THE HEAT CAPACITIES OF LIQUIDS IN THE SYSTEM $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$

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The composition dependencies of molar heat capacity, molar heat capacity of mixing, partial molar heat capacity for constituents and partial molar heat capacity of mixing for constituents of liquids in the $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ *system were determined from experimental relative enthalpy data. The heat capacity values related to one atom of a formula molecule in these liquids exceeds the 3R-value by about 5 to 16 J* mol^{-1} K^{-1}. *The largest changes in the number and/or kind of degrees of freedom of particles in the melt arise when the liquid of* $Ca_2Al_2SiO_7$ *or* $CaAl_2Si_2O_8$ *is added to large amount of* $CaSiO_3$ *liquid and when the liquid of* $CaSiO_3$ *or supercooled liquid of* Al_2O_3 *is added to large amounts of* $Ca_2Al_2SiO_7$ *or* $CaAl_2Si_2O_8$ *liquids.*

INTRODUCTION

The heat capacity data of aluminosilicate liquids are widely exploited in several fields of engineering as well as in the geological sciences. Despite an expanding data set of heat capacities on silicate melts additional data are needed, especially on aluminosilicate liquids, to describe satisfactorily their behaviour in more general form.

In recent time, Richet and Neuville [1] studied the composition dependence of the heat capacity of $MAlO_2$—SiO_2 aluminosilicate melts (M = Na, $Ca_{0.5}$, $Mg_{0.5}$). They found out that $C_p(l)$ varies linearly with composition for magnesium aluminosilicates whereas calcium aluminosilicates show deviations from linearity smaller than sodium aluminosilicate melts. Ideal behaviour of liquids in the system MgO—Al_2O_3—SiO_2 with respect to the heat capacity was confirmed by Courtial and Richet [2].

Molar relative enthalpy (H_{rel}) of melts in $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ system as a function of temperature and composition within the temperature range from 1600 to 1950 K was derived by Kosa et al. [3], using experimentally determined relative enthalpies of melts in this system. The relative enthalpy H_{rel} was obtained as

$$H_{rel}(l) = -(\Delta_{cool}H + \Delta_{sol}H) \quad (1)$$

$\Delta_{cool}H$ being the change in enthalpy on cooling of a sample from a chosen temperature T to 298 K, measured by the use of a drop calorimeter, and $\Delta_{sol}H$ being the change in enthalpy on dissolution of the products of cooling in a mixture of inorganic acids at 298 K, measured by the use of a solution calorimeter [4]. Determined relative enthalpies of liquids in $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ system were related to one mole of the melt mixture of both mineral and oxide components. Linear temperature dependence of relative enthalpies of liquids in the investigated system implies molar heat capacities $C_p(l)$ independent of temperature.

The aim of the present study is to determine the molar heat capacities, molar heat capacities of mixing - the changes in heat capacity on formation of 1 mol of a solution from liquid components and partial molar heat capacities of single constituents as functions of composition using experimental results published previously and to discuss the correlation between these quantities and some structural properties of these liquids.

CALCULATIONS

Heat capacities and heat capacities of mixing

The function for the relative enthalpy of liquids in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ found out by measurements of Kosa et al. [3] is written in the form

$$H_{rel}(l) = \sum_j A_j\,[x(C)]^{a_j}\,[x(A)]^{b_j}\,T^{c_j} \quad (2)$$

$x(C)$ and $x(A)$ in this equation are mole fractions of CaO and Al_2O_3 in both $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ and CaO—Al_2O_3—SiO_2 systems, T is a temperature, A_j's are coefficients gained by multiple regression analysis, a_j, b_j and c_j are powers of variables $x(C)$, $x(A)$ and T, respectively.

The molar heat capacity of a liquid, $C_p(l)$, is closely connected with the kinds of motion of particles and therefore also with its structure. Composition dependencies of $C_p(l)$ were calculated by the relation

$$C_p(l) = \sum_j A_j \, [x(C)]^{a_j} \, [x(A)]^{b_j} \qquad (3)$$

obtained deriving equation (1) with respect to temperature, at constant pressure and composition. The values of A_j's, a_j's and b_j's for both systems are given in tables 1 and 2. The values of A_j's used in this work are to a certain extent different with respect to those of Kosa et al. [3] due to the modified statistical treatment of the same input data set.

Table 1. Powers a_j, b_j and coefficients A_j with standard deviations σ_j in the equation (3) for the heat capacity of liquids in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$.

j	a_j	b_j	A_j (kJ mol^{-1} K^{-1})	σ_j (kJ mol^{-1} K^{-1})
1	0	0	0.3189	0.0018
2	2	0	-0.6751	0.0201
3	0	2	-13.3859	0.9778
4	0	3	51.9769	3.1716
5	1	1	3.9222	0.1957
6	1	2	-11.1714	0.6126
7	0	3	29.4333	2.0100

Table 2. Powers a_j, b_j and coefficients A_j with standard deviations σ_j in the equation (3) for the heat capacity of liquids in the system CaO—Al_2O_3—SiO_2.

j	a_j	b_j	A_j (kJ mol^{-1} K^{-1})	σ_j (kJ mol^{-1} K^{-1})
1	0	0	0.0920	0.0077
2	0	3	0.1623	0.0165
3	1	2	1.0200	0.6174
4	1	3	-4.9082	1.7182

The deviations of liquid systems from ideal behavior are given by composition dependencies of molar heat capacities of mixing $\Delta_{mix}C_p(l)$:

$$\Delta_{mix}C_p(l) = C_p(l) - \sum_i x(X_i)\, C_p^0(X_i, l) \qquad (4)$$

where $C_p^0(X_i, l)$ is molar heat capacity of pure liquid component X_i. Plot of $\Delta_{mix}C_p(l)$ vs. composition in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ is shown in figure 1.

The number and the kind of degrees of freedom of particles in the considered phase affect the proportional part of $C_p(l)$ per one atom of the formula molecule

$${}^1C_p(l) = \frac{C_p(l)}{N} \qquad (5)$$

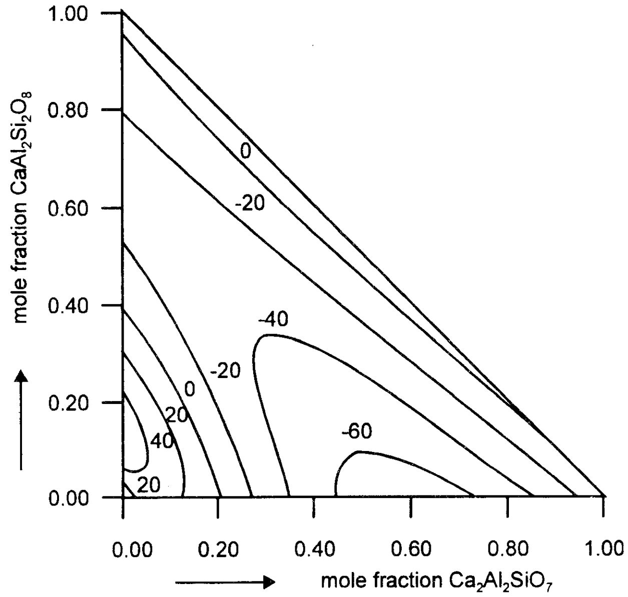

Figure 1. Map of composition dependence of $\Delta_{mix}C_p(l)$ (J mol^{-1} K^{-1}) in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$. Heat capacities relate to 1 mol of mixture of components $CaSiO_3$, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$.

In this relation N denotes the number of atoms in the corresponding formula molecule. For the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$

$$N_1 = 5x(CaSiO_3) + 12x(Ca_2Al_2SiO_7) + \\ + 13x(CaAl_2Si_2O_8) \qquad (6)$$

and for the system CaO—Al_2O_3—SiO_2

$$N_2 = 2x(CaO) + 5x(Al_2O_3) + 3x(SiO_2) \qquad (7)$$

The values of ${}^1C_p(l)$ were used by Richet and Bottinga [5] as a criterion to assess the structure of glasses and liquids for some minerals. Plots of ${}^1C_p(l)$ vs. composition for the studied system are shown in figures 2 and 3.

The differences between the number and kind of degrees of freedom of particles in liquid and crystalline phases can be seen from the composition dependence of a quantity Δ^1C_p which is given by the equation

$$\Delta^1C_p = {}^1C_p(l) - \sum_i x(X_i)\, {}^1C_p^0(X_i, cr) \qquad (8)$$

where ${}^1C_p^0(X_i, cr)$ is molar heat capacity of pure crystalline component X_i per one atom of its formula molecule. The plot of this dependence vs. composition for the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ at the temperature of fusion of $CaSiO_3$, 1821 K, can be seen

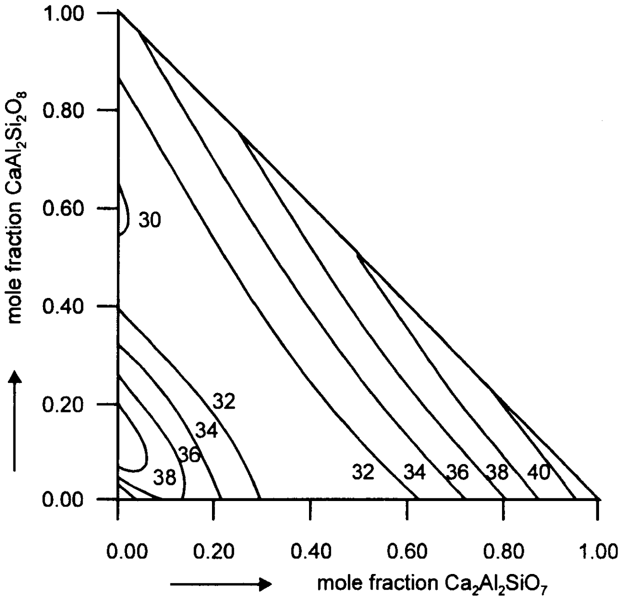

Figure 2. Map of composition dependence of $^{l}C_p(l)$ (J mol^{-1} K^{-1}) in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$. Heat capacities relate to 1 mol of mixture of components $CaSiO_3$, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$.

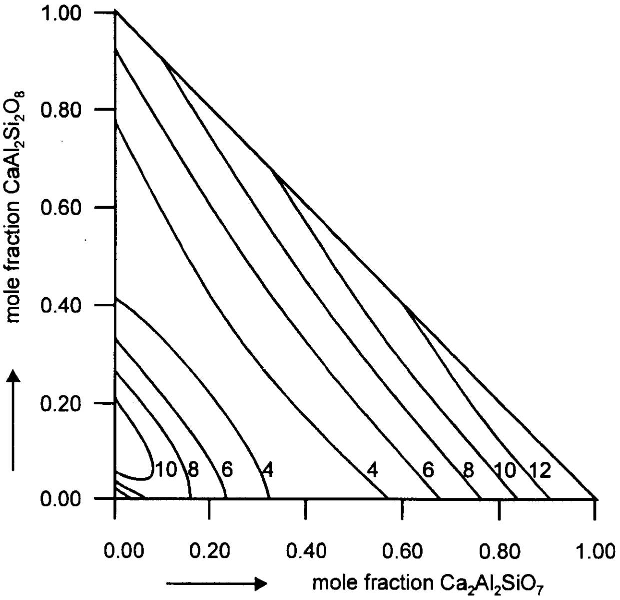

Figure 4. Map of composition dependence of $\Delta^{l}C_p$ (J mol^{-1} K^{-1}) in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ at 1821 K. Heat capacities relate to 1 mol of mixture of components $CaSiO_3$, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$.

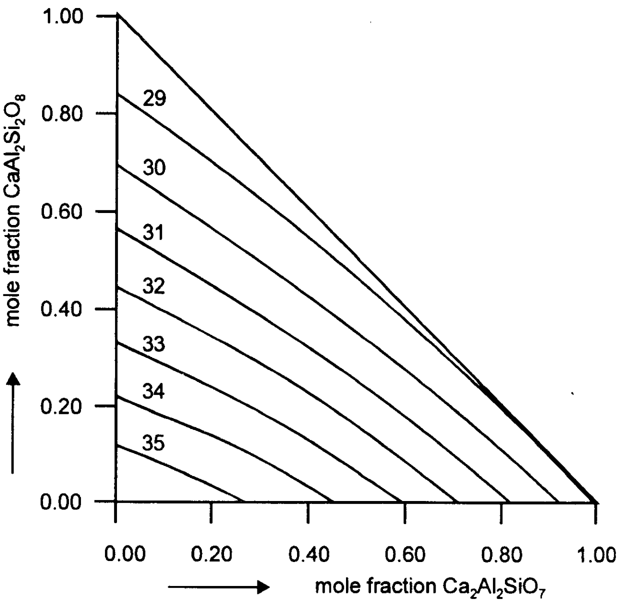

Figure 3. Map of composition dependence of $^{l}C_p(l)$ (J mol^{-1} K^{-1}) in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$. Heat capacities relate to 1 mol of mixture of components CaO, Al_2O_3 and SiO_2.

in figure 4. The data for $^{l}C_p^0(X_i, cr)$ calculation of $X_i = Ca_2Al_2SiO_7$, $CaSiO_3$ and $CaAl_2Si_2O_8$ were taken from Saxena and Chatterjee [6], Holland and Powell [7] and Richet and Fiquet [8], respectively.

Partial molar heat capacity and partial molar heat capacity of mixing

The partial molar heat capacity of constituent X_i, $\bar{C}_p(X_i, l)$, is the change in the heat capacity of a large amount of liquid when one mole of this constituent is added. The values of this quantity for all constituents in both mineral and oxide systems were calculated from the following relations:

$$\bar{C}_p(X_3, l) = C_p(l) - x(X_1)\left[\frac{\partial C_p(l)}{\partial x(X_1)}\right]_{x(X_2)} - x(X_2)\left[\frac{\partial C_p(l)}{\partial x(X_2)}\right]_{x(X_1)} \qquad (9)$$

$$\bar{C}_p(X_2, l) = C_p(l) - x(X_1)\left[\frac{\partial C_p(l)}{\partial x(X_1)}\right]_{x(X_2)} + (1-x(X_2))\left[\frac{\partial C_p(l)}{\partial x(X_2)}\right]_{x(X_1)} \qquad (10)$$

$$\bar{C}_p(X_1, l) = C_p(l) + (1-x(X_1))\left[\frac{\partial C_p(l)}{\partial x(X_1)}\right]_{x(X_2)} - x(X_2)\left[\frac{\partial C_p(l)}{\partial x(X_2)}\right]_{x(X_1)} \qquad (11)$$

The value of $\bar{C}_p(X_i, l)$ includes both the molar heat capacity of added pure liquid constituent and changes in the heat capacity of a liquid caused by differences in geometrical and energetic arrangements inside and outside the particles of this constituent. As an example the plot of the partial molar heat capacity of the constituent $CaAl_2Si_2O_8$ in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ vs. composition is shown in figure 5.

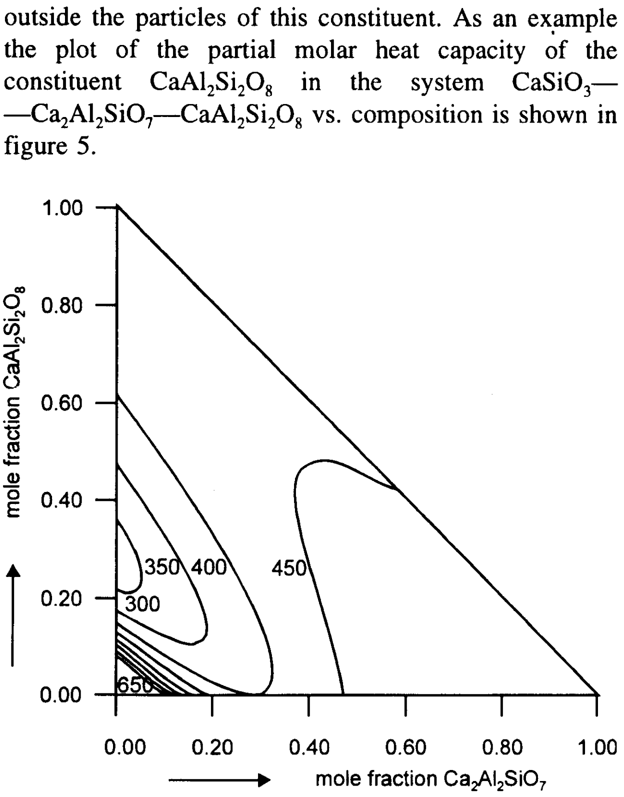

Figure 5. Map of composition dependence of $\bar{C}_p(CaAl_2Si_2O_8, l)$ (J mol^{-1} K^{-1}) in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$. Heat capacities relate to 1 mol of mixture of components $CaSiO_3$, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$.

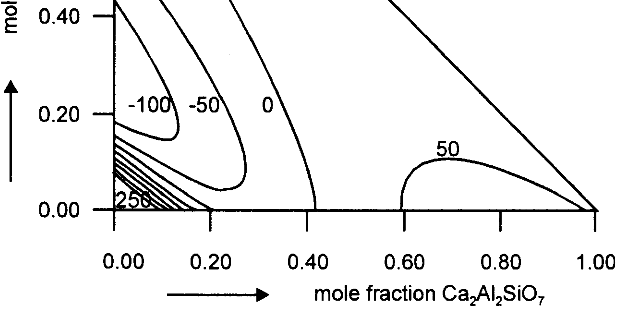

Figure 6. Map of composition dependence of $\Delta_{mix}\bar{C}_p(CaAl_2Si_2O_8, l)$ (J mol^{-1} K^{-1}) in the system $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$. Heat capacities relate to 1 mol of mixture of components $CaSiO_3$, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$.

The partial molar heat capacity of mixing of the constituent X_i is given by

$$\Delta_{mix}\bar{C}_p(X_i, l) = \bar{C}_p(X_i, l) - C^0_p(X_i, l) \qquad (12)$$

This value is equal to the total change in the heat capacity of a system caused by the changes in the structure of added particles and particles around them as a consequence of mixing of liquids. The composition dependence of the partial molar heat capacity of mixing of the constituent mentioned in the above paragraph is shown in figure 6.

DISCUSSION AND CONCLUSIONS

The composition dependencies of C_p(l) are not planar which means that the molar heat capacities of mixing are not equal to zero (figure 1). The same conclusion also follows from the non-constant values of $\bar{C}_p(X_i, !)$, $(\bar{C}_p(X_i, l) \neq C^0_p(X_i, l))$ (figure 5) and non-zero values of $\Delta_{mix}\bar{C}_p(X_i, l)$ (figure 6). Therefore the heat capacity of liquids in this system is not an additive function of the heat capacities of molten pure constituents.

The quantities ^1C_p(l) exceeds the 3*R* value (24.9 J mol^{-1} K^{-1}), corresponding to the high temperature limit of C_v (the isochoric heat capacity) for solids with harmonic vibrations, by about 5 to 16 J mol^{-1} K^{-1} (figure 4). This difference is caused both by the appearance of additional degrees of freedom and by the additional motion of particles the energy of which is no longer a linear, homogeneous function of the squares of their spatial and momentum coordinates. Such phenomenon can be observed in the crystalline phases of compounds with the strong ionic bonds and, to a certain extent, also in the pure crystalline constituents of the investigated system. ($^1C^0_p$ ($CaSiO_3$, cr) = 27.6 J mol^{-1} K^{-1}, $^1C^0_p$ ($Ca_2Al_2SiO_7$, cr) = 27.2 J mol^{-1} K^{-1}, $^1C^0_p$ ($CaAl_2Si_2O_8$, cr) = 26.9 J mol^{-1} K^{-1}). As it can be seen in figure 4, both influences are more exposed in the liquid than in the crystalline phases (positive values of Δ^1C_p), the largest value being at compositions close to $Ca_2Al_2SiO_7$.

Note that quantities $\bar{C}_p(X_i, l)$ and $\Delta_{mix}\bar{C}_p(X_i, l)$ (see figures 5 and 6) are mixed second derivatives so their values could have quite large errors especially in the system CaO—Al_2O_3—SiO_2 where additional data of relative enthalpy for undercooled liquids of CaO, Al_2O_3, and SiO_2 have been used.

Despite these limitations, the following qualitative conclusions can be made:

- The largest changes in structures of the melts occur when the liquid of $Ca_2Al_2SiO_7$ or $CaAl_2Si_2O_8$ is put into a large excess of $CaSiO_3$ liquid (figures 5 and 6) and when liquid $CaSiO_3$ or undercooled liquid Al_2O_3 is put into a large excess of $Ca_2Al_2SiO_7$ or $CaAl_2Si_2O_8$ liquid, provided that the corresponding molar quantities are related to one mole of the mixture of $CaSiO_3$, $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ or to one mole of the mixture of CaO, Al_2O_3 and SiO_2.

- It also follows from these figures that the $Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ binary system behaves as a mechanical mixture. Considering that the phase diagram of this system does not correspond to the ideal solutions and that $\Delta_{mix}H$ is, within the limits of experimental error, equal to zero over the entire range of compositions and a wide range of temperatures [9], the melts of this system can be considered to be athermal solutions.

Acknowledgments

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TEPELNÉ KAPACITY TAVENÍN V SÚSTAVE $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$

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S použitím nameraných hodnôt mólovej relatívnej entalpie [3] sa stanovili závislosti mólovej tepelnej kapacity, mólovej zmiešavacej tepelnej kapacity, parciálnych mólových tepelných kapacít zložiek a parciálnych mólových zmiešavacích tepelných kapacít zložiek tavenín v sústave $CaSiO_3$—$Ca_2Al_2SiO_7$—$CaAl_2Si_2O_8$ od zloženia, v teplotnom rozmedzí 1600 až 1950 K.

Relatívna entalpia je definovaná ako záporný súčet zmeny entalpie pri ochladení vzorky z teploty T na 298 K, nameraný vhadzovacím kalorimetrom a zmeny entalpie pri rozpustení ochladenej vzorky vo vhodnej zmesi anorganických kyselín, nameranej rozpúšťacím kalorimetrom pri teplote 298 K (1), [4].

Mólová zmiešavacia tepelná kapacita je zmena tepelnej kapacity pri vzniku 1 mólu roztoku z kvapalných zložiek, definovaná vzťahom (4).

Získané hodnoty tepelných kapacít sa vztiahli na jeden mól taveniny, počítaný vzhľadom na minerálové i oxidové zložky. Výsledky sa korelovali s počtom možných stupňov voľnosti pohybu častíc v tavenine. Tepelné kapacity, vztiahnuté na jeden atóm formálnej vzorcovej molekuly taveniny, prekračujú hodnotu $3R$ o 5 až 16 J mol^{-1} K^{-1}, čo svedčí o zvýšení počtu stupňov voľnosti, alebo druhov pohybu častíc v tavenine. Najväčšie zmeny v štruktúre častíc pridávanej zložky a častíc v ich okolí nastávajú pri pridávaní taveniny $Ca_2Al_2SiO_7$ alebo $CaAl_2Si_2O_8$ do veľkého prebytku taveniny $CaSiO_3$, resp. pri pridávaní taveniny $CaSiO_3$ alebo podchladenej taveniny Al_2O_3 do veľkého množstva tavenín $Ca_2Al_2SiO_7$ alebo $CaAl_2Si_2O_8$, za predpokladu, že príslušné mólové veličiny sa vzťahujú na jeden mól zmesi $CaSiO_3$, $Ca_2Al_2SiO_7$ a $CaAl_2Si_2O_8$, resp. na jeden mól zmesi CaO, Al_2O_3 a SiO_2.