

The liquidus of sodium chloride in the system sodium chloride—calcium fluoride*

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The system NaCl—CaF₂ was investigated in the range of 0–5 mole % CaF₂ by the TA method. The coordinates of the eutectic point (95.5 mole % NaCl, 4.5 mole % CaF₂; $T_E = 779.5^\circ\text{C}$) as well as the course of the liquidus curve of NaCl were determined. Inaccurate literature data were corrected. The thermodynamic analysis of the liquidus curve of NaCl was performed with respect to the possible dissociation of CaF₂. The composition of the eutectic point may be explained on the assumption that CaF₂ forms not only ions but also molecules in solution. Experimental results and theoretical analysis are in agreement with the concept according to which the system NaCl—CaF₂ has the character of a quasi-binary diagonal section of the ternary reciprocal system Na,Ca || F,Cl. The solubility of CaF₂ in the solid state in NaCl was proved to be negligible.

The interaction of the substances NaCl and CaF₂ in the melt along the liquidus curve of NaCl is significant both from the practical and from the theoretical viewpoint.

It is known that for electrolytic production of magnesium the melt NaCl—KCl—MgCl₂ with an addition of CaF₂ or NaF ([1], pp. 281 and 304) serves as electrolyte. With respect to the comparatively high melting point of CaF₂ the maximum addition of it should not exceed its content in the eutectic point of the given system. The substances NaCl and CaF₂ are also components of several types of aluminium electrolytes and their interaction is significant also from this point of view [2].

The system NaCl—CaF₂ has also some theoretical importance. The study of the course of the liquidus curve of NaCl can help to solve the question whether CaF₂ in the liquid phase forms not only Ca²⁺ ions but also the complex cations CaF⁺, as indicated by measurements of the phase diagram in the system Li₃AlF₆—CaF₂ [3].

Besides, the possibility of the formation of solid solutions on NaCl basis is also interesting. The arguments in favour of this possibility are: the approximately equal size of the cations Ca²⁺ ($r = 0.99$ [4]) and Na⁺ ($r = 0.95$ [4]) and the fact that $r_{F^-} < < r_{Cl^-}$ [4]. The replacement of the cations Na⁺ by Ca²⁺ in the system NaCl—CaCl₂ is reported by Flood *et al.* [5].

The thermodynamic analysis of the liquidus course in the system NaCl—CaF₂ has not been reported up to now.

The substances NaCl and CaF₂ form a diagonal subsystem (section) of the ternary reciprocal system Na,Ca || F,Cl. This system as a whole was investigated for the first

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time by *Ishaque* [6]. It has been shown that the system under investigation is irreversibly reciprocal and thus in solidification of the equivalent mixture of the ions of the system the following reaction takes place

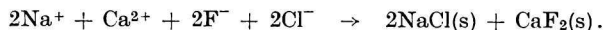


Table 1

Phase diagram of the system NaCl—CaF₂

T_{NaCl}^f [°C]	$T_{\text{CaF}_2}^f$ [°C]	E		Research methods	Ref.	Notes
		mole % CaF ₂	T_E [°C]			
800	1380	3.9	780	VPT ^a	[7]	<i>e</i>
801	1360	10.865	778	TA ^b	[6]	SES ^d
800.5	1411	3.3	780	V ^c + TA	[2]	SES
800	1411	4.12	770	VPT	[8]	SES
800	1410	3.4	775	VPT ^f	[9]	—
800	1410	4.12	773	VPT ^f	[9]	—

a) VPT — visual-polythermal method.

b) TA — thermal analysis.

c) V — visual method.

d) SES — simple eutectic system.

e) Liquidus given only.

f) In paper [9] two different data concerning the eutectic point E are given.

Thus the system NaCl—CaF₂ is a stable diagonal section of the reciprocal system Na₂Ca || F, Cl.

The “solidus—liquidus” equilibrium in the quasi-binary system NaCl—CaF₂ was investigated by several authors. Their results are confronted in Table 1. As it may be seen, the data are appreciably different from each other, particularly regarding the composition of the eutectic point reported from 3.3 to 10.865 mole % CaF₂ [2, 6]. This difference considerably exceeds some possible inaccuracies of the measurements. Since from the description of the experiments realized by different authors none of the measurements could be unambiguously found to be incorrect, it appeared necessary to verify the data concerning the equilibrium “solidus—liquidus” in the quasi-binary system NaCl—CaF₂.

Experimental

To investigate the course of the liquidus curve of NaCl in the given system the TA method was applied. The chemicals used were: NaCl, anal. grade, $T^f = 800.8^\circ\text{C}$, and CaF₂ “single crystals” grade, $T^f = 1418^\circ\text{C}$ [10].

The salts were calcinated in a Pt dish at 400–500°C and stored in ground-in bottles in an exsiccator. The samples were weighed in Pt crucibles with Pt lids and melted in a silite furnace during 30–45 min. The overheating above the temperature of primary crystallization of NaCl did not exceed 40°C. The temperature was measured with a Pt/Pt10Rh thermocouple and its calibration was performed by means of the binary mixtures: 34 mole % NaF + 66 mole % NaCl, T_E (temperature of the eutectic point) =

Table 2

Composition, temperature of the primary crystallization and T_E of the system NaCl—CaF₂

Mole %		Weight %		Temperature of primary crystallization [°C]	T_E [°C]
NaCl	CaF ₂	NaCl	CaF ₂		
99.75	0.25	99.67	0.33	798.5	—
99.50	0.50	99.33	0.67	796.5	778.0
99.25	0.75	99.00	1.00	795.0	779.0
99.00	1.00	98.67	1.33	793.0	777.5
98.50	1.50	98.00	2.00	790.0	779.0
98.00	2.00	97.34	2.66	787.0	778.5
97.50	2.50	96.69	3.31	784.0	779.5
97.00	3.00	96.03	3.97	782.9	779.5
96.50	3.50	95.38	4.62	782.0	779.5
96.00	4.00	94.73	5.27	780.7	779.5
95.50	4.50	94.08	5.92	—	779.5
95.00	5.00	93.43	6.57	—	779.5

= 681°C [11]; 11 mole % Na₃AlF₆ + 89 mole % NaCl, $T_E = 737^\circ\text{C}$ [2] and of NaCl, anal. grade, m.p. 800.8°C [10].

The cooling curves were recorded with an EZ 11 line recorder. The rate of cooling did not exceed 2°C/min.

The reproducibility and the accuracy of the process was checked by repeated measurements. Twelve mixtures were investigated, each of them three times. The results obtained are in Table 2. The error in measurements does not exceed $\pm 1^\circ\text{C}$.

Experimental results and discussion

The phase diagram of the system NaCl—CaF₂ exhibits a eutectic point of the composition of 95.5 mole % NaCl, 4.5 mole % CaF₂, $T_E = 779.5^\circ\text{C}$. The eutectic halt on the cooling curves could be recorded even at the concentration of 0.5 mole % CaF₂, indicating a practically complete insolubility of CaF₂ in NaCl in the solid phase. The liquidus of NaCl was to the concentration axis expressively convex.

The experimental results are in agreement with the concept according to which the system NaCl—CaF₂ has the character of a quasi-binary diagonal section of the ternary reciprocal system Na,Ca || F,Cl.

Direction of the reaction in the system



may be found by determining the value of ΔG_r for this reaction at $T_E = 780^\circ\text{C}$. The ΔG_i° values were taken from the JANAF Tables [10]. The resultant $\Delta G_r = -83.8 \text{ kcal mol}^{-1}$. All the constituents were considered in their standard state. This circumstance does not, however, essentially influence the results of the calculation, according to which the equilibrium in reaction (A) is shifted entirely to the right. This conclusion was confirmed by the results of the X-ray phase analysis. In the quenched samples of the melt, which corresponded to the eutectic composition there were identified besides the characteristic curves of NaCl only those of CaF₂.

Thermodynamic analysis of the liquidus of NaCl

The equation of the liquidus of the i -th component in a simple eutectic system is

$$T = \frac{\Delta H_i^f}{\Delta S_i^f - R \ln a_i}, \quad (1)$$

where T – temperature of primary crystallization of the substance i (TPC),

ΔH_i^f – the heat of fusion of the pure substance i ; $\Delta H_{\text{NaCl}}^f = 6730 \text{ cal mol}^{-1}$ [10],

ΔS_i^f – the entropy of fusion of the pure substance i ; $\Delta S_{\text{NaCl}}^f = 6.2675 \text{ cal K}^{-1} \text{ mol}^{-1}$,

a_i – the activity of the liquid i -th substance in the discussed solution saturated with substance i .

The state of the pure i -th substance in the liquid phase at the temperature T was taken for the standard state (that means that the given substance was in the under-cooled state). It was assumed that the quantity ΔH_i^f was temperature independent. Since for $i = \text{NaCl}$ the difference of $T_i^f - T_E$ makes about 20°C , such a simplification is quite admissible.

a) Let us suggest that the molten mixture $\text{NaCl} + \text{CaF}_2$ behaves as an ideal molecular solution. Then $a_i = x_i$, where x_i is the mole fraction of NaCl in the mixture. The corresponding values of the TPC are plotted in Fig. 1.

If we compare the values of TPC obtained in this way with the experimental data it is evident that the liquidus of NaCl in the whole range expressively deviates from the behaviour of an ideal molecular solution.

b) Let us suggest that the mixture under consideration forms an ideal ionic solution and its constituents dissociate as follows

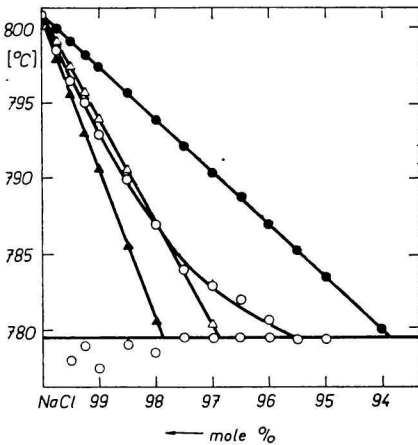


Fig. 1. Comparison of the experimental and calculated course of the liquidus of NaCl in the system $\text{NaCl}-\text{CaF}_2$.

○ experiment; ● $a_i = x_i$; △ $a_i = x_i^2$;

$$\blacktriangle a_i = \frac{x_i^2}{2 - x}$$

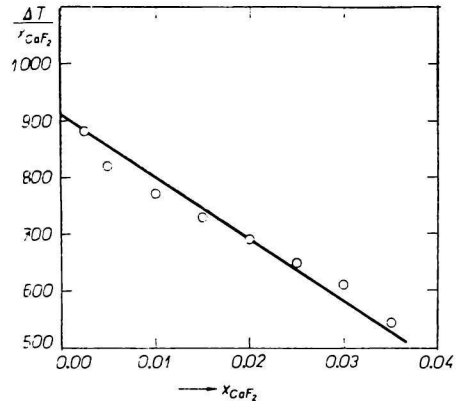


Fig. 2. Dependence $\Delta T/x_{\text{CaF}_2} = f(x_{\text{CaF}_2})$.



Let us take the Temkin model of ideal ionic solutions [12]. The mole fraction of NaCl let be x . Then for $i = \text{NaCl}$ it holds

$$a_i = x_{\text{Na}^+} \cdot x_{\text{Cl}^-} = \frac{x}{x + (1 - x)} \cdot \frac{x}{x + 2(1 - x)} = \frac{x^2}{2 - x}$$

The limiting coefficient is then determined [13]

$$\lim_{x_i \rightarrow 1} \frac{da_i}{dx_i} = 3.$$

This result is in accordance with the suggested scheme of dissociation of CaF_2 . Comparison of the calculated values of TPC with those found experimentally shows that these values agree with each other only in the range of very low concentrations, *i.e.* of 0–0.25 mole % CaF_2 (when the inaccuracy of measurements is suggested to be less than 1°C).

c) Let us suggest that the given mixture forms an ideal ionic solution with its components dissociating according to the following relations



Then for $i = \text{NaCl}$ it holds

$$a_i = x_i^2.$$

From the comparison of the computed and the experimental values of TPC it follows that an agreement between them may be found only in the interval of 0–2.5 mole % CaF_2 .

In order to determine whether for the very low concentration range of CaF_2 the model *b* is valid, or even if in the interval of 0–0.25 mole % CaF_2 the TPC values may be computed according to the model *c*, the results of TA were treated in a cryometric way, *i.e.* the dependence $\Delta T/x_{\text{CaF}_2} = f(x_{\text{CaF}_2})$ was plotted and extrapolated to the zero concentration of CaF_2 (Fig. 2).

Since it holds that

$$K_0^{\text{td}} = \frac{R(T_i^f)^2}{\Delta H_i^f} \quad (2)$$

and

$$K_{\text{exp}}^{\text{td}} = K_0^{\text{td}} \cdot k_{j/i}^{\text{St}} \quad (3)$$

(where $i = \text{NaCl}$, $j = \text{CaF}_2$), it is possible to calculate the Stortenbeker correction factor $k_{j/i}^{\text{St}}$, which is numerically equal to the number of new particles introduced by 1 molecule CaF_2 in the melt of pure NaCl.

From the graph in Fig. 2 it may be seen that $K_{\text{exp}}^{\text{td}} = 910$. Using this value and applying relations (2) and (3) we find that $k_{j/i}^{\text{St}} = 2.7 \approx 3$.

This result is very important because

1. it demonstrates that in diluted solutions of CaF_2 in NaCl (up to 0.25 mole % CaF_2) calcium fluoride yields three particles, *i.e.* Ca^{2+} and 2F^- and therefore the model *b* is valid:

2. it confirms that CaF_2 does not form with NaCl any solid solutions. It may be proved that the presence of solid solutions manifests itself by shifting the liquidus above its theoretically calculated course [14].

Consequently, if the experimental liquidus (within the limits of inaccuracy of measurements) coincides with that calculated theoretically, for the case of the highest possible dissociation of the second component there are no solid solutions in the system under consideration.

As Fig. 1 shows for the CaF_2 content over 2.5 mole % the model, which suggests the dissociation of CaF_2 into CaF^+ and F^- ions, is not suitable any more.

For the interpretation of the liquidus of NaCl the "universal" relation was applied [15]:

$$\ln x_i^{k_{ji}} = \frac{\Delta H_i^f}{R} \left[\frac{1}{T_i^f} - \frac{1}{T} \right]. \quad (4)$$

The exponential factor k_{ji} is in general a function of the concentration x_i , and it holds that

$$\lim_{x_i \rightarrow 1} k_{ji} = k_{ji}^{\text{St}}.$$

By inserting the coordinates of the eutectic point in the system $\text{NaCl}-\text{CaF}_2$ into relation (4), it may be seen that $k_{ji} = 1.385 \approx 1.4$.

This result throws a new light on the problem of the dissociation of CaF_2 in NaCl , because it appears necessary to assume that CaF_2 forms besides ions also molecular solution. The eutectic mixture thus contains the ions Na^+ , Ca^{2+} , CaF^+ , Cl^- , F^- and the molecules of CaF_2 , or simply, Na^+ , Ca^{2+} , Cl^- , F^- , and CaF_2 . The use of the TA method cannot show which of these two alternatives is the more probable.

In conclusion let us analyze the results reported by Ishaque [6] from another point of view.

For systems containing solid solutions the following relation holds

$$\ln \frac{a_i^l}{a_i^s} = \frac{\Delta H_i^f}{R} \left[\frac{1}{T^f} - \frac{1}{T} \right]. \quad (5)$$

For the sake of simplicity we may suggest that in the discussed system there exists the ideal molecular solution of CaF_2 in NaCl and that the solid solution of CaF_2 in NaCl is ideal, too. Therefore it holds

$$\ln x_i^s = \ln x_i^l - \frac{\Delta H_i^f}{R} \left[\frac{1}{T^f} - \frac{1}{T} \right].$$

Introducing for x_i^l and T_E the data reported by Ishaque we obtain $x_i^s = 0.9545$. That would mean that the range of the solid solution of CaF_2 in NaCl at the eutectic temperature extends up to the concentration of 4.55 mole % CaF_2 . This result is, however, contradictory to our measurements (the eutectic halt occurs even at 0.50 mole % CaF_2) as well as to the conclusions drawn from the cryometric measurements. Also from this point of view the results reported by Ishaque are open to criticism.

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