

The Phase Diagram of the System MgCl_2 - CaCl_2 , and Thermodynamic Properties of Molten Mixtures in this System

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The system magnesium chloride-calcium chloride has been examined by thermal analysis, differential thermal analysis and equilibration followed by quenching. Identification of phases present in the system was performed by optical microscopy, and by high temperature X-ray diffraction technique. The system is a eutectic one with a eutectic point at 52.8 mole % (49 weight %) MgCl_2 and $620 \pm 1^\circ\text{C}$. A solid solubility of about 17 mole % MgCl_2 was found on the CaCl_2 -side of the system at 620°C . The solid solubility decreases rather fast with the temperature.

The partial excess free energy of magnesium chloride has been calculated from the freezing-point depression measurements on the MgCl_2 -side of the system, and compared with values obtained from EMF measurements using the galvanic cell:



Integral Gibbs excess free energies for MgCl_2 - CaCl_2 mixtures were calculated and excess entropies were obtained from the enthalpies of mixing in the system. The excess entropy curve is S-shaped, the entropy being negative for compositions $0 < N_{\text{MgCl}_2} < 0.25$ and positive for $N_{\text{MgCl}_2} > 0.25$. The entropy effect is discussed qualitatively, and compared with available entropy data in the AlkCl-MgCl_2 systems.

I. INTRODUCTION

The phase diagram of the system magnesium chloride-calcium chloride was examined for the first time by Menge¹ in 1911. Later, the system has been reexamined by Ivanov² and by Matiasovsky.³ While their results differ somewhat with respect to eutectic composition and temperature, they all indicate solid solubilities of magnesium chloride in calcium chloride ranging from about 10 to 15 mole % MgCl_2 . The results referred to above are summarized in Table 1.

The limit of the solid solubilities was in all three cases found by plotting the time of the thermal arrest as a function of composition. It is well known that this method can indicate solid solubility in a system, but it does not

Table 1. Phase relations in the system $\text{MgCl}_2\text{-CaCl}_2$.

References	Eutectic composition		Solid solution mole % MgCl_2
	mole % MgCl_2	temp.°C	
Menge (1911)	60.9	621	14.7
Ivanov (1953)	52.8	611	about 10
Matiasovsky (1959)	53.3	614	larger than 11.5
This work (1969)	52.8 ± 0.8	620 ± 1	17.2 ± 1.0

necessarily prove that solid solubility really exists. The present work was therefore undertaken with the main object of trying to establish the solidus curve in the system better than before.

The following methods were used in this study: Thermal analysis, differential thermal analysis, quenching technique with microscopic and X-ray investigations of quenched samples, and high-temperature X-ray investigations.

II. EXPERIMENTAL

1) *Chemicals*. The anhydrous magnesium chloride used in this investigation was prepared by removing the water from the hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, analytical reagent

Table 2. The system $\text{MgCl}_2\text{-CaCl}_2$. Results from thermal analysis.

Composition molefraction MgCl_2	Temperature °C	
	liquidus curve	solidus curve
0	771.7	—
0.074	756.6	—
0.143	739.0	—
0.184	726.0	—
0.228	712.2	616.3
0.310	685.4	618.4
0.403	653.5	619.6
0.467	632.6	620.4
0.516	—	621.3
0.549	621.1	620.5
0.579	628.9	620.4
0.659	647.9	618.1
0.724	661.5	618.1
0.825	682.7	617.1
0.909	696.5	615.6
1.000	712.7	—

grade from Merck, Germany). Anhydrous CaCl_2 was made from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (analytical reagent grade from Merck, Germany). The processes used for purification and handling of these chemicals are described elsewhere.⁴

2) *Thermal analysis.* The equipment used in the present work for the cooling curve investigation was the same as described in previous papers^{5,6} from this Institute.

A graphite crucible, 55 mm in diameter and of 120 mm height, containing 40–100 g melt was placed inside a "thermal gradient free" standard type furnace. The temperature was recorded by a Pt/Pt 10 % Rh thermocouple calibrated at the melting point of silver, 960.5°C. Supercooling of the melt was prevented by stirring and by seeding with small crystals of magnesium chloride or calcium chloride. The uncertainty in determining temperature by this method is $\pm 0.2^\circ\text{C}$. However, due to supercooling effects the uncertainty in some experiments could be as large as $\pm 0.5^\circ\text{C}$.

3) *Differential thermal analysis.* Samples of different compositions were also examined by differential thermal analysis. The cooling curves were recorded by a Varian G 2022 Dual Channel Recorder connected to a D. C. Microvolt Amplifier (range 50–2000 μV , Leeds and Northrup, U.S.A.). Samples were placed in a platinum crucible mounted in a nickel block in a furnace of the same standard type as used in the thermal analysis experiments. Fired alumina, Al_2O_3 , was used as reference material.

4) *Quenching experiments.* The technique of quenching, after equilibration at predetermined temperatures, was used to supplement the information obtained by thermal analysis. One sample containing 8 mole % MgCl_2 was homogenized to a very fine powder in waterfree acetone, dried, and put into small platinum capsules, and heated in the furnace at the predetermined temperature. After equilibration for 1–2 h, the sample was quenched in oil, and examined by optical microscopy. A petrographic microscope was used for identification of the phases present, and to observe the first appearance of a liquid phase.

5) *The high-temperature X-ray equipment.* The high-temperature X-ray experiments were carried out in a metal ribbon furnace similar to the type described by Smith.⁷ The heating element was a flat strip made from platinum/10 % rhodium. The temperature was recorded with a Pt/Pt 10 % Rh thermocouple and was constant within $\pm 1^\circ\text{C}$ with time. Calibration at the transition point of Na_3AlF_6 ($\alpha \rightarrow \beta$) at 560°C, showed the recorded temperature to be correct to within $\pm 5^\circ\text{C}$.

III. RESULTS AND DISCUSSION

Results obtained by thermal analysis are listed in Table 2 and plotted in a phase diagram in Fig. 1. In the course of the differential thermal analysis, both heating and cooling curves were recorded. The points are plotted in the same diagram, Fig. 1. The DTA method was used to detect small heat changes associated with formations of solid solutions and small amounts of eutectic mixture. It was quite clear that this taxed the equipment and the procedures to the limit. The points given in Fig. 1, marked DTA, are not taken from well established peaks in the DTA diagram, but rather from small changes in the heat content recorded during heating and cooling. Three of these curves are shown in Fig. 2, a-c. It is clear from other phase diagram examinations at this Institute, that the DTA equipment may be used for detection of solidus curves in certain systems where the solid solubility exceeds 10–20 mole %, as in the two systems NaCl-KCl ⁸ and $\text{Na}_3\text{AlF}_6\text{-Li}_3\text{AlF}_6$.⁹ On the MgCl_2 -side a eutectic reaction was recorded for a sample containing 98.7 mole % MgCl_2 at 613°C. It is therefore assumed that the solid solubility of calcium chloride in magnesium chloride is less than 1 mole %.

On the CaCl_2 -side of the system the eutectic reaction was recorded at 18.5 mole % MgCl_2 on cooling and 17.0 mole % MgCl_2 on heating. This reaction could not be detected for samples containing less than 17 mole % MgCl_2 .

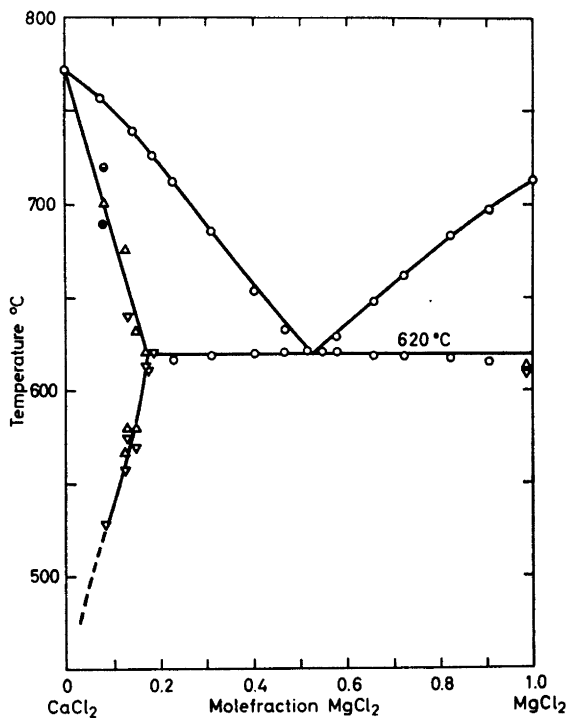


Fig. 1. The phase diagram of the system $\text{MgCl}_2\text{-CaCl}_2$ from the present work.

○ points obtained from thermal analysis; △ points obtained from thermal heating curves; ▽ points obtained from DTA cooling curves; ●● points obtained from quenching experiments; half-filled indicating that both one solid phase and a liquid phase are present, filled indicating that solid phases only are present.

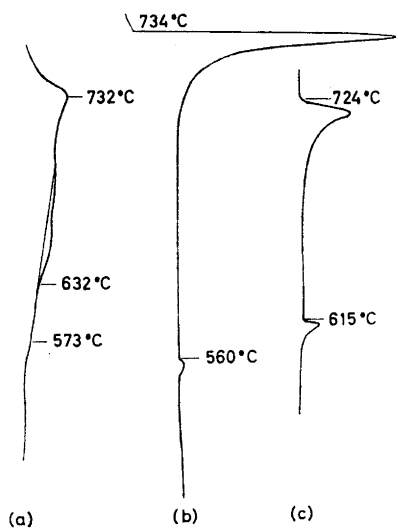
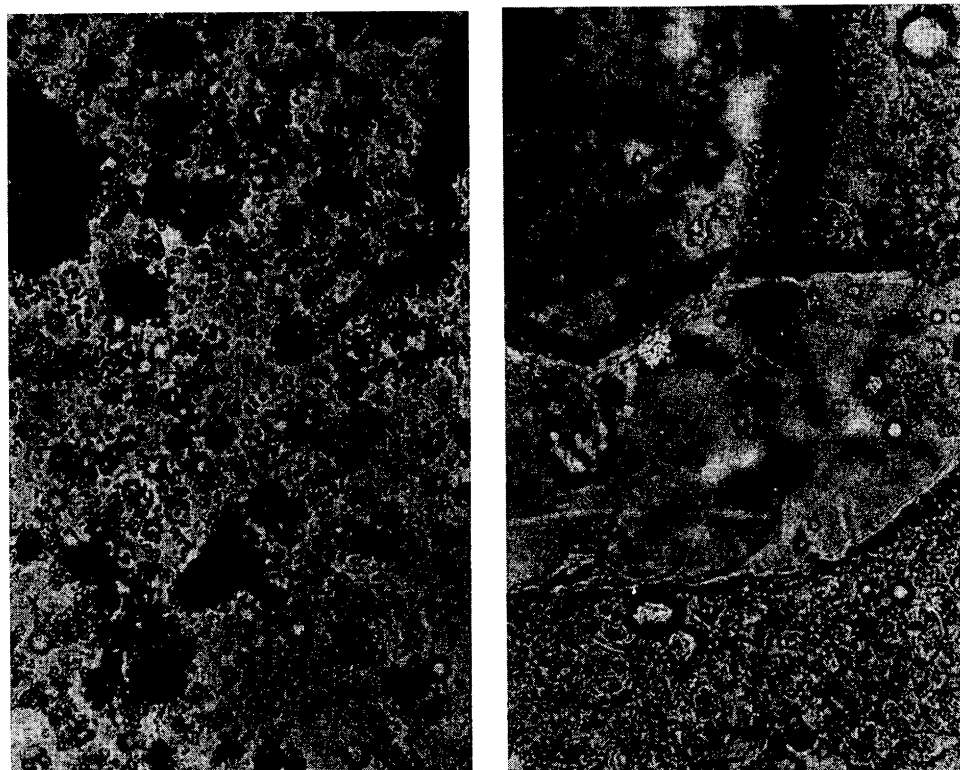


Fig. 2. DTA cooling curves. (a) and (b) 14.8 mole % MgCl_2 ; (a) heating curve, $\times 200$; (b) cooling curve, $\times 100$; (c) 17.6 mole % MgCl_2 , cooling curve, $\times 200$.

However, in the concentration range 0–17 mole % MgCl_2 it was sometimes possible to observe changes in the slope of the heating and cooling curves (Fig. 2a). It is assumed that these changes in the heat content are due to the formation of solid solutions. These points are plotted in Fig. 1 as well.

The results from the microscopic examinations of a sample containing 8 mole % MgCl_2 and quenched from different temperatures can be summarized as follows: The sample showed no presence of a liquid phase when quenched from 680°C (Fig. 3a). When the sample was quenched from 710°C the appearance of a liquid phase was quite clear. (Fig. 3b).



(a)

(b)

Fig. 3. Photomicrographs of phases in the system $\text{MgCl}_2\text{-CaCl}_2$ at composition 8.1 mole % MgCl_2 . Magnification $\times 300$. (a) Quenched from 680°C . Sample not melted. (b) Quenched from 710°C . Sample partly melted.

A sample containing 10 mole % MgCl_2 was also examined by high-temperature X-ray at 620°C and compared with the diagram of pure CaCl_2 at the same temperature. No peaks corresponding to magnesium chloride could be found in the diagram. Nor could any shift in the X-ray diagram of CaCl_2

due to a change in any of the lattice parameters of CaCl_2 be observed. This is probably due to the difference in the size of the magnesium and the calcium ions, *i.e.* the smaller Mg^{2+} ion will easily fit into the CaCl_2 -lattice. On the basis of the experimental work it is assumed that the system MgCl_2 - CaCl_2 constitutes a simple eutectic system, with a eutectic point at 52.8 mole % (49 weight %) MgCl_2 and $620 \pm 1^\circ\text{C}$. On the CaCl_2 -side of the system the solid solubility does not exceed 17 mole % MgCl_2 at 620°C .

IV. THERMODYNAMIC PROPERTIES OF MOLTEN MIXTURES OF MAGNESIUM CHLORIDE AND CALCIUM CHLORIDE

The excess partial Gibbs energy of magnesium chloride can be calculated from the observed freezing point depressions by using the relation

$$\bar{G}_{\text{MgCl}_2}^e = -\Delta H_f \left(1 - \frac{T}{T_f}\right) + \frac{\Delta C_p}{2} \frac{(\Delta T)^2}{2} - RT \ln N_{\text{MgCl}_2} \quad (1)$$

Here ΔH_f is the enthalpy of fusion of magnesium chloride, $\Delta H_f = 10.3$ kcal/mole, Moore,¹⁰ and ΔC_p is the difference in specific heat of the pure liquid and pure solid magnesium chloride. $\Delta T = T_f - T$ where T is the melting temperature of the mixture and T_f the melting temperature of pure magnesium chloride. The excess partial free energy of magnesium chloride can be expressed by

$$\bar{G}_{\text{MgCl}_2}^e = \lambda N_{\text{MgCl}_2}^2 \quad (2)$$

where λ is a function of the molefraction N_{CaCl_2} .

The best fit for $\bar{G}_{\text{MgCl}_2}^e/N_{\text{MgCl}_2}^2$ is obtained by the relation

$$\bar{G}^e/N_{\text{CaCl}_2}^2 = 1300 - 1670 N_{\text{CaCl}_2} \quad (3)$$

In Table 3 the partial excess free energies obtained from phase diagram data are compared with the excess partial free energies obtained by using the galvanic cell:¹¹

$\text{Cl}_{2(g)}$, graphite/ $\text{NaCl}_{(l)}$ / $\text{Na-glass}/(\text{Na-Mg-Ca})\text{Cl}_{(l)}$ /graphite $\text{Cl}_{2(g)}$ at 850°C . Since the \bar{G}^e -values obtained from the EMF-data are calculated * and not measured, we believe that the phase diagram data in this case are better than the EMF data in the composition range 100–60 mole % MgCl_2 . However,

* The partial excess free energies of MgCl_2 were obtained from the following expression:

$$\begin{aligned} \bar{G}_{\text{MgCl}_2}^e = & \left\{ \int_1^0 \frac{\bar{G}_{\text{NaCl}}^e}{(1-X_{\text{NaCl}})^2} dx_{\text{NaCl}} \right\}_{y=1} \\ & + \left\{ (1-y) \int_1^{X_{\text{NaCl}}} \frac{\partial \bar{G}_{\text{MgCl}_2}^e}{\partial y} \frac{1}{(1-X_{\text{NaCl}})^2} dx_{\text{NaCl}} \right. \\ & \left. - \int_1^{X_{\text{NaCl}}} \frac{\partial \bar{G}_{\text{NaCl}}^e}{\partial X_{\text{NaCl}}} dX_{\text{NaCl}} \right\}_y \end{aligned}$$

Table 3. Excess Gibbs energies for molten $\text{MgCl}_2\text{-CaCl}_2$ mixtures.

Molefraction MgCl_2	$\bar{G}_{\text{MgCl}_2}^e$ cal/mole		$\bar{G}_{\text{CaCl}_2}^e$ cal/mole	G^e cal/mole
	this work	EMF ¹¹		
0				0
0.1		331	0	33
0.2		322	0	64
0.3		292	0	88
0.4		239	37	118
0.5	115	172	87	130
0.6	101	73	202	140
0.7	72	31	325	148
0.8	39	0	407	111
0.9	12	0	516	63
1.0	0	0	0	0

the EMF data should certainly be preferred in the low magnesium chloride concentration range. Excess partial free energies of calcium chloride are also evaluated from the EMF data and given in Table 3. This permits us to calculate the integral free energy of mixing from the relation

$$G^e = N_{\text{MgCl}_2} \cdot \bar{G}_{\text{MgCl}_2}^e + N_{\text{CaCl}_2} \cdot \bar{G}_{\text{CaCl}_2}^e \quad (4)$$

The G^e values are plotted in Fig. 4 together with the enthalpies of mixing given by Papatheodorou and Kleppa¹² as:

$$\Delta H^M/N_{\text{MgCl}_2} (1 - N_{\text{MgCl}_2}) = 0.06 + 0.99N_{\text{MgCl}_2} + 1.30N_{\text{MgCl}_2}^2$$

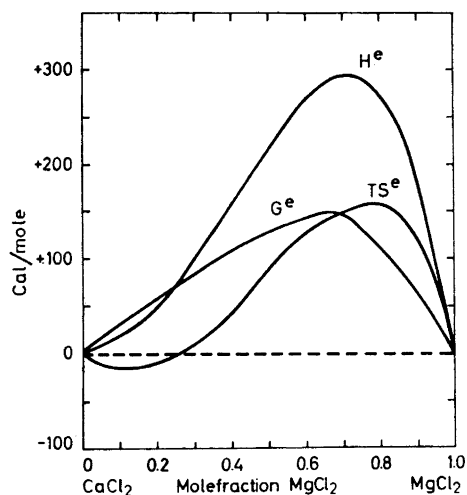


Fig. 4. The excess functions H^e , G^e , and TS^e in the system $\text{MgCl}_2\text{-CaCl}_2$.

The excess entropy of mixing given in the same diagram was obtained from eqn. (5).

$$TS^e = H^e - G^e \quad (5)$$

As can be seen the three thermodynamic functions are all positive except the excess entropy which is negative in the region 0–25 mole % MgCl_2 . The deviations from ideality are, however, rather small in all three cases. It should be

Table 4. Excess entropies in the system CaCl_2 – MgCl_2 .

Molefraction MgCl_2	TS^e		$T\bar{S}^e/N_1N_2$	$\bar{S}_{\text{MgCl}_2}^e$	$\bar{S}_{\text{MgCl}_2}^{\text{ideal}}$
	obs.	calc.			
	cal/mole		cal/mole	cal/mole degree	
0	0	0			
0.1	–17	–15	–188		
0.2	14	–13	–88		
0.3	12	6	57		
0.4	42	41	175		
0.5	91	85	364	0.289	1.38
0.6	130	128	542	0.206	1.02
0.7	145	158	690	0.180	0.71
0.8	159	161	994	0.116	0.44
0.9	118	115	1311	0.036	0.21
1.0	0	0			

stressed that the negative deviation in entropy on the CaCl_2 -side is of the same magnitude as the estimated accuracy in TS^e , namely $\pm 20^\circ$ cal. The excess entropies are given in Table 4 together with the entropy interaction parameter

$$\lambda_S = \frac{TS^e}{N_{\text{MgCl}_2} N_{\text{CaCl}_2}} \quad (6)$$

The data were fitted by the least-square method to polynomials of the form

$$TS^e = N_1N_2(a + bN_1 + cN_1N_2) \quad (7)$$

The following equation was obtained:

$$TS^e = N_{\text{MgCl}_2}N_{\text{CaCl}_2}(-0.233 + 1.811 N_{\text{MgCl}_2} - 1.336 N_{\text{MgCl}_2}N_{\text{CaCl}_2}) \quad (8)$$

The partial molar excess entropy of magnesium chloride, $T\bar{S}_{\text{MgCl}_2}^e$, is found by differentiation of eqn. (8).

$$T\bar{S}_{\text{MgCl}_2}^e = N_{\text{CaCl}_2}(4.725 - 8.966 N_{\text{CaCl}_2} + 4.010 N_{\text{CaCl}_2}^2) \quad (9)$$

Values for $\bar{S}_{\text{MgCl}_2}^e$ are given in Table 4 and compared with the partial ideal entropy of mixing. As can be seen the difference between the real and ideal entropy is always less than 25 %. At the composition $N_{\text{MgCl}_2} = 0.8$, the ideal

entropy of mixing $\Delta S^{\text{ideal}}=0.40$ e.u. This value should be compared with the excess entropy $\Delta S^e=0.14$ e.u. The excess partial entropies of mixing are therefore inconsistent with earlier analysis of cryoscopic data on the MgCl_2 -side of the systems $\text{MgCl}_2\text{-AlkCl}$.¹³ This model predicted that additions of AlkCl should give a double freezing point depression in liquid magnesium chloride. This should correspond to an excess entropy of the same size as the ideal one.

In the systems AlkCl-MgCl_2 it has been shown that the excess entropies are all negative¹⁴ increasing from Na^+ to Cs^+ in the same direction as the enthalpies of mixing.¹⁵ When considering changes in configurational entropy only, negative deviations from ideality seem to occur in all simple systems of the type AX-BX having a nonideal enthalpy of mixing. However, in the AlkCl-MgCl_2 systems and in the present system $\text{CaCl}_2\text{-MgCl}_2$, the problem is not as simple as before, since new species will be introduced by mixing of the two components.

The configurational contribution to the excess entropy can be expected to arise at least from the sum of two effects given by $S^e=S_1^e+S_2^e$. The first of these effects, S_1^e , is due to a reduction in the number of independent units in the system, which results in a negative contribution and is the major factor in the case of very strong association. Secondly the introduction of new species will make a positive contribution and is the controlling factor when the association is feeble, *i.e.* in systems where the enthalpy of mixing is small and negative, or positive.

If we apply this to the systems mentioned above, we find that the S_1^e term always determines the sign of S^e in the systems AlkCl-MgCl_2 , where $\text{Alk}^+=\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$. The excess entropy will in this case probably be associated with the loss in the number of orientations of the chloride ions, due to formation of complex species. In the system $\text{MgCl}_2\text{-CaCl}_2$ the interactions are weak and the S_2^e term will in this case be the most important.

Species like MgCl^+ , MgCl_2 , CaCl^+ , CaCl_2 , and Cl^- may be expected to be present in the melt and contribute to the positive excess entropy of mixing.

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