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THERMODYNAMIC ANALYSIS OF THE SYSTEM $2\,CaO\,.\,MgO\,.\,2\,SiO_2$—$CaO\,.\,MgO\,.\,2\,SiO_2$

II. Isobaric analysis of the Gibbs energy

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The paper is concerned with the calculation of mixing entropy, Gibbs energy, activities and activity coefficients of components in the melt region of the system akermanite ($Ca_2MgSi_2O_7$) — *diopside* ($CaMgSi_2O_6$). *The calculations are based on the determination of partial molar mixing entropy of the components* $\Delta S_{mix,i}$ *using experimentally determined relative enthalpies* H_{rel} *in the temperature range of 1700 K to 1873 K [1] and the phase diagram [2] of the system in question. The calculated concentration dependences of mixing entropy* ΔS_{mix} *and those of additional entropy* ΔS^{E}_{mix} *are asymmetrical, thus exhibiting positive values with solutions containing for the most part* C_2MS_2 *and negative values with solutions comprising mostly* CMS_2. *The additional Gibbs energy* ΔG^{E}_{mix} *is positive at all* x, *showing a maximum at* $x = 0.6$. *The activity coefficients* γ *are larger than unity with the exception of those of the pure components. The system therefore exhibits a positive deviation from the properties of ideal solutions.*

INTRODUCTION

The present study makes use of the following symbols:

The system components, the composition of which is given by the formal formulas $CaO\,.\,MgO\,.\,2\,SiO_2$ and $2\,CaO\,.\,MgO\,.\,2\,SiO_2$ are designated by the respective symbols CMS_2 and C_2MS_2. The concentrations are specified by the molar fraction of CMS_2 (x — molar fraction of CMS_2 in melt; y — molar fraction of CMS_2 in solid phase).

The dependent quantities are given as functions of independent state variables in the following order: x, y and temperature T; all the data refer to atmospheric pressure.

The indexes designate processes, states, substances or phases to which the dependent quantities are related. They are ascribed in the following order:

1. mix (mixing), fus (fusion), eq (equilibrium state), eut (eutectic equilibrium), m (state of system as measured).
2. A (C_2MS_2), B (CMS_2), i (both components).
3. l (liquid phase), s (solid phase).

Calculation of mixing entropy, Gibbs energy and other thermodynamic functions within the melt region of the system C_2MS_2—CMS_2 is based on its enthalpic analysis [1] and application of the eutectic-type phase diagram (Fig. 1), [2]. In the system there arise solid solutions showing limited solubility of components at the side of high concentrations of diopside CMS_2. The fusion temperature of akermanite C_2MS_2 T_{eq} (0,0) is 1727 K and that of diopside T_{eq} (1,1) is 1665 K; eutectic melt has the composition $x_{eut} = 0.638$ at 1634 K. The solid solutions exist in equilibrium with the melt within the concentration range y ($T_{eq} = 1634 \div 1665$ K) $= 0.931 \div 1.0$.

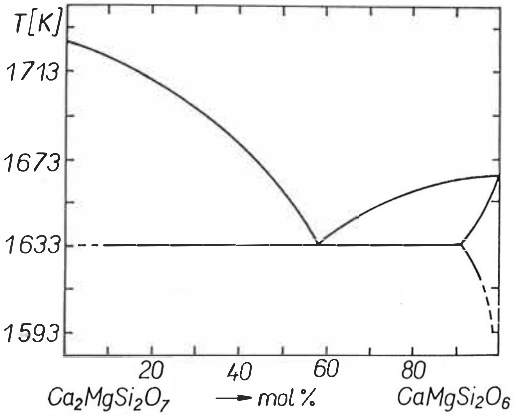

Fig. 1. Phase diagram of the system C_2MS_2 — CMS_2.

The first part of the present study [1] dealt with the measurement of mixing enthalpies ΔH_{mix} of melts in the given system in the temperature interval of 1723—1873 K. The determination of concentration dependences of the other thermodynamic quantities within the same temperature limits, as described below, is based on the calculation of mixing entropy ΔS_{mix} of these phases (another procedure is described in [3]). In this calculation use was made of H_{rel} values obtained by extrapolation of the respective temperature dependences towards the equilibrium temperatures which are ordinates of points on the liquidus lines in the phase diagram.

CALCULATION OF MIXING ENTROPY ΔS_{mix}

General relations

Mixing entropy $\Delta S_{mix,l}(x, T_m)$ was determined by the procedure described in [3]; the procedure is based on a mathematical description of equilibrium between phases present in the system in question.

For the concentration range $x \leqq x_{eut}$ in which the melt co-exists with almost pure crystalline akermanite, the following equation holds for equilibrium chemical potential of component C_2MS_2 in melt and in solid phase:

$$\mu_{A,l}(x, T_{eq}(x, 0)) = \mu_{A,s}(0, T_{eq}(x, 0)). \qquad (1)$$

After rearrangement equation (1) acquires the form

$$\bar{H}_{A,l}(x, T_{eq}(x, 0)) - T_{eq}(x, 0) \, . \, \bar{S}_{A,l}(x, T_{eq}(x, 0)) = H_{A,s}(0, T_{eq}(x, 0)) - T_{eq}(x, 0) \, . \, S_{A,s}(0, T_{eq}(x, 0)). \qquad (2)$$

Equation (2) allows to calculate partial molar entropy of C_2MS_2 under equilibrium conditions. When temperature is raised up to T_m the value of partial molar entropy increases, with respect to $\bar{S}_{A,l}(x, T_{eq}(x, 0))$, by

$\int\limits_{T_{\mathrm{eq}}(x,0)}^{T_{\mathrm{m}}} \frac{\bar{C}_{\mathrm{A,l}}(x,\, T_{\mathrm{m}})}{T}\, \mathrm{d}T$. Partial molar mixing entropy can then be described in the form

$$\Delta \bar{S}_{\mathrm{mix,A,l}}(x,\, T_{\mathrm{m}}) = \bar{S}_{\mathrm{A,l}}(x,\, T_{\mathrm{m}}) - S_{\mathrm{A,l}}(0,\, T_{\mathrm{m}}) =$$

$$= \frac{\bar{H}_{\mathrm{A,l}}(x,\, T_{\mathrm{eq}}) - H_{\mathrm{A,s}}(0,\, T_{\mathrm{eq}})}{T_{\mathrm{eq}}(x,\, 0)} + \int\limits_{T_{\mathrm{eq}}(x,0)}^{T_{\mathrm{m}}} \frac{\bar{C}_{\mathrm{A,l}}(x,\, T)}{T}\, \mathrm{d}T + S_{\mathrm{A,s}}(0,\, T_{\mathrm{eq}}(x,\, 0)) -$$

$$- \Bigg[S_{\mathrm{A,s}}(0,\, T_{\mathrm{eq}}(x,\, 0)) + \int\limits_{T_{\mathrm{eq}}(x,0)}^{T_{\mathrm{eq}}(0,0)} \frac{C_{\mathrm{A,s}}(0,\, T)}{T}\, \mathrm{d}T + \frac{\Delta H_{\mathrm{fus,A}}(0,\, T_{\mathrm{eq}})}{T_{\mathrm{eq}}(0,\, 0)} + \qquad (3)$$

$$+ \int\limits_{T_{\mathrm{eq}}(0,0)}^{T_{\mathrm{m}}} \frac{C_{\mathrm{A,l}}(0,\, T)}{T}\, \mathrm{d}T \Bigg].$$

Partial molar mixing entropy of component CMS$_2$ for $x \leqq x_{\mathrm{eut}}$ was calculated from integrated Gibbs—Duhem equation

$$\Delta \bar{S}_{\mathrm{mix,B,l}}(x,\, T_{\mathrm{m}}) = \Delta \bar{S}_{\mathrm{mix,B,l}}(x_{\mathrm{eut}},\, T_{\mathrm{m}}) - \int\limits_{\Delta \bar{S}_{\mathrm{mix,A,l}}(x_{\mathrm{eut}},\, T_{\mathrm{m}})}^{\Delta \bar{S}_{\mathrm{mix,A,l}}(x,\, T_{\mathrm{m}})} \frac{1-x}{x}\, \mathrm{d}\Delta \bar{S}_{\mathrm{mix,A,l}}(x,\, T_{\mathrm{m}}). \qquad (4)$$

The value of partial molar entropy of CMS$_2$ $\Delta \bar{S}_{\mathrm{mix,B,l}}(x_{\mathrm{eut}},\, T_{\mathrm{m}})$ for the eutectic composition was calculated from equation (8) below.

Within the concentration range $x \geqq x_{\mathrm{eut}}$ the equilibrium state of the system is described by the relationship

$$\mu_{\mathrm{B,l}}(x,\, T_{\mathrm{eq}}(x,\, \mathrm{y})) = \mu_{\mathrm{B,s}}(y,\, T_{\mathrm{eq}}(x,\, y)). \qquad (5)$$

Equation (5) can be written in the form

$$\bar{H}_{\mathrm{B,l}}(x,\, T_{\mathrm{eq}}(x,\, y)) - T_{\mathrm{eq}}(x,\, y)\,.\, \bar{S}_{\mathrm{B,l}}(x,\, T_{\mathrm{eq}}(x,\, y)) = \bar{H}_{\mathrm{B,s}}(y,\, T_{\mathrm{eq}}(x,\, y)) -$$

$$- T_{\mathrm{eq}}(x,\, y)\,.\, \bar{S}_{\mathrm{B,s}}(y,\, T_{\mathrm{eq}}(x,\, y)) = H_{\mathrm{B,s}}(1,\, T_{\mathrm{eq}}(x,\, y)) - T_{\mathrm{eq}}(x,\, y)\,.$$

$$.\, S_{\mathrm{B,s}}(1,\, T_{\mathrm{eq}}(x,\, y)) + RT_{\mathrm{eq}}(x,\, y)\,.\, \ln a_{\mathrm{B,s}}(y,\, T_{\mathrm{eq}}(x,\, y)). \qquad (6)$$

In view of the high concentration of CMS$_2$ in solid solutions the approximate values of the CMS$_2$ activity coefficients can be considered as being equal to unity, and the equilibrium activity of diopside in (6) can be substituted from equation

$$a_{\mathrm{B,s}}(T_{\mathrm{eq}}(x,\, y)) = y_{\mathrm{B,s}}(T_{\mathrm{eq}}(x,\, y)). \qquad (7)$$

(Application of equation (7) is likewise permissible with respect to the relatively low value of the last term of the right-hand side of equation (6).)

By the procedure indicated in the deriving of equation (3), the following expression for partial molar mixing entropy of CMS$_2$ in the melt of the system in question can be obtained from formally rearranged equation (6):

$$\Delta\bar{S}_{\mathrm{mix,B,l}}(x,T_\mathrm{m}) = \frac{\bar{H}_{\mathrm{B,l}}(x,T_\mathrm{eq}(x,y)) - H_{\mathrm{B,s}}(1,T_\mathrm{eq}(x,y))}{T_\mathrm{eq}(x,y)} + \int\limits_{T_\mathrm{eq}(x,y)}^{T_\mathrm{m}} \frac{\bar{C}_{\mathrm{B,l}}(x,T)}{T}\,\mathrm{d}T - \int\limits_{T_\mathrm{eq}(x,y)}^{T_\mathrm{eq}(1,1)} \frac{C_{\mathrm{B,s}}(1,T)}{T}\,\mathrm{d}T - \frac{\Delta H_{\mathrm{fus,B}}(T_\mathrm{eq}(1,1))}{T_\mathrm{eq}(1,1)} - \int\limits_{T_\mathrm{eq}(1,1)}^{T_\mathrm{m}} \frac{C_{\mathrm{B,l}}(1,T)}{T}\,\mathrm{d}T - R\ln y(x,T_\mathrm{eq}(x,y)) = \Delta\bar{S}'_{\mathrm{mix,B,l}}(x,T_\mathrm{m}) - R\ln y(x,T_\mathrm{eq}(x,y)). \tag{8}$$

The value of $\Delta\bar{S}'_{\mathrm{mix,B,l}}(x,T_\mathrm{m})$ would pertain to partial molar mixing entropy of CMS_2 if no solid solutions were formed.

Partial molar mixing entropy of component C_2MS_2 was again calculated from the integrated Gibbs — Duhem equation

$$\Delta\bar{S}_{\mathrm{mix,A,l}}(x,T_\mathrm{m}) = \Delta\bar{S}_{\mathrm{mix,A,l}}(x_\mathrm{eut},T_\mathrm{m}) - \int\limits_{\Delta\bar{S}'_{\mathrm{mix,B,l}}(x_\mathrm{eut},T_\mathrm{m})}^{\Delta\bar{S}'_{\mathrm{mix,B,l}}(x,T_\mathrm{m})} \frac{x}{1-x}\,\mathrm{d}\Delta\bar{S}'_{\mathrm{mix,B,l}}(x,T_\mathrm{m}) + R\int\limits_{\ln y_\mathrm{eut}}^{\ln y(x,T_\mathrm{eq}(x,y))} \frac{x}{1-x}\,\mathrm{d}\ln y\,(T_\mathrm{eg}(x,y)). \tag{9}$$

The value of $\Delta\bar{S}_{\mathrm{mix,A,l}}(x_\mathrm{eut},T_\mathrm{m})$ was obtained with the use of equation (3). The mixing entropy in the system was calculated from the equations

$$\Delta S_{\mathrm{mix,l}}(x,T) = (1-x)\,\Delta\bar{S}_{\mathrm{mix,A,l}}(x,T) + x\,\Delta\bar{S}_{\mathrm{mix,B,l}}(x,T) \tag{10}$$

$$\Delta S^\mathrm{E}_{\mathrm{mix,l}}(x,T) = \Delta S_{\mathrm{mix,l}}(x,T) - [-(1-x)\ln(1-x) - x\ln x]. \tag{11}$$

The dependence of mixig entropy of the system C_2MS_2—CMS_2 on composition and temperature

In the calculation of $\Delta\bar{S}_{\mathrm{mix,A}}$ and $\Delta\bar{S}_{\mathrm{mix,B}}$, the values H_rel and $\bar{H}_\mathrm{rel}$ measured by the 'two-calorimeter method' [1] were substituted into equations (3) and (8). (In study [3] its author has suggested a procedure for calculating the mixing entropy using the ΔH_mix values, also based on equations (1) and (5). However, the method is advantageous only when the mixing enthalpies can be determined directly.)

The following values and relations were employed in numerical solving of equations (10) and (11):

Fusion heat of akermanite $\Delta H_{\mathrm{fus,A}}(T_\mathrm{eq}(0,0)) = 123.9 \pm 3.2$ [kJ mol^{-1}] [4].

The temperature dependences of molar thermal capacities of fused and crystalline akermanite are as follows:

$C_{\mathrm{A,l}} = 0.3815$ [kJ mol^{-1} K^{-1}], measured in the temperature range of 1740 to 1870 K [4], and

$C_{\mathrm{A,s}} = 0.2014 + 8.84 \times 10^{-5}\,T$ [kJ mol^{-1} K^{-1}], measured in the temperature range of 1469 to 1690 K [4].

The heat of fusion of diopside $\Delta H_{\mathrm{fus,B}}(T_{\mathrm{eq}}(1, 1)) = 128.5$ kJ mol^{-1} [5]. The temperature dependences of molar thermal capacities of molten and crystalline diopside, respectively, are given by the following equations [5]:

$$C_{\mathrm{B,l}} = 0.3558 \ [\mathrm{kJ\ mol^{-1}\ K^{-1}}], \text{ and}$$

$$C_{\mathrm{B,s}} = 0.279 - 1.781 \times 10^4\, T^2 \qquad [\mathrm{kJ\ mol^{-1}\ K^{-1}}].$$

The dependences hold in the temperature interval of 298 to 1885 K. The values of the integrals on the right-hand sides of equations (4) and (9) were determined graphically.

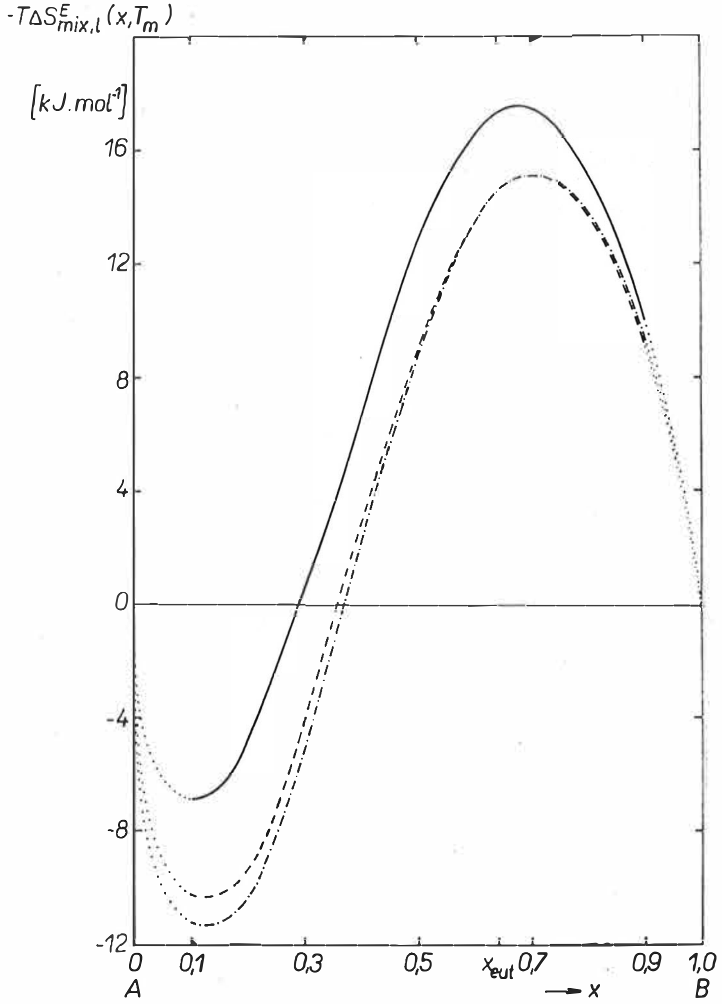

Fig. 2. Isothermic concentration dependences of the product $-T\,\Delta S^{\mathrm{E}}_{\mathrm{mix,l}}(x, T_{\mathrm{m}})$ *(x is the molar fraction of* CMS$_2$*);*
——— $T_{\mathrm{m}} = 1723$ K, — — — $T_{\mathrm{m}} = 1773$ K, —·—·— $T_{\mathrm{m}} = 1823$ K.

The isothermic concentration dependences of excess entropy in the system, $\Delta S^{E}_{mix,l}(x, T_m)$ have an S-shaped course similarly to those of $\Delta H_{mix,l}(x, T_m)$. The range of maximum values of $\Delta S^{E}_{mix,l}(x, T)$ curves at $x = 0.1$ amounts to $3.97 \div 6.16$ [J mol^{-1} K^{-1}] for the temperature interval in question. The transition through zero values to the region of negative ones arises in the composition range of $x = 0.3$ to 0.4; at $x = 0.7$ the curves attain their minimum values of —10.0 [J mol^{-1} K^{-1}] (1723 K) down to —8.34 [J mole^{-1} K^{-1}] (1823 K). Fig. 2 shows three curves of $-T\ \Delta S^{E}_{mix,l}(x, T)$ for temperatures $T_m = 1723$, 1773 and 1823 K (their course is thus 'mirror-symmetrical' as compared to the relationships of $\Delta S^{E}_{mix,l}(x, T)$ described above).

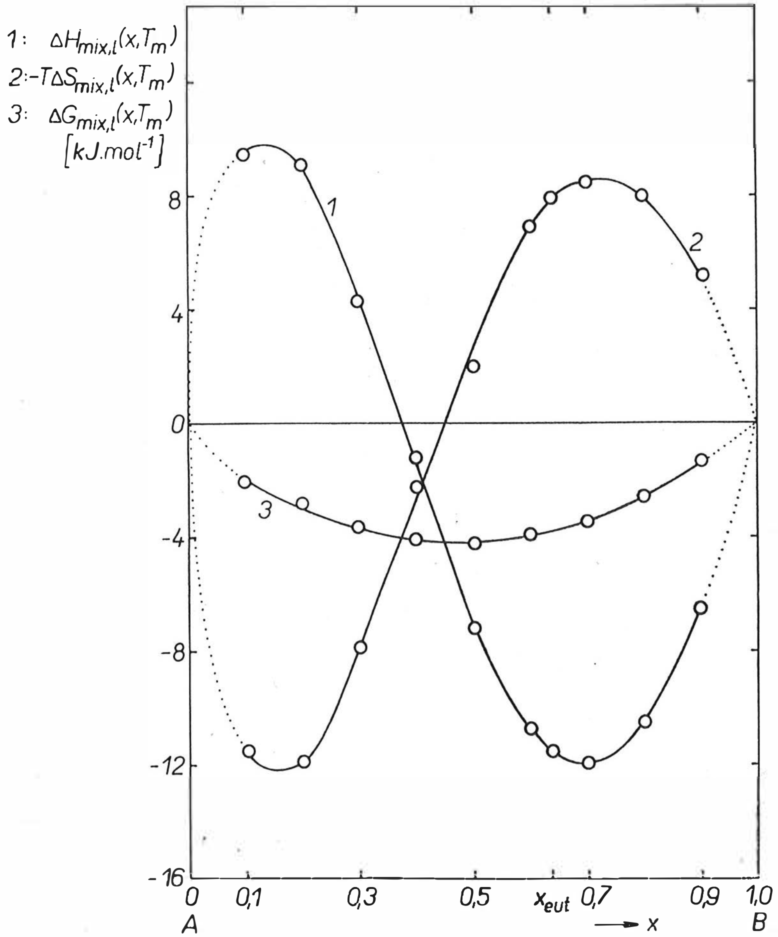

Fig. 3. Isothermic concentration dependences of:
1. mixing enthalpy of the system $\Delta H_{mix,l}(x, T_m)$ (curve 1),
2. the product — $T\ \Delta S_{mix,l}(x, T_m)$ (curve 2),
3. Gibbs energy of the system $\Delta G_{mix,l}(x, T_m)$ (curve 3);
$T_m = 1723$ K, o — experimental points.

The positive value of excess entropy in the high-concentration C_2MS_2 region results from at least the following two reasons:

a) there is a considerable difference in the sizes of basic particles (anions) of the components in the given system (similarly to organic polymers), [6], [7],

b) there are the changes in structure due to mixing. In the analysis of the $\Delta H_{\mathrm{mix,l}}(x, T)$ isotherms in [1] it was assumed that at $x < 0.3$, pyroxene

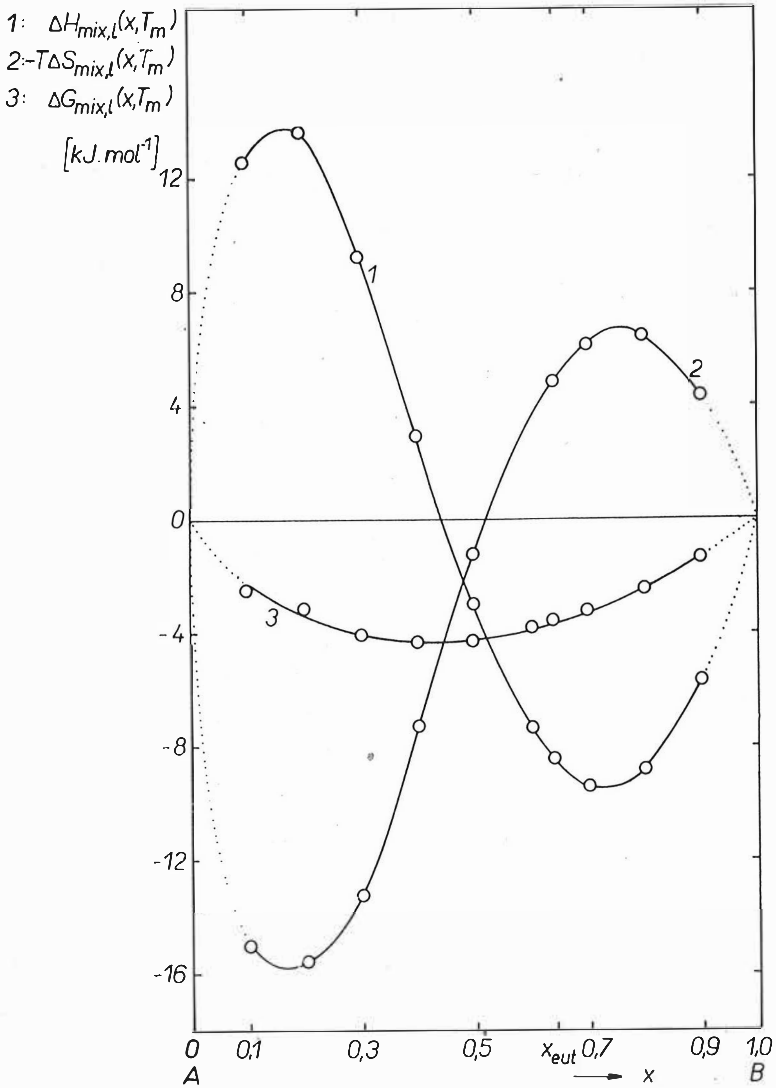

Fig. 4. Isothermic concentration dependences of:
1. mixing enthalpy of the system $\Delta H_{\mathrm{mix,l}}(x, T_{\mathrm{m}})$ *(curve 1),*
2. the product — $T\,\Delta S_{\mathrm{mix,l}}(x, T_{\mathrm{m}})$ *(curve 2),*
3. Gibbs energy of the system $\Delta G_{\mathrm{mix,l}}(x, T_{\mathrm{m}})$ *(curve 3);*
$T_{\mathrm{m}} = 1773$ K, *o — experimental points.*

chains $[SiO_3]^{2-}_n$ split up and shorter chains are formed. The increase in melt disarrangement due to creation of a larger number of new particles results in an increase in excess entropy ΔS^E_{mix}.

At higher concentrations of CMS_2 the shorter (pyrosilicate) chains tend to associate forming longer chains with stronger bonds between bridging oxygens

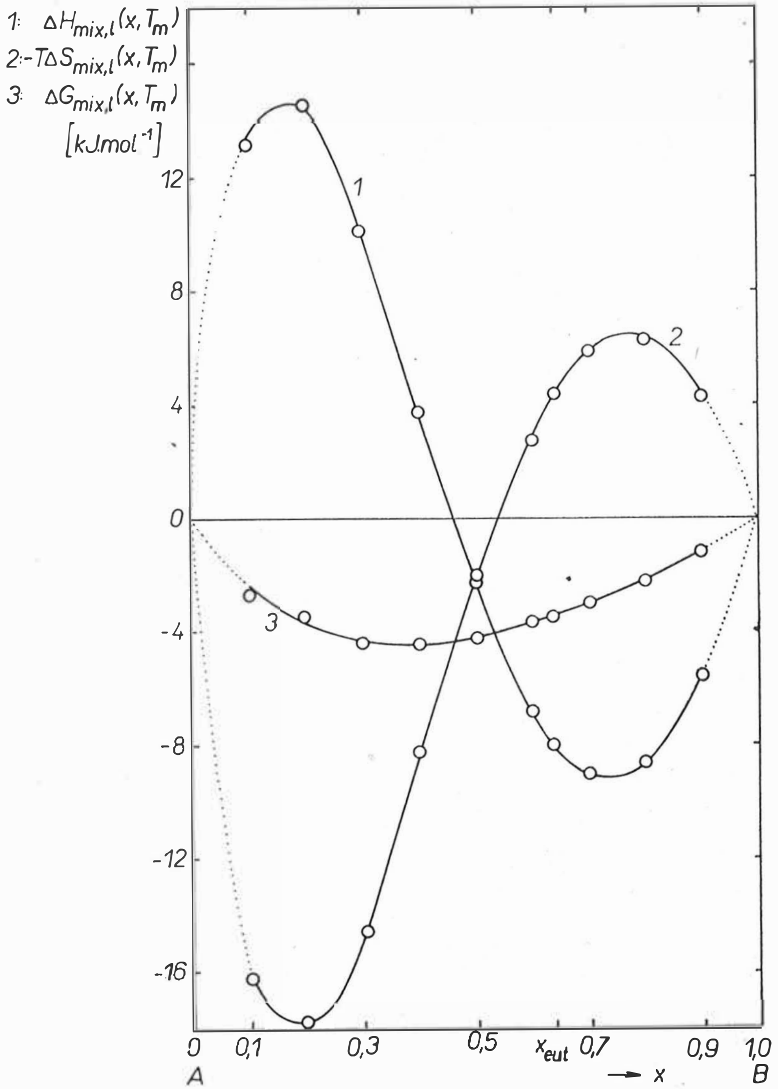

Fig. 5. Isothermic concentration dependences of:
1. mixing enthalpy of the system $\Delta H_{mix,l}(x, T_m)$ *(curve 1),*
2. the product — $T\,\Delta S_{mix,l}(x, T_m)$ *(curve 2),*
3. Gibbs energy of the system, $\Delta G_{mix,l}(x, T_m)$ *(curve 3);*
$T_m = 1823$ K, *o — experimental points.*

and silicon. The excess entropy $\Delta S^{\mathrm{E}}_{\mathrm{mix}}$ is negative (while, however, $\Delta G^{\mathrm{E}}_{\mathrm{mix}}$ is positive).

In Figs. 3, 4 and 5 (marked *2*) are plotted the relationships of $-T\,\Delta S_{\mathrm{mix,l}}(x, T_{\mathrm{m}})$ for temperatures of 1723, 1773 and 1823 K. The positions of the 'minima' are shifted towards $x = 0.2$; zero values are attained by this quantity within the range of $x = 0.4$ to 0.6. The position of the 'maxima' is in the range of $x = 0.7$ to 0.8.

Calculation of mixing and excess Gibbs energy in the system C_2MS_2—CMS_2

The mixing Gibbs energy $\Delta G_{\mathrm{mix,l}}(x, T)$ and the excess Gibbs energy $\Delta G^{\mathrm{E}}_{\mathrm{mix,l}}(x, T)$ in the given system were calculated with the use of the definition equations

$$\Delta G_{\mathrm{mix,l}}(x, T) = \Delta H_{\mathrm{mix,l}}(x, T) - T\Delta S_{\mathrm{mix,l}}(x, T) \tag{12}$$

and

$$\Delta G^{\mathrm{E}}_{\mathrm{mix,l}}(x, T) = \Delta H_{\mathrm{mix,l}}(x, T) - T\Delta S^{\mathrm{E}}_{\mathrm{mix,l}}(x, T) \tag{13}$$

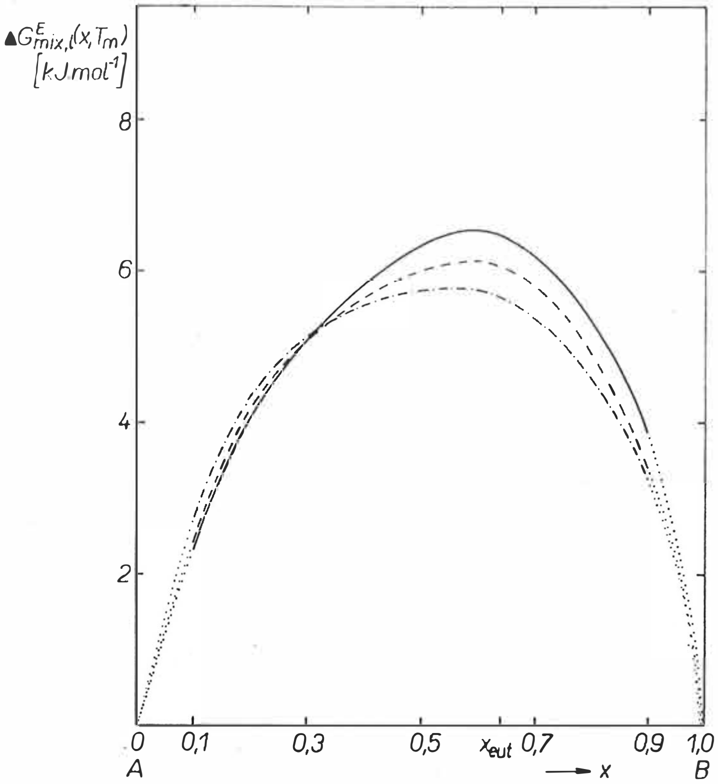

Fig. 6. Isothermic concentration dependences of excess Gibbs energy $\Delta G^{\mathrm{E}}_{\mathrm{mix,l}}(x, T_{\mathrm{m}})$ in the system (x — molar fraction of CMS_2);
—·—·— $T_m = 1723$ K, — — — — $T_m = 1773$ K, ——— $T_m = 1823$ K.

where the values of $\Delta H_{\mathrm{mix,l}}(x, T)$ were obtained by calculations from equation (14) of study [1] and the values of $\Delta S_{\mathrm{mix,l}}(x, T)$ and $\Delta S^{\mathrm{E}}_{\mathrm{mix,l}}(x, T)$ were calculated according to equations (10) and (11) as given in the present study.

The activity coefficients of the two components were calculated on the basis of partial molar Gibbs energies of the components determined according to the following equations:

$$\Delta \bar{G}^{\mathrm{E}}_{\mathrm{mix,\,i,\,l}}(x, T) = \Delta \bar{H}_{\mathrm{mix,\,i,\,l}}(x, T) - T\Delta \bar{S}^{\mathrm{E}}_{\mathrm{mix,\,i,\,l}}(x, T). \qquad (14\mathrm{a,\ b})$$

The following equations hold for the activity coefficients of both components, $\gamma_{\mathrm{A,\,l}}(x, T)$ and $\gamma_{\mathrm{B,\,l}}(x, T)$:

$$\gamma_{\mathrm{i,\,l}}(x, T) = \exp\left(\frac{\Delta G^{\mathrm{E}}_{\mathrm{mix,\,i,\,l}}(x, T)}{RT}\right). \qquad (15\mathrm{a,\ b})$$

The activities of C_2MS_2 and CMS_2 are given by the equations

$$a_{\mathrm{A,\,l}}(x, T) = (1 - x)\,\gamma_{\mathrm{A,\,l}}(x, T) \qquad (16)$$

and

$$a_{\mathrm{B,\,l}}(x, T) = x\gamma_{\mathrm{B,\,l}}(x, T). \qquad (17)$$

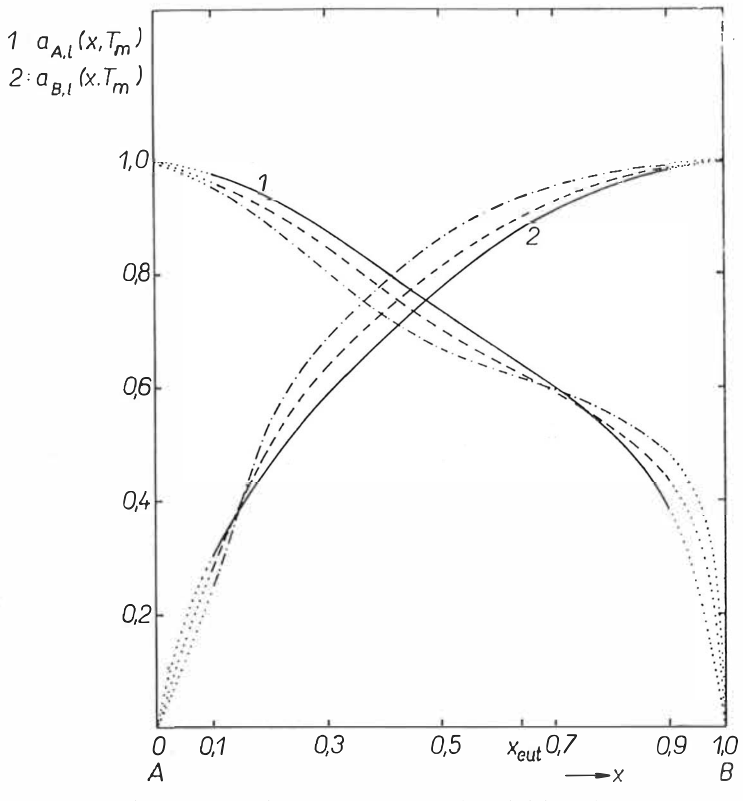

Fig. 7. *Isothermic concentration dependences of activities of the components.*
1. $a_{\mathrm{A,\,l}}(x, T_{\mathrm{m}})$ *— activity of* C_2MS_2,
2. $a_{\mathrm{B,\,l}}(x, T_{\mathrm{m}})$ *— activity of* CMS_2;
——— $T_{\mathrm{m}} = 1723$ K, — — — $T_{\mathrm{m}} = 1773$ K, —·—·— $T_{\mathrm{m}} = 1823$ K.

Fig. 6 shows a plot of isothermic concentration dependences for excess Gibbs energy $\Delta G^{\mathrm{E}}_{\mathrm{mix,\,l}}(x, T_{\mathrm{m}})$ for the temperatures of 1723, 1773 and 1823 K. The curves are mildly asymmetrical and within the entire concentration range pass through the region of positive values, exhibiting a maximum at $x_{\mathrm{m}} = 0.6$. At the maximum the values attained by the quantity within the given temperature interval amount to 5.7 to 6.6 [kJ mol^{-1}].

The course of isothermic concentration dependences of $\Delta G_{\mathrm{mix,\,l}}(x, T_{\mathrm{m}})$ is in the range of negative values, showing a minimum at $x \doteq 0.5$ (1723 and 1823 K) and at $x = 0.4$ (1773 K); the range of extreme values is from —4.19 to —4.36 [kJ mol^{-1}].

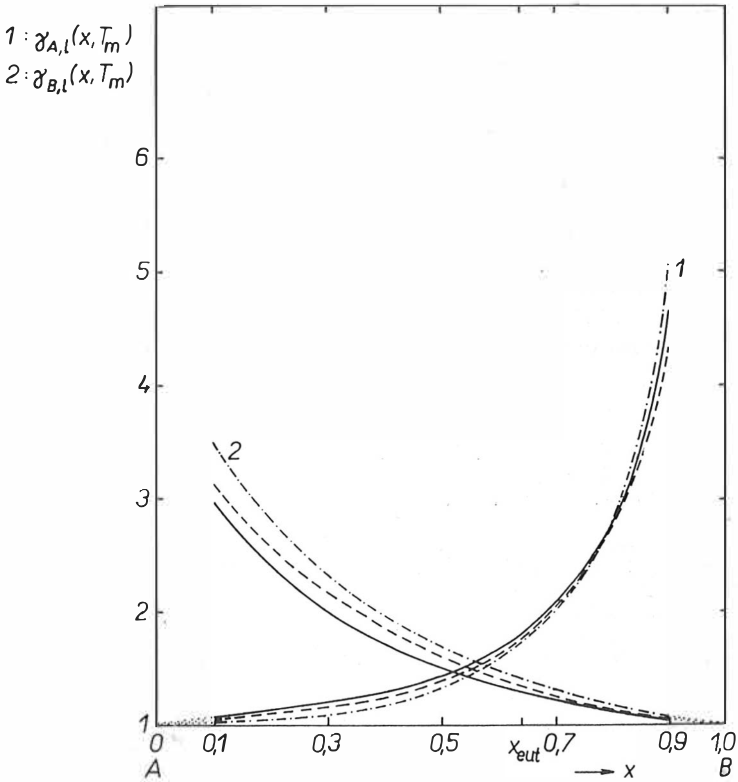

Fig. 8. Isothermic concentration dependences of activity coefficients of the components:
1. $\gamma_{\mathrm{A,l}}(x, T_{\mathrm{m}})$ *— activity coefficient of* $\mathrm{C_2MS_2}$,
2. $\gamma_{\mathrm{B,l}}(x, T_{\mathrm{m}})$ *— activity coefficient of* $\mathrm{CMS_2}$;
——— $T_{\mathrm{m}} = 1723$ K, — — — $T_{\mathrm{m}} = 1773$ K, —·—·— $T_{\mathrm{m}} = 1823$ K.

Isothermic concentration dependences of activities $a_{\mathrm{A,l}}(x, T_{\mathrm{m}})$ and $a_{\mathrm{B,l}}(x, T_{\mathrm{m}})$ are plotted in Fig. 7 for $T_{\mathrm{m}} = 1723$, 1773 and 1823 K, respectively. The activity curves of both components are higher within the entire concentration range than those of molar fractions and substantially deviated from the 'ideal' course (when expressing the molar fractions of the components of the given system by means of formal molecular weights the Raoult law does not hold even at the limit concentrations). The activity values except for those of the pure components, are higher than the values of molar fractions, i.e. the activity coefficients of the two components are higher than, or equal to unity at all the x (Fig. 8).

All the calculated excess quantities are mildly temperature-dependent. The probable course of the graphic relationships of all the thermodynamic quantities in question within the concentration intervals of $x < 0; 0.1 >$ and $x < 0.9; 1.0>$ is represented by the dotted line.

CONCLUSION

The results given above indicate that the system C_2MS_2—CMS_2 is non-ideal in its melt region. The considerable difference between the structures of the basic particles of the components and the structural changes taking place in the course of mixing are obviously the cause of an asymmetrical and temperature-dependent course of all the excess quantities, in particular of mixing enthalpy and excess mixing entropy ΔS^{E}_{mix}. The system exhibits a positive deviation from the Raoult law. The thermodynamic properties of the solutions of C_2MS_2—CMS_2 can be more advantageously described by 'flexible' mathematical functions than by using inadequately substantiated and frequently quite formal thermodynamic models. The unsuitability of application of such models in the case of some, often much simpler systems, has been demonstrated experimentally and evaluated critically by Holm [8], [9].

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TERMODYNAMICKÝ ROZBOR SÚSTAVY
$2\,CaO \,.\, MgO \,.\, 2\,SiO_2$ — $CaO \,.\, MgO \,.\, 2\,SiO_2$

II. Izobarický rozbor Gibbsovej energie

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Obsahom predloženej práce sú výpočty zmiešavacej entropie, Gibbsovej energie, aktivít a aktivitných koeficientov zložiek v taveninovej oblasti sústavy akermanit ($2\,CaO \,.\, MgO \,.\, 2\,SiO_2$) — diopsid ($CaO \,.\, MgO \,.\, 2\,SiO_2$). Tieto výpočty sa zakladajú:

1. na použití experimentálnych hodnôt zmiešavacej entalpie v sústave v teplotnom intervale 1700—1873 K [1],
2. na použití fázového diagramu eutektického typu s oblasťou existujúcich tuhých roztokov s obmedzenou rozpustnosťou zložiek na strane vysokých koncentrácií CMS_2 [2].

Zmiešavacia entropia $\Delta S_{\mathrm{mix},1}(x, T_{\mathrm{m}})$ sa stanovila postupom, ktorý sa zakladá na matematickom opise rovnováhy medzi fázami, prítomnými v študovanej sústave [3]. Pre koncentračné rozmedzie $x \leqq x_{\mathrm{eut}}$, v ktorom tavenina koexistuje s takmer čistým kryštalickým akermanitom, dá sa odvodiť z rovnosti chemických potenciálov C_2MS_2 pre parciálnu mólovú zmiešavaciu entropiu C_2MS_2 vzťah:

$$\Delta S_{\mathrm{mix,A,1}}(x, T_{\mathrm{m}}) = \frac{\bar{H}_{\mathrm{A,1}}(x, T_{\mathrm{eq}}) - H_{\mathrm{A,s}}(0, T_{\mathrm{eq}})}{T_{\mathrm{eq}}(x, 0)} + \int_{T_{\mathrm{eq}}(x,0)}^{T_{\mathrm{m}}} \frac{\bar{C}_{\mathrm{A,1}}(x, T)}{T} \mathrm{d}T -$$

$$- \int_{T_{\mathrm{eq}}(x,0)}^{T_{\mathrm{eq}}(0,0)} \frac{C_{\mathrm{A,s}}(0, T)}{T} \mathrm{d}T - \frac{\Delta H_{\mathrm{fus,A}}(0, T_{\mathrm{eq}})}{T_{\mathrm{eq}}(0, 0)} - \int_{T_{\mathrm{eq}}(0,0)}^{T_{\mathrm{m}}} \frac{C_{\mathrm{A,1}}(0, T)}{T} \mathrm{d}T. \tag{1}$$

Obdobný výraz platí pre parciálnu mólovú zmiešavaciu entropiu CMS_2 v tavenine v koncentračnom rozmedzí $x \geqq x_{\mathrm{eut}}$:

$$\Delta S_{\mathrm{mix,B,1}}(x, T_{\mathrm{m}}) = \frac{\bar{H}_{\mathrm{B,1}}(x, T_{\mathrm{eq}}(x, y) - H_{\mathrm{B,s}}(1, T_{\mathrm{eq}}(x, y))}{T_{\mathrm{eq}}(x, y)} + \int_{T_{\mathrm{eq}}(x,y)}^{T_{\mathrm{m}}} \frac{\bar{C}_{\mathrm{B,1}}(1, T)}{T} \mathrm{d}T -$$

$$- \int_{T_{\mathrm{eq}}(x,y)}^{T_{\mathrm{eq}}(1,1)} \frac{C_{\mathrm{B,s}}(1, T)}{T} \mathrm{d}T - \frac{\Delta H_{\mathrm{fus,B}}(T_{\mathrm{eq}}(1, 1))}{T_{\mathrm{eq}}(1, 1)} - \int_{T_{\mathrm{eq}}(1,1)}^{T_{\mathrm{m}}} \frac{C_{\mathrm{B,1}}(1, T)}{T} \mathrm{d}T -$$

$$- R \ln y(x, T_{\mathrm{eq}}(x, y)). \tag{2}$$

Hodnoty veličín H_{rel}, resp. $\bar{H}_{\mathrm{rel}}$ v rovniciach (1) a (2) sa prevzali z práce [1], hodnoty tavných entalpií čistých zložiek a závislostí tepelných kapacít jednotlivých fáz čistých zložiek z práce [4] a [5].

Parciálne mólové zmiešavacie entropie CMS_2 pre $x \leqq x_{\mathrm{eut}}$ a C_2MS_2 v koncentračnej oblasti $x \geqq x_{\mathrm{mix}}$ sa vypočítali z integrovaných Gibbsových—Duhemových rovníc.

Vypočítané koncentračné závislosti zmiešavacej entropie ΔS_{mix} a dodatkovej entropie $\Delta S^{\mathrm{E}}_{\mathrm{cut}}$ sú nesymetrické a pre zloženia roztokov s prevahou C_2MS_2 nadobúdajú kladné hodnoty, zatiaľ čo pre zloženia roztokov s prevahou CMS_2 nadobúdajú záporné hodnoty.

Dodatková Gibbsova energia $\Delta G^{\mathrm{E}}_{\mathrm{mix}}$ je pre všetky x kladná a má mierne asymetrický priebeh s maximom pri $x = 0{,}6$. Aktivitné koeficienty γ obidvoch zložiek sú s výnimkou čistých zložiek väčšie ako 1.

Asymetrický a mierne teplotne závislý priebeh všetkých dodatkových veličín je zrejme spôsobený značným rozdielom medzi štruktúrami základných častíc zložiek a štrukturálnymi zmenami pri zmiešaní.

Obr. 1. Fázový diagram sústavy C_2MS_2 — CMS_2.
Obr. 2. Izotermické koncentračné závislosti súčinu — $T\, \Delta S^{\mathrm{E}}_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$
(x — *mólový zlomok* CMS_2);
——— $T_{\mathrm{m}} = 1723$ K, — — — $T_{\mathrm{m}} = 1773$ K, —·—·— $T_{\mathrm{m}} = 1823$ K.
Obr. 3. Izotermické koncentračné závislosti;
1. zmiešavacej entalpie sústavy $\Delta H_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$ (*krivka 1*),
2. súčinu — $T\, \Delta S_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$ (*krivka 2*),
3. Gibbsovej energie sústavy $\Delta G_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$ (*krivka 3*);
$T_{\mathrm{m}} = 1723$ K, *o — experimentálne body.*
Obr. 4. Izotermické koncentračné závislosti.
1. zmiešavacej entalpie sústavy $\Delta H_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$ (*krivka 1*),
2. súčinu — $T\, \Delta S_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$ (*krivka 2*),
3. Gibbsovej energie sústavy $\Delta G_{\mathrm{mix,1}}(x, T_{\mathrm{m}})$ (*krivka 3*);
$T_{\mathrm{m}} = 1773$ K, *o — experimentálne body.*

Obr. 5. Izotermické koncentračné závislosti:
1. zmiešavacej entalpie sústavy $\Delta H_{\mathrm{mix,\,l}}(x,\ T_{\mathrm{m}})$ *(krivka 1),*
2. súčinu — $T\ \Delta S_{\mathrm{mix,\,l}}(x,\ T_{\mathrm{m}})$ *(krivka 2),*
3. Gibbsovej energie sústavy $\Delta G_{\mathrm{mix,\,l}}(x,\ T_{\mathrm{m}})$ *(krivka 3);*
$T_{\mathrm{m}} = 1823$ K, *o — experimentálne body.*

Obr. 6. Izotermické koncentračné závislosti dodatkovej Gibbsovej energie $\Delta G^{\mathrm{E}}_{\mathrm{mix,\,l}}(x,\ T_{\mathrm{m}})$ *v sústave (x — mólový zlomok* CMS$_2$);
—·—·— $T_{\mathrm{m}} = 1723$ K, ———— $T_{\mathrm{m}} = 1773$ K, ——— $T_{\mathrm{m}} = 1823$ K.

Obr. 7. Izotermické koncentračné závislosti aktivít zložiek:
1. $a_{\mathrm{A,\,l}}(x,\ T_{\mathrm{m}})$ *— aktivita* C$_2$MS$_2$,
2. $a_{\mathrm{B\,l}}(x,\ T_{\mathrm{m}})$ *— aktivita* CMS$_2$;
——— $T_{\mathrm{m}} = 1723$ K, ———— $T_{\mathrm{m}} = 1773$ K, —·—·— $T_{\mathrm{m}} = 1823$ K.

Obr. 8. Izotermické koncentračné závislosti aktivitných koeficientov zložiek:
1. $\gamma_{\mathrm{A,\,l}}(x,\ T_{\mathrm{m}})$ *— aktivitný koeficient* C$_2$MS$_2$,
2. $\gamma_{\mathrm{B,\,l}}(x,\ T_{\mathrm{m}})$ *— aktivitný koeficient* CMS$_2$;
——— $T_{\mathrm{m}} = 1723$ K, – – – – $T_{\mathrm{m}} = 1773$ K, –.–.– $T_{\mathrm{m}} = 1823$ K.

ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ СИСТЕМЫ
2 CaO . MgO . 2 SiO$_2$ — CaO . MgO . 2 SiO$_2$

II. Изобарический анализ энергии Гиббса

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Целью предлагаемой работы являются расчеты энтропии смешивания, энергии Гиббса, активностей и активных коэффициентов компонентов в области расплава системы акерманит (2 CaO . MgO . 2 SiO$_2$) — диопсид (CaO . MgO . 2 SiO$_2$). Приводимые расчеты основываются:
1. на применении экспериментальных величин энтальпии смешивания в системе в температурном интервале 1700—1873 K [1], 2. на применении диаграммы фаз эвтектического типа с областью существующих твердых растворов с органиченной растворимостью компонентов относительно высоких концентраций CMS$_2$ [2].

Энтропию смешивания $\Delta S_{\mathrm{mix,l}}(x,\ T_{\mathrm{m}})$ установили методом, основывающимся на математическом описании равновесия между фазами, присутствующими в исследуемой системе [3]. Для пределов концентрации $x \leqq x_{\mathrm{eut}}$, в которых расплав сосуществует с почти чистым кристаллическим акерманитом можно выводить на основании равенства химических потенциалов C$_2$MS$_2$ для парциальной молярной энтропии смешивания C$_2$MS$_2$ отношение:

$$\Delta S_{\mathrm{mix,\,A,\,l}}(x,\ T_{\mathrm{m}}) = \frac{\bar{H}_{\mathrm{A,\,l}}\,(x,\ T_{\mathrm{eq}}) - H_{\mathrm{A,\,s}}\,(0,\ T_{\mathrm{eq}})}{T_{\mathrm{eq}}(x,\ 0)} + \int_{T_{\mathrm{eq}}(x,\,0)}^{T_{\mathrm{m}}} \frac{\bar{C}_{\mathrm{A,\,l}}(x,\ T)}{T}\,\mathrm{d}T -$$

$$- \int_{T_{\mathrm{eq}}(x,\,0)}^{T_{\mathrm{eq}}(0,\,0)} \frac{C_{\mathrm{A,\,s}}(0,\ T)}{T}\,\mathrm{d}T - \frac{\Delta H_{\mathrm{fus,\,A}}(0, T_{\mathrm{eq}})}{T_{\mathrm{eq}}(0,\ 0)} - \int_{T_{\mathrm{eq}}(0,\,0)}^{T_{\mathrm{m}}} \frac{C_{\mathrm{A,\,l}}(0,\ T)}{T'}\,\mathrm{d}T \qquad (1)$$

Подобное отношение действует для парциальной молярной энтропии смешивания CMS$_2$ в расплаве в пределах концентрации $x \geqq x_{\mathrm{eut}}$:

$$\Delta S_{\mathrm{mix,\,B,\,l}}(x,\ T_{\mathrm{m}}) = \frac{\bar{H}_{\mathrm{B,\,l}}(x.\ T_{\mathrm{eq}}(x,\ y) - H_{\mathrm{B,\,s}}(1 T_{\mathrm{eq}}(x,\ y))}{T_{\mathrm{eq}}(x,\ y)} + \int_{T_{\mathrm{eq}}(x,y)}^{T_{\mathrm{m}}} \frac{\bar{C}_{\mathrm{B,\,l}}(x,\ T))}{T}\,\mathrm{d}T -$$

$$- \int_{T_{\mathrm{eq}}(x,\,y)}^{T_{\mathrm{eq}}(1,1)} \frac{C_{\mathrm{B,\,s}}(1,\ T)}{T}\,\mathrm{d}T - \frac{\Delta H_{\mathrm{fus,\,B}}(T_{\mathrm{eq}}(1,\ 1)}{T_{\mathrm{eq}}(1,\ 1)} - \int_{T_{\mathrm{eq}}(1,\,1)}^{T_{\mathrm{m}}} \frac{C_{\mathrm{B,\,l}}(1,\ T)}{T}\,\mathrm{d}T - R \ln y(x,\ T_{\mathrm{eq}}(x,\ y)). \qquad (2)$$

Величины H_{rel} или $\bar{H}_{rel}$ в уравнениях (1) и (2) взяты из работы [1], величины энтальпий плавления чистых компонентов и зависимостей теплоемкостей отдельных фаз чистых компонентов из работ [4] и [5].

Парциальные молярные энтропии смешивания CMS_2 для $x \leqq x_{eut}$ и C_2MS_2 в концентрационной области $x \geqq x_{eut}$ расчитали из интегрированных уравнений Гиббса—Дюэма.

Расчитанные зависимости энтропии смешивания ΔS_{mix} и добавочной энтропии ΔS^E_{mix} от концентрации являются несимметричными и для состава растворов с преобладающим C_2MS_2 получают положительные величины, в то время как для состава растворов с преобладающим CMS_2 — отрицательные величины.

Добавочная энегрия Гиббса ΔS_{mix} для всех x положительна и имеет умеренно симметричный ход с максимумом при $x = 0{,}6$. Коэффициенты активности обоих компонентов больше 1, за исключением чистых компонентов.

Асимметричный и умеренно зависимый от температуры ход всех добавочных величин вероятно вызывается значительным различием между структурами основных частиц компонентов и структурными изменениями при смешивании.

Рис. 1. Диаграмма фаз системы C_2MS_2 — CMS_2.

Рис. 2. Изотермические зависимости концентрации произведения $-T\ \Delta S_{mix.1}(x, T_m)$ (x — *молярная доля* CMS_2); ——————— $T_m = 1723$ K, — — — — — — $T_m = 1773$ K, -.-.-.-.-.-. $T_m = 1823$ K.

Рис. 3. Изотермические зависимости концентрации: 1. энтальпии смешивания системы $\Delta H_{mix.1}(x, T_m)$ (*кривая 1*), *2. произведения* $-T\ \Delta S_{mix.1}(x, T_m)$ (*кривая 2*), *3. энергии Гиббса системы* $\Delta G_{mix.1}(x, T_m)$ (*кривая 3*); $T_m = 1723$ *K*, *o — экспериментальные точки.*

Рис. 4. Изотермические зависимости концентрации: 1. энтальпии смешивания системы $\Delta H_{mix.1}(x, T_m)$ (*кривая 1*), *2. произведения* $-T\ \Delta S_{mix.1}(x, T_m)$ (*кривая 2*), *3. энергии Гиббса системы* $\Delta G_{mix.1}(x, T_m)$ (*кривая 3*) $T_m = 1773$ *K*; *o — экспериментальные точки.*

Рис. 5. Изотермiческие зависимости концентрации: 1. энтальпии смешивания системы $\Delta H_{mix.1}(x, T_m)$ (*кривая 1*), *2. произведения* — $T\ \Delta S_{mix.1}(x, T_m)$ (*кривая 2*), *3. энергии Гиббса системы* $\Delta G_{mix.1}(x, T_m)$ (*кривая 3*); $T_m = 1823$ *K*, *o — экспериментальные точки.*

Рис. 6. Изотермические зависимости концентрации добавочной энергии Гиббса $\Delta G^E{}_{mix.1}(x, T_m)$ *в системе* (x — *молярная доля* CMS_2), -.-.-.-.-.-. $T_m = 1723$ *K*, — — — — — — $T_m = 1773$ *K*, ——————— $T_m = 1823$ *K*.

Рис. 7. Изотермические зависимости активностей компонентов; 1. $a_{A,1}$ (x, T_m) — *активность* C_2MS_2, *2.* $a_{B,1}$ (x, T_m) — *активность* CMS_2; ——————— $T_m = 1723$ K, - - - - - - $T_m = 1773$ K, -.-.-.- $T_m = 1823$ K.

Рис. 8. Изотермические зависимости концентраци активных коэффициентов компонентов; 1. $\gamma_{A,1}$ (x, T_m) — *активный коеффициент* C_2MS_2, *2.* $\gamma_{B,1}$ (x, T_m) — *активный коеффициент* CMS_2; ——————— $T_m = 1723$ K, - - - - - - $T_m = 1773$ K, -.-.-.- $T_m = 1823$ K.