THE PHYSICAL CHEMISTRY OF SIMPLE MOLTEN GLASSES

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I. INTRODUCTION

A liquid is now generally regarded as a disordered version of a solid rather than as a compressed gas. Although the long-range order exhibited by crystals is no longer present in the liquid state, a short-range order still persists. The application of this concept to the inorganic melts of systems such as metal oxide–silica, metal oxide–boron trioxide, and metal oxide–phosphorus pentoxide is of particular importance and interest, since the structures of the crystalline solids have been extensively studied, and most of these liquids upon cooling form glasses, in which the liquid structure is to some extent retained.

From a technological point of view, the properties and constitution of these molten glasses are of importance not only to the glass technologist but also to the extraction metallurgist as slags, and to other industrial chemists as, for instance, condensed phosphates. However, predominant industrial interest has led to a concentration of experimental work on polycomponent systems, the complexity involved making interpretations difficult. Another cause of this tardy progress is the usual experimental difficulties encountered in high-temperature studies, such as the corrosive properties of most inorganic melts.

Recently, an increasing number of basic studies have been made on the simpler binary systems by the application of a wide range of physicochemical methods. A considerable amount of work has been reported on the molten silicates and some on the borates and phosphates. Because of the divergence of the immediate interests of the workers, the approaches have been different and the information scattered. The object of this review is to present a systematic treatment of the results on these three different binary molten systems with particular emphasis on the structural aspects. Thermodynamic studies in this field have been concentrated on slag–metal equilibria; since they have made few impressive contributions to our knowledge of the structure of these melts, they will not be treated here. Two reviews on this topic are available (47, 48). Most of the work treated here has been published only in the last few years and is confined to measurements above the liquidus temperatures. Results of earlier workers, mainly on the more complex multicomponent silicates, are to be found elsewhere (18).

II. ELECTRIC MEASUREMENTS

Up to the beginning of the last decade, controversial views existed concerning the constitution of molten glasses and slags. According to the "molecular theory," undissociated molecules and compounds such as Ca_2SiO_4 and $Na_2Si_2O_5$ are present in the melt (46, 52, 67). The "ionic theory," however, maintains that electrolytic dissociation is complete and that electroneutral molecules are entirely absent in the molten state (21, 26, 42, 66). Liquid silicates, borates, and phosphates are, therefore, high-temperature ionic liquids, similar to the molten salts, in which a coulombic force field exists. A direct test of the correctness of this latter hypothesis should be possible from studies of conductivity, electrolysis, and transport number, and it was the result of these electric measurements which has led to the eventual rejection of the "molecular" concept (10).

A. Conductance

Most of the electrochemical studies on binary oxide melts have been focused on conductivity measurements because of the possibility of obtaining a measure of the magnitude and nature of the intermolecular forces in these liquids (4). The first systematic study on the silicates was carried out on the systems Li_2O–SiO_2, Na_2O–SiO_2, and K_2O–SiO_2 over the temperature range 1250–1450°C. and the composition range 10–50 weight per cent metal oxide (20, 21). The specific conductivity increased with increasing metal-ion concentrations and fluidity; for similar ionic concentrations, it increased with the cationic radii. It was suggested that conductance was a property governed solely by the cations in the melt. This was confirmed by recent more extensive studies (7, 8) up to 1800°C. covering the systems Li_2O–SiO_2 (33–57 mole per cent Li_2O), Na_2O–SiO_2 (20–34 mole per cent Na_2O), K_2O–SiO_2 (17–34 mole per cent K_2O), MgO–SiO_2 (39–55 mole per cent MgO), CaO–SiO_2 (27–60 mole per cent CaO), SrO–SiO_2 (24–58 mole per cent SrO), BaO–SiO_2 (21–54 mole per cent BaO), MnO–SiO_2 (35–77 mole per cent MnO), Al_2O_3–SiO_2 (1–7 mole per cent Al_2O_3), and TiO_2–SiO_2 (8 mole per cent TiO_2). The composition limits were imposed by the volatility of the metal oxides, by their immiscibility, and by refractory failures at the higher temperatures. Some of these and other results are summarized in table 1.

All the results obeyed the Rasch–Hinrichsen law (50):

$$\kappa = A_\kappa \exp(-E_\kappa/RT) \qquad (1)$$

where κ is the specific conductance, A_κ is a constant, and E_κ is the energy of activation for conductance.

The predominant ionic nature of the liquid silicates is demonstrated by the following evidence (8): (*a*) conductivity is of the same order of magnitude as for

TABLE 1

Specific conductivity of molten binary silicates

System	Metal Oxide	Temperature	Specific Conductivity	Reference
	mole per cent	°C.	*ohm*$^{-1}$ *cm.*$^{-1}$	
Li_2O-SiO_2	33	1750	2.5	(8)
	50	1750	5.5	(8)
	66	1750	23.2*	(8)
	50	1300	0.12	(21)
Na_2O-SiO_2	33	1750	2.1	(8)
	50	1750	4.8*	(8)
	50	1300	0.07	(21)
K_2O-SiO_2	33	1750	1.5	(8)
	50	1750	2.4*	(8)
	50	1300	0.16	(21)
MgO-SiO_2	33	1750	0.23*	(8)
	50	1750	0.72	(8)
CaO-SiO_2	33	1750	0.31	(7)
	50	1750	0.83	(7)
SrO-SiO_2	33	1750	0.21	(8)
	50	1750	0.63	(8)
BaO-SiO_2	33	1750	0.18	(8)
	50	1750	0.60	(8)
MnO-SiO_2	50	1750	1.8	(7)
	66	1750	6.3	(7)
Al_2O_3-SiO_2	6	1750	3×10^{-3}	(7)
TiO_2-SiO_2	8	1750	6×10^{-4}	(8)
PbO-SiO_2	30	1000	5×10^{-3}	(43)
	50	1000	0.11	(43)
	70	1000	0.72	(43)
	90	1000	2.4	(43)
FeO-SiO_2	50	1350	0.68	(70)
	66	1350	4.6	(70)
	83	1400	24.0	(31)
	95	1400	125	(31)

* Extrapolated values.

the molten salts; (*b*) the temperature coefficient of conductance is positive; (*c*) the ratio of the conductance above and below the liquidus temperature is about 100; and (*d*) passage of current through the melt produces electrolysis. Although further support of the ionic concept is available from independent measurements on the systems Na_2O–SiO_2, CaO–SiO_2, and MnO–SiO_2 (44), an unambiguous conclusion can only be reached from studies of the applicability of Faraday's laws. Results of the PbO–SiO_2 system are also in general agreement with the above evidence, although individual conductance data showed slight variance (32, 43, 51).

The system FeO–SiO_2 is of special interest because both solid and liquid FeO are semiconductors (30). Early results on melts containing 50, 57, and 66 mole per cent FeO indicated that the conduction was ionic and decreased with increasing silica content (70). Similar values of specific conductance were obtained for the orthosilicate by later workers (3, 31). A negative temperature coefficient of conductance has been reported (22), but this was later shown to be in error (30) because the conduction due to the iron cell had not been taken into consideration. A single observation that FeO–SiO_2 melts exhibited only cationic

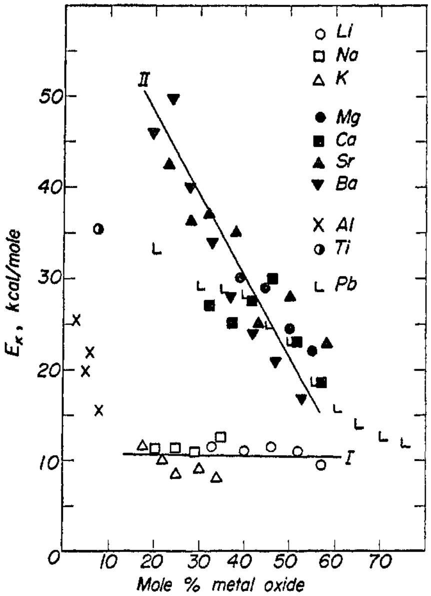

FIG. 1

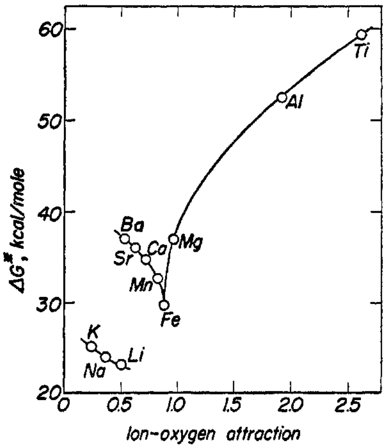

FIG. 2

FIG. 1. Activation energy for electrical conduction in molten binary silicates (8)
FIG. 2. Free energy of activation and ion–oxygen attraction relationship (10)

conduction at low temperatures but anionic conduction at higher temperatures (45) is not in agreement with both past and recent more reliable studies (30).

The activation energies for conduction, E_κ, can be evaluated from equation 1 and are shown in figure 1 for the various systems. A marked difference is observed between systems containing alkali and alkaline earth metal oxides, although within each group E_κ is nearly independent of the cationic species. In Group I E_κ seems to be independent of composition, but in Group II it increases with decreasing metal oxide content. The aluminum and titanium ions occupy further different positions. It is evident that the cationic charge is an important factor in the mechanism of conduction. A satisfactory explanation of these results may be achieved (10) by assuming that the addition of a metal oxide to silica results in the breakdown of the three-dimensional network to give different ions and then correlating the free energy of activation for conduction, ΔG^*, with a function of the electrical interaction in the melt, the ion–oxygen attraction, defined as

$$I = \frac{2ze^2}{r^2} \tag{2}$$

where z is the valency of the cation, e is the electronic charge, and r is the internuclear distance between the metal and oxygen ions. ΔG^* can be derived by the application of the theory of absolute reaction rates (24) to the conduction process, from which the following expression is obtained (8):

$$\Lambda = 3.62 \times 10^{19} z d^2 \exp(-\Delta H^*/RT) \exp(\Delta S^*/R) \tag{3}$$

Λ is the equivalent conductance, d is half the distance between the initial and final states along the reaction coordinate, and ΔH^* and ΔS^* are the enthalpy and entropy of activation for conduction, respectively. ΔH^* and ΔS^* can be evaluated from equation 1 and ΔG^* is obtained from equation 4.

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{4}$$

The relationship between ΔG^* and I is shown in figure 2. For the ions of one valency group, ΔG^* decreases steadily as the ionic radius is reduced and it is therefore probable that a steric effect predominates. However, when I reaches a value of about 0.9 for Fe^{++}, an anomalous increase of ΔG^* occurs, indicating an increasing difficulty of cationic movement. It is likely that this is due to the multivalent cations Al^{+++} and Ti^{++++} competing with the Si^{++++} ions for the oxygen of the lattice to form, for instance, TiO_4^{----} anions, thus leaving fewer cations for electrical transport. There is some resemblance between this and the concept of network modifiers and formers in the theories of solid glasses.

The binary molten borates have received relatively less attention. Results on the systems Li_2O–B_2O_3 (0–37 mole per cent Li_2O), Na_2O–B_2O_3 (0–39 mole per cent Na_2O), and K_2O–B_2O_3 (0–41 mole per cent K_2O) up to 1200°C. (35, 56), CaO–B_2O_3 (31–54 mole per cent CaO), SrO–B_2O_3 (22–45 mole per cent SrO), and BaO–B_2O_3 (18–64 mole per cent BaO) from 900° to 1300°C. (57) are scat-

TABLE 2

Specific conductivity of molten B_2O_3 *and binary borates*

System	Metal Oxide	Temperature	Specific Conductivity	Reference
	mole per cent	°*C.*	*ohm*$^{-1}$ *cm.*$^{-1}$	
Li_2O-B_2O_3	2.5	1007	0.0034	(56)
	9.9	990	0.054	(56)
	28.8	1006	1.12	(56)
Na_2O-B_2O_3	1.0	1003	0.0017	(56)
	6.2	1002	0.022	(56)
	15.7	1005	0.11	(56)
	34.4	1008	1.36	(56)
K_2O-B_2O_3	1.1	995	0.0011	(56)
	3.9	997	0.009	(56)
	15.9	1000	0.11	(56)
	31.5	994	0.76	(56)
CaO-B_2O_3	31.2	1204	0.10	(57)
	42.5	1193	0.19	(57)
	54.4	1197	0.29	(57)
SrO-B_2O_3	22.4	1117	0.025	(57)
	33.8	1100	0.062	(57)
	45.3	1154	0.16	(57)
BaO-B_2O_3	17.8	1204	0.057	(57)
	32.1	1100	0.063	(57)
	45.9	1104	0.16	(57)
	63.8	1119	0.26	(57)
PbO-B_2O_3	1.0	1050	0.0002	(43)
	5.0	1050	0.002	(43)
	30.0	1050	0.16	(43)
	50.0	1050	0.51	(43)
	80.0	1050	1.8	(43)
B_2O_3	—	900	2×10^{-6}	(43)
	—	900	6×10^{-5}	(56)
	—	900	2×10^{-4}	(35)

tered and void of structural interpretations. The magnitude of the specific conductivities, shown in table 2, is similar to the values for the silicates, and the temperature coefficient of conductance is again positive. There is little doubt, therefore, that these are also ionic liquids. The present author has made use of the available data on these systems and evaluated the activation energies for conduction. These are presented as a function of composition in figure 3, which shows a remarkable similarity to figure 2 for the silicates. The metal oxides are again separated into two distinct groups, within each of which E_κ is independent of the specific cation. As for the silicates, E_κ seems to be independent of composition for the alkali oxides but increases with decreasing amounts of alkaline earth oxides. Although E_κ is similar for the Group II silicates and borates, values for the alkali borates are much larger than for the corresponding silicates. Melts of the system $PbO–B_2O_3$ are also typically ionic over the entire composition range (43), but the E_κ/composition relationship shows an anomalous behavior. In figure 2 values of E_κ for the lead silicates are similar to those for the Group II melts and are much higher than for the Group I silicates. However, in figure 3 values of E_κ for $PbO–B_2O_3$ are very different from those for the Group II melts and are even lower than the corresponding values for the Group I borates.

Various values for the specific conductance have been reported for pure boron trioxide (35, 43, 56). However, these may be due to traces of impurities present, and therefore the smallest value, 2×10^{-6} ohm^{-1} cm.$^{-1}$ at 900°C., is more correct (43).

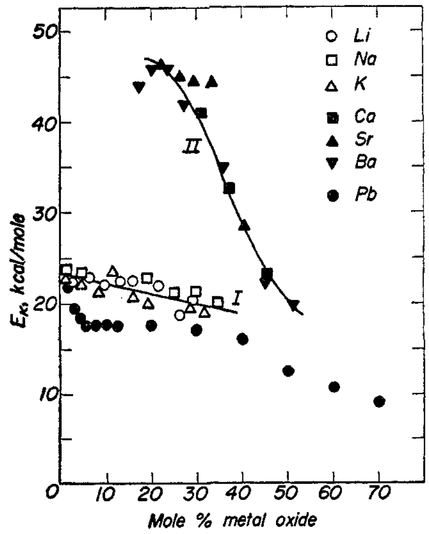

FIG. 3

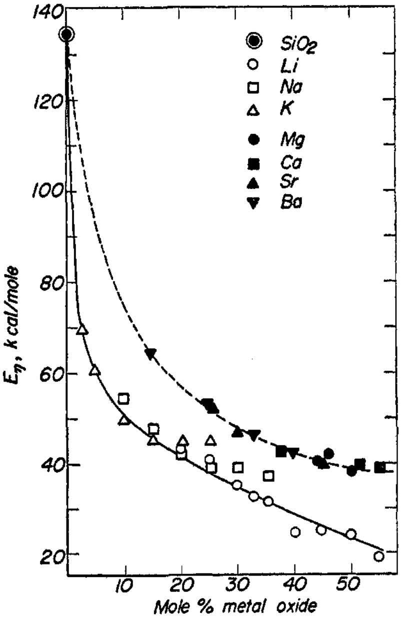

FIG. 4

FIG. 3. Activation energy for electrical conduction in molten binary borates
FIG. 4. Activation energy for viscous flow in molten binary silicates (40)

TABLE 3

Electrolysis of molten binary silicates

System	Metal Oxide	Temperature Range	Conduction Mechanism	References
	mole per cent	°C.		
$LiO-SiO_2$	34–62	1300–35	Ionic	(5)
$CaO-SiO_2$	34–57	1550–1650	Ionic	(6)
$MnO-SiO_2$	54–59	1240–1450	Ionic	(6)
$PbO-SiO_2$	49	920	Ionic	(6)
	50–100	875–950	Ionic	(43)
$FeO-SiO_2$	90–100	1400	10% ionic	(61, 62)
	75	1400	55% ionic	(61, 62)
	66	1400	90% ionic	(61, 62)
	66	1200–1400	Ionic	(2)
$CoO-SiO_2$	71.5	1440–1500	95% ionic	(2)
	73.5	1450	72% ionic	(2)
	75.0	1450	Semiconductor	(2)

B. Electrolysis

Studies of the applicability of Faraday's laws, by measuring the amounts of oxygen liberated at the anode or of the metal deposited at the cathode, have confirmed that for most binary silicates conduction is wholly ionic. These results are summarized in table 3. Semiconduction is exhibited by melts containing large amounts of CoO and FeO, but in the $PbO-SiO_2$ system the Faradaic yield is 100 per cent even at a melt composition of 90 mole per cent PbO. No electrolysis experiments have been reported on the binary borates but by analogy to the silicates, the conduction is probably entirely ionic as well (43).

C. Transport number

As conductance is wholly ionic, increases with the concentration of metal oxides, and is greatest for melts with univalent metals of small ionic radius, it is probable that the current is carried predominantly by the cations (8). The silicon–oxygen network is much larger and therefore relatively immobile. The correctness of this hypothesis has been demonstrated for four binary silicate melts by different methods. The transport numbers of the cations in the systems K_2O-SiO_2 (22–34 mole per cent K_2O) and Li_2O-SiO_2 (47 mole per cent Li_2O) have been found by a Hittorf-type method to be unity (6). For melts containing more than 66 mole per cent metal oxide, when the maximum Si:O ratio of 1:4 is reached, it is possible that a share of the current is carried by oxygen ions. However, it has been found by a moving-boundary method that in the systems $FeO-SiO_2$ and $CoO-SiO_2$, containing 66 and 71.5 mole per cent metal oxides, respectively, the transport number of the cations is still 1. Electric conductance in the liquid silicates, and by inference in the borates, is therefore entirely unicationic over the whole range of composition.

D. Electromotive forces

Although E.M.F. measurements at room temperature permit the evaluation of thermodynamic functions of the specific constituents in a solution, their application to melts at high temperatures involves great experimental difficulties, first in obtaining a satisfactory electrode system, and secondly, to make the necessary corrections for the thermal E.M.F. With one end immersed in a melt at high temperature and the other at room temperature, electrodes of different materials become essentially a thermocouple. Thus the thermal E.M.F. at 1500°C. was found to be five to seven times larger than the actual reversible E.M.F. (about 0.02 v.) due to a $CaO–SiO_2$ melt (15). In this system, a variation of the temperature coefficient of E.M.F. with composition was observed and interpreted as an indication of a progressive change of some properties of the melt, such as dissociation or association.

Recently (17), an attempt was made to obtain the oxygen-ion activity in molten silicates from E.M.F. measurements at 800–900°C. of the cell:

$$\text{Pt}\ (O_2)\ |\ \text{silicate solvent}\ |\ \text{silicate solvent} + M_xO_y\ (n)\ |\ (O_2)\ \text{Pt}$$

M_xO_y denotes oxides of all the alkali metals, all the alkaline earth metals, thallium, lead, cadmium, zinc, bismuth, boron, aluminum, titanium, silicon, and germanium; n is the concentration such as to give 0.2 mole of the metal ion M per mole of the solvent. Lead silicate containing 50 mole per cent PbO was selected as the solvent because of its low melting point. A variation of the potential due to the presence of different dissolved metal oxides was observed and considered to be a measure of the change in oxygen-ion activity of the silicate solvent, taken as the standard. As this change must be related to the attraction exerted by the added cations on the negative oxide ions, the observed E.M.F. was plotted against z/r^2, where z is the charge on the cation and r is the distance between the cation and the oxygen ion. Results for cations with a completed noble gas shell and those with eighteen outer electrons fall on two different hyperbolic curves. The so-called acid oxides like BeO, Al_2O_3, B_2O_3, TiO_2, and SiO_2 gave increasing positive potentials, whereas the E.M.F.'s of the basic alkali and alkaline earth oxides are negative. Although these observations are of structural interest, the cells are not amenable to exact thermodynamic treatment because the liquid-junction potentials are not known.

Cells of the type

$$\text{Pt}\ (O_2)\ |\ \text{molten}\ B_2O_3\ |\ \text{molten}\ B_2O_3 + M_2O\ (n)\ |\ (O_2)\ \text{Pt}$$

where M denotes lithium, sodium, and potassium, have also been studied (16, 65). At equimolar compositions below 22 mole per cent metal oxide the E.M.F. increased in the order K_2O, Na_2O, Li_2O. Above this composition, where the E.M.F. is about 0.6 v., this order is reversed; the change is attributed to the differential variation of the basicity of the melts. Because of the uncertainty regarding the potential-determining reaction in the cell, no quantitative interpretation was possible (23).

III. VISCOSITY

Complementary to the many important cationic properties revealed by electric measurements, studies of viscous flow have yielded much valuable information on the anionic nature of molten glasses. The viscosities of almost all binary silicates, borates, and phosphates, even at temperatures far above the liquidus, are much greater than those for other liquids like water, benzene, and liquid metals. In general, the empirical relation

$$\eta = Ae^{E_\eta/RT} \tag{5}$$

is obeyed, where η is the viscosity, A is a constant, and E_η is the energy of activation for viscous flow. Some typical viscosity values for various systems are shown in table 4.

Early results of work on the systems CaO–SiO_2 (25, 49) and Na_2O–SiO_2 (38, 46) were highly controversial with regard to the existence of minima in the viscosity isotherms, attributed to compound formation in the melts. These have since been shown to be erroneous (39, 40). The first mechanism postulated for viscous flow resulted from studies of the three alkali oxide–silica systems (21). The observed large decrease of viscosity when the metal oxides were added to silica was interpreted as the result of a progressive breakdown of the three-dimensional lattice to give silicon–oxygen ions, the limit being reached at the orthosilicate composition, when the melt consisted only of discrete SiO_4^{4-} anions and metal ions. At compositions corresponding to 50 and 33 mole per cent metal oxide, analogous to the pyroxenes and micas of solid silicates, infinite silicon–oxygen chains and sheets were postulated. Between 66 and 50 mole per cent metal oxide the chains were formed by the linking of SiO_4^{4-} tetrahedra.

TABLE 4

Viscosity of some molten silicates, borates, and phosphates

System	Metal Oxide	Temperature	Viscosity	References
	mole per cent	°C.	*poises*	
Li_2O-SiO_2	30	1300	55	(11, 59)
	50	1300	2.3	(11, 19)
Na_2O-SiO_2	10	1400	4,000	(11, 25)
	30	1400	42	(11, 38)
K_2O-SiO_2	2.5	1600	4,700	(11)
	10	1400	1,180	(11)
	30	1400	60	(11, 59)
MgO-SiO_2	50	1700	1.8	(11)
SrO-SiO_2	20	1700	80	(11)
	50	1700	2.0	(11)
BaO-SiO_2	15	1700	195	(11)
	50	1700	1.9	(11)
CaO-SiO_2	50	1700	1.1	(9)
FeO-SiO_2	66	1400	0.6	(38, 69)
	88	1400	0.3	(37, 69)
SiO_2	—	2060	24,000	(11)
		1960	90,000	(11)
		1860	160,000	(64)
B_2O_3	—	1280	22	(63)
		1000	75	(63)
		700	550	(56)
Li_2O-B_2O_3	2.5	900	31	(56)
	25	900	5.3	(56)
Na_2O-B_2O_3	1.0	900	58	(56)
	10	900	12	(56)
K_2O-B_2O_3	1.0	900	63	(56)
	28	900	3.8	(56)
Na_2O-P_2O_5	50	1013	0.9	(13)
	67	1030	0.3	(13)

Recently, however, a detailed study of the CaO–SiO_2 system has furnished results which are not compatible with this model (9). The use of the activation energy for flow, E_η, evaluated from equation 5, in the interpretation of viscosity data has proved to be more fruitful in obtaining structural information. It was shown that the variation of E_η over long ranges of composition was slight and gave no significant deviation at the two compositions corresponding to the presence of infinite chains and sheets. As the movement of infinite sheets is associated with large activation energies and, as is true for polyesters and hydrocarbons, long chains tend to collapse to give shorter segments when flow occurs, the concept of infinite sheets and chains in molten silicates is untenable. In their place, smaller discrete anions were postulated which were entirely satisfactory in explaining the observed variations of the activation energies with composition. Thus at 50 and 33 mole per cent metal oxides, puckered $Si_3O_9^{6-}$ rings and tetrahedral $Si_4O_{10}^{4-}$ anions were the respective predominant ions in the melt. From 33 to about 12 mole per cent metal oxide, these anions increase gradually in size with the $Si_4O_{10}^{4-}$ tetrahedron as the basic building unit, until they become unstable and rearrangement occurs to give a continuous silica-type lattice. This theory was not only compatible with the available E_η–composition relationship but received support from partial molar volume studies of solid glasses (14), the solubility of fluorides in silicates (27), and the crystallite theory of glasses (29).

Although later more extensive measurements covering the alkali and the alkaline earth silicates (11) have added confirmation to the concept of the discrete ion, two objections have arisen on account of the geometry of the anions postulated. Both the puckered $Si_3O_9^{6-}$ rings and the $Si_4O_{10}^{4-}$ type anions necessitate a tetrahedral Si—O—Si angle of 109°, which is not found in solid silicates (40). Further, this angle is about 140° in vitreous silica, and density studies of binary alkali silicates (72) have shown that the partial molar volume of silica does not alter appreciably at about 12 mole per cent metal oxide, where it was suggested that rearrangement involving a large change of the oxygen angle should occur. Thus if discrete anions are present, the Si—O—Si angle must be larger than 109° and not deviate appreciably from about 140°.

A new series of discrete anions which involve a larger oxygen angle and satisfactorily explain the variation of E_η over the whole range of composition, as shown in figure 4, has recently been suggested (11). These are based on a planar $Si_3O_9^{6-}$ ring, present at 50 mole per cent, with a Si—O—Si angle of 133° as the building unit. For instance, the addition of silica to a metasilicate may be formally represented by an overall reaction

$$6M^+ + Si_3O_9^{6-} + 3SiO_2 \rightarrow 6M^+ + Si_6O_{15}^{6-}$$

The idealized $Si_6O_{15}^{6-}$ ion, present at the composition 33 mole per cent metal oxide and essentially formed by the linking of two $Si_3O_9^{6-}$ rings, is shown in figure 5. The discrete ions proposed which obey the general formula $(Si_nO_{2n+3})^{6-}$ are given in table 5. Low-angle scattering of x-rays by solid glasses has revealed the presence of "inhomogeneities" with dimensions down to about 20 A. (28) in support of this new concept of discrete ions.

The extremely high viscosity of molten silica (1.5×10^5 poises at 1920°C.)

TABLE 5

Silicate ions present at compositions between 10 and 50 mole per cent metal oxide

Composition of Melt	Metal Oxide	Discrete Ion	Approximate Chain Length	Composition of Melt	Metal Oxide	Discrete Ion	Approximate Chain Length
	mole per cent		*A.*		*mole per cent*		*A.*
SiO_2:MO	50	$Si_3O_9^{6-}$		$5SiO_2$:MO	16.7	$Si_{15}O_{33}^{6-}$	15
$2SiO_2$:MO	33	$Si_6O_{15}^{6-}$	6	$6SiO_2$:MO	14.3	$Si_{18}O_{39}^{6-}$	18
$3SiO_2$:MO	25	$Si_9O_{21}^{6-}$	9	$7SiO_2$:MO	12.5	$Si_{21}O_{45}^{6-}$	21
$4SiO_2$:MO	20	$Si_{12}O_{27}^{6-}$	12	$8SiO_2$:MO	11.1	$Si_{24}O_{51}^{6-}$	23

and the very high energy of activation for flow (134 kcal./mole) suggest that much of the three-dimensional bonding remains and that viscous flow involves the rupture of Si—O bonds of energy 104 kcal./mole. From a relationship between the free energy for flow and the energy of vaporization, silica molecules can be shown to be the most likely flow units (9). When metal oxides are progressively added to silica, "weak points" are introduced into the lattice, their increasing concentrations thus leading to the subsequent breakdown of the three-dimensional continuous structure to give discrete anions. This collapse of the silica lattice occurs at about 10 mole per cent for a Group I metal oxide and at a slightly higher composition for the Group II oxides. The observed difference between the alkali and the alkaline earth silicates shown in figure 4 is explicable by the valencies of the cations. The divalent cations induce a "bridging" effect by attracting two singly charged oxygen ions located on different discrete anions; hence relative movement between the latter is made more difficult.

Viscosity results for molten boron trioxide do not obey equation 5 but follow

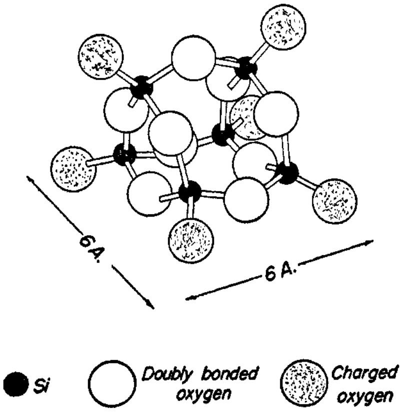

FIG. 5

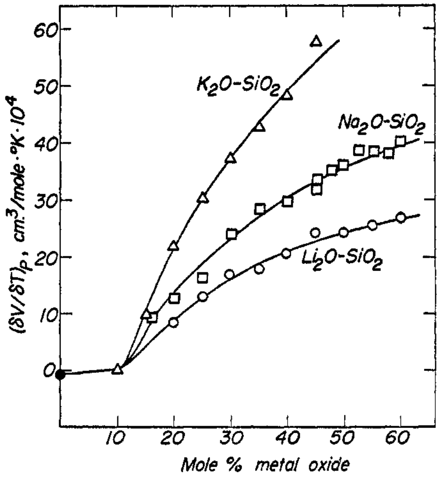

FIG. 6

FIG. 5. Idealized $Si_6O_{15}^{6-}$ ion at 33 mole per cent metal oxide (40)
FIG. 6. Thermal expansion of binary alkali silicates at 1400°C. (72)

a pattern described by typical associated liquids. This and other physicochemical properties indicated the presence of crystallites in liquid B_2O_3 (41). Unlike the silicates, pronounced maxima and minima are found in the viscosity isotherms for the alkali borates (56), attributed to the effects of changes of the oxygen coordination of boron from three to four. Theoretical treatments parallel to those attempted for the silicates are lacking at present.

The only binary phosphate examined is the system Na_2O–P_2O_5 from 50 to 68 mole per cent Na_2O (13). The viscosity decreases with increasing concentration of metal oxide and obeys the empirical equation 5. Treatment of the results according to the rate process theory (24) suggests that viscous flow, similar to that of the long-chain hydrocarbons, involves small flow units of not more than eight phosphorus atoms, although the chain lengths in the quenched glass may be much greater. This is in harmony with the discrete-ion concept for the silicates.

IV. DENSITY

Although the variation of the density with composition of a melt may yield important evidence indicative of any structural changes, very few such studies have been made and only in one instance were the measurements made with sufficient accuracy to permit the evaluation of partial molar volumes. The only binary silicate systems examined are Li_2O–SiO_2, Na_2O–SiO_2, and K_2O–SiO_2 (25, 59, 72). Addition of metal oxide to silica causes a progressive decrease in density, and the molar volumes of the melts increase from lithium to the potassium silicates. At equimolar compositions the observed thermal expansivity is in the order $K > Na > Li$. This is in agreement with the values of ion–oxygen attraction for these ions, defined by equation 2. The weakly bound potassium ions are unable to prevent thermal expansion as readily as the more strongly bound sodium and lithium ions (59). Some data on the density and expansivity of silicates, borates, and phosphates are shown in table 6.

Two noteworthy features regarding the structures of molten silicates are revealed by the more accurate studies of density (72). The first is that 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 long ranges of composition. Secondly, it is evident from figure 6 that the thermal expansions show a sudden increase when the content of alkali metal oxide exceeds about 12 mole per cent. This sudden inflection indicates that a fundamental change in the structure of the liquid silicates occurs at this composition, thus furnishing direct evidence in support of the discrete-ion theory (11).

The density and expansivity of the binary alkali and alkaline earth borates increase with increasing concentration of metal oxides. At 800–1000°C. the addition of the alkali metal oxides to boron trioxide causes a large contraction of the B_2O_3 lattice. This effect, which reaches a maximum at about 20 mole per cent metal oxide, is in the order $Li > Na > K$ (55). A similar tendency is indicated in the case of the divalent metal oxides but because of insufficient data, the effect is not as well defined (57). These are evidently related to the variation of the coordination number of boron from three to four.

TABLE 6

Density and expansivity of some molten silicates, borates, and phosphates

System	Metal Oxide	Temperature	Density	Expansivity per °C. × 10^5	Reference
	mole per cent	*°C.*	*g./cm.^{3}*		
Li_2O-SiO_2	20	1400	2.169	3.5	(72)
	40	1400	2.098	9.0	(72)
	60	1400	1.980	12.6	(72)
Na_2O-SiO_2	20	1400	2.222	4.4	(72)
	40	1400	2.201	10.7	(72)
	60	1400	2.163	14.3	(72)
K_2O-SiO_2	10	1400	2.216	0	(72)
	20	1400	2.184	7.0	(72)
	40	1400	2.136	14.0	(72)
B_2O_3	—	898	1.522	9.6	(55)
Li_2O-B_2O_3	2.5	903	1.574	11.5	(55)
	9.9	899	1.731	16.0	(55)
	21.6	900	1.919	22.4	(55)
Na_2O-B_2O_3	3.0	898	1.598	11.7	(55)
	10.0	899	1.779	13.4	(55)
	34.4	900	2.048	28.9	(55)
K_2O-B_2O_3	1.1	907	1.538	10.5	(55)
	11.6	899	1.788	18.7	(55)
	31.5	892	1.954	32.6	(55)
CaO-B_2O_3	31.2	999	2.288	24.7	(57)
	37.1	1105	2.306	21.9	(57)
SrO-B_2O_3	22.4	1015	2.431	21.8	(57)
	40.6	1120	2.885	20.6	(57)
BaO-B_2O_3	17.8	1002	2.477	19.2	(57)
	36.3	1003	3.231	22.8	(57)
	51.6	996	3.512	17.5	(57)
Na_2O-P_2O_5	50	950	2.142	—	(12)
	66	1043	2.196	—	(12)

The density of melts of the system Na_2O–P_2O_5 also increases with increasing metal oxide content and, from 50 to 66 mole per cent Na_2O, obeys the relation

$$\rho = 2.372 + 0.089(Na_2O/P_2O_5) - 0.000338t$$

where t is the temperature in degrees Centigrade and Na_2O/P_2O_5 is the molar ratio of the two components (12). Structural interpretations of the results obtained for the density of the borates and phosphates have not been reported.

V. SURFACE TENSION

The surface tension of a liquid is directly related to the binding forces between the constituents and should therefore provide some structural information. This is immediately evident if the values shown in table 7 are compared with those for other liquids. The surface tensions of molecular liquids and liquid metals are respectively smaller and greater than those for the molten silicates, borates, and phosphates by approximately factors of ten. The molten phosphates, however, have values similar to those for the molten salts and are therefore essentially ionic liquids.

The most interesting feature revealed by studies of the silicates is the positive temperature coefficient of surface tension, which increases with the ion–oxygen attraction but for each system decreases with increasing concentration of metal

TABLE 7

Surface tension of some molten silicates, borates, and phosphates

System	Metal Oxide	Temperature	Surface Tension	Temperature Coefficient	References
	mole per cent	°C.	*dynes/cm.*	*dynes/cm./°C.*	
Li_2O-SiO_2	29	1300	315	+0.02	(1, 58)
	33.4	1300	320	0	(1, 58)
	50.3	1300	352	−0.03	(1, 58)
Na_2O-SiO_2	19.5	1300	275	−0.01	(1, 58)
	49.2	1300	289	−0.05	(1, 58)
K_2O-SiO_2	16.7	1300	221	−0.02	(1, 58)
	33.0	1300	211	−0.05	(1, 58)
FeO-SiO_2	50	1400	360	+0.08	(33)
	66	1400	400	+0.01	(36)
CaO-SiO_2	50	1550	400	+0.02	(34)
B_2O_3	—	1000	84	+0.04	(54)
Li_2O-B_2O_3	2.8	1000	88	+0.04	(54)
	8.0	1000	123	+0.01	(54)
	48.4	1000	225	−0.05	(54)
Na_2O-B_2O_3	9.0	1000	108	+0.04	(54)
	38.7	1000	187	−0.10	(54)
K_2O-B_2O_3	3.9	1000	88	+0.03	(54)
	41.0	1000	121	−0.18	(54)
CaO-B_2O_3	28.8	1300	124	−0.03	(57)
	50.3	1300	270	−0.03	(57)
SrO-B_2O_3	22.4	1300	122	0.	(57)
	50.6	1300	276	−0.05	(57)
BaO-B_2O_3	17.8	1300	122	+0.02	(57)
	51.6	1300	252	−0.09	(57)
PbO-B_2O_3	10	900	85	+0.40	(60)
	20	900	110	−0.30	(60)
ZnO-B_2O_3	60	1200	240	Positive	(53)
	75	1200	340	Positive	(53)
Na_2O-P_2O_5	50	977	179	−0.04	(12)
	66	1012	250	−0.03	(12)

oxides. Thus the systems containing the multivalent ions Ca^{++}, Fe^{++}, Mg^{++}, and Mn^{++} have highly positive coefficients (33). The causes attributed to the presence of asymmetric groups (71) or to the dissociation of large anions at high temperatures (34) are not entirely satisfactory in explaining all the observed results.

On addition of the alkali metal oxides to boron trioxide, the initial increase of surface tension is slight and the temperature coefficient is positive and similar to that for pure B_2O_3 up to about 20 mole per cent metal oxide (54). The same behavior is noted for melts of the system PbO–B_2O_3 (60) and the alkaline earth borates exhibit a similar tendency, although no measurements are available over this range of composition (57). This property and the tendency to immiscibility over this range strongly suggest that the surface layer is essentially boron trioxide which differs a great deal from the interior of the liquid (60).

The surface tension of sodium phosphate melts increases with the concentration of sodium oxide and obeys the relation

$$\gamma = 150.6 - 0.0379t + 677(Na_2O/P_2O_5)$$

over the composition range 50 to 68 mole per cent Na_2O (12). The temperature coefficient is negative. As for the silicates and borates, no structural interpretations have been drawn from surface tension measurements.

VI. SUMMARY

From the results of the various physicochemical studies discussed, little doubt remains that simple molten silicates, borates, and phosphates are ionic liquids similar to the molten salts. Further systematic measurements on the latter two liquids are necessary before the evaluation of the structures of the anions is possible. As in the case of the silicates, studies of viscosity and density will be most fruitful in this respect.

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