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Determination of the mixing properties of granitic and other aluminosilicate melts by Knudsen Cell Mass Spectrometry

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Abstract—The entropies, enthalpies and free energies of mixing of melts in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 have been determined by Knudsen Cell Mass Spectrometry (KCMS). The enthalpies of mixing have an accuracy and precision (1-σ) of around 1.0 and 0.5 KJ/mol, respectively (FRASER and BOTTINGA, 1985), and are thus comparable with the best solution calorimetric data available for glasses. The mixing properties of the melts are related to the topology of the underlying liquidus surface so that marked changes in the entropy, enthalpy and free energy of mixing of the melts accompany changes in the nature of the crystalline phase in equilibrium with the melt at lower temperatures. These data and the results of X-ray diffraction, NMR and Raman spectroscopic studies of glasses of similar composition indicate that clustering may occur in the melts to produce regions which differ in structure and composition on the approximately 20 Å scale. The equilibrium liquids are thus inhomogeneous on the micro-scale and may contain structures more closely related to the crystalline phase on the liquidus than to a mineral phase of the same composition as the liquid.

INTRODUCTION

ACCURATE MEASUREMENTS of the activities of silicate components in magmas and their interpretation in terms of molecular structure are essential for the construction of predictive models for a wide range of igneous phenomena. Several independent thermodynamic studies of the mixing properties of melts and glasses in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 (Ne–Ks–Qz) have recently been made using a range of experimental techniques. These include vapour pressure measurements made on the melts themselves at high temperature by KCMS (RAMMENSEE and FRASER, 1982; FRASER *et al.*, 1983, 1985; ROGEZ *et al.*, 1983), HF and borate melt solution calorimetry on quenched and annealed glasses (ROGEZ *et al.*, 1983; HENRY *et al.*, 1982; HERVIG and NAVROTSKY, 1984; HOVIS, 1984) and drop calorimetry on melts and glasses (STEBBINS *et al.*, 1983; RICHET and BOTTINGA, 1984). In addition, measurements of the structures of glasses and melts in this and allied systems have been made by X-ray diffraction (TAYLOR and BROWN, 1979a, 1979b), Raman spectroscopy (MYSEN *et al.*, 1981; MCMILLAN *et al.*, 1982) and NMR spectroscopy (MURDOCH *et al.*, 1985; STEBBINS *et al.*, 1985; FRASER and CLAYDEN, 1986) so that considerable structural information is also available.

Estimates of the activities of silicate components in melts have been obtained until recently mainly from depression of freezing-point calculations (*e.g.*, WOOD and FRASER, 1976; BOTTINGA and RICHET, 1978). These suffer from large inaccuracies resulting from the combination of uncertainties in the positions of liquidus surfaces and in the heats of fusion used in the calculations. In the present series of measurements we set out to determine the activities of silicate components in melts directly by measuring their equilibrium vapour pressures by KCMS.

The purpose of the present paper is to review the application of KCMS to the study of the thermodynamic properties of silicate melts, to report the entropies of mixing of $NaAlSi_3O_8$–$KAlSi_3O_8$ melts and to comment on possible relationships between these measurements and the atomic and molecular structures of the melts.

METHOD

The measurement of activities in solution by KCMS is a standard technique in modern physical chemistry. It is based on the fundamental relationship between activity and equilibrium vapour pressure:

$$a_i = f_i/f_i^0 = p_i/p_i^0 \tag{1}$$

where a_i is the activity of component i, and f_i and f_i^0, p_i and p_i^0 are the fugacities and partial pressures of the component over a solution and standard state respectively.

For the very low partial pressures of components in equilibrium with most silicate melts the fugacity is equal to the partial pressure. Thus, by measuring the equilibrium vapour pressures of silicate melts, the activities of the silicate components may be determined directly using equation (1).

The volatilization of Na and, to a lesser extent, K, from silicate melts and glasses is well known to experimental petrologists (*e.g.*, KRACEK, 1930; O'HARA *et al.*, 1970) and to analysts of glasses using the electron microprobe. The volatility and the absolute Na/K ratio of the vapour depend on the temperature, oxygen activity and chemical properties of the melt or glass in question. Since silicate melts thus vaporize incongruently, great care was taken in all our experiments to identify all possible species present and to consider the effects of these on the results. In the case of the alkali aluminosilicate melts considered in the present paper, we have shown (RAMMENSEE and FRASER, 1982) that at temperatures up to about 1600°C the vapour species consist almost entirely of monatomic Na and K atoms (Figure 1). Measurements made with low ionization energies in the ionization chamber failed to show any evidence of Na– or K–oxide species and so the possibility of fragmentation of oxide species in the ionization chamber can be excluded. At the highest temperatures studied, very small amounts of SiO are measurable.

The equilibrium vapour pressures of alkali aluminosilicate melts are the sums of the partial pressures of all the species present. Thus the vapour pressures of, for example, $NaAlSi_3O_8$ and $KAlSi_3O_8$ melts are given by:

$$\mathrm{P}_{NaAlSi_3O_8} = p_{Na} + p_{NaO} + p_O + p_{SiO} + \cdots \qquad (2)$$

$$\mathrm{P}_{KAlSi_3O_8} = p_K + p_{KO} + p_O + p_{SiO} + \cdots \qquad (3)$$

Because the vapours above melts in this system are composed almost entirely of monatomic Na and K atoms and the oxygen fugacity is buffered at low values by the Mo Knudsen cells, then the equilibrium vapour pressures of pure $NaAlSi_3O_8$ and $KAlSi_3O_8$ melts are to a first approximation simply the partial pressures of Na and K:

$$P_{NaAlSi_3O_8} = p_{Na} \qquad (4)$$

$$P_{KAlSi_3O_8} = p_K. \qquad (5)$$

The activities of the $NaAlSi_3O_8$ and $KAlSi_3O_8$ components in mixed melts can therefore be obtained by combining equations (4) or (5) with (1)

$$a_{NaAlSi_3O_8} = p_{Na}/p^0_{Na} \qquad (6)$$

$$a_{KAlSi_3O_8} = p_K/p^0_K \qquad (7)$$

where p_{Na} and p_K are the partial pressures of Na and K above the mixed melts and p^0_{Na} and p^0_K are the partial pressures of Na and K above pure molten $NaAlSi_3O_8$ and $KAlSi_3O_8$ respectively.

It should be noted that although these melts vaporize incongruently to give vapours consisting almost entirely of alkali metal atoms, the activities obtained by taking the ratio of the partial pressure of an alkali metal atom above a mixed melt to that of the same alkali metal atom species in equilibrium with an aluminosilicate melt as standard state, are the activities of the aluminosilicate components and not, for example, Na metal or Na_2O. Activities relative to the latter standard states could be obtained if, for example, the partial pressures were compared with those above pure liquid Na metal or Na_2O respectively.

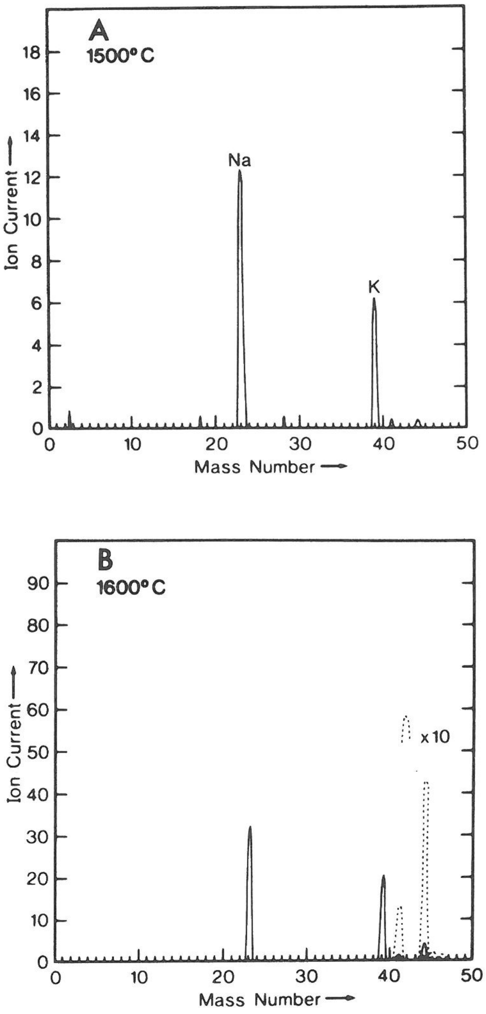

FIG. 1. Mass spectra for the 50:50 (mol) composition in the system $NaAlSi_3O_8$–$KAlSi_3O_8$ in arbitrary units of ion current. The spectra are dominated by ^{23}Na and ^{37}K. Minor amounts of ^{41}K can also be seen, and at higher temperatures small peaks due to ^{28}SiO, ^{29}SiO and ^{30}SiO are visible.

In the Knudsen effusion technique (KNUDSEN, 1909), equilibrium partial pressures are determined by measuring the flux of vapour species through a minute aperture in an inert container (the Knudsen cell) into an evacuated space. So long as the area of the effusion aperture is small relative to the surface area of the lid, which is bombarded inside the cell by the vapour molecules thus setting up the intrinsic vapour pressure, the rate of effusion is related to the equilibrium vapour pressure inside the cell by the Herz-Knudsen equation:

$$dN_i/dt = (p_i AK)/(2\pi RM_iT)^{1/2} \qquad (8)$$

where N_i is the number of moles of component i evaporated in time t, p_i is the partial pressure, A the orifice area, K the Clausing emission efficiency factor, R is the gas constant, M_i the molecular weight, and T the temperature (PAULE and MARGRAVE, 1976).

In our experiments, the fluxes of vapour components in the resulting molecular beam were determined using a quadrupole mass spectrometer and the partial pressures obtained from the measured ion currents using the relationship (Chatillon *et al.*, 1975):

$$p_i = (I_i^+ T)/S_i \tag{9}$$

where I_i^+ is the ion current of species i and S_i is the sensitivity of the spectrometer to species i.

EXPERIMENTAL

The apparatus used for making these measurements consists of a rotatable tantalum block containing four Mo Knudsen cells. The block can be heated by a Ta rod furnace to 1650°C. The molecular beam of Na and K atoms effusing from each cell passes through a rotating beam-chopper to enable automatic subtraction of background by distinguishing between atoms which effuse directly from the cells and those originating above the chopper from elsewhere in the apparatus. The chopped beam then passes into the ionization chamber of a quadrupole mass spectrometer. The apparatus has been described in detail in previous papers (Rammensee and Fraser, 1981; Fraser and Rammensee, 1982; Fraser *et al.*, 1985) and a diagram is shown in Figure 2. Gel starting materials used in our earlier experiments were replaced by pre-melted mixed glasses to improve equilibration times and temperatures were measured using Pt6%Rh/Pt30%Rh thermocouples calibrated by observing changes in the vapour pressure of pure Ag at the melting point (Fraser *et al.*, 1985).

Considerable care was taken in all experiments to ensure that equilibrium was achieved. Vapour pressure measurements were always made in both increasing and decreasing temperature sequences so that the equilibrium value was approached from both sides. In addition, because the Knudsen effusion technique depends on the loss of small amounts of material from the system, it is important to show that no systematic changes in sample composition occurred during the experiments. For this reason, the temperatures at which measurements were made were non-sequential as is shown in Figure 3, so that any change in sample composition would be immediately visible as a systematic error. Some samples quenched at the end of an experiment were also sectioned longitudinally and analyzed for Na and K using the electron microprobe. No significant surface depletion effects could be observed. The consistency of measurements made throughout any experiment and the homogeneity of glass compositions analyzed by the electron microprobe imply that no significant changes in sample composition occurred during these experiments. This conclusion is in accord with calculations of the very small weight loss which occurs during an experiment and the high diffusivities of Na and K in these melts (Jambon, 1982) which allow any surface loss by evaporation to be immediately restored. Even for an average vapour pressure of 10^{-5} torr and the most unfavourable case in which the Clausing emission factor is 1, the total loss of material during a typical six to ten hour experiment is of the order of only 3 μg. A detailed description of the experimental technique is given in previous papers (Rammensee and Fraser, 1982; Fraser *et al.*, 1985).

MEASUREMENTS IN THE SYSTEM $NaAlSiO_4$–$KAlSiO_4$–SiO_2

We have investigated the mixing properties of four binary and pseudobinary joins in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 having fixed Si/Al ratios, and a series of compositions on the join $Na_{0.7}K_{0.3}AlSiO_4$–SiO_2 (Rammensee and Fraser, 1982, 1986; Fraser *et al.*, 1983, 1985) as shown in Figure 4. In addition, the heats of mixing of quenched and annealed glasses in this system have been measured by HF and high temperature oxide melt solution calorimetry (Rogez *et al.*, 1983; Hovis, 1984; Henry *et al.*, 1982; Hervig and Navrotsky, 1984) and these have been reviewed recently by Fraser and Bottinga (1985).

In the Knudsen effusion experiments, the Na/K ratios of vapours in equilibrium with mixed Na, K aluminosilicate melts were measured as functions of bulk composition. Typical results for the system $NaAlSi_5O_{12}$–$KAlSi_5O_{12}$ which is near the granite minimum at 1 atmosphere pressure in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 (Schairer 1957), are shown in Figure 3. Note that results were obtained both down– and up–temperature as shown by the run numbers. The activities of the aluminosilicate components can, in principle, be obtained by comparing the partial pressures of Na and K above the melts with those measured above pure liquid $NaAlSi_5O_{12}$ and $KAlSi_5O_{12}$ respectively. However such "direct" activity measurements are experimentally very difficult because small differences in the temperature and size and shape of the Knudsen aperture between sample and reference, quickly lead to significant errors when the ratios are taken. These problems are very greatly reduced if the variation of the Na/K ratio with bulk composition is determined instead of the individual ion currents of Na and K. The activities and activity coefficients of the end member components may then be extracted from the rates of change with composition by applying the Gibbs-Duhem equation:

$$\ln a_{NaAlSi_3O_8} = -\int_{X_K=0}^{X_K=X_K} X_K d\ln(I_K/I_{Na}) \tag{10}$$

$$\ln \gamma_{NaAlSi_3O_8} = -\int_{X_K=0}^{X_K=X_K} X_K d\ln(I_K/I_{Na}\cdot X_{Na}/X_K). \tag{11}$$

In addition, because the temperature dependence of the ion current ratios is related to the heat of mixing, enthalpies of mixing may be obtained from the composition dependence of the *slopes* of data of the sort shown in Figure 3:

$$\Delta h_1 = -R\int_{X_2=0}^{X_2=X} X_2 d(\partial \ln(I_2/I_1)/1/T) \tag{12}$$

where Δh_1 is the partial molar enthalpy of mixing of component 1.

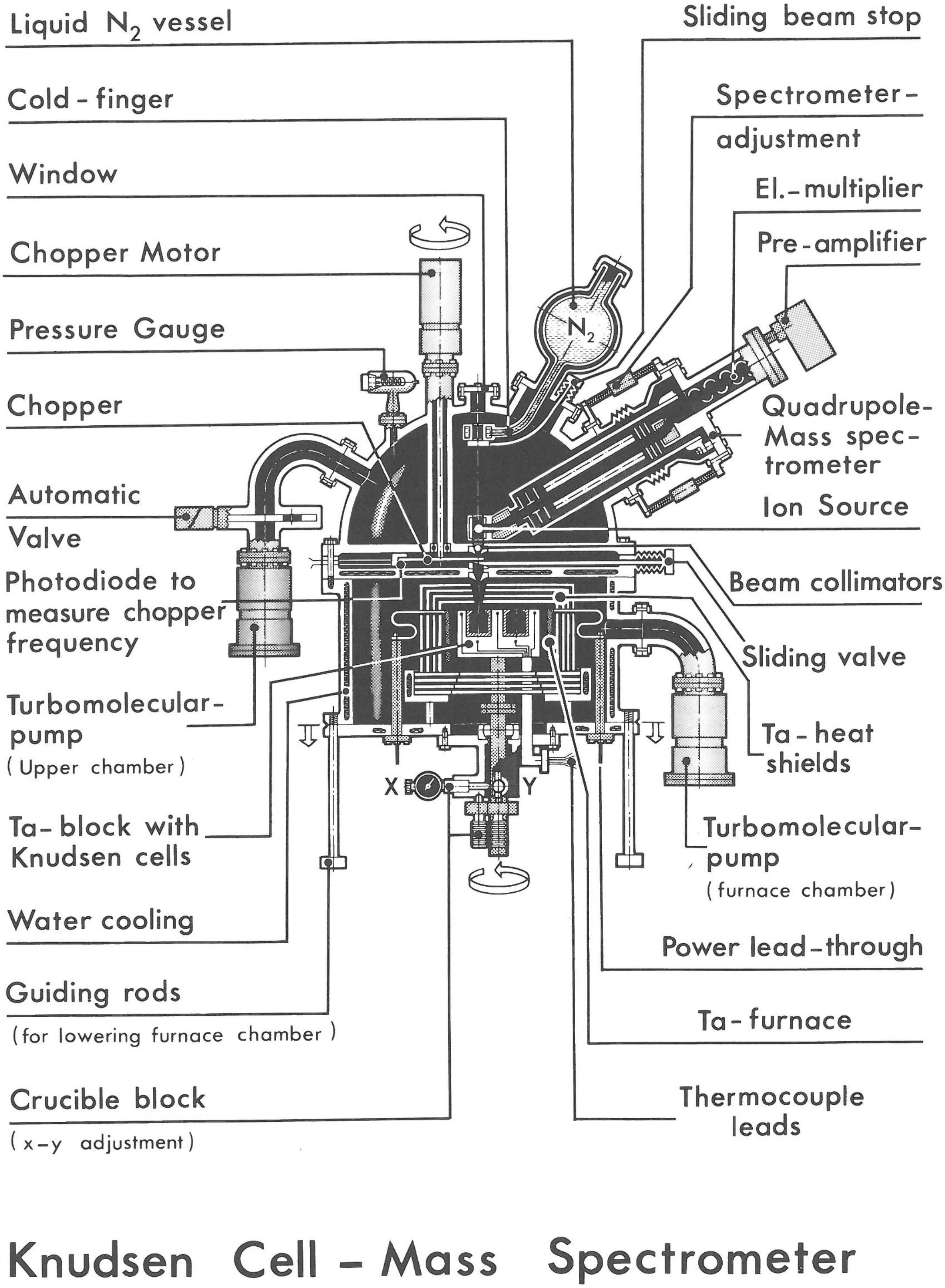

FIG. 2. Diagram of the Knudsen Cell Mass Spectrometer apparatus.

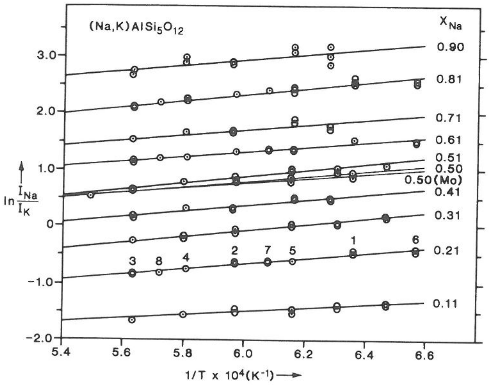

FIG. 3. Variations in ln (I_{Na}/I_K) with $1/T$. Compositions are indicated at the right hand side. Results were obtained both up– and down–temperature as a check on possible systematic errors occurring during each run and the numbers indicate the order in which the measurements were made. The data marked (Mo) were obtained in an experiment in which a Mo plate was inserted inside the Knudsen cell so as to block the direct line of flight of vapour species from the melt through the Knudsen orifice.

RESULTS

Heats of mixing

The partial molar enthalpies of mixing of melts on the joins $NaAlSi_2O_6$–$KAlSi_2O_6$ (FRASER *et al.*, 1983), $NaAlSi_3O_8$–$KAlSi_3O_8$ (RAMMENSEE and FRASER, 1982) $NaAlSi_4O_{10}$–$KAlSi_4O_{10}$ and $NaAlSi_5O_{12}$–$KAlSi_5O_{12}$ (FRASER *et al.*, 1985) have been determined from the temperature dependence of the Na/K ion current ratios using Equation (12) and have been reported previously. In addition, the Knudsen cell data of ROGEZ *et al.* (1983) for the system $NaAlSi_3O_8$–$KAlSi_3O_8$ have been analyzed to obtain an independent set of enthalpy measurements (FRASER and BOTTINGA, 1985). These data are summarized in Figure 4. The enthalpies of mixing along the three most silicic joins are all close to zero. The $NaAlSi_4O_{10}$–$KAlSi_4O_{10}$ and $NaAlSi_5O_{12}$–$KAlSi_5O_{12}$ joins have slight negative heats of mixing with symmetrical minima at the $X_{Na} = 0.5$ compositions. Heats of mixing on the $NaAlSi_3O_8$–$KAlSi_3O_8$ join vary with Na/K ratio. They are slightly negative in Na-rich compositions, but show significant positive enthalpies of mixing at the potassium rich side of the join, with a maximum at $X_K = 0.8$. The two independent Knudsen cell studies are in excellent agreement (FRASER and BOTTINGA, 1985) even though substantially different types of apparatus were used with Mo Knudsen cells used in one set of measurements and Pt cells in the other. Comparison of the two sets of data indicates precisions ($\pm 1\sigma$) of the order of 500 J and an accuracy of better than 1.0 KJ/mol. The precision of our more recent experiments is a factor of two better (FRASER *et al.*, 1985).

The heats of mixing obtained from these Knudsen cell studies may be compared with the heats of mixing obtained from calorimetric studies of glasses in the system $NaAlSi_3O_8$–$KAlSi_3O_8$ (HERVIG and NAVROTSKY, 1984; HOVIS, 1984). However this can only be done if corrections are applied to take account of the differences between the properties of glasses and liquids. In particular, enthalpies of mixing measured by solution calorimetry on glasses, must be corrected for thermal effects associated with the glass transition. This can only be done at present for one composition in the system $NaAlSi_3O_8$–$KAlSi_3O_8$ for which measurements of the fictive temperature are available. The relevant calculations indicate (FRASER and BOTTINGA, 1985) that for the $X_{Na} = 0.5$ composition in the system $NaAlSi_3O_8$–$KAlSi_3O_8$, around 2.0 KJ/mol must be added to the enthalpy of mixing reported for the particular glasses used for the calorimetric measurements. The absolute value of this correction varies with the thermal history of the glasses and with bulk composition. When this correction is made, the calorimetric data on glasses are consistent with the Knudsen cell measurements made on the equilibrium liquids at high temperature. Accordingly, care should be taken in using data obtained from glasses below their fictive temperatures to apply to the properties of melts unless measurements of the fictive temperatures of the glasses are available for all compositions and the associated thermal corrections are made.

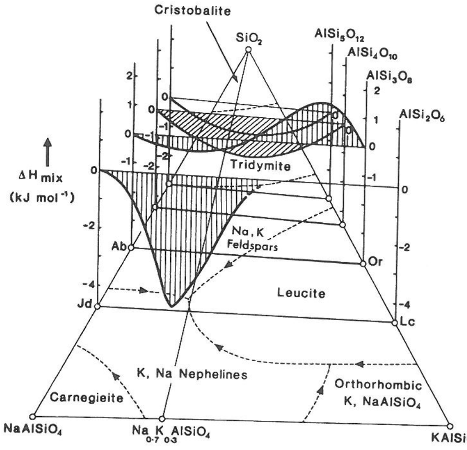

FIG. 4. Enthalpies of mixing for four different joins in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2. The values on the $NaAlSi_2O_6$–$KAlSi_2O_6$ join refer to the partial molar enthalpy of mixing of the $NaAlSi_2O_6$ component.

Free energies and entropies of mixing

The free energies of mixing of binary aluminosilicate melts may be obtained from the vapour pressure data using Equations (10) or (11) and excess entropies of mixing may then be calculated by combining these values with the heats of mixing derived from Equation (12). The free energies of mixing of melts in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 have been previously reported (RAMMENSEE and FRASER, 1982; FRASER *et al.*, 1985) and behave in a closely similar way to the enthalpies of mixing shown in Figure 4 and discussed above. Melts on the two most siliceous joins examined mix essentially ideally and their excess free energies of mixing vary symmetrically with composition. The maximum values at the $X_{Na} = 0.5$ composition are 70 ± 160 J mol^{-1} on the $NaAlSi_4O_{10}$–$KAlSi_4O_{10}$ join and −240 ± 160 J/mol for $NaAlSi_5O_{12}$–$KAlSi_5O_{12}$ join. The excess free energies of mixing of $NaAlSi_3O_8$–$KAlSi_3O_8$ melts are more interesting. Significant positive deviations from ideality occur throughout with a maximum at the K–rich side of the join (RAMMENSEE and FRASER, 1982, ROGEZ *et al.*, 1983). This tendency to unmixing may be related to the structural mismatch that causes unmixing and perthite formation in the solid state. However, X–ray determinations of the radial distribution functions RDFs of $KAlSi_3O_8$ glass (TAYLOR and BROWN, 1979a) suggest a closer similarity to the structures of leucite or tridymite than that of sanidine, and the positive deviation from ideality in the melts is more probably related to the incongruent melting of sanidine at low pressures and the resulting large stability field of leucite and this will be discussed below.

Excess entropies of mixing of melts on the four joins can be calculated by combining the results obtained using Equations (11) and (12) and are shown in Figure 5. The excess entropies of mixing are similar in form to the heats of mixing shown in Figure 4. The $NaAlSi_4O_{10}$–$KAlSi_4O_{10}$ and $NaAlSi_5O_{12}$–$KAlSi_5O_{12}$ joins have small symmetrical excess entropies of mixing (FRASER *et al.*, 1985). Melts on the join $NaAlSi_3O_8$–$KAlSi_3O_8$ show significant positive excess entropies of mixing (ΔS^{xm}) at the potassic side of the join. Similar behaviour was observed for the high–temperature alkali feldspars (THOMPSON and HOVIS, 1979). In addition, measurements of the densities of mixed $NaAlSi_3O_8$–$KAlSi_3O_8$ glasses show a pronounced excess volume of mixing (HAYWARD, 1977) with a maximum near $X_K = 0.8$ and the viscosities of $KAlSi_3O_8$ melts have different Arrhenian activation energies below and above 1550°C (URBAIN *et al.*, 1982).

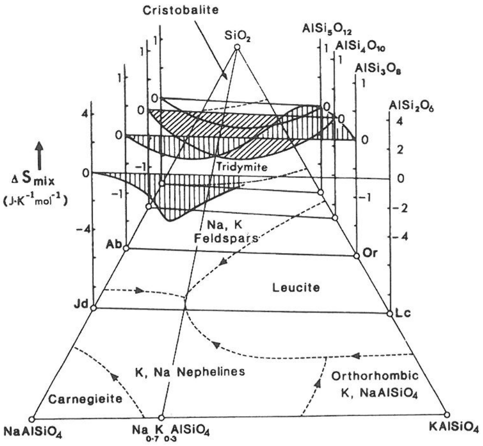

FIG. 5. Entropies of mixing for four different joins in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2. The values on the $NaAlSi_2O_6$–$KAlSi_2O_6$ join refer to the partial molar entropy of mixing of the $NaAlSi_2O_6$ component. Note the different scale for the latter compositions.

The positive non–ideal entropies of mixing shown in Figure 5 cannot be interpreted on the basis of non–random clustering of Na and K ions on sites within a constant aluminosilicate network because such an effect could only produce negative values of ΔS^{xm}. Any negative contribution to ΔS^{xm} must therefore be exceeded by the effect of a positive excess in the heat capacity or, if medium range ordering effects lead to the formation of more than one different sub–network structure in the melts, additional configurational entropy terms may result. In the case of the high temperature crystalline alkali feldspars, it was suggested (THOMPSON and HOVIS, 1979) that the asymmetry in the positive values of ΔS^{xm} is consistent with the argument that the smaller Na ion would have greater vibrational freedom on a large–ion site than vice versa. The values of ΔS^{xm} reported for the $NaAlSi_3O_8$–$KAlSi_3O_8$ join in Figure 5 have a maximum positive value of 0.64 J K^{-1} mol^{-1} at the $X_K = 0.8$ composition and are thus smaller than the maximum of around 3.3 J K^{-1} mol^{-1} reported by THOMPSON and HOVIS (1979) for the feldspars taking ΔH^{xm} to be asymmetrical. This difference is unlikely to be caused by the difference in temperature between the low temperature experiments used by THOMPSON and HOVIS (1979) and the high temperatures at which the melt data were obtained because ΔC_p^{xm} is probably positive as noted above. However, mixing in the melts is complicated by the additional degrees of freedom which allow variations in the aluminosilicate network structure. The RDFs reported by TAYLOR and BROWN (1979a,b) indicate that there is a close correspondence between the local structures of $NaAlSi_3O_8$ glass and crystalline high albite out to 4 Å. This includes the Si–O(1), Si–Si(1) and Si–O(2) vectors. The peak at 4.0–4.5 Å characteristic of the second nearest neighbour Si–Si(2) distance across the four–membered rings of the feldspar structure is still present, but is weaker in the glass RDF whereas a new peak appears in the glass structure at around 5.1 Å. There are no interatomic distances in the high albite structure which have this value. This distance correlates instead with the Si–Si(2) distance across the six–membered rings of a stuffed tridymite structure. The correspondence between the RDFs of $KAlSi_3O_8$ glass and sanidine is less good. There is a clear minimum in the $KAlSi_3O_8$ glass radial distribution function at 4.5 Å where there is a maximum for sanidine, whereas the reverse is true of a maximum in the glass RDF at around 5.1 Å. The minimum agrees well with a minimum at 4.5 Å in the leucite structure which contains both four and six–membered rings of $(Si,Al)O_4$ tetrahedra. However, at larger distances the correspondence is weaker. Neither the leucite nor a stuffed tridymite structure describes all the features of the glass X–ray data. The glass and hence presumably also melts, may therefore be inhomogeneous on the scale of 20 Å containing regions of leucite–like and stuffed tridymite structures. Other ring configurations such as five–membered rings may also be present. This view which we originally proposed to explain the positive heats of mixing observed in $NaAlSi_3O_8$–$KAlSi_3O_8$ melts (RAMMENSEE and FRASER, 1982) is further supported by a recent Raman spectral study of $KAlSi_3O_8$ glasses (MATSON *et al.*, 1986) which indicated regions of leucite–like and tridymite–like structure in $KAlSi_3O_8$ glasses. Similar ideas involving the presence of 4– and 6–membered rings have been proposed by MAMMONE *et al.* (1981) and SEIFERT *et al.* (1982) who have suggested that the proportion of 4–membered rings increases with increasing Al/(Al + Si) ratio in the melt.

The Raman spectra of $NaAlSi_3O_8$ and $KAlSi_3O_8$ glasses show small differences with the weak band at 1100 cm^{-1} being more prominent in the $KAlSi_3O_8$ composition (MCMILLAN *et al.*, 1982). It has been suggested by the latter authors that these differences indicate increased clustering of aluminosilicate groups in the Na-bearing system than in $KAlSi_3O_8$ glasses and similar conclusions were reached by FLOOD and KNAPP (1968) based on cryoscopic arguments. Using the $Q^n(x\mathrm{Al})$–notation familiar from NMR spectroscopy in which n represents the number of bridging oxygen atoms around the Si, and x the number of next–nearest neighbour Al atoms, this can be represented by:

$$Q^4 + Q^4(2\mathrm{Al}) = 2Q^4(1\mathrm{Al}). \qquad (13)$$

Replacement of K by Na moves the equilibrium distribution to the left forming Al–rich and Si–rich clusters in the melt. This is similar to the mechanism proposed recently to explain deviations in the ^{29}Si NMR spectra of $NaAlSi_3O_8$–$CaMgSi_2O_6$ glasses (FRASER and CLAYDEN, 1986).

The excess entropies of mixing of $NaAlSi_2O_6$ and $KAlSi_2O_6$ melts stand in marked contrast to those on the more SiO_2–rich joins. $NaAlSi_2O_6$–$KAlSi_2O_6$ melts show a pronounced negative partial molar entropy of mixing of the $NaAlSi_2O_6$ component with a maximum deviation at the Na–rich side near the Na:K = 3:1 composition. The most likely interpretation of this negative excess entropy of mixing is that Na–K clustering takes place in these liquids (FRASER *et al.*, 1983). The coincidence of the maximum negative value with the 3:1 composition suggests that the melts may contain regions similar in structure to that of Na_3K–nepheline which is stable on the liquidus on this join because of the incongruent melting of jadeite.

DISCUSSION

The enthalpies and entropies of Na–K mixing shown in Figures 4 and 5 carry important implications for the structures and general mixing properties of aluminosilicate melts and hence the theoretical modelling of crystal–liquid equilibrium in these systems.

On the basis of the mixing properties of the melts, the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 may be considered in three parts:

(1) Compositions near the join $NaAlSi_2O_6$–$KAlSi_2O_6$ where strongly negative partial molar entropies and enthalpies of mixing are observed near the Na:K = 3:1 composition.

(2) Compositions near the feldspar join on which a significant positive deviation from ideality is observed at the potassic side.

(3) More SiO_2–rich liquids near the 1–atmosphere granite minimum which mix nearly ideally and for which no abrupt changes in mixing properties are observed.

If these groups are compared with the ternary phase diagram (SCHAIRER, 1957), it can be seen that the mixing properties observed in the equilibrium liquids at high temperatures above the liquidus are broadly correlated with changes in the nature of the crystalline phase at lower temperatures. Somewhat similar suggestions have been made previously by us (RAMMENSEE and FRASER, 1982; FRASER *et al.*, 1983) and by Burnham (BURNHAM, 1981; BURNHAM and NEKVASIL, 1986, 1987). Both jadeite and sanidine melt incongruently at low pressure so that the joins $NaAlSi_2O_6$–$KAlSi_2O_6$ and $NaAlSi_3O_8$–$KAlSi_3O_8$ are pseudobinaries and are each cut by a large field representing the crystalline phase of lowest free energy which is in equilibrium with these liquids. The $NaAlSi_2O_6$–$KAlSi_2O_6$ join is cut by the primary phase volume of Na,K–nephelines. X–ray diffraction studies of crystalline Na,K–nepheline indicate a structure containing small and large cation sites in the ratio 3:1 so that the equilibrium composition is close to $Na_3K(AlSiO_4)_4$ (BUERGER *et al.*, 1954). The pronounced negative heats and entropies of mixing observed on the $NaAlSi_2O_6$–$KAlSi_2O_6$ join near the Na_3K composition indicate that ordering also occurs in the liquids so that the structures of Na–rich liquids on the $NaAlSi_2O_6$–$KAlSi_2O_6$ join probably contain regions of nepheline–like structure rather than that of jadeite or leucite.

The join $NaAlSi_3O_8$–$KAlSi_3O_8$ shows different but analogous behaviour. Here the sharp change in mixing properties and the positive enthalpy and entropy of mixing correlate qualitatively, but not exactly, with the composition at which the join is cut by the primary phase volume of leucite, the break in mixing properties indicated by the Knudsen cell studies of vapour pressures occurring near $X_K = 0.8$. The positive enthalpy, entropy and free energy of mixing at the potassic side of the join are supported by the positive excess volumes of mixing of glasses in the system (HAYWARD, 1977) and by the analogous behaviour of the high temperature feldspars which show positive excess entropies of mixing (ΔS^{xm}) at the potassic side of the join (THOMPSON and HOVIS, 1979). Radial distribution function studies of $KAlSi_3O_8$ glasses show a clear minimum at 4.5 Å. This is consistent with a leucite–like structure for $KAlSi_3O_8$ glass and not with a sanidine–like structure although features at higher radial distances suggest a stuffed tridymite structure (TAYLOR and BROWN, 1979a,b). We, therefore, previously suggested (RAMMENSEE and FRASER, 1982) that $KAlSi_3O_8$ melts are inhomogeneous and contain medium-range domains of leucite-like structure composed of 4– and 6–membered rings on the approximately 20 Å scale linked to regions of tridymite–like structure consisting of cross-linked sheets of 6–membered rings. Other sub–network structures are also possible, but the whole linked three–dimensional network must be homogeneous on the optical scale. Recent support for this model has been provided by the Raman spectral study of MATSON *et al.* (1986) which indicates T–O–T modes which correspond with regions of leucite–like and tridymite–like structure. The effect of adding potassium across the join seems to be to stabilize 4–membered rings and a similar effect has been noted in vitreous silica in which 4–rings are stabilized by broken Si–O defect centres (SHARMA *et al.*, 1981).

Finally the two silicic joins which lie almost entirely within the single–phase mixed feldspar field in which no change of crystallizing phase occurs on the liquidus show no analogous breaks in mixing properties.

CONCLUSIONS

The overriding conclusion of these studies is that the structures of aluminosilicate melts may bear little relationship to those of minerals of the same composition. This is seen most clearly in the case of the minerals which melt incongruently in this system, jadeite and sanidine. Melts on the $NaAlSi_2O_6$–$KAlSi_2O_6$ join are probably composed of inter–linked regions of nepheline–like and tridymite–like structure. Melts on the $NaAlSi_3O_8$–$KAlSi_3O_8$ join are unlike the feldspars, but contain regions of tridymite–like and, at the potassic side, leucite–like structure. The implication of these models is that aluminosilicate melts are inhomogeneous on the medium–range scale and may contain two or more topologically distinct domains linked to form an optically homogeneous three–dimensional network. It is likely that the crystal chemical factors which determine the structures of minimum free energy in the liquid operate similarly to determine the crystalline phase of minimum free energy on the liquidus. The consequence of these models is that the sharp changes in mixing properties observed in the melts at high temperature above the liquidus may often occur at similar compositions to those at which a change occurs in the stable phase on the liquidus.

The development of models which relate the thermodynamic properties of silicate melts to their structures requires, in particular, accurate measurements of the entropies and free energies of mixing. KCMS allows these quantities to be determined directly together with the enthalpies of mixing. The latter can be shown to have accuracy and precision comparable to or slightly better than the best measurements of the enthalpies of mixing of glasses by solution calorimetry currently available. In addition, because measurements are made at high temperature on the melts themselves, KCMS data are not affected by problems related to the glass transition or quenching.

The data now available for the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 suggest that medium range clustering occurs in the melts. These melts are probably inhomogeneous on the approximately 20 Å scale and may contain local structures which, in part, resemble the crystalline phase which is in equilibrium with a melt of given composition rather than that necessarily of a crystalline phase of the same composition. The distinction between the latter two is particularly important in systems containing phases which melt incongruently.

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