Cryometric Analysis of the Phase Diagrams of Pseudobinary Systems of the System $CaO \cdot SiO_2$ (CS)–$2CaO \cdot Al_2O_3 \cdot SiO_2$ (C_2AS)–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2)

II. Results of the Analysis

[a]M. ELIÁŠOVÁ, [b]O. ŽIGO, and [a]I. PROKS

[a]*Institute of Inorganic Chemistry, Slovak Academy of Sciences,*
CS-842 36 Bratislava

[b]*Institute of Construction and Architecture, Slovak Academy of Sciences,*
CS-842 20 Bratislava

Received 26 November 1991

Using the cryometric analysis described in [1], we determined a mean value of the sum of number of moles of products $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{M}))_\ell$ that were formed when a unit substance amount of "formula" admixture M was dissolved in solvent N under the condition of infinitely dilute solutions L(M in N), formed out of components of the system CS—C_2AS—CAS_2. The value $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{M}))_\ell$ is independent of ions Ca^{2+} present in all investigated melts. For solutions L(CS in C_2AS or in CAS_2) the value of $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{CS}))_\ell \in \langle 0.02; 0.06\rangle$. Hence admixture CS contains polymeric ions of probable mean composition $(SiO_3)_n^{2n-}$ ($n >> 2$). For solutions L(C_2AS or CAS_2 in CS) $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{M}))_\ell \in \langle 1.1; 1.5\rangle$. When C_2AS or CAS_2 is added to the melt CS, a formal dissociation of one "formula" particle occurs and "foreign" particles are formed ($n > 1$). Approximately we can assume that both types of particle may occur in the melts C_2AS and CAS_2: *a*) polymeric ions formed out of *n* (*n* is probably a small integer — 2, 3, 4) "formula" particles C_2AS or CAS_2; *b*) ions Al^{3+} that are released from the "formula" particles at the formal polymerization reaction. For the mutual solutions C_2AS and CAS_2 it is apparent from the values $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{C_2AS}))_\ell \in \langle 0.3; 0.4\rangle$ and $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{CAS_2}))_\ell \in \langle 0.1; 0.3\rangle$ that mutually different polymeric ions of effective molar mass $M_{\mathrm{eff}} \approx (2.5—10) M_{\mathrm{form}}(\mathrm{M})$ ($M_{\mathrm{form}}(\mathrm{M})$ is the "formula" molar mass of M) occur in the melts C_2AS and CAS_2. Number of types of the polyanions in the melts C_2AS and CAS_2, respectively, can be > 1. Ions Al^{3+} occur in the melts C_2AS and CAS_2 as well.

The aim of this work is application of the cryometric method on the pseudobinary systems $2CaO \cdot Al_2O_3 \cdot SiO_2$ (C_2AS) (in crystallic phase gehlenite)—$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2) (in crystallic phase anorthite), $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot SiO_2$ (CS) (in crystallic phase wollastonite), and $CaO \cdot Al_2O_3 \cdot 2SiO_2$—$CaO \cdot SiO_2$. As it follows from theoretical analysis [1], the method is applicable in the region of infinite dilution of one component (admixture M) in the other component (solvent N), hence in the region of existence of infinitely dilute solution L(M in N). The result of cryometric analysis is a relation determining a mean value of the sum of number of moles of products $\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{M}))_\ell$ which are formed when a unit amount of molten substance M is dissolved in solvent N under the condition of infinitely dilute solution L(M in N).

If in the system M—N no solid solutions are formed, then for the relation a formula holds as follows [1]

$$\sum_i {}^1\nu(\mathrm{P}_i(\mathrm{M}))_\ell = \lim_{w_{\mathrm{eq}}(\mathrm{M})_\ell \to 0} \left(- \frac{\mathrm{d}T}{\mathrm{d}w(\mathrm{M})_\ell} \right) M(\mathrm{M}) \frac{\Delta h_{\mathrm{fus}}(\mathrm{N}, T_{\mathrm{fus,\,eq}}(\mathrm{N}))}{R(T_{\mathrm{fus,\,eq}}(\mathrm{N}))^2} \qquad (1)$$

where

$$\Delta h_{\mathrm{fus}}(\mathrm{N}, T_{\mathrm{fus,\,eq}}(\mathrm{N})) \equiv \frac{\Delta H_{\mathrm{fus}}(\mathrm{N}, T_{\mathrm{fus,\,eq}}(\mathrm{N}))}{M(\mathrm{N})}$$

is the specific enthalpy of solvent N, $M(\mathrm{X})$ is the molar mass of substance X, indices "fus" and "eq" denote the quantities which characterize melting and equilibrium state, respectively.

The Data Used

Values of the molar enthalpy of fusion $\Delta H_{\mathrm{fus}}(\mathrm{N}, T_{\mathrm{fus,eq}}(\mathrm{N}))$ of pure substances of the investigated

Table 1. Values of the Molar Enthalpy of Fusion $\Delta H_{fus}(N, T_{fus,eq}(N))$ of Pure Components of the Investigated Systems, Obtained by Various Ways

Wollastonite $CaO \cdot SiO_2$ $T_{fus,eq}(N) = (1821 \pm 2)$ K			Anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$ $T_{fus,eq}(N) = (1830 \pm 2)$ K			Gehlenite $2CaO \cdot Al_2O_3 \cdot SiO_2$ $T_{fus,eq}(N) = (1868 \pm 2)$ K		
$\Delta H_{fus,eq}(N)$ / kJ mol^{-1}	Method	Ref.	$\Delta H_{fus,eq}(N)$ / kJ mol^{-1}	Method	Ref.	$\Delta H_{fus,eq}(N)$ / kJ mol^{-1}	Method	Ref.
27.4	*c*	[2]	74.1	*e*	[8, 9]	142.3	*b*	[6]
50.2	*b*	[3]	81.0	*c*	[2, 10]	156.2	*e*	[18]
56.1	*e*	[4]	93.5	*c*	[11]	172.9 ± 6.0	*a*	[19]
57.3 ± 2.9	*a*	[5]	120.1	*b*	[3]			
59.0	*c*	[6]	122.2	*e*	[12, 13]			
62.8	*b*	[6]	123.0	*e*	[14]			
68.2	*d*	[6]	133.0 ± 4.0	*a*	[15]			
82.8	*e*	[7]	135.6 ± 8.8	*a*	[16]			
			162.3	*c*	[6]			
			167.0	*a*	[17]			
			389.5	*d*	[6]			

a) Calorimetric measurement; *b*) calculation using the course of boundary lines of phase diagram; *c*) calculation from the difference between entropies of glass and crystallic phase; *d*) calculation using the Clapeyron—Clausius equation; *e*) the way was not specified.

system are presented in Table 1. The data were obtained by various ways. The authors consider as most reliable the values corresponding to the calorimetrically measured difference of enthalpy of liquid and crystallic phases of a given substance N at the temperature of fusion $T_{fus,eq}(N)$.

The equilibrium data of pure components of the investigated system were chosen from phase diagrams [21—25] for the temperatures of fusion $T_{fus,eq}(N)$ of pure components. The data were corrected according to the International Practical Temperature Scale 1968 (IPTS-68). The data practically do not differ from the data corrected according to the IPTS-90 [34].

To evaluate $\sum_i^1 \nu(P_i(M))_\ell$, the following values were used in this work

$$\Delta H_{fus}(CS,\ 1821\ K) = (57.3 \pm 2.9)\ kJ\ mol^{-1} \quad [5]$$

$$\Delta H_{fus}(CAS_2,\ 1830\ K) = (133.0 \pm 4.0)\ kJ\ mol^{-1} \quad [15]$$

$$\Delta H_{fus}(C_2AS,\ 1868\ K) = (172.9 \pm 6.0)\ kJ\ mol^{-1} \quad [19]$$

The quantity $\lim_{w_{eq}(M)_\ell \to 0}(-dT/dw(M)_\ell)$ is a limit value of derivation of regression function which describes the liquidus curve of phase diagram of the investigated binary system M—N at the temperature of fusion $T_{fus,eq}(N)$ of the pure solvent. Equilibrium composition in the used phase diagrams is given in mass fractions $w_{eq}(X)$ of components.

Phase diagrams measured by *Rankin* and *Wright* [20], *Osborn* and *Schairer* [21], *Osborn* [22, 23] and revised Rankin's and Wright's phase diagram by *Osborn* and *Muan* [24] and by *Gentile* and *Foster* [25] were used as sources of phase diagrams for particular binary systems.

The phase diagram of $CaO—Al_2O_3—SiO_2$ was measured by *Rankin* and *Wright* in 1915 [20]. The phase equilibria of binary subsystems, studied in our work, were also measured by the above authors. These three phase diagrams were later remeasured again. In 1941 *Osborn* and *Schairer* measured the phase diagram of the system $CS—C_2AS$ (Fig.1) [21], in 1942 *Osborn* measured the phase diagram of $CS—CAS_2$ (Fig. 2) [22] and of $C_2AS—CAS_2$ (Fig. 3); the latter phase diagram was presented by *Goldsmith* in [23].

The whole ternary phase diagram of $CaO—Al_2O_3—SiO_2$ by Rankin and Wright was revised by *Osborn* and *Muan* in 1960 [24] and then by *Gentile* and *Foster* in 1963 [25].

Phase diagrams of the pseudobinary subsystems of the system $CS—C_2AS—CAS_2$ are also presented in the monograph by *Levin et al.* [26]. In the case of the system $C_2AS—CAS_2$, liquidus curve on the side of primary crystallization of component C_2AS is not consistent with the equilibrium data measured by *Rankin* and *Wright* presented in the original work [20] and cited in [26].

The temperature values that are presented in the studies of phase equilibria of the investigated subsystems are based on the following international temperature scales:

a) The temperature scale GL-12 determined in the Carnegie Institution of Washington. The scale was used in the Rankin—Wright phase diagram and in the binary diagrams by Osborn and Schairer and by Osborn alone.

b) The International Practical Temperature Scale 1948 (IPTS-48). Taking this scale into account, Osborn with Muan in 1960 and Foster with Gentile in 1963 corrected the temperature data in the phase diagram of $CaO—Al_2O_3—SiO_2$.

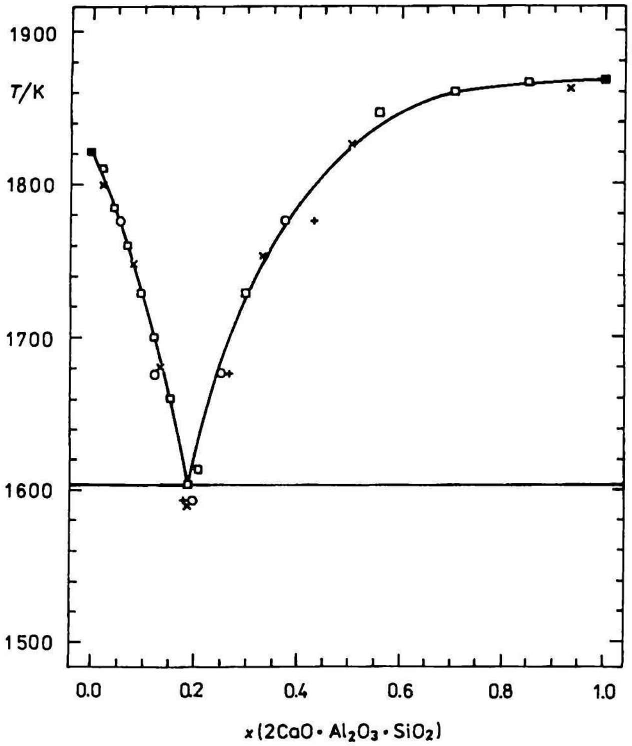

Fig. 1. Phase diagram of the system $CaO \cdot SiO_2$—$2CaO \cdot Al_2O_3 \cdot SiO_2$. Experimental data according to Ref.: x [20], □ [21], ○ [24], + [25], ■ [34].

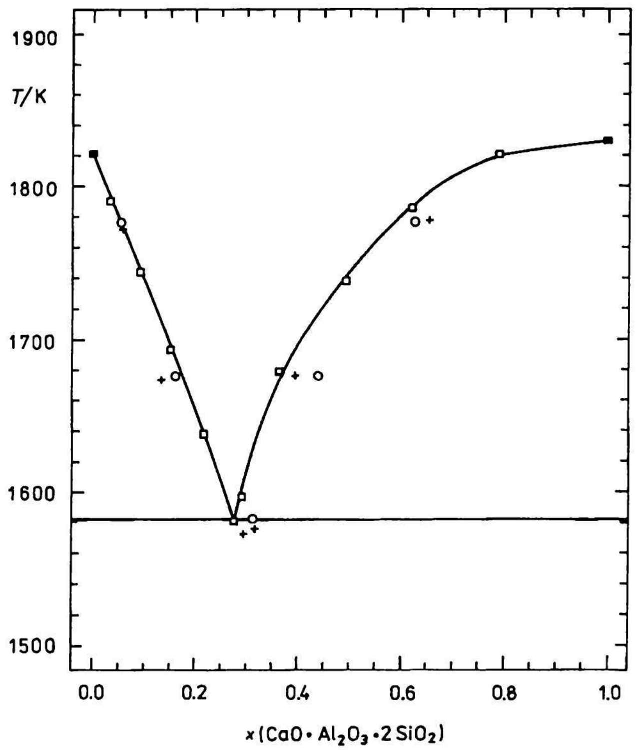

Fig. 2. Phase diagram of the system $CaO \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$. Experimental data according to Ref.: □ [22], ○ [24], + [25], ■ [34].

c) The International Practical Temperature Scale 1968 (IPTS-68). Considering the IPTS-68, the authors of this work corrected the temperature data in the binary phase diagrams by Osborn and Osborn—Schairer.

d) Scale corrections determined after 1968 are substantially less than errors of temperature measurement in the presented diagrams.

Osborn and *Schairer*'s [21] or *Osborn*'s [22, 23] measurements of phase equilibria of the studied pseudobinary subsystems contain relatively a large number of experimental data published in the form of tables or diagrams. Therefore these data were above all used in the cryometric analysis, which is the aim of this work. To optimize results, all available phase diagrams of the studied subsystems were mathematically treated.

Regression functions describing the course of liquidus curves, were found out employing two ways:

a) By the "spline functions" method that determines a curve which goes through experimental data. This is the disadvantage of the method.

b) By the least-squares method which gives a regression function in the form of a power polynomial. Such a curve does not go through experimental data. Therefore limit values of $\lim_{w_{\mathrm{eq}}(\mathrm{M})_\ell \to 0} (-\mathrm{d}T/\mathrm{d}w(\mathrm{M})_\ell)$ determined through these two methods are not consistent.

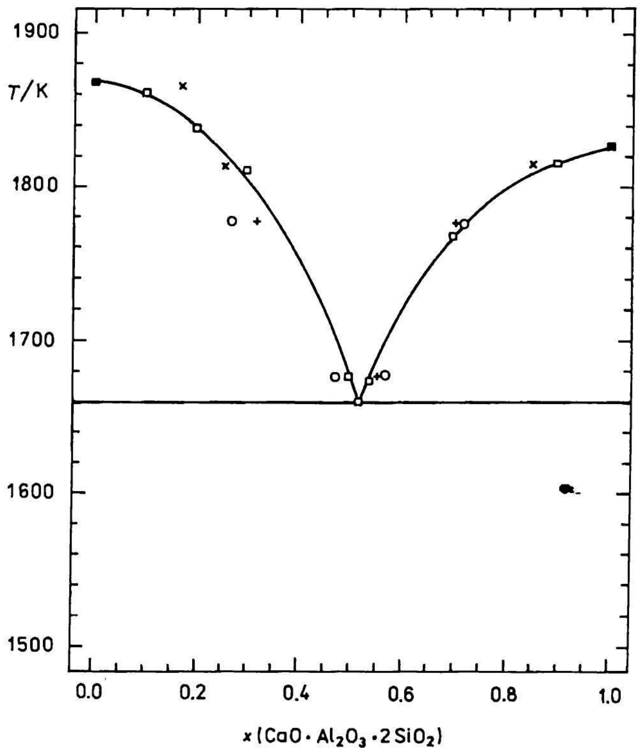

Fig. 3. Phase diagram of the system $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$. Experimental data according to Ref.: x [20], □ [23], ○ [24], + [25], ■ [34].

Table 2. Values of $\lim_{w_{eq}(M)_\ell \to 0} (-\,\mathrm{d}T/\mathrm{d}w(M)_\ell)$ and $\Sigma_i{}^1\nu(P_i(M))_\ell$ in Infinitely Dilute Solutions of L(M in N) in the Pseudobinary Subsystems of the System CaO · Al_2O_3 · $2SiO_2$—2CaO · Al_2O_3 · SiO_2—CaO · SiO_2

Solvent N	Admixture M	$\lim_{w_{eq}(M)_\ell \to 0} (-\,\mathrm{d}T/\mathrm{d}w(M)_\ell)$	$\Sigma_i{}^1\nu(P_i(M))_\ell$	Calculation	Authors of phase diagram
C_2AS	CS	− 23.8	0.06	*a*	*Osborn*
		− 13.8	0.04*	*b*	*Schairer* [21]
CS	C_2AS	− 220.8	1.10	*a*	*Osborn*
		− 308.5	1.50	*b*	*Schairer* [21]
CAS_2	CS	− 11.5	0.02	*a*	*Osborn* [22]
		− 22.3	0.05	*b*	
CS	CAS_2	− 273.4	1.40	*a*	*Osborn* [22]
		− 291.9	1.50	*b*	
CAS_2	C_2AS	− 91.2	0.44	*a*	*Osborn* [23]
		− 64.6	0.32	*b*	
C_2AS	CAS_2	− 25.5	0.13	*a*	*Osborn* [23]
		− 60.8	0.30	*c*	

a) Spline functions; *b*) 3rd deg. polynomial; *c*) 2nd deg. polynomial.

* Because of complexity of the liquidus curve, eutectic was not included in the experimental data used for calculation of the regression function (2). The values of $\lim_{w_{eq}(M)_\ell \to 0} (-\,\mathrm{d}T/\mathrm{d}w(M)_\ell)$ and $\Sigma_i{}^1\nu(P_i(M))_\ell$ are then less reliable.

Experimental data were used in the calculation of regression functions.

While Rankin and Wright presented individual equilibrium temperatures in their measurements, Osborn and Schairer carried out their measurements predominantly in 5 K intervals and presented upper and lower temperatures (in some cases only the lower ones) of melts that were quenched to form pure glass or a glass with an admixture of crystallic phase. In our work we considered mean values of the mentioned intervals as the temperatures of equilibrium. In case we did not have a value of upper limit of the interval, 3 K were added to the temperature which corresponded to the formation of crystallic phase.

A region of solid solutions of one component in the other was not found out in any of the given phase diagrams.

From the power polynomial which describes the dependence of equilibrium temperature of primary crystallization of solvent N on composition in the shape

$$T_{eq}(N) = a + bw_{eq}(M)_\ell + c(w_{eq}(M)_\ell)^2 + \\ + d(w_{eq}(M)_\ell)^3 + \dots \qquad (2)$$

we evaluated the limit value of derivation of this function at the temperature of fusion of pure component N according to the formula

$$\lim_{w_{eq}(M)_\ell \to 0} \left(-\frac{\mathrm{d}T}{\mathrm{d}w(M)_\ell} \right) = b \qquad (3)$$

From eqn (*3*) and eqn (*1*) the values of $\Sigma_i{}^1\nu(P_i(M))_\ell$ were figured out. The values are presented in Table 2.

RESULTS AND DISCUSSION

The mean value of the sum of number of moles of products $\Sigma_i{}^1\nu(P_i(M))_\ell$, which is the result of cryometric analysis based on the thermodynamic account in [1], does not provide a detailed information on the composition and structure of individual particles of products $(P_i(M))_\ell$. Indeed, these results can serve as an additional information to the knowledge about the structure of melts and glasses of silicates that are published *e.g.* in the monograph [27].

As it follows from theoretical analysis in [1], the value of $\lim_{w_{eq}(M)_\ell \to 0} (-\mathrm{d}T/\mathrm{d}w(M)_\ell)$ is influenced only by particles of admixture M in infinitely dilute solution L(M in N), structurally different from the particles of solvent N. Therefore cations Ca^{2+} present in all melts M in N of the studied binary systems have no influence on the calculated limit values $\lim_{w_{eq}(M)_\ell \to 0} (-\mathrm{d}T/\mathrm{d}w(M)_\ell)$. Since these values (Table 2) are nonzero for all types of infinitely dilute solutions L(M in N) of the investigated subsystems CS—C_2AS—CAS_2, some products formed when M is added to L(M in N) must be mutually different in all cases.

The Probable Values of $\Sigma_i{}^1\nu(P_i(M))_\ell$ in Particular Binary Subsystems of the System CS—C_2AS—CAS_2

The Systems CS—C_2AS and CS—CAS_2

For solutions L(M in N) with admixture M—C_2AS or CAS_2 and solvent N—CS it holds: $\Sigma_i{}^1\nu(P_i(M))_\ell \in \langle 1.1;\, 1.5 \rangle$.

So in the melts of pure components C_2AS and CAS_2, there must be reactions yielding larger number of products than that of particles of reactant. The particles of products differ from those present in the melt CS.

For solutions L(M in N) with M—CS and N—CAS_2 or C_2AS $\sum_i^1 \nu(P_i(M))_\ell \in \langle 0.02; 0.06\rangle$. If formation of disthetic point is excluded, as it is proved below, the low mean values of the quantity $\sum_i^1 \nu(P_i(M))_\ell$ can be explained by a predominant formation of polymeric anions $(SiO_3)_n^{2n-}$ in both types of solution. The anions may be taken as the formal polymers of "formula" particles CS. From the data in Table 2 the limit values of the degree of polymerization are $n \approx$ 17 and 50. Of course, the error of calculation of these values may be large, because determination of the quantity $\sum_i^1 \nu(P_i(M))_\ell$ requires a very precise measurement of the corresponding data for liquidus curves at low values of $-\mathrm{d}T/\mathrm{d}w(M)_\ell$.

In accordance with the considerations in [1], in a very dilute solution L(M in N) particles formed when M is added to N cannot polymerize. Hence polymeric ions $(SiO_3)_n^{2n-}$ are already present in the pure melt of CS. A similar result was found out in the systems $CaSiO_3$—$2CaO \cdot MgO \cdot SiO_2$ [28] and $CaO \cdot MgO \cdot 2SiO_2$—$2CaO \cdot MgO \cdot 2SiO_2$ [29].

The idea about a high content of polymeric anions $(SiO_3)_n^{2n-}$ in the melt CS is consistent with the data reported by Mysen *et al.* [30], according to which in the melt CS there occur predominantly $(SiO_3)_n^{2n-}$, while the content of polymeric ions $(Si_2O_5)_n^{2n-}$ and monomers $(SiO_4)^{4-}$ is significantly lower.

The System CAS_2—C_2AS

a) For infinitely dilute solutions L(C_2AS in CAS_2) it holds: $\sum_i^1 \nu(P(C_2AS))_\ell \in \langle 0.3; 0.4\rangle$,

b) for infinitely dilute solutions L(CAS_2 in C_2AS) it holds: $\sum_i^1 \nu(P(CAS_2))_\ell \in \langle 0.1; 0.3\rangle$.

In the case of *a*) the mean degree of association η is approximately in the interval $\langle 2.5; 3.3\rangle$, in the case of *b*) η is in the interval $\langle 3.3; 10\rangle$. So in the melts of pure components C_2AS or CAS_2, mutually different polymeric particles (or one mean polymeric particle) are formed out of several "formula" particles.

The value of $\sum_i^1 \nu(P_i(M))_\ell > 1$ calculated for solutions L(C_2AS in CS) and L(CAS_2 in CS) must correlate with the value of $\sum_i^1 \nu(P_i(M))_\ell \in \langle 0.1; 0.4\rangle$ for solutions L(C_2AS in CAS_2) and L(CAS_2 in C_2AS). The condition leads to a conclusion that there are particles of two types in the melts CAS_2 and C_2AS: *a*) mutually different polymeric particles, *b*) identical particles which have no influence on the value of $\sum_i^1 \nu(P_i(M))_\ell$ at formation of solutions L(C_2AS (or CAS_2) in CAS_2 (or C_2AS)), however, they are active when molten components C_2AS and CAS_2 are added to the melt CS.

From nonzero values of $\sum_i^1 \nu(P_i(M))_\ell$ for the solutions which contain as admixture C_2AS or CAS_2 it follows that in the studied binary systems the disthetic point of fusion of gehlenite and anorthite does not exist.

On the basis of the results presented we can derive for the processes in the melts of pure C_2AS or CAS_2 the following simplified reaction scheme

$$n(X)_\ell \rightleftarrows 1(\text{polymer}) + \sum_i k_i(P(X))_\ell \qquad (4)$$

$n(X)$ is the number of particles of reactant X, $k_i(P(X))_\ell$ is the number of particles of the *i*-th product $P(X)_\ell$ formed out of *n* particles of X, X is C_2AS and CAS_2, respectively.

From eqn (*4*) it follows

$$\frac{1 + \sum_i k_i(P(X))_\ell}{n(X)_\ell} = \sum_i \nu(P(X))_\ell \in \langle 1.1; 1.5\rangle$$

Initially we may take into account that n = 2 (3), $\sum_i^1 \nu(P_i(X))_\ell = 1.5$ and $i = 1$. Then $\sum_i k_i(P(X))_\ell = 2$ (3.5). The following formal model reaction schemes fulfil these conditions

$$2Ca_2Al_2SiO_7 \leftrightharpoons (Ca_4Al_2Si_2O_{14})^{6-} + 2Al^{3+} \quad (A)$$

and

$$2CaAl_2Si_2O_8 \leftrightharpoons (Ca_2Al_2Si_4O_{16})^{10-} + 2Al^{3+} \quad (B)$$

respectively

$$3Ca_2Al_2SiO_7 \leftrightharpoons (Ca_6Al_{2.5}Si_3O_{21})^{10.5-} + 3.5Al^{3+} \quad (C)$$

and

$$3CaAl_2Si_2O_8 \leftrightharpoons (Ca_3Al_{2.5}Si_6O_{24})^{10.5-} + 3.5Al^{3+} \quad (D)$$

Polymeric ions in schemes (*A*—*D*) are formal. In real situation they may be a mean of more than one particle. From radial distribution function *Scamehorn* and *Angell* [30] came to the assumption that there are Al and Si atoms with coordination number higher than 4 and Al polyhedrons with edge sharing of bridge oxygen in anorthite glass at 300 K. If the assumption is true, application of the proposed model schemes is acceptable.

Daněk [31] and *Liška* [32] used a similar model as (*A*), (*B*) calculating equations of the boundary region of the phase diagram of CaO—Al_2O_3—SiO_2 and achieved results well consistent with experimental data.

The obtained interval of values $\sum_i^1 \nu(P_i(M))_\ell \in \langle 1.1; 1.5\rangle$ for solutions L(C_2AS or CAS_2 in CS) allows us to design a set of reaction schemes different from (*A*—*D*). All these schemes, however, are based on the assumption of low-polymerized structure of the melts of C_2AS and CAS_2.

There is a lot of works on correlation between the properties and structure of anorthite glass and melt. Navrotsky *et al.* [27] assume on the basis of the course of the curves of enthalpies of dissolution and of mixing, ΔH_{soln} and ΔH_{mix}, and the curves describing the dependence of molar volume *vs.* ratio $n(\text{Al})/(n(\text{Al}) + n(\text{Si}))$ on the connecting line SiO_2—$Ca_{0.5}AlO_2$ [27] that there is a high degree of arrangement and polymerization with a maximum number of Si—O—Al bindings for anorthite glass. Taylor and Brown [27] considering the similarity of X-ray radial distribution functions for crystallic anorthite and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ glass draw a conclusion that both phases probably had a very similar structure. Taking this assumption into account, the structure of glass and melt of CAS_2 is a three-dimensional net consisting of mutually bound 4-link "circles" of tetrahedrons $(Al_2Si_2O_8)^{2-}$. On the basis of the Raman spectra, *Seifert et al.* [33] came to an idea that the quenched melts of the composition from the connecting line SiO_2—$Ca_{0.5}AlO_2$ consist of three-dimensional coupled chains of 4-link "circles" of anions $(Al_2Si_2O_8)^{2-}$, 6-link "circles" of Si_6O_{12} and 6-link "circles" of anions $(Al_6O_{12})^{6-}$. According to their results cited in [28], CAS_2 glass consists of approximately 62 mole % $(Al_2Si_2O_8)^{2-}$, 35 mole % SiO_2 and 3 mole % $(AlO_2)^-$. This composition would support the idea that all atoms of Al^{III} do not contribute to the formation of SiO_4 and AlO_4 tetrahedral net. From the analysis of the dependence of viscosity of aluminosilicates on temperature in [30], it follows that the melt of an anorthite composition shows a very low viscosity when compared to the melt of SiO_2 exhibiting strictly the Arrhenius temperature dependence of viscosity. Hence the data about viscosity support the assumptions following from this work that at transition of CAS_2 glass into the state of melt, the tetrahedral net breaks up and a certain amount of Al^{3+} cations escape from the net and do not take part in netting of present polymeric anions. The same assumption on the basis of the results achieved in this work may be expressed for the melt C_2AS as well.

REFERENCES

1. Proks, I., Eliášová, M., and Žigo, O., *Chem. Papers 46*, 7 (1992).
2. Robie, R. A., Hemingway, B. S., and Fisher, J. R., *U.S. Geol. Surv. Bull. 1452,* 456 (1978).
3. Adams, L. H. and Cohen, L. H., *Am. J. Sci. 264*, 543 (1966).
4. Barin, I. and Knacke, O., *Thermochemical Properties of Inorganic Substances,* p. 921. Springer-Verlag, Berlin, 1973.
5. Adamkovičová, K., Kosa, L., and Proks, I., *Silikáty 24*, 193 (1980).
6. Bottinga, Y. and Richet, P., *Earth Planet. Sci. Lett. 40*, 382 (1978).
7. Spencer, P. J., *Natl. Phys. Lab. Rep. Chem. 21*, 36 (1973).
8. Kelley, K. K., *U.S. Bur. Mines Bull. 584*, 232 (1960).
9. De Wys, E. C., *Miner. Mag. 38*, 632 (1972).
10. Robie, R. A., Hemingway, B. S., and Wilson, W. H., *Am. Mineral. 63*, 110 (1978).
11. Stebbins, J. F., Carmichael, I. S. E., and Weill, D. E., *Am. Mineral. 68*, 717 (1983).
12. Hariya, Y. and Kennedy, G. C., *Am. J. Sci. 266*, 193 (1968).
13. Carmichael, I. S. E., Turner, F. J., and Verhoogen, J., *Igneous Petrology*, p. 739. McGraw-Hill, New York, 1975.
14. Rossini, F. D., Wagman, D. D., Ewans, W. H., Levine, S., and Jaffe, I., *U. S. Natl. Bur. Stand. Circ. 500* (1952).
15. Richet, P. and Bottinga, Y., *Earth Planet. Sci. Lett. 67*, 415 (1984).
16. Weill, D. F., Stebbins, J. F., Hon, R., and Carmichael, I. S. E., *Contrib. Mineral. Petrol. 74*, 95 (1980).
17. Ferrier, A., *C. R. Acad. Sci., Ser. C 269*, 951 (1969).
18. Scholze, H. and Kumm, K. A., *Tonind. Ztg. 93*, 360 (1969).
19. Žigo, O., Adamkovičová, K., Kosa, L., Nerád, I., and Proks, I., *Chem. Papers 41,* 171 (1987).
20. Rankin, G. A. and Wright, F. E., *Am. J. Sci. 39*, 4th Ser., 1 (1915).
21. Osborn, E. F. and Schairer, J. F., *Am. J. Sci. 239*, 715 (1941).
22. Osborn, E. F., *Am. J. Sci. 240*, 751 (1942).
23. Goldsmith, J. R., *J. Geol. 15*, 387 (1947).
24. Osborn, E. F. and Muan, A., *Phase Equilibrium Diagrams of Oxide Systems*, Plate 1. American Ceramic Society and the Edward Orton, Ir., Ceramic foundation, Columbus, Ohio, 1960.
25. Gentile, A. L. and Foster, W. R., *J. Am. Ceram. Soc. 46*, 76 (1963).
26. Levin, E. M., Robbins, C. R., and McMurdie, F., *Phase Diagrams for Ceramics* No. 1, p. 221. American Ceramic Society, Columbus, Ohio, 1969.
27. Mysen, B. O., *Structure and Properties of Silicate Melts,* Vol. *4*: *Developments in Geochemistry*. Elsevier, Amsterdam, 1988.
28. Eliášová, M., Kosa, L., and Proks, I., *Chem. Zvesti 34*, 602 (1980).
29. Proks, I. and Eliášová, M., *Silikáty 22*, 293 (1978).
30. Scamehorn, C. A. and Angell, C. A., *Geochim. Cosmochim. Acta 55*, 721 (1991).
31. Daněk, V., *Silikáty 30*, 97 (1986).
32. Liška, M. and Daněk, V., *Silikáty 34*, 215 (1990).
33. Seifert, F., Mysen, B. O., and Virgo, D., *Am. Mineral. 67*, 696 (1982).
34. Mangum, B. W., *J. Res. Natl. Inst. Stand. Technol. 95*, 69 (1990).

Translated by P. Eliáš