Structural Aspects of Slags

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ABSTRACT

The structures of silicate and aluminosilicate melts and glasses have been infered from measurement of the dependence on composition of structure-sensitive properties, from application of polymer theory, from identification of trimethylsilyl (TMS) derivatives of anionic species and from interpretation of the spectra obtained in various spectrometry studies. The discrete ion theory and the polymer theory are briefly discussed and the conclusions drawn from spectroscopic studies are compared with the results of TMS studies. Raman spectra of silicate and aluminosilicate glasses have been interpreted in terms of the existence of "structural units", and various reaction equilibria among these structural units have been presented in the literature. It is concluded that these equilibria are meaningless and suggestions are made as to the forms of the discrete ions which contain the units. For example, the trimeric cyclic ion $Si_3O_9^{6-}$ consists of three SiO_3^{2-} "units" and the disilicate anion $Si_6O_{15}^{6-}$ consists of three $Si_2O_5^{2-}$ units. It is also concluded that the results of the TMS studies are more credible than the interpretations of Raman spectra.

1. INTRODUCTION

The structures of oxide slags, which are determined by the extents to which the various component acidic and basic oxides interact with one another, influence important physical properties such as viscosity, density, surface tension, thermal conductivity and electrical conductivity. These interactions also determine the thermodynamic activities of the oxides, which, in turn, determine important practical properties such as liquidus and solidus temperatures. Consequently the structures of slags has been a topic of interest in the metallurgical community since the 1920's. Although the level of this interest is still high, most recent activity in the area has been occurring in the geological community, where the emphasis has been on obtaining an understanding of the behavior of magma. The object of this paper is to present a critical review of conclusions drawn as to the structures of slags.

In general, the structures of molten and glassy silicates have been determined

1. by inference from observation of the dependence on composition and temperature of physical properties such as viscosity, density and electrical conductivity,
2. from application of polymer theory to silicate melts,
3. by chemical extraction, separation and identification of anions in quenched melts, and
4. by inference from the results of spectroscopic studies.

2. THE DISCRETE ION MODEL

Bockris *et. al.*[1,2] showed that the only type of structure consistent with the observed influence of composition and temperature on the viscosities of binary silicate melts is one containing discrete silicate anions, formed by the depolymerization of silica when dissolved in a liquid basic oxide. The orthosilicate ion, SiO_4^{4-} occurs at the orthosilicate composition, $2MO.SiO_2$, and the pyrosilicate ion, $Si_2O_7^{6-}$, formed by polymerization of two orthosilicate ions, occurs at the pyrosilicate composition, $3MO.2SiO_2$. Further addition of silica causes continued linear polymerization to form discrete chain anions which are the flow units in the viscous flow process. According to this scheme the chain length would approach infinity as the melt composition approachs the metasilicate, $MO.SiO_2$. However the measured activation energies for viscous flow of metasilicate melts are not consistent with the occurrence of infinite chains, and thus Bockris *et. al.* suggested that a new type of flow unit must form. They suggested the cyclic trimer $Si_3O_9^{6-}$ and/or the cyclic tetramer $Si_4O_{12}^{8-}$, both of which fulfil the requirements of stoichiometry, electroneutrality and stereochemistry. The cyclic trimeric anion and the cyclic tetramic anion occur, respectively, in wollastonite and poryphyllite. At higher silica contents the rings ions polymerize face to face to form $Si_6O_{15}^{6-}$ at the disilicate composition, $MO.2SiO_2$ and $Si_9O_{21}^{6-}$ at the trisilicate composition, $MO.3SiO_2$.

The constancy of the partial molar volume of silica and zero thermal expansivity of alkali silicate melts in the range of composition $0 < N_{SiO_2} < 0.12$ lead Bockris *et. al.*[3] and Tomlinson *et. al.*[4] to suggest that these melts exist as randomly damaged three-dimensional networks in which the alkali cations are contained within cages in the structure. Since the cages are made up of strong Si-O-Si bridges having negligible thermal expansivity, the expansion associated with the ionic bonds is not displayed. The sudden increase in thermal expansivity at 12 mole percent M_2O indicates that, at this composition, the network structure breaks down and the Si-O-Si bonds are confined within discrete polyanions, which, in turn, are joined only by ionic bonds through metal cations.

In the discrete ion model of silicate melts, although a particular anion predominates at a particular composition, all melt compositions contain a distribution of anions, which gives rise to the smooth variation, with composition, of the physical properties of the system.

2. THE POLYMER MODELS

The application of polymer theory to silicate melts[5–11] identifies the orthosilicate ion SiO_4^{4-} as the mer unit. In the initial model[5–6] the SiO_4^{4-} ion is considered to be a pseudo-bifunctional mer which undergoes self-condensation reactions to form linear chain polyions $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$ ... $Si_xO_{3x+1}^{(2x+2)-}$ Each condensation reaction produces a free oxygen ion, O^{2-}, and polymerization produces the general equilibrium

$$SiO_4^{4-} + Si_xO_{3x+1}^{(2x+2)-} = Si_{3x+4}^{2(x+2)-} + O^{2-} \quad (1)$$

The assumption of Temkin mixing of the anions allows the equilibrium constant for the equilibrium given by Eq. (1) to be written as

$$k_{1,x} = \frac{N_{Si_{x+1}O_{3x+4}^{2(x+2)-}}\, N_{O^{2-}}}{N_{SiO_4^{4-}}\, N_{Si_xO_{3x+1}^{(2x+2)-}}}$$

in which N_i is the anion fraction of the species i. The further assumption that the value of $k_{1,x}$ is independent of x gives rise to a geometric array of polysilicate anions in which

$$\frac{N_{x+1}}{N_x} = k_{1,1}\frac{N_{SiO_4^{4-}}}{N_{O^{2-}}}$$

Consequently at all melt compositions, SiO_4^{4-} is the most abundant silicate anion, followed by $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, etc. and the anion fractions of SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$ etc. exhibit maxima at the compositions $2MO.SiO_2$, $3MO.SiO_2$, $4MO.3SiO_2$ etc. Specification of the value of $k_{1,1}$ quantifies the degree of polymerization in the system and gives the variation of the thermodynamic activity of the basic metal MO as

$$a_{MO} = N_{O^{2-}}$$

In the later polymer model[7–9] the SiO_4^{4-} ion is considered to be a 4-functional mer unit, in which case all four of its O^- can undergo condensation to form linear and branching chain ions. Polymerization is quantified by the value of $k_{1,1}$ and the degree of polymerization, α, given as the fraction of functional O^- on the monomers which have undergone condensation. Temkin mixing is assumed and the activity of the basic metal oxide is given by

$$\frac{a_{MO}}{1-a_{MO}} = \frac{k_{1,1}\left[1-\frac{2\alpha}{3}\right]}{2\alpha}$$

or

$$\alpha = \frac{1-(1-a_{MO})\left[\frac{1}{N_{SiO_2}}-2\right]}{2}$$

The linear and branched chain models are shown in Fig. 1 which shows the theoretical activities (calculated with $k_{1,1} = 0.196$) and the measured activities of PbO in the system PbO-SiO_2 at 1000°C. The limitations of polymer theory do not allow the formation of anions other than linear and branching chains to be considered and thus the polymer models are restricted to compositions with $N_{SiO_2} < 0.5$.

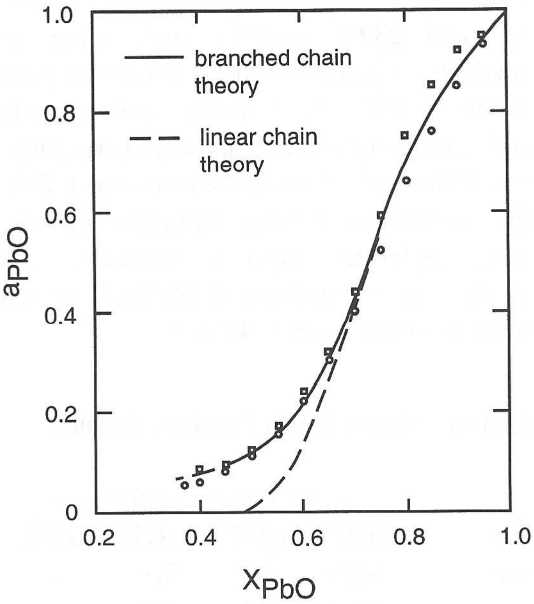

Fig. 1. The activity of PbO in the system PbO–SiO_2 at 1000°C. The lines are theoretical with $k_{1,1} = 0.196$. (ref 11).

3. TRIMETHYLSILYLATION

Lentz[12] identified the silicate anions occurring in mineral silicates and aqueous sodium silicate solutions using what is now referred to as the Lentz technique of trimethylsilylation, which involves reacting a powdered silicate sample with hexamethyldisiloxane, HCl and water. The HCl reacts with the hexamethyl disiloxane according to

$$(CH_3)_3Si{:}O{:}Si(CH_3)_3 + HCl =$$

$$(CH_3)_3SiCl + (CH_3)_3SiOH$$

and one or both of the reaction products causes trimethylsilylation, TMS, as shown schematically in Fig. 2. The TMS derivatives are separated from one another by gas-liquid chromatography and are identified by mass spectrometry. TMS derivatives of sodium silicate solutions contained the chain ions SiO_4^{4-}, $Si_2O_7^{6-}$, and $Si_3O_{10}^{8-}$, the tetrameric ring ion $Si_4O_{12}^{8-}$ and polysilicate ions. A solution of sodium metasilicate contained 25.7% monomer, 12.0% dimer, 6.9% trimer, 10.0% cyclic tetramer and 23.3% polysilicates. In all of the compositions studied by Lentz the monomer was found in greater quantity than the dimer, which was always present in greater quantity than the trimer. However, when Lentz treated the mineral hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$, which contains only the dimer, he obtained a yield of 77.6% $Si_2O_7^{6-}$ and 22.0% SiO_4^{4-}, which indicated that depolymerization had occurred during the procedure.

The side reactions which can occur during the procedure, namely polymerization, depolymerization and hydrolysis of the TMS derivatives, have been studied by Gotz and Masson[13,14] who examined the influence of the experimental variables time, temperature and make-up of the reaction medium. This lead to the development of the direct trimethylsilylation procedure which involved the use of isopropyl alcohol, hexamethyldisiloxane and trimethyl chloride. Using the Lentz technique with hemimorphite, Gotz and Masson[13] obtained a yield of 28.8% SiO_4^{4-}, 27.4% $Si_2O_7^{6-}$, 15.2% $Si_3O_{10}^{6-}$ and 28.6% $Si_4O_{12}^{8-}$, and, using an optimized direct TMS procedure, obtained a yield of 96.8% $Si_2O_7^{6-}$, 2.1% SiO_4^{4-} and scarcely detectable traces of trimeric and tetrameric rings. Gotz and Masson[14] then applied the direct TMS to the naturally-occurring minerals olivene, fosterite, tephroite, fayalite, andradite and laumonite, and to synthetic $K_4H_4(Si_4O_{12})$ and obtained the yields listed in Table I.

Table 1. Direct TMS of various silicates.

Silicate	Si, wt% in the products as SiO_4^{4-}	$Si_2O_7^{6-}$	$Si_3O_{10}^{8-}$	$Si_4O_{12}^{8-}$
Olivine	88.0	9.7	2.3	-
Fosterite	81.9	15.2	2.9	-
Tephroite	87.2	11.3	1.5	-
Fayalite	84.9	14.1	1.0	-
Andradite	83.0	11.6	5.4	-
$K_4H_4(Si_4O_{12})$	14.7	0.9	0.4	84.0
Laumontite	3.8	-	-	96.2

Gotz and Masson suggested that the higher proportion of side-reactions with the orthosilicates is due to the higher lability of the SiO_4^{4-} anion, which makes it difficulty to suppress entirely the self-condensation of the monomers to form dimers. They also pointed out that relatively high amount of orthosilicate ions in the products from the synthetic $K_4H_4(Si_4O_{12})$ may have been caused by the presence of K_2SiO_3 as an impurity in the synthesized material. Overall the unified direct TMS method reproduced the structures in the TMS derivatives with an accuracy of 94% for the pyrosilicate and 82-88% for the orthosilicates.

The types and amounts of silicate grouping existing in glassy and crystalline $2PbO.SiO_2$ have been studied by Gotz *et.al.*[15] who used paper chromatography, direct TMS combined with gas-liquid partition chromatography and the molybdate method. They found that glassy $2PbO.SiO_2$ and each of the three main crystalline polymorphs is characterized by its own specific distribution of silicate ions. The distribution in

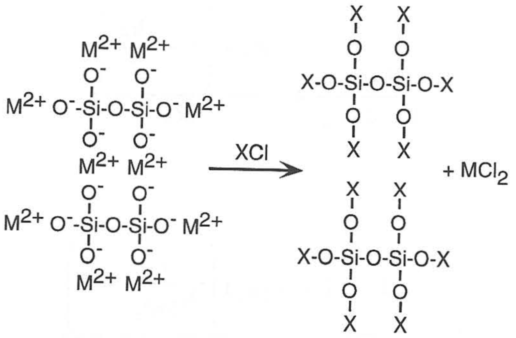

Fig. 2. The trimethylsilylation of a dimer. X represents a trimethylsilyl group. (ref 13).

vitreous $2PbO.SiO_2$ is of a polyanionic nature, dimeric anions prevail in T-Pb_2SiO_4, $Si_4O_{12}^{8-}$ ions are predominant in M_1-Pb_2SiO_4 and H-Pb_2SiO_4 is a typical polysilicate with chain ions of the type $[SiO_3^{2-}]_n$.

The progress of crystallization of lead orthosilicate glass has been studied by Gotz *et.al.*[16] who heated powdered samples of the glass at 500°C for various times before quenching to room temperature and subjecting to TMS and gas-liquid chromatography. Their results are shown in Fig. 3, in which the % area on the *y*-axis is the area under the peak for a particular TMS derivative in the chromatographic pattern divided by the total area under all of the peaks. Fig. 3 shows a smooth decrease in the monomer derivative, a maximum in the dimer derivative after some 30 minutes of heat treatment and the establishment of a plateau for the tetrameric ring structure. The dominance of the tetrameric ring structure in the crystalline orthosilicate was not expected and Gotz *et. al.* pointed out that stoichiometry requires the existence of four O^{2-} ions for each $Si_4O_{12}^{8-}$ ion in the crystalline orthosilicate. Although the crystal structure of the orthosilicate is not known, the results of the study showed that the SiO_4^{4-} ions which predominate in the glass undergo dimerization initially, with elimination of free O^{2-} ions, before finally transforming to the stable structure which contains $Si_4O_{12}^{8-}$ ring ions.

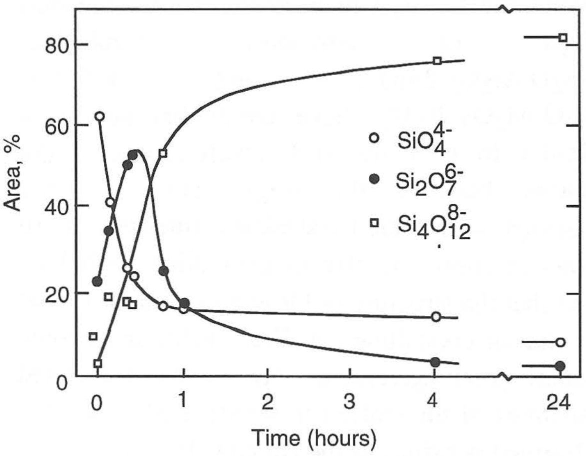

Fig. 3. The change in the constitution of lead orthosilicate glass during crystallization at 500°C. (ref 16).

4. SPECTROSCOPY

A variety of absorption, emission and scattering techniques has been applied to the study of silicate glasses, using electrons, neutrons and radiation with wavelengths ranging from γ-ray to infrared. Although these techniques yield limited information on the local environments of atoms in vitreous materials (co-ordination numbers, first and second neighbor bond distances and bond angles), measured spectra have been interpreted in terms of structure.

The application of X-ray diffraction to the study of structures of glasses began in the 1930's using what are now[17] considered to be crude experimental methods and theories which involved serious approximations. In 1969 an X-ray study of vitreous silica, using "greatly improved conditions"[18] lead to the following conclusions. Practically all of the silicon atoms are tetrahedrally-bonded to 4 oxygen atoms, with an average Si-O distance of 0.162 nm. Practically all of the oxygen atoms are bonded to 2 silicon atoms. The Si-O-Si bond angle varies from 120° to 180° with a maximum at about 144°. On the average there seems to be a random orientation about the Si-O bond directions, except where prevented by the close approach of neighbors. This lead to attempts to refine the Random Network Theory, RNT, which considers vitreous silica to consist of a three-dimensional random network of tetrahedral SiO_4 molecular units. Neighboring units share a common bridging oxygen atom and the mutual orientation of adjacent units can vary widely in a random manner. In an attempt to confirm the RNT Bell and Dean[19] constructed ball and spoke models of vitreous silica and calculated their theoretical X-ray radial distribution functions, (RDF's). They found that a model with a mean bond angle of 153° reproduced the experimental RDF in detail out to an interatomic distance of 0.8 nm. Bell and Dean concluded that the distribution of bond angles may not be a critical factor in determining the overall agreement between theory and experiment, but that the distribution of molecular loops in the network could be important. In this context a loop of length *n* is a closed path in the network which passes once, and only once, through *n* silicons and along *n* Si-O-Si bond pairs. With a mean bond angle of 153° the percentages of shortest loops of length 4, 5 and at least 6 were, respectively, 19, 28 and 53. Dean and Bell were not able to determine what set of statistical parameters, if any, can best serve to characterize a random molecular network, and could not determine whether a given RDF can be consistent with just one type of structures or with a wide range of different structures.

The RN model of Bell and Dean has been re-examined by Gaskell and Tarrant[20] who took the original coordinates of the atoms in the model and used a strain energy minimization procedure in which each atom is moved in a direction which decreases the local elastic strain due to stretched bonds and distorted angles. This "relaxed" model was made consistent with the assumed interatomic potential energy function and the calculated elastic energy, density, radial distribution and scattering functions of the model were compared with experimental values. The relaxed structure gave approximately correct values for the density, enthalpy of crystallization and X-ray and neutron scattering data, and hence confirmed the general validity of the Bell-Dean RN model. However the re-examination did not support some of the detailed reasons suggested by Bell and Dean for the success of the model. For example different bond angles were required to give the best fit with experimental data - 144-149° for stability, 149° for density and 142° for scattering measurements - and no single structure reproduced all of the experimental data. Also Gaskell and Tarrant found that the best fit would require a mean oxygen angle close to 145°, in contrast with Bell and Dean's choice of 153°, and they disagreed with Bell and Dean's suggestion that the oxygen bond angle may not be critical in determining the overall agreement between theory and experiment.

In comparing the Raman spectra of silica glass with those of the crystalline polymorphs coesite and α-quartz, Mammone *et. al.*[21] concluded that silica glass contains randomly oriented four- and six-membered rings. The breadth of the strongest band at 437 cm^{-1} was considered to be due to either a variation in the Si-O-Si bond angle or to the presence of five-, seven- and higher-membered rings. The four-membered rings are possibly stabilized by the occurrence of a defect structure involving partially-broken Si-O bonds.

Taylor and Brown[22] have inferred structures from the X-ray RDF's of the feldspar glasses albite, ($Na_2O.Al_2O_3.6SiO_2$ - Ab), orthoclase, ($K_2O.Al_2O_3.6SiO_2$ - Or), and anorthite, ($CaO.Al_2O_3.2SiO_2$ - An). The similarity in the RDF's of silica, Al and Or glass lead them to suggest that Ab and Or have a tridymite-like structure based on a three-dimensional framework of six-membered rings of tetrahedra in which Al is substituted for Si. The alkali cations are contained in 12-fold coordination in the interstices between the rings, with one interstice for every two tetrahedral atoms. This model is known as the "stuffed tridymite model". The structures of the glasses thus differ from those of the corresponding crystalline forms, which contain four-membered rings of tetrahedra. Nepheline, $Na_2O.Al_2O_3.2SiO_2$, and kalsilite, $K_2O.Al_2O_3.2SiO_2$, have tetrahedral structures similar to tridymite with alkali atoms in the spaces between the rings. Thus, on the assumption that the tetrahedral framework of Ab glass is similar to that of crystalline nepheline, and that the structure of Or glass is similar to that of that of crystalline kalsilite, Taylor and Brown found good agreement between the calculated densities of the stuffed tridymite models and the observed densities of the Ab and Or glasses.

Further support for the model is obtained from the observation that nucleation and growth of crystalline Ab and Or from their melts is difficult. Crystallization requires that at least two (Si,Al)-O bonds be broken and reformed to form a four-membered ring in the crystal from a six-membered ring in the melt. Similarly, in melting experiments, Taylor and Brown found that crystals of Ab and Or persisted for 48 hours at a superheat of 60 centigrade degrees.

In contrast with Ab and Or glasses, Taylor and Brown concluded that An glass has a feldspar-like structure containing four-membered rings of AlO_4 and SiO_4 connected to other tetrahedra in a random manner. The similarity between the glass and the crystalline structure is responsible for the ease with which An crystallizes. A schematic representation of the feldspar four-membered ring structure is shown in Fig. 4(a) and the stuffed tridymite six-membered ring structure is shown in Fig. 4(b). The circles indicate the positions of the alkali cations. The vertical ring on the left side of Fig. 4 (b) is known as the "boat" conformation and the horizontal top and bottom rings have the "chair" conformation.

From X-ray DRF studies Taylor and Brown[23] also concluded that jadeite ($Na_2O.Al_2O_3.4SiO_2$ - Jd) and nepheline ($Na_2O.Al_2O_3.2SiO_2$ - Ne) have the stuffed tridymite structure. Thus in Jd two thirds of the interstices are occupied by sodium ions and one

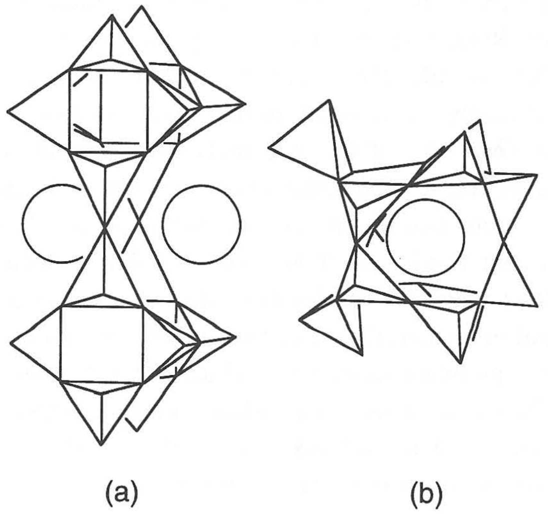
(a) (b)

Fig. 4. Schematic representation of (*a*) feldspar-type four-membered rings of tetrahedra, (*b*) stuffed tridymite six-memberes rings of tetrahedra. (ref 22).

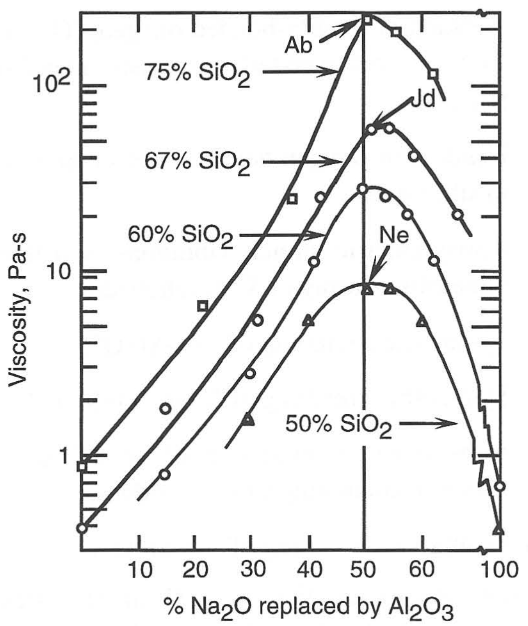

Fig. 5. The viscosities of melts in the system $Na_2O–Al_2O_3–SiO_2$ at 1700°C. (ref 24).

third of the tetrahedral sites are occupied by aluminum ions, and in Ne all of the interstitial sites are occupied by sodium ions and half of the tetrahedral sites are occupied by aluminum ions. The RDF's show that interatomic distances increase as Al is substituted for Si, which is caused by a higher percentage of larger AlO_4 tetrahedra and an overall expansion as the interstitial sites are filled with Na. Taylor and Brown found that the amount of structural detail in the DRF's beyond 0.47 nm decreases in the order silica < Ab < Jd < Ne, and suggested that this was caused by the increased chance of a structural "irregularity" with increasing substitution of Al for Si. Suggested irregularities included two sodium atoms in a single interstice and an Al coordinated by six oxygens rather than four. They referred to measurements of the viscosities of melts in the system $Na_2O–Al_2O_3–SiO_2$ made at 1500°C by Riebling[24]. Some of these data are shown in Fig. 5. The compositions of the most viscous melts occur at Na/Al = 1.0, which is to be expected when the charge balance between Na^+ and Al^{3+} facilitates a fully polymerized structure in which all of the oxygens are doubly-bonded between $(Si,Al)O_4$ tetrahedra. Taylor and Bell suggested that the decrease in viscosity at Na/Al = 1 with progressive relacement of SiO_2 by $NaAlO_2$ could be attributed to the type of irregularities mentioned above and the replacement of Si-O bonds by weaker Al-O bonds. Melts with Na/Al < 1.0 are expected to have Al in six-fold coordination[25] causing a decrease in viscosity due to local disruption of the tetrahedral network and the presence of $Al^{VI}–O$ bonds which are weaker than $Al^{IV}–O$ bonds, and melts of Na/Al > 1.0 contain non-bridging oxygens which changes the mechanism of viscous flow.

Mysen *et. al.*[26] have interpreted the Raman spectra of silicate and aluminosilicate glasses in terms of ionic structure. This involved deconvoluting the measured spectra into gaussian bands centered on specific wave numbers. In sodium silicate glasses the deconvoluted bands were assigned to, or were described as being most likely due to:

i. Rocking of doubly-bonded oxygen, (O°), in a fully polymerized three-dimensional structure.

ii. Bending of oxygen bonds in defect structures in silica glass.

iii. Antisymmetric stretch vibrations in a three-dimensional array of SiO_4 tetrahedra.

iv. Symmetric stretching of $^{-}O{-}Si{-}O^{\circ}$.

v. Symmetric stretching of O° in $^{-}O{-}Si{-}O^{\circ}$.

vi. Antisymmetric stretching of of O° in any structure containing oxygen bridges.

vii. Symmetric stretching of $^{-}O{-}Si{-}O^{-}$.

It was considered that the $^{-}O{-}Si{-}O^{-}$ stretch vibrations may be derived from a chain or a ring structure (NBO/Si = 2) and the $^{-}O{-}Si{-}O^{\circ}$ vibration from a structural unit that has NBO/Si = 1 (e. g., a sheet). The ratio NBO/Si is the ratio of nonbonding oxygens to silicons in the structure, which, in the absence of free oxygen, (O^{2-}), ions in the structure, is a simple function of the mole fraction of SiO_2.

Mysen *et. al.* stated that the most important observation made from the assignment of the Raman spectra is that there is a unique set of coexisting anionic "structural units" for specific ranges of NBO/Si. These units are listed in Table II.

Table II. Specific structural units in silicate melts.

Structural unit	NBO/Si	Composition
SiO_4^{4-}	4	orthosilicate
$Si_2O_7^{6-}$	3	pyrosilicate
$Si_2O_6^{4-}$	2	metasilicate
$Si_2O_5^{2-}$	1	disilicate
SiO_2	0	silica

The authors thus considered their model to be simple in comparison with models such as the polymer model, and they discard the validity of the conclusions drawn from the TMS-chromatograph studies, (i) because the results of the TMS differ from the conclusions drawn from the Raman spectroscopy study and (ii) because they consider the results of the TMS work to be internally inconsistent, in that Lentz' proportions of TMS derivatives of $2Na_2O.SiO_2$ did not add up to 100%. The authors did not see an influence of composition on the frequency of the Si-O stretch bands and thus concluded that structural units with NBO/Si between that of a dimer and that of a chain (3 and 2, respectively) do not exist in significant amounts in silicate melts - which effectively denies the validity of the polymers models. The authors also consider that the occurrence of branched chain ions is unlikely, (i) because there is no experimental evidence of branching chain ions in silicate melts and (ii) branched chains are not found in crystalline silicates. Instead chains and sheets are formed, and there is no clear reason why branched chains would be expected to form in a melt.

The suggestion was made that monomers are the most abundant species in melts with compositions close to that of the orthosilicate and that they become increasingly unstable with increasing silica content, although they still occur at the disilicate sheet composition. In contrast the dimer has a restricted range of stability with an apparent maximum in abundance between the ortho- and metasilicate compositions. The instability of the dimer appears to coincide with the appearance of the sheet unit and with increasing NBO/Si the sheet and chain species increase in abundance relative to the monomer. The authors propose that the equilibria among the coexisting anionic species (units) can be expressed as follows.

For 4 > NBO/Si > 2;

$$2Si_2O_7^{6-} = 2SiO_4^{4-} + Si_2O_6^{4-} \tag{2}$$

for 2 > NBO/Si > 1

$$3Si_2O_6^{4-} = 2SiO_4^{4-} + 2Si_2O_5^{2-} \tag{3}$$

and for 1 > NBO/Si > 0.1

$$2Si_2O_5^{2-} = Si_2O_6^{4-} + 2SiO_2 \tag{4}$$

Thus the model delineates three distinct ranges of composition, in each of which a combination of three structural units occurs.

Mysen *et. al.*[27] obtained Raman spectra from quenched melts of compositions (in mole percent) 90% SiO_2 - 10% Al_2O_3 (designated SA10) and 84% SiO_2 - 10% Al_2O_3 - 6% Na_2O (designated SAN6) and concluded that non-bridging oxygens are formed when Na/Al < 1.0, i.e., Al^{3+} is a network modifier existing in octahedral coordination with oxygen. They presented the formalized equation

$$Al(IV)Si_7O_{18}^- = Al^{3+}(VI) + 7SiO_2 + 2O^{2-} \quad (5)$$

where $Al^{3+}(VI)$ denotes Al^{3+} as a network modifier (e.g. VI-coordinated), SiO_2 is the silicate component with tetrahedrally-coordinated Si^{4+} and O^{2-} is the (sic) nonbridging oxygen formed as a result of the change in coordination of aluminum. It can be noted that the charge balance in Eq. (5) requires that O^{2-} be a free, as opposed to nonbridging, oxygen. Mysen *et. al.* claimed that Eq (5) was written for the stoichiometry of composition SAN6, which is Si:Al:Na = 24:10:6. The stoichiometry in Eq. (5) is Si:Al:Na = 140:10:10. The equilibrium given by Eq. (4) occurs in SA10, and the authors combined this with that given by Eq. (5) to give

$$3Al(IV)Si_7O_{16}^- =$$

$$3Al^{3+}(VI) + 13SiO_2 + 2Si_2O_5^{2-} + 2Si_2O_6^{4-} \quad (6)$$

which is taken as the description of the reaction along the composition path SA10 - SAN6. The authors then state that "As written, Eq. (6) rigorously describes the proportions in structural units in the SA10 melt when the reaction has gone to completeion. Anywhere along the join between SAN6 and SA10 there will be an equilibrium constant with a finite value, a value that will increase as Na/Al decreases."

Mysen *et. al.* concluded that within the first 10 mole percent in the system $Na_2O.2SiO_2$ - $Na_2O.Al_2O_3$ all of the added aluminum enters three-dimensional structures. Designating the aluminate structural units with NBO/Al = 0, 1 and 2 as, respectively, $NaAlO_2$, $(NaAl)_2O_5^{2-}$, and $(NaAl)_2O_6^{4-}$, the equilibrium in the range 10-20 mole percent Al_2O_3 was given as

$$2NaAlO_2 + 3Si_2O_5^{2-} =$$

$$4SiO_2 + Si_2O_6^{4-} + (NaAl)_2O_5^{2-} \quad (7)$$

and, in the concentration range 20-40 mole percent Al_2O_3 was given as

$$4NaAlO_2 + 5Si_2O_5^{2-} =$$

$$8SiO_2 + Si_2O_6^{4-} + (NaAl)_2O_5^{2-} + (NaAl)_2O_6^{4-} \quad (8)$$

Only two composition regions were discerned in the corresponding system $CaO.2SiO_2$ - $CaO.Al_2O_3$. In the range up to 10 mole percent Al_2O_3 aluminum enters both the three-dimensional network units and the sheet units and the equilibrium is identical with that given by Eq. (7), except that Na^+ is replaced with Ca^{2+}. In the composition range with more than 10 mole percent Al_2O_3 aluminum enters all of the structural units in which it mixes randomly with the silicate counterparts. The equilibrium is given by

$$2CaAl_2O_4 + 5Si_2O_5^{2-} = 8SiO_2$$

$$+ Si_2O_6^{4-} + CaAl_2O_5^{2-} + CaAl_2O_6^{4-} \quad (9)$$

From study of the Raman spectra of glasses in the system SiO_2 - $Na_2O.SiO_2$ Seifert *et. al.*[28] concurred with Taylor and Brown[23] that the SiO_2 framework is largely preserved when $NaAlO_2$ is incorporated into the network. They implied that the Al^{3+} occurs mainly in the six-fold rings of silica, and suggested that two types of six-membered rings occur in silica - a "puckered" ring which has a maximum Si-O-Si angle which is 5 - 10° smaller than the other one. The Raman spectra of glasses in the systems SiO_2 -

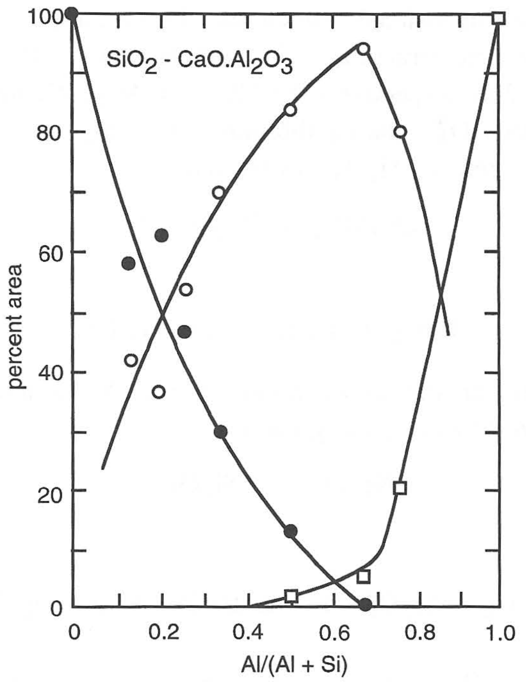

Fig. 6. Proportion of areas of band stemming from different structural units in the system SiO_2–$CaO.Al_2O_3$ as a function of bulk Al/(Al + Si) in the glasses. Closed circles, six-membered SiO_2 rings; open circles, $Al_2Si_2O_8^{2-}$ four-membered rings; open squares, six-membered $Al_2O_4^{2-}$ rings. (ref 28).

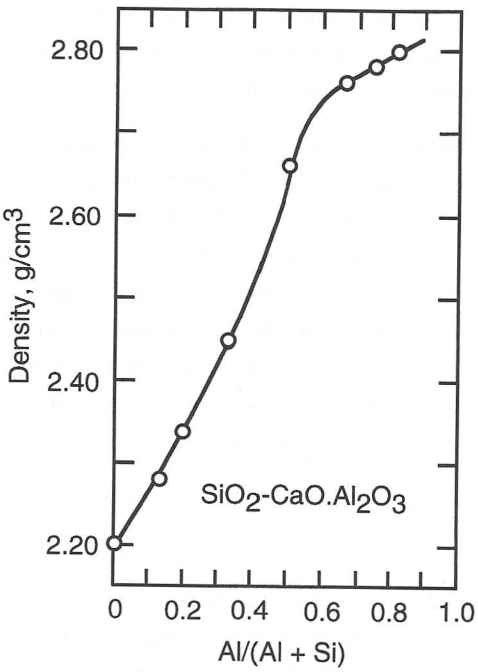

Fig. 7. The densities of glasses in the system SiO_2–$CaO.Al_2O_3$. (ref 28).

$CaO.Al_2O_3$ and SiO_2 - $MgO.Al_2O_3$ lead Seifert *et. al.* to suggest that a structural unit with stoichiometry "similar" to $Al_2Si_2O_8^{2-}$ occurs in these systems. Also, the similarity of the $CaO.Al_2O_3$ glass spectrum to that of the corresponding crystalline phase lead them to suggest that $Al_2O_4^{2-}$ units occur in the quenched melt as six-membered rings. Consequently, melts in the systems SiO_2 - $CaO.Al_2O_3$ and SiO_2 - $MgO.Al_2O_3$ are mixtures of SiO_2, $Al_2Si_2O_8^{2-}$ and $Al_2O_4^{2-}$ interconnected three-dimensional structures, the relative concentrations of which vary with composition as shown in Fig. 6. The densities of glasses in the system SiO_2 - $CaO.Al_2O_3$, shown in Fig. 7, were explained in terms of this model. The dependence of density on composition shows two, almost straight lines; a segment between SiO_2 and the An composition, and a less steep segment between the An composition and $CaO.Al_2O_3$. Seifert *et. al.* rationalized this behavior in terms of mixing of SiO_2, $CaAl_2Si_2O_8$ and $CaAl_2O_4$ units. Similar density-composition behavior occurs in the system SiO_2 - $MgO.Al_2O_3$.

Nuclear magnetic resonance spectroscopy, NMR, has been used by Murdoch *et. al.*[29] in an attempt to study the environments of silicon in silicate and aluminosilicate glasses. It is claimed that NMR spectra give information on the degree of polymerization of the silicate anions, the variation in the Si-O-Si bond angle and the distribution of silicate and aluminate tetrahedra in three-dimensional framework aluminosilicate glasses. Murdoch *et. al.* measured the NMR spectra of alkali and alkaline earth metasilicates and disilicates and compared them with the NMR spectra of the corresponding crystalline compounds. This analysis required the assumption that no significant difference in distribution of Si-O-Si bond angles exists between the corresponding glassy and crystalline states, in which case differences in spectra can be attributed to variations in silicate polymerization. The NMR spectra are interpreted in terms of Q^n, where Q represents a tetrahedrally-coordinated silicon and n is the number of doubly-bonded oxygen in its coordination sphere. Thus at the disilicate composition the equilibrium of interest is

$$2Q^3 = Q^2 + Q^4 \tag{10}$$

which is equivalent to the equilibrium given by Eq. (4). Similarly, at the metasilicate composition, the relevant equilibria are

$$2Q^2 = Q^1 + Q^3 \tag{11}$$

and/or

$$2Q^2 = Q^0 + Q^4 \tag{12}$$

Murdoch *et. al.* stated an expectation that different network-modifying cations shift these equilibria to the left or to the right. A shift to the left implies the same type of silicate polymerization as is found in the corresponding crystal with a more or less evenly-spaced distribution of cations, and a shift to the right implies a bunching of cations near those silicate units with extra non-bridging oxygens. The conclusions drawn from interpretation of the NMR spectra were somewhat limited. The spectra showed, not surprizingly, that the dominant silicate species in the glass is that found in the corresponding crystalline material and that the range of silicate species present increases with smaller, more highly charged cations. It was also concluded that such cations probably induce greater variety in the distribution of Si and Al in aluminosilicate glasses. Typical results are shown in Fig. 8, which shows the variations of the integrated linewidths (peak area/height) with ionic potential of the cation (charge/radius). Although Fig. 8 shows a definite correlation between linewidth and ionic potential, Murdoch *et. al.* found it "curious" that the two lines are displaced from one another and attributed this to artifacts of peak broadening in the NMR spectra. Similarly, Stebbins *et. al.*[30] found that line broadening in the NMR spectra for ^{27}Al in $Na_2O.Al_2O_3.4SiO_2$ and $0.35Na_2O:0.15Al_2O_3:0.5SiO_2$ melts made it difficult to draw conclusions about the coordination of Al in the liquids. From study of the NMR spectra of alkali silica melts Farnan and Stebbins[31] and Liu *et. al.*[32] have shown that the lifetimes of silicate species in melts are short. In $Na_2O.2SiO_2$ the lifetimes range from a few microseconds at temperatutes above the liquidus to times approaching a nanosecond at the melting temperature of silica. These authors thus concluded that although polymeric "molecules" may be present in glasses in the sense of topological connectivity, they do not persist as discrete entities in the melt at temperatures much above the glass transition.

5. DISCUSSION

The TMS studies of Masson and Gotz have provided a direct indication of the the forms and relative concentrations of anions occurring in silicate melts. Masson *et. al.*[33] subjected iron blast furnace slags and open hearth steelmaking slags to the direct trimethylsilylation method and extracted, in decreasing order of abundance, silicate monomers, dimers, trimeric chains and

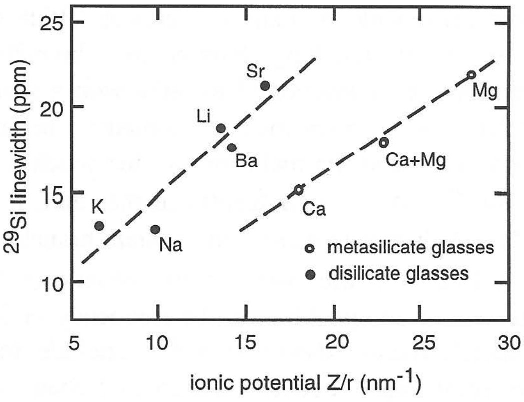

Fig. 8. Integrated linewidths (peak area/height) of disilicate and metasilicate glasses as a function of the ionic potential (charge/ionic radius) of the cation. (ref 29).

tetrameric rings from both slags. In addition, they extracted PO_4^{3-} and the silico-phosphate anions $SiPO_7^{5-}$, $Si_2PO_{10}^{7-}$ and $Si_3PO_{12}^{7-}$ from the open hearth slags and $Si_7O_{19}^{10-}$ and $Si_{13}O_{15}^{10-}$ from the more acidic blast furnace slags. They also detected tetrameric chain silicate anions, pentameric ring anions and several more complex ring and spherical anions. Of particular significance is the identification of the trimeric and tetrameric ring silicate ions first postulated by Bockris *et. al.*[1,2]

In discarding the validity of the results of TMS studies Mysen *et. al.*[26] are disingenuous in that they cite the work of Kuroda and Kato[34], which showed that the TMS derivatives of hemimorphite vary with the type of organic solvent used with the TMS reagant, and did not cite the work of Gotz and Masson[13] which yielded almost 97% of the TMS dimer derivative from hemimorphite, in spite of the fact that the results of the latter study were published nine years after the results of the former were published. Inasmuch that TMS derivatives are identified by their molecular weight, the technique cannot distinguish between a linear chain *n*-mer and a branching chain *n*-mer. However, the observation that branched chain silicate anions are not found in crystalline silicates is a poor reason to dismiss their existence in the liquid state. By definition the crystalline state is one of long range order and it is not reasonable to expect a crystal lattice to accommodate branching chain anions - branched chains will be transformed to units with a more regular or symmetrical geometry during crystallization of the melt. Indeed, inasmuch that the SiO_4^{4-} ion is a four-functional mer unit, it is highly likely that silicate melts contain branching chain ions. On the basis of not observing an influence of composition on the frequency of Si-O stretch bands Mysen *et. al.*[26] conclude that "structural units" between dimers and chains of NBO/Si = 3 do not exist in significant amounts in silicate melts. It is logical to conclude that a silicate melt capable of forming infinite chains is capable of forming chains of finite length.

Inconsistences occur in the conclusions drawn from examination of the Raman spectrum of $CaO.2SiO_2$ glass[27]. The spectrum shows that, while co-existing chain and sheet units predominate, the structure contains monomers but the spectrum also shows no evidence of three-dimensional network structures. Mysen *et. al.* point out the mass balance considerations require the presence of structural units which are more polymerized than a sheet and thus conclude "It is likely, therefore, that this composition, in fact, contains three-dimensional units." This raises the question - if the structure contains three-dimensional units, why do they not appear in the Raman spectrum?

Of the five "structural units" postulated by Mysen *et. al.*[26] and listed in Table II, two, SiO_4^{4-} and $Si_2O_7^{6-}$ are discrete anions and two $Si_2O_6^{4-}$ and $Si_2O_5^{2-}$ are designated, respectively, as units of "chain" and "sheet" structures. Consequently, as partial molar free energies cannot be assigned to sub-units of chemical species, the equilibria given by Eqs. (2), (3) and (4) have no thermodynamic basis. However if the unit $Si_2O_6^{4-}$ is considered to be two SiO_3^{2-} units, then, as shown in Fig. 9, three of the latter units can be combined to form the trimeric cyclic $Si_3O_9^{6-}$ anion and four can be combined to form the tetrameric cyclic $Si_4O_{12}^{8-}$ anion. Similarly, as shown in Fig.10, three $Si_2O_5^{2-}$ units can be

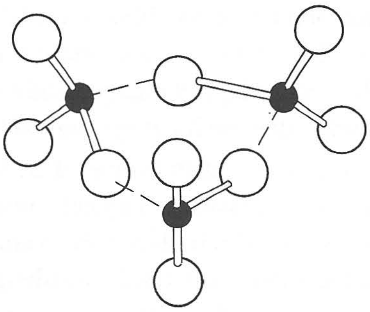

Fig. 9. Combination of three SiO_3^{2-} units to form an $Si_3O_9^{6-}$ anion.

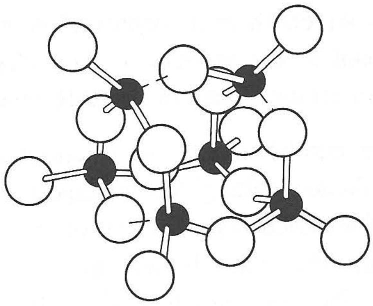

Fig. 10. Combination of three $Si_2O_5^{2-}$ units to form an $Si_6O_{15}^{6-}$ anion

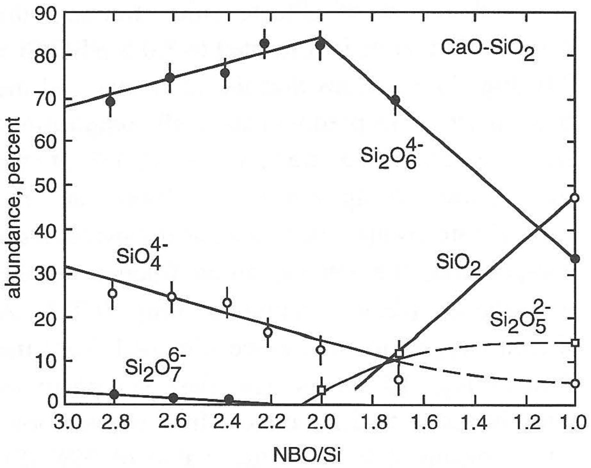

Fig. 11. The abundance of structural units in CaO–SiO_2 glasses as a function of composition. (ref 34).

combined to form the $Si_6O_{15}^{6-}$ anion (formed by face to face polymerization of two $Si_3O_9^{6-}$ rings) or four of them can be combined to form the $Si_8O_{20}^{8-}$ anion. By means of this postulate interpretation of the Raman spectra of silicate melts is in accord with the results of the TMS studies and reference need not be made to the infinite chain and sheet structures originally proposed by Endell and Hellbrugge[33]. The equilibria given by Eqs. (2), (3) and (4) become, respectively,

$$3Si_2O_7^{6-} = 3SiO_4^{4-} + Si_3O_9^{6-} \tag{13}$$

$$3Si_3O_9^{6-} = 3SiO_4^{4-} + Si_6O_{15}^{6-} \tag{14}$$

and

$$Si_6O_{15}^{6-} = Si_3O_9^{6-} + 3SiO_2 \tag{15}$$

which, involving discrete silicate species, have a thermodynamic basis. Eqs. (13), (14) and (15) can also be written in terms of the ions $Si_4O_{12}^{8-}$ and $Si_8O_{20}^{8-}$. The conclusions drawn from the Raman studies can be reviewed in terms of the above equilibria. Fig. 11 shows the variation with composition of the "structural units" in the system CaO–SiO_2 as proposed by Mysen *et. al.*[34]. The composition ranges from the pyrosilicate at NBO/Si = 3.0 to the disilicate at NBO/Si = 1.0 with the compositions of the glasses being incremented by 0.2 NBO/Si units. $Si_2O_6^{4-}$, which is the most abundant unit in all compositions, has a maximum concentration at the metasilicate composition, NBO/Si = 2.0. Converting the $Si_2O_6^{4-}$ and $Si_2O_5^{2-}$ units to, respectively, $Si_3O_9^{6-}$ and $Si_6O_{15}^{6-}$ ions, the silicate ion fractions of the four silicate anions are shown in Fig. 12. Since the SiO_2 unit cannot be included

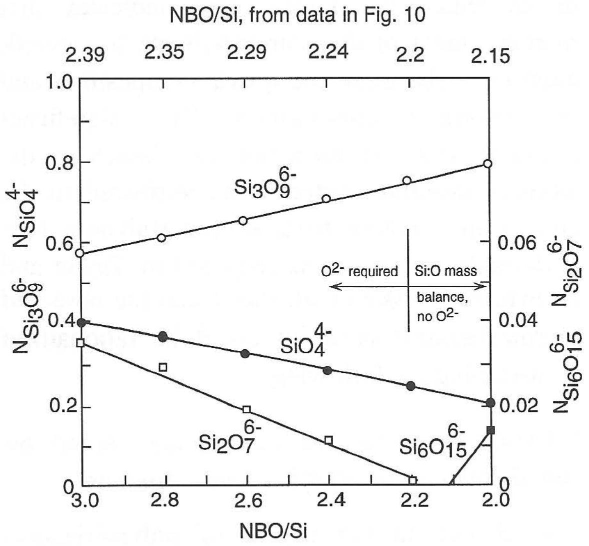

Fig. 12. Silicate anion fractions as a function of composition calculated from the data in Fig. 10.

in a calculation of silicate anion fraction, the composition range is restricted to 3.0 > NBO/Si > 2.0. Fig. 12 indicates that the monomer and the trimeric ring ions predominate at all compositions (from a combined fraction of 96.5% at the pyrosilicate composition to 99% at the metasilicate composition) and, at the pyrosilicate composition, the silicate anion fraction of the pyrosilicate (dimer) anion is only 0.035. A silicon-oxygen mass balance obtained from the data in Fig. 10 shows that glass compositions with NBO/Si > 2.2 contain free oxygen ions which means that the actual value of NBO/Si, given by the upper scale in Fig. 12, is less than the nominal value calculated by Mysen *et. al.*

The thermochemical measurements of Navrotsky *et. al.*[37] support the structural conclusions of Taylor and Brown[22,23]. Navrotsky *et. al.* found that the heat of formation of glasses in the system SiO_2-$Na_2O.Al_2O_3.6SiO_2$, (quartz - albite), is zero, and suggested that this indicates that the substitution of Na + Al for Si occurs randomly with no specific energy constraints in the stuffed-tridymite structure. The situation in the SiO_2-$CaO.Al_2O_3.2SiO_2$ system is more complex in that endothermic mixing occurs in quartz-rich glasses and exothermic mixing occurs in anorthite-rich glasses. This indicates that rearrangement of the aluminosilicate framework must occur between the quartz composition and the anorthite composition. The significant negative heats of formation of glasses in the albite - anorthite system were attributed to the change in structure from stuffed tridymite to a feldspar-like structure as proposed by Taylor and Brown. Navrotsky *et. al.* stated that the observed thermochemical behavior could be rationalized by assuming the following.

1. Exothermic heats of mixing are caused by breakdown of the anorthite glass structure.
2. A change in the degree of polymerization (from framework silicate composition in quartz, albite or anorthite to chain silicate composition in $CaO.MgO.2SiO_2$) causes a small positive heat of mixing.
3. The mixing of non-framework cations produces an exothermic contribution which is proportional to the product of their charges of some other factor related to size difference.

The equilibria among structural units in aluminosilicate melts given by Eqs. (6)-(9) are not credible. Each involves five or six types of unit with the equilibrium given Eq. (8) involving 20 units and that given by Eq. (6) involving 23 units.

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