Cryometric Analysis of the Phase Diagrams of Pseudobinary Systems of the System CaO · SiO$_2$ (CS)— 2 CaO · Al$_2$O$_3$ · SiO$_2$ (C$_2$AS)—CaO · Al$_2$O$_3$ · 2 SiO$_2$ (CAS$_2$)

I. Theoretical Part

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Applicability of cryometric analysis of phase diagrams of binary silicate systems (the systems having peritectic melting are not included) for determination of structure of molten silicates is discussed. The method is based on application of the Le Chatelier—Shreder equation in the region of infinite dilution of one component (admixture A) in the second component (solvent S). Knowledge of experimental values of enthalpy of fusion of pure components S and of experimentally determined courses of liquidus (and solidus) curves in a binary system is required. Result of the analysis is determination of the mean value of the sum of number of moles of all products $\Sigma_i {}^1 v(P_i(A))_i$ which are formed when 1 mol of "formula" admixture A is dissolved in an infinite amount of solvent S and an infinitely diluted solution L(A in S) is formed.

Main errors sources of this method are: error in determination of the enthalpy of fusion of S; incorrect or not sufficiently precise determination of liquidus or solidus curves in the phase diagram, which gives a wrong value of the limit $dT/d(w(A))_l$ and $dT/d(w(A))_s$ at infinite dilution; the method is unable to distinguish among the products $P_i(A)$ which a) form in the liquid and solid phases solutions having similar composition, b) are identical with the products of dissociation of solvent S.

In this paper the cryometric analysis of the phase diagram of the ternary system CaO · SiO$_2$ (CS, crystallic phase, pseudowollastonite)— 2 CaO · Al$_2$O$_3$ · SiO$_2$ (C$_2$AS, crystallic phase, gehlenite)—CaO · Al$_2$O$_3$ · 2 SiO$_2$ (CAS$_2$, crystallic phase, anorthite) was used for obtaining information about the structure of melts of given composition at the temperatures of melting of crystallic phases. Application of the cryometry assumes knowledge of enthalpies and temperatures of fusion of pure components which are considered as solvents and of data on the decrease of melting temperature of pure component (solvent S) when an infinitely small amount of investigated substance (admixture A) is added. The experimental values of enthalpies of fusion of pseudowollastonite, gehlenite, and anorthite have been recently published [1—3]. The value of the decrease of melting temperature of solvent at infinite dilution of admixture can be determined from the experimental courses of liquidus and solidus curves in all three pseudobinary subsystems of the ternary system.

In the first part of this work theoretical analysis of applicability of the cryometric method is presented. In the following considerations we assume that properties of particles S in infinitely diluted solutions of admixture A in solvent S (spec-ification of solution is L(A in S)) cannot be experimentally distinguished by common methods from the properties of the same particles in the pure solvent S (the activity coefficient γ(S, L(A in S)) $\approx$ 1). Also the mutual interaction of particles $P_i(A)$ formed in the solution from A can be neglected. Interaction of solvent S with particles $P_i(A)$ can be taken into account by choosing an appropriate standard state so that for activity coefficients it holds $\gamma(P_i(A),$ L(A in S)) $\approx$ 1.

Cryometric analysis of the phase diagram enables us to determine time and space mean values of the sum of number of moles of products P_i(A) which are formed from one "formula" mole of admixture A in L(A in S) by the reaction according to the scheme

$$1 A + {}^1v(S)\, S = \sum_i {}^1v(P_i(A))\, P_i(A) \qquad (A)$$
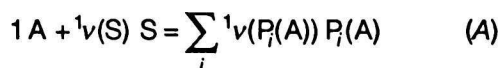
Further changes of the products P_i(A) cannot be found by the used method. The following mass balance corresponds to the equation (A)

$$1 \text{ mol } M(A) + {}^1n(S)\, M(S) =$$
$$= \sum_i {}^1n(P_i(A))\, M(P_i(A)) \qquad (1)$$

where $M(X)$ is the molar mass of component X, $^{1}v(X)$ is the stoichiometric coefficient corresponding to the unit amount of substance of "formula" particles of admixture A, $^{1}n(X)$ is the amount of substance of compound X corresponding to the unit amount of "formula" particles of admixture A. "Formula" particle means a set of basic particles (atoms, ions, molecules, etc.) in which each of basic particles exists at least once. The stoichiometric coefficient $^{1}v(X)$ equals the numerical value of the amount of substance $^{1}n(X)$

$$^{1}v(X) = \left\{ ^{1}n(X) \right\} \qquad (2)$$

From the value of $\Sigma_i\, ^{1}v(P_i(A))$ obtained by cryometric analysis of the phase diagram one cannot determine the composition and mass of the individual particles $P_i(A)$ which are formed by the reactions in infinitely diluted solution L(A in S) from one "formula" mole of admixture A. These reactions between the particles of pure melt (X ≡ A) can be of two types, viz. dissociation or nondissociation (e.g. polymerization). In the pure melt of substance X (X ≡ A) the reactants and products of dissociation are present and their contents are determined by the corresponding equilibrium constants. In infinitely diluted solution L(A in S) the equilibria of dissociation reactions are disturbed and these reactions are shifted to complete dissociation. Thus only the products of dissociation reactions are present. It means that at infinite dilution of solution L(A in S) there are not necessarily present the particles which exist in important detectable concentrations in the melt of pure admixture A.

When the nondissociation (e.g. polymerization) reactions between particles take place in the pure melt (X ≡ A) the particles of reactants and probably also of products remain in L(A in S). This complicated reaction mechanism of formation of L(A in S) results in a non-integer value of $\Sigma_i\, ^{1}v(P_i(A))$.

If $^{1}v(S)$ equals zero then the reaction according to scheme (A) will proceed without participation of solvent.

Even at the limitations discussed above the value of $\Sigma_i\, ^{1}v(P_i(A))$ obtained from cryometric measurements can be considered as an important characteristic of the system. Together with the results of direct experimental methods (diffraction and spectroscopic methods, electron microscopy, molecular dynamics calculation, etc.) cryometry contributes to the investigation of structure of melt A.

The value of $\Sigma_i\, ^{1}v(P_i(A))$ can be calculated from the general form of the Le Chatelier—Shreder equation (p = const)

$$d\ln a(S_l, T) - d\ln a(S_s, T_{eq}) =$$
$$= \frac{\Delta H_{fus}(S, T_{eq})}{R T_{eq}^2}\, dT \qquad (3)$$

$a(S_{l,s}, T_{eq})$ is the activity of solvent S in liquid and solid phase, respectively, at the equilibrium temperature T_{eq}. $\Delta H_{fus}(S, T_{eq})$ is the enthalpy of fusion of solvent S at temperature T_{eq}.

After introducing eqns (4—6) into eqn (3) it holds for an arbitrary one from both phases

$$\lim_{x(S)\to 1} d\ln a(S) = d\ln x(S) = dx(S) =$$
$$= -\sum_i dx(P_i(A)) = -\sum_i x(P_i(A)) \qquad (4)$$

$$\lim_{x(S)\to 1} \sum_i x(P_i(A)) = \sum_i \frac{\dfrac{dm(P_i(A))}{M(P_i(A))}}{\dfrac{m(S)}{M(S)}} =$$
$$= \sum_i \frac{\dfrac{dw(P_i(A))}{M(P_i(A))}}{\dfrac{1}{M(S)}} = M(S)\sum_i \frac{dw(P_i(A))}{M(P_i(A))} \qquad (5)$$

where $m(X)$ is the mass of substance X, $x(P_i(A))$ and $w(P_i(A))$ are the mole and mass fraction of product $P_i(A)$ in L(A in S), respectively. According to the reaction scheme (A) it holds

$$\frac{dm(P_i(A))}{-dm(A)} = \frac{dw(P_i(A))}{-dw(A)} =$$
$$= \frac{^{1}n(P_i(A))\, M(P_i(A))}{-1\ mol\ M(A)} =$$
$$= {^{1}v(P_i(A))}\frac{M(P_i(A))}{-M(A)} \qquad (6)$$

Then from the Le Chatelier—Shreder equation applied to infinite dilution of admixture A in both coexisting solutions of A in solvent S we obtain

$$\lim_{x(S)\to 1}\left[-\sum_i {^{1}v(P_i(A))}_l\, d(w(A))_l + \right.$$
$$\left. + \sum_i {^{1}v(P_i(A))}_s\, d(w(A))_s \right] =$$
$$= M(A)\frac{\Delta H_{fus}(S, T_{fus,\, eq}(S))}{M(S)\, R(T_{fus,\, eq}(S))^2}\, dT =$$
$$= M(A)\frac{\Delta h_{fus,\, eq}(S, T_{fus,\, eq}(S))}{R(T_{fus,\, eq}(S))^2}\, dT \qquad (7)$$

$\Delta h_{fus}(S, T_{fus, eq}(S))$ is the specific enthalpy of fusion of substance S at the equilibrium melting temperature $T_{fus}(S)$. When no solid solutions are formed in the system S—A eqn (7) gives after rearrangement the relationship

$$\sum_i {}^1 v(P_i(A))_l =$$

$$= -\frac{dT}{d(w(A))_l} M(A) \frac{\Delta h_{fus}(S, T_{fus, eq}(S))}{R(T_{fus, eq}(S))^2} \quad (8)$$

Thus it follows that for calculation of the value of $\sum_i {}^1 v(P_i(A))_l$ we need to know the quantities $T_{fus}(S)$, $\Delta h_{fus}(S, T_{fus, eq}(S))$, and $\lim_{x(S)\to 1}(dT/d(w(A))_l)$.

When solid solutions are formed in the system S—A we need to know also the value of $\lim_{x(S)\to 1}(dT/d(w(A))_s)$ and the relation between $\sum_i {}^1 v(P_i(A))_l$ and $\sum_i {}^1 v(P_i(A))_s$. The values of $\lim_{x(S)\to 1}(dT/d(w(A))_{l,s})$ equal to the limit values of derivation of the regression equation describing the course of liquidus and solidus curves in the system S—A, S being the solvent. We can write

$$(T_{eq})_l = \sum_i b_{i,l}(w_i(A))_l^{r_i} \quad (9)$$

and

$$(T_{eq})_s = \sum_i b_{i,s}(w_i(A))_s^{r_i} \quad (10)$$

The main reasons for differences between experimental and calculated value of $\sum_i {}^1 v(P_i(A))_l$ are:

1. Error in determination of the specific enthalpy of fusion of solvent S. High-temperature calorimetry yields values which can have a relative error up to 10 %. Less accurate are the enthalpies of fusion calculated from the liquidus curves of phase diagrams. Lowest reliability can be expected when the enthalpies of fusion are estimated using some empirical and semiempirical rules.

2. Incorrect or not sufficiently precise data on the solid—liquid equilibria in the phase diagram which give a wrong value of the limit $dT/d(w(A))_l$ or $dT/d(w(A))_s$.

Most of phase diagrams used in the field of silicate technologies have been measured in the first half of this century. These measurements are experimentally difficult and time-consuming because of difficulties with investigations at high temperatures and establishment of equilibria between condensed phases. These phase diagrams were rarely reinvestigated or revised (only recently some of them were reinvestigated and more precise data were obtained [1, 2]). The main difficulty is in reaching equilibrium coexistence of condensed phases because it takes a very long time before the equilibrium is achieved.

3. The value of $\sum_i {}^1 v(P_i(A))_{l,s}$ can be influenced also by a chosen regression method used for description of the liquidus or solidus curves.

4. Missing or incorrect information about formation of solid solution of A in S. Neglecting of the existence of solid solution decreases the value of $\sum_i {}^1 v(P_i(A))_l$.

When the products $P_i(A)$ formed according to scheme (A) form in liquid and solid phase solutions having similar composition, limits of the slopes of tangents to the liquidus and solidus curves in the melting point of solvent S (see eqn (3)) approach zero. Then also the change in temperature dT approaches zero. This case can occur when the difference between properties of particles A and S diminishes.

5. The value of the tangent to the liquidus curve approaches zero at the melting point of S also in the case when the molar mass of $P_i(A)$, i.e. $M(P_i(A))$, has an "experimentally infinite" high value.

6. The slope of tangent to the liquidus curve at the melting point of S is not influenced by the products $P_i(A)$ the particles of which are identical with the particles existing in the melt of substance S. When particles of all products $(P_i(A))_l$ formed according to scheme (A) are identical with products of dissociation of solvent S the melting point is called a "distectic point" For an arbitrary nonzero degree of dissociation of melt S it holds [4, 5]

$$\frac{dT}{d(x(A))_l} = 0 \quad (11)$$

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