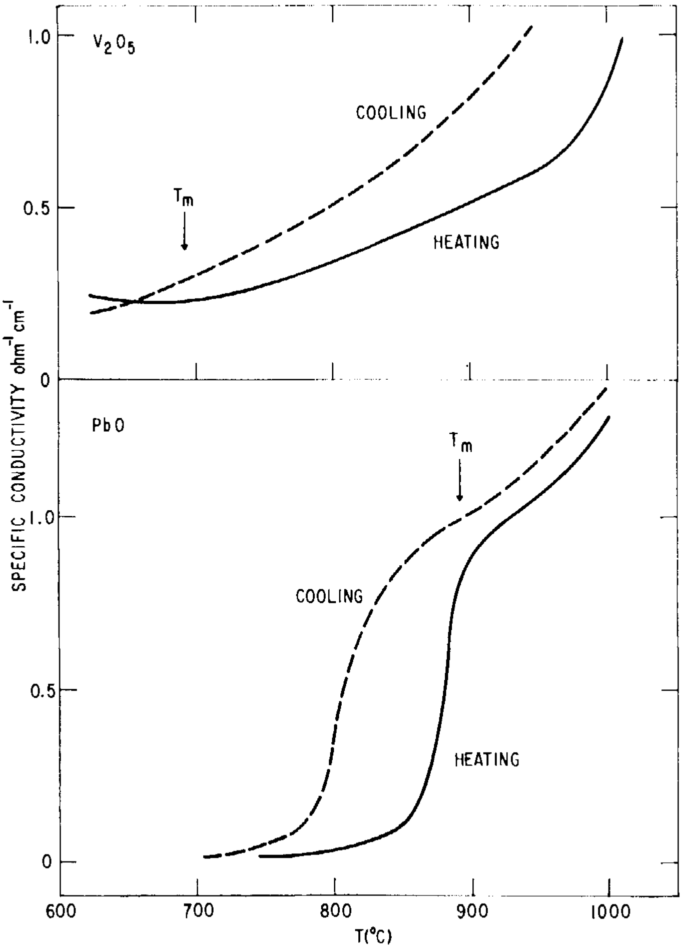


FIG. 1. Specific conductivity of V_2O_5 (semiconductor) and PbO (ionic conductor) (*16*).

the absence of electrolysis. A value of 5 kcal/mole evaluated for E_K was considered to be not meaningful by the authors since the Fe/O ratio is temperature dependent. Other predominantly electronic conductors are liquid CoO, NiO, and Cu_2O. The ionic transport numbers of these melts at the fusion temperature are estimated to be less than 10^{-3} (*46*). The negligible participation of ions in the conduction process in a highly fluid melt is not understood. The addition of SiO_2 to these oxides causes the ionic transport numbers to increase. Thus the mechanism of conduction in liquid FeO containing 25 mole-% of SiO_2 is 50% ionic (*53*) and that in liquid CoO with 27 mole-% SiO_2 is 70% ionic (*1*).

By comparing the specific conductivity/temperature relationships of both solid and liquid V_2O_5 and PbO, Esin and Ziazev (*16*) were able to demonstrate that liquid V_2O_5 was a semiconductor. Their results are reproduced in Fig. 1. It is seen that for V_2O_5, no marked change of specific conductivity is found in the vicinity of the melting point. Other semiconducting oxide melts are CuO (*16*), Bi_2O_3 (*22*), MnO (*15*), and TiO_2 (*57*). The addition of substantial amounts of ionic oxides ($>20\%$, say) such as PbO, MgO, and CaO to V_2O_5 generally results in an ionic melt (*65*). Ziazev and Esin (*65*) have pointed out that the composition at which the mechanism of conduction changes sharply usually corresponds to that of a stable crystalline phase. It is thus suggested that short-range order is an important factor in the predominance of one mechanism over another.

2. Ionic Conductors

Besides PbO which shows a large change in conductivity in the vicinity of the melting point (Fig. 1), liquid Li_2O is probably an ionic melt. The specific conductivity of the solid near the melting temperature of 1570°C is about 10^5 ohm^{-1} cm^{-1} but that of the melt is 7 ohm^{-1} cm^{-1} (*57*). The latter value is comparable to that of molten LiCl, but the increase on fusion is even greater than the halides. By analogy, other molten alkali oxides are probably also ionic conductors.

For the oxides in Table IV, specific mention was made by Van Arkel *et al.* (*57*) that liquid TiO_2 is expected to be a semiconductor. No suggestion was made regarding the nature of the other melts. Ziazev and Esin (*65*) however, suggest that liquid CaO and MgO are ionic conductors whereas Tomlinson (*54*) maintained that these are semiconductors. The values of the conductivity of these two liquid oxides obtained by Tomlinson are not markedly different from the *extrapolated* values of the corresponding solids to the melting points. Conductivity data obtained at below 1800°C for the systems CaO—SiO_2 and MgO—SiO_2 were extrapolated to 2580°C and 2800°C respectively. (Melting temperatures of CaO and MgO.) These extrapolated values are some 10–100 times larger than the values of the pure liquid oxides obtained by Tomlinson. This was interpreted as an indication of semiconduction since the conductivity is so sensitive to minor additions of SiO_2. However, it can be demonstrated that such conclusions are not entirely valid. Firstly, it is *not* a characteristic of liquid oxide semiconductors that the conductivity is highly sensitive to small amounts of impurities. Both Tomlinson's own work on FeO (*21*) and other studies

(*1, 53, 65*) have clearly established this fact. Secondly, the use of Eq. (2), for instance, to make extrapolations over a range of as much as 1000°C is questionable. Thirdly, if the values of Van Arkel *et al.*, for liquid CaO and MgO are adopted instead, then (a) a large change in conductivity is seen to occur at the melting temperature and (b) the effects of the addition of SiO_2 to CaO and MgO are only gradual. This latter treatment would suggest that liquid CaO and MgO are both ionic liquids.

The data of Inouye *et al.* (*21*) on the system FeO—Al_2O_3 containing only 5 mole-% Al_2O_3 were incorrectly interpreted by Ioffe and Regel (*22*) that pure liquid Al_2O_3 is a semiconductor. Actually, the extrapolated specific conductivity of solid single-crystal Al_2O_3 at the melting temperature of 2050°C is approximately 10^{-2} ohm^{-1} cm^{-1} (*45*). The value for the melt at this temperature is 15 ± 8 ohm^{-1} cm^{-1} (*57*). There is thus a large increase of conductivity on fusion. In the absence of more reliable data, the present interpretation is that liquid Al_2O_3 is probably an ionic conductor as well.

C. MOLECULAR LIQUIDS

In the preceding sections it has been shown that most metal oxides are high melting and that on fusion, two general types of melts are obtained: (a) the network liquids which are characterized by high viscosity and low electrical conductivity, and (b) the ionic and semiconductors which are highly fluid. The oxides OsO_4 and RuO_4 yield yet another different liquid type on fusion.

The melting temperature of OsO_4 is 41°C and the boiling point is 130°C. The melt is fluid and nonconducting (*57*). The crystal is composed of OsO_4 tetrahedra separated by Van der Waals forces (*63*). Raman and infrared absorption studies have revealed that this structure persists in the melt (*61*). Other physical properties of liquid OsO_4 such as density-temperature relationship (*12*), are also similar to those of normal liquids like CCl_4. Much less information is available on liquid RuO_4. At the even lower melting temperature of 25°C, the melt is also nonconducting (*26*). It is likely, therefore, that similar to liquid OsO_4, molten RuO_4 is a molecular liquid.

III. Binary Systems

Primarily because of industrial interests in glass and slags, and, to a less extent, of the relative ease of experimentation, most of the binary liquid oxide systems studied have been silicates and borates. Hence these will be the only systems to be discussed in this section.

A. BINARY SILICATES

In silica and in almost all crystalline silicates, the basic "building" unit is the SiO_4 tetrahedron (*60*). Within the limits of experimental uncertainty, this is also true for glassy silicates (*56*). It is generally agreed that no departure is expected in binary silicate melts at temperatures not far above the liquidus or melting point (*28*). By binary liquid silicates, we mean a homogeneous single liquid containing silica and one other metal oxide such as Na_2O or CaO. In liquid SiO_2, it has been shown (*vide supra*) that these SiO_4 tetrahedra are bonded together to give large polymeric units or a network liquid. The main structural problem in the case of the binary liquid silicates is thus the manner in which these SiO_4 groups are linked together when the composition or the temperature is varied. In this section, some of the physicochemical properties of liquid silicates are first examined. A discussion of the present structural concepts will then be made.

1. Electrochemical Measurements

A detailed review of these studies has already been made elsewhere (*28*) and hence only a summary of the more important findings are presented here. With no known exceptions, the addition of metal oxides to SiO_2 increases the specific conductance of the melt. When the concentration of metal oxides is appreciable, say, 50 mole-%, the magnitude of the specific conductivity is comparable to that of the fused halides (*4*). Over fairly wide ranges of temperature, for instance, 100–200°C, Eq. (2) is obeyed. The activation energies for conduction, E_K, for a large number of binary melts are shown in Fig. 2. It is seen that a marked difference exists between

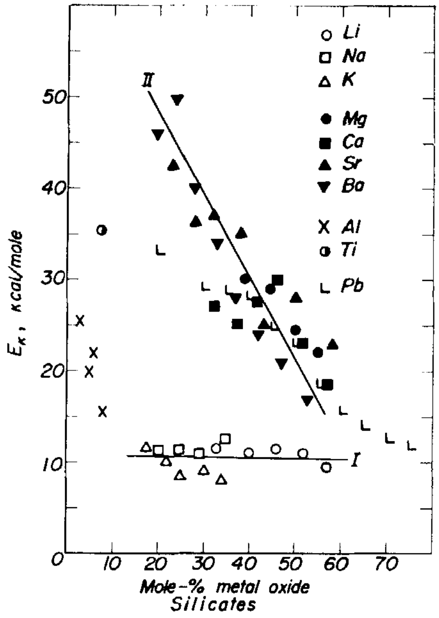


FIG. 2. Energy of activation for electrical conduction in binary liquid silicates (*28*).

TABLE V
ELECTRICAL CONDUCTION IN BINARY LIQUID SILICATES

System and composition	T (°C)	Specific conductivity ($\text{ohm}^{-1}\ \text{cm}^{-1}$)	Conduction mechanism	Reference
$Li_2O{\cdot}SiO_2$	1300	0.1	Ionic	(*4, 5*)
$CaO{\cdot}2SiO_2$	1650	0.2	Ionic	(*3, 5*)
$PbO{\cdot}SiO_2$	1000	0.1	Ionic	(*8*)
$1.2MnO{\cdot}SiO_2$	1350	1.0	Ionic	(*3, 5*)
$19FeO{\cdot}SiO_2$	1400	125	10% Ionic	(*21, 53*)
$2FeO{\cdot}SiO_2$	1400	5	90% Ionic	(*53, 59*)
$3CoO{\cdot}SiO_2$	1450	—	Electronic	(*1*)
$2.75CoO{\cdot}SiO_2$	1450	—	72% Ionic	(*1*)
$2.5CoO{\cdot}SiO_2$	1440	—	95% Ionic	(*1*)

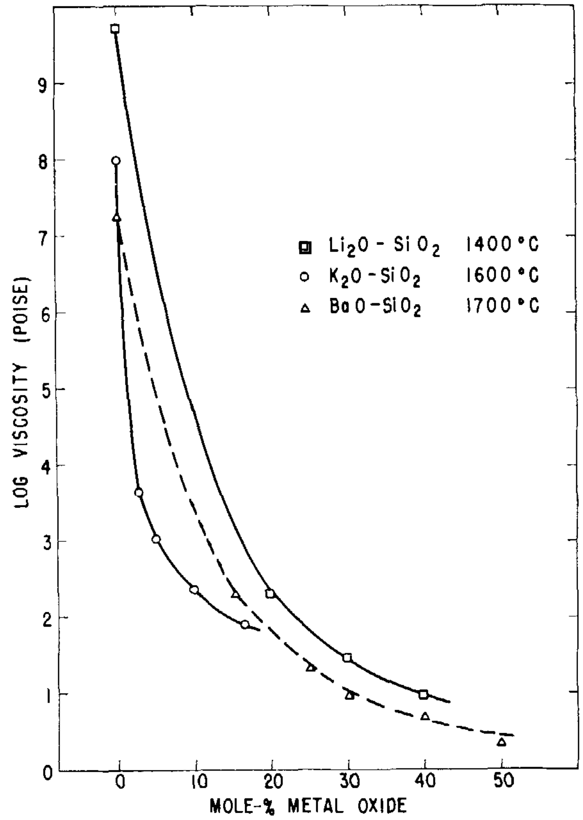


FIG. 3. Effects of metal oxides on the viscosity of binary liquid silicates (*37*).

the alkali and the alkaline earth silicates. Electrolysis and transport number measurements have been carried out on a number of binary liquid silicates (*1*, *5*, *8*). Except for melts containing a large amount of some metal oxides, for instance, 75 mole-% of FeO and CoO, the mechanism of conduction is predominantly ionic. The transport number of the cations is invariably unity. Some of these results are given in Table V.

2. Viscous Flow

Whereas electric conduction in the molten silicates is predominantly a cationic process, viscous flow involves the motion of both ionic species and is expected to furnish more information on the larger anions. Some recent systematic studies have indeed confirmed this (*5*, *6*). The addition of even small amounts of metal oxides to silica can reduce the viscosity very appreciable. In Fig. 3, for instance, the addition of only 2.5 mole-% of K_2O to SiO_2 is seen to reduce the viscosity at 1600°C from 2×10^7 poise to 2×10^3 poise. In general, over temperature ranges up to 200°C, Eq. (1) is applicable. Large reductions of the energy of activation for flow E_η are also brought about by the presence of metal oxides. The variations of E_η with composition are shown in Fig. 4. These studies reveal that a large structural change

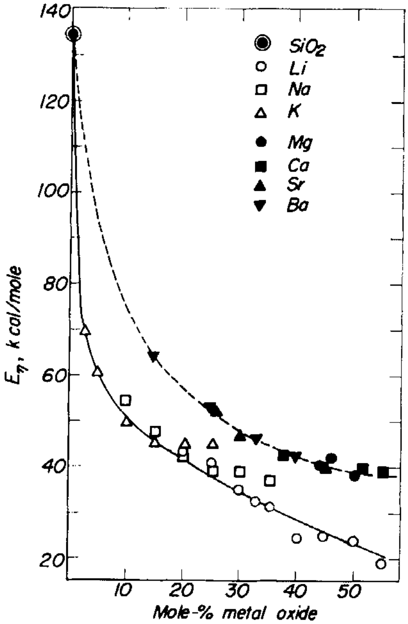


FIG. 4. Energy of activation for viscous flow in binary liquid silicates (*28*).

occurs when small amounts of metal oxides are present. When the concentration of metal oxides is in excess of about 20 mole-%, the change becomes more gradual. The higher values of E_η over E_K (Figs. 4 and 2) are indicative of the different roles played by the two ionic species in the two processes of viscous flow and electrical conduction.

3. Thermal Expansion and Partial Molar Volume

Some important features regarding the structures of liquid silicates are revealed by recent volumetric studies of both alkali (*9*) and alkaline earth systems (*55*). First, the partial molar volume of silica in the alkali silicates is nearly equal to that of pure fused silica and is independent of the cation over wide compositional ranges. Second, at about 10–15 mole-% metal oxides, the thermal expansions show a sudden increase. The results for the alkali silicates are shown in Fig. 5. A similar behavior is found in the system $BaO—SiO_2$ (*55*). At equimolar compositions above 20 mole-% metal oxides, the expansivity is in the descending order of K, Na, Li, Ba, Sr, Ca, and Mg and is inversely proportional to the so-called "ion-oxygen attraction" defined as $I = 2ze^2/r^2$ where z is the cationic valence, e is the electronic charge, and r is the separation between the metal and oxygen ions (*55*). The ionic nature of these melts is further confirmed. Relationships were also obtained between the cationic radii and molar volumes which suggest that the volumes of the *silicon-oxygen anions* at any composition are comparable for all the binary systems (*55*).

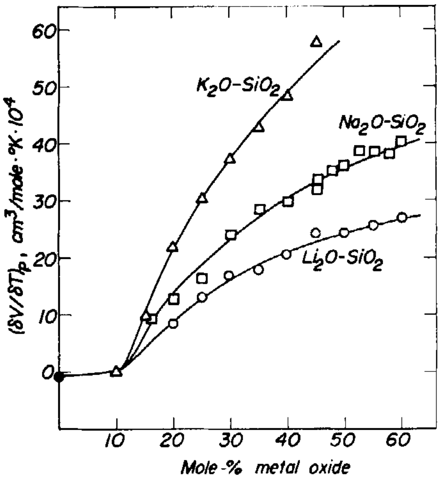
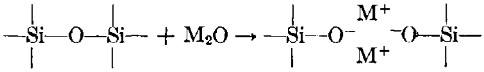


FIG. 5. Thermal expansion of binary alkali silicates at 1400°C (*9*).

4. Structural Models

Physicochemical measurements on the binary silicates have revealed the following features: (1) the melt is made up of small cations and relatively large anions; (2) the anions are made up of SiO_4 tetrahedra linked together in such a way that the partial molar volume of SiO_2 is not subject to large variations with composition; (3) there is a large change of structure at between 10–20 mole-% metal oxides; (4) from this approximate composition to about 66 mole-%, i.e., the orthosilicate composition, structural variations have become more gradual; and (5) over a temperature range of 100–200°C from the melting or liquidus temperatures upwards, there is probably no dissociation of the anions. Any structural model postulated must therefore be compatible with these experimental findings.

The first detailed "ionic" model of melt structure is that of Endell and Hellbrügge (*14*). According to these workers, the addition of a metal oxide to silica causes the progressive breakdown of the three dimensional network. The reaction may be formally represented by:



$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + M_2O \rightarrow -\overset{|}{\underset{|}{Si}}-O^{-}\overset{M^+}{\underset{M^+}{\quad}}{}^{-}O-\overset{|}{\underset{|}{Si}}-$$

The limit of this "breakdown" is reached at the orthosilicate composition (66 mole-%) when the melt consisted primarily of discrete SiO_4^{4-} anions and the cations. In analogy with the crystalline silicates, it was postulated that at 50 mole-% metal oxide, infinite chains or rings are present in the melt. The mineral, wollastonite, ($CaO{\cdot}SiO_2$), is built up of $Si_3O_9^{6-}$ rings and Ca^{2+} ions. It is not unreasonable to expect that at the melting temperature, the liquid may be depicted by the idealized two dimensional representation of Fig. 6. Between 50 and 33 mole-% metal oxides, analogous to the pyroxenes and micas, infinite silicon-oxygen chains and sheets constitute respectively the anionic portion of the melt. This model is not entirely satisfactory in view of the large structural change occurring at 10–20 mole-% metal oxide and the subsequent more gradual variations.

Recently, Bockris and co-workers (*6*, *7*, *9*) have modified the above model to satisfy the experimental findings outlined in (1) to (5). In place of infinite chains and sheets, smaller anions the sizes of which are directly proportional to the concentration of SiO_2 in the melt, were postulated. Thus at 33 mole-% metal oxide, the anions present may be $(Si_6O_{15})^{6-}$ or $(Si_8O_{20})^{8-}$. Although this later "ionic" model is entirely compatible with available physicochemical data, it must be emphasized that, at present, direct proofs of the existence of the anions postulated are lacking.

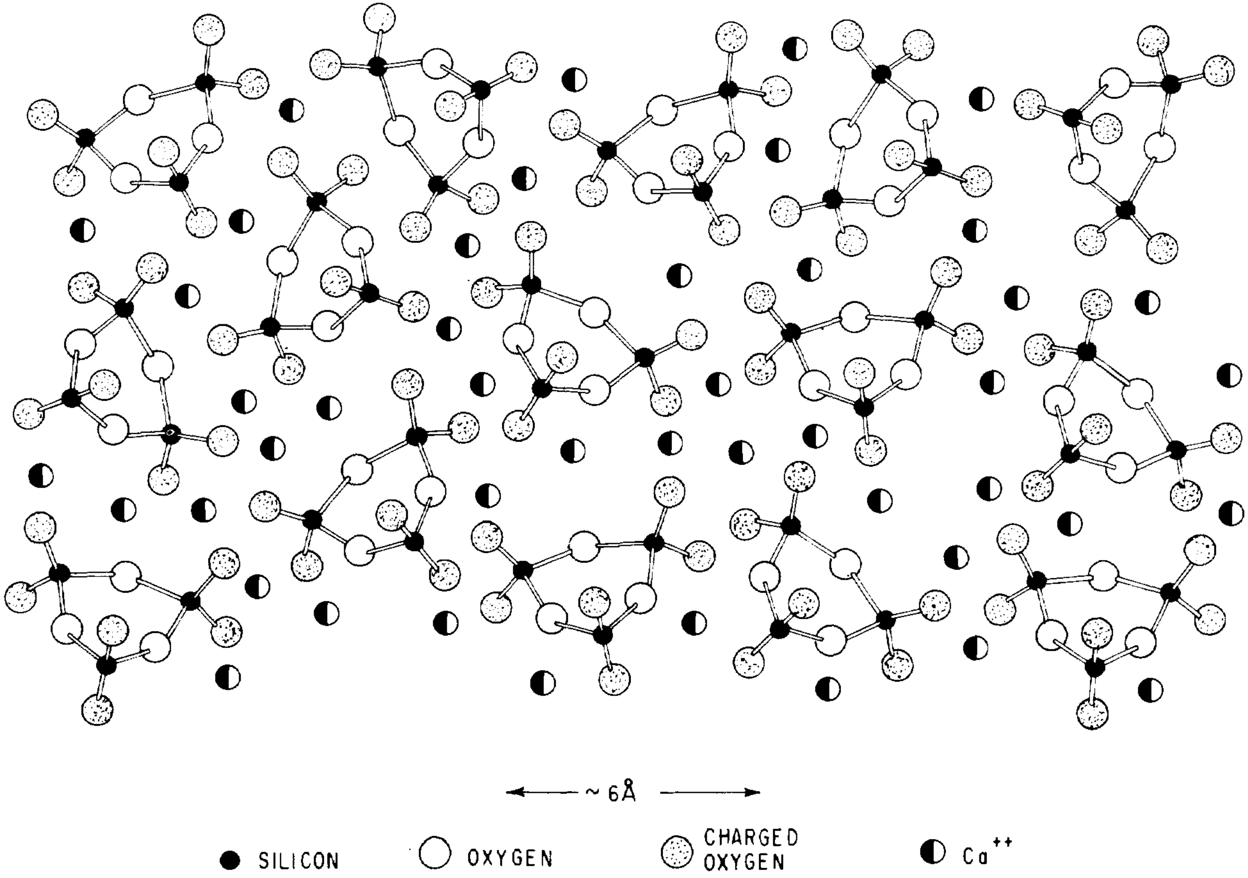


FIG. 6. Idealized two dimensional representation of liquid wollastonite ($CaO{\cdot}SiO_2$) at the melting temperature.

B. BINARY BORATES

Compared to the silicates, only a few systematic physico-chemical measurements have been carried out on the binary borates. Whereas in silica and silicates the SiO_4 tetrahedron is the only "building" unit, both BO_3 and BO_4 groups are known to be present in crystalline and glassy borates (*52*, *60*). Structural interpretations similar to those for the silicates are thus more difficult. At present, no satisfactory model exists for the binary borates. Some very interesting results are, however, available and these will be discussed below.

1. *Electrical Measurements*

As expected of a network liquid, the electrical conductivity of liquid B_2O_3 increases with increasing concentration of metal oxides. The specific conductivity of liquid alkali borates containing only 1 mole-% metal oxide is approximately ten times greater than that of "pure" B_2O_3 (*47*). Some typical conductance values of liquid borates are shown in Table VI. At high concentration of metal oxides, the specific conductivity may be in excess of 1 ohm^{-1} cm^{-1}, similar in magnitude to those of the fused salts and fused silicates. The energy of activation for conduction is also similar to the liquid silicates as shown in Fig. 7. It is interesting to note that although the behavior of the alkali and the alkaline earth borates and silicates is similar, the systems containing PbO are very different. The temperature coefficient of conductance is again positive, and although no electrolysis and transference experiments have been reported on the melts, measurements on glassy $Na_2O—B_2O_3$ at 300°C indicated that Faraday's laws are obeyed and that the transport number of the Na^+ ion is unity (*43*). It seems certain, therefore, that the liquid borates may also be classified as ionic liquids.

TABLE VI
SPECIFIC CONDUCTIVITY OF LIQUID BINARY BORATES

System	Mole-% metal oxide	T (°C)	Specific conductivity (ohm^{-1} cm^{-1})	Reference
$Li_2O—B_2O_3$	9.9	990	0.054	(*47*)
	28.8	1006	1.12	(*47*)
$Na_2O—B_2O_3$	1.0	1003	0.0017	(*47*)
	34.4	1008	1.36	(*47*)
$CaO—B_2O_3$	31.2	1204	0.10	(*48*)
	54.4	1197	0.29	(*48*)
$PbO—B_2O_3$	1.0	1050	0.0002	(*8*)
	50.0	1050	0.51	(*8*)

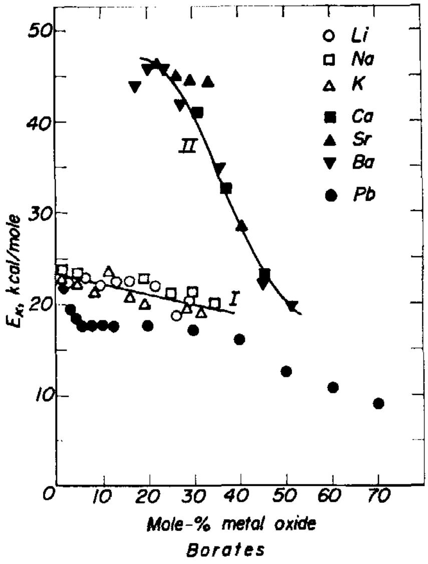


FIG. 7. Energy of activation for electrical conduction in binary liquid borates (*28*).

2. Viscosity

Although the addition of small amounts of metal oxide to B_2O_3 is effective in reducing the viscosity, the decrease is much less than that for the silicates. Thus the ratio of the viscosity of silica to that of a silicate containing 2.5 mole-% alkali oxide at 1700°C is about 10^4. The corresponding ratio for the borates vary from only 1.5 at 600°C to 6 at 1000°C (*47*). Some of these results are shown in Fig. 8. Further, the energy of activation for flow *increases* with increasing alkali metal oxide (Fig. 9). This is directly opposite to the behavior of the liquid silicates. In solid borate glasses, BO_4 groups are formed as a result of the addition of alkali metal oxides to B_2O_3 (*52*). It is likely that similar reactions occur in the liquid borates to cause the anomalous flow behavior.

3. Density

A number of interesting phenomena related to the structure of binary liquid borates have been revealed by the work of Shartsis *et al.* (*48*, *49*). The density of the alkali borates increases with increasing metal oxides up to a maximum at about 30 mole-% and then decreases sharply. The results at 1000°C are shown in Fig. 10. The expansivity at high temperatures, similar to the silicates, also increases with metal oxide content. However, unlike the silicates, there is no sharp "break" (cf. Fig. 5) and, secondly, the expansivity of the systems $Li_2O—B_2O_3$, $Na_2O—B_2O_3$, and $K_2O—B_2O_3$

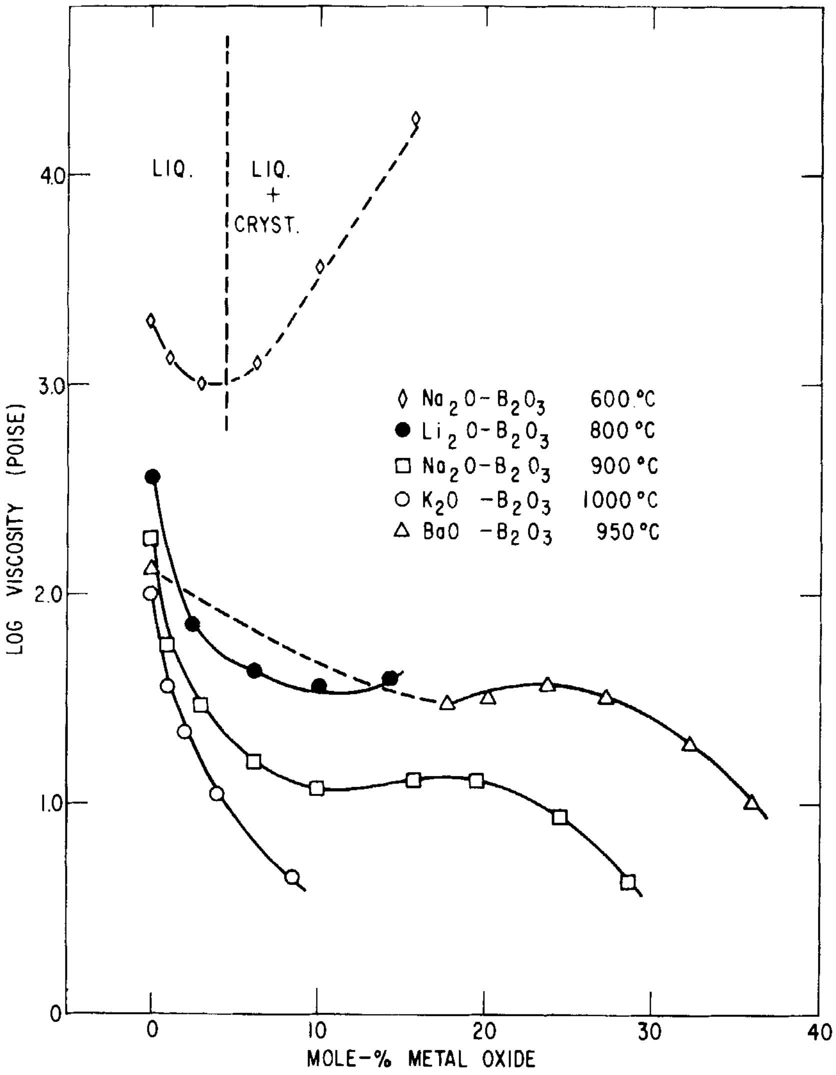


FIG. 8. Effects of metal oxide on the viscosity of binary liquid borates (*47*, *49*).

is similar over wide ranges of composition (Fig. 10). At low concentrations of metal oxides, below about 10 mole-%, the expansivities over the range 25–1000°C are higher than both of those of the liquid at 900°C and of the solid glass. There is thus a temperature range between the glass transition and the liquid regions in which a large expansion must take place. Unfortunately, no actual measurements are made over this temperature range.

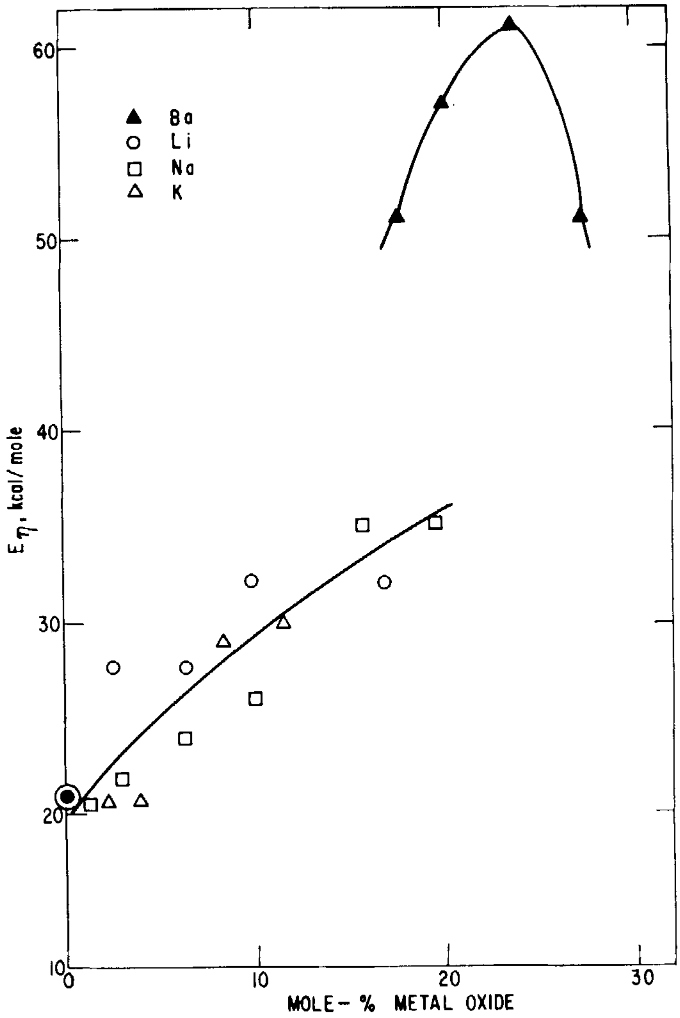


FIG. 9. Energy of activation for viscous flow in binary liquid borates at 900–1000°C (*37*).

From the volume of melt containing one mole of boron, Shartsis *et al.* (*48*) have estimated the average B—B distance as a function of composition. When small amounts of metal oxides are added to B_2O_3, there appears to be a contractive effect giving rise to a decreasing B—B distance in the order Li > Na > K. At 1000°C, for instance, the average B—B distance in liquid B_2O_3 is estimated to be 3.35 Å. In a liquid borate with 20 mole-% Li_2O, this distance is now only 3.22 Å. Similar tendency is exhibited by the alkaline earth melts although the effect is less well defined (*49*).

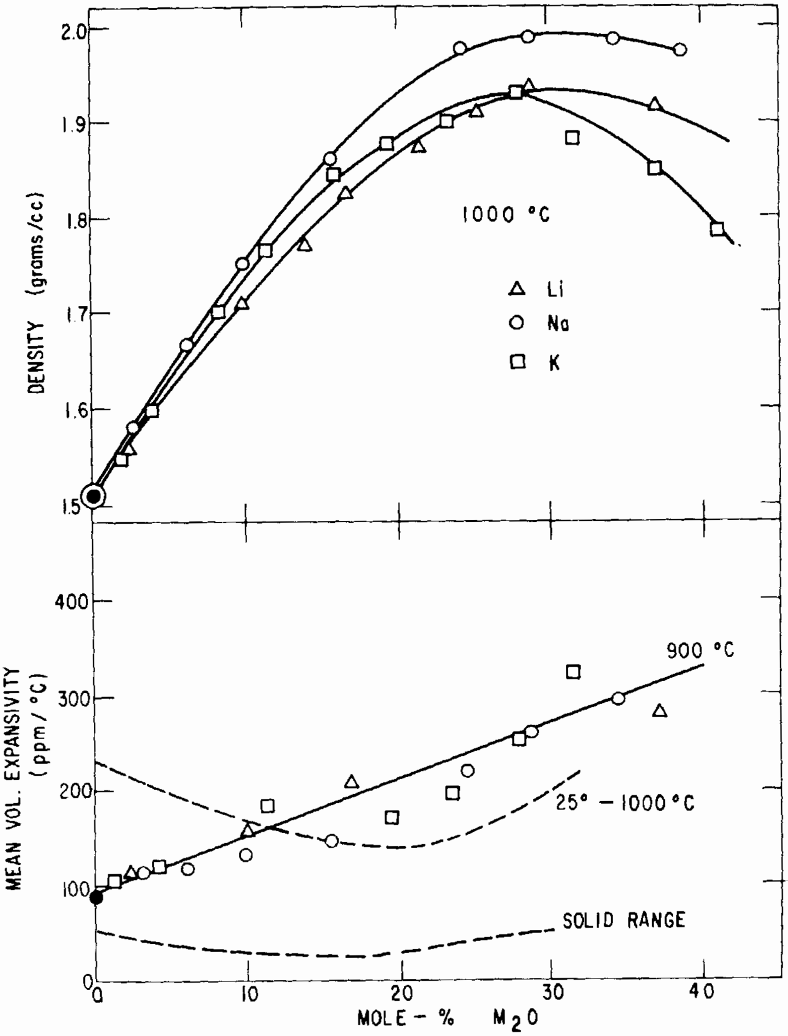


FIG. 10. Density and expansivity of binary alkali borates (*48*).

4. Structural Considerations

Although electrical measurements have confirmed the ionic nature of borate melts, viscous flow and volumetric studies clearly indicated their difference from liquid silicates. Shartsis and co-workers (*47*) have suggested that an equilibrium exists in the melt between BO_3 triangles and BO_4 tetrahedra, this being both temperature and composition dependent. The only ionic model for the borates is that of Bockris and Mellors (*8*) which does not take into consideration the presence of BO_4 groups. Such treatment is thus not entirely satisfactory. It may be concluded that the present status regarding the structures of borate melts is far less satisfactory than that for the silicates.

IV. Polycomponent Systems

Polycomponent systems of liquid oxides studied have mostly been silicates. Detailed discussions of these systems are beyond the scope of the present review. Perhaps the most important feature regarding polycomponent liquid silicates is their ionic nature. This may be conveniently illustrated by recent studies on the viscosity of some of these melts.

In Fig. 4, it is seen that for the alkali silicates, over wide composition ranges; the energy of activation for flow E_η is similar for the different cationic species present. This is also true for the binary alkaline earth systems. It has been found that the pre-exponential factor A_η of Eq. (1) is also independent of the cation within each group (*32*). Thus the mechanism of flow and possibly, the viscosity, in a binary melt containing one cation of a particular group should be similar to that of any polycomponent melt with two or more cations of the same group as long as the *total* molar concentrations of metal oxides are equal. If liquid silicates are regarded as ideal mixtures, then the energy of activation for flow should be given by:

$$E_\eta = N_A E_A + N_B E_B \tag{3}$$

where N_A and N_B are the mole fractions of two binary melts and E_A and E_B their respective activation energies. The viscosity of polycomponent melts too can be similarly calculated if the composition and the viscosity of the binary systems are known. Based on this simple picture of a similar silicon-oxygen anionic species for different systems at the same composition, surprisingly good agreement has been obtained between calculated and measured values of E_η and η for a large number of complex melts (*32*).

Polycomponent liquid oxides containing Al_2O_3, however, are not amenable to such simple treatment on account of the possibility of the formation of both AlO_4 and AlO_6 groups (*25*). No hypothesis regarding the nature and molecular structure of such anions has been made.

V. Summary and Conclusions

Pure oxide melts can be divided into three general types: (a) network liquids, for example, SiO_2, (b) ionically (Li_2O) or electronically conducting (FeO) melts, and (c) molecular liquids, for instance, OsO_4. Binary melts containing SiO_2 and a metal oxide such as Na_2O or CaO are ionically conducting. It seems probable that the melt is composed of small cations and large silicon-oxygen anions the "building" unit of which is the SiO_4 tetrahedron. Although the ionic nature of binary borate melts is established, little is known of the anionic species because of the ability of boron to form both BO_3 and BO_4 groups. The simple ionic model for the binary silicates is applicable to polycomponent melts except in the presence of Al_2O_3 which may result in the formation of AlO_4 or AlO_6 groups.

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