The Phase Diagram of the System NaF-NaCl* and Thermodynamic Properties of Fused Mixtures

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1. The phase diagram. The phase diagram of the system NaF—NaCl has been re-examined by thermal analysis (cooling curve technique). The results from the thermal analysis are given in Table 1 and plotted in a phase diagram in Fig. 1.

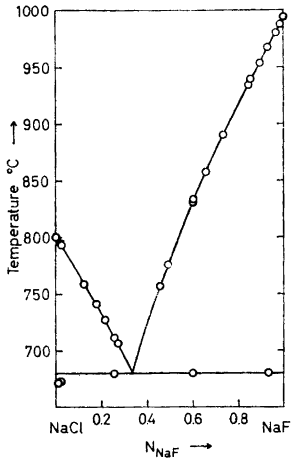

Fig. 1. The phase diagram of the system NaCl—NaF.

An eutectic point is found at 680°C and 33.5 mole% NaF. Since thermal arrests were obtained at the eutectic temperature for mixtures containing 1 and 2 mole% NaF, it is assumed that formations of solid solutions above 1 mole% do not occur in the system.

* This work is based on a thesis by Tor Halvorsen submitted to The Technical University of Norway in 1956 in partial fulfillment of requirements for the degree of Sivilingeniør in Chemistry.

Table 1. The system NaCl—NaF. Temperatures obtained by thermal analysis (cooling curves).

Composition, mole fraction NaF	Liquidus curve °C	Solidus curve °C
0.0000	800.5	
0.0100	—	672.0
0.0217	793.5	671.0
0.0240	793.3	
0.1249	759.5	
0.1807	741.2	
0.2164	726.6	
0.2580	710.7	679.9
0.2694	706.6	
0.4563	756.5	
0.4937	776.4	
0.6001	831.1	680.1
0.6028	832.8	
0.6581	857.8	
0.7346	890.2	
0.8450	934.1	
0.8573	939.0	
0.8961	953.8	
0.9313	967.7	
0.9343	968.7	680.0
0.9649	980.5	
0.9673	981.8	
0.9838	987.8	
1.0000	994.5	

Earlier investigations of the system have been carried out by Wolters,[1] Plato [2] and others.

These authors report liquidus temperatures about 7—8 degrees lower than the results obtained by the present authors.

2. Thermodynamic properties of the mixture. The excess partial free energies have been calculated from the observed freezing point expressions by using the relation

$$\bar{G}^{e} = -\Delta H_f\left(1-\frac{T}{T_f}\right) + \frac{\Delta Cp}{2}\frac{(\Delta T)^2}{T} - RT \ln N \qquad (1)$$

Here ΔH_f is the heat of fusion of NaF or NaCl, $\Delta H_{f,NaF} = 8030$ cal/mole (Kelley and O'Brien [3]), $\Delta H_{f,NaCl} = 6690$ cal/mole (Dworkin and Bredig [4]), ΔCp is the difference in specific heat of the pure liquid and pure solid salt. $\Delta T = T_f - T$ where T is the melting temperature of the mixture, and N is the mole fraction of the component

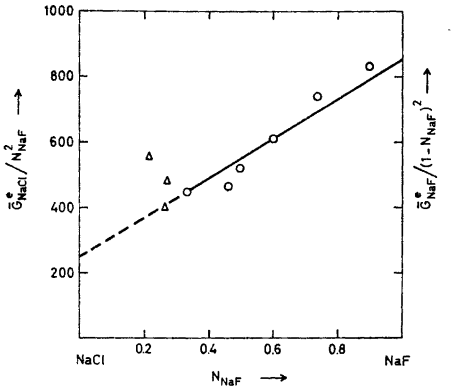

Fig. 2. The interaction parameter $\bar{G}^e/N^2$ as a function of the mole fraction of sodium fluoride in the mixture.

○ Points from the NaF-side of the system;
△ Points from the NaCl-side of the system.

for which the excess partial free energy is calculated.

The mole fractions of NaCl and NaF are defined by

$$N_{NaCl} = \frac{n_{NaCl}}{n_{NaCl} + n_{NaF}}$$

$$N_{NaF} = \frac{n_{NaF}}{n_{NaCl} + n_{NaF}}$$

The mixture is treated as a regular mixture where the excess partial free molar energies of the two components are expressed by

$$\bar{G}^e_{NaF} = b \times N^2_{NaCl} \quad (2a)$$

$$\bar{G}^e_{NaCl} = b \times N^2_{NaF} \quad (2b)$$

The interaction parameter, b, is plotted as a function of composition on Fig. 2. A straight line corresponding to

$$\bar{G}^e_{NaF} = (1-N_{NaF})^2 (250 + 600\, N_{NaF}) \quad (3)$$

is obtained on the NaF-side of the system.

At 50:50 composition we find

$$\bar{G}^e_{NaF}/(1-N_{NaF})^2 = +\ 550 \text{ cal/mole}$$

This is in good agreement with a value reported by Murgulescu and Sternberg,[5] $G^e = +\ 153$ cal/mole or $G^e/(1-N_{NaF})N_{NaF} = +\ 612$ cal/mole. This value should be compared with interaction parameters obtained by Flood, Førland and Toguri [6] for anion mixtures of the type Me(Cl—Br), Table 2. We note that all these systems show positive deviation from ideality, as does the system Na(F—Cl).

Table 2. Interaction parameters for some anion mixtures of alkali halogenides based on free energy data.

System	Interaction parameter cal/mole	References
K(Cl—Br)	+ 530	Flood, Førland, Toguri [6]
Na(Cl—Br)	+ 350	—»—
Li(Cl—Br)	+ 150	—»—
Na(Cl—F)	+ 550	This work

Experimental. The chemicals used in the studies were commercially available reagent grade sodium fluoride (Merck, Darmstadt Germany) m.p. 994.5°C and reagent grade sodium chloride, *fusum*, (Merck, Darmstadt Germany), m.p. 800.5°C.

The equipment for the cooling work consisted of a Pt—Pt 10 % Rh thermocouple connected to a precision potentiometer with a mirror galvanometer. The furnace was a standard type furnace used at this institute. Both the furnace and the technique used during the work has been described in a previous paper.[7] A platinum crucible of about 37 mm in diameter and 45 mm height was used as a container for the melt.

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