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The Phase Diagrams of the Systems NaCl-MgCl₂ and KCl-MgCl₂

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As a part of our investigations of the physicochemical properties of the magnesium chloride-calcium chloride-alkali chloride electrolyte for the production of magnesium, the phase diagrams of the two systems NaCl-MgCl₂ and KCl-MgCl₂ have been reinvestigated.

The methods used in the investigation were: Thermal analysis, differential thermal analysis, and X-ray diffraction studies at room temperature. These methods and techniques have been described in previous papers¹⁻³ from this institute.

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The chemicals NaCl, KCl, and MgCl₂ were the same as used in the density measurements on molten mixtures in the same systems.⁴ The two phase diagrams are presented in Figs. 1 and 2.

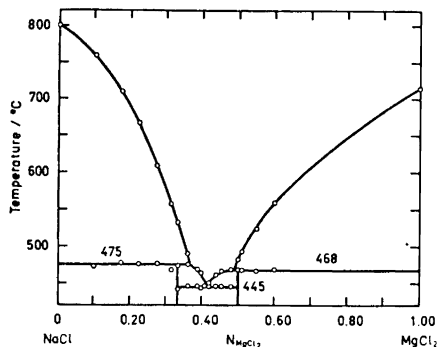


Fig. 1. The phase diagram of the system NaCl-MgCl₂.

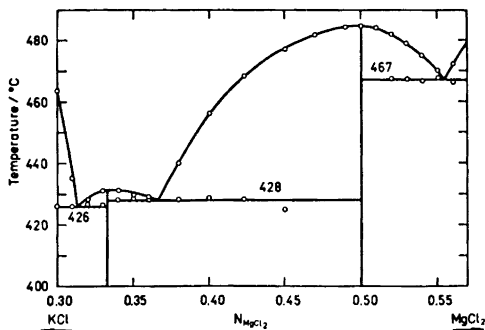
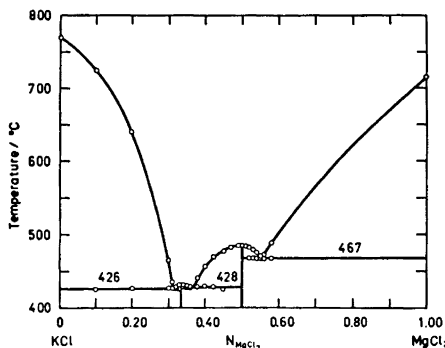


Fig. 2. a. The phase diagram of the system KCl-MgCl₂; b. The main part of the phase diagram KCl-MgCl₂.

Table 1. Some characteristic data for the system NaCl-MgCl₂.

Melting points °C		Eutectic point		Peritectic points				Reference
NaCl	MgCl ₂	mol % MgCl ₂	Temp. °C	mol % MgCl ₂	Temp. °C	mol % MgCl ₂	Temp. °C	
803	711	44.0	430	38.1	464	48.6	448	5
—	—	39.9	450	35.6	485	46.9	465	6
800	712	48.0	442	37.6	476	49.8	462	7
815	720	43–44	450	38.0	480	(49.0)	470) ^a	8
798	711	47.0	444	39.0	476	(44.0)	462) ^a	9
—	712	47.0	442	34.0	476	(50.0)	462) ^a	10
800.5	713.9	41.5	445	37.0	475	49.0	468	This work

^a Peritectic point for NaMg₂Cl₅ instead of NaMgCl₃.

Table 2. Some characteristic data for the system KCl-MgCl₂.

Melting points °C				Eutectic points				Reference		
KCl	K ₂ MgCl ₄	KMgCl ₃	MgCl ₂	mol % MgCl ₂	Temp. °C	mol % MgCl ₂	Temp. °C			
776	437	484	711	32.9	426	34.8	433	57.2	473	5
785	440	500	720	32.5	440	40.0	440	58.0	480	8
772	433	488	715	30.0	430	36.0	431	60.0	470	11
770.3	431.2	484.8	713.9	31.5	426	36.5	428	55.5	467	This work

In Tables 1 and 2 our values for the melting points, eutectic and peritectic points are compared with literature data.

In our phase examinations we find two *incongruently* melting compounds, corresponding to Na₂MgCl₄ and NaMgCl₃ in the NaCl-MgCl₂ system, while we find two *congruently* melting compounds, K₂MgCl₄ and KMgCl₃, in the KCl-MgCl₂ system.

As can be seen our results for both systems are in relatively good accordance with those obtained by Klemm,^{6,11}

Our data for the system NaCl-MgCl₂ are also in fair agreement with the results given by Matiasovsky.⁷

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