DIFFERENTIAL ENTHALPIES OF SOLUTION OF COMPONENTS IN BINARY SYSTEMS 2 CaO . Al_2O_3 . SiO_2–CaO . Al_2O_3 . 2 SiO_2, CaO . SiO_2–CaO . Al_2O_3 . 2 SiO_2 and CaO . SiO_2–2 CaO . Al_2O_3 . SiO_2

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Differential enthalpies of solution of components in binary systems 2 CaO . Al_2O_3 . SiO_2–CaO . Al_2O_3 . 2 SiO_2, CaO . SiO_2–CaO . Al_2O_3 . 2 SiO_2 and CaO . SiO_2–2 CaO . Al_2O_3 . SiO_2 as the functions of composition and temperature were determined on the base of isothermal composition dependences of enthalpies of mixing and temperature dependences of heats of fusion of their pure components. From the values of the first differential heat of solution of CaO . Al_2O_3 . 2 SiO_2 and 2 CaO . Al_2O_3 . SiO_2 in CaO . SiO_2 over temperature range considered we can conclude that the reactions where closed chains of SiO_4 tetrahedra in CaO . SiO_2 melt break, are exothermic. On the other hand positive values of this quantity for CaO . SiO_2 in CaO . Al_2O_3 . 2 SiO_2 and 2 CaO . . Al_2O_3 . SiO_2 led us to the conclusion that the progressive breaking originally closed chains in CaO . . SiO_2 melt has endothermic character.

Gehlenite, anorthite and wollastonite are the minerals belonging to the group of aluminosilicates or silicates that are widely spread in nature and occur in many basic types of rocks. Systems that contain these minerals are important subjects of geochemical and geophysical research. They are not only the part of many technically important products, e.g., some types of ceramics and glass but also by-products of some large-scale productions, e.g., slags. Knowledge of enthalpic balance of partial processes occurring in these systems is of great importance to optimize the production or work up these products and to study geological changes.

General composition and temperature dependence of relative enthalpy in the 2 CaO . . Al_2O_3 . SiO_2 (C_2AS)–CaO . Al_2O_3 . 2 SiO_2 (CAS_2)–CaO . SiO_2 (CS) system[1] enabled to calculate the enthalpies of mixing as a function of composition and temperature $\Delta H_{mix}(x,T)$ in all three binary subsystems[2-4]. In our previous paper[1] the experimental methods of relative enthalpies determination are also described. Knowing $\Delta H_{mix}(x,T)$ in all three binary subsystems and temperature dependences of heats of fusion $\Delta H_{fus}(T)$ of CAS_2, C_2AS and CS obtained using relative enthalpies of pure component melts[1] and crystalline phases[5-9] we can determine heats of solution.

The aim of this work is to determine temperature and composition dependences of differential enthalpies of solution for components in binary systems mentioned.

THEORETICAL

Differential enthalpy of solution of crystalline components M,cr and N,cr which we denote as $\Delta H_{\mathrm{sol,diff}}(\mathrm{M,cr},x_\mathrm{N})$ and $\Delta H_{\mathrm{sol,diff}}(\mathrm{N,cr},x_\mathrm{N})$, respectively, is by definition[10] enthalpy accompanying isobaric-isothermal dissolution of 1 mole of crystalline component M or N in infinite amount of homogeneous liquid solution of both components at composition x_N. N is the component chosen to express composition of binary system studied (C_2AS–CAS_2 : N ≡ CAS_2; CS–CAS_2 : N ≡ CAS_2; CS–C_2AS : N ≡ C_2AS). The quantity defined in this manner is also equal to molar increase in enthalpy for the reaction when from crystalline components M and N arises liquid homogeneous solution, which we will call $\Delta H_{\mathrm{melt}}(x_\mathrm{N})$, by the relations

$$\Delta H_{\mathrm{sol,diff}}(\mathrm{M,cr},x_\mathrm{N}) = \left(\frac{\partial \Delta H_{\mathrm{melt}}(x_\mathrm{N})}{\partial n_\mathrm{M}}\right)_{n_\mathrm{N}} \tag{1}$$

and

$$\Delta H_{\mathrm{sol,diff}}(\mathrm{N,cr},x_\mathrm{N}) = \left(\frac{\partial \Delta H_{\mathrm{melt}}(x_\mathrm{N})}{\partial n_\mathrm{N}}\right)_{n_\mathrm{M}}, \tag{2}$$

where

$$\begin{aligned}\Delta H_{\mathrm{melt}}(x_\mathrm{N}) &= H(\mathrm{l},x_\mathrm{N}) - n_\mathrm{M}H^0_\mathrm{m}(\mathrm{M,cr}) - n_\mathrm{N}H^0_\mathrm{m}(\mathrm{N,cr}) = \\ &= n_\mathrm{M}\overline{H}(\mathrm{M,l},x_\mathrm{N}) + n_\mathrm{N}\overline{H}(\mathrm{N,l},x_\mathrm{N}) - n_\mathrm{M}H^0_\mathrm{m}(\mathrm{M,cr}) - n_\mathrm{N}H^0_\mathrm{m}(\mathrm{N,cr}) = \\ &= n_\mathrm{M}\Delta\overline{H}_{\mathrm{melt}}(\mathrm{M},x_\mathrm{N}) + n_\mathrm{N}\Delta\overline{H}_{\mathrm{melt}}(\mathrm{N},x_\mathrm{N}) .\end{aligned} \tag{3}$$

In the latest relation $H(\mathrm{l},x_\mathrm{N})$ is the enthalpy of homogeneous liquid solution at composition x_N, $H^0_\mathrm{m}(\mathrm{M,cr})$ and $H^0_\mathrm{m}(\mathrm{N,cr})$ are the molar enthalpies of pure crystalline components M and N, $\overline{H}(\mathrm{M,l},x_\mathrm{N})$ and $\overline{H}(\mathrm{N,l},x_\mathrm{N})$ are the partial molar enthalpies of components M and N in solution at composition x_N, $\Delta\overline{H}_{\mathrm{melt}}(\mathrm{M},x_\mathrm{N})$ and $\Delta\overline{H}_{\mathrm{melt}}(\mathrm{N},x_\mathrm{N})$ are partial molar enthalpies of fusion of components M and N, n_M and n_N are amounts of substance of component M and N, respectively. The right sides of Eqs (*1*) and (*2*) are thus partial molar enthalpies of fusion for components M and N. Equation (*3*) may be then expressed in the form

$$\frac{\Delta H_{\mathrm{melt}}(x_{\mathrm{N}})}{n_{\mathrm{M}} + n_{\mathrm{N}}} = \Delta H_{\mathrm{melt,m}}(x_{\mathrm{N}}) = x_{\mathrm{M}}\Delta\bar{H}_{\mathrm{melt}}(\mathrm{M},x_{\mathrm{N}}) + x_{\mathrm{N}}\Delta\bar{H}_{\mathrm{melt}}(\mathrm{N},x_{\mathrm{N}}) . \qquad (4)$$

Hence by Eq. (4) one can obtain by the method of intercepts, $\Delta H_{\mathrm{sol,diff}}(\mathrm{M,cr},x_{\mathrm{N}})$ and $\Delta H_{\mathrm{sol,diff}}(\mathrm{N,cr},x_{\mathrm{N}})$. Equation (4) can be written as

$$\Delta H_{\mathrm{melt,m}}(x_{\mathrm{N}}) = x_{\mathrm{M}}\{\bar{H}(\mathrm{M,l},x_{\mathrm{N}}) - H^0_{\mathrm{m}}(\mathrm{M,cr})\} + \\ + x_{\mathrm{N}}\{\bar{H}(\mathrm{N,l},x_{\mathrm{N}}) - H^0_{\mathrm{m}}(\mathrm{N,cr})\} . \qquad (5)$$

If we substitute into Eq. (5) from

$$H^0_{\mathrm{m}}(\mathrm{M,cr}) = H^0_{\mathrm{m}}(\mathrm{M,l}) - \Delta H^0_{\mathrm{fus,m}}(\mathrm{M}) \qquad (6)$$

and

$$H^0_{\mathrm{m}}(\mathrm{N,cr}) = H^0_{\mathrm{m}}(\mathrm{N,l}) - \Delta H^0_{\mathrm{fus,m}}(\mathrm{N}) , \qquad (7)$$

where $\Delta H^0_{\mathrm{fus,m}}(\mathrm{M})$ and $\Delta H^0_{\mathrm{fus,m}}(\mathrm{N})$ are the molar enthalpies of fusion of components M and N, $H^0_{\mathrm{m}}(\mathrm{M,l})$ and $H^0_{\mathrm{m}}(\mathrm{N,l})$ are the molar enthalpies of molten components M and N, respectively, Eq. (5) will be of the form

$$\Delta H_{\mathrm{melt,m}}(x_{\mathrm{N}}) = \Delta H_{\mathrm{mix,m}}(\mathrm{l},x_{\mathrm{N}}) + \Delta H^0_{\mathrm{fus,m}}(\mathrm{M,N},x_{\mathrm{N}}) , \qquad (8)$$

where

$$\Delta H^0_{\mathrm{fus,m}}(\mathrm{M,N},x_{\mathrm{N}}) = x_{\mathrm{M}}\Delta H^0_{\mathrm{fus,m}}(\mathrm{M}) + x_{\mathrm{N}}\Delta H^0_{\mathrm{fus,m}}(\mathrm{N}) . \qquad (9)$$

During calculations the functions $\Delta H_{\mathrm{mix,m}}(\mathrm{l},x_{\mathrm{N}})$ (refs[2 - 4]) and temperature dependences $\Delta H^0_{\mathrm{fus,m}}(\mathrm{M},T)$ and $\Delta H^0_{\mathrm{fus,m}}(\mathrm{N},T)$ obtained by above mentioned manner were substituted in Eq. (8). Enthalpies of mixing were calculated in the way used in ref.[2] and thus they are consistent with phase diagrams as well as Gibbs–Duhem equation for ΔG_{mix}.

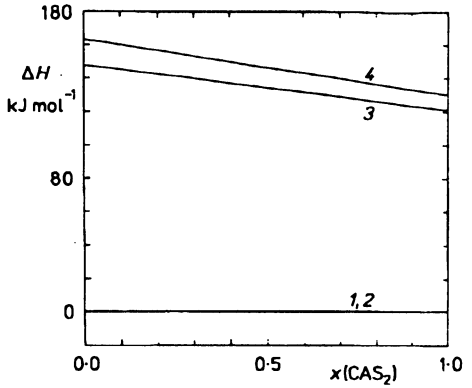

FIG. 1

Plots of $\Delta H_{mix,m}(l)$, $\Delta H^0_{fus,m}(C_2AS,CAS_2)$ and $\Delta H_{melt,m}$ versus composition in the C_2AS–CAS_2 system. *1* $\Delta H_{mix,m}(l)$, 1 700 K; *2* $\Delta H_{mix,m}(l)$, 1 800 K; *3* $\Delta H_{melt,m} \equiv \Delta H^0_{fus,m}(C_2AS,CAS_2)$, 1 700 K; *4* $\Delta H_{melt,m} \equiv \Delta H^0_{fus,m}(C_2AS,CAS_2)$, 1 800 K

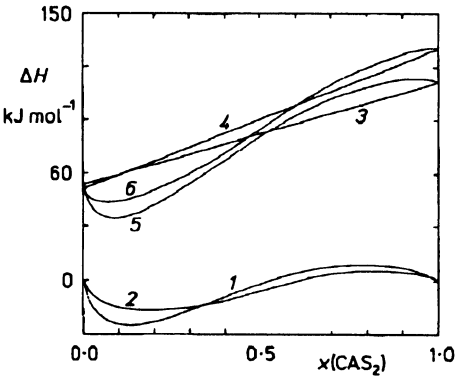

FIG. 2

Plots of $\Delta H_{mix,m}(l)$, $\Delta H^0_{fus,m}(CS,CAS_2)$ and $\Delta H_{melt,m}$ versus composition in the CS–CAS_2 system. *1* $\Delta H_{mix,m}(l)$, 1 600 K; *2* $\Delta H_{mix,m}(l)$, 1 800 K; *3* $\Delta H^0_{fus,m}(CS,CAS_2)$, 1 600 K; *4* $\Delta H^0_{fus,m}(CS,CAS_2)$, 1 800 K; *5* $\Delta H_{melt,m}$, 1 600 K; *6* $\Delta H_{melt,m}$, 1 800 K

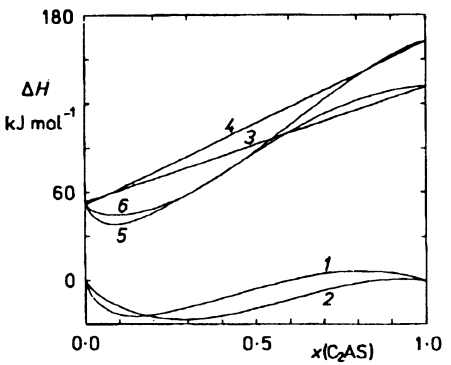

FIG. 3

Plots of $\Delta H_{mix,m}(l)$, $\Delta H^0_{fus,m}(CS,C_2AS)$ and $\Delta H_{melt,m}$ versus composition in the CS–C_2AS system. *1* $\Delta H_{mix,m}(l)$, 1 600 K; *2* $\Delta H_{mix,m}(l)$, 1 800 K; *3* $\Delta H^0_{fus,m}(CS,C_2AS)$, 1 600 K; *4* $\Delta H^0_{fus,m}(CS,C_2AS)$, 1 800 K; *5* $\Delta H_{melt,m}$, 1 600 K; *6* $\Delta H_{melt,m}$, 1 800 K

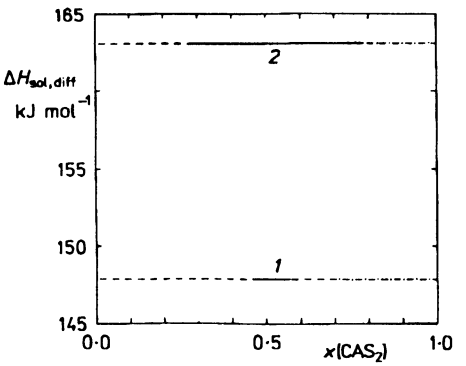

FIG. 4

Composition dependences of $\Delta H_{sol,diff}(C_2AS)$ in the C_2AS–CAS_2 system at the temperatures 1 700 K (*1*) and 1 800 K (*2*)

RESULTS AND DISCUSSION

Plots of $\Delta H_{mix,m}(l,x_N)$, $\Delta H^0_{fus,m}(M,N,x_N)$ and $\Delta H_{melt,m}(x_N)$ versus x_N in the C_2AS–CAS_2 system at the temperatures 1 700 K and 1 800 K, in the CS–CAS_2 and CS–C_2AS systems at the temperatures 1 600 K and 1 800 K are shown in Figs 1, 2 and 3.

In Figs 4 to 9 are presented isothermal plots of $\Delta H_{sol,diff}(M,cr,x_N,T_c)$ and $\Delta H_{sol,diff}(N,cr,x_N,T_c)$ calculated from Eq. (*4*) by the method of intercepts (T_c is chosen

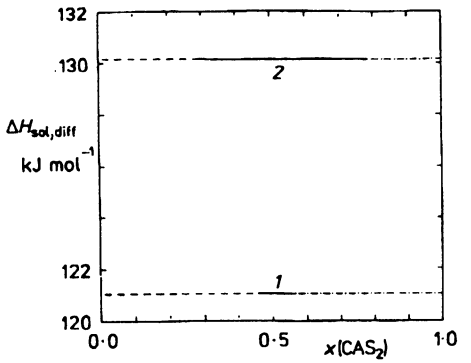

FIG. 5
Composition dependences of $\Delta H_{sol,diff}(CAS_2)$ in the C_2AS–CAS_2 system at the temperatures 1 700 K (*1*) and 1 800 K (*2*)

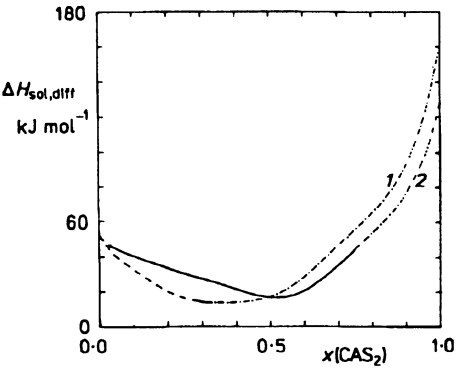

FIG. 6
Composition dependences of $\Delta H_{sol,diff}(CS)$ in the CS–CAS_2 system at the temperatures 1 600 K (*1*) and 1 800 K (*2*)

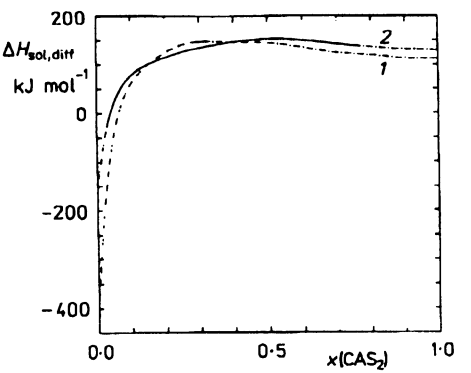

FIG. 7
Composition dependences of $\Delta H_{sol,diff}(CAS_2)$ in the CS–CAS_2 system at the temperatures 1 600 K (*1*) and 1 800 K (*2*)

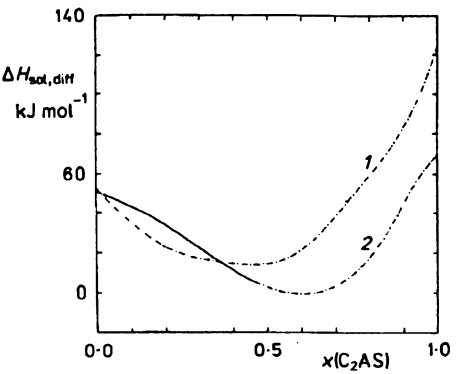

FIG. 8
Composition dependences of $\Delta H_{sol,diff}(CS)$ in the CS–C_2AS system at the temperatures 1 600 K (*1*) and 1 800 K (*2*)

temperature). Parts of curves plotted by solid line refer to stable solutions region, those plotted by dashed line refer to oversaturated solutions corresponding to component M while those plotted by dashed and dotted line go through an oversaturated solution region of component N. The value of differential enthalpy of solution of components M

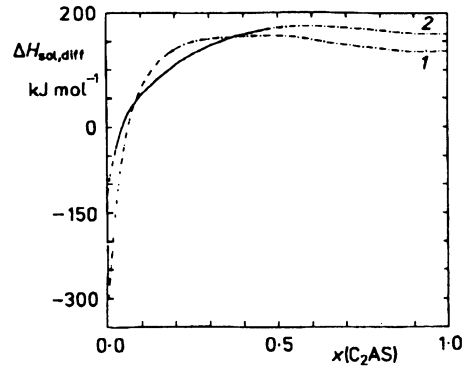

FIG. 9
Composition dependences of $\Delta H_{sol,diff}(C_2AS)$ in the CS–C_2AS system at the temperatures 1 600 K (*1*) and 1 800 K (*2*)

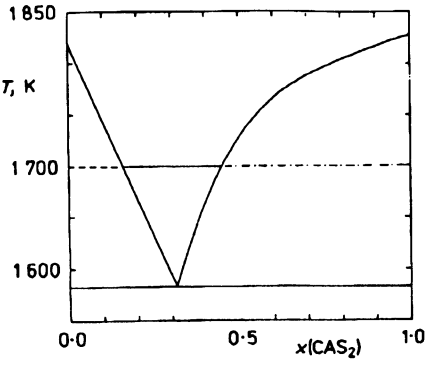

FIG. 10
The phase diagram of the CS–CAS_2 system with marked regions of oversaturated solutions of CS (dashed line), stable solutions (solid line) and oversaturated solutions of CAS_2 (dashed and dotted line) at the temperature 1 700 K

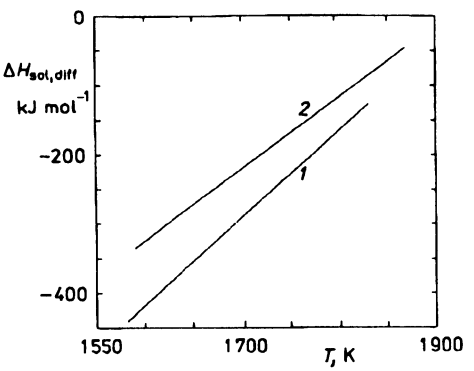

FIG. 11
Plots of $\Delta H_{sol,diff}(CAS_2,cr,x(CS) = 1)$ (*1*) and $\Delta H_{sol,diff}(C_2AS,cr,x(CS) = 1)$ (*2*) versus temperature

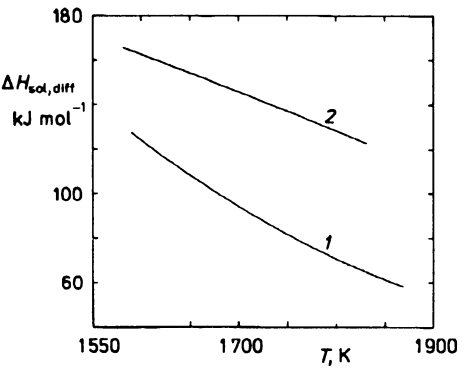

FIG. 12
Plots of $\Delta H_{sol,diff}(CS,cr,x(C_2AS) = 1)$ (*1*) and $\Delta H_{sol,diff}(CS,cr,x(CAS_2) = 1$ (*2*) versus temperature

or N at $x_N(T_c) = 0$ is the heat of fusion of M or the first differential heat of solution of N, respectively. Differential enthalpy of solution for the components M or N referred to $x_{N,eq}(l,M,cr,T_c)$ is called differential heat of solution for the component M in saturated solution of the same component, i.e., the last differential heat of solution for the component M or differential heat of solution for the component N in saturated solution of the component M, respectively. Differential enthalpy of solution for the components M or N referred to $x_{N,eq}(l,N,cr,T_c)$ is called differential heat of solution for the component M in saturated solution of the component N or differential heat of solution for the component N in saturated solution of the same component, i.e., the last differential heat of solution for the component N, respectively. Differential enthalpy of solution for the components M or N referred to $x_N(T_c) = 1$ is the first differential heat of solution for the component M or heat of fusion of the component N, respectively.

An example of composition ranges of oversaturated solutions for CS, CAS_2 and stable solutions in the CS–CAS_2 system at the temperature 1 700 K is shown in Fig. 10.

Temperature dependences of the first differential heat of solution for CAS_2 in the CS–CAS_2 system and for C_2AS in the CS–C_2AS system are shown in Fig. 11. The same dependences for CS in the CS–CAS_2 system and in the CS–C_2AS system are shown in Fig. 12.

Because the C_2AS–CAS_2 system has within the limits of our experimental errors athermic behavior[2], all three types of differential enthalpies of solution are equal to the heats of fusion of corresponding components (Figs 4 and 5). Their temperature dependences can be obtained from refs[1,5 - 7]. As we can see from Figs 6 to 9, temperature dependences of the last differential heats of solution for all components in the CS–CAS_2 and CS–C_2AS systems are inexpressive.

Composition dependences of $\Delta H_{sol,diff}$ for CS in the systems mentioned reach the minima (Figs 6 and 8). These quantities strongly decrease with increasing mole fraction of CS whereas the first differential heat of solution of this mineral has greater value than its heat of fusion in both systems.

Figures 7 and 9 illustrate than for small mole fractions of CAS_2 and C_2AS in the CS–CAS_2 and CS–C_2AS systems $\Delta H_{sol,diff}$ of CAS_2 and C_2AS are strongly dependent on composition and increase from negative to positive values close to the enthalpies of fusion of CAS_2 and C_2AS. Near middle values of mole fractions are these quantities even higher than this value.

The first differential heats of solution of CAS_2 and C_2AS in CS over the whole temperature range (Fig. 11) point out that the reactions where closed chains of SiO_4 tetrahedra in the CS melt break, are exothermic. Although the differences of the first differential heats of solution between CAS_2 and C_2AS are greater than the differences of heats of fusion between the same components at chosen temperature, similar temperature dependences of both differential heats of solution (Fig. 11) show that the configuration of both component particles is similar. Positive values of the first differential

heats of solution of CS in CAS_2 and C_2AS point out that the progressive breaking of originally closed chains in the CS melt is endothermic. Different sign of the first differential heat of solution of CAS_2 or C_2AS in CS and CS in CAS_2 or C_2AS is probably due to greater amount of energy in the closed SiO_4 chains in the melt structure of CS than in the SiO_4 chains in the melt structure of C_2AS or CAS_2.

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