Thermodynamic proof of the existence of compounds in the phase diagrams of systems without solid solutions III. The system CaF_2—AlF_3

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The thermodynamic analysis indicates that in the system CaF_2—AlF_3 the nearest neighbour of CaF_2 is the compound $3CaF_2 \cdot 2AlF_3$ the existence of which has not been experimentally confirmed yet. The published experimental data on the system CaF_2—AlF_3 do not contradict this forecast.

Используемый метод указывает на образование в системе CaF_2—AlF_3 как ближайшего соседа CaF_2 соединения $3CaF_2 \cdot 2AlF_3$. Существование последнего еще экспериментально не доказано, но опубликованные экспериментальные данные не противоречат этому выводу.

The system CaF_2—AlF_3 was studied first time by *Fedotiev* and *Ilyinskii* by the method of thermal analysis [1]. The authors write about the eutectic reaction and about a possibility of formation of chemical compound of the type $Ca_5Al_6F_{28}$. The authors also admit a possibility of formation of solid solution on the base of CaF_2. The presence of the incongruently melting compound $CaAlF_5$ has been proved first time by *Holm* [2] by means of an X-ray analysis. This result was confirmed by our investigation of the system CaF_2—AlF_3 by the method of thermal analysis which was carried out in the concentration range 40—70 mole % CaF_2 [3]. In paper [3] also the coordinates of the peritectic point have been published. Solid solutions were found neither in work [2] nor in [3].

The existence of a chemical compound in the system CaF_2—AlF_3 can be considered experimentally proved. In the present paper we shall give the thermodynamic proof of its existence. Further we shall verify if the above given composition of the compound, *viz.* $CaAlF_5$, is thermodynamically possible and if in this system another chemical compound can exist.

The method of application of the Le Chatelier—Shreder equation to the analysis of nonvariant points of the liquidus curve of pure component, as it is described in papers [4, 5], is to be modified in that respect that it is necessary to take into account the polymorphic transition β-$CaF_2 \rightarrow \alpha$-CaF_2 which takes place at temperature 1424 K. This fact influences the liquidus curve of CaF_2 and coordinates of

the eutectic point. In the analysis of the course of liquidus curve between the temperature of polymorphic transition and eutectic temperature it is not possible to neglect the temperature dependence of the change in enthalpy of fusion of the modification α-CaF_2. However, the values $\Delta H^f(\alpha\text{-}CaF_2)$ and $T^f(\alpha\text{-}CaF_2)$ have not been published yet and therefore it was necessary to estimate them on the basis of the other thermodynamic data for CaF_2 which are known.

Calculation of $\Delta H^f(\alpha\text{-}CaF_2)$ and $T^f(\alpha\text{-}CaF_2)$

The calculations are based on the following data [6]

$\Delta H^f_\beta = 29\,707$ J mol^{-1}, $T^f_\beta = 1697$ K for the modification β-CaF_2
$\Delta H^{tr} = 4\,770$ J mol^{-1}, $T^{tr} = 1424$ K for the polymorphic transition
β-$CaF_2 \rightarrow \alpha$-CaF_2
$\Delta C_p^{l/\beta}$/J mol^{-1} K^{-1} $= -7.99 - 10.46 \times 10^{-3}\ T$/K
$\Delta C_p^{l/\alpha}$/J mol^{-1} K^{-1} $= 40.17 - 30.46 \times 10^{-3}\ T$/K $- 1.97 \times 10^5\ (T/K)^{-2}$

Calculation of $\Delta H^f(\alpha\text{-}CaF_2)$ and $T^f(\alpha\text{-}CaF_2)$ is based on the equality of activities of both modifications in liquid phase at the temperature of polymorphic transition

$$a_\beta^{tr} = a_\alpha^{tr} \tag{1}$$

For the activity on liquidus curve it generally holds

$$\ln a_i = \frac{\Delta H_i^f}{R}\left(\frac{1}{T_i^f} - \frac{1}{T}\right) + f(\Delta C_{pi}^{l/s}) \tag{2}$$

When we apply eqn (2) to the thermodynamic data known for the β modification we obtain

$$\ln a_\beta^{tr} = \frac{\Delta H_\beta^f}{R} \cdot \frac{T^{tr} - T_\beta^f}{T^{tr} T_\beta^f} + \frac{\Delta a_\beta}{R}\left(\frac{T_\beta^f}{T^{tr}} - 1 - \ln \frac{T_\beta^f}{T^{tr}}\right) +$$

$$+ \frac{\Delta b_\beta}{2R}\left[\frac{(T_\beta^f)^2}{T^{tr}} - 2T_\beta^f + T^{tr}\right] \tag{2a}$$

where

$$\Delta a_\beta = -7.99 \text{ J mol}^{-1} \text{ K}^{-1}; \quad \Delta b_\beta = -10.46 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-2}$$

Solution of eqn (2a) yields the value a_β^{tr} and because of the validity of eqn (1) we have also a_α^{tr}.

For $\ln a_\alpha^{tr}$ we can write simultaneously the expression analogous to eqn (*2a*)

$$\ln a_\alpha^{tr} = \frac{\Delta H_\alpha^f}{R} \cdot \frac{T^{tr} - T_\alpha^f}{T^{tr} T_\alpha^f} + \frac{\Delta a_\alpha}{R}\left(\frac{T_\alpha^f}{T^{tr}} - 1 - \ln \frac{T_\alpha^f}{T^{tr}}\right) +$$

$$+ \frac{\Delta b_\alpha}{2R}\left[\frac{(T_\alpha^f)^2}{T^{tr}} - 2T_\alpha^f + T^{tr}\right] + \frac{\Delta c_\alpha}{2R}\left(\frac{T_\alpha^f - T^{tr}}{T_\alpha^f T^{tr}}\right)^2 \qquad (3)$$

where

$$\Delta a_\alpha = 40.17 \text{ J mol}^{-1} \text{ K}^{-1}; \quad \Delta b_\alpha = -30.46 \times 10^{-3} \text{ J mol}^{-1}$$

$$\Delta c_\alpha = -1.97 \times 10^5 \text{ J mol}^{-1} \text{ K}$$

The expression (*3*) contains two unknown quantities: ΔH_α^f and T_α^f. However, it holds also

$$\Delta H_\alpha^f = \Delta H^{l/\alpha}(T^{tr}) + \int_{T^{tr}}^{T_\alpha^f} \Delta C_p^{l/\alpha} \, dT \qquad (4)$$

Thus the simultaneous solution of eqns (*3*) and (*4*) allows to calculate both unknown quantities.

The term $\Delta H^{l/\alpha}(T^{tr})$ in eqn (*4*) can be determined easily from the relation

$$\Delta H^{l/\alpha}(T^{tr}) = \Delta H_\beta^f - \int_{T^{tr}}^{T_\beta^f} \Delta C_p^{l/\beta} \, dT + \Delta H^{tr} \qquad (5)$$

Using the above-mentioned procedure we obtained the desired values of thermodynamic quantities

$$\Delta H^f(\alpha\text{-}CaF_2) = 39\,632 \text{ J mol}^{-1}, \quad T^f(\alpha\text{-}CaF_2) = 1646 \text{ K}$$

which were applied in the further calculations instead of direct experimental data.

Thermodynamic proof of the existence of compound

At the application of the method the following coordinates of the eutectic point on the liquidus curve of α-CaF_2 were used [3]

$$T^E = 1102 \text{ K}, \quad x^E(CaF_2) = 0.625$$

(x denotes the concentration in the system CaF_2—AlF_3.)

After inserting these values into eqn (*2*) we obtain the thermodynamic activity of CaF_2 in solution which is in the eutectic point in equilibrium with the phase α-CaF_2

$$a^E(\alpha\text{-}CaF_2) = 0.228$$

The proof of the existence of chemical compound which is the nearest neighbour of CaF_2 in the system CaF_2—AlF_3 is done in the following way. We choose different systems CaF_2—$(CaF_2)_r(AlF_3)_s$ in which $(CaF_2)_r(AlF_3)_s$ is the sought compound. For each case we make transformation of the concentration coordinate according to the scheme

$$x\ CaF_2 + (1-x)\,AlF_3 \rightarrow y\ CaF_2 + (1-y)(CaF_2)_r(AlF_3)_s \qquad (6)$$

Then

$$y^E = \frac{(s+r)x - r}{(s+r-1)x - r + 1} \qquad (7)$$

It was assumed that the tested systems are close to ideality and therefore that a correct choice of concentration base minimizes the difference between y^E and $a^E(\alpha\text{-}CaF_2)$ or, in other words, that the ratio

$$D = a^E(\alpha\text{-}CaF_2)/y^E \rightarrow 1 \qquad (8)$$

Simultaneously we calculated for each system the value $\Delta H_\alpha^{t,*}$ using the relation

$$\Delta H_\alpha^{t,*} = R\,\frac{T_\alpha^t T^E}{T^E - T_\alpha^t}\ln y^E \qquad (9)$$

and we compared it with the value $\Delta H^t(\alpha\text{-}CaF_2) = 39\,632\ J\ mol^{-1}$ calculated from eqn (4).

The agreement between $\Delta H_\alpha^{t,*}$ and $\Delta H^t(\alpha\text{-}CaF_2)$ and approaching of the coefficient D to 1 was considered to be the criterion of correctness of the choice of concentration base and consequently the thermodynamic proof of the presence of the presumed compound.

From the results, which are summarized in Table 1, it follows that the best agreement was achieved for the assumption that the nearest neighbour of CaF_2 in the system CaF_2—AlF_3 is the compound $Ca_3Al_2F_{12}$.

Table 1

Calculation of $\Delta H^{t,*}(\alpha\text{-}CaF_2)$ and of the coefficient D for different systems of the type CaF_2—$(CaF_2)_r(AlF_3)_s$

System	$y^E = f(x^E)$	$\Delta H^{t,*}(\alpha\text{-}CaF_2)/J\ mol^{-1}$	D
CaF_2—AlF_3	$x = 0.625$	13 030	0.365
CaF_2—$CaF_2 \cdot AlF_3$	$(2x-1)/x = 0.400$	25 402	0.536
CaF_2—$CaF_2 \cdot 2AlF_3$	$(3x-1)/2x = 0.700$	9 888	0.329
CaF_2—$2CaF_2 \cdot 3AlF_3$	$(4x-2)/(3x-1) = 0.571$	7 976	0.309
CaF_2—$3CaF_2 \cdot 2AlF_3$	$(5x-2)/(4x-1) = 0.750$	38 433	0.921
CaF_2—$CaF_2 \cdot 3AlF_3$	$(4x-1)/3x = 0.800$	6 186	0.289

Discussion

The compound $3CaF_2 \cdot 2AlF_3$ can be regarded as an analogue of similar compounds which have been found in the systems BaF_2—AlF_3 and SrF_2—AlF_3 [7—9]. It supports the conclusion drawn on the basis of thermodynamic analysis about existence of the compound $3CaF_2 \cdot 2AlF_3$. It is to be hoped that it will be possible to prove the existence of this compound also experimentally. The published experimental results [2, 3] do not exclude this possibility because this compound can decompose incongruently and in solid state it can be stable only in a narrow temperature interval.

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