The Magnesium Chloride-Potassium Chloride Phase Diagram

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The $MgCl_2$-KCl binary phase diagram has been redetermined experimentally by cooling curve analysis. It has three eutectics—at 427 °C (31 mol% $MgCl_2$), at 426 °C (35 mol% $MgCl_2$), and at 470 °C (57 mol% $MgCl_2$)—and two congruently melting compounds—K_2MgCl_4 at 428 °C (33 mol% $MgCl_2$) and $KMgCl_3$ at 488.5 °C (50 mol% $MgCl_2$). A peritectic of $K_3Mg_2Cl_7$ was found at 440 °C (36 mol% $MgCl_2$). Another phase change, for which we have not been able to offer a satisfactory explanation, was found at 424 °C in the 40 to 50 mol% $MgCl_2$ region.

1. Introduction

The $MgCl_2$-KCl phase diagram has been determined by a number of workers[1-7] (Fig. 1 to 7) employing various methods, but discrepancies exist. Seifert and coworkers[7-9,11,12] have studied the system more thoroughly than earlier investigators using, not only DTA, but a novel electrochemical approach. They have also determined the crystal structures of four compounds.[7,8] Although the work by Seifert is very thorough, the most often quoted phase diagram is that of Grjotheim and coworkers.[6] This paper describes our determination of the $MgCl_2$-KCl phase diagram using the cooling curve thermal analysis method.

The main discrepancy in the phase diagram is over the existence of the two incongruently melting compounds, K_4MgCl_6 and $K_3Mg_2Cl_7$, reported by only Seifert *et al.*[7-9,11,12] The existence of K_2MgCl_4 is reported by the majority of the authors, while others indicate only a single congruently melting compound, $KMgCl_3$. The melting point of K_2MgCl_4 is reported to be between 428 to 433 °C, and $KMgCl_3$ reportedly melts between 485 to 492 °C. Three eutectic points are reported: two between 426 to 431 °C and one at 470 to 487 °C at compositions of approximately 31, 36, and 58 mol% $MgCl_2$, respectively. Klemm, Beyersdorfer, and Oryschkewirsch[3] and Ivanov[4] report an additional phase change around the 40 mol% $MgCl_2$ region, and Seifert *et al.* established the existence of two incongruently melting compounds—K_4MgCl_6, melting point 429 °C (30 mol% peritectic point) and $K_3Mg_2Cl_7$, melting point 442 °C (38 mol% peritectic point). $KMgCl_3$ transforms at 297 °C (orthorhombic to cubic).

2. Experimental

2.1 Materials

The KCl used was Merck analar grade (99.5%). (Before use, the KCl was heated to 800 °C in a furnace in a nitrogen atmos-

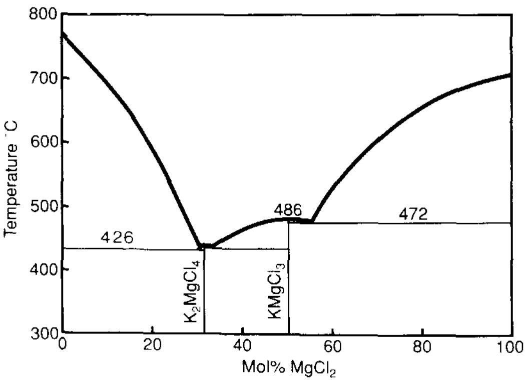

Fig. 1 $MgCl_2$-KCl phase diagram. From O. Menge[1] (1911).

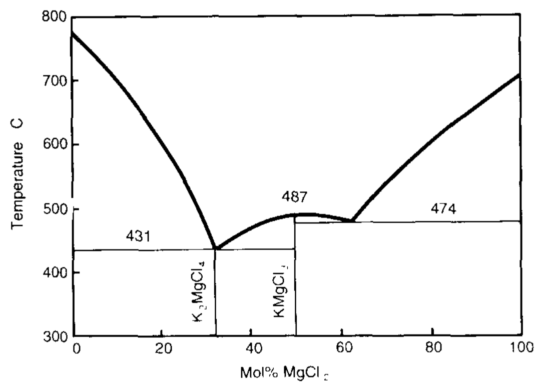

Fig. 2 $MgCl_2$-KCl phase diagram. From K. Scholich[2] (1920).

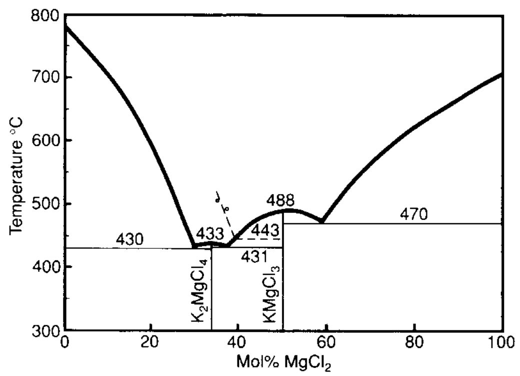

Fig. 3 $MgCl_2$-KCl phase diagram. From W. Klemm *et al.*[3] (1948).

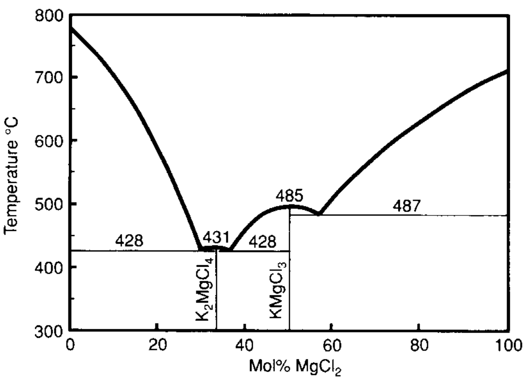

Fig. 4 $MgCl_2$-KCl phase diagram. From A.I. Ivanov[4] (1953).

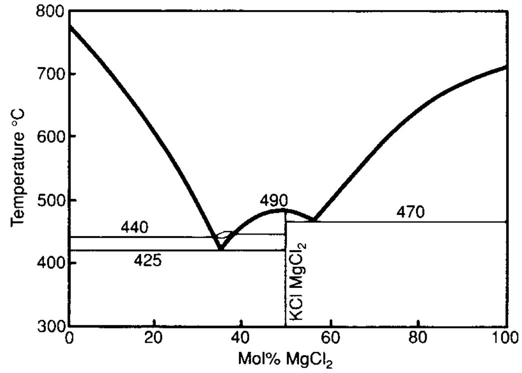

Fig. 5 $MgCl_2$-KCl phase diagram. From N.D. Chikanov *et al.*[5] (1966).

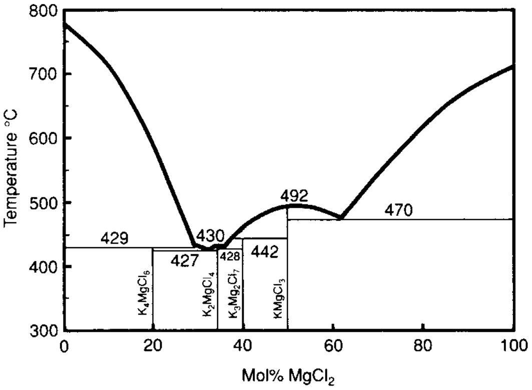

Fig. 6 $MgCl_2$-KCl phase diagram. From K. Grjotheim *et al.*[6] (1972).

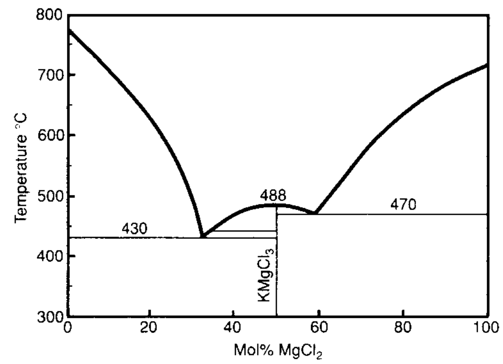

Fig. 7 $MgCl_2$-KCl phase diagram. From H.J. Seifert *et al.*[7] (1974).

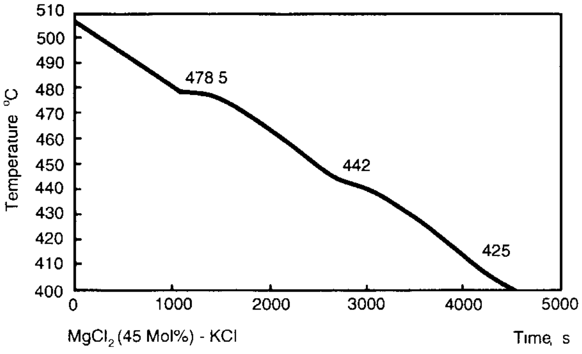

Fig. 8 Example of a cooling curve for $MgCl_2$ (45 mol%)-KCl.

phere glovebox, held at 800 °C for one hour, and then allowed to cool.) Karl Fischer analysis showed the product to contain 0.09% water ±0.02%), and Fast Neutron Activation Analysis (FNAA) determined the oxygen content to be 0.05%. Spectrographic analysis showed the major impurity was magnesium at 170 ppm. The melting point was 768 °C.[10]

The $MgCl_2$ used was Merck technical grade anhydrous. The $MgCl_2$ was heated to 750 °C in a silica tube in an argon atmosphere. Once the salt was molten, HCl was bubbled through for 30 minutes before allowing the $MgCl_2$ to cool under argon. This treatment was necessary to prevent the $MgCl_2$ from hydrolyzing and forming the oxychloride. The product was a

Table 1 Chemical Analysis of KCl and $MgCl_2$

Element	KCl, ppm	$MgCl_2$, ppm
Lithium	<10	<10
Beryllium	<1	<1
Sodium	<50	<50
Magnesium	170	...
Potassium	...	290±30
Calcium	70	140
Scandium	<1	<1
Titanium	<20	<20
Vanadium	<50	<50
Chromium	<10	<10
Manganese	<50	<50
Iron	20±5	55±5
Cobalt	<1	<1
Nickel	<20	<20
Copper	<20	<20
Zinc	<100	<100
Rubidium	<1	<1
Strontium	<10	<10
Cesium	<1	<1
Water	0.09±0.02 mass%	0.46±0.05 mass%
Oxygen	0.05±0.10 mass%	0.86±0.10 mass%

Note: In ppm except where stated.

white salt with some grey material deposited in the bottom of the tube. The grey impurities were removed, and the white salt was ground for use. Karl Fischer analysis showed the product to contain 0.46% water (±0.05%); FNAA gave 0.86% oxygen. Major cationic impurities were potassium (290 ppm) and calcium (140 ppm), and the melting point was 712 °C (cf., 714 °C[10]).

Table 1 lists chemical analysis of KCl and $MgCl_2$. Table 2 provides average temperature arrests for $MgCl_2$-KCl.

2.2 Method

2.2.1 Thermal Analysis

A free-standing furnace in a nitrogen atmosphere glovebox was used for the cooling curve determinations. The furnace was designed to hold up to five silica tubes ~180 mm long and 25 mm diameter within a graphite holder.

About 20 g of the required compositions of KCl-$MgCl_2$ were weighed into the dry silica test tubes in a nitrogen dry box (~100 ppm water). Previously calibrated Chromel-Alumel thermocouples (Hoskins Manufacturing Co., 10778 Hall Rd., Hamburg, MI), each protected by a closed-end recrystallized alumina tube, were inserted into the salt mixtures, and the thermocouple output leads were connected to an analog input interface board. The temperatures of the salts were monitored by a microcomputer using a data acquisition program. The furnace was controlled by a West 2050 furnace controller* that was programmed to heat to 800 °C in 3 hours, to dwell for 30 minutes, and to cool at a rate of ~1.5 °C/min. The samples were stirred while molten to ensure mixing and to eliminate the possibility of supercooling.

Table 2 Temperature Arrests for Various Compositions of $MgCl_2$-KCl

$MgCl_2$, mol%	Average temperature arrests, °C		
0	768	...	...
10	710	429	...
20	635	427	...
25	560.5	427	...
30	443	426.5	...
31	427	...	...
32	426	426	...
33	428	...	...
34	429	...	...
35	440	426	...
37	437	...	...
40	467	442	426
42	473	443	427
45	487	440	425
47	488	439.5	420.5
50	488.5	...	...
52	488.5	465.5	...
55	488.5	465.5	...
57	479	473	...
60	475	...	...
65	474	...	...
68	473	...	...
70	595	470	...
80	635.5	473	...
90	683.5	473	...
100	712	...	...

Phase changes occurring during the cooling of the molten salt produced temperature arrests that were detected visually on plotted traces of the cooling curves, *e.g.* Fig. 8. The temperature arrest was read at the highest point on the plateau and quoted to the nearest 0.5 °C. From the temperature arrests, a phase diagram was constructed of $MgCl_2$ mol% against temperature (Fig. 9).

2.2.2 Differential Thermal Analysis (DTA)

Several samples were analyzed by DTA using a Perkin-Elmer DTA 1700 System (Perkin-Elmer Corp., 761-T Main Ave., Norwalk, CT) to establish the temperature at which the phase changes occurred.

The samples were crushed, and 10 to 15 mg of each were loaded into a platinum sample cup. The sample was surrounded by alumina powder to prevent contact with the air and platinum, and a control cup was filled with alumina powder. The sample and the inert reference sample (lead) were heated under identical conditions, and any temperature difference that developed between them was recorded. The samples were analyzed over the temperature range 30 to 1200 °C at a heating rate of 10 °C/min in an atmosphere of air or argon at 50 ml/min. An example of a trace obtained is shown in Fig. 10, and a determination with pure aluminum showed the temperature to have an accuracy of ±1 °C.

2.2.3 X-Ray Analysis

Several samples were analyzed by XRD.

Two samples (20 and 33 mol% $MgCl_2$) were analyzed to establish the presence of the K_4MgCl_6 and the K_2MgCl_4 compounds; a $MgCl_2$ (40 mol%)-KCl sample was examined for

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*West Instruments, Mark IV Instruments Ltd., The Hyde, Brighton, E. Sussex, BN2 4JU, UK; or East Greenwich, RI 02818-0962, USA.

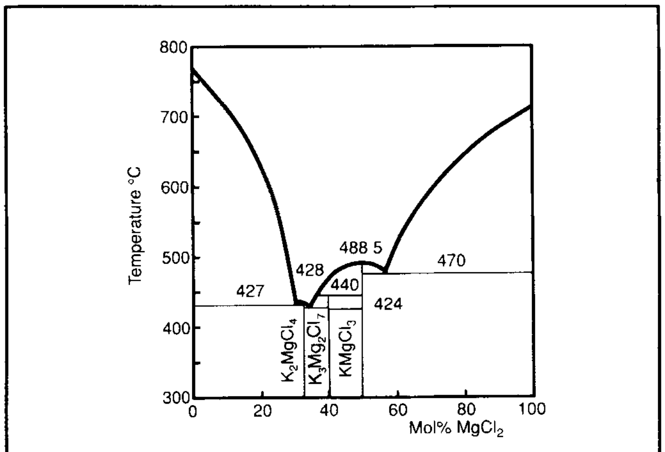

Fig. 9 $MgCl_2$-KCl phase diagram. From this work.

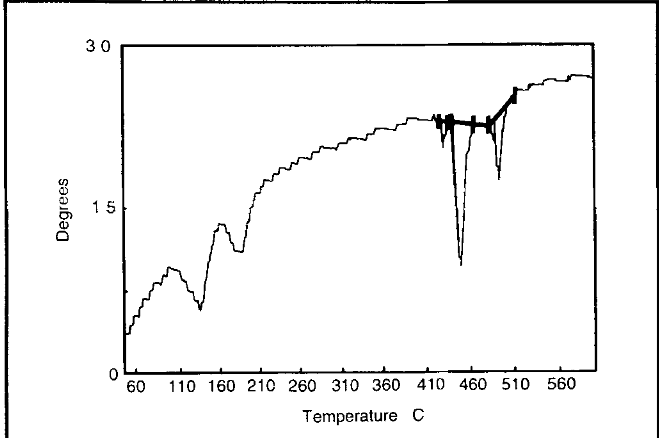

Fig. 10 Example of DTA trace for $MgCl_2$ (45 mol%)-KCl.

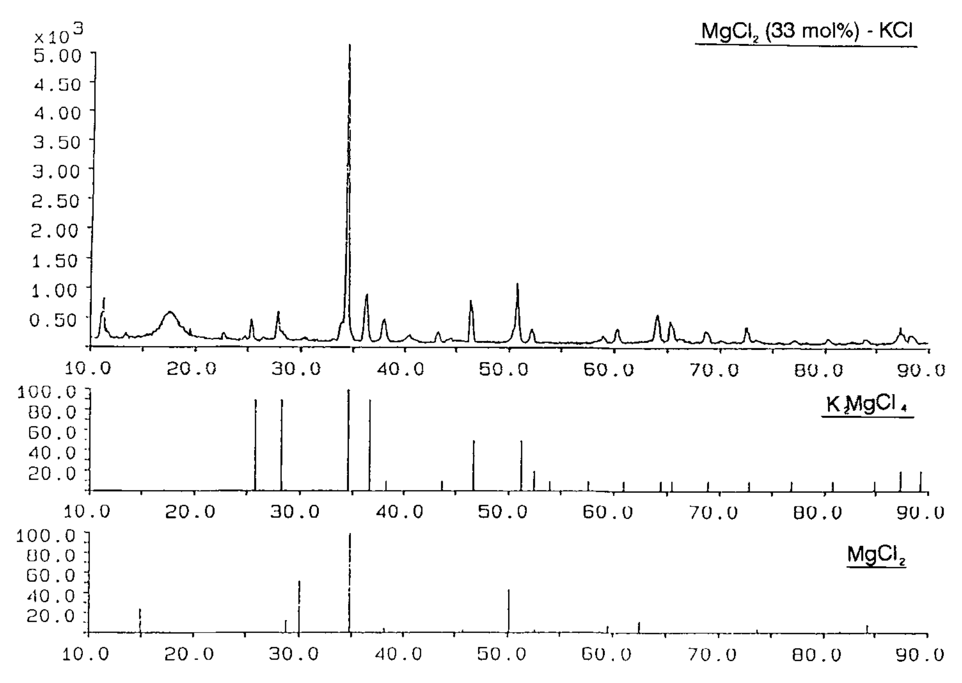

Fig. 11 XRD pattern for $MgCl_2$ (33 mol%)-KCl.

$K_3Mg_2Cl_7$. This sample was first heated to 800 °C, cooled to 434 °C (a temperature just above the additional phase change), and held at this temperature for four hours. The sample was then quenched by being removed from the furnace and poured into a platinum crucible.

Several other samples, quenched and slow cooled, were submitted from the region of $MgCl_2$ (35 to 50 mol%)-KCl.

A finely powdered sample of each composition was prepared, and a thin film of the salt was loaded into a sample holder, care being taken to ensure a smooth surface for deflection.

The sample was covered with polycarbonate film and transported in a sealed container for immediate analysis. Analysis was carried out using a diffractometer with Cu Kα radiation. The peaks in the resulting diffraction pattern were assigned "d" values and intensities, and these values were matched with possible compounds. The diffraction patterns obtained for the $MgCl_2$ (33 mol%)-KCl sample and the $MgCl_2$ (40 mol%)-KCl sample are shown in Fig. 11 and 12.

3. Results and Discussion

The thermal analyses gave the temperature arrests for the various compositions of $MgCl_2$-KCl with the constructed phase diagram in Fig. 9, which shows $MgCl_2$-KCl is a system with three eutectic points and two congruently melting compounds. The melting points of $KMgCl_3$ and K_2MgCl_4 were found at 488.5 °C and 428 °C, respectively. The eutectic temperatures

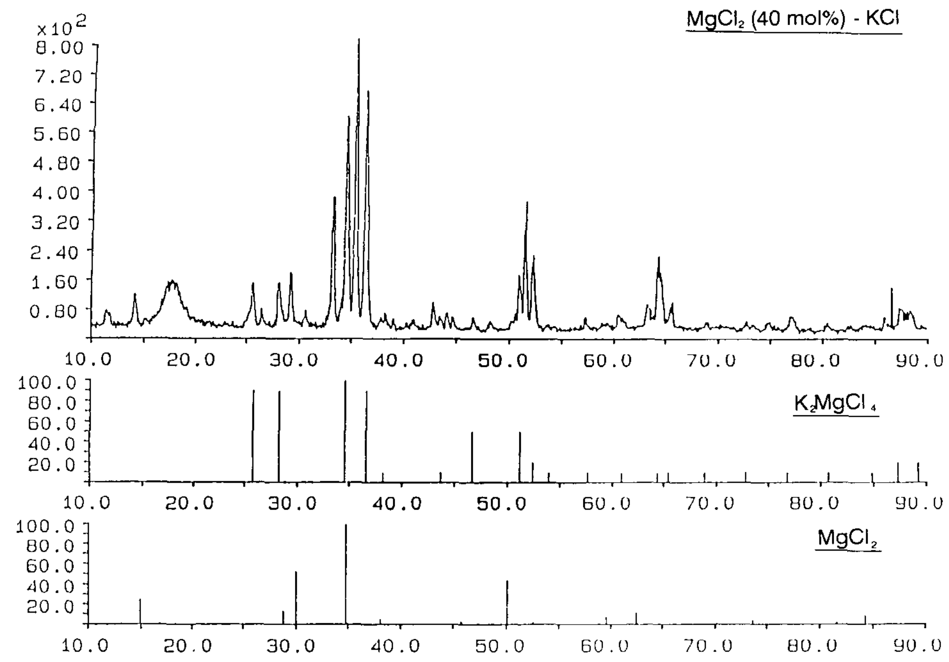

Fig. 12 XRD pattern for $MgCl_2$ (40 mol%)-KCl.

were 427 °C, 426 °C, and 470 °C, at 31, 35, and 57 mol% $MgCl_2$, respectively. These results are in good agreement with the work of Grjotheim[6] and Seifert *et al.*[7-9,11,12] However, there was no evidence from XRD for the existence of the K_4MgCl_6 compound found by Seifert at 20 mol% $MgCl_2$. The peritectic of $K_3Mg_2Cl_7$ (melting point 440 °C) was ~36 mol% $MgCl_2$, cf 442 °C and 35 mol% $MgCl_2$ found by Seifert and Fink.[7] The peritectic at 30 mol% $MgCl_2$ (429 °C) was not observed because our measurement system is not sufficiently sensitive.

The melting temperature (428 °C) of K_2MgCl_4 was difficult to establish, and this region was examined in detail.

The maximum here is very flat, and the analysis of the X-ray pattern for the $MgCl_2$ (33 mol%)-KCl sample showed two phases, one crystalline and one amorphous, but the compound present could not be identified using the JCPDS database of patterns. The pattern agreed with the XRD pattern of K_2MgCl_4, published by Klemm[3] (Fig. 11). The pattern was subsequently confirmed by Seifert[8] and Gibbons, Reinsborough, and Whitla[13] as tetragonal K_2MgCl_4, although with slightly differing C values.

Klemm *et al.*[3] point out additional thermal effects at 12 °C above the eutectic between the two compounds (Fig. 3). They disputed the existence of the second compound because the maxima is very flat and could be interpreted as a eutectic between $KMgCl_3$ and KCl. However, evidence for the formation of K_2MgCl_4 was confirmed by their X-ray analysis, although the rate of cooling and dwell seems to play a part in its formation. Grjotheim, Holm, and Rotnes[6] (Fig. 6) also only found this congruently melting compound at 431 °C on close examination of the area and using X-ray analysis.

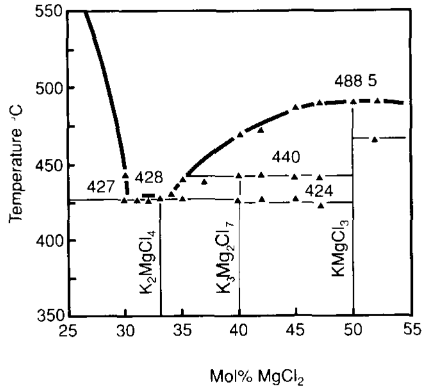

Fig. 13 $MgCl_2$-KCl phase diagram showing 25 to 55 mol% $MgCl_2$ region.

The most interesting results were between 40 to 50 mol% $MgCl_2$ where additional thermal effects take place at 424 °C (Fig. 13). To investigate further, XRD (room temperature) and DTA were carried out on compositions in this region.

The XRD pattern for the quenched $MgCl_2$ (40 mol%)-KCl sample showed a major amount of K_2MgCl_4 with small amounts of $KMgCl_3$ and $K_3Mg_2Cl_7$ (Fig. 12).

Only Klemm *et al.*[3] and Ivanov[4] show the additional phase change at ~443 °C on their phase diagrams. Ivanov[4] shows four phase changes (which infringes on the phase rule) in the 0 to 50 mol% $MgCl_2$ region, but the diagram as a whole differs from any previous interpretations (Fig. 4). We have examined Ivanov's original results,[4] and interpret the system as similar to our own.

Table 3 Differential Thermal Analysis Results

$MgCl_2$, mol%	Temperature of identified phase changes, °C				
33	138.9	183	432.1	...	...
40	120	180.3	429.8	445.6	...
45	134.3	187.2	428	445.3	489.9
40	...	158.85	426.6	444.8	489.65
42	133.7	179.1	425.5	444.7	492.3
47	...	...	...	441.7	497.7
47 (Merck)	...	...	440.6	467.3	488.5

The existence of additional thermal effects in the 40 to 50 mol% $MgCl_2$ region is firmly established in this work as the cooling curves for this region clearly show the three temperature arrests (see Fig. 8). Several experiments were carried out on 40 to 50 mol% $MgCl_2$ compositions to confirm the presence of the additional phase change at ~424 °C.

Heating and cooling curves were recorded for four of the compositions in this region, following an overnight dwell of the samples in the molten state. The results were similar to those obtained earlier. Several compositions were reanalyzed using ultrapure $MgCl_2$* with a longer dwell period and slower cooling rate. This did not produce any significant difference in the values obtained for the temperature arrests. An experiment was also carried out by heating a composition under argon until molten and by bubbling HCl through it for 30 minutes to eliminate the possibility of oxychlorides forming. The cooling curve was then redetermined, but the temperature arrests did not change significantly.

The DTA results (Table 3) also verify the three phase changes between 400 and 500 °C at 33 to 50 mol% $MgCl_2$. The 33 mol% $MgCl_2$ sample gave one peak in the 400 to 500 °C region, as expected for the formation of a congruently melting compound. Samples 42 and 45 mol% $MgCl_2$ showed three peaks in the 400 to 500 °C range. The 40 mol% $MgCl_2$ samples showed two peaks on the DTA trace with a possible, poorly resolved third peak, which appears as a shoulder. Another 40 mol% $MgCl_2$ sample gave three fully resolved peaks. Two samples of 47 mol% $MgCl_2$ were analyzed, one containing $MgCl_2$ anhydrous from Merck. (Table 4 shows the chemical analysis.) This was to eliminate the possibility of the additional phase change on the DTA trace being due to impurities in the HCl dried $MgCl_2$. The anhydrous sample gave three peaks. The DTA also indicated the presence of water in the salts, shown by the peaks between 100 and 200 °C. However, no evidence for water was shown on the cooling curves carried out in this temperature range. It was therefore assumed that the samples had been exposed to air while awaiting DTA.

Following a suggestion by Seifert,[14] four samples were annealed (360 °C for 9 days) before carrying out heating and cooling curves (100 °C/h). The "phase change" was still observed in all the samples.

Several explanations for the additional thermal effects at ~424 °C have been considered. The possible formation of solid solutions was investigated through the application of the Roozeboom[15] criteria, which link them to idealized cooling curves. Tammann plots were also made. However, neither approach yielded a sensible correlation with the experimental data. Stabilization of a new compound through impurities in the $MgCl_2$ (such as oxide) was eliminated through the experiments with HCl and the use of pure $MgCl_2$.

Table 4 Analysis of Merck Magnesium Chloride Anhydrous

Element	Chemical analysis
Water content	0.1 mass%
Aluminum	4.7 ppm
Barium	0.4 ppm
Calcium	11 ppm
Copper	<0.6 ppm
Iron	0.8 ppm
Manganese	0.4 ppm
Sodium	9.0 ppm
Nickel	<1.1 ppm
Silicon	344 ppm
Strontium	0.1 ppm
Zinc	4.7 ppm

The most favored explanation is a lack of equilibrium in the 40 to 50 mol% $MgCl_2$ region, although this appears to be unsupported by the measurements on samples held at 360 °C. Indeed the results of those experiments and the degree of agreement with our earlier data and the results of Ivanov[4] suggest the opposite. Unfortunately, Ivanov denies the formation of the compound K_2MgCl_4 during the solidification process. Instead, he says "no third thermal effect representing decomposition of the variable composition phase is found on the cooling curves, and that the phase (called A), covering the 4% $MgCl_2$ concentration region, only exists in pure form at temperatures of 425 to 440 °C ...". We have noted that two earlier workers (Klemm *et al.*[3] and Fink,[14] Ph.D. thesis transcript) also observed these thermal effects. Although we are inclined to agree with the hypothesis of nonequilibria, the phase diagram of this system is still far from settled.

4. Conclusions

The redetermination of the $MgCl_2$-KCl phase diagram has shown it to be a system with three eutectics and two congruently melting compounds, $KMgCl_3$ and K_2MgCl_4, which is in agreement with most of the previous references. The peritectic of $K_3Mg_2Cl_7$ was found at 36 mol% $MgCl_2$. The peritectic near 30 mol% $MgCl_2$ was not detected.

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*Obtained from APL Engineered Materials Inc., 2401 N. Willow Road, Urbana, IL 61801-7332.

An additional phase change was found in the $KMgCl_3$-$K_3Mg_2Cl_7$ phase field at 424 °C between 40 to 50 mol% $MgCl_2$. No explanation is offered for the additional thermal effects.

Acknowledgments

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