

# The equilibrium "solidus—liquidus" in the system lithium fluoride—calcium fluoride\*

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The phase diagram of the binary system LiF—CaF<sub>2</sub> was measured, the liquidus curve of LiF was determined more precisely, and the coordinates of the eutectic point E were established: 80.5 mole % LiF, 19.5 mole % CaF<sub>2</sub>; the temperature of the eutectic crystallization was found to be 769°C. The thermodynamic analysis of the liquidus curve of LiF was performed and the Dodé—Hagège relation was applied to the course of the liquidus curves of both components in the proximity of the eutectic point. For the calculation of the course of the liquidus curve of CaF<sub>2</sub> a new method was used. The phase and liquidus diagrams of the system LiF—CaF<sub>2</sub> published till now were critically discussed.

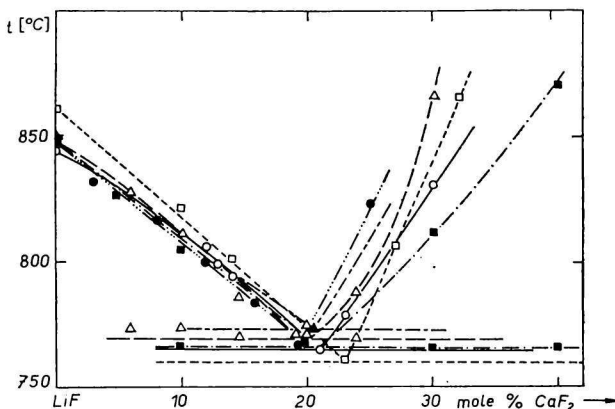


Fig. 1. Comparison of the phase diagram of LiF—CaF<sub>2</sub> as reported by different authors:  
○ [1]; ● [2]; △ [3]; ▲ [5]; □ [6]; ■ [8].

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The binary system  $\text{LiF}-\text{CaF}_2$  was experimentally studied by several authors [1–8]. According to these papers it is a simple eutectic system, in which the composition of the eutectic point is within the interval of 76.2–80.5 mole %  $\text{LiF}$  (23.8–19.5 mole %  $\text{CaF}_2$ ). The temperature of the eutectic crystallization is reported to be in the range of 760–773°C.

A more detailed study of the published diagrams of  $\text{LiF}-\text{CaF}_2$  showed that papers, in which two of the mentioned parameters are essentially in accordance, report different character of the course of the liquidus curve, particularly in the proximity of the eutectic point (Fig. 1).

The  $\text{LiF}-\text{CaF}_2$  system has not been analyzed thermodynamically so far, neither from the point of view of the course of the liquidus curves and their deviations from an ideal run, nor with respect to the criteria of the thermodynamic consistency that hold for binary systems of the simple eutectic type.

### Experimental

The methods of TA and X-ray phase analysis were applied in this investigation. The system was studied in the concentration range of 0–30 mole %  $\text{CaF}_2$  (the rest being  $\text{LiF}$ ). The temperature was measured with a Pt/Pt10Rh thermocouple and recorded with a compensating line recorder EZ 11. The thermocouple was calibrated at the melting points of  $\text{Na}_2\text{SO}_4$  (884.8°C),  $\text{NaCl}$  (800.8°C),  $\text{KCl}$  (772°C), and the eutectic temperature of the mixture  $\text{NaCl}-\text{Na}_2\text{SO}_4$  628°C. The rate of cooling was 1–2°/min, the sample weight 20 g; Pt crucibles were used. The purity of the fused salts was of “single crystals” grade. Twenty various mixtures were studied and main attention was paid to the proximity of the eutectic point. Reproducibility was  $\pm 1^\circ$ .

The results of the TA and X-ray phase analysis confirmed that this was a simple eutectic system, where solid solutions were either absent, or they did not exceed 1 mole %  $\text{CaF}_2$ .

### Theoretical

#### *A. Deviation of the liquidus from the ideal course in the $\text{LiF}-\text{CaF}_2$ system*

The activity of the  $i$ -th component of a simple eutectic system is defined by the generalized Le Chatelier–Schröder equation

$$\ln a_i = \frac{1}{R} \left( \int_T^{T^r} \Delta H_i^f - \int_T^{T^r} \Delta C_{P,i}^{l/s} dT \right) \frac{dT}{T^2}. \quad (1)$$

#### *The liquidus of $\text{LiF}$*

For calculation of the liquidus of  $\text{LiF}$  by using eqn (1) the following values were used: for the heat of fusion the value of 6.471 kcal mol<sup>-1</sup> reported by Douglas and Dever [9] was taken. Its accuracy was verified by cryometric measurements of the system  $\text{LiF}-\text{AlF}_3$  [10]. The values of the heat capacities were taken from Kelley's Tables [11].

The ideal course of the liquidus of  $\text{LiF}$  (*i.e.*  $a_i = x_i$ ) was calculated for the melting point of  $\text{LiF} = 845^\circ\text{C}$ , because this was the melting point of the used salt. The enthalpy of fusion of  $\text{LiF}$  is given for the melting temperature of 848°C (*i.e.* the melting point of the salt used by Douglas and Dever); therefore it has been corrected on the assumption that the entropy of fusion is constant

$$\Delta H_{1118}^f = \frac{\Delta H_{1121}^f}{T^f} 1118,$$

$$\Delta H_{1118}^f = 6.452 \text{ kcal mol}^{-1}.$$

With respect to the results obtained this correction may be shown to be more favourable.

The calculation of the liquidus of LiF was carried out for two cases:

a)  $\Delta H^f = \Delta H^{l/s} = \text{const},$

$$\Delta H^f = 6.452 \text{ kcal mol}^{-1}, T^f = 1118 \text{ K};$$

b)  $\Delta H^{l/s} = f(T),$

$$C_{P(s)} = 10.41 + 3.9 \times 10^{-3} T - 1.38 \times 10^5 T^{-2},$$

$$C_{P(l)} = 15.5 \text{ cal K}^{-1}.$$

The results are listed in Table 1.

Table 1

Theoretical values of the temperature of primary crystallization (TPC) of LiF

T [K]	t [°C]	(TPC) LiF	
		$\Delta H^{l/s} = \text{const}$	$\Delta H^{l/s} = f(T)$
1100	827	0.9536	0.9536
1085	812	0.9156	0.9156
1080	807		0.9031
1075	802		0.8906
1070	797	0.8779	0.8782
1060	787		0.8536
1050	777	0.8286	0.8293
1030	757		0.7815

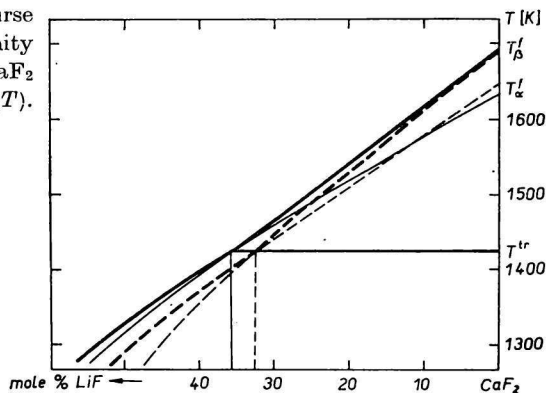
#### The liquidus of CaF<sub>2</sub>

For the heat of fusion of CaF<sub>2</sub> the value of the calorimetric study by *Naylor* [12], *i.e.* 7.1 kcal mol<sup>-1</sup> was used. This value was confirmed by high-temperature cryometric measurements by *Delbove* [13], who had found the value of 7.25 kcal mol<sup>-1</sup>. Besides, it is recommended by the *Rossini* Tables [14].

*Naylor* [12] measured the enthalpy of calcium fluoride for both the solid and the liquid phases by means of calorimetry and found that in the temperature range of 1320–1440 K the temperature coefficient of the enthalpy (heat capacity) showed a marked increase. On the basis of these measurements *Naylor* suggested the existence of two modifications of CaF<sub>2</sub>: the low-temperature  $\alpha$ -modification and the high-temperature  $\beta$ -modification. For thermodynamic calculations he chose the transition temperature of these two modifications (1424 K) and determined the change of enthalpy due to this process to be 1.14 kcal mol<sup>-1</sup>.

The supposition of the existence of two modifications of CaF<sub>2</sub> requires a special procedure for the calculation of the activities. The activities of liquid CaF<sub>2</sub> in a solution,

Fig. 2. Detail of the calculated course of the liquidus of  $\text{CaF}_2$  in the proximity of the transition temperature of  $\text{CaF}_2$  under the condition of  $\Delta H^{1/s} = f(T)$ .



coexisting with its high-temperature  $\beta$ -modification can be obtained for the temperature range of 1424–1691 K from eqn (1). To calculate the activities of  $\text{CaF}_2$  in a solution coexisting with the low-temperature  $\alpha$ -modification we have to determine a hypothetical melting point of  $\alpha$ - $\text{CaF}_2$ , as shown in Fig. 2, as well as the enthalpy of fusion at this temperature.

a) Calculation of the activities of  $\text{CaF}_2$  in a solution, when  $\Delta C_P = 0$ .

In this case the following relation holds

$$\Delta H_{\alpha}^{1/s} = \Delta H_{\beta}^{1/s} + \Delta H^{\text{tr}}. \quad (2)$$

According to Naylor [12] we obtain

$$\Delta H_{\alpha}^{1/s} = 7.1 + 1.14 = 8.24 \text{ kcal mol}^{-1}.$$

To obtain the hypothetical melting point of the  $\alpha$ -modification eqn (1) may be used at the transition temperature of 1424 K for both the modifications, since they are in equilibrium with the liquid phase

$$\frac{\Delta H_{\beta}^f}{R} \left[ \frac{1}{T_{\beta}^f} - \frac{1}{T^{\text{tr}}} \right] = \frac{\Delta H_{\alpha}^f}{R} \left[ \frac{1}{T_{\alpha}^f} - \frac{1}{T^{\text{tr}}} \right]. \quad (3)$$

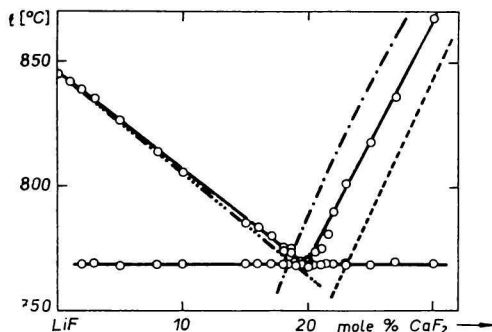


Fig. 3. The phase diagram of  $\text{LiF}-\text{CaF}_2$ .  $-\circ-\circ-$  experimental course of the liquidus;  $-\cdot-\cdot-$  calculated course of the liquidus for  $\Delta H^{1/s} = f(T)$ ;  $-----$  calculated course of the liquidus for  $\Delta H^{1/s} = \text{const.}$

The only unknown value is the hypothetical melting temperature of the  $\alpha$ -modification; calculation yields  $T_{\alpha}^f = 1648$  K. This value has to be introduced into eqn (1) to obtain the activities of the low-temperature  $\alpha$  form of  $\text{CaF}_2$  in a solution. The obtained values may be found in Table 2.

*Table 2*  
Theoretical values of the temperature of primary crystallization (TPC) of  $\text{CaF}_2$  if  $\Delta H^{1/s} = \text{const}$

$T$ [K]	$t$ [°C]	TPC	
		$\beta\text{-CaF}_2$	$\alpha\text{-CaF}_2$
1600	1327	0.887	
1500	1227	0.764	
1450	1177	0.704	
1424	1151	0.673	0.673
1400	1127		0.640
1300	1027		0.510
1200	927		0.391
1100	827		0.285
1050	777		0.239
1000	727		0.196

*b) Calculation of the activities of  $\text{CaF}_2$  in a solution, when the enthalpy of fusion is not constant.*

The activities of the high-temperature modification may be calculated from eqn (1) using the following values

*Table 3*  
Theoretical values of the temperature of primary crystallization (TPC) of  $\text{CaF}_2$  if  $\Delta H^{1/s} \neq \text{const}$

$T$ [K]	$t$ [°C]	TPC	
		$\beta\text{-CaF}_2$	$\alpha\text{-CaF}_2$
1600	1327	0.883	0.935
1550	1277	0.816	0.849
1500	1227	0.747	0.764
1450	1177		0.683
1424	1151	0.642	0.642
1400	1127		0.605
1350	1077		0.531
1300	1027		0.462
1250	977		0.400
1200	927		0.337
1100	827		0.232
1000	727		0.150

$$\Delta H_{\beta}^f = 7.1 \text{ kcal mol}^{-1}; \quad T_{\beta}^f = 1691 \text{ K}; \quad C_{P(l)} = 23.88;$$

$$C_{P(s)} = 25.81 + 2.5 \times 10^{-3} T.$$

At the transition temperature (denoted as  $T^{\text{tr}}$  (transition)) of 1424 K,  $\alpha^{\text{tr}} = 0.642$ . This point is determining for the extrapolation of the course of the liquidus line of  $\alpha\text{-CaF}_2$  since the temperature and the enthalpy of fusion are known. Let us apply the transformation of coordinates so that the activity of  $\text{CaF}_2$  in the transition point would be the unit one. Then we extrapolate the heat capacity values of the low-temperature  $\alpha$ -modification to the hypothetical region and calculate from eqn (1) the melting temperature of this modification of  $\text{CaF}_2$ . For this temperature we determine the enthalpy of fusion of this modification. The method of calculation is discussed in detail in paper [15].

The calculation shows that the hypothetical melting temperature of the low-temperature  $\alpha$ -modification of  $\text{CaF}_2$  is 1637 K, the enthalpy of fusion belonging to this temperature and to this modification being 9.428 kcal mol<sup>-1</sup>. The values of the activities of  $\text{CaF}_2$  in a solution are summarized in Table 3.

By plotting these calculated values in an experimental graph (Fig. 3), we obtain the deviation of the studied system from ideality.

### B. Determination of $\Delta H_{\text{LiF}}^f$ from the course of the liquidus curve of LiF

For the slope of the tangent  $k_{\text{LiF}}^0$  to the liquidus curve for  $x_{\text{LiF}} \rightarrow 1$  in a simple eutectic system the following relation holds

$$k_{\text{LiF}}^0 = \lim_{x_{\text{LiF}} \rightarrow 1} \frac{dT}{dx} = \frac{R(T_{\text{LiF}}^f)^2}{\Delta H_{\text{LiF}}^f} k_{\text{CaF}_2/\text{LiF}}^{\text{St}}.$$

The Stortenbeker correction factor is the unit for the given case and then

$$k_{\text{LiF}}^0 = \frac{1.98716 \times 1118^2}{6.452} = 384 \text{ K}.$$

Since the experimentally found liquidus of LiF is practically a straight line, the slope of the tangent to this experimental liquidus curve is

$$k_{\text{exp}} = \frac{845 - 769}{0.195} = 389.9 \doteq 390 \text{ K}.$$

Table 4

Evaluation of the published phase diagrams of LiF— $\text{CaF}_2$  based on criteria of thermodynamic consistence

$k_{\text{LiF}}^0$	Deviation [%]	$x^E \cdot \Delta H^{1/2} \cdot k^E$ LiF	$x^E \cdot \Delta H^{1/2} \cdot k^E$ $\text{CaF}_2$	Deviation [%]	Ref.
376.2	2.3	1895	1306	31	[1]
400	3.7	2028	2314	14	[2]
320	16.9	2258	1100	51	[3]
420	9.1	1601	3005	88	[6]
400	3.7	1511	1306	14	[8]
390	1.5	1990	1800	10	Our measurement

Both these data show a very good agreement, the deviation being less than 2%. All the published phase diagrams of LiF-CaF<sub>2</sub> have been evaluated in this way. The results are listed in Table 4.

### C. Application of Dodé-Hagège's relation

According to Dodé-Hagège [16] for the eutectic point in simple binary systems the following relation is valid

$$x_A \cdot \Delta \bar{H}_A^{l/s} \cdot k_A^E = x_B \cdot \Delta \bar{H}_B^{l/s} \cdot k_B^E \quad (4)$$

Since the system under investigation, LiF-CaF<sub>2</sub>, is not very different from an ideal one, the partial molar change of enthalpy for the phase transition "solidus-liquidus"  $\Delta \bar{H}^{l/s}$ , for the eutectic composition and temperature may be replaced by the enthalpy of fusion of the same component at the eutectic temperature. For the calculation of the fusion enthalpy the above-described values of the heat capacities according to [11] and [12] were used. Then we obtain for the eutectic temperature of 1042 K

$$\Delta H_{\text{LiF}}^{0,l/s} = 6.376 \text{ kcal mol}^{-1},$$

$$\Delta H_{\text{CaF}_2}^{0,l/s} = 9.564 \text{ kcal mol}^{-1}.$$

The slopes of tangents to the liquidus lines,  $k^E$ , in the eutectic point may be taken from the experimental courses of liquidus curves

$$k_{\text{LiF}}^E = 390; \quad k_{\text{CaF}_2}^E = 980.$$

These values introduced into Dodé-Hagège's relation give

$$\text{for LiF:} \quad 0.805 \times 6.376 \times 390 = 1990,$$

$$\text{for CaF}_2: \quad 0.195 \times 9.564 \times 980 = 1800.$$

The deviation represents less than 10%, which is, with respect to the sensitivity of the tangent methods, a satisfactory result. The values for the other published diagrams computed on the basis of this relation are listed in Table 4.

### Discussion

The calculated and measured liquidus lines of LiF are nearly identical. This is, however, different for CaF<sub>2</sub>. The liquidus of CaF<sub>2</sub> calculated for the condition  $\Delta H^{l/s} = \text{const.}$ , lies below the experimental values. If the liquidus is calculated for the condition  $\Delta H^{l/s} = f(T)$  and the heat capacities used are according to [12], the obtained liquidus lies above the experimental data. This difference may be caused by two reasons:

1. The experimental data of the liquidus of CaF<sub>2</sub> may be shifted to the lower temperature values; this case occurs rather often, when the liquidus of the given component shows a strong slope.

2. The transition temperature 1424 K reported by [12] seems to be arbitrary to a certain extent, since irregularities in the course of the enthalpies may be found in the range of 1320-1440 K [12]. If the correct value of the transition temperature were lower than reported by [12], then the calculated liquidus would also be shifted towards the higher CaF<sub>2</sub> content.

Nevertheless, the computed eutectic point has the parameters 81.5 mole % LiF, 18.5 mole % CaF<sub>2</sub>, and  $T_E = 771^\circ\text{C}$ . The difference between them and the experimental data makes 1 mole % and  $2^\circ$  indicating only a small deviation of this system from ideality.

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