

Původní práce

THERMODYNAMIC ANALYSIS OF THE SYSTEM 2 CaO . MgO . 2 SiO₂—CaO . MgO . 2 SiO₂

I. Enthalpic Analysis of the System

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Mixing enthalpy $\Delta H_{\text{mix},i}(x, T)$ of the melts in the system 2 CaO . MgO . 2 SiO₂—CaO . MgO . 2 SiO₂ and the temperature dependence of enthalpy of the pure components were determined within the temperature range of approx. 1 700—1 873 K. Use was made of the double calorimetry method by which the values of relative enthalpy $H_{\text{rel},i}(x_m, T_m)$ in the system are determined from the sum of increases in enthalpy measured in the course of cooling in the drop calorimeter (ΔH_{cool}) as well as during dissolving in a calorimeter for the measurement of dissolution heat (ΔH_{sol}). The states of solutions in a mixture of concentrated hydrofluoric and nitric acids (2 : 1) at temperature $T_{\text{bas}} = 298$ K were chosen as the reference state. The values measured were used for plotting the relationship of $H_{\text{rel},i}(x, T)$ for temperatures $T_m = 1\,723, 1\,773$ and $1\,823$ K; the $H_{\text{rel},i}(x, T)$ was described mathematically by an exponential function.

INTRODUCTION

The present paper is concerned with an isobaric thermodynamic analysis of the system 2 CaO . MgO . 2 SiO₂—CaO . MgO . 2 SiO₂ carried out on the basis of determining the mixing enthalpies of the melts, the melting enthalpies of the pure components, and by means of equilibrium values found in the phase diagram of the system [1].

The crystalline phases of the components comprising the given system belong to the following two structurally different types of silicate compounds: Diopside CaMg(SiO₃)₂ is a metasilicate from the group of monoclinic pyroxenes. The structure of diopside contains continuous broken chains of metasilicate tetrahedra [SiO₃]_n²⁻ linked together by their apexes. The free oxygen ions in each tetrahedron constitute a bond with calcium and magnesium cations [2]. Melting brings about destruction of the linearly linked anions and formation of [SiO₃]_n²⁻ closed chains.

The crystals of akermanite Ca₂MgSi₂O₇ exhibit a tetragonal symmetry. The structure is based on broken chains of [Si₂O₇]⁶⁻ groups, [MgO₄]⁶⁻ tetrahedra and calcium ions co-ordinated by eight oxygen atoms. Akermanite melts likewise consist for the most part of [Si₂O₇]⁶⁻ anions [3].

The thermodynamic study of the given system had the aim to determine the relationships between the entire complex of thermodynamic quantities and the composition and temperature of the system. Knowledge of these relationships allows to characterize the thermodynamic properties of the system

as well as to form a certain idea of the structure of the melts and of the mechanism of their formation.

In the present paper the authors present a description of the isobaric enthalpic analysis of the system in question. The calculation of entropy and that of the Gibbs energy of the melts will be dealt with in a separate paper.

The principle of isobaric enthalpic analysis

Direct measurements of the changes in enthalpy taking place in the course of physico-chemical processes in some silicate systems are intrinsically inaccurate for the following two main reasons:

- a) The processes in question are frequently very slow.
- b) The thermal losses due to dissipation into the calorimeter environment taking place during high-temperature processes in silicate systems are difficult to calculate of compensate.

However, an enthalpic balance of significant processes in all systems can be evaluated by means of the equation

$$\psi(H, \text{composition}, T) = 0. \quad (1)$$

For this reason the aim of a complete enthalpic analysis is ascribing an unambiguous assignment of the enthalpy values (measured or calculated ones) to the individual figurative points in the phase diagram of the system in question, i.e. determination of the function of ψ . As the absolute value of internal energy cannot be determined, the ψ is established merely for the increase in enthalpy from the basic value corresponding to a certain reference state of the system. This is for instance the enthalpy value of the elementary particles the combination of which yields the respective system at 298 K. When designating the increase in enthalpy due to combination of the building blocks into the given system $\Delta H_f(T_{\text{bas}} = 298 \text{ K})$, the absolute enthalpy value of the system at an experimental temperature T_m is given by the equation

$$H_{\text{abs}}(T_m) = \sum \nu_i H_i(T_{\text{bas}}) + \Delta H_f(T_{\text{bas}}) + \int_{T_{\text{bas}}}^{T_m} C_{\text{syst}}(T) dT \quad (2)$$

where $H_i(T_{\text{bas}})$ are absolute enthalpies of particles constituting the system in its reference state;

ν_i are the stoichiometric coefficients in the equation according to which the system in question is formed from the elementary particles;

$C_{\text{syst}}(T)$ is the isobaric molar heat of the system.

In the present study the enthalpic balance is related to the heating up of the system and to the general reaction taking place in the system. In both cases the initial and the final states of the system comprise the same number of elementary particles so that the first term on the right-hand side of equation (2) is always cancelled in the respective relations. When calculating the changes in enthalpy in the two types of processes one can thus operate with the relative enthalpy value $H_{\text{rel}}(T_m)$,

$$H_{\text{rel}}(T_m) = H_f(T_{\text{bas}}) + \int_{T_{\text{bas}}}^{T_m} C_{\text{syst}}(T) dT. \quad (3)$$

The state of the subsystems in solution in a 2 : 1 mixture of concentrated hydrofluoric and nitric acids at $T_{\text{bas}} = 298 \text{ K}$ was chosen as the basic state. Relative enthalpy $H_{\text{rel}}(T_m)$ was measured by the indirect method of double calorimetry. This procedure permits to determine $H_{\text{rel}}(T_m)$ from a sum of increases in enthalpy measured in the course of cooling the system down in a drop calorimeter (ΔH_{cool}), as well as during its dissolving in a calorimeter for dissolution heat measurements (ΔH_{sol}). Equation (3) can thus be written in the form

$$H_{\text{rel}} = -(\Delta H_{\text{cool}} + \Delta H_{\text{sol}}). \quad (4)$$

The H_{rel} values determined by double calorimetry are independent of the values of the addends on the right-hand side of equation (4), the magnitudes of which frequently vary when measuring repeatedly one and the same sample. This is so because the value of ΔH_{cool} (and thus also that of ΔH_{sol}) depends on the poorly reproducible state of the sample after this has cooled down in the drop calorimeter. With the system $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ — $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ the samples after concluded ΔH_{cool} measurement often consisted of a mixture of glass and crystalline phases including not only the system components but also the products of their decomposition (above all merwinite).

When a reaction takes place in a system, the respective reaction enthalpy is given by the following relationship when using the method being described:

$$\begin{aligned} \Delta H_r &= \sum \Delta H_{\text{cool, start}} + \sum \Delta H_{\text{sol, start}} - \sum \Delta H_{\text{cool, prod}} - \sum \Delta H_{\text{sol, prod}} = \\ &= \sum \Delta H_{\text{rel, prod}} - \sum \Delta H_{\text{rel, start}}. \end{aligned} \quad (5)$$

Utilization of the dissolution enthalpies in equation (5) is justified when the individual phases are adequately dilute in the solvent of the chosen mass. Only then it is possible to neglect, with respect to the dissolution calorimetry errors, the values of mixing enthalpies pertaining to the formation of the common solution of all the initial (final) phases, as well as the values of dilution enthalpy which results from diluting the common solution of the sum of initial phases so that the solvent mass in the solution being formed be identical with that of the common solution of all the final phases.

The results of enthalpic analysis are presented by means of isoplethic relations of $H_{\text{rel}}(x_m, T)$ and isothermic relations of $H_{\text{rel}}(x, T_m)$.

EXPERIMENTAL

Sample preparation

Samples of glasses of the pure components and mixtures in the system $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ — $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ were prepared from precursor compounds MgO , SiO_2 and CaCO_3 [SPECPURE, JMC] the weights having been corrected for water content. By slow heating of homogenized initial mixtures up to 1823 K for a period of 3 days the samples were relieved of the carbon dioxide freed by decomposition of CaCO_3 . The platinum crucible containing the sample was sealed by welding on a PtRh10 lid and heated for 4 hours at 1823 K ; then it was quenched rapidly in water. The samples obtained in this way were ground in an agate mortar to a grain size of $< 40 \mu\text{m}$. Before calorimetric measurement the samples were once more homogenized by remelting.

Samples of crystalline akermanite and diopside were prepared by the precursor method according to [4].

The calorimetric methods employed

The increases in enthalpy ΔH_{cool} between the temperature chosen and 298 K in the $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ — $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ mixtures were measured in a drop calorimeter which has been described in [5].

The weights of powdered samples in the sealed crucibles of PtRh10 were in the range of 1.0 to 1.1 g. After concluded measurement in the drop calorimeter the crucible was opened by careful cutting off the lid at the weld; the entire sample was removed from the crucible, ground and homogenized. The sample was then subjected to X-ray and IR analyses and dissolution heat measurements (in amounts of approx. 0.05 g). There were on the average 3 parallel ΔH_{sol} values determined per one ΔH_{cool} value.

THE RESULTS AND DISCUSSION

The relative enthalpies $H_{\text{rel},l}(x, T)$ of melt mixtures $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ — $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ were measured in the temperature range of approx. 1 700 to 1 873 K at temperature intervals of roughly 50 K and at concentration intervals of 10 mole % including pure components (x is the mole fraction of $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$). The experimental values were arranged into quadratic relationships of $H_{\text{rel},l}(x_m, T)$ (Fig. 1); in eight concentration cross sections including the pure components these isopleths are constructed from at least four experimental points; isopleths for $x = 0$; 5 and 0.9 are based on three, those for $x = 0.1$ on two experimental points. The calculation was based on the assumption that the temperature course of all the isopleths was similar. The temperature dependences of $H_{\text{rel},l}(0.1, T)$ of pure components are linear. The measuring results were also used for the calculation of the fusion enthalpy of akermanite at its melting temperature [6].

The values read from the graphic temperature dependences in Fig. 1 were used for plotting the graphic relations of $H_{\text{rel},l}(x, T_m)$ for the respective temperatures $T_m = 1\,723$, $1\,773$ and $1\,823$ K (rings in the diagrams in Fig. 2). The S-shaped curves obtained exhibit their inflexion point at about $x = 0.4$ and with respect to a connection line of the terminal points are characterized by a "relative maximum peak" close to composition $x = 0.2$ and by a "relative minimum peak" at approx. $x = 0.7$.

The following mathematical treatments have been chosen for the description of the $H_{\text{rel},l}(x, T_m)$ isotherms:

a) power polynomial of the 3rd degree in the form

$$y = A + Bx + Cx^2 + Dx^3, \quad (6)$$

where the coefficients A , B , C and D were linearly or quadratically dependent on temperature. However, these polynomials were not sufficiently flexible to comport with the shape of the relationships determined by measurement.

b) exponential function in the form

$$y = A + BC^x + DE^x, \quad (7)$$

where the coefficients A , B , C , D and E are generally temperature-dependent [7]. However, within the temperature range in question the changes of coefficients C and E in terms of temperature were little significant; the most suitable values of these coefficients were therefore determined by iteration. In the function chosen (8) these values were considered as independent of concentra-

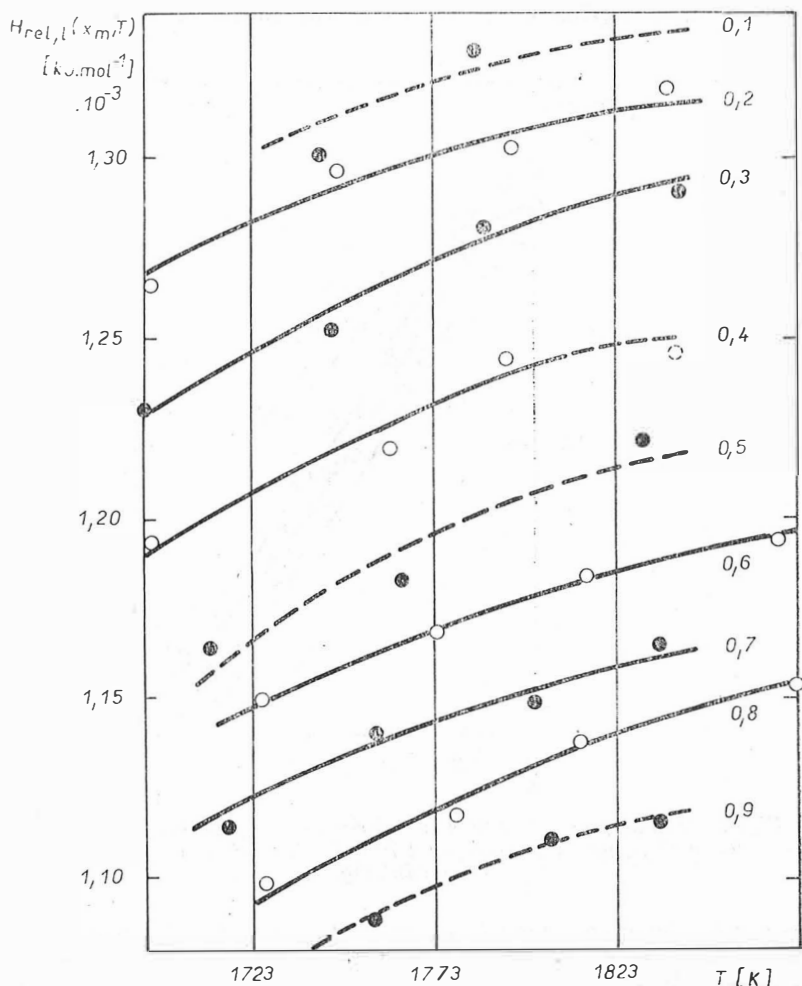


Fig. 1. Graphic plots of relative enthalpies $H_{rel,i}(x_m, T)$ vs. temperature for chosen melt concentrations x in the system $2 \text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2 - \text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2$;

- — experimental values of $H_{rel,i}(x_m, T)$ for un paired x
- — experimental values of $H_{rel,i}(x_m, T)$ for paired x .

tion and temperature. The temperature dependence of coefficients A , B and D was described by a quadratic function in the form $y = p + qT + rT^2$. The final form of the the function is as follows:

$$H_{\text{rel},l}(x, T) = \{(-3.0639 \times 10^{-1} + 1.0809 \times 10^{-3}T - 2.16 \times 10^{-7}T^2) + \\ + (-7.73083 + 9.1292 \times 10^{-3}T - 2.496 \times 10^{-6}T^2) \times \\ \times (2.3802)^x - (8.8023 + 9.9315 \times 10^{-3}T - 2.736 \times 10^{-6}T^2) \times \\ \times (1.8316 \times 10^{-2})^x\} \times 10^3 \quad [\text{kJ mole}^{-1}]. \quad (8)$$

From the values of function (8) and from 43 experimental values of $H_{\text{rel},l}(x_m, T_m)$ (rings in Fig. 1) an estimate of standard deviation was calculated ($\delta = 11.215 \text{ kJ mole}^{-1}$) [this value varies in the range of about 1.1 to 0.8 %]

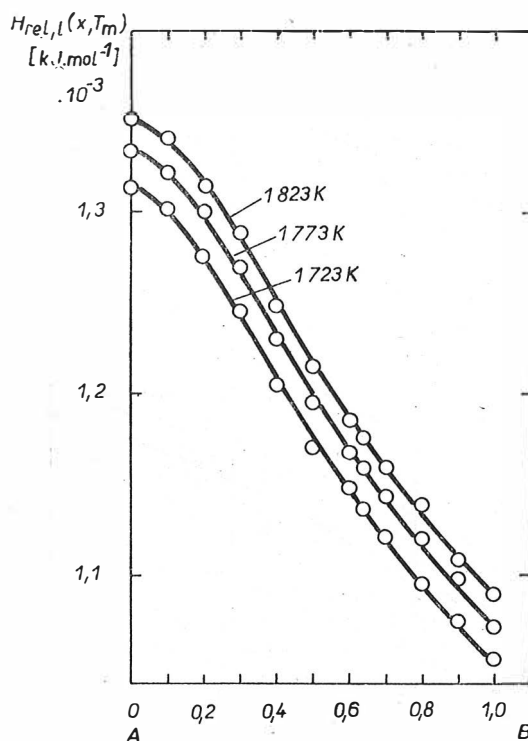


Fig. 2. Graphic plots of relative enthalpies vs. composition $H_{\text{rel},l}(x, T_m)$; $\circ$ — values of $H_{\text{rel},l}(x, T_m)$ read for 1 723 K, 1 773 K and 1 823 K from the curves in Fig. 1.

with respect to the experimental values of $H_{\text{rel},l}(x_m, T_m)$]. Isotherms obtained from the values calculated from equation (8) are plotted in full lines while the rings represent the values of $H_{\text{rel},l}(x, T_m = 1\,723, 1\,773 \text{ and } 1\,823 \text{ K})$ read for the given temperatures from the curves in Fig. 1.

The following quantities were calculated on the basis of known integral relative enthalpy $H_{\text{rel},l}(x, T_m)$ of the mixture:

1. Partial molar relative enthalpy of $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ in melt $\bar{H}_{\text{rel},A,l}(x, T_m)$ and that of $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ in melt $\bar{H}_{\text{rel},B,l}(x, T_m)$, according to the relationships

$$\bar{H}_{\text{rel},A,l}(x, T_m) = H_{\text{rel},l}(x, T_m) - x \left[\frac{\partial(H_{\text{rel},l}(x, T_m))}{\partial x} \right]_{T_m} \quad (9)$$

and

$$H_{\text{rel}, B, l}(x, T_m) = H_{\text{rel}, l}(x, T_m) + (1 - x) \left[\frac{\partial(H_{\text{rel}, l}(x, T_m))}{\partial x} \right]_{T_m} \quad (10)$$

The concentration dependences of $\bar{H}_{\text{rel}, A, l}(x, T_m)$ attain their maximum value, and the corresponding curves of $\bar{H}_{\text{rel}, B, l}(x, T_m)$ their minimum value at composition $x \doteq 0.4$ (Figs. 3 and 4).

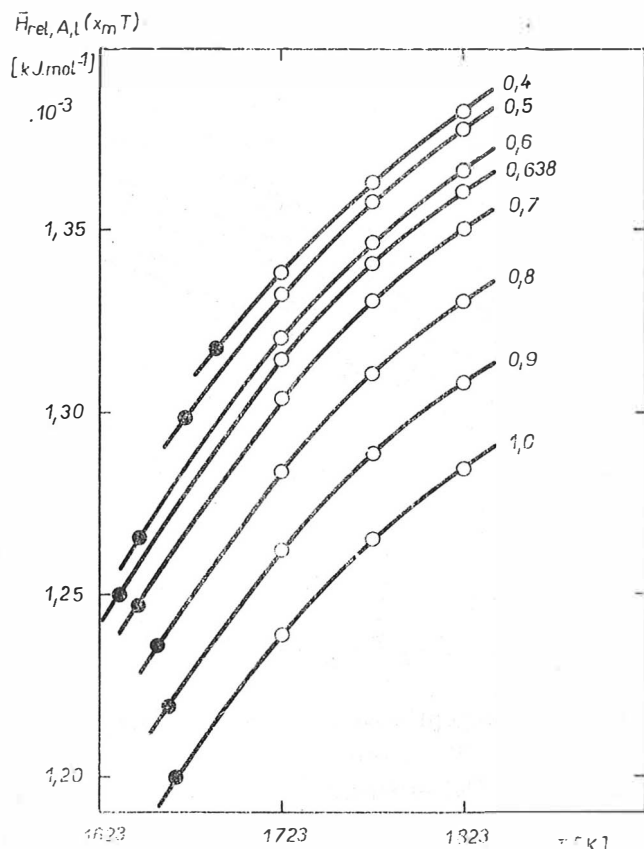


Fig. 3. Graphic plots of partial molar relative enthalpies of $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ in melt $\bar{H}_{\text{rel}, l, A}(x_m, T)$ for concentrations $x = 0.4$ to 1.0 .

The temperature dependence of partial molar enthalpy $\bar{H}_{\text{rel}, i, l}(x, T_m)$ of the melt of $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ and $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ was described by equation

$$\bar{H}_{\text{rel}, i, l}(x_m, T) = a_i + b_i T + c_i T^2. \quad (11)$$

Equation (11) was employed for calculating the values of partial molar relative enthalpies of mixtures of akermanite and diopside melts at equilibrium temperatures along the liquidus lines corresponding to composition x_m ;

knowledge of these quantities is indispensable for calculation of partial molar mixing entropies in the system.

2. From equation (11), differentiation of $\bar{H}_{\text{rel},i,l}(x_m, T)$ with respect to temperature yields partial molar heat capacities of components $\bar{C}_{A,l}(x_m, T)$ and $\bar{C}_{B,l}(x_m, T)$.

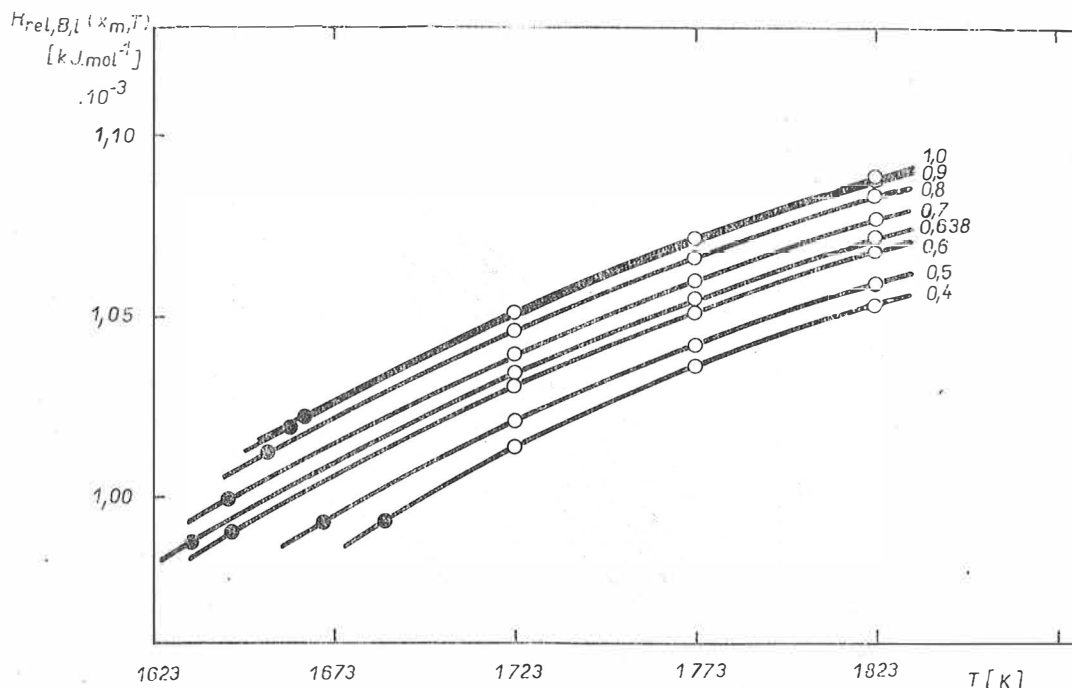


Fig. 4. Graphic plots of partial molar relative enthalpies of $\text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2$ $\bar{H}_{\text{rel},B,l}(x_m, T)$.

3. Partial molar mixing enthalpies of the two components were calculated from the respective equations

$$\Delta \bar{H}_{\text{mix},A,l}(x, T_m) = \bar{H}_{\text{rel},A,l}(x, T_m) - H_{\text{rel},A,l}(0, T_m) \quad (12)$$

and

$$\Delta \bar{H}_{\text{mix},B,l}(x, T_m) = \bar{H}_{\text{rel},B,l}(x, T_m) - H_{\text{rel},B,l}(1, T_m). \quad (13)$$

By substituting (12) and (13) into the equation

$$\Delta H_{\text{mix},l}(x, T_m) = (1 - x) \Delta \bar{H}_{\text{mix},A,l}(x, T_m) + x \Delta \bar{H}_{\text{mix},B,l}(x, T_m) \quad (14)$$

the mixing enthalpies due to formation of melt mixtures in the given system were calculated for temperatures $T_m = 1\,723$, $1\,773$ and $1\,823$ K.

At compositions with prevailing $2 \text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2$ (in the range of $x \doteq 0.1$ to 0.4) these quantities exhibit a region of positive values with a maximum from about 9.5 to $10.5 \text{ kJ mole}^{-1}$ for $x = 0.1$ ($1\,723$ K) and $x = 0.2$ ($1\,773$ K and $1\,823$ K). Within the concentration range of $x \doteq 0.4$ to 1.0 the $\Delta H_{\text{mix},l}(x, T_m)$ curves pass through a region of negative values with a minimum

from approx. -12.0 to -9.0 kJ mole $^{-1}$ at $x \doteq 0.7$ (1 723 K) and $x \doteq 0.8$ at 1 773 K and 1 823 K. Dissolution of akermanite melt in diopside melt is therefore an exothermic process, and vice versa, dissolution of diopside melt in akermanite melt is an endothermic process.

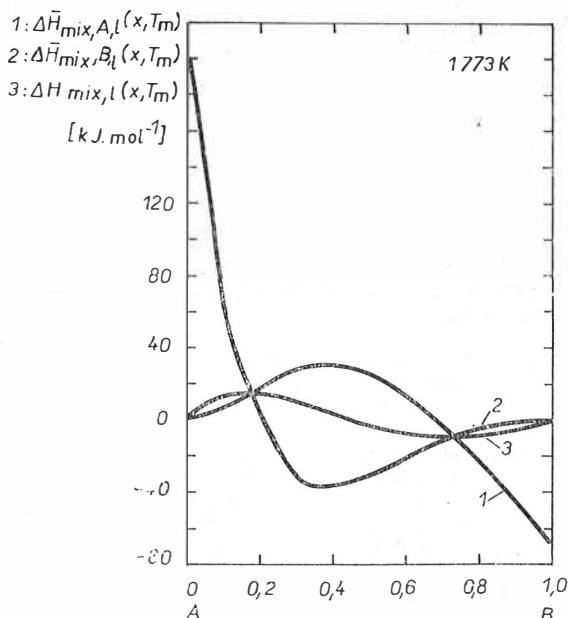


Fig. 5. Graphic plots of partial molar mixing enthalpies of the components, and mixing enthalpy vs. composition at 1 773 K;

- 1 — partial molar mixing enthalpy of $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ $\Delta \bar{H}_{\text{mix}, A, l}(x, T_m)$,
- 2 — partial molar mixing enthalpy of $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ $\Delta \bar{H}_{\text{mix}, B, l}(x, T_m)$,
- 3 — mixing enthalpy $\Delta \bar{H}_{\text{mix}, l}(x, T_m)$.

The courses of mixing enthalpy curves and those of partial molar mixing enthalpies of the components indicate to a non-ideal character of $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ and $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ solutions within the temperature interval in question. However, this non-ideality is insignificant when compared with the values of relative enthalpies of the components and their thermodynamic mixtures.

The results of mixing enthalpy measurements in the melt region of the given system can be interpreted qualitatively as follows:

At high concentrations of $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$, where the diopside melt is dissolved in the akermanite melt, the long pyroxene chains of $[\text{SiO}_3]_n^{2-}$ are split into shorter ones in the stronger field of Ca^{2+} and Mg^{2+} cations (the concentration of cations being higher in the akermanite melt than in the diopside one). This complex reaction comprises at least four simultaneous partial processes:

1. The actual splitting of the pyroxene chain.
2. Linking of the pyrosilicate, orthosilicate or oxygen anion to the "freed"

silicon atom at the end of one of the two products of splitting. The anions may be formed in the course of fusion of akermanite as a result of partial association of pyrosilicate anions.

3. Dissociation of the bond between the non-bridging oxygen of the pyrosilicate anion, and by the Ca^{2+} or the Mg^{2+} cations.

4. Formation of a bond between the non-bridging oxygen of the product of splitting and the Ca^{2+} or the Mg^{2+} cation.

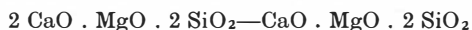
The mechanism of splitting the lattice of the original pyroxene tetrahedron chains therefore yields shorter formations in which the bonds formed by bridging oxygens are less strong than the "long" chains. The frequencies corresponding to these bonds are lower in the case of the shorter chains than in that of the longer ones [8]. Splitting up of this type is therefore an endothermic reaction.

On the other hand, when the akermanite melt is being dissolved in the diopside melt the shorter (mostly pyrosilicate) chains become associated. Stronger bonds between bridging oxygens and silicon are formed so that the total reaction is exothermic.

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TERMODYNAMICKÝ ROZBOR SÚSTAVY



I. Entalpický rozbor sústavy

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Prvá časť práce o izobarickom termodynamickom rozbere systému $2 \text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2 - \text{CaO} \cdot \text{MgO} \cdot 2 \text{SiO}_2$ obsahuje opis entalpického rozboru sledovanej sústavy. Cieľom entalpického rozboru je priradiť každému figuratívne bodu fázového diagramu sústavy v uvažovanej teplotnej oblasti a v celom koncentračnom rozmedzí hodnotu tzv. „relatívnej entalpie“ H_{rel} . Je to prírastok entalpie, počítaný od základnej hodnoty, odpovedajúcej určitému referenčnému stavu sústavy. Za referenčný stav bol zvolený stav roztoku študovaných subsystémov v zmesi koncentrovaných kyselín fluorovodíkovej a dusičnej (2 : 1) pri teplote $T_{\text{bas}} = 298 \text{ K}$. Relatívne entalpie sa merali metódou dvojakej kalorimetrie, pomocou ktorej sa ich hodnoty stanovili ako záporne vzatý súčet entalpických prírastkov, nameraných jednak pri ochladení systému vo vhadzovacom kalorimetri (ΔH_{cool}), jednak pri jeho rozpúšťaní v kalorimetri na určovanie rozpúšťacích tepiel (ΔH_{sol}) podľa rovnice

$$H_{\text{rel}} = - (\Delta H_{\text{cool}} + \Delta H_{\text{sol}}) .$$

Релятивне ентальпії $H_{\text{rel},i}(x, T)$ тавенинових змеші 2 CaO . MgO . 2 SiO₂—CaO . MgO . 2 SiO₂ са мерали в розмездзі теплôt пблїзно 1 700—1 873 К в теплотнѣх интервалах са по 50 К а в концентрачнѣх интервалах по 10 мѡл. % вратане чистѣх зложіек. З намеранѣх годнѡт $H_{\text{rel},i}(x_m, T_m)$ са зоставили теплотнѣ (кватратіекѣ) а концентрачнѣ графіекѣ зăвїсlostи. Пре математіекїй опис релятивнѣй ентальпії $H_{\text{rel},i}(x, T)$ була зволена експоненціална функція tvarу

$$H_{\text{rel},i}(x, T) = \{(-3,0639 \cdot 10^{-1} + 1,0809 \cdot 10^{-3} T - 2,16 \cdot 10^{-7} T^2) + \\ + (-7,730 \cdot 83 + 9,1292 \cdot 10^{-3} T - 2,496 \cdot 10^{-6} T^2) (2,3802)^x - \\ - (8,8023 + 9,9315 \cdot 10^{-3} T - 2,736 \cdot 10^{-6} T^2) (1,8316 \cdot 10^{-2})^x\} \cdot \\ \cdot 10^3 \quad [\text{kJ мѡл}^{-1}].$$

З годнѡт tejto функції а зо 43 експериментальних годнѡт $H_{\text{rel},i}(x_m, T_m)$ са вypoчїтал одхад снеродайнѣй одхылкы функції $\delta = 11,215 \text{ kJ.мѡл}^{-1}$.

На зăклáде знálosti інтегральной релятивнѣй ентальпії змеші $H_{\text{rel},i}(x, T_m)$ са вypoчїтали:

1. парціалне мѡлѡве релятивне ентальпії алкерманиту а діопсиду в тавеніне а парціалне мѡлѡве тепелне капáцити зложіек $\bar{C}_{A,i}(x, T)$ а $\bar{C}_{B,i}(x, T)$,

2. змїшавачіе ентальпії а парціалнѣ мѡлѡвѣ змїшавачіе ентальпії обидвох зложіек.

Годнѡты змїшавачей ентальпії а парціалнѣх мѡлѡвѣх змїшавачіе ентальпії зложіек сведіа о мїерне неїдеальном характере розтоков 2 CaO . MgO . 2 SiO₂ а CaO . MgO . 2 SiO₂ в поужитом теплотном интервале. Кладнѣ годнѡты змїшавачіе ентальпії в концентрачном розмездзі $x = 0 - 0,4$ мѡжно вьсветліт ендотерміекїм штієпенїм пьрохѡновѣх ретазцов $[\text{SiO}_3]_a^-$ на кратшіє; зăпорнѣ годнѡты змїшавачіе ентальпії є мѡжнѣ наopak вьсветліт асоціаціоу пьрокремїчановѣх ретазцов на длїшіє.

Обр. 1. Графіекѣ зăвїсlostи релятивнѣх ентальпії од теплоты $H_{\text{rel},i}(x_m, T)$ пре зволенѣй концентрації x тавеніны в сїстáве 2 CaO . MgO . 2 SiO₂—CaO . MgO . 2 SiO₂;

● — експериментальне годнѡты $H_{\text{rel},i}(x_m, T)$ пре непáрне x ,

○ — експериментальне годнѡты $H_{\text{rel},i}(x_m, T)$ пре пáрне x .

Обр. 2. Графіекѣ зăвїсlostи релятивнѣх ентальпії од зложїенія $H_{\text{rel},i}(x, T_m)$;

○ — годнѡты $H_{\text{rel},i}(x, T_m)$ одѣїтанѣ пре 1 723, 1 773 а 1 823 К з кривіек на обр. 1.

Обр. 3. Графіекѣ зăвїсlostи парціалнѣх мѡлѡвѣх релятивнѣх ентальпії 2 CaO . MgO . 2 SiO₂ в тавеніне $H_{\text{rel},i}(x_m, T)$ пре концентрації $x = 0,4 - 1,0$.

Обр. 4. Графіекѣ зăвїсlostи парціалнѣх мѡлѡвѣх релятивнѣх ентальпії CaO . MgO . 2 SiO₂ $\bar{H}_{\text{rel},B,i}(x_m, T)$.

Обр. 5. Графіекѣ зăвїсlostи парціалнѣх мѡлѡвѣх змїшавачіе ентальпії зложіек а змїшавачей ентальпії од зложїенія при теплоте 1 773 К;

1. парціална мѡлѡва змїшавачіа ентальпіа 2 CaO . MgO . 2 SiO₂

$\Delta \bar{H}_{\text{mix},A,i}(x, T_m)$,

2. парціална мѡлѡва змїшавачіа ентальпіа CaO . MgO . 2 SiO₂

$\Delta \bar{H}_{\text{mix},B,i}(x, T_m)$,

3. змїшавачіа ентальпіа $\Delta H_{\text{mix},i}(x, T_m)$.

ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ СИСТЕМЫ

2 CaO . MgO . 2 SiO₂ — CaO . MgO . 2 SiO₂

1. Энтальпический анализ системы

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В первую часть работы о изобарическом термодинамическом анализе системы 2 CaO . MgO . 2 SiO — CaO . MgO . 2 SiO₂ входит описание энтальпического анализа исследуемой системы. Целью энтальпического анализа является соотношение каждой фигуративной точки фазовой диаграммы системы в рассматриваемой температурной области и во всем диапазоне концентрации с так наз. „относительной энтальпией“ H_{rel} . Это прирост энтальпии, рассчитываемый от основной величины, соответствующей определенному состоянию системы. Как референтное состояние подбирали состояние рас-

творя исследуемых субсистем в смеси концентрированных фтористоводородной и азотной кислот (2 : 1) при температуре $T_{\text{bas}} = 298 \text{ K}$. Относительные энтальпии измеряли методом двукратной калориметрии, с помощью которой их величины устанавливали как отрицательно взятую сумму энтальпических приростов, измеряемых с одной стороны при охлаждении системы в опускающем калориметре ΔH_{cool} , с другой стороны при её растворении в калориметре для определения теплоты растворения (ΔH_{sol}) согласно уравнению

$$H_{\text{rel}} = -(\Delta H_{\text{cool}} + \Delta H_{\text{sol}}).$$

Относительные энтальпии $H_{\text{rel},i}(x, T)$ смесей расплавов $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ — $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ измеряли в пределах температуры приблизительно 1700—1873 K в температурных интервалах приблизительно по 50 K и концентрационных интервалах по 10 мол. % включая чистые компоненты. Измеренные величины $H_{\text{rel},i}(x_m, T_m)$ обрабатывали в виде температурных (квадратических) и концентрационных графических зависимостей. Для математического описания относительной энтальпии $H_{\text{rel},i}(x, T)$ подобрали показательную функцию в виде

$$H_{\text{rel},i}(x, T) = t(-3,0639 \cdot 10^{-1} + 1,0809 \cdot 10^{-3} T - 2,16 \cdot 10^{-7} T^2) + \\ + (-7,73083 + 9,1292 \cdot 10^{-3} T - 2,496 \cdot 10^{-6} T^2)(2,3802)^x - (8,8023 + 9,9315 \cdot 10^{-3} T - \\ - 2,736 \cdot 10^{-6} T^2)(1,8316 \cdot 10^{-2})^x \cdot 10^3 \text{ [кж. моль}^{-1}\text{]}$$

Из величин приводимой функции и 43 экспериментальных величин $H_{\text{rel},i}(x_m, T_m)$ выводили предполагаемое стандартное отклонение функции $\delta = 11,215 \text{ кж. моль}^{-1}$.

На основании имеющейся интегральной относительной энтальпии смеси $H_{\text{rel},i}(x, T_m)$ рассчитали:

1. парциальные молярные относительные энтальпии акерманита и диоксида в расплаве и парциальные молярные теплоемкости компонентов; $C_{A,i}(x, T)$ и $C_{\Lambda,i}(x, T)$,
2. смешивающие энтальпии и парциальные молярные смешивающие энтальпии обоих компонентов.

Величины смешивающей энтальпии и парциальных молярных смешивающих энтальпий компонентов являются свидетельством умеренно неидеального характера растворов $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ и $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ в применяемом температурном интервале. Положительные величины смешивающих энтальпий в пределах концентрации $x = 0-0,4$ можно объяснить эндотермическим расщеплением пироксеновых цепей $[\text{SiO}_3]_n^-$ на более короткие; наоборот, отрицательные величины смешивающих энтальпий объясняются ассоциацией пироксилантных цепей на более длинные.

Рис. 1. Графические зависимости относительных энтальпий от температуры $H_{\text{rel},i}(x_m, T)$ для подобранных концентраций x расплава в системе $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ — $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$;

● — экспериментальные величины $H_{\text{rel},i}(x_m, T)$ для нечетных x , ○ — экспериментальные величины $H_{\text{rel},i}(x_m, T)$ для четных x .

Рис. 2. Графические зависимости относительных энтальпий от состава $H_{\text{rel},i}(x, T_m)$; ○ — величины $H_{\text{rel},i}(x, T_m)$ вычитаемые для 1723, 1773 и 1823 K из кривых, приводимых на рис. 1.

Рис. 3. Графические зависимости парциальных молярных относительных энтальпий $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ в расплаве $H_{\text{rel},iA}(x_m, T)$ для концентраций $x = 0,4-0$.

Рис. 4. Графические зависимости парциальных молярных относительных энтальпий $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ $H_{\text{rel},iB}(x_m, T)$.

Рис. 5. Графические зависимости парциальных молярных смешивающих энтальпий компонентов и смешивающей энтальпии от состава при температуре 1773 K; 1 — парциальная молярная смешивающая энтальпия $2 \text{ CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ $\Delta \bar{H}_{\text{mix},A,i}(x, T_m)$, 2 — парциальная молярная смешивающая энтальпия $\text{CaO} \cdot \text{MgO} \cdot 2 \text{ SiO}_2$ $\Delta \bar{H}_{\text{mix},B,i}(x, T_m)$, 3 — смешивающая энтальпия $\Delta H_{\text{mix},i}(x, T_m)$.