ACTIVITIES OF COMPONENTS IN THE $Ca_2MgSi_2O_7$–$CaSiO_3$ MOLTEN SYSTEM

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Received October 6, 1995
Accepted March 11, 1996

Activities of the components, the Gibbs energy of mixing, and the excess entropy of mixing have been calculated for the $Ca_2MgSi_2O_7$–$CaSiO_3$ system. The mole fractions of the components were calculated assuming that in the point of the formal component $Ca_2MgSi_2O_7$, the molar mass of the quasi-real particle in the melt corresponds to its formula molar mass, whereas in the point of the formal component $CaSiO_3$ the molar mass of the quasi-real particle in the melt is 8.5 times higher than as corresponds to its formula. The fact that the enthalpy of mixing is zero whereas the excess entropy of mixing is non-zero suggests that $Ca_2MgSi_2O_7$–$CaSiO_3$ melts behave as athermal solutions.
Keywords: Akermanite; Wollastonite; Thermodynamics of mixing.

Knowledge of the thermodynamic quantities of the CaO–MgO–SiO_2 melt system is a prerequisite for a quantitative characterization of the properties of this system, which are of theoretical as well as practical interest, e.g. for thermodynamic analysis and geophysical considerations on the one hand, and for ceramic and metallurgical technologies on the other hand. In this paper we deal with the akermanite–wollastonite ($Ca_2MgSi_2O_7$–$CaSiO_3$) binary system.

In our previous papers[1,2] we calculated the mean numbers of SiO_4 tetrahedra in anions present in $CaMgSi_2O_6$ and $CaSiO_3$ melts based on the $Ca_2MgSi_2O_7$ liquidus curves of the $Ca_2MgSi_2O_7$–$CaMgSi_2O_6$ and $Ca_2MgSi_2O_7$–$CaSiO_3$ phase diagrams, respectively. The molar mass of the component anions has been determined as a multiple of that of the formula unit using the cryometrical principle, whereas the molar mass of the quasi-real particle was calculated by employing the Le Chatelier–Shreder equation in the region of infinitesimally diluted solutions[1,2]. The experimental basis for this calculation comprised the enthalpy of fusion of akermanite[3] and the phase diagrams of the $Ca_2MgSi_2O_7$–$CaMgSi_2O_6$ and $Ca_2MgSi_2O_7$–$CaSiO_3$ systems[4,5].

Over the temperature range of 1 673–1 950 K, the enthalpy of mixing in the $Ca_2MgSi_2O_7$–$CaSiO_3$ melt calculated based on the temperature and composition dependences of the relative enthalpy, determined from the relative enthalpies of selected melts in this system, is zero within the experimental error[6,7]. The relative enthalpy of the phase at a given temperature is defined as the negative sum of the heat of cooling from that temperature to the temperature of dissolution and the heat of solution of the cooled sample; both heats are determined calorimetrically[8].

In this paper, the activities of the quasi-real components, the Gibbs energy of mixing, and the excess entropy of mixing are calculated based on the use of the $Ca_2MgSi_2O_7$–$CaSiO_3$ phase diagram[5] taking into account the above facts.

THEORETICAL

As in refs[2,9], we assume that the melt of pure $Ca_2MgSi_2O_7$ contains mostly disilicate anions $Si_2O_7^{6-}$ and Ca^{2+} and Mg^{2+} cations, as follows both from the infrared spectra of akermanite glass[9] and from the molar mass of $Ca_2MgSi_2O_7$ (ref.[2]) calculated based on the experimental liquidus curve of $CaSiO_3$ (ref.[5]) and the experimental value of the enthalpy of fusion of wollastonite[10]. The liquidus curves of akermanite in phase diagrams of the two systems indicate that the mean number of SiO_4 tetrahedra in the quasi-real anions in melts of the two monosilicates is $\overline{N}(CaSiO_3) = \overline{N}(CaMgSi_2O_6) = 8.5$. Mean numbers of tetrahedra in the monosilicates and disilicate anions have been established in their mutual ideal (infinitely diluted) solutions at temperatures close to the melting points of the end-members. Consequently, the activities of the quasi-real anions of the solvents are identical with their mole fractions in those composition regions.

The temperature dependence of activity of a component X in a solution having a chosen composition x_c can be written in general as

$$\ln a(X,x_c,T_2) = \ln a(X,x_c,T_1) - \int_{T_1}^{T_2} \frac{\Delta_{mix}\overline{H}(X,x_c,T)}{RT^2}\,dT \ , \qquad (1)$$

where $\Delta_{mix}\overline{H}(X,x_c,T)$ is the temperature-dependent partial molar enthalpy of mixing of component X in the solution of composition x_c. The activities of components in $Ca_2MgSi_2O_7$–$CaSiO_3$ melts do not depend on temperature owing to the fact that both $\Delta_{mix}H$ and $\Delta_{mix}\overline{H}$ are zero[6]. This implies that the mole fractions of the prevailing components, and thus also the molar masses of the quasi-real particles constituting them, are temperature independent in infinitely diluted solutions.

Three types of processes can be considered during mixing $Ca_2MgSi_2O_7$ and $CaSiO_3$ melts:

1. No chemical reaction occurs. In this case $\Delta_{mix}H$ is zero within the limits of experimental error, and the numbers of SiO_4 tetrahedra in anions of the two components are composition-independent.

2. Mutual equilibrium reactions of the two types of anions giving rise to linear chain anions according to scheme (*A*)

$$[SiO_3]_{\overline{N}}^{2\overline{N}-} + Si_2O_7^{6-} = [[SiO_3]_{(\overline{N}+2)}O]^{(2\overline{N}+6)-} \qquad (A)$$

which can contribute to the enthalpy of mixing of the $Ca_2MgSi_2O_7$–$CaSiO_3$ melts. (In this scheme $\bar{N} \equiv \bar{N}(CaSiO_3)$ is the mean number of SiO_4 tetrahedra constituting the quasi-real anion in the $CaSiO_3$ melt.) The numbers of bridging and terminal oxygen atoms remain unchanged. The reaction enthalpy can be assumed to be zero or close to zero. It is conceivable that the linear chain anions produced by reaction (*A*) might undergo further decomposition due to the additional effect of the $Si_2O_7^{6-}$ anions; actually, however, this is rather improbable because there is no reasonable explanation why such reaction should terminate at the relatively high value of $\bar{N}(CaSiO_3) = 8.5$. Thus also in this case, addition of 8.5 formal moles of $CaSiO_3$ to the $Ca_2MgSi_2O_7$ melt is equivalent to the addition of one mole of the quasi-real component. The mole fraction of the quasi-real component corresponds to $(CaSiO_3)_{8.5}$ over the entire melt composition range.

3. Mutual reactions of the monosilicate anions described by the equations

$$[SiO_3]_{N_1}^{2\bar{N}_1-} + [SiO_3]_{N_2}^{2\bar{N}_2-} \longleftrightarrow 2[SiO_3]_{N}^{2\bar{N}-} \tag{B}$$

and

$$[SiO_3]_{2N}^{4\bar{N}-} \longleftrightarrow 2[SiO_3]_{N}^{2\bar{N}-} \ . \tag{C}$$

Reaction (*B*) cannot reach its equilibrium in infinitely diluted solution in which $\bar{N}(CaSiO_3) = 8.5$. This indicates that the melt of pure monosilicate itself consists of anions with $\bar{N}(CaSiO_3) = 8.5$. Again, it is improbable that the particles with $\bar{N}(CaSiO_3) = 8.5$ in infinitely dilute solutions of $CaSiO_3$ in the $Ca_2MgSi_2O_7$ melt are products of reaction (*C*), because if such dissociative decomposition took place, it would hardly stop at $\bar{N}(CaSiO_3) = 8.5$. Hence, the particles in question are apparently present in the very melt of pure $CaSiO_3$. Since monosilicate anions consist of closed strings irrespective of the number of SiO_4 tetrahedra present in them (which implies that for both types of the reactions mentioned the number and kinds of bonds are constant), the reaction enthalpies of these processes and thus also the mixing enthalpies in this system are virtually zero.

The mean values of $\bar{N}(Ca_2MgSi_2O_7) = 2$ and $\bar{N}(CaSiO_3) = 8.5$ remain constant over the entire temperature and composition ranges. So, they can be used to the mole fractions of the quasi-real components, $x(X_{real})$, corresponding to the particles actually existing in the melt. The mole fractions of the quasi-real components in the melt of the system investigated were calculated assuming that in the point of the formal component $Ca_2MgSi_2O_7$, the molar mass of the quasi-real particle in the melt is equal to that corresponding to its formula, whereas in the point of the formal component $CaSiO_3$, the molar mass of the quasi-real particle in the melt is 8.5 times larger than as corresponds to its formula. The mole fractions of the quasi-real components are more suitable to express the composition of the melts than the formal ones.

Figure 1 shows the phase diagram of the $Ca_2MgSi_2O_7$–$CaSiO_3$ system measured by Schairer and Bowen[5], expressed in terms of the mole fractions of both the formal (dotted line) and quasi-real (solid line) components.

RESULTS AND DISCUSSION

Activities of the Quasi-Real Components at Temperature T_c

The activity of a quasi-real component in the melt which is in equilibrium with the corresponding crystalline phase at temperature T_{eq} is obtained by using the LeChatelier–Shreder equation

$$\ln a(X_{real}, x_c, T_{eq}) = \int_{T_{fus}(X)}^{T_{eq}} \frac{\bar{\nu}(X_{form}) \Delta_{fus} H(X_{form}, T)}{RT^2} \, dT \ , \qquad (2)$$

where X_{real} and X_{form} are the quasi-real and formal components in the melt, respectively, $\bar{\nu}(X_{form})$ is the mean value of the quasi-real-to-formal component molar mass ratio in the melt ($\bar{\nu}(X_{form}) = M(X_{real})/M(X_{form})$; $\bar{\nu}(Ca_2MgSi_2O_7) = 1$ and $\bar{\nu}(CaSiO_3) = 8.5$), and $\Delta_{fus}H(X_{form},T)$ is the temperature dependence of the enthalpy of fusion of the formal component, calculated from the equation

$$\Delta_{fus} H(X_{form}, T) = H_{rel}(\text{melt}, X_{form}, T) - H_{rel}(\text{cryst}, X_{form}, T) \ , \qquad (3)$$

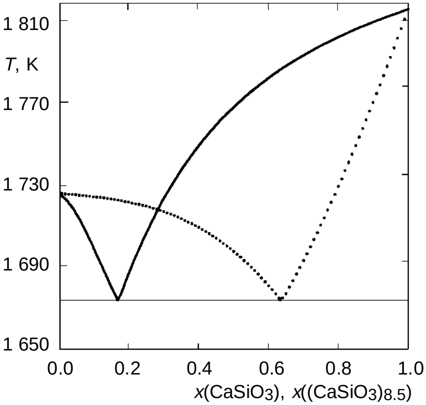

FIG. 1

Phase diagram of the $Ca_2MgSi_2O_7$–$CaSiO_3$ system. The dotted line refers to the formal mole fractions, the solid line refers to the quasi-real mole fractions where $H_{rel}(\mathrm{melt},X_{form},T)$ and $H_{rel}(\mathrm{cryst},X_{form},T)$ are the temperature dependences of the relative enthalpies of the melt and of the crystalline component X, respectively. The relative enthalpy of the melt or crystalline component is defined as

$$H_{rel}(X_{form},T) = H(X_{form},T) - H(X_{form},298\ \mathrm{K}) - \Delta_{sol}H(X_{form},298\ \mathrm{K})\ , \qquad (4)$$

where $\Delta_{sol}H(X_{form},298\ \mathrm{K})$ is the heat of solution of the cooled melt or crystalline component at 298 K. The values of $H_{rel}(\mathrm{melt},X_{form},T)$ for $Ca_2MgSi_2O_7$ and $CaSiO_3$ were taken from ref.[6]. The $H_{rel}(\mathrm{cryst},X_{form},T)$ values were obtained from the temperature dependences of the heat capacities[11,12] and from the heats of solution of the crystalline phases[3,10].

The equilibrium temperature T_{eq}, corresponding to the chosen mole fraction $x_c(X_{real})$ of the quasi-real component in the phase diagram in Fig. 1 was inserted in Eq. (*2*). From Eqs (*1*) and (*2*) where $T_1 = T_{eq}$ and $T_2 = T_c$ it follows the calculated activity of the quasi-real component X_{real} at the equilibrium temperature T_{eq} and the selected mole fraction $x_c(X_{real})$, $a(X_{real},T_{eq},x_c(X_{real}))$, is also equal to its activity at any other temperature T_c. The activities $a((CaSiO_3)_{8.5})$ for $x_c((CaSiO_3)_{8.5}) \in \langle 0;x_e((CaSiO_3)_{8.5})\rangle$ and $a(Ca_2MgSi_2O_7)$ for $x_c((CaSiO_3)_{8.5}) \in \langle x_e((CaSiO_3)_{8.5});1\rangle$ were calculated using the Gibbs–Duhem and Margules equations[13].

The activities of the two quasi-real components in dependence on $x((CaSiO_3)_{8.5})$ for temperatures within the interval from the eutectic temperature T_e to 1 950 K are plotted in Fig. 2.

Excess Entropy of Mixing $\Delta_{mix}S^E$

The Gibbs energies of mixing $\Delta_{mix}G$ in dependence on the composition were calculated for the temperature of 1 800 K using the composition dependences of the acti-

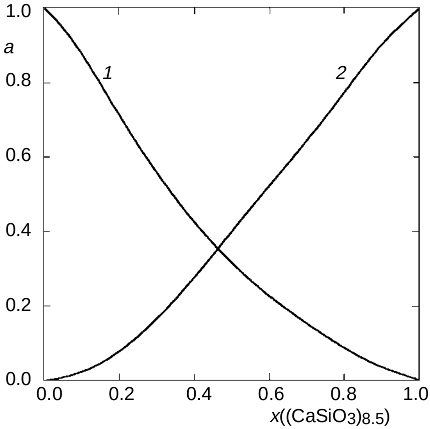

FIG. 2
Activities $a(Ca_2MgSi_2O_7, T_c)$ (*1*) and $a((CaSiO_3)_{8.5}, T_c)$ (*2*) in dependence on $x((CaSiO_3)_{8.5})$ at 1 673–1 950 K

vities. The values of $T\Delta_{mix}S$ and $T\Delta_{mix}S^E$ were obtained from the following equations, which are derived based on the definition of $\Delta_{mix}S$ and the fact that $\Delta_{mix}H = 0$:

$$T\Delta_{mix}S = -\Delta_{mix}G \qquad (5)$$

$$T\Delta_{mix}S^E = -\Delta_{mix}G + RT[x(Ca_2MgSi_2O_7) \ln x(Ca_2MgSi_2O_7) + + x((CaSiO_3)_{8.5}) \ln x((CaSiO_3)_{8.5})] \ . \qquad (6)$$

The composition dependences of $\Delta_{mix}G$, $T\Delta_{mix}S$ and $T\Delta_{mix}S^E$ at 1 800 K are plotted in Fig. 3.

Discussion and Conclusions

Small or zero values of the reaction contributions to the enthalpy of mixing of the melts are consistent with the zero value of $\Delta_{mix}H$. The zero enthalpies of reactions (*B*) and (*C*) leading to the equilibrium distribution of anion sizes in the monosilicate melt implies that the mean number of SiO_4 tetrahedra in the monosilicate anions is independent of temperature.

The non-ideality of the molten solutions of the system studied can be explained by:

a) the difference between the real component activities calculated from Eq. (*2*) and the mole fractions (Fig. 2) found using the liquidus curves in the phase diagram (Fig. 1);

b) the non-zero value of the excess entropy of mixing (Fig. 3);

c) the asymmetrical shapes of the activity–composition curves and of the composition dependences of $\Delta_{mix}G$, $T\Delta_{mix}S$ and $T\Delta_{mix}S^E$. The maximum of the $T\Delta_{mix}S^E$ curve is

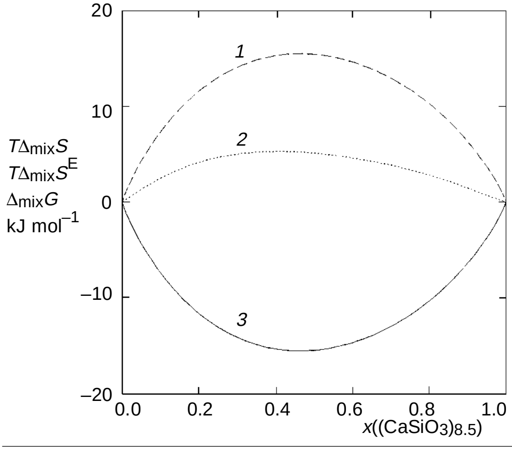

FIG. 3
Composition dependences of $T\Delta_{mix}S$ (*1*), $T\Delta_{mix}S^E$ (*2*) and $\Delta_{mix}G$ (*3*) at 1 800 K

shifted towards the composition region of higher $Ca_2MgSi_2O_7$ contents implying a better order in the melt in this region.

The largest contribution to the excess entropy of mixing is due to the differences in the size and shape of anions of the two components. The activities of the quasi-real components in the composition regions close to the pure components (Fig. 2) must agree with their mole fractions owing to the application of the cryometrical method of calculation of $\overline{N}(Ca_2MgSi_2O_7)$ and $\overline{N}(CaSiO_3)$ to the determination of the mole fraction of the components. The differences in the slope of the tangent lines to the $\Delta_{mix}G$ and $T\Delta_{mix}S$ curves at the initial and final points with respect to the theoretical values are due to the large mole fraction increment step used in the calculation.

The considerable deviations from the ideal behaviour of activities of the two components in the region of validity of Henry's law (Fig. 2), derived using the phase diagram with the quasi-real mole fractions, may be due either to the non-zero excess entropy of mixing or to the occurrence of reactions expressed by scheme (*A*).

The fact that the enthalpy of mixing is zero while the excess entropy of mixing is non-zero suggests that melts of the $Ca_2MgSi_2O_7$–$CaSiO_3$ system can be regarded as athermal solutions.

This work was supported by the Slovak Grant Agency for Sciences (Grant No. 2/1170/95).

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