

Structure of diluted solutions of the molten system C_2MS_2 —CS at temperatures near the melting point of pure components

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Received 23 January 1980

Discussion of the structure model of the melts of pure components and their very diluted solutions in the system $CaO \cdot SiO_2(CS) + 2CaO \cdot MgO \cdot 2SiO_2(C_2MS_2)$ is based on:

a) calculation of molar weights of molten components using cryometry for infinitely diluted solutions,

b) calorimetric data on enthalpy of mixing for the studied system.

From comparison of the calculated value of molar weight of metasilicate CS with formula molar weight $M_{\text{form,CS}} = 116.16 \text{ g mol}^{-1}$ it follows that in molten CS prevail the anions $(SiO_3)_8^{16-}$. Positive values of ΔH_{mix} indicate reactions between species in solution. It is probable that anions of the melt C_2MS_2 react with added anions $(SiO_3)_8^{16-}$, which results in the formation of open chains having the number of SiO_4 -tetrahedrons changing from 8 to 10. From the value of molar weight of akermanite calculated for very diluted solution of C_2MS_2 in CS it follows that at the dissolution of the additive the amount of substance does not appreciably change.

Структурная модель расплавов чистых компонентов и взаимных, очень разбавленных растворов $CaO \cdot SiO_2(CS)$ и $2CaO \cdot MgO \cdot 2SiO_2(C_2MS_2)$ обсуждалась на основании следующих данных:

a) Расчётов мольной массы расплавленных компонентов с использованием криометрии для предельно разбавленных растворов.

б) Измеренных энтальпий смешивания ΔH_{mix} и энтропий смешивания ΔS_{mix} изучаемой системы.

Из сравнения рассчитанного значения мольной массы метасиликата CS прибавляемого к расплавленному C_2MS_2 с мольной массой $M_{\text{form,CS}} = 116,16 \text{ г моль}^{-1}$, соответствующей данной формуле, вытекает, что анионы в расплаве CS имеют преимущественно состав $(SiO_3)_8^{16-}$. Положительные значения ΔH_{mix} являются доказательством реакций между составляющими раствора. Анионы в расплаве C_2MS_2 , вероятно,

Abbreviations used:

In this paper the formula abbreviations are used instead of stoichiometric formulae. C — CaO, M — MgO, S — SiO_2 .

реагируют с прибавляемыми анионами $(\text{SiO}_3)_8^{16-}$ с образованием открытых цепей с числом тетраэдров SiO_4 равным от 8 до 10.

Значение молярной массы акерманита, рассчитанное для очень разбавленного раствора C_2MS_2 в CS показывает, что при растворении примеси не наблюдается изменение молярного количества.

For elucidation the correlation between structure and thermodynamic properties of molten binary systems the temperature region of coexistence of pure crystal phases with melt at high dissolution of one component in the melt appears to be the most suitable. This work deals with the determination of an effective molar weight of CS and C_2MS_2 in their melts using cryometric method. Further the structure of anions and their mutual reactions in solution are discussed. The treatment is based on the assumption that the components CS and C_2MS_2 do not form mutual solid solutions [1].

This paper employs the calorimetric determination of the enthalpy of fusion of akermanite [2] and wollastonite [3] and the results of calculation of SiO_4 -tetrahedrons in anions of molten CMS_2 which was added to the melt C_2MS_2 [4]. It is continuation of papers dealing with thermodynamic treatment of the systems C_2MS_2 — CMS_2 [5, 6] and C_2MS_2 —CS [7].

Calculation of effective molar weights of pure molten components in the system C_2MS_2 —CS

There are three kinds of molar weights used in the paper which are defined as follows:

the real molar weight of substance X ($M_{\text{real},X}$) which corresponds to 1 mole of identical particles really existing in the system,

the formula molar weight of substance Y ($M_{\text{form},Y}$) corresponding to the stoichiometric formula of substance Y,

the effective molar weight of substance Y ($M_{\text{ef},Y}$) equal to the fraction of formula molar weight corresponding to 1 mole of particles which arise in the system from 1 formula mole of substance Y. If in the melt of pure solvent n moles of "distinguishable" particles are formed from 1 formula mole of the solvent Y or from 1 formula mole of an additive Y, the values of $M_{\text{form},Y}$ and $M_{\text{ef},Y}$ are connected by the relation

$$M_{\text{ef},Y} = M_{\text{form},Y}/n \quad (1)$$

The equilibrium between crystals of pure component A and melt in the binary system A—B can be described (assuming pressure to be constant) by the LeChatelier—Shreder equation

$$\frac{d \ln a_A}{dT} = \frac{\Delta H_{\text{fus},A}(x=0, T)}{RT^2} \quad (2)$$

x is the total equilibrium mole fraction of all distinguishable particles which are formed in the solution according to the general reaction scheme



where $n_{P,i}$ are the rational numbers and $n_A \geq 0$.

For $x \rightarrow 0$ it holds $a_A \rightarrow (1-x)$ and thus from eqn (2) it results

$$\lim_{x \rightarrow 0} \frac{d \ln(1-x)}{d(1/T)} = - \frac{\Delta H_{\text{fus},A}(x=0, T_{\text{fus},A})}{R} \quad (4)$$

Eqn (4) can be rearranged to the expression

$$\lim_{x \rightarrow 0} \frac{dx}{d(1/T)} = \frac{\Delta H_{\text{fus},A}(x=0, T_{\text{fus},A})}{R} \quad (5)$$

The dependence of the composition on temperature for equilibrium between crystal phase A and melt, as it follows from the LeChatelier—Shreder equation, is graphically given by the liquidus curve in the corresponding phase diagram in which the composition of components must be expressed in accordance with eqns (4) and (5) by the real (and not by formula) mole fractions. The total equilibrium mole fraction x in binary system is defined by the relation (m is the equilibrium mass fraction)

$$x = \frac{\sum_i \frac{m_{P,i}}{M_{\text{real},P,i}}}{\frac{m_A}{M_{\text{ef},A}} + \sum_i \frac{m_{P,i}}{M_{\text{real},P,i}}} \quad (6)$$

Differentiating of eqn (6) with respect to $(1/T)$ gives for $x \rightarrow 0$ ($m_{P,i} \rightarrow 0$ or $m_A \rightarrow 1$)

$$\begin{aligned} \lim_{x \rightarrow 0} \frac{dx}{d(1/T)} &= M_{\text{ef},A} \lim_{m_{P,i} \rightarrow 0} \sum_i \frac{1}{M_{\text{real},P,i}} \frac{dm_{P,i}}{d(1/T)} = \\ &= M_{\text{ef},A} \lim_{m_{P,i} \rightarrow 0} \sum_i \frac{1}{M_{\text{real},P,i}} \frac{dm_{P,i}}{d(\Delta(1/T))} \end{aligned} \quad (7)$$

where $\Delta(1/T) = 1/T - 1/T_{\text{fus},A}$.

From eqn (3) it follows

$$\frac{dm_{P,i}}{dm_B} = \frac{n_{P,i} M_{\text{real},P,i}}{M_{\text{form},B}} \quad (8)$$

Substituting eqn (7) and eqn (8) to eqn (5) and rearranging gives

$$\sum_i n_{P,i} = n \doteq \frac{M_{\text{form,B}} \Delta H_{\text{fus,A}} (m_{\text{B}} = 0, T_{\text{fus,A}})}{R M_{\text{ef,A}} \lim_{m_{\text{B}} \rightarrow 0} \frac{dm_{\text{B}}}{d(\Delta(1/T))}} \quad (9)$$

resp.

$$n \doteq \frac{M_{\text{form,B}} \Delta h_{\text{fus,A}} (m_{\text{B}} = 0, T_{\text{fus,A}})}{R \lim_{m_{\text{B}} \rightarrow 0} \frac{dm_{\text{B}}}{d(\Delta(1/T))}} \quad (10)$$

where $\Delta h_{\text{fus,A}} (m_{\text{B}} = 0, T_{\text{fus,A}})$ is the specific heat of fusion of component A.

Calculation of the effective molar weights of components CS and C_2MS_2 in the studied systems is based on the following data:

a) calorimetric values of the enthalpy of fusion of pure akermanite C_2MS_2 $\Delta h_{\text{fus,C}_2\text{MS}_2} (T_{\text{fus}} = 1727 \text{ K}) = 454.4 \pm 20.2 \text{ kJ kg}^{-1}$ [2] and the enthalpy of fusion of pure wollastonite CS $\Delta h_{\text{fus,CS}} (T_{\text{fus}} = 1817 \text{ K}) = 493.3 \pm 30.0 \text{ kJ kg}^{-1}$ [3],

b) equilibrium values of the composition and temperature corresponding to the points on liquidus curves of the system C_2MS_2 —CS in composition interval 10 wt %; parameters of eutectic point of the system are as follows: $m_{\text{eut,C}_2\text{MS}_2} = 0.57$; $T_{\text{eut}} = 1673 \text{ K}$ [1].

The experimental data on both branches of the liquidus curve were fitted to polynomial $m_{\text{B,calc}} = f(\Delta(1/T))$ using the least squares method and then the expression

$$\lim_{m_{\text{B}} \rightarrow 0} \frac{dm_{\text{B,calc}}}{d(\Delta(1/T))}$$

was calculated. After substitution to eqn (10) the value of n was determined.

It was found that for description of the liquidus curve it is useful to use the polynomial of the type

$$m_{\text{B,calc}} = A_1(\Delta(1/T)) + A_2(\Delta(1/T))^2 + A_3(\Delta(1/T))^3 + \dots \quad (11)$$

The advantage of this approach is that one of statistically treated points (melting point of pure component) is considered to be known "exactly" because it had been measured many times. The absolute term of general polynomial (11) equals zero: $A_0 = 0$. Thus for the temperature of fusion of pure component it follows $m_{\text{B,calc}} = 0$, which is in agreement with reality.

The degree of polynomial was chosen according to the standard deviation of the regression function. Thus the concentration dependence of the added component CS vs. $\Delta(1/T)$ for the curve of primary crystallization of component C_2MS_2 was fitted by the polynomial

$$m_{\text{CS,calc}} = 5.309949 \times 10^4 (\Delta(1/T)) - 3.024925 \times 10^9 (\Delta(1/T))^2 + 7.575104 \times 10^{13} (\Delta(1/T))^3 \quad (12)$$

standard deviation δ being 7.422×10^{-3} .

For the dependence of concentration of added component C_2MS_2 vs. $\Delta (1/T)$ on the curve of primary crystallization of component CS it holds

$$m_{C_2MS_2,calc} = 1.484909 \times 10^4 (\Delta (1/T)) - 5.889771 \times 10^7 (\Delta (1/T))^2 \quad (13)$$

$$\delta = 8.329 \times 10^{-3}.$$

Using the relationships (10), (12), and (13) and the values of specific enthalpies of fusion of both components the following values of n were obtained

$$n_{(12)} \doteq 0.1198 \quad (M_{form,CS} = 116.16 \text{ g mol}^{-1}) \quad (14)$$

and

$$n_{(13)} \doteq 1.091 \quad (M_{form,C_2MS_2} = 272.64 \text{ g mol}^{-1}) \quad (15)$$

From eqn (1) and eqn (14) it follows for $M_{ef,CS}$

$$M_{ef,CS} \doteq 971 \text{ g mol}^{-1} \quad (16)$$

From eqn (1) and eqn (16) it follows

$$M_{ef,C_2MS_2} \doteq 250 \text{ g mol}^{-1} \quad (17)$$

Results and discussion

Diluted solution of metasilicate in disilicate

From the measurement of enthalpy in the system C_2MS_2 —CS and on the basis of calculations described the following results can be drawn:

a) Let us consider solution of component CS in C_2MS_2 . Then (according to eqns (1), (13), and (14)) in each mole of particles distinguishable from the matrix of solvent there are k formula moles of substance CS, where

$$k = 1/n = M_{ef,CS}/M_{form,CS} \doteq 8.36 \quad (18)$$

Because the formation of distinguishable species by association of species having formula molar weight of CS is not possible in very diluted solutions of CS in C_2MS_2 it may be assumed that the value $M_{ef,CS}$ corresponds approximately to the mean value of the real molar weight of CS ($M_{real,CS}$) in the melt of this substance. Anions are formed by closed circles having 8 tetrahedrons SiO_4 and therefore their composition is $[(SiO_3)_8]^{16-}$. Similar conclusion has been obtained for the system C_2MS_2 — CMS_2 [4].

b) The enthalpy of mixing ΔH_{mix} in both silicate systems, i.e. C_2MS_2 —CS and C_2MS_2 — CMS_2 , is positive in the concentration region with surplus of C_2MS_2 .

Therefore it follows that endothermic reactions occur between components of the systems in question [5, 7]. It was found [5, 7] that ΔH_{mix} practically does not depend on the ratio of concentrations of cations Ca^{2+} and Mg^{2+} .

Explanation of observed phenomena

It is probable that both silicate anions take part in the chemical reactions in the solution discussed above. It is proved by the change in frequency of i.r. spectra of glasses of the studied systems [8]. The following types of reactions can be assumed:

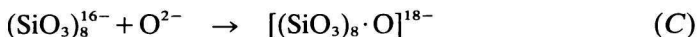
1. Reaction of disilicate anions $(\text{O}_3\text{Si}-\text{O}-\text{SiO}_3)^{6-}$ of solvent with metasilicate anions of added component according to the reaction scheme



2. Less probable are reactions of the type



and



The proposed schemes (A—C) were chosen considering the structure properties of the anions in question and taking into account also the sign of corresponding reaction heat and other thermodynamic properties of the studied systems.

Cleavage of closed circles composed of SiO_4 -tetrahedrons is caused by the action of a lone electron pair of oxygen anion on the bond between bridge atom O and atom Si. The electron pairs in oxide anion O^{2-} possess the greatest ability to cleave the chains of SiO_4 -tetrahedrons. Lone electron pairs of unbridged oxygen atoms in the chains of SiO_4 -tetrahedrons are influenced also by induction interaction of adjacent unbridged or even more of bridged oxygen atoms. Thus the intensity of cleavage ability decreases in the series from O^{2-} to unbridged oxygen atoms in groups $(\text{SiO}_4)^{4-}$, $-(\text{SiO}_3)^{3-}$, and $-(\text{SiO}_2)^{2-}$. Due to a low content of ions $(\text{SiO}_4)^{4-}$ and O^{2-} [9] it follows that the reaction (A) prevails in solution.

The back reactions (A), (B), and (C) can be retarded by surrounding of resulting anions by anions $(\text{Si}_2\text{O}_7)^{6-}$ which hinder the open chains from closing back to the circle. Mutual reactions between anions in silicate melts can be either exothermic or endothermic. Considering the reactions (A—C), which are supposed to exist in the studied systems $\text{C}_2\text{MS}_2-\text{CMS}_2$ and $\text{C}_2\text{MS}_2-\text{CS}$, we should take into account several simultaneous and subsequent events accompanied by energy changes which may be partially compensated.

In all cases an opening of closed 8-link metasilicate chain occurs as a result of reaction with smaller anions. It results in relative shortage of originally "infinite" chain and in decrease of bond strength between bridged oxygen atoms and silicon atoms. The decrease of bond strength is proved by lower frequency of bridged

oxygen atoms in i.r. spectra of silicate glasses which results from the decrease of number of bridge bonds in silicate formations (chains, planar and space network) [8]. Decrease in bond strength in species is accompanied with increase of its potential energy and therefore also with absorption of energy. By opening of the chain weaker bonds between bridged oxygen atom and Si atom are destroyed and they are replaced by stronger bonds in groups — $(\text{SiO}_3)^{3-}$. Stronger bonds between unbridged O atom in inner groups — $(\text{SiO}_2)^{2-}$ — are changed to weaker bonds in terminal groups — $(\text{SiO}_3)^{3-}$. From the above discussion it follows that for total reaction enthalpy ΔH_r , all signs are possible

$$\Delta H_r \geq 0 \quad (19)$$

However, it has been found experimentally that in the studied systems the reaction enthalpy is positive $\Delta H_{\text{mix}} = \Delta H_r > 0$. Therefore endothermic character of reactions prevails, which is connected with the opening of chain and replacement of two bonds in the group — $(\text{SiO}_2)^{2-}$ — with two bonds in terminal group — $(\text{SiO}_3)^{3-}$. As examples for validity of relation (19) the enthalpy changes of the following reactions of crystal silicates ($T_0 = 298 \text{ K}$) can be given [10, 11]

- a) $\text{C} + \text{CS} \rightarrow \text{C}_2\text{S} (\gamma); \quad \Delta H_r = -47.73 \text{ kJ mol}^{-1}$
 b) $\text{CS} + \text{C}_2\text{S} (\beta) \rightarrow \text{C}_3\text{S}_2; \quad \Delta H_r = 0 \text{ kJ mol}^{-1}$
 c) $\text{CS} + \text{CMS} \rightarrow \text{C}_2\text{MS}_2; \quad \Delta H_r = 20.93 \text{ kJ mol}^{-1}$

Opening of metasilicate chains which results by mixing of the melt C_2MS_2 with the melt CS (or CMS_2) is connected with relatively high positive change in entropy ΔS_r because the mobility of single parts of chain increases when compared with closed chain. This increase of entropy determines the sign of change in Gibbs energy of reactions (A—C) and thus

$$\Delta G_r = \Delta H_r - T\Delta S_r < 0 \quad (20)$$

which determines whether the reaction proceeds spontaneously.

Diluted solution of C_2MS_2 in CS

The value of $n_{\text{calc}} = 1.09$ calculated using relation (13) is close to 1. It indicates that in the melt of pure C_2MS_2 besides cations Ca^{2+} , Mg^{2+} and anions $(\text{Si}_2\text{O}_7)^{6-}$ also ions resulting from reactions of $(\text{Si}_2\text{O}_7)^{6-}$ can be present. However the total amount of substance (in moles) does not change. As an example the reaction $2(\text{Si}_2\text{O}_7)^{6-} = (\text{Si}_3\text{O}_{10})^{8-} + (\text{SiO}_4)^{4-}$ can be given. Low negative value of enthalpy of mixing (which is in some cases comparable with uncertainty of measurement [7]) proves that the reactions of the type (A) are hindered in solutions having concentration of cations lower than is their concentration in diluted solution of CS in C_2MS_2 .

The reasons for nonzero difference ($n_{\text{calc}} - 1$) may be as follows:

a) Error of measurement $\Delta H_{\text{fus,CS}}$, $T_{\text{fus,CS}}$ and errors in determination of equilibrium values of temperature and concentration which were used for fitting the function (13).

b) Besides distinguishable complex C_3S_2 also 1 mole of the complex $\text{Ca}_7\text{MgSi}_8\text{O}_{24}$ can be formed in solution as a result of its reaction with 1 formula mole of C_2MS_2 . The properties of the latter complex are similar but not identical with those of the complexes $\text{Ca}_8\text{Si}_8\text{O}_{24}$ which are present, according to eqn (A), in the melt of wollastonite.

c) Solid solutions which have not been detected are formed in the systems in question.

Acknowledgements. The authors wish to express deep gratitude to RNDr. Ing. M. Zikmund, CSc. for his valuable comments to the work and his help by interpretation of the experimental and calculated results presented in this paper.

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Translated by P. Fellner