

The Quinary Reciprocal Salt System Na,K,Mg,Ca/Cl,SO₄—A Review of the Literature With New Data

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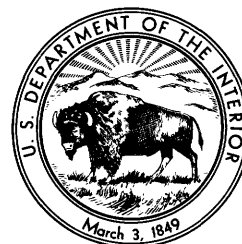


The Quinary Reciprocal Salt System Na,K,Mg,Ca/Cl,SO₄—A Review of the Literature With New Data

By J. J. ROWE, G. W. MOREY and C. S. ZEN

G E O L O G I C A L S U R V E Y P R O F E S S I O N A L P A P E R 7 4 1

*A discussion of the melting relations and interactions of
components of the NaCl-K₂SO₄-MgSO₄-CaSO₄ system as
applied to the crystallization-differentiation of the
Gnome melt*



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PREFACE

The $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ system and its component subsystems were studied by the authors under the direction of G. W. Morey. This work, supported by the U.S. Atomic Energy Commission, was undertaken to develop a theory for the crystallization, during cooling, of the mass of salt melted by the underground nuclear explosion Gnome near Carlsbad, N. Mex.

With the death of G. W. Morey on October 3, 1965, it was decided to conclude the major experimental work and present the data assembled in this report. This report is not a completed study of the extremely complex systems; there is considerable experimental work yet to be performed. Nevertheless, the comprehensive data presented herein can be of value to future studies of these and related systems.

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THE QUINARY RECIPROCAL SALT SYSTEM $\text{Na,K,Mg,Ca/Cl,SO}_4$ — A REVIEW OF THE LITERATURE WITH NEW DATA

By J. J. ROWE, G. W. MOREY, and C. S. ZEN

ABSTRACT

Data from the literature, supplemented by new experimental results, are presented for 28 binary systems, 13 ternary systems, six ternary reciprocal salt systems, and four quaternary reciprocal salt systems that make up the quinary reciprocal salt system $\text{Na,K,Mg,Ca/Cl,SO}_4$. The data were extrapolated to the pseudoquaternary system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ to develop a theory for the crystallization-differentiation of the salt melted by the Gnome underground nuclear explosion in the Salado Formation near Carlsbad, N. Mex.

INTRODUCTION

The Gnome experiment, an underground nuclear explosion, was one event in the Plowshare program to evaluate the peaceful uses of atomic energy. To resolve problems such as the recovery of the radioisotopes generated by the device and absorbed by the surrounding rocks, it was necessary to study the course of crystallization of the molten mass of salt during cooling after the explosion in the Salado Formation near Carlsbad, N. Mex.

To develop an understanding of the phase relations of the $\text{Na,K,Mg,Ca/Cl,SO}_4$ system, a critical compilation was made of the data in the literature. This was supplemented by additional experimental study to determine the stable parts of the system and to resolve some of the discrepancies in the literature.

The system consists of NaCl , K_2SO_4 , MgSO_4 , and CaSO_4 . The approximate mineralogical composition of the Gnome material according to Nathans (1965) is 72 percent halite, 12.5 percent polyhalite, 8 percent silt and clay, 5.5 percent anhydrite, and 2 percent water. Neglecting silt, clay, and water, the composition of the material is 80.7 percent NaCl , 4 percent K_2SO_4 , 2.8 percent MgSO_4 , and 12.5 percent CaSO_4 . Projected to the base of the tetrahedron as shown in figure 1, the composition, in terms of sulfate, is 21 percent K_2SO_4 , 15 percent MgSO_4 , and 64 percent CaSO_4 . This system is of geologic interest insofar as the compounds and minerals represent

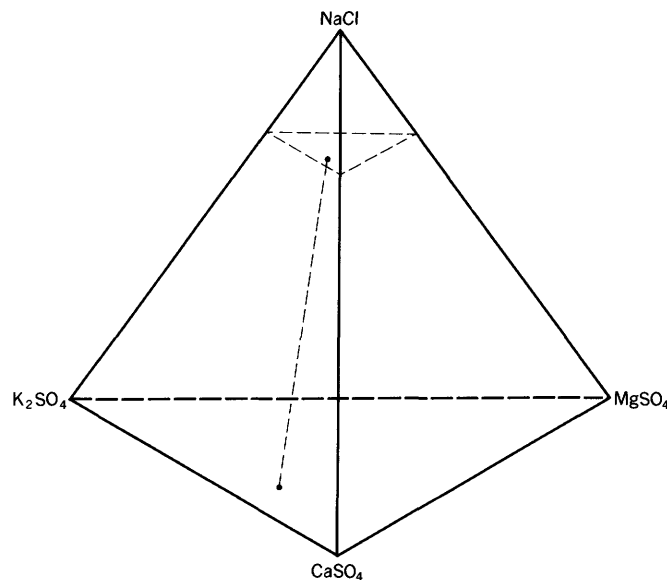
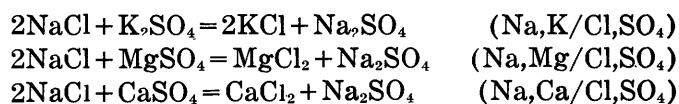


FIGURE 1.—The system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ with the Gnome composition projected to the base.

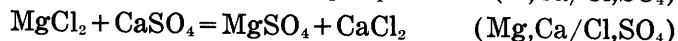
anhydrous end members of many naturally occurring hydrated mineral systems.

The four component system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ is represented by a tetrahedron (fig. 1) bounded by the following ternary systems: $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$, $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$, $\text{NaCl-K}_2\text{SO}_4\text{-CaSO}_4$, and $\text{NaCl-MgSO}_4\text{-CaSO}_4$. The ternary system K,Mg,Ca/SO_4 , shown as the base of the tetrahedron, is a straightforward ternary system which has been studied by Mukimov, Krylova, and Bergman (1949) and restudied by Rowe, Morey, and Silber (1967).

The other three ternary systems are made complex by the formation of reciprocal salts. NaCl reacts with each of the sulfates to form the following three ternary reciprocal salt systems, each consisting of two anions and two cations:



The secondary reactions of MgCl_2 , CaCl_2 , and KCl with the sulfates provide three more systems:



Each of the three ternary sides of the tetrahedron (fig. 1) can be considered as a plane across a prism representing a quaternary reciprocal salt system. A quaternary reciprocal salt system is bounded by three ternary reciprocal salt systems. For example, we can show the $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ system as a plane across the Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system, as in figure 2. Another plane across the prism from two chlorides to one sulfate will further subdivide the prism into three quaternary systems. If the planes represent true ternary sys-

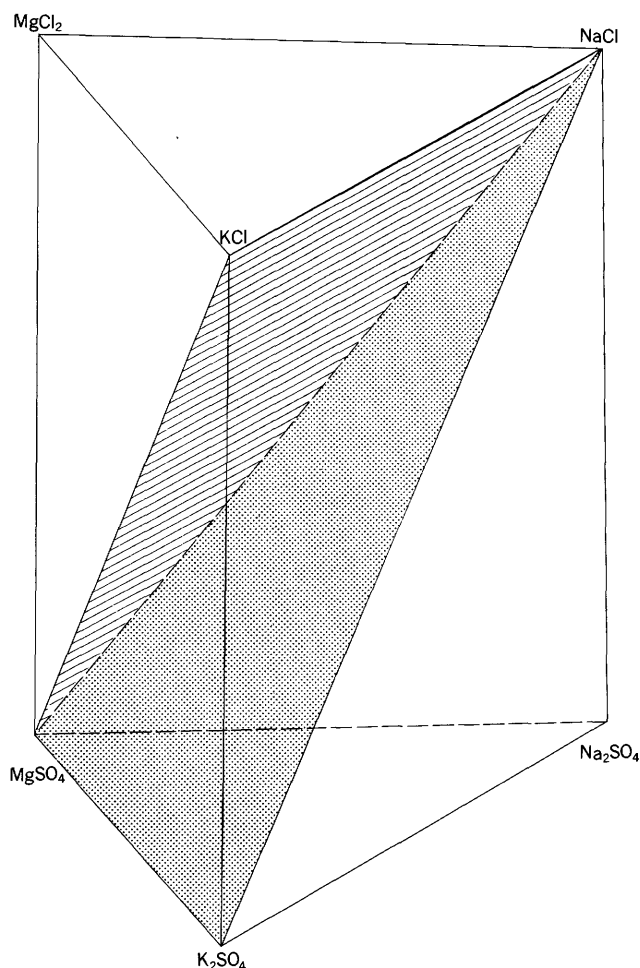


FIGURE 2.—The systems $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ (shaded) and KCl-NaCl-MgSO_4 (ruled) as planes across the quaternary reciprocal salt system Na,K,Mg/Cl,SO_4 .

tems, then each quaternary system formed can be treated as an individual system.

The complexity of the system under study is apparent. The quaternary system of figure 1 can be considered to be part of the quinary reciprocal salt system $\text{Na,K,Mg,Ca/Cl,SO}_4$. Ricci (1964) discussed some of the problems of representing phase diagrams of the molten salts in reciprocal salt systems. The entire problem is further complicated by the high temperature decomposition of MgSO_4 and CaSO_4 to MgO and CaO , respectively; the volatilization of NaCl ; and the extensive occurrence of complex solid solutions.

We summarize data from the literature supplemented by some experimental study of the eight possible components (five of which are independent), 28 binary systems, 13 of the 56 ternary systems, six ternary reciprocal salt systems, and four quaternary reciprocal salt systems shown in figure 3. Our presentation of this extremely complex problem will be to develop information for the $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ system which is the base of the tetrahedron of figure 1 and then to describe each ternary side as a plane across the quaternary reciprocal salt system. Finally, we will discuss the tetrahedron and its component sections as related to the crystallization of the Gnome material.

EXPERIMENTAL METHODS

Charges to be studied were prepared from purified reagents that were checked by X-ray diffraction and by spectrographic analysis. These mixtures were repeatedly melted, ground, mixed, and remelted.

Compositions rich in MgSO_4 or CaSO_4 could not be prepared by melting because of the decomposition of MgSO_4 to MgO and CaSO_4 to CaO at high temperatures. We found that we could achieve reactions in the solid state without decomposition by heating the charges at $700^\circ\text{--}800^\circ\text{C}$ over a period of several weeks. The heating was interrupted periodically for mixing and grinding. X-ray diffraction patterns were run during this process to check on the progress of the reactions. We found that compositions could also be prepared hydrothermally. The mixed and ground components were placed in a 10-ml (milliliter) platinum crucible which was inserted into a Morey bomb (Morey and Ingerson, 1937). The crucible was loosely covered with a platinum cover and the bomb was closed. After heating to 600°C in a furnace, water was pumped into the bomb to generate 7,500 psi (pounds per square inch) of steam pressure. The pressure and temperature

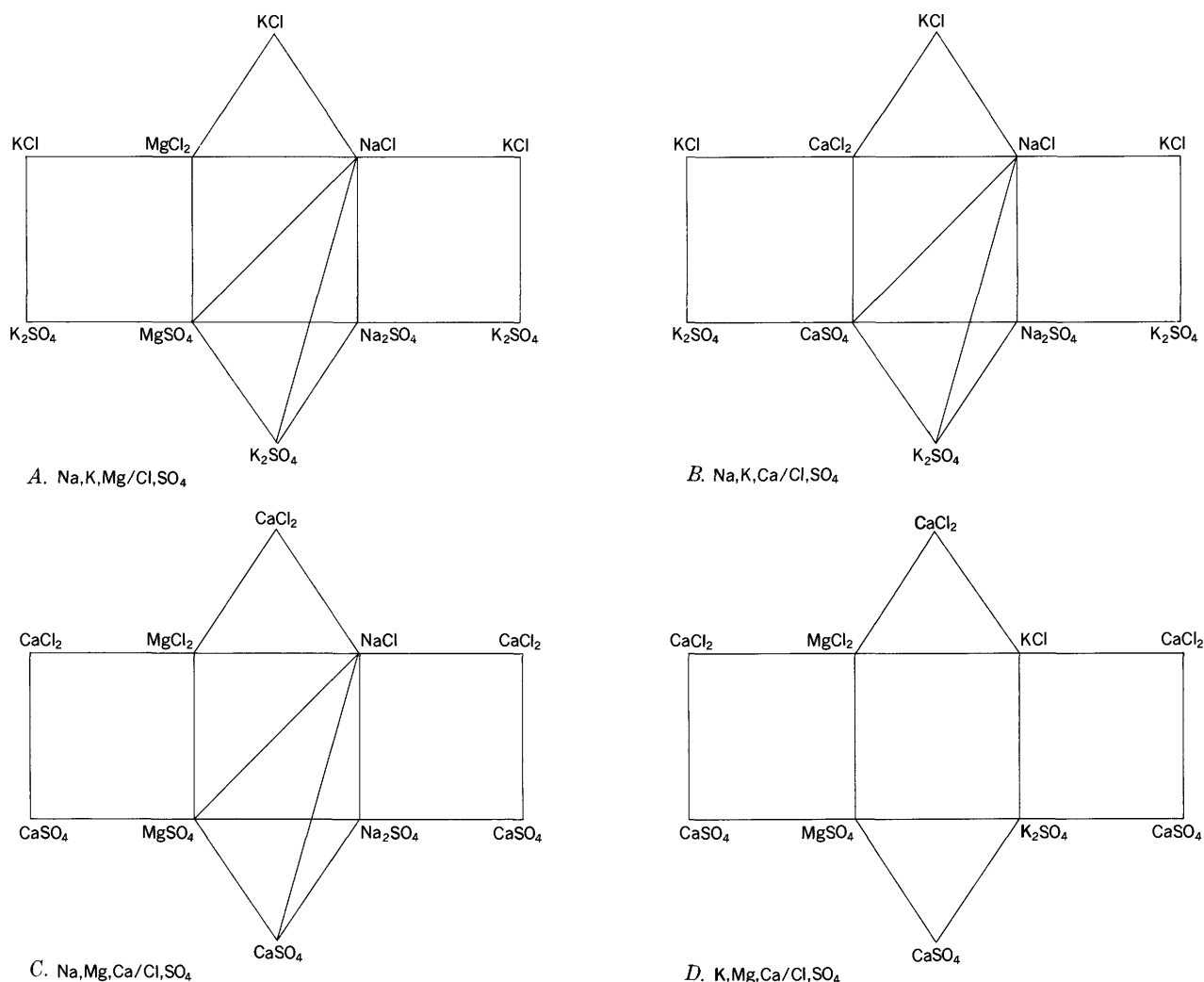


FIGURE 3.—The four quaternary reciprocal salt systems (A, B, C, and D) and their constituent binary, ternary, and ternary reciprocal salt systems which compose the quinary reciprocal salt system Na,K,Mg,Ca/Cl,SO₄.

were maintained for 1 to 2 days. Pressure was then reduced to atmospheric and heating continued for about 15 minutes to eliminate water. The bomb was permitted to cool slowly before opening. The crucible with the powders was weighed to determine whether any loss occurred and also to assure that water which might form hydrates was not absorbed.

Thermocouples used for quenching and heating-cooling studies were standardized against a thermocouple calibrated by the Bureau of Standards. Thermocouples were also checked using the known melting temperatures of NaCl (800.4°C), Na_2SO_4 (884°C), $Na_2Si_2O_5$ (874°C), and the alpha-beta quartz inversion (573°C).

Quenching studies were made by the usual method (Morey, 1923) of placing a small amount of the powdered material in a platinum foil envelope and dropping the envelope into mercury after the ma-

terial had been subjected to a definite temperature for a suitable time to assure equilibrium. The quenched material was then examined using the petrographic microscope and X-ray diffractometer to identify crystalline phases and to determine whether melting had occurred. If the equilibrium temperature was below the liquidus temperature, crystalline material represents the primary phase, whereas glass or quenched crystals represent liquid in equilibrium with the crystals.

For quenching study of compositions which decompose before melting, such as $MgSO_4$ above 900°C, the powder was sealed in a platinum tube. The decomposition of some $MgSO_4$ to SO_3 plus MgO produced the pressure necessary to prevent further decomposition of the balance of the $MgSO_4$.

Heating-cooling curves were made for many of the compositions to determine subsolidus, eutectic,

and liquidus thermal effects. A small platinum crucible containing the sample was suspended in an electric furnace. A thermocouple of platinum versus platinum with 10-percent rhodium measured the temperature of the samples, and a thermocouple of "platinel" (Donne, 1964) with one junction in the sample and the other junction in refractory tubing just above the sample measured the difference in temperature between the sample and its environment. These measurements were simultaneously plotted by a multichannel strip chart recorder. A furnace temperature controller was programmed to automatically cycle at a uniform rate between set limits. Usually the rate was 5° to 10° per minute but was varied to achieve the best results for the particular composition under study.

Thermal analysis utilizing heating-cooling curves or a modified DTA (differential thermal analysis) is a classical method which provides data regarding structure inversions, unmixing, solidus reactions, and eutectics, as well as liquidus temperatures. Thermal analysis methods, however, are nonequilibrium procedures. Sluggish reactions may not give detectable thermal effects. When metastable phases persist during cooling (undercooling), erroneous results may be obtained.

Hot-stage microscopy was also used to determine liquidus temperatures. The sample was placed directly on the loop of a thermocouple and inserted into a small furnace on the microscope stage. The behavior of the sample was observed during heating and cooling under low magnification with transmitted light.

The large number of systems to be examined for this study required that we refer to results of many other investigators. Most of the German work was done using thermal analysis. The Russian studies were made using the so-called visual polythermal method of Kurnakov as modified by Kumanin and described by Bergman (1955). This method is based on the observation of the surface of the liquid in a platinum crucible. The liquidus temperature is the temperature at which the last crystals will disappear during heating or the first crystals will appear on cooling. Little or no information regarding primary phases or subsolidus effects can be derived from this method.

For some systems, there are differences in the data reported by various investigators. These differences are to be expected considering that each study is based on an individual interpretation of observations using a variety of methods. When inconsistencies were found, we generally made laboratory

studies to resolve discrepancies; when this was not possible, we show the results of the various studies.

Some workers have reported their results in terms of mole percent, others have used weight percent. Unless otherwise indicated results given here will be in weight percent.

COMPONENTS

The system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ is not limited to four components. Reciprocal salt reactions generate four more compounds— KCl , MgCl_2 , CaCl_2 , and Na_2SO_4 —resulting in a total of eight components as follows:

NaCl: Sodium chloride melts at 800.4°C and boils at 1,445°C according to Kracek (1942).

K_2SO_4 : Potassium sulfate has a reported melting temperature of 1,069.1°C and a transition from orthorhombic to hexagonal at 583°C (Roberts, 1924). The latter has been verified by many studies including an X-ray diffractometer study by Bernard and Hocart (1961). We confirmed these results.

KCl: Potassium chloride has a reported melting temperature of 770.3°C and boils at 1,465°C (Roberts, 1924).

MgCl_2 : Magnesium chloride melts at 712°C as reported by Klemm, Beyersdorfer, and Oryschke-witsch (1948).

CaCl_2 : The melting temperature for CaCl_2 is 777°C (Scholich, 1920).

Na_2SO_4 : Sodium sulfate melts at 884.7°C (Roberts, 1924). It occurs in five enantiotropic modifications with a complicated pattern of inversion which has been described by Kracek (1929). The existence of a new high temperature form above 548°C was reported by Simanov and Kirkina (1957).

CaSO_4 : Calcium sulfate decomposes to CaO and SO_3 on heating above 1200°C in open crucibles. Numerous temperatures have been reported for the melting, decomposition, and inversion of CaSO_4 as shown in table 1.

We made our studies of the melting temperature for CaSO_4 in sealed platinum tubes by the quenching technique and found it to be 1,462°C (Rowe and others, 1965). This temperature represents a minimum, because of the formation of CaO , which would reduce the liquidus temperature as the system becomes binary (CaO-CaSO_4). Decomposition starts at about 1,200°C, making the system binary, with a eutectic at 1,365°C, 20 percent CaO according to Newman (1941).

TABLE 1.—*Compilation of reported temperatures in degrees Celsius, for the inversion, eutectic, decomposition, and melting of CaSO₄*

Reference	α - β inversion	CaSO ₄ -CaO eutectic	Decom- position	Melting
Bellanca (1942) -----	1,195	----	----	1,380
Briner, Pamm, and Paillard (1948) -----	----	----	1,000	----
Bye and Kiehl (1948) -	----	----	> 1,000	1,297
Flörke (1952) -----	> 1,110	----	----	1,450
Gay (1965) -----	----	----	1,150	----
Golubeva and Bergman (1956) ----	1,196	----	----	1,450
Grahmann (1913) ----	1,196	----	none	1,450
Gruver (1951) -----	1,230	1,350	----	----
Jänecke and Mühlhäusser (1936) -	----	----	----	1,450
Kracek (1942) -----	----	----	1,230	1,450
Masuda (1932) -----	1,232	----	----	----
Müller (1910) -----	----	----	----	1,350
Newman (1941) -----	1,214	1,365	> 1,200	----
Ostroff and Sanderson (1959) ---	----	----	1,149	----
Rowe, Morey and Silber (1967) -----	1,195	1,360	> 1,200	1,462

The inversion to a high temperature form has been questioned by Gay (1965). We observed a reversible thermal effect at 1,195°C in our heating-cooling studies but were unable to obtain crystals of the high-temperature form from our quenching experiments. We presume, as did Flörke (1952), that the high-temperature form reverts to the low-temperature form very rapidly on cooling.

MgSO₄: The determination of the temperature at which MgSO₄ melts is complicated by the decomposition to MgO and SO₃. Rowe, Morey, and Silber (1967) found by thermogravimetric analysis that MgSO₄ starts to decompose at 895°C. It was therefore necessary to use the sealed tube method to determine its approximate melting temperature.

Various temperatures have been reported for the melting of MgSO₄. Some of these are 1,185°C (Jänecke, 1912), 1,125°C (Grahmann, 1913), 1,124°C (Nacken, 1907), 1,120°C (Ginsberg, 1909), 1,187°C (Mukimov, Krylova, and Bergman, 1949), and 1,185°C (Kracek, 1942). From quenching experiments in sealed tubes, Rowe, Morey, and Silber (1967) found that MgSO₄ melts at 1,136°±4°C. Because of the formation of a small amount of MgO, this represents a minimum melting temperature.

We found that MgSO₄ exists in two enantiotropic forms. The beta form described by Coing-Boyat (1926) was easily prepared by dehydration of MgSO₄·H₂O at 700°C. The high temperature form was found after heating the β -MgSO₄ which was sealed in platinum tubes. The temperature of

the reversible transition of one form to the other is uncertain. Our results suggest that the inversion is between 997° and 1,095°C, probably close to 1,090°. The X-ray diffraction patterns for this new form are given in Rowe, Morey, and Silber (1967). Dewing and Richardson (1959) performed experiments in which N₂, SO₂, and O₂ were passed over MgSO₄ during heating while thermal effects were measured with a differential thermocouple. They report a transition at 1,010°±10°C.

THE SYSTEM K₂SO₄-MgSO₄-CaSO₄

The ternary system K₂SO₄-MgSO₄-CaSO₄ is the base of the tetrahedron for the quaternary system shown in figure 1. It consists of three binary systems: K₂SO₄-MgSO₄, K₂SO₄-CaSO₄, and MgSO₄-CaSO₄.

BINARY SYSTEMS

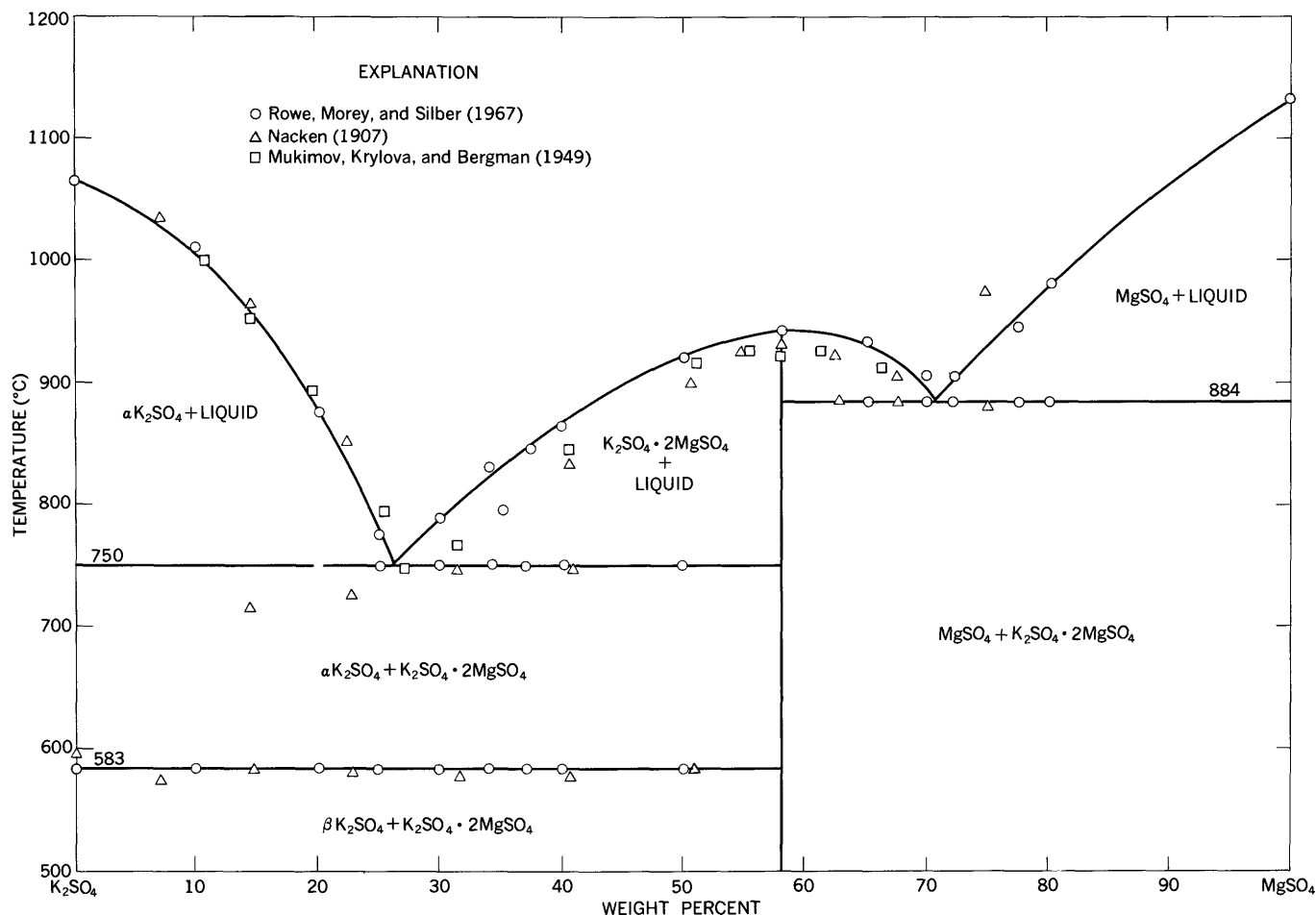
K₂SO₄-MgSO₄

The K₂SO₄-MgSO₄ system was studied by Nacken (1907), Grahmann (1913), Mukimov, Krylova, and Bergman (1949), and Rowe, Morey, and Silber (1967). Some of these results are shown in figure 4. Only one binary compound, langbeinite (K₂SO₄·2MgSO₄), is found in this system. Grahmann (1913) and also Mukimov, Krylova, and Bergman (1949) reported its melting temperature to be 930°C. By quenching techniques and heating-cooling studies, Morey, Rowe, and Fournier (1964) found that langbeinite melted at 943°C. The eutectic between langbeinite and K₂SO₄ occurs at 750°C and 27.5 percent MgSO₄. Nacken (1907) and Grahmann (1913) reported this eutectic at 750°C and 29.6 percent MgSO₄. The eutectic between langbeinite and MgSO₄ was given by Nacken (1907) as 884°C and 70.9 percent MgSO₄. We verified this value. Mixtures containing more than 80 percent MgSO₄ could not be melted in air without decomposition.

K₂SO₄-CaSO₄

The system K₂SO₄-CaSO₄ had been previously studied by Müller (1910), Grahmann (1913), Bellanca (1942), Mukimov, Krylova, and Bergman (1949), and Golubeva and Bergman (1956). The study by Rowe, Morey, and Hansen (1965) to resolve the differences between the results reported by previous investigators confirmed the results of Bellanca with only slight differences.

Calcium langbeinite (K₂SO₄·2CaSO₄) is the only compound in this binary system. It melts incongruently at 1,011°C to CaSO₄ plus a liquid of com-

FIGURE 4.—The binary system K_2SO_4 – MgSO_4 (from Rowe and others, 1967).

position 57.5 percent CaSO_4 . X-ray diffraction studies provided no evidence of the 1:1, 2:3, 1:3, or 1:4 ratios for $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4$ compounds reported by Mukimov, Krylova, and Bergman (1949) and by Golubeva and Bergman (1956). There is limited solid solution of CaSO_4 in K_2SO_4 . The eutectic between calcium langbeinite and K_2SO_4 is, at 875°C , 34 percent CaSO_4 . Figure 5, from Rowe, Morey, and Hansen (1965) shows our data plotted with that of Bellanca (1942).

MgSO_4 – CaSO_4

The binary system MgSO_4 – CaSO_4 has not been previously studied. Ramsdell (1935) and Mukimov, Krylova, and Bergman (1949) presumed that this was a simple binary eutectic system, containing no compounds. Bodaleva and Lepeshkov (1956) reported no compound formation in the system MgSO_4 – CaSO_4 – H_2O .

Investigation of this system was hampered by the decomposition of MgSO_4 above 890°C and CaSO_4

above $1,200^\circ\text{C}$. We carried out a limited study of the system by investigating (1) subsolidus reactions by long-time heating at temperatures below decomposition temperatures, (2) liquidus relationships by quenching studies of charges sealed in platinum capsules to limit the amount of decomposition of the sulfate mixtures, and (3) subsolidus reactions during hydrothermal heating at 600°C and 7,500 psi of steam pressure.

A new compound, $\text{CaSO}_4 \cdot 3\text{MgSO}_4$, containing 28.3 percent CaSO_4 was discovered, and the X-ray diffraction pattern was reported by Rowe, Morey, and Silber (1967). Compositions containing less than 28.3 percent CaSO_4 gave patterns for MgSO_4 plus $\text{CaSO}_4 \cdot 3\text{MgSO}_4$; those containing more than 28.3 percent CaSO_4 gave patterns for CaSO_4 plus $\text{CaSO}_4 \cdot 3\text{MgSO}_4$. In studies on the NaCl – CaSO_4 – MgSO_4 system, compositions on the join NaCl – $\text{CaSO}_4 \cdot 3\text{MgSO}_4$ showed the presence of NaCl plus $\text{CaSO}_4 \cdot 3\text{MgSO}_4$ (fig. 51).

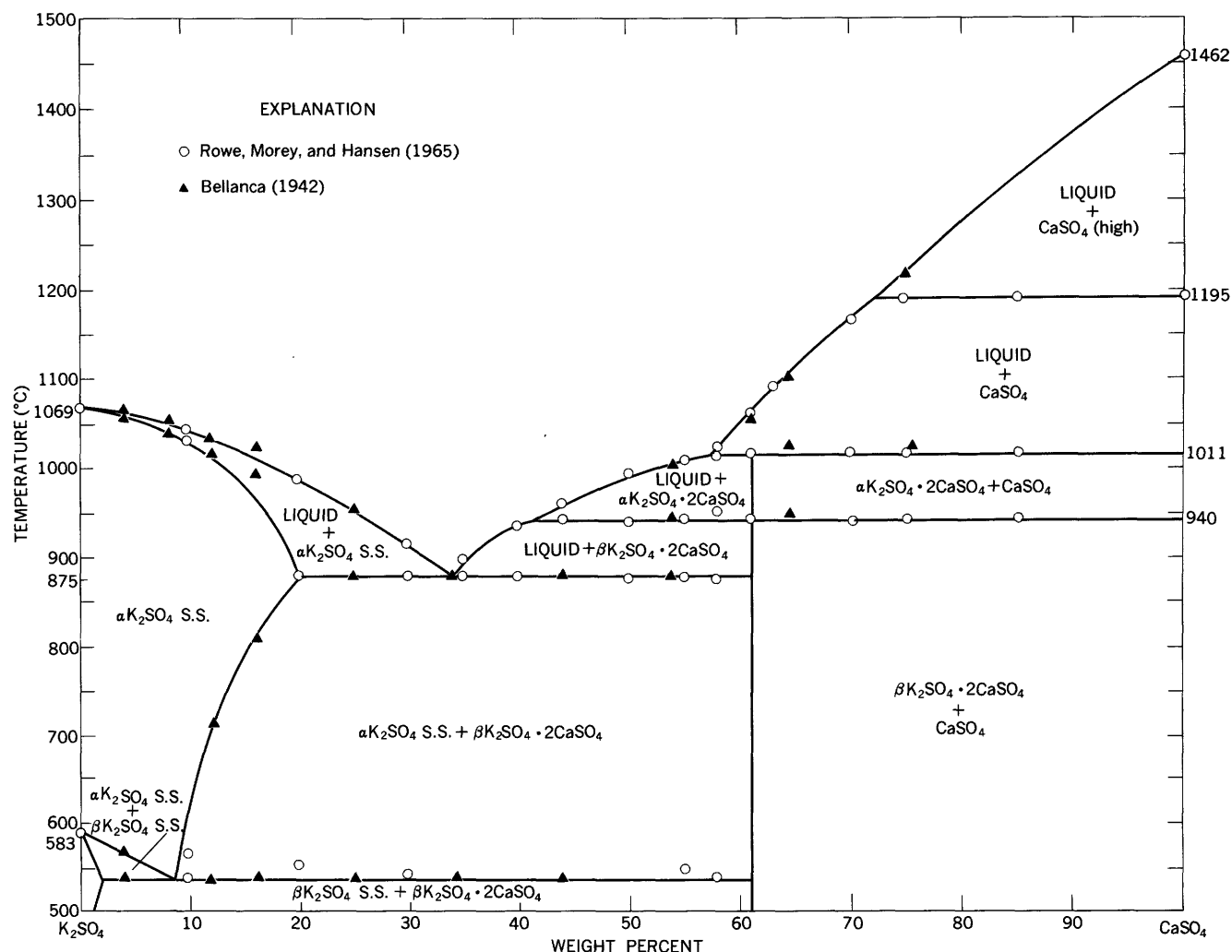


FIGURE 5.—The binary system K_2SO_4 - $CaSO_4$ (from Rowe and others, 1965). S.S. indicates solid solution.

Liquidus temperatures, determined by the sealed tube quenching technique are given in table 2. These results are subject to uncertainties which are in-

TABLE 2.—Compositions in the binary system $MgSO_4$ - $CaSO_4$

$CaSO_4$ (wt. percent)	Phases present	Liquidus temperature (°C)	Primary phase
0	$MgSO_4$	1,136	α - $MgSO_4$
5	$MgSO_4 + CaSO_4 \cdot 3MgSO_4$	-----	$MgSO_4$
10	$MgSO_4 + CaSO_4 \cdot 3MgSO_4$	-----	$MgSO_4$
13.91	$MgSO_4 + CaSO_4 \cdot 3MgSO_4$	-----	-----
15	$MgSO_4 + CaSO_4 \cdot 3MgSO_4$	-----	-----
20	$CaSO_4 \cdot 3MgSO_4 + MgSO_4$	-----	$CaSO_4 \cdot 3MgSO_4$
28.3	$CaSO_4 \cdot 3MgSO_4$	$1,201 \pm 4$	$CaSO_4 \cdot 3MgSO_4$
30	$CaSO_4 \cdot 3MgSO_4 + CaSO_4^*$	-----	-----
40	$CaSO_4 \cdot 3MgSO_4 + CaSO_4$	1,165	$CaSO_4 \cdot 3MgSO_4$
50	$CaSO_4 \cdot 3MgSO_4 + CaSO_4$	1,130	-----
53	$CaSO_4 \cdot 3MgSO_4 + CaSO_4$	1,116	$CaSO_4 \cdot 3MgSO_4$
60	$CaSO_4 + CaSO_4 \cdot 3MgSO_4$	1,140	$CaSO_4$
70	$CaSO_4 + CaSO_4 \cdot 3MgSO_4$	1,210	$CaSO_4$
80	$CaSO_4 + CaSO_4 \cdot 3MgSO_4$	1,275	$CaSO_4$
90	$CaSO_4 + CaSO_4 \cdot 3MgSO_4$	1,385	$CaSO_4$
100	$CaSO_4$	1,462	-----

* Trace $CaSO_4$.

herent in the experimental procedures. As the sulfates in the sealed tubes start to decompose, the partial pressure of SO_3 increases to prevent further sulfate decomposition. Depending on the amount of sulfate that decomposed, the final compositions may have changed slightly from those listed in table 2.

Quenching experiments using sealed platinum tubes gave erratic results in regard to phase identification. In some charges which were quenched from high temperatures, there were shifts in the X-ray lines for the $CaSO_4 \cdot 3MgSO_4$ compound, suggesting a possible partial solid solution with other compounds. Another compound may possibly be formed at high temperature in compositions containing 50 percent $CaSO_4$. Still another X-ray pattern was obtained from some charges of starting composition between $MgSO_4$ and $CaSO_4 \cdot 3MgSO_4$. However, these results do not permit positive conclusions, since some of the

observed effects may be due to decomposition reactions.

To completely describe this binary system, additional work should be performed using controlled partial pressures of SO_3 . For the scope of this study, we are assuming the binary to be a simple eutectic system with a congruently melting compound ($\text{CaSO}_4 \cdot 3\text{MgSO}_4$). The eutectics may be near 15 percent and 55 percent CaSO_4 .

DISCUSSION

The ternary system K_2SO_4 – MgSO_4 – CaSO_4 had been studied by Mukimov, Krylova, and Bergman (1949) and parts had been investigated by Ramsdell (1935). A complete restudy was made by Rowe, Morey, and Silber (1967) of compositions shown in figure 6.

The ternary system as determined by Rowe, Morey, and Silber (1967) is shown in figure 7. There are five fields of primary crystallization. Three of these are the pure components K_2SO_4 , CaSO_4 , and MgSO_4 . A solid solution field has a minimum between congruently melting langbeinite and incongruently melting calcium langbeinite. The compound $\text{CaSO}_4 \cdot 3\text{MgSO}_4$ has a field extending into the ternary system. A ternary eutectic occurs at 67.5 percent MgSO_4 , 27.5 percent K_2SO_4 , 5 percent CaSO_4 , where liquid plus MgSO_4 plus $\text{CaSO}_4 \cdot 3\text{MgSO}_4$ plus langbeinite solid solution coexist at 882°C. Another

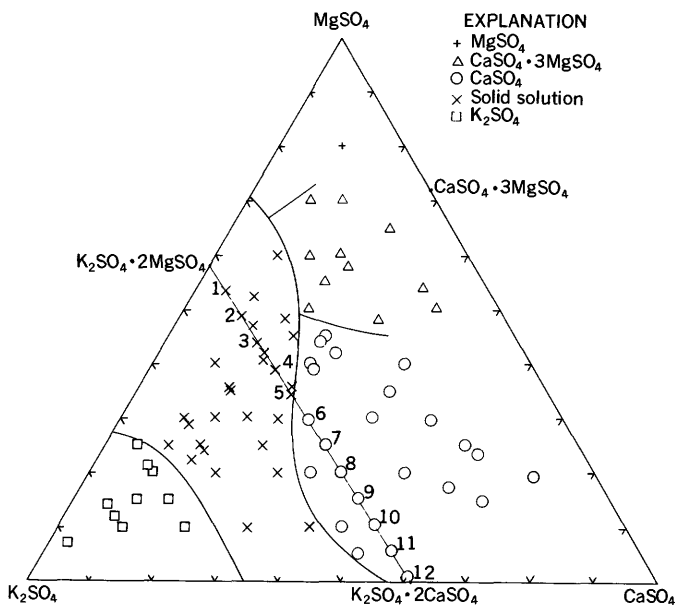


FIGURE 6.—Compositions in weight percent, studied in the ternary system K_2SO_4 – MgSO_4 – CaSO_4 . Primary phases are shown. Compositions on the join langbeinite–calcium langbeinite are numbered 1 through 12 (from Rowe and others, 1967).

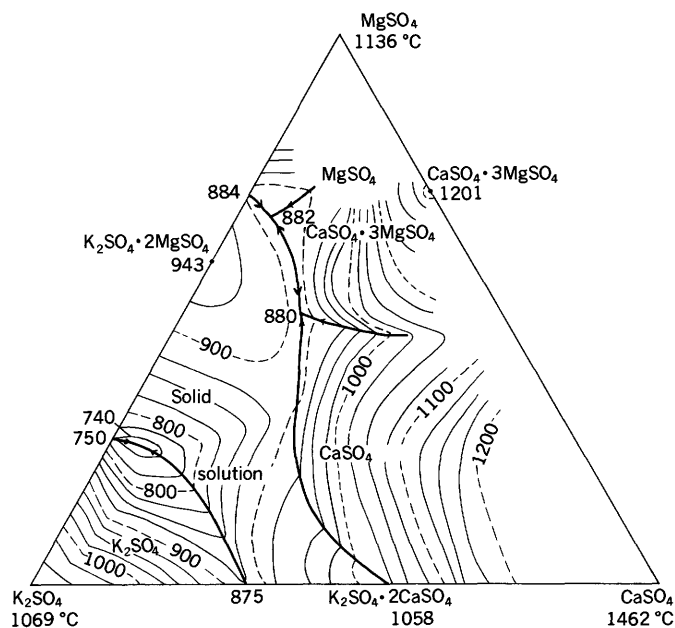


FIGURE 7.—The ternary system K_2SO_4 – MgSO_4 – CaSO_4 plotted in weight percent. Contours show liquidus temperatures; contour interval is 25°C (from Rowe and others, 1967).

eutectic at 880°C occurs at 49 percent MgSO_4 , 32 percent K_2SO_4 , and 19 percent CaSO_4 , where liquid plus CaSO_4 plus $\text{CaSO}_4 \cdot 3\text{MgSO}_4$ plus langbeinite solid solution coexist. A minimum in the system occurs at 740°C at 25 percent MgSO_4 , 69 percent K_2SO_4 , and 6 percent CaSO_4 , where liquid plus K_2SO_4 plus langbeinite solid solution coexist. This minimum is at the intersection of the trough of the solid solution field and the boundary between K_2SO_4 and the langbeinite solid solution field.

The Gnome composition, projected to the base of the tetrahedron of figure 1, in terms of sulfate, is in the field where anhydrite (CaSO_4) is the primary phase.

THE SYSTEM NaCl – K_2SO_4 – MgSO_4

The system NaCl – K_2SO_4 – MgSO_4 can be considered as a plane across the prism representing compositions in the quaternary reciprocal salt system $\text{Na}, \text{K}, \text{Mg}/\text{Cl}, \text{SO}_4$ (fig. 2). The phase relations on this plane provide one ternary side of the tetrahedron (fig. 1) representing the quasi-quaternary system NaCl – MgSO_4 – K_2SO_4 – CaSO_4 . The prism representing the $\text{Na}, \text{K}, \text{Mg}/\text{Cl}, \text{SO}_4$ system consists of the reciprocal salt systems $\text{Na}, \text{K}/\text{Cl}, \text{SO}_4$; $\text{Na}, \text{Mg}/\text{Cl}, \text{SO}_4$; $\text{K}, \text{Mg}/\text{Cl}, \text{SO}_4$; and ternary systems $\text{Na}, \text{K}, \text{Mg}/\text{Cl}$ and $\text{Na}, \text{K}, \text{Mg}/\text{SO}_4$ (fig. 3A).

Na,K/Cl,SO_4 RECIPROCAL SALT SYSTEM

The Na,K/Cl,SO_4 reciprocal salt system consists of the NaCl-KCl , $\text{NaCl-Na}_2\text{SO}_4$, $\text{KCl-Na}_2\text{SO}_4$, and $\text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ systems as edges and the $\text{NaCl-K}_2\text{SO}_4$ and $\text{KCl-Na}_2\text{SO}_4$ systems as diagonals.

BINARY SYSTEMS **NaCl-KCl**

Kurnakov and Zemczuznyj (1907) found that NaCl and KCl form a complete series of solid solutions which unmix at lower temperatures. The liquidus temperatures have been studied by Treis (1914), Jänecke (1908), Gemsky (1913), and Akopov and Bergman (1954). A minimum in the solid solution series is at 664°C and 50 mole percent (43.6 wt percent) KCl . The unmixing was studied, using X-ray diffraction methods, by Bunk and Tichelaar (1953) and also by Nguyen-Ba-Chanh (1964) who found the upper consolute temperature to be $500^\circ \pm 5^\circ\text{C}$ at 69.5 mole percent KCl (fig. 8).

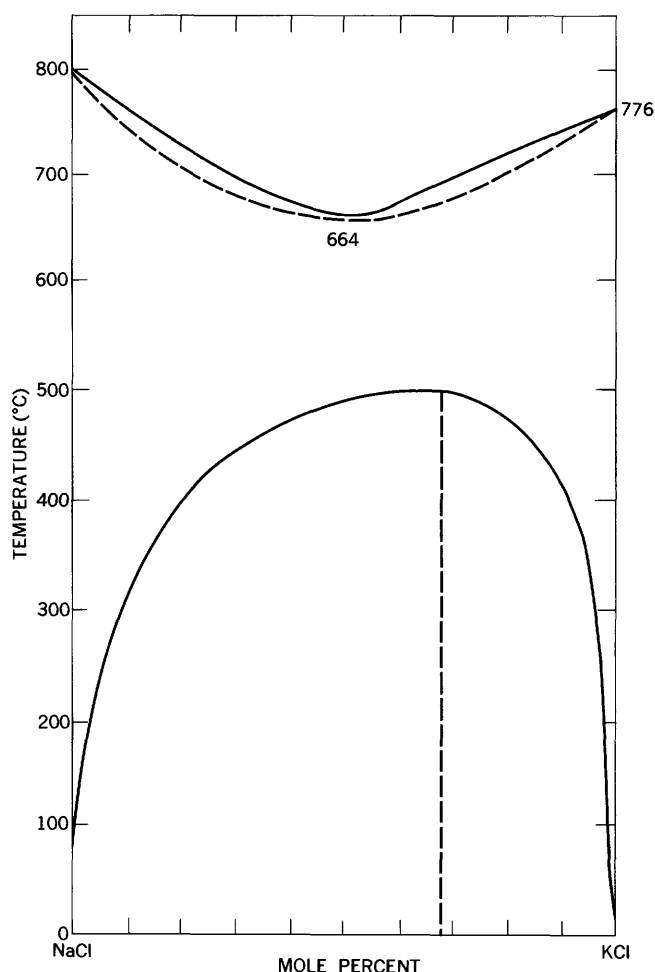


FIGURE 8.—The binary system NaCl-KCl (from Nguyen-Ba-Chanh, 1964).

 $\text{NaCl-Na}_2\text{SO}_4$

The $\text{NaCl-Na}_2\text{SO}_4$ system studied by Jänecke (1908) is a simple system with the eutectic at 628°C , and 65 mole percent (69.3 wt percent) Na_2SO_4 (fig. 9). Akopov and Bergman (1954) confirmed Jänecke's results.

 $\text{KCl-K}_2\text{SO}_4$

The $\text{KCl-K}_2\text{SO}_4$ system studied by Jänecke (1908) is a simple system with a eutectic at 690°C , 58 mole percent (55.2 wt percent) KCl (fig. 10). There was no solid solution as evidenced by the inversion temperature of K_2SO_4 , 587°C , remaining unchanged with addition of KCl . Akopov and Bergman (1954) and Golubeva and Bergman (1956) agreed with the results of Jänecke.

 $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$

Jänecke (1908), Perrier and Bellanca (1940), Bellanca (1942), and Mukimov, Krylova, and Fillipova (1949) all found a solid solution series between Na_2SO_4 and K_2SO_4 with the following temperatures reported for the minimum: 823°C (Bellanca) 845°C (Jänecke), and 830°C (Mukimov, Krylova, and Fillipova). They agreed that the minimum is at 20 mole percent K_2SO_4 . The complicated solid phase transitions were studied by Hilmy (1953). X-ray

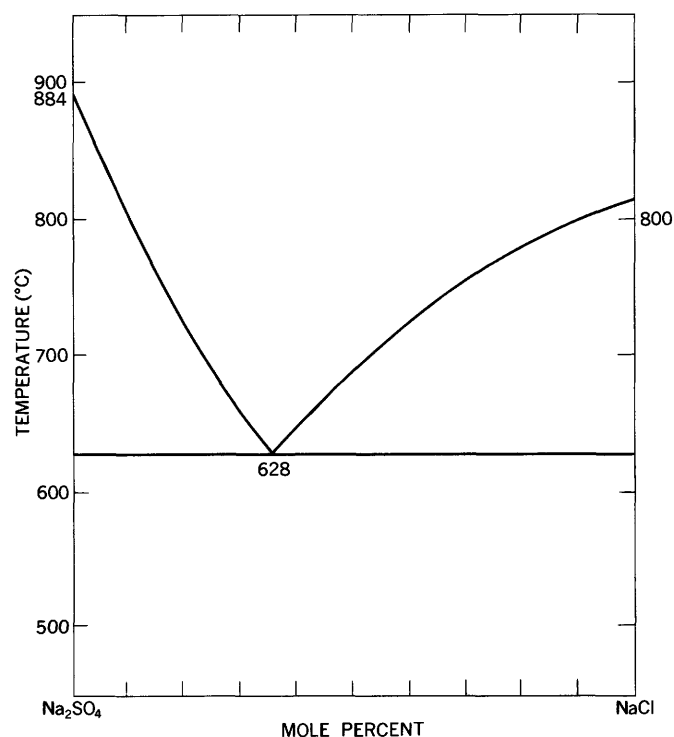


FIGURE 9.—The binary system $\text{NaCl-Na}_2\text{SO}_4$ (from Jänecke, 1908).

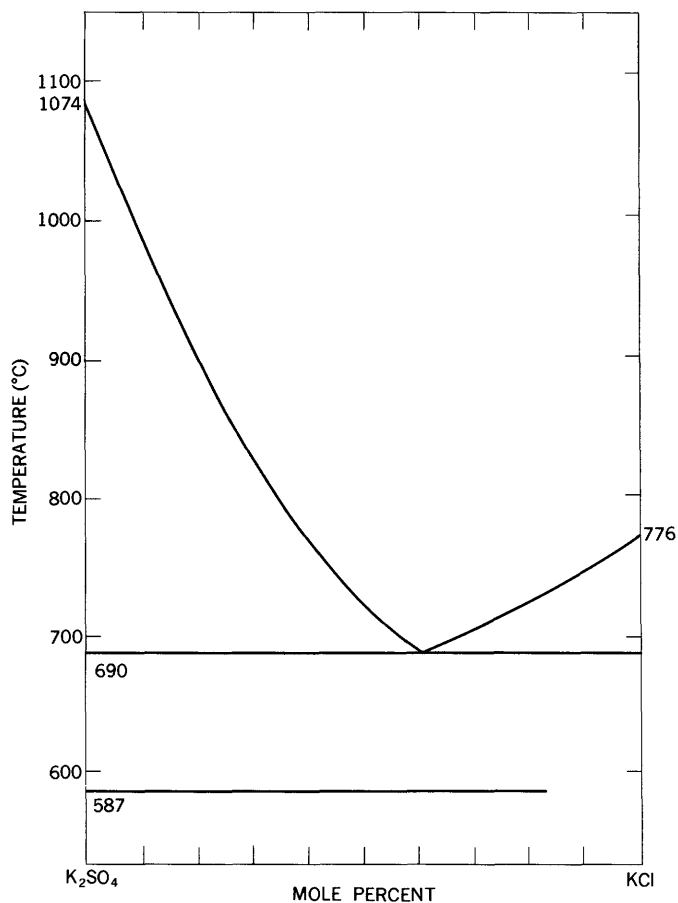


FIGURE 10.—The binary system $\text{KCl-K}_2\text{SO}_4$ (from Jänecke, 1908).

measurements of the thermal expansion of $\text{K}_3\text{Na}(\text{SO}_4)_2$ were made by Fischmeister and Rönquist (1960). Figure 11 is from Perrier and Bellanca (1940).

$\text{NaCl-K}_2\text{SO}_4$

We found the join $\text{NaCl-K}_2\text{SO}_4$ in the reciprocal salt system Na,K/Cl,SO_4 to be a pseudobinary diagonal crossing the fields of NaCl ; $(\text{Na,K})\text{Cl}$ solid solution; KCl ; $(\text{Na,K})\text{SO}_4$ solid solution; and K_2SO_4 . KCl was the primary phase from 66.4 percent K_2SO_4 to 54 percent K_2SO_4 .

Jänecke (1908) treated this diagonal as a binary system with a eutectic at 540°C and 65 mole percent (60 wt percent) K_2SO_4 . Akopov and Bergman (1954, 1959) found that it was not a binary but a pseudobinary diagonal. Our results and those of Jänecke and Akopov and Bergman are plotted in figure 12.

Many of the subsolidus thermal effects observed in heating-cooling studies represent the complex

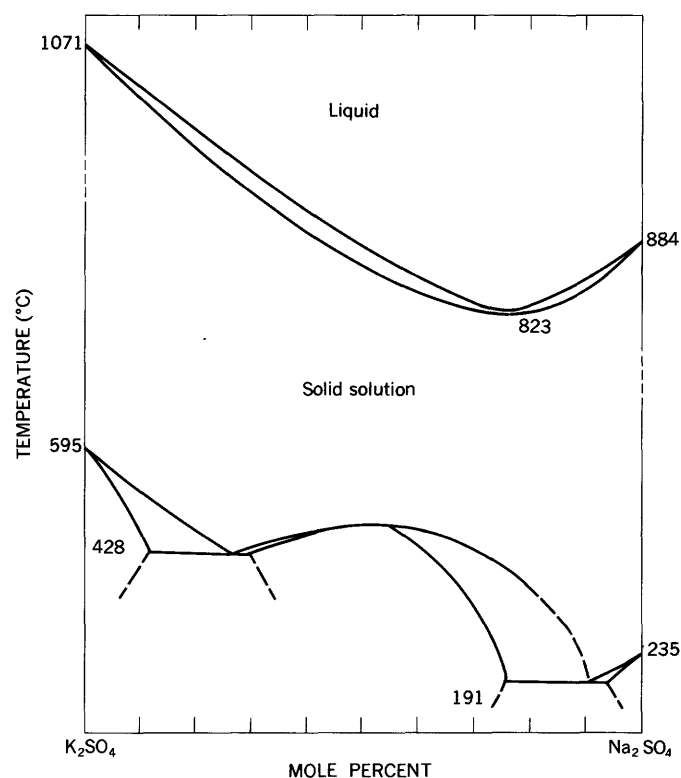


FIGURE 11.—The binary system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ (from Perrier and Bellanca, 1940).

unmixing of the $(\text{Na,K})\text{Cl}$ solid solution and reactions of the $(\text{Na,K})\text{SO}_4$ solid solution series. We and Jänecke did not attempt to resolve these thermal effects.

This join is one side of the plane $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ and the plane $\text{NaCl-K}_2\text{SO}_4\text{-CaSO}_4$.

$\text{KCl-Na}_2\text{SO}_4$

Jänecke (1908) studied the system $\text{KCl-Na}_2\text{SO}_4$ by means of heating-cooling curves and reported a complete solid solution series with complicated inversions and unmixing at lower temperatures which he did not attempt to clarify. Akopov and Bergman (1954) reported that this join crossed the field of a compound, probably $2\text{Na}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$, that formed by the decomposition of the solid solution. The later work done by Akopov and Bergman (1959) on this pseudobinary diagonal indicated that it goes from Na_2SO_4 through a field of $(\text{Na,K})\text{SO}_4$ solid solution, across fields of two of the three compounds formed from the breakdown of the $(\text{Na,K})\text{SO}_4$ solid solution with a minimum at 525°C , and finally through the $(\text{Na,K})\text{Cl}$ solid solution field to KCl . Jänecke used heating-cooling curves, whereas Akopov and Bergman relied on the visual polythermal method. Both results are shown in figure 13. Neither of the pre-

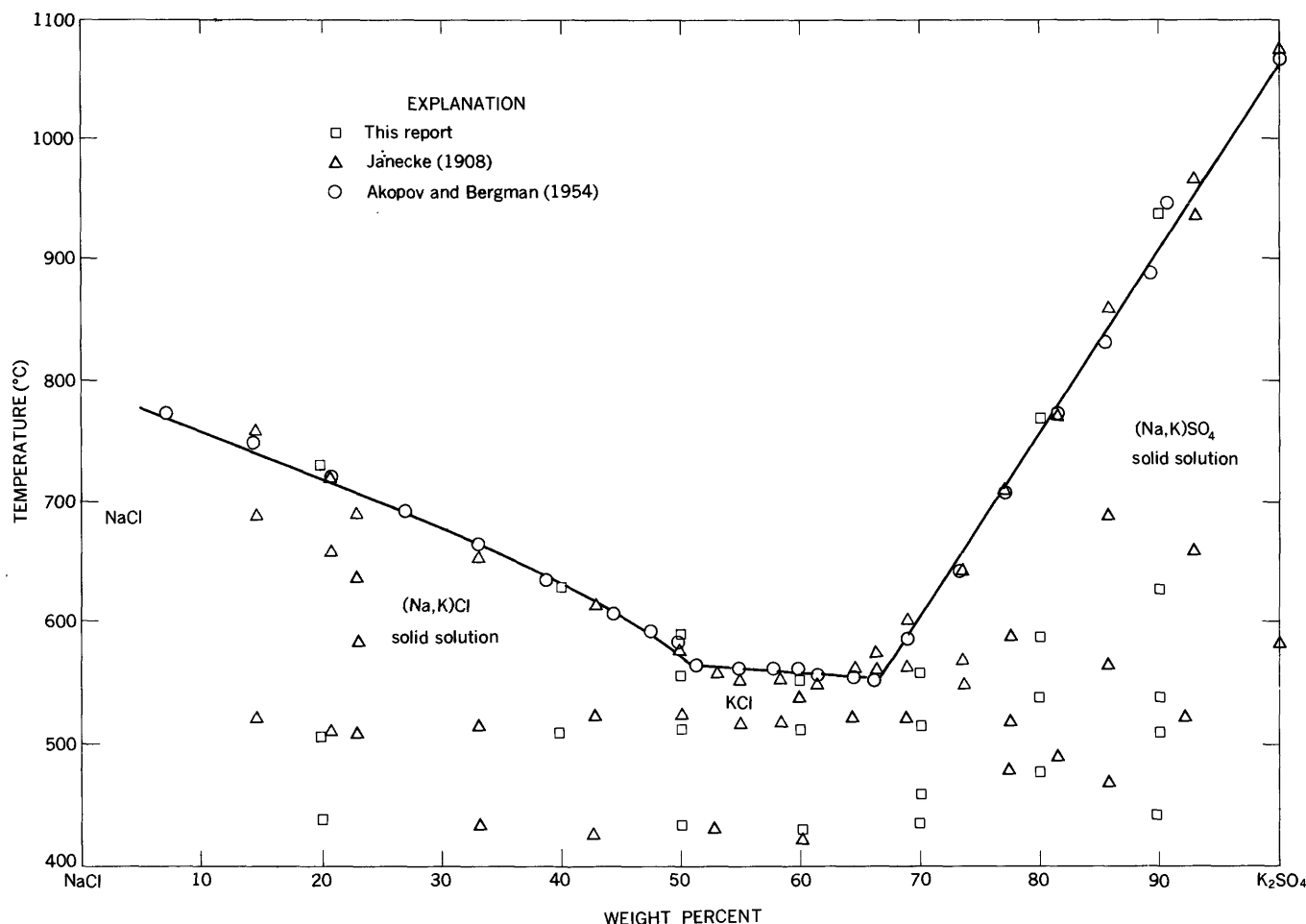


FIGURE 12.—The pseudobinary join $\text{NaCl-K}_2\text{SO}_4$ across the Na,K/Cl,SO_4 reciprocal salt system. Symbols represent thermal effects observed in heating-cooling study.

vious investigators used X-ray or optics to identify primary phases.

DISCUSSION

The representation of reciprocal salt systems developed by Jänecke (1908) is made by plotting compositions on a square, with the four salts as corners, one axis giving the fraction of the cations (in equivalents) and the other, the fraction of the anions. With temperature as the vertical axis, the diagram is a square prism, and the orthogonal projection of the liquid-solid relations on the composition square is the usual phase diagram.

Jänecke (1908, 1950) (fig. 14) described the Na,K/Cl,SO_4 reciprocal salt system as consisting of two complete series of solid solutions $(\text{Na,K})\text{Cl}$ and $(\text{Na,K})_2\text{SO}_4$ which meet in a boundary curve. He reported a minimum liquidus on the boundary curve at 515°C at a composition of 43 percent

Na_2 , 57 percent K_2 , 46 percent Cl_2 , and 54 percent SO_4 (in mole percent). In terms of weight percent the composition of this point is 20.6 percent NaCl , 19.8 percent KCl , 16.0 percent Na_2SO_4 , and 43.6 percent K_2SO_4 .

Akopov and Bergman (1954, 1959) and Akopov (1960) reported the existence of three $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ double compounds of unknown composition. These result from the breakdown of the continuous solid solutions of sodium and potassium sulfates below 736°C . They reported that the double compounds form limited solid solutions with one another and the other components of the system. In the binary system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$, the solid solutions break down at a much lower temperature forming the 1:1 compound at 476°C . There has been no X-ray confirmation of the double compounds in this system.

We did not attempt to resolve the differences between Jänecke and Akopov and Bergman regarding

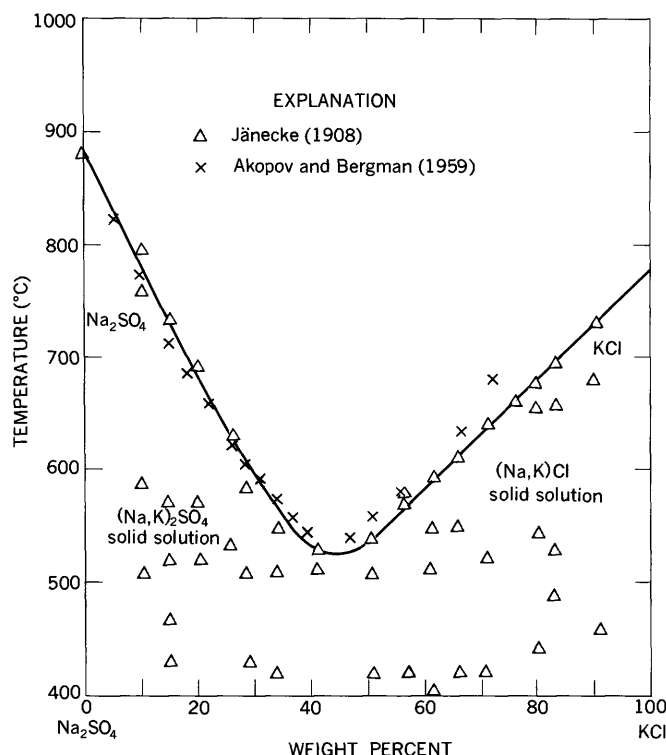


FIGURE 13.—The pseudobinary join $\text{KCl-Na}_2\text{SO}_4$ across the Na,K/Cl,SO_4 reciprocal salt system. Symbols represent thermal effects observed in heating-cooling study.

the complex subsolidus reactions in the system. Additional study should be performed to clarify the Na,K/Cl,SO_4 reciprocal salt system.

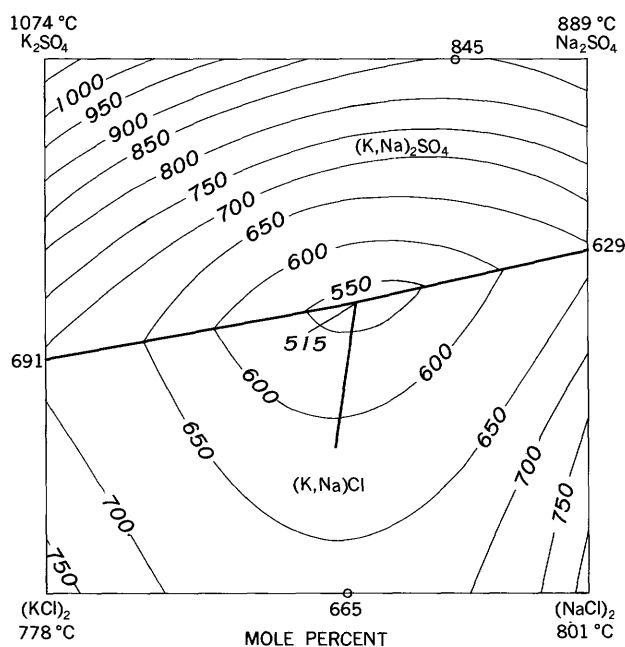


FIGURE 14.—The reciprocal salt system Na,K/Cl,SO_4 (from Jänecke, 1950).

Na,Mg/Cl,SO_4 RECIPROCAL SALT SYSTEM

The reciprocal salt system Na,Mg/Cl,SO_4 forms the second side of the prism representing the quaternary reciprocal salt system Na,K,Mg/Cl,SO_4 (fig. 2A). The diagonal NaCl-MgSO_4 is one side of the ternary plane $\text{NaCl-MgSO}_4\text{-K}_2\text{SO}_4$ (fig. 1). This reciprocal salt system is bounded by NaCl-MgCl_2 , $\text{MgCl}_2\text{-MgSO}_4$, $\text{Na}_2\text{SO}_4\text{-MgSO}_4$, and $\text{NaCl-Na}_2\text{SO}_4$.

BINARY SYSTEMS

NaCl-MgCl_2

Klemm and Weiss (1940) (fig. 15) and Klemm, Beyersdorfer, and Oryschkewitsch (1948) studied the binary system NaCl-MgCl_2 using X-ray techniques to identify phases. They reported two incongruently melting compounds $2\text{NaCl} \cdot \text{MgCl}_2$ (melting point 485°C) and $\text{NaCl} \cdot \text{MgCl}_2$ (mp 465°C). Bondarenko (1962) agreed with these results. The eutectic is at 450°C and 62 mole percent NaCl .

Menge (1911) reported only one compound ($\text{NaCl} \cdot \text{MgCl}_2$) in this system. Scholich (1920) and Speranskaya (1938) reported two compounds, $2\text{NaCl} \cdot \text{MgCl}_2$ (mp 476°C) and $\text{NaCl} \cdot 2\text{MgCl}_2$ (mp 462°C), and the eutectic at 444°C and 53 mole percent NaCl . The latter compound was found to be a mixture of $\text{NaCl} \cdot \text{MgCl}_2$ and MgCl_2 by Klemm and Weiss (1940).

$\text{MgCl}_2\text{-MgSO}_4$

Jänecke (1912) found $\text{MgCl}_2\text{-MgSO}_4$ to be a simple system with the eutectic at 667°C and 20 mole percent MgSO_4 . Speranskaya (1938) found the eutectic at 656°C and 22.5 mole percent MgSO_4 (fig. 16).

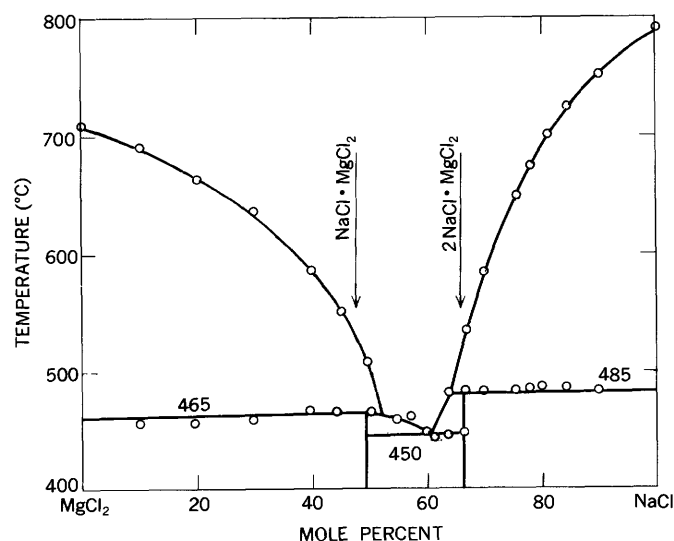


FIGURE 15.—The binary system NaCl-MgCl_2 (from Klemm and Weiss, 1940).

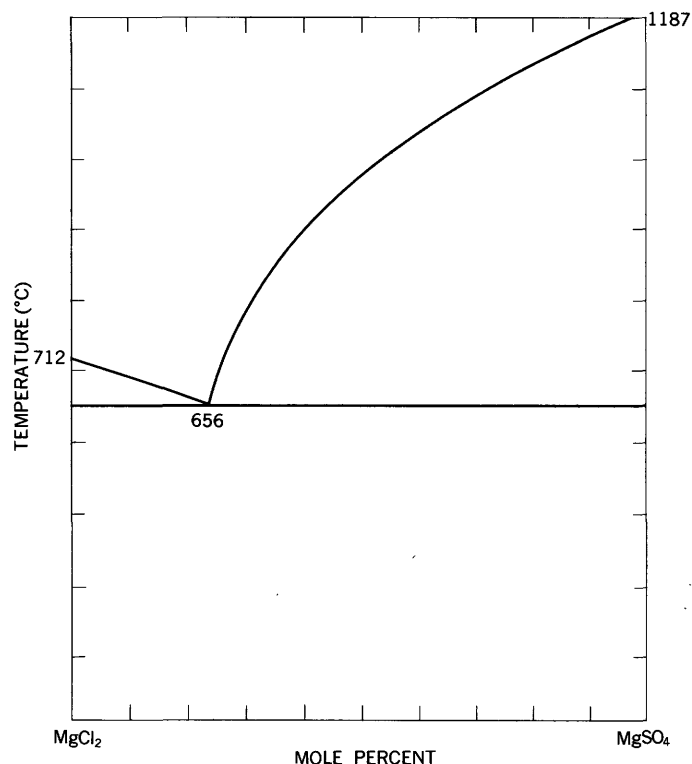


FIGURE 16.—The binary system $\text{MgCl}_2\text{-MgSO}_4$ (from Speranskaya, 1938).

$\text{Na}_2\text{SO}_4\text{-MgSO}_4$

The system $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ was studied by Nacken (1907), who reported that $\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4$ melts congruently. Ginsberg (1909) (fig. 17) found three compounds in the system: $\text{Na}_2\text{SO}_4\cdot 3\text{MgSO}_4$ (antivanthoffite) which melts incongruently at 814°C to MgSO_4 plus liquid of composition 70 mole percent MgSO_4 ; $\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4$ which decomposes at 604°C to solid solution plus $\text{Na}_2\text{SO}_4\cdot 3\text{MgSO}_4$; and vanthoffite, $3\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4$ which forms solid solution plus $\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4$ above 506°C . The eutectic for the system is at 670°C and 43 mole percent MgSO_4 . The Na_2SO_4 -rich solid solution series contains 36 mole percent MgSO_4 at the eutectic and becomes poorer in MgSO_4 as the temperature is lowered. Speranskaya (1938) and Mukimov, Krylova, and Fillipova (1949) accepted Ginsberg's results.

NaCl-MgSO_4

Speranskaya (1938) (fig. 18) found the system NaCl-MgSO_4 to be of the simple eutectic type with no binary compounds. The eutectic is at 642°C and 48.5 mole percent MgSO_4 (49.2 wt percent). This system is assumed to be a stable diagonal in the reciprocal salt system. We obtained liquidus results agreeing with Speranskaya but our MgSO_4 -rich

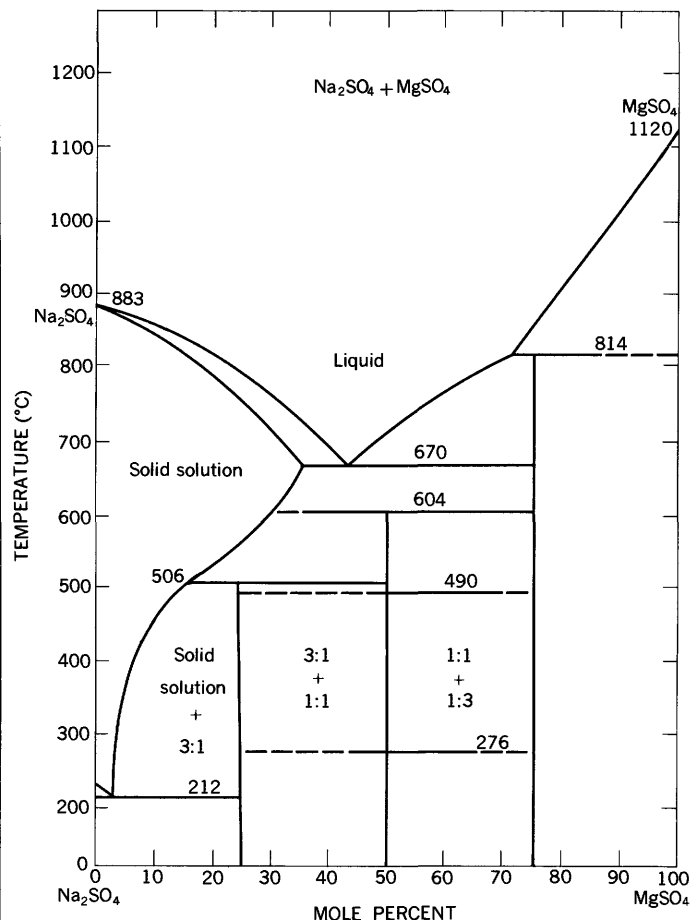


FIGURE 17.—The binary system $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ (from Ginsburg, 1909).

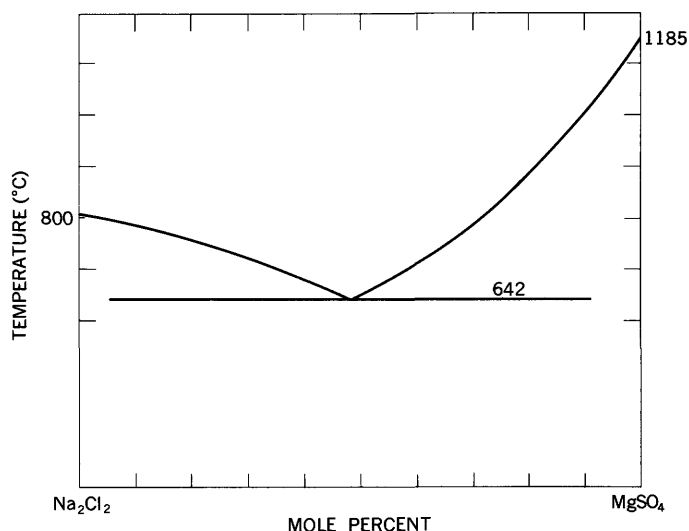


FIGURE 18.—The stable join NaCl-MgSO_4 in the Na,Mg/Cl,SO_4 reciprocal salt system (from Speranskaya, 1938).

melts were milky indicating some decomposition of MgSO_4 . We also experienced considerable difficulty with creeping of the melt and volatilization of NaCl . From our heating-cooling curves, we confirmed the eutectic at 642°C .

$\text{MgCl}_2\text{--Na}_2\text{SO}_4$

Speranskaya (1938) (fig. 19) studied the pseudobinary diagonal $\text{MgCl}_2\text{--Na}_2\text{SO}_4$ in the reciprocal salt system Na,Mg/Cl,SO_4 . On addition of MgCl_2 to Na_2SO_4 , the liquidus falls rapidly from 884°C to about 575°C where the field of NaCl is met at about 19 mole percent MgCl_2 . The temperature of the liquidus then rises to a maximum at 662°C (40 mole percent MgCl_2) while crossing the NaCl primary field. It then descends to the $\text{MgSO}_4\text{--NaCl}$ boundary at 642°C (49 mole percent MgCl_2) where MgSO_4 becomes the primary phase until the $\text{MgCl}_2\text{--MgSO}_4$ boundary is met at 588°C (86 mole percent MgCl_2) after which the liquidus rises to the melting point of MgCl_2 , 712°C .

DISCUSSION

The reciprocal salt system Na,Mg/Cl,SO_4 as studied by Speranskaya (1938) (fig. 20) shows the following seven fields of primary crystallization: Na_2SO_4 , $\text{Na}_2\text{SO}_4\cdot 3\text{MgSO}_4$, NaCl , MgSO_4 , MgCl_2 , $\text{NaCl}\cdot 2\text{MgCl}_2$, and $2\text{NaCl}\cdot\text{MgCl}_2$. The differences between the results of Speranskaya (1938) and those of Klemm and Weiss (1940) and Klemm, Beyersdorfer, and Oryschkewitsch (1948) regarding the compound $\text{NaCl}\cdot 2\text{MgCl}_2$ were discussed on page 12.

Orlova and Yanat'eva (1963) in a study of the $\text{Na,Mg/Cl,SO}_4\text{--H}_2\text{O}$ system at 100°C reported the

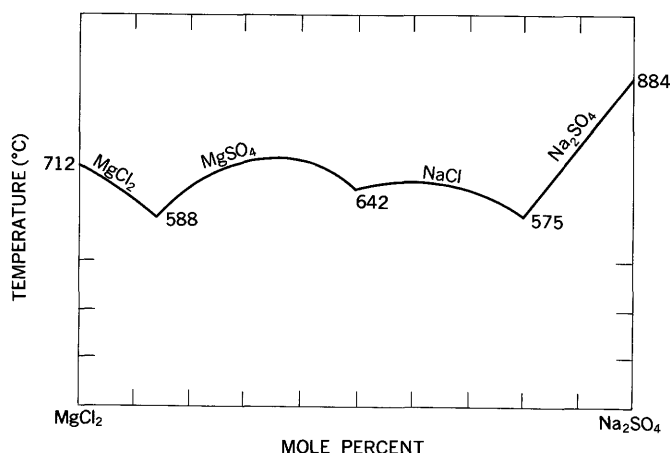


FIGURE 19.—The pseudobinary join $\text{MgCl}_2\text{--Na}_2\text{SO}_4$ in the Na,Mg/Cl,SO_4 reciprocal salt system (modified from Speranskaya, 1938).

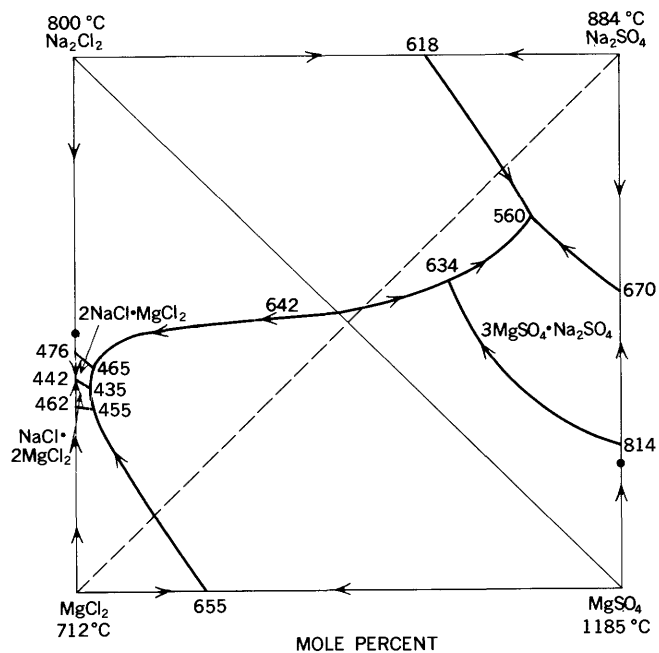


FIGURE 20.—The reciprocal salt system Na,Mg/Cl,SO_4 (from Speranskaya, 1938).

existence of a compound of composition $\text{MgSO}_4\cdot 3\text{NaCl}\cdot 9\text{Na}_2\text{SO}_4$, which gave DTA effects at 525°C , 620°C , and 720°C . At 525°C , the compound decomposes to $\text{NaCl} + \text{Na}_2\text{SO}_4\cdot\text{MgSO}_4 + (\text{Na,Mg})\text{SO}_4$ solid solution.

The join from MgCl_2 to Na_2SO_4 represents a pseudobinary diagonal which crosses the field of MgSO_4 . NaCl--MgSO_4 is a stable diagonal which divides the system into two stable ternary systems.

K,Mg/Cl,SO_4 RECIPROCAL SALT SYSTEM

The reciprocal salt system K,Mg/Cl,SO_4 consists of KCl--MgCl_2 , $\text{MgCl}_2\text{--MgSO}_4$ (fig. 16), $\text{K}_2\text{SO}_4\text{--MgSO}_4$ (fig. 4), and $\text{KCl--K}_2\text{SO}_4$ (fig. 10) as edges and KCl--MgSO_4 and $\text{MgCl}_2\text{--K}_2\text{SO}_4$ as diagonals.

BINARY SYSTEMS

KCl--MgCl_2

Klemm, Beyersdorfer, and Oryschkewitsch (1948) studied the system KCl--MgCl_2 using X-ray methods to identify phases. They reported the two compounds: anhydrocarnallite, $\text{KCl}\cdot\text{MgCl}_2$ (mp 488°C), and $2\text{KCl}\cdot\text{MgCl}_2$ (mp 433°C), both melting congruently as shown in figure 21.

This is in agreement with Menge (1911) and Ivanov (1952). Jänecke (1912) and Scholich (1920) reported only $\text{KCl}\cdot\text{MgCl}_2$ in the binary system but did not use X-ray methods in their work.

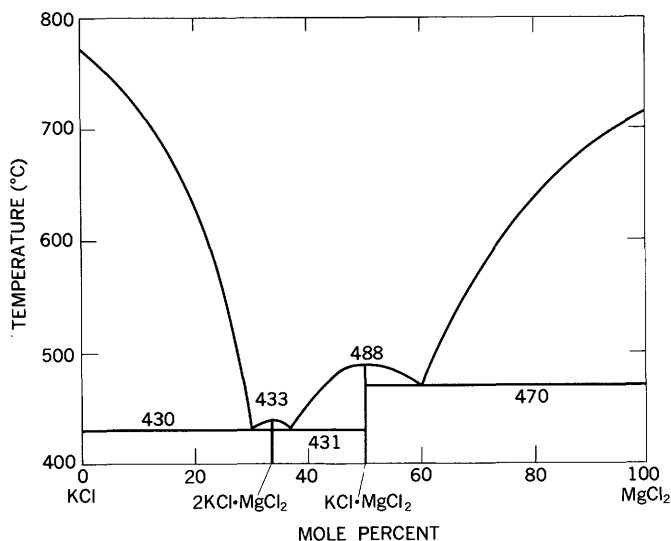


FIGURE 21.—The binary system KCl-MgCl_2 (from Klemm and others, 1948).

KCl-MgSO_4

The KCl-MgSO_4 system is a stable diagonal according to Jänecke (1912) (fig. 22). The compound KCl·MgSO_4 (anhydrokainite) is isotropic, probably tetrahedral, and melts congruently about 920°C .

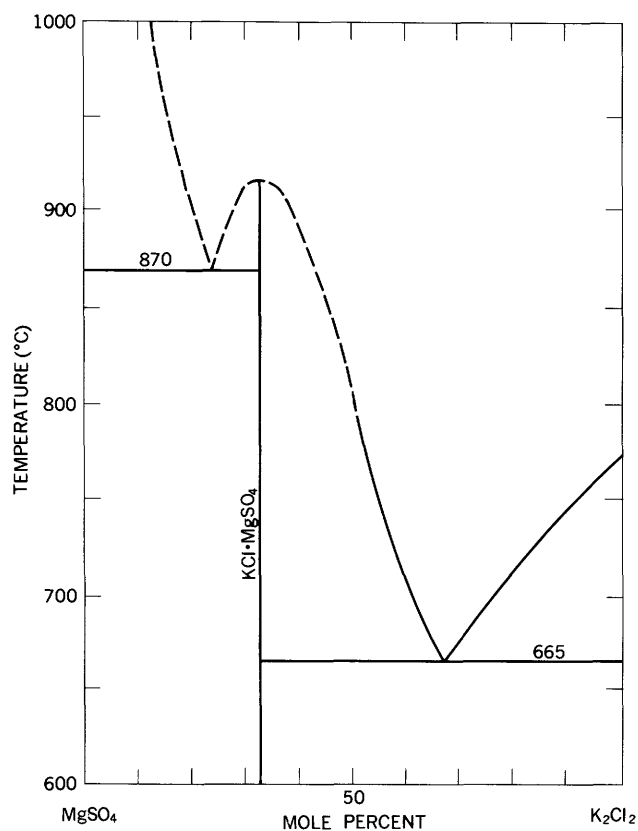


FIGURE 22.—Stable diagonal KCl-MgSO_4 in the reciprocal salt system K,Mg/Cl,SO_4 (from Jänecke, 1912)

The melting point could not be determined precisely by Jänecke because the decomposition of MgSO_4 prevented synthesis of the pure compound. The eutectic between KCl and KCl·MgSO_4 is at 665°C and 33.3 mole percent (30 wt percent) MgSO_4 . Jänecke (1912), from results slightly off of this diagonal, assumed the eutectic between KCl·MgSO_4 and MgSO_4 to be at 870°C . Bergman and Selivanova (1938) accepted Jänecke's results in their study of the plane NaCl-KCl-MgSO_4 .

There has been some question regarding the existence of KCl·MgSO_4 . We prepared a melt of composition KCl·MgSO_4 (38.2 percent KCl +61.8 percent MgSO_4) which gave an X-ray diffraction pattern of langbeinite plus KCl plus a trace of MgCl_2 or KCl·MgCl_2 , whereas we should have observed anhydrokainite. Heating-cooling curves of the composition KCl·MgSO_4 indicate thermal effects at 418° , 490° , 610° , and 885°C . Linstedt (1952) made heavy liquid separation of a melt of KCl·MgSO_4 composition and found langbeinite. He also questioned the existence of a KCl·MgSO_4 compound. Additional study is therefore indicated to resolve the discrepancies and to revise Jänecke's (1912) diagram of the K,Mg/Cl,SO_4 system.

$\text{MgCl}_2\text{-K}_2\text{SO}_4$

The join $\text{MgCl}_2\text{-K}_2\text{SO}_4$ was studied by Jänecke (1912, 1950) as part of the system K,Mg/Cl,SO_4 . On the addition of MgCl_2 to K_2SO_4 , the liquidus is lowered from $1,069^\circ\text{C}$ to about 650°C at 33 mole percent (9 wt percent) MgCl_2 where KCl·MgSO_4 becomes the primary phase. The liquidus then rises to about 790°C as the anhydrokainite field is crossed. At 650°C and 76 mole percent (63 wt percent) MgCl_2 , MgSO_4 becomes the primary phase. At 580°C and 87 mole percent (76 wt percent) MgCl_2 , the field of MgCl_2 is entered. The liquidus temperature then rises to the melting point of MgCl_2 , 712°C . Figure 23 is from data of Jänecke (1912).

DISCUSSION

This reciprocal salt system, studied by Jänecke (1912), is shown in figure 24. The binary $\text{K}_2\text{SO}_4\text{-MgSO}_4$ system has eutectics at 725°C and 875°C , according to Jänecke. We found eutectics at 750°C and 884°C (fig. 4). There are seven fields of primary crystallization: the four pure compounds and the binary compounds $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$ (langbeinite), KCl·MgCl_2 (anhydrocarnallite) (fig. 21), and possibly KCl·MgSO_4 (anhydrokainite) (fig. 22). Additional study, using modern methods, should be performed to verify the phase diagram for this system.

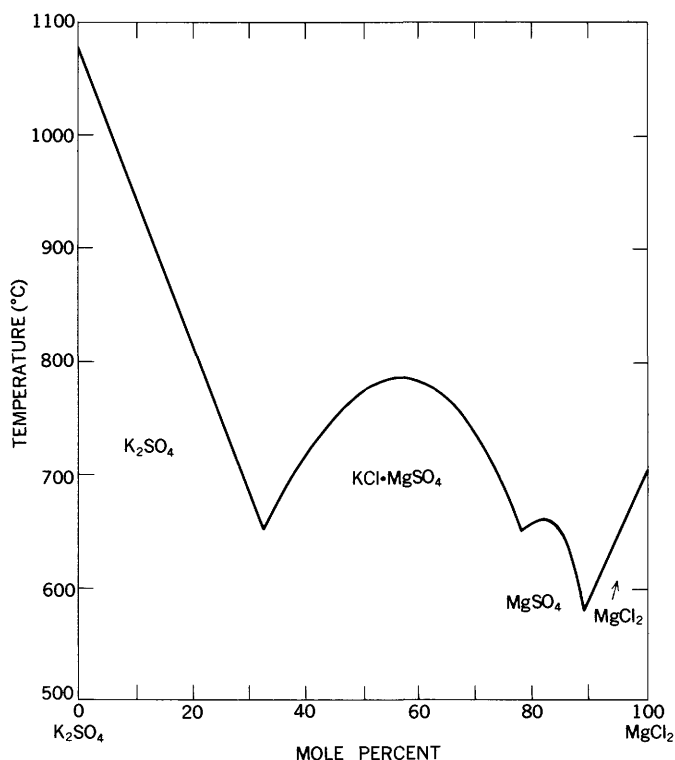


FIGURE 23.—Pseudobinary diagonal $\text{MgCl}_2\text{--K}_2\text{SO}_4$ in the reciprocal salt system K,Mg/Cl,SO_4 (data from Jänecke, 1912).

$\text{NaCl--MgCl}_2\text{--KCl}$ TERNARY SYSTEM

The ternary system $\text{NaCl--MgCl}_2\text{--KCl}$ represents the three chlorides in the quaternary reciprocal system Na,Mg,K/Cl,SO_4 . It can be considered to be

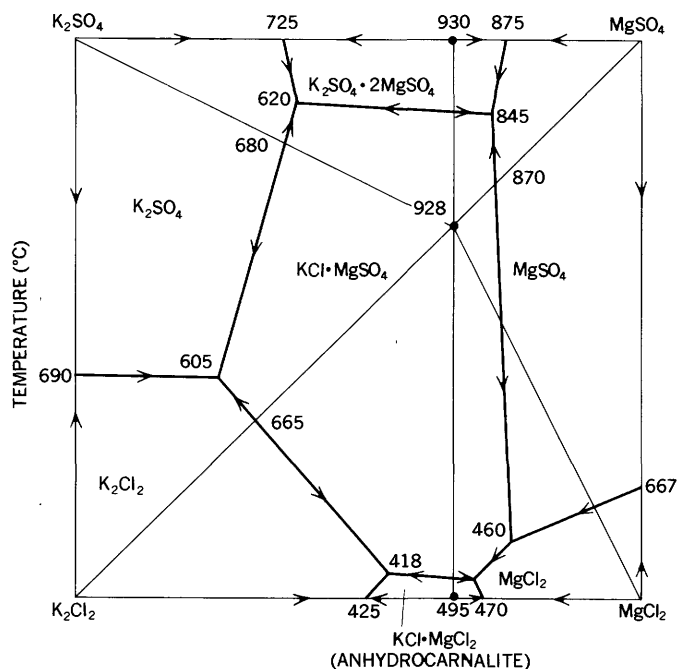


FIGURE 24.—The reciprocal salt system K,Mg/Cl,SO_4 (from Jänecke, 1912).

the end of the prism formed from the three reciprocal salt systems: K,Mg/Cl,SO_4 ; Na,K/Cl,SO_4 ; and Na,Mg/Cl,SO_4 . The $\text{NaCl--MgCl}_2\text{--KCl}$ system was studied by Scholich (1920) (fig. 25). He reported no ternary compounds. Fields are shown for the incongruently melting binary compounds $\text{NaCl}\cdot 2\text{MgCl}_2$, $2\text{NaCl}\cdot \text{MgCl}_2$ and the congruently melting $\text{KCl}\cdot \text{MgCl}_2$ (anhydrocarnallite). Below about 480°C , the solid solution $(\text{Na,K})\text{Cl}$ unmixes.

The results shown by Scholich (1920) are different from those later reported by Klemm, Beyersdorfer, and Oryschkewitsch (1948) for the binary systems NaCl--MgCl_2 (fig. 15) and KCl--MgCl_2 (fig. 21).

$\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--K}_2\text{SO}_4$ TERNARY SYSTEM

Jänecke (1950), in compiling the data on the ternary reciprocal salt system K,Mg,Na/Cl,SO_4 , found that the system $\text{Na}_2\text{SO}_4\text{--MgSO}_4\text{--K}_2\text{SO}_4$ had not been previously studied. He deduced the phase diagram shown in figure 26 from the phase diagrams of the component binary systems. Jänecke's diagram will be used for our compilation of the Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system.

Mukimov, Krylova, and Fillipova (1949), using the visual polythermal method, reported that the field of MgSO_4 extended between the fields for langbeinite and $\text{Na}_2\text{SO}_4\cdot 3\text{MgSO}_4$ (fig. 27). They agreed with Jänecke regarding the extension of the $(\text{Na,K})\text{SO}_4$ solid solution into the ternary system.

Additional study should be done on this ternary

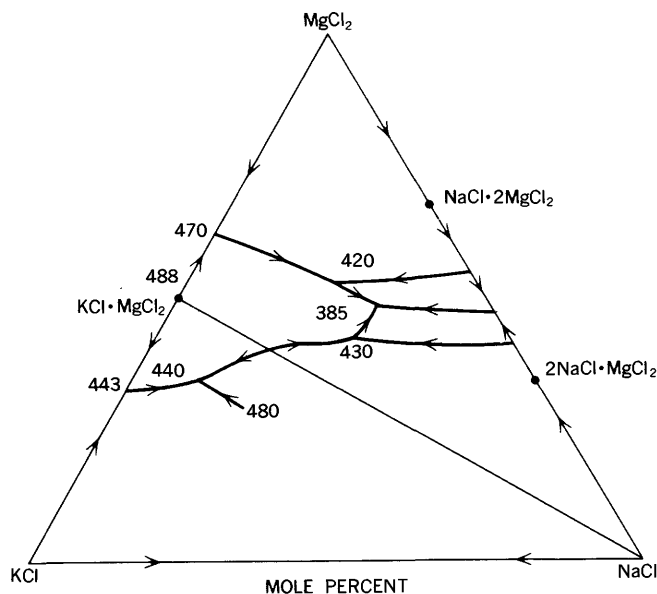


FIGURE 25.—The ternary system $\text{NaCl--MgCl}_2\text{--KCl}$ (from Scholich, 1920).

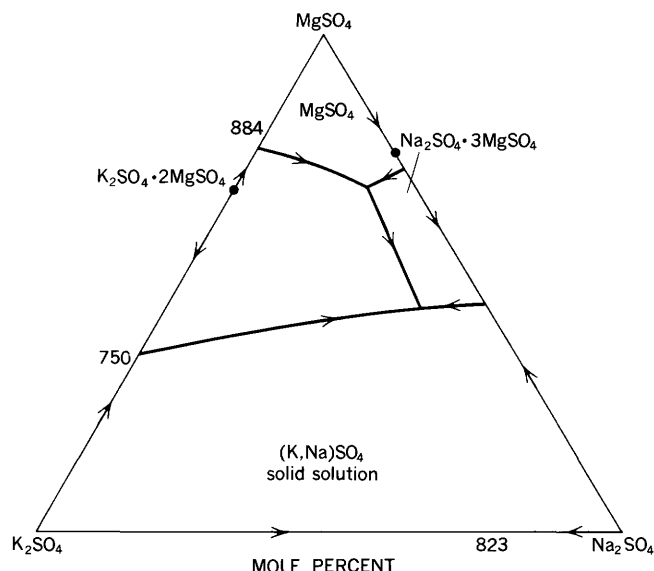


FIGURE 26.—The ternary system $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-K}_2\text{SO}_4$ (modified from Jänecke, 1950).

system using X-ray diffraction to identify the primary phases.

NaCl-KCl-MgSO_4 PLANE

The NaCl-KCl-MgSO_4 plane across the prism representing the quaternary reciprocal salt system Na,K,Mg/Cl,SO_4 was studied by Bergman and Selivanova (1938) as shown in figure 28. There are no ternary compounds. Ternary eutectics are at 616° and 624° . The field for anhydrokainite (KCl-MgSO_4) extends into the ternary system. The study of Bergman and Selivanova was done entirely

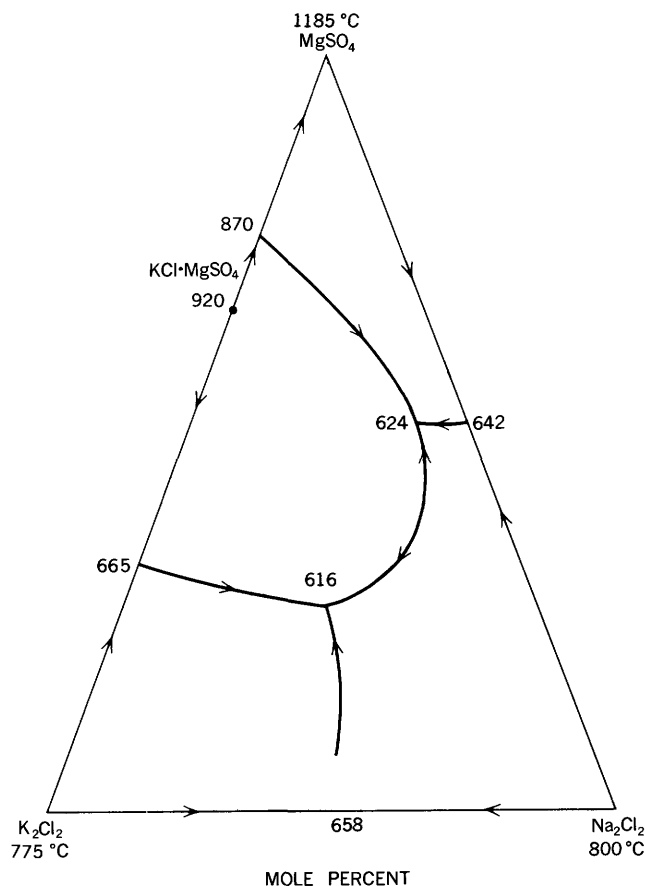


FIGURE 28.—The ternary plane NaCl-KCl-MgSO_4 across the Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system (modified from Bergman and Selivanova, 1938).

by the visual polythermal method. There was no phase identification by X-ray or optical methods, hence, the existence of the field shown for anhydrokainite should be reexamined.

For this compilation and for preparation of the phase diagrams of the quaternary reciprocal salt system, we will show this ternary system as a stable plane in the system.

SUMMARY OF $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ AS A PLANE IN THE Na,K,Mg/Cl,SO_4 SYSTEM

The system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ is a plane across the prism representing the quaternary reciprocal salt system Na,K,Mg/Cl,SO_4 as shown in figures 2 and 3A. The phase relations will be discussed in relation to the phase volumes intersected.

The prism may be further subdivided into subsystems by various joins between the components and the compounds KCl-MgCl_2 , NaCl-2MgCl_2 , $\text{Na}_2\text{SO}_4\cdot 3\text{MgSO}_4$, $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$, and KCl-MgSO_4 . We did not attempt to determine which of these joins would form stable binary, ternary, and quaternary

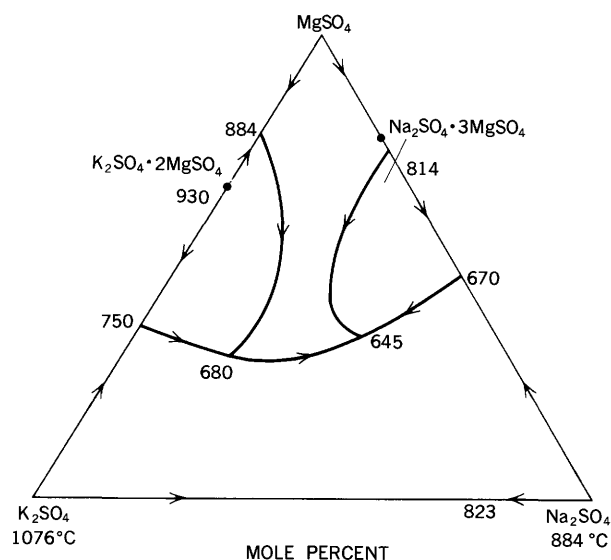


FIGURE 27.—The ternary system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-MgSO}_4$ (from Mukimov, Krylova, and Fillipova, 1949).

subsystems. Within each of the quaternary subsystems are invariant points or "stars" of liquid plus four solid phases.

Jänecke (1950) derived the phase relations in the quaternary reciprocal salt system Na,K,Mg/Cl,SO_4 , which he called double-ternary. The following internal phase volumes were deduced from the bounding ternary reciprocal salt systems: Na,K/Cl,SO_4 (fig. 14), Na,Mg/Cl,SO_4 (fig. 20), and K,Mg/Cl,SO_4 (fig. 24). Internal information was from the study by Bergman and Selivanova (1938) of the plane NaCl-KCl-MgSO_4 (fig. 28), which intersects phase volumes of NaCl , KCl , MgSO_4 , and KCl-MgSO_4 and also forms one ternary side of the quaternary system $\text{NaCl-KCl-MgCl}_2\text{-MgSO}_4$ (fig. 2).

To determine the phases that occur on the plane $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ and to learn whether the plane will further subdivide the prism into two more stable quaternary systems, we prepared compositions shown in table 3. The data for compositions on the join $\text{NaCl-K}_2\text{SO}_4\cdot 2\text{MgSO}_4$ are shown in figure 29. From the coexistence of langbeinite and NaCl for all compositions on this join, we can assume that it is a true binary system. A minimum at 632°C was found at 47.5 percent NaCl . Other compositions on this plane, between the NaCl -langbeinite join and the $\text{NaCl-K}_2\text{SO}_4$ join, show NaCl ; KCl ; $(\text{Na,K})\text{SO}_4$ solid solution (aphthitalite); and $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$ (langbeinite). The $\text{NaCl-K}_2\text{SO}_4$ join is a pseudo-ternary join. The system is not ternary but is quinary in this part of the plane, hence it does not divide the prism into two more stable quaternary systems.

The join NaCl-MgSO_4 is a stable diagonal of the

Na,Mg/Cl,SO_4 system. Hence we can assume that the plane is stable between the NaCl -langbeinite join and the NaCl-MgSO_4 binary system. NaCl , MgSO_4 , and $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$ are the three phases found in this part, as shown in figure 30. Additional study is necessary to completely delineate this plane.

To aid in visualizing the complex quaternary reciprocal salt system Na,K,Mg/Cl,SO_4 , we prepared figure 31, which shows the prism opened. A stereopair, representing the prism and the internal planes, is shown in figure 32. The graphic representation of the system is complicated by the solid solution series $(\text{Na,K})\text{Cl}$, $(\text{Na,K})\text{SO}_4$, and $(\text{Na,Mg})\text{SO}_4$.

It can be seen from figures 30-32 that the plane $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ intersects phase volumes of $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$ (langbeinite), NaCl , MgSO_4 , K_2SO_4 , KCl , and $(\text{Na,K})\text{SO}_4$ solid solution. The phase volume of langbeinite extends a greater distance into the prism than was thought by Jänecke (1950). Anhydrokainite (KCl-MgSO_4) (figs. 22-24) is reported to have a field in the NaCl-KCl-MgSO_4 plane (fig. 28).

To determine completely this complex system and the numerous invariant points requires considerable additional experimental study of the many sections across the various subsystems.

THE SYSTEM $\text{NaCl-K}_2\text{SO}_4\text{-CaSO}_4$

The system $\text{NaCl-K}_2\text{SO}_4\text{-CaSO}_4$ can be considered as a plane across the prism representing compositions in the quaternary reciprocal salt system Na,K,Ca/Cl,SO_4 . The phase relations on this plane will provide us with another ternary side of the tetra-

TABLE 3.—Compositions on the $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ plane in the Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system

NaCl (wt percent)	K_2SO_4 (wt percent)	MgSO_4 (wt percent)	Phases present	Liquidus temperature ($^\circ\text{C}$)	Temperature of other thermal effects ($^\circ\text{C}$)	Primary phase
Compositions on the join NaCl -langbeinite ($\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$)						
100	0	0	NaCl -----	800.4	-----	NaCl .
90	4.2	5.8	NaCl +langbeinite -----	775	540	NaCl .
80	8.4	11.6	----- do -----	740	630, 540	NaCl .
70	12.59	17.41	----- do -----	715	632, 540	NaCl .
60	16.79	23.21	----- do -----	675	632, 540	NaCl .
50	20.99	29.01	----- do -----	645	632, 510	NaCl .
40	25.19	34.81	----- do -----	688	635, 510	Langbeinite.
30	29.39	40.61	----- do -----	745	635, 510	Do.
20	33.59	46.41	----- do -----	805	635, 510	Do.
10	37.78	52.22	----- do -----	877	510	Do.
0	41.8	58.2	Langbeinite -----	943	-----	Do.
Other compositions [ss indicates solid solution]						
40	50	10	NaCl +langbeinite ----- + KCl + $(\text{Na,K})\text{SO}_4$ ss	640	540, 510	KCl .
40	40	20	----- do -----	560	510	Langbeinite.

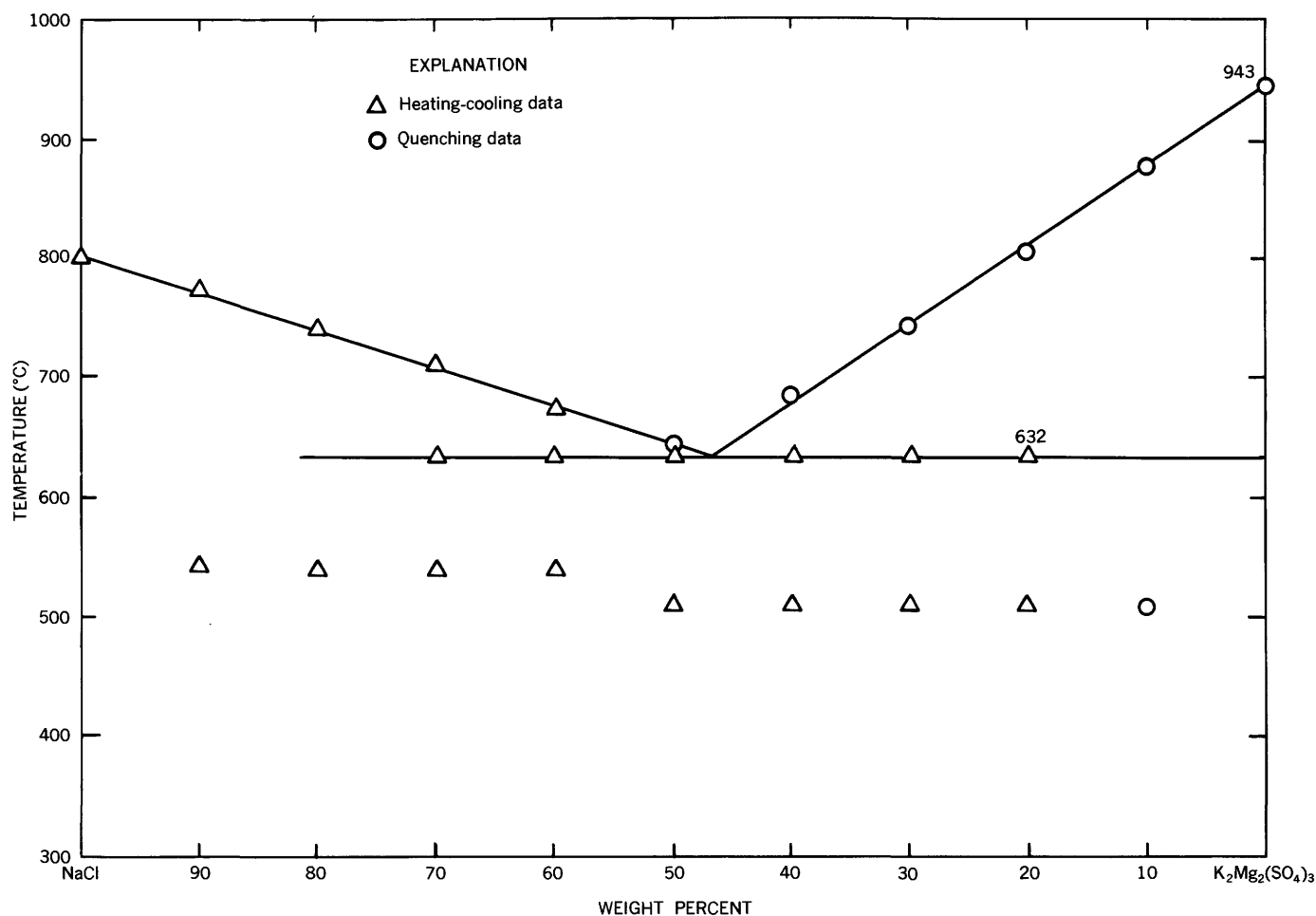


FIGURE 29.—The join NaCl to $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (langbeinite) on the plane $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$.

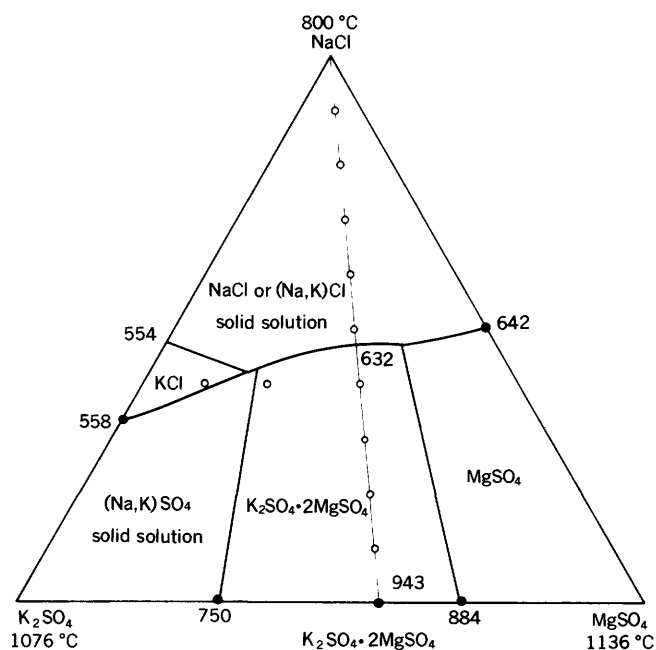


FIGURE 30.—The plane $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$ across the Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system.

hedron for the quasi-quaternary system $\text{NaCl-MgSO}_4\text{-K}_2\text{SO}_4\text{-CaSO}_4$ (fig. 1).

The prism representing the Na,K,Ca/Cl,SO_4 system consists of the reciprocal salt systems Na,K/Cl,SO_4 ; Na,Ca/Cl,SO_4 ; and Ca,K/Cl,SO_4 and the ternary systems NaCl-KCl-CaCl_2 and $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-CaSO}_4$ (fig. 3B).

Na,Ca/Cl,SO_4 RECIPROCAL SALT SYSTEM

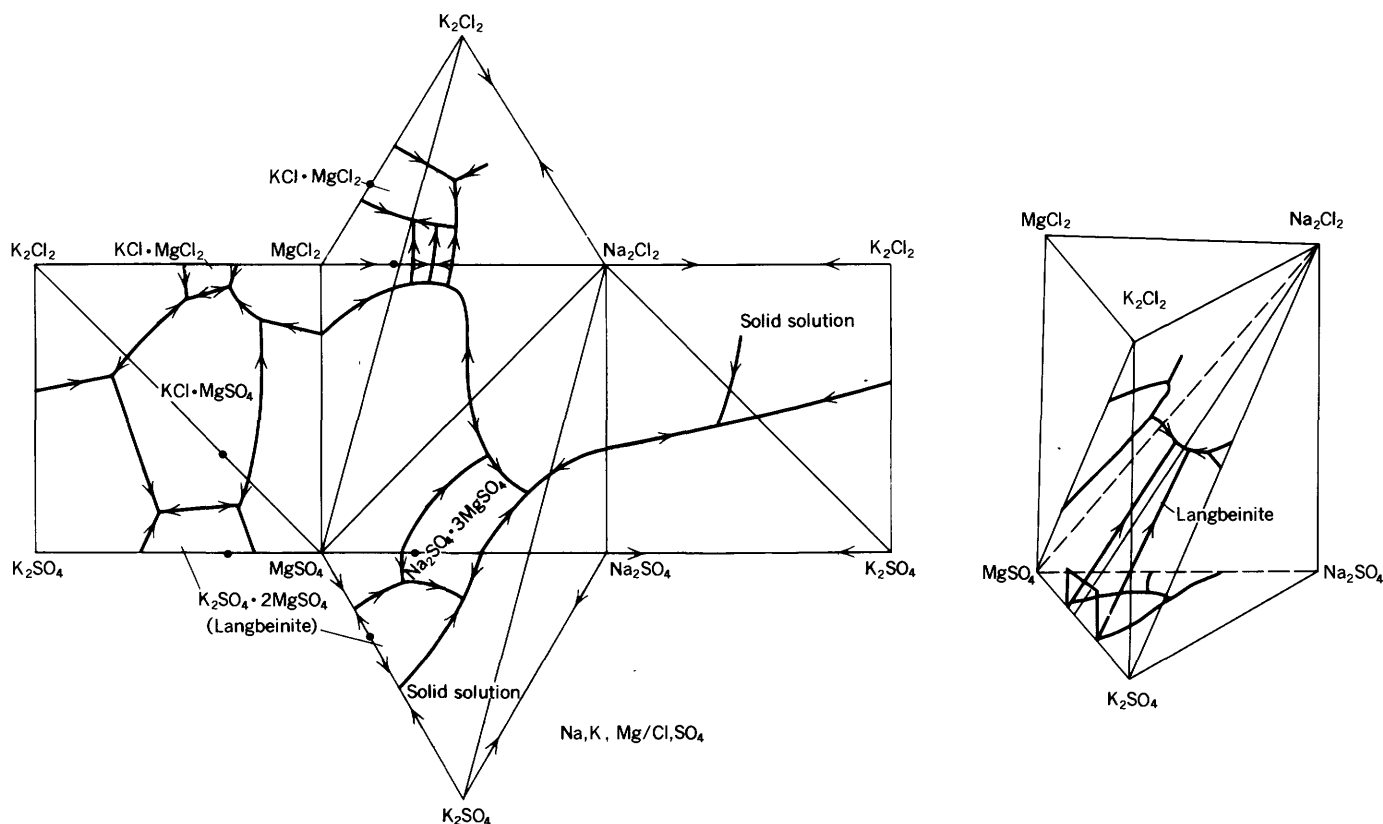
This reciprocal salt system consists of the NaCl-CaCl_2 , $\text{NaCl-Na}_2\text{SO}_4$, $\text{CaCl}_2\text{-CaSO}_4$, and $\text{Na}_2\text{SO}_4\text{-CaSO}_4$ systems as edges and NaCl-CaSO_4 and $\text{CaCl}_2\text{-Na}_2\text{SO}_4$ as diagonals.

BINARY SYSTEMS

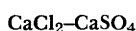
NaCl-CaCl_2

Schlich (1920) found the NaCl-CaCl_2 system to be a simple binary system with a eutectic at 506°C and 53 mole percent (68.2 wt percent) CaCl_2 , as shown in figure 33.

Menge (1911) had reported an incongruently melting compound 4NaCl-CaCl_2 . Examination of

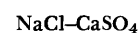
FIGURE 31.—The Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system.

Menge's data shows a thermal effect for the eutectic in compositions containing more than 80 mole percent NaCl , which would preclude the existence of the $4\text{NaCl}\cdot\text{CaCl}_2$ compound.

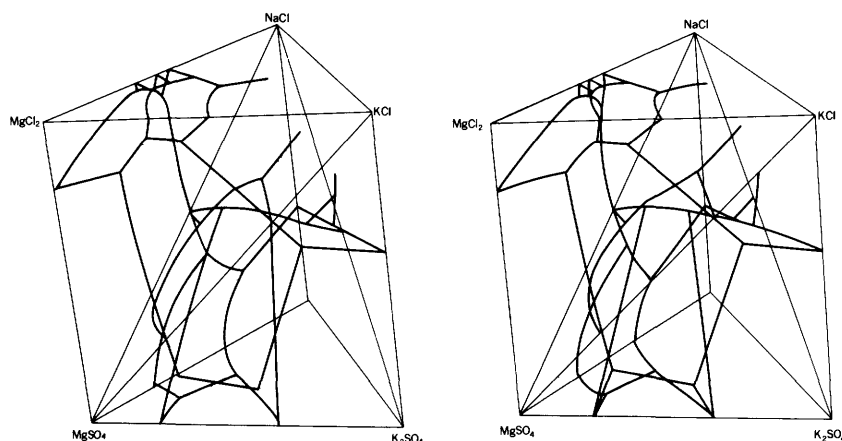


Jänecke and Mühlhäusser (1936), in a study of the reciprocal salt system K,Ca/Cl,SO_4 indicated that this was a simple system with a eutectic at 730°C and about 10 percent (8.7 mole percent) CaSO_4 .

However, they did not specifically study this binary system. Golubeva and Bergman (1956) (fig. 34), repeated this system and reported a eutectic at 706°C and 12.5 mole percent CaSO_4 . Palkin (1949) and Zimina, Bergman, and Nagornyi (1965) report this eutectic to be at 712°C .



The system $\text{Na}_2\text{SO}_4\text{--CaSO}_4$ (fig. 35) has been studied by many, starting with Le Chatelier (1887),

FIGURE 32.—Stereopair for the Na,K,Mg/Cl,SO_4 quaternary reciprocal salt system.

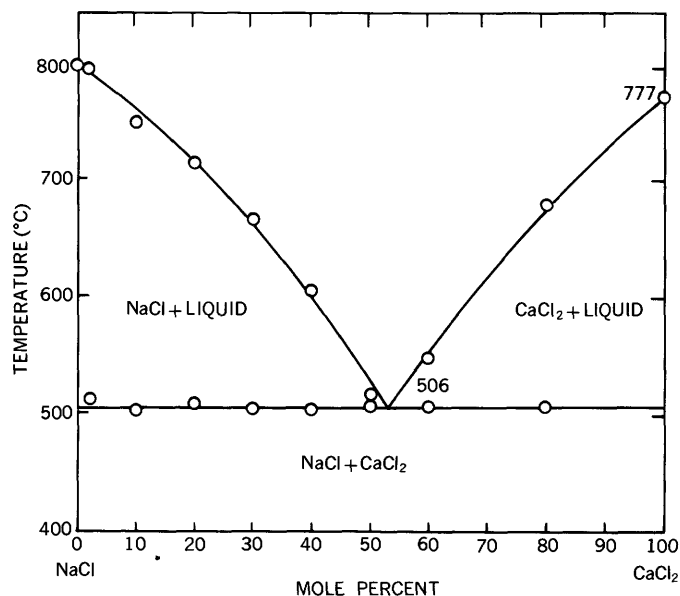


FIGURE 33.—The binary system NaCl-CaCl_2 (from Scholich, 1920).

with many contradictions and different interpretations of the experimental data. There is general agreement on the liquidus exhibiting solid solution with a maximum between 20 and 25 mole percent CaSO_4 , and a temperature between 944° and 950°C . The greatest differences are in the nature and composition of phases formed. Müller (1910) reported a $4\text{Na}_2\text{SO}_4\cdot\text{CaSO}_4$ compound. La Chatelier (1887) found a $2\text{Na}_2\text{SO}_4\cdot\text{CaSO}_4$ compound, which was confirmed by Speranskaya and Barskaya (1961) by an X-ray study. Komissarova, Plyushchev, and Stepina (1955) in a study using thermal, optical, and X-ray methods reported finding glauberite ($\text{Na}_2\text{SO}_4\cdot\text{CaSO}_4$) in the solidus as did Plyushchev (1962). Bellanca (1942), also using X-ray methods, reported no compounds but found that solid solution was formed of approximately $3\text{Na}_2\text{SO}_4\cdot\text{CaSO}_4$. Kracek (1942) gave the melting temperature of naturally occurring glauberite as 905°C with decomposition below the liquidus to CaSO_4 and solid solution, and he stated that glauberite cannot be prepared from the melt. This was confirmed by Speranskaya and Barskaya (1961).

There are also some differences in the reported temperature and composition of the eutectic. Müller (1910) found the eutectic at 913°C (40 mole percent CaSO_4); Komissarova, Plyushchev, and Stepina (1955), at 890°C (40 mole percent CaSO_4); Speranskaya and Barskaya (1961) and also Mukimov and Fillipova (1949), at 918°C (49 mole percent CaSO_4); Zimina, Bergman, and Nagornyi (1965), at 910°C (49 mole percent CaSO_4); Plyushchev (1962,

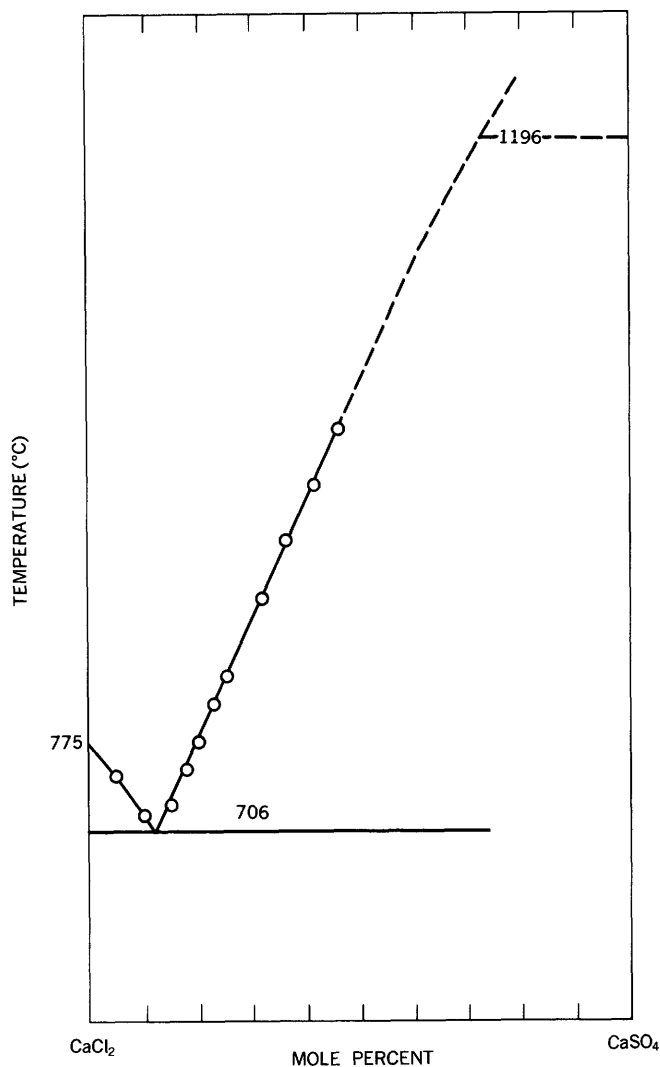
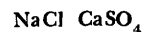


FIGURE 34.—The binary system $\text{CaCl}_2\text{-CaSO}_4$ (from Golubeva and Bergman, 1956).

at 890°C (40 mole percent CaSO_4); and Bellanca (1942), at 912°C (50 mole percent CaSO_4).

The eutectoid in the solidus was reported by Komissarova, Plyushchev, and Stepina (1955) and Plyushchev (1962) as 185°C (6 mole percent CaSO_4) which confirmed the interpretation of Müller (1910). Bellanca (1942) found it to be 225°C (5 mole percent CaSO_4).

Additional study of this system is needed, using differential thermal analysis, longtime subsolidus heating, quenching techniques, and the heating stage X-ray diffractometer to clarify the differences and to determine if, and at what temperature, glauberite melts incongruently or decomposes.



Bye and Kiehl (1948) studied this binary diagonal of the reciprocal salt system Na,Ca/Cl,SO_4 . The

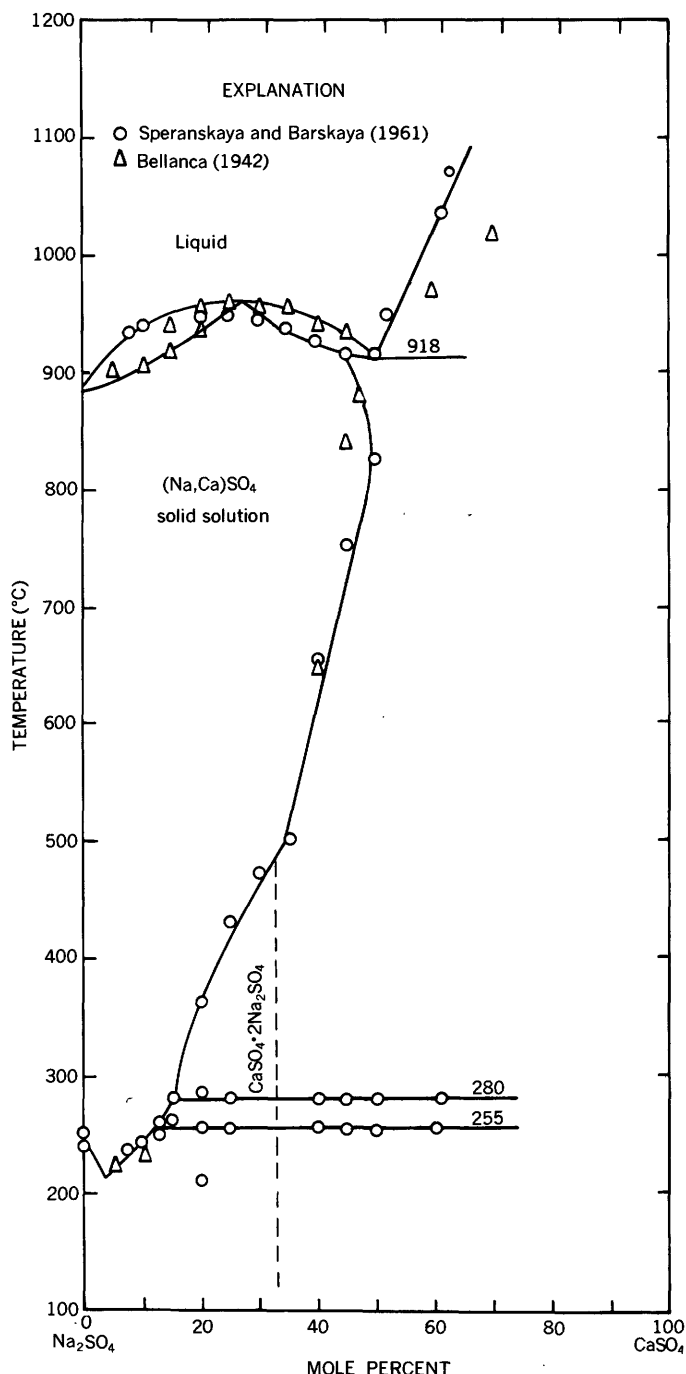


FIGURE 35.—The binary system Na₂SO₄-CaSO₄ (from Speranskaya and Barskaya, 1961, and Bellanca, 1942).

eutectic is at 725°C and 37 percent CaSO₄. The study was not carried beyond 70 percent CaSO₄ because of the decomposition of CaSO₄. Palkin (1949) and also Rubleva and Bergman (1956) repeated this system and found the eutectic at 726° and 33 weight percent (30 mole percent) CaSO₄. We experienced difficulty in trying to verify their results because of

gravitative differentiation in the melts. Calcium sulfate settled out in the thin liquid. We prepared several compositions in the system and verified the eutectic thermal effect at 725°C. Figure 36 shows the results of Bye and Kiehl (1948) and of Rubleva and Bergman (1956).

CaCl₂-Na₂SO₄

This is a pseudobinary diagonal in the reciprocal salt system Na,Ca/Cl,SO₄. Palkin (1949), without giving any experimental data or actual temperatures, reported that upon the addition of CaCl₂ to Na₂SO₄, the liquidus was lowered from 884°C until the composition reaches the boundary where CaSO₄ becomes the primary phase. The CaSO₄ field is crossed to where CaCl₂ becomes the primary phase; the liquidus then rises to the melting point of CaCl₂, 775°C. (See fig. 37.)

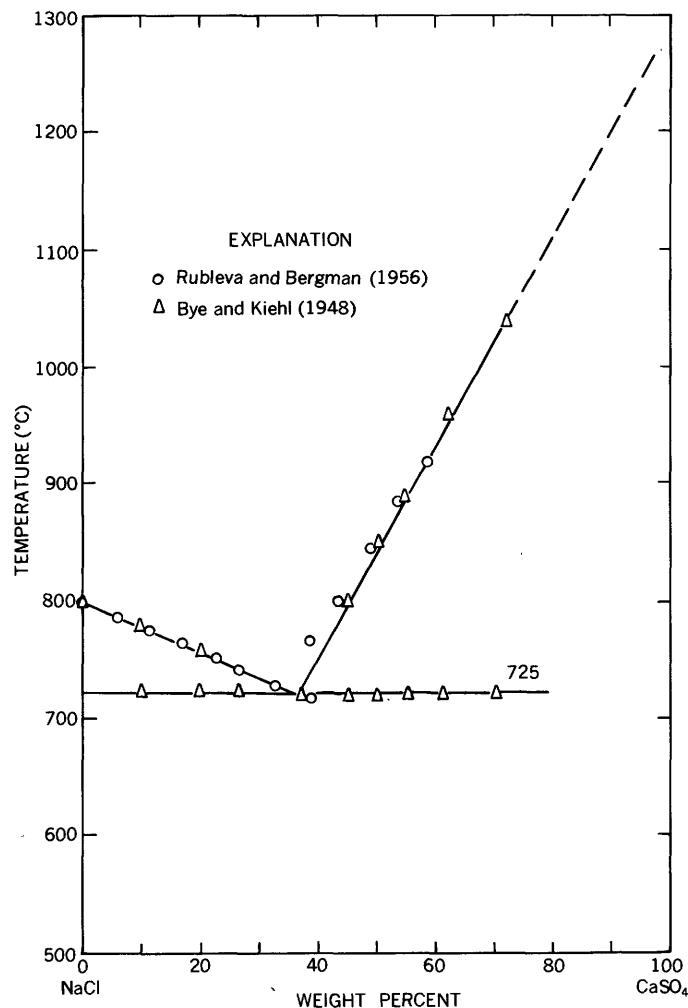


FIGURE 36.—The join NaCl-CaSO₄ in the Na,Ca/Cl,SO₄ reciprocal salt system (from Bye and Kiehl, 1948, and Rubleva and Bergman, 1956).

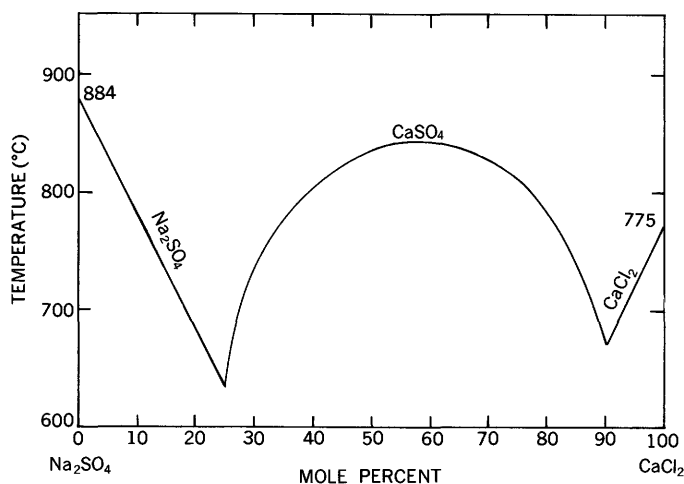


FIGURE 37.—The pseudobinary diagonal $\text{CaCl}_2\text{-Na}_2\text{SO}_4$ in the Na,Ca/Cl,SO_4 reciprocal salt system (from Palkin, 1949).

DISCUSSION

This system was reported by Palkin (1949) and by Zimina, Bergman, and Nagornyi (1965) (fig. 38). The liquidus minimum at 628°C in the $\text{NaCl-Na}_2\text{SO}_4$ system rose to a maximum at 640°C because of the Na_2SO_4 solid solution, and then descended to a eutectic at 634°C (Zimina and others, 1965). There are primary fields for CaSO_4 , $(\text{Na,Ca})\text{SO}_4$ solid solution, NaCl , and CaCl_2 with no ternary compounds shown. The stable join NaCl-CaSO_4 divides the system into two stable ternary systems,

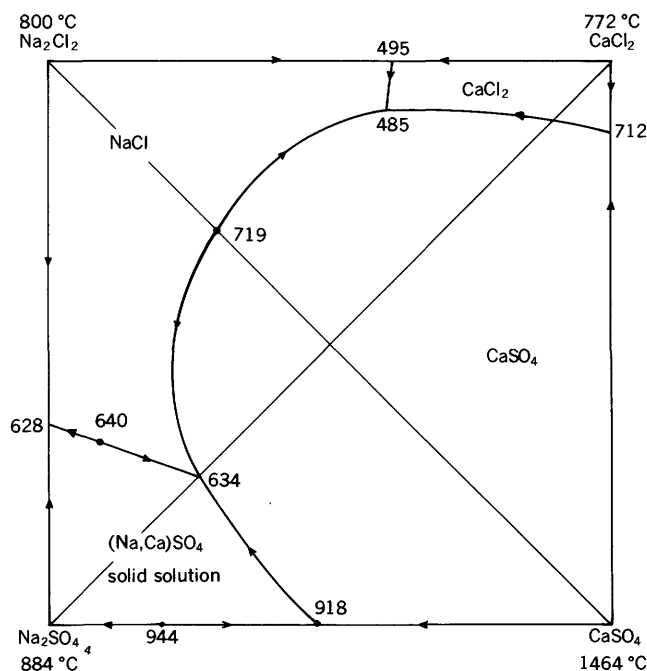


FIGURE 38.—The reciprocal salt system Na,Ca/Cl,SO_4 (from Zimina and other, 1965).

$\text{NaCl-CaSO}_4\text{-Na}_2\text{SO}_4$ and $\text{NaCl-CaSO}_4\text{-CaCl}_2$. Eutectics are at 634°C and 485°C , but there is no indication of a field for glauberite or the extent of the solid solution field of $(\text{Na,Ca})\text{SO}_4$.

Ca,K/Cl,SO_4 RECIPROCAL SALT SYSTEM

The third reciprocal salt system in the quaternary reciprocal salt system Na,K,Ca/Cl,SO_4 is the Ca,K/Cl,SO_4 system (fig. 3B). This system consists of $\text{CaCl}_2\text{-KCl}$, $\text{CaCl}_2\text{-CaSO}_4$, $\text{KCl-K}_2\text{SO}_4$, and $\text{CaSO}_4\text{-K}_2\text{SO}_4$ as edges and $\text{CaCl}_2\text{-K}_2\text{SO}_4$ and KCl-CaSO_4 as diagonals.

BINARY SYSTEMS

$\text{CaCl}_2\text{-KCl}$

The system $\text{CaCl}_2\text{-KCl}$ was studied by Menge (1911) (fig. 39) who found only one compound, $\text{KCl}\cdot\text{CaCl}_2$, which melts congruently at 754°C . Eutectics are found with KCl at 597°C and 65 percent KCl and with CaCl_2 at 641°C and 19 percent KCl . Menge's results were essentially confirmed by Golubeva and Bergman (1956), Jänecke and Mühlhäusser (1936), and Scholich (1920).

$\text{CaCl}_2\text{-K}_2\text{SO}_4$

The pseudobinary join $\text{CaCl}_2\text{-K}_2\text{SO}_4$ in the system Ca,K/Cl,SO_4 was studied by Jänecke and Mühlhäusser (1936). They found that the addition of CaCl_2 to K_2SO_4 lowered the liquidus from $1,069^\circ\text{C}$ to about 770° near 26 mole percent CaCl_2 where calcium langbeinite becomes the primary phase (fig. 40).

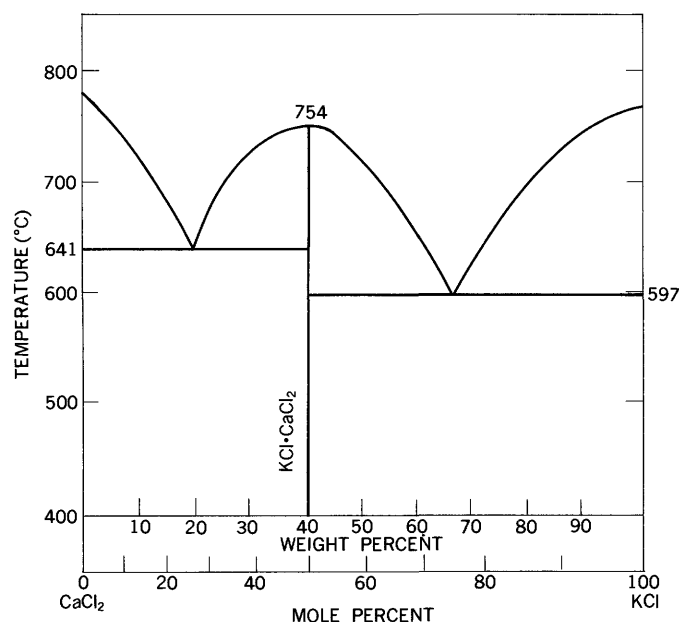


FIGURE 39.—The binary system KCl-CaCl_2 (from Menge, 1911).

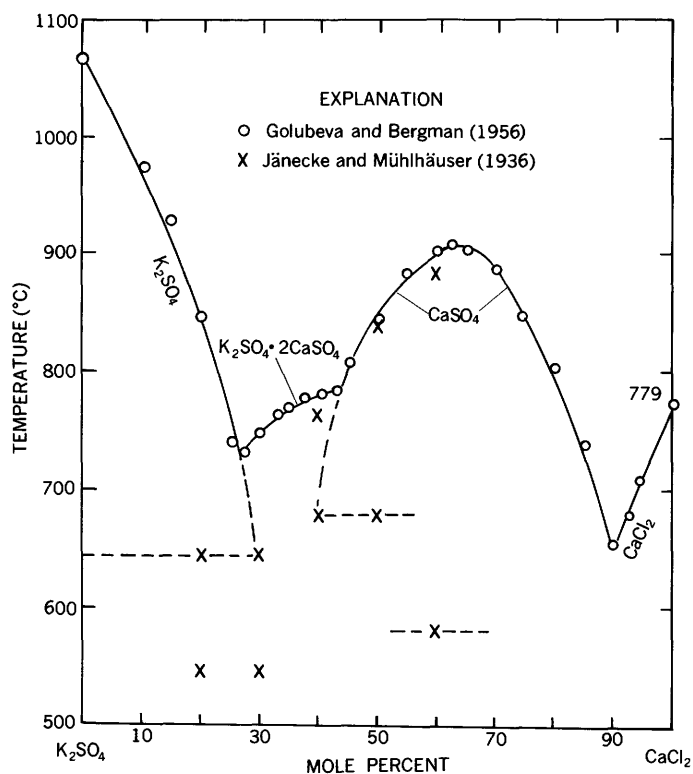


FIGURE 40.—The pseudobinary diagonal $\text{CaCl-K}_2\text{SO}_4$ in the K,Ca/Cl,SO_4 reciprocal salt system (from Golubeva and Bergman, 1956, and Jänecke and Mühlhäusser, 1936).

The liquidus rises as it crosses the calcium langbeinite primary phase to 790°C and 43.5 mole percent CaCl_2 where CaSO_4 becomes the primary phase. It then rises and falls again as it crosses the CaSO_4 field to meet the boundary of the CaCl_2 field, whence it rises to the melting point of CaCl_2 , 779°C . The part of the system high in CaCl_2 was not investigated but was extrapolated from the internal sections and binary data.

According to Golubeva and Bergman (1956) the diagonal passes through five fields: CaCl_2 , CaSO_4 , $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ (calcium langbeinite), $2\text{K}_2\text{SO}_4 \cdot 3\text{CaSO}_4$, and K_2SO_4 , intersecting the boundaries at 720°C and 26.5 mole percent CaCl_2 , 785°C and 42.5 mole percent CaCl_2 , and 645°C and 90 mole percent CaCl_2 . The study of the $\text{K}_2\text{SO}_4\text{--CaSO}_4$ system by Rowe, Morey and Hansen (1965) failed to find any evidence of the $2\text{K}_2\text{SO}_4 \cdot 3\text{CaSO}_4$ compound reported by Golubeva and Bergman (1956). Figure 40 is from data of Golubeva and Bergman (1956) and Jänecke and Mühlhäusser (1936); the plot of Golubeva's data seems to confirm the interpretation of Jänecke.

KCl--CaSO_4

Jänecke and Mühlhäusser (1936) reported that the KCl--CaSO_4 join was a stable binary system with a

eutectic at 685°C and 31 mole percent (29 wt percent) CaSO_4 . Golubeva and Bergman (1956) found the eutectic to be 688°C and 32 mole percent CaSO_4 and reported an incongruently melting compound, $2\text{KCl} \cdot \text{CaSO}_4$, with a peritectoid at 790°C and 44.5 mole percent CaSO_4 . Rubleva and Bergman (1965) also studied this binary and reported the eutectic to be 687°C and 30.5 mole percent CaSO_4 and the peritectoid to be 827°C and 47.5 mole percent CaSO_4 .

The data of Golubeva and Bergman (1956), Rubleva and Bergman (1956), and Jänecke and Mühlhäusser (1936) are plotted in figure 41. Liquidus determinations provide slight evidence of an incongruently melting compound of possible composition $2\text{KCl} \cdot \text{CaSO}_4$. Jänecke and Mühlhäusser, however, detected a thermal effect at 688°C for a composition containing 60 mole percent CaSO_4 which would indicate that such a compound does not exist. We prepared, by melting and annealing, a composition containing 52 mole percent (50 wt percent) CaSO_4 . X-ray examination showed only KCl and CaSO_4 . Heating-cooling study of this composition showed a

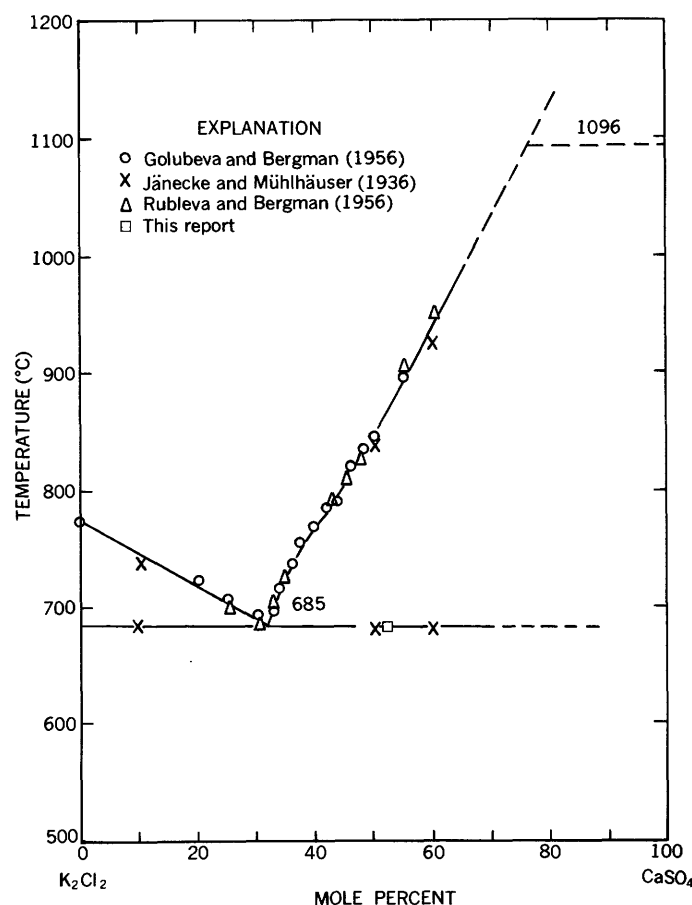
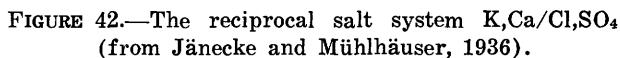


FIGURE 41.—The binary join KCl--CaSO_4 in the K,Ca/Cl,SO_4 reciprocal salt system.

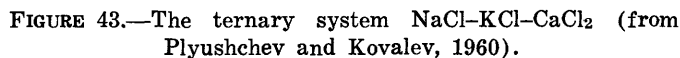
DISCUSSION

Figure 42 is from Jänecke and Mühlhäusser (1936). We did not include the fields for $2K_2SO_4 \cdot 3CaSO_4$ and $2KCl \cdot CaSO_4$ reported by Golubeva and Bergman (1956).

The ternary system NaCl-KCl-CaCl_2 formed by the three chlorides of the quaternary reciprocal salt system Na,K,Ca/Cl,SO_4 was studied by Scholich (1920). There are no ternary compounds. The field of the binary compound KCl-CaCl_2 extends into the ternary system. Plyushchev and Kovalev (1960) (see fig. 43) restudied the system and confirmed most of the results of Scholich but obtained different temperatures for the invariant points. They reported the eutectic to be 465°C and the minimum on the boundary between solid solution $(\text{Na,K})\text{Cl}$ and KCl-CaCl_2 to be 515°C .



This ternary system, formed by the three sulfates of the quaternary reciprocal salt system, was studied by Bellanca (1942). The phase diagram (fig. 44) shows three fields: CaSO_4 , $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4$, and $(\text{K}, \text{Na}, \text{Ca})\text{SO}_4$ solid solution.



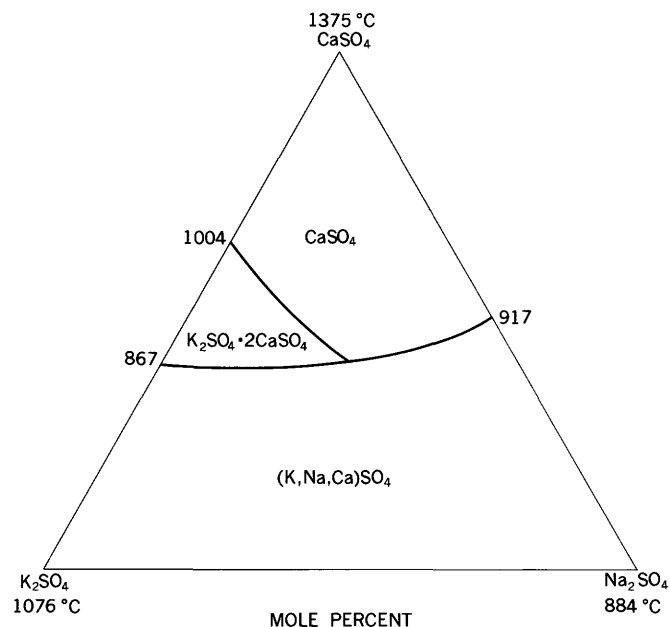


FIGURE 44.—The ternary system $\text{Na}_2\text{SO}_4\text{--CaSO}_4\text{--K}_2\text{SO}_4$ (modified from Bellanca, 1942).

$\text{NaCl}\text{--KCl}\text{--CaSO}_4$ PLANE

The $\text{NaCl}\text{--KCl}\text{--CaSO}_4$ plane across the quaternary reciprocal salt system Na,K,Ca/Cl,SO_4 was studied by Rubleva and Bergman (1956). They reported that the compound $2\text{KCl}\cdot\text{CaSO}_4$ had a field which extended from the side face of the ternary reciprocal salt system K,Ca/Cl,SO_4 into the ternary system. They found a minimum in the system at 605°C , 38.5 mole percent 2KCl , 19.0 mole percent CaSO_4 , and 42.5 mole percent 2NaCl . Decomposition of the $(\text{Na,K})\text{Cl}$ solid solution was found at temperatures below about 515°C .

We did not find evidence for the $2\text{KCl}\cdot\text{CaSO}_4$ compound in the $\text{KCl}\text{--CaSO}_4$ binary system. Examination of the liquidus curves of Rubleva and Bergman (1956) and those of Golubeva and Bergman (1956) provide only meager evidence for the existence of this compound, considering that they used only the visual polythermal method. We are therefore discounting the field for the $2\text{KCl}\cdot\text{CaSO}_4$ compound. Figure 45 is modified from Rubleva and Bergman (1956).

SUMMARY OF $\text{NaCl}\text{--K}_2\text{SO}_4\text{--CaSO}_4$ AS A PLANE IN THE Na,K,Ca/Cl,SO_4 SYSTEM

The $\text{NaCl}\text{--K}_2\text{SO}_4\text{--CaSO}_4$ side of the quaternary system $\text{NaCl}\text{--K}_2\text{SO}_4\text{--MgSO}_4\text{--CaSO}_4$ (fig 1) is a plane across the prism representing the quaternary reciprocal salt system Na,K,Ca/Cl,SO_4 (figs. 3B and

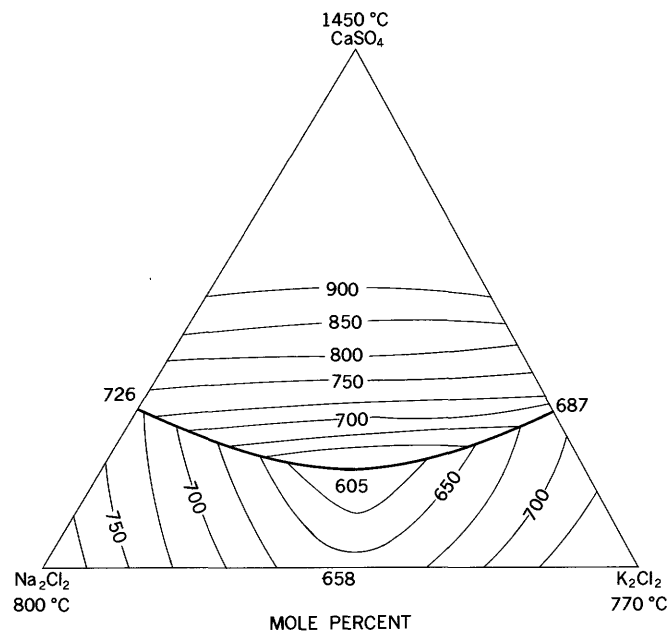
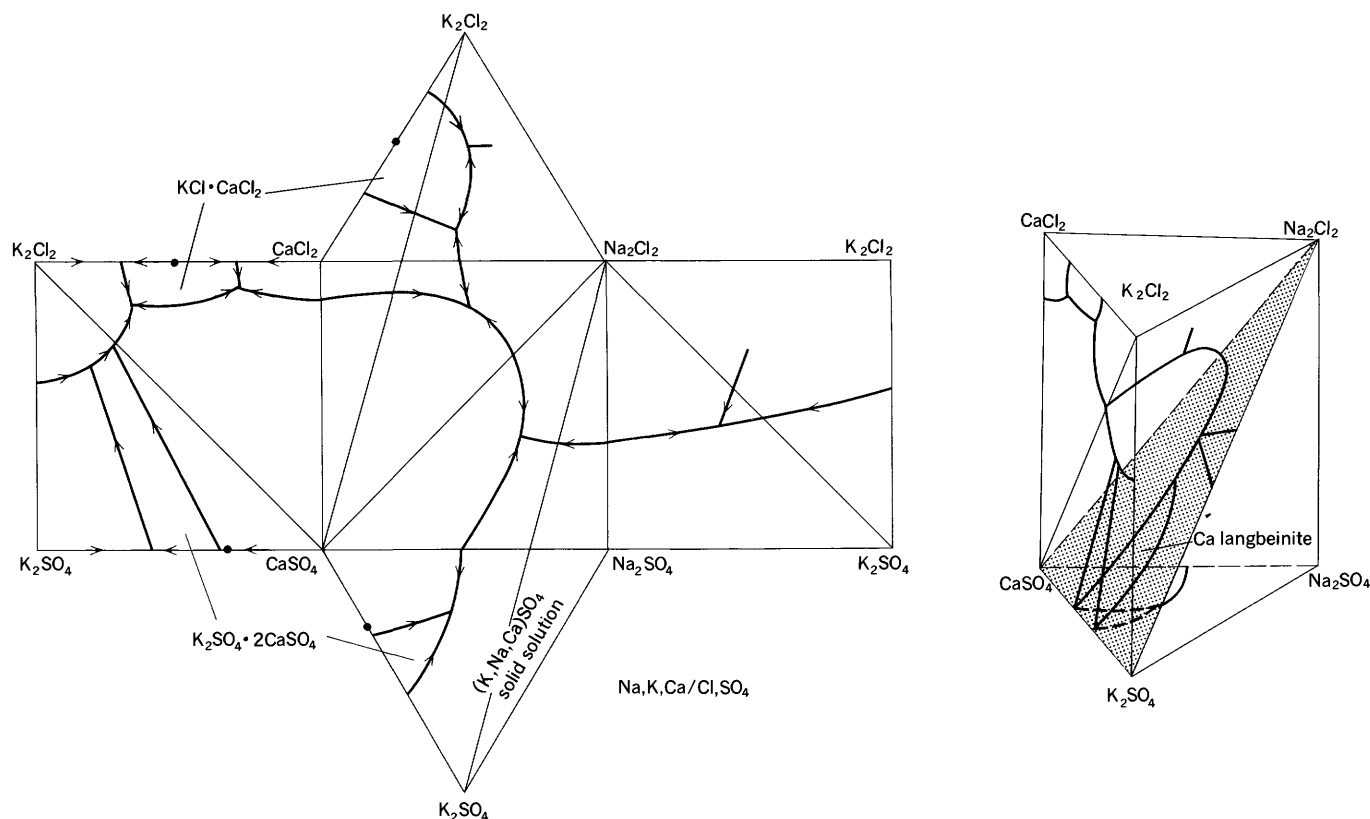


FIGURE 45.—The plane $\text{NaCl}\text{--KCl}\text{--CaSO}_4$ in the Na,K,Ca/Cl,SO_4 quaternary reciprocal salt system (modified from Rubleva and Bergman, 1956).

46). We will discuss the phase relations on this plane with respect to the phase volumes of the quaternary reciprocal salt system which it intersects.

In the manner used for discussion of the Na,K,Mg/Cl,SO_4 system (p. 17), we will consider whether or not two planes, as in figure 2, will divide the system into three stable quaternary systems. The $\text{NaCl}\text{--KCl}\text{--CaSO}_4$ system, which is a stable ternary system according to Rubleva and Bergman (1956), can be shown as a plane across the prism. It subdivides the prism to give a stable quaternary system, $\text{NaCl}\text{--KCl}\text{--CaSO}_4\text{--CaCl}_2$, in which phase volumes can be represented in the usual manner.

The $\text{NaCl}\text{--K}_2\text{SO}_4\text{--CaSO}_4$ plane represents a pseudoternary system which does not subdivide the prism into two more stable quaternary systems (fig. 46). Four compositions on the plane $\text{NaCl}\text{--K}_2\text{SO}_4\text{--CaSO}_4$ were prepared as shown in table 4 and figure 47 to determine the phase volumes intersected. We found the presence of KCl and $(\text{Na,K,Ca})\text{SO}_4$ solid solution in addition to NaCl and $\text{K}_2\text{SO}_4\cdot 2\text{CaSO}_4$ (calcium langbeinite). Hence this plane is one of greater than ternary complexity, probably of five components, crossing through the two subquaternary systems within the prism, $\text{KCl}\text{--Na}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--CaSO}_4$ and $\text{NaCl}\text{--KCl}\text{--Na}_2\text{SO}_4\text{--CaSO}_4$.

FIGURE 46.—The quaternary reciprocal salt system Na,K,Ca/Cl,SO₄.

Although the KCl-CaSO₄-Na₂SO₄ plane had never been studied, it must also be a pseudoternary system because the KCl-Na₂SO₄ join is a pseudobinary system. (See fig. 13.) It will also fail to subdivide the prism into the aforementioned subquaternary systems.

Nevertheless, from the limited data available, we can conclude that the phase volume for CaSO₄ occupies a considerable part of the prism, intersecting the planes NaCl-K₂SO₄-CaSO₄ and NaCl-KCl-CaSO₄. The calcium langbeinite (K₂SO₄·2CaSO₄) phase volume extends from the ternary Na₂SO₄-K₂SO₄-CaSO₄ system to intersect the NaCl-K₂SO₄-

CaSO₄ plane; it does not occur in the NaCl-KCl-CaSO₄ plane. The phase volumes of (Na,K,Ca)SO₄ and (Na,K)Cl solid solutions intersect the NaCl-K₂SO₄-CaSO₄ plane. Other arrangements of the boundary curves are possible, although all the fields shown are required by their presence in the bounding systems.

Additional study is needed to resolve the differences between previous investigators regarding KCl-CaSO₄ and the Na,K/Cl,SO₄ system. Study should also be made of the KCl-CaSO₄-Na₂SO₄ plane and the further subdivision of the prism by joins to calcium langbeinite and to KCl·CaCl₂.

TABLE 4.—Compositions on the NaCl-K₂SO₄-CaSO₄ plane in the Na,K,Ca/Cl,SO₄ quaternary reciprocal salt system

NaCl (wt percent)	K ₂ SO ₄ (wt percent)	CaSO ₄ (wt percent)	Phases present	Liquidus temperature (°C)	Temperature of other thermal effects (°C)	Primary phase
10.0	35.1	54.9	K ₂ SO ₄ ·2CaSO ₄ +NaCl+(Na,K,Ca)SO ₄ + KCl+CaSO ₄	946	800, 515	CaSO ₄
20.0	31.2	48.8	K ₂ SO ₄ ·2CaSO ₄ +NaCl+KCl+ (Na,K,Ca)SO ₄ +CaSO ₄	825	630, 515	CaSO ₄
50.0	19.5	30.5	CaSO ₄ +NaCl+KCl+(Na,K,Ca)SO ₄	660	630, 515	(Na,K)Cl
35	30	35	CaSO ₄ +NaCl+KCl+(Na,K,Ca)SO ₄	---	560, 515	CaSO ₄

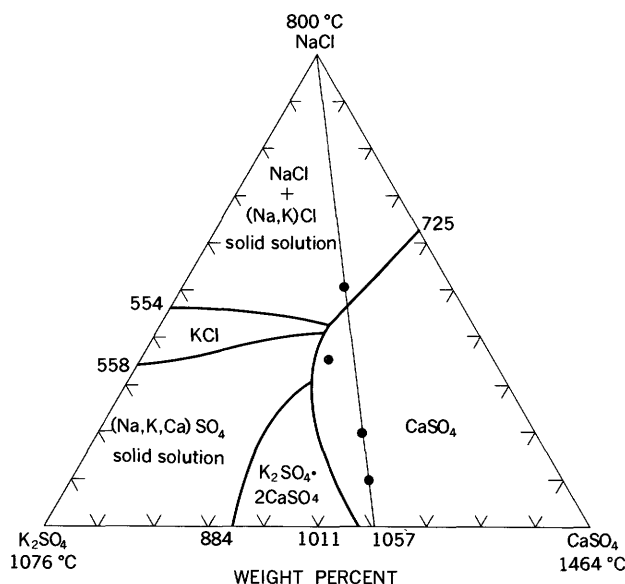


FIGURE 47.—The plane $\text{NaCl-K}_2\text{SO}_4\text{-CaSO}_4$ in the Na,K,Ca/Cl,SO_4 quaternary reciprocal salt system.

THE SYSTEM $\text{NaCl-MgSO}_4\text{-CaSO}_4$

The system $\text{NaCl-MgSO}_4\text{-CaSO}_4$ is a plane across the prism representing the quaternary reciprocal salt system Na,Mg,Ca/Cl,SO_4 , which consists of the reciprocal salt systems Na,Ca/Cl,SO_4 ; Na,Mg/Cl,SO_4 ; and Mg,Ca/Cl,SO_4 and the ternary systems of $\text{NaCl-MgCl}_2\text{-CaCl}_2$ and $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ (fig. 3C).

Mg,Ca/Cl,SO_4 RECIPROCAL SALT SYSTEM

The Mg,Ca/Cl,SO_4 reciprocal salt system consists of $\text{CaCl}_2\text{-MgCl}_2$, $\text{CaCl}_2\text{-CaSO}_4$, $\text{MgCl}_2\text{-MgSO}_4$, and $\text{CaSO}_4\text{-MgSO}_4$ as edges and $\text{CaCl}_2\text{-MgSO}_4$ and $\text{MgCl}_2\text{-CaSO}_4$ as diagonals.

BINARY SYSTEMS

$\text{CaCl}_2\text{-MgCl}_2$

Menge (1911) found $\text{CaCl}_2\text{-MgCl}_2$ to be a simple eutectic system with the eutectic at 621°C and 39.1 mole percent (42.8 wt. percent) CaCl_2 (fig. 48). Ivanov (1952) reported the eutectic to be 611°C .

$\text{CaCl}_2\text{-MgSO}_4$

We found no information in the literature regarding the $\text{CaCl}_2\text{-MgSO}_4$ diagonal of the reciprocal salt system Mg,Ca/Cl,SO_4 nor did we study it.

$\text{MgCl}_2\text{-CaSO}_4$

No information is available for this binary diagonal.

DISCUSSION

We have no reference to any previous study of the Mg,Ca/Cl,SO_4 reciprocal salt system. There is information regarding each of the binary side systems including an incomplete study we made of the

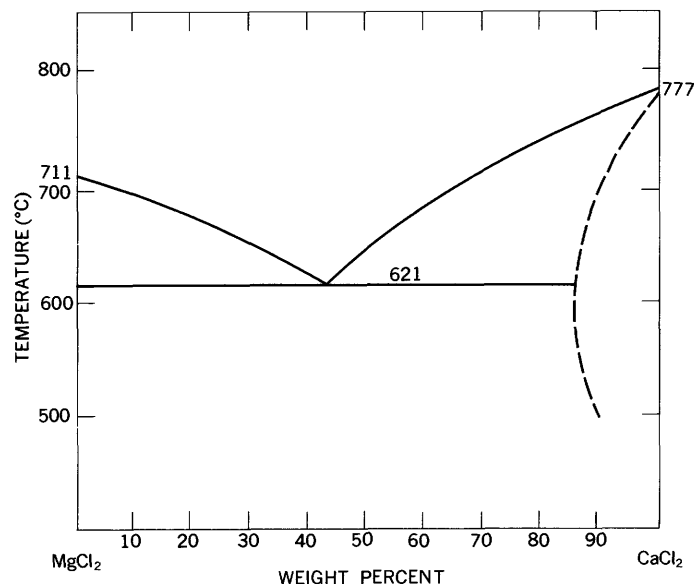


FIGURE 48.—The binary system $\text{CaCl}_2\text{-MgCl}_2$ (from Menge, 1911).

$\text{MgSO}_4\text{-CaSO}_4$ system. No binary compounds are reported for three of the four side systems. In the $\text{CaSO}_2\text{-MgSO}_4$ system we found at least one compound, $\text{CaSO}_4\cdot 3\text{MgSO}_4$. It is not known how far into the reciprocal salt system its field will extend. The internal sections of this reciprocal salt system should be studied to determine the extent of the $\text{CaSO}_4\cdot 3\text{MgSO}_4$ field and the boundaries of the fields of MgSO_4 , CaSO_4 , MgCl_2 , and CaCl_2 , and to learn if any heteroionic compounds formed. If any such compounds are found, it would be necessary to determine the phase volumes in the quaternary reciprocal salt system Na,Ca,Mg/Cl,SO_4 .

$\text{NaCl-MgCl}_2\text{-CaCl}_2$ TERNARY SYSTEM

This ternary chloride system formed from the three reciprocal salt systems Na,Mg/Cl,SO_4 , Na,Ca/Cl,SO_4 , and Ca,Mg/Cl,SO_4 has not been previously studied. In the $\text{CaCl}_2\text{-MgCl}_2$ system there are no binary compounds. In the NaCl-MgCl_2 system, Klemm and Weiss (1940) found two incongruently melting compounds, $2\text{NaCl}\cdot\text{MgCl}_2$ and $\text{NaCl}\cdot\text{MgCl}_2$. Scholich (1920) reported that the NaCl-CaCl_2 system was a simple eutectic system with no binary compounds. Because of the limited data, the ternary system $\text{NaCl-MgCl}_2\text{-CaCl}_2$ is shown in figure 50 as an incomplete system.

$\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ TERNARY SYSTEM

This ternary sulfate system had been studied by Mukimov and Fillipova (1949) (fig. 49), using the

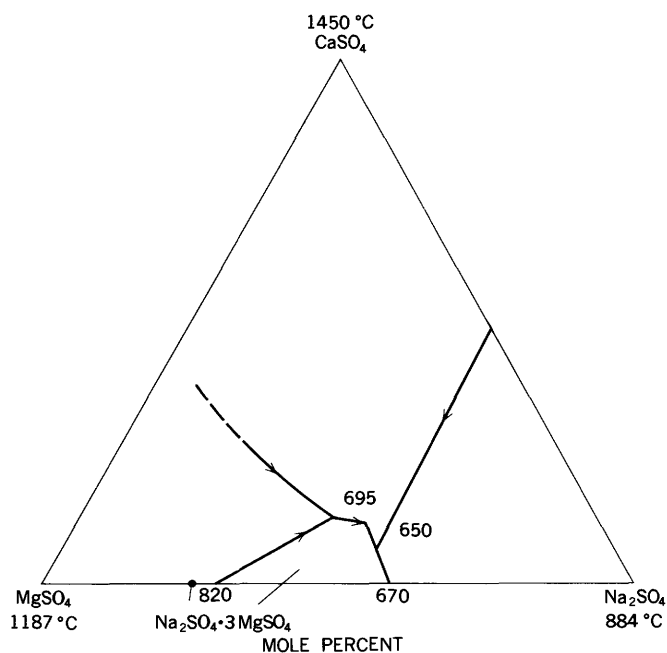


FIGURE 49.—The ternary system $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ (from Mukimov and Fillipova, 1949).

visual polythermal method. They reported that they were unable to study the $\text{MgSO}_4\text{-CaSO}_4$ binary system and the part of the ternary system adjacent to

it. They presumed the $\text{CaSO}_4\text{-MgSO}_4$ system to be a simple binary system with no compounds. The problems associated with study of this system were discussed on page 6, where the results of our studies are presented.

Mukimov and Fillipova (1949) reported a ternary eutectic at 650°C , 7 mole percent CaSO_4 , 40 mole percent MgSO_4 , and 53 mole percent Na_2SO_4 and a transition point at 695°C , 13 mole percent CaSO_4 , 44 mole percent MgSO_4 , and 43 mole percent Na_2SO_4 . There is a ternary field for the incongruently melting $\text{Na}_2\text{SO}_4\cdot 3\text{MgSO}_4$ (antivanthoffite).

This system should be restudied to determine the field of $\text{CaSO}_4\cdot 3\text{MgSO}_4$ and the extent of the $(\text{Na,Ca})\text{SO}_4$ and $(\text{Na,Mg})\text{SO}_4$ solid solutions.

SUMMARY OF $\text{NaCl-MgSO}_4\text{-CaSO}_4$ AS A PLANE IN THE Na,Mg,Ca/Cl,SO_4 SYSTEM

The system $\text{NaCl-MgSO}_4\text{-CaSO}_4$ is one side of the tetrahedron representing the quaternary system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4$, shown in figure 1. It can be considered to be a plane across the prism for the quaternary reciprocal salt system Na,Mg,Ca/Cl,SO_4 , as shown in figure 50.

Compositions on this plane, as shown in table 5 and figure 51, were prepared and studied using heating-cooling, quenching, and hot-stage microscopy.

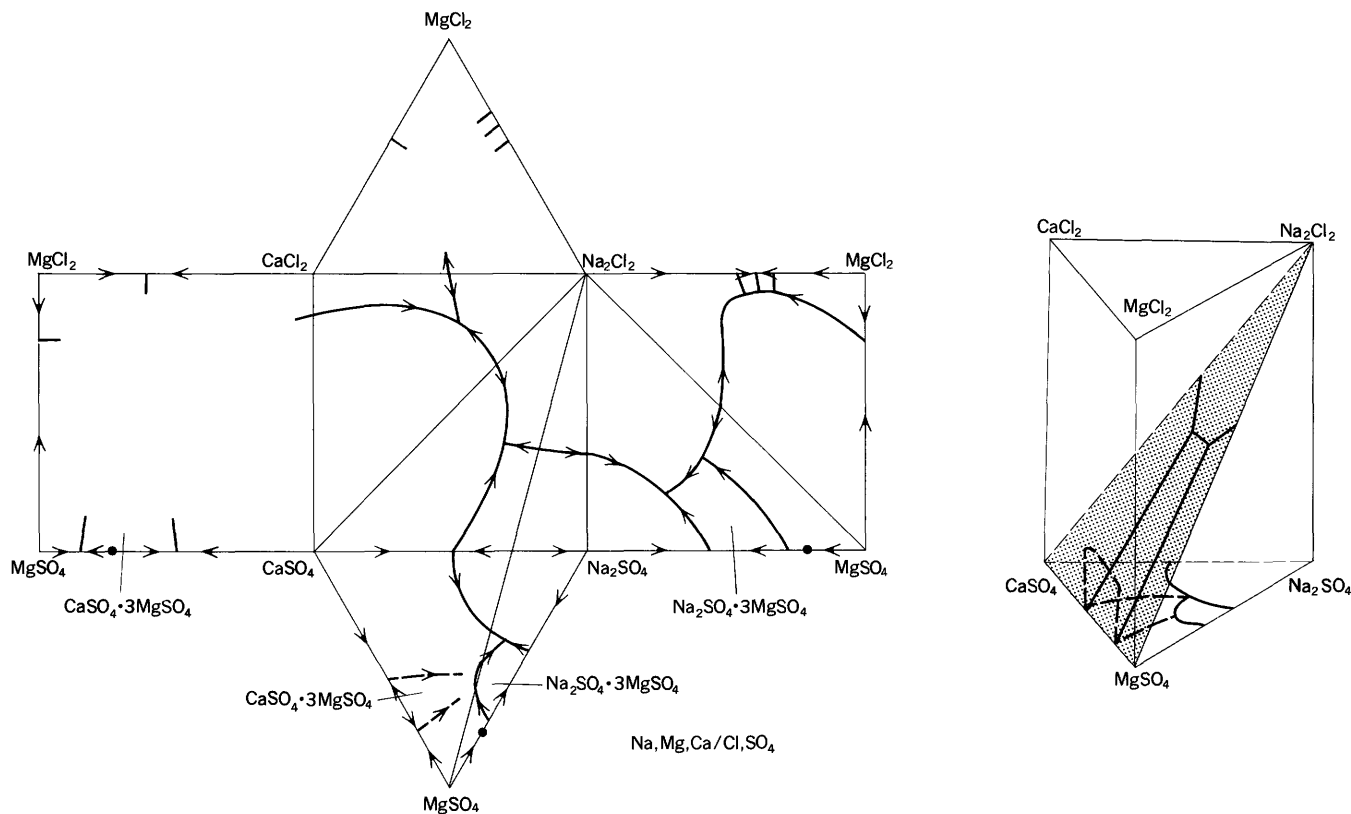


FIGURE 50.—The Na,Mg,Ca/Cl,SO_4 quaternary reciprocal salt system.

TABLE 5.—Compositions on the NaCl-MgSO₄-CaSO₄ plane in the Na,Mg,Ca/Cl,SO₄ quaternary reciprocal salt system

NaCl (wt percent)	MgSO ₄ (wt percent)	CaSO ₄ (wt percent)	Phases present	Liquidus temperature (°C)	Temperature of other thermal effects (°C)	Primary phase
Compositions of the join NaCl to CaSO ₄ ·3MgSO ₄						
0	72.5	28.5	CaSO ₄ ·3MgSO ₄	1201	-----	CaSO ₄ ·3MgSO ₄
20	57	23	NaCl+CaSO ₄ ·3MgSO ₄	880	645, 575	CaSO ₄ ·3MgSO ₄
30	50	20	NaCl+CaSO ₄ ·3MgSO ₄	-----	-----	CaSO ₄ ·3MgSO ₄
40	43	17	NaCl+CaSO ₄ ·3MgSO ₄	660	645, 630, 575	CaSO ₄ ·3MgSO ₄
50	36	14	NaCl+CaSO ₄ ·3MgSO ₄	-----	-----	CaSO ₄ ·3MgSO ₄
60	28.5	11.5	NaCl+CaSO ₄ ·3MgSO ₄	660	645, 630, 580	NaCl
70	21.5	8.5	NaCl+CaSO ₄ ·3MgSO ₄	-----	-----	NaCl
80	13.5	5.5	NaCl+CaSO ₄ ·3MgSO ₄	-----	-----	-----
Other compositions						
40	50	10	NaCl+MgSO ₄ +CaSO ₄ ·3MgSO ₄	640	-----	MgSO ₄
50	30	20	NaCl+CaSO ₄ +CaSO ₄ ·3MgSO ₄	680	640, 585	CaSO ₄
50	20	30	NaCl+CaSO ₄ +CaSO ₄ ·3MgSO ₄	700	675, 645, 580	CaSO ₄
40	30	30	NaCl+CaSO ₄ +CaSO ₄ ·3MgSO ₄	710	640, 580	CaSO ₄

Coexisting phases in the cooled melt and in quenches were identified by X-ray and optical properties. Because extensive experimental study was not completed, only limited data are available. Nevertheless, we can conclude that it is a ternary plane across the prism, intersecting phase volumes of MgSO₄, CaSO₄, NaCl, and CaSO₄·3MgSO₄ as shown in figures 50 and 51.

The join from NaCl to CaSO₄·3MgSO₄ is a stable join. We found NaCl plus CaSO₄·3MgSO₄ in the cooled melt for all compositions on this join. Com-

positions richer in CaSO₄ showed CaSO₄ plus CaSO₄·3MgSO₄ and NaCl, while compositions richer in MgSO₄ showed MgSO₄ plus CaSO₄·3MgSO₄ and NaCl.

Additional study should be made to determine the subdivision of the quaternary reciprocal salt system Na,Mg,Ca/Cl,SO₄ into stable subsystems by additional planes and joins. These studies should include the plane NaCl-MgCl₂-CaSO₄ and the various joins to Na₂SO₄·3MgSO₄, NaCl-MgCl₂, and 2NaCl-MgCl₂. The systems for which data are lacking should also be included in future studies.

THE QUATERNARY RECIPROCAL SALT SYSTEM K,Mg,Ca/Cl,SO₄

The K,Mg,Ca/Cl,SO₄ quaternary reciprocal salt system consists of the reciprocal salt systems K, Ca/Cl,SO₄; K,Mg/Cl,SO₄; and Mg,Ca/Cl,SO₄ and the ternary systems KCl-MgCl₂-CaCl₂ and K₂SO₄-MgSO₄-CaSO₄ (fig. 3D). All of these systems have been considered earlier except for the KCl-MgCl₂-CaCl₂ ternary system.

KCl-MgCl₂-CaCl₂

This ternary system was studied by Ivanov (1952) (fig. 52), who found no ternary compounds in the system. There are fields in the ternary system for the binary compounds KCl-MgCl₂, 2KCl-MgCl₂, and KCl-CaCl₂.

DISCUSSION

No study has been made of the internal planes of the prism representing compositions in the quaternary reciprocal salt system K,Mg,Ca/Cl,SO₄. Figure 53 shows the three ternary reciprocal salt sys-

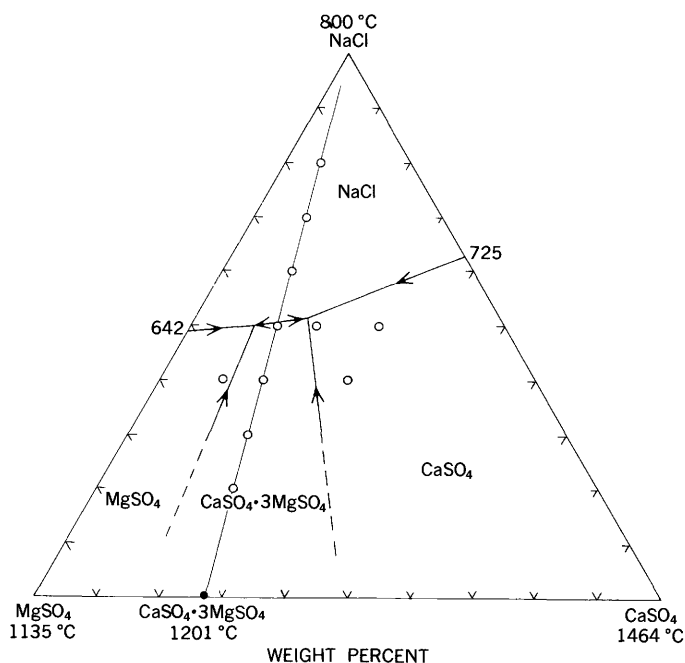


FIGURE 51.—The plane NaCl-MgSO₄-CaSO₄ in the Na,Mg,Ca/Cl,SO₄ quaternary reciprocal salt system.

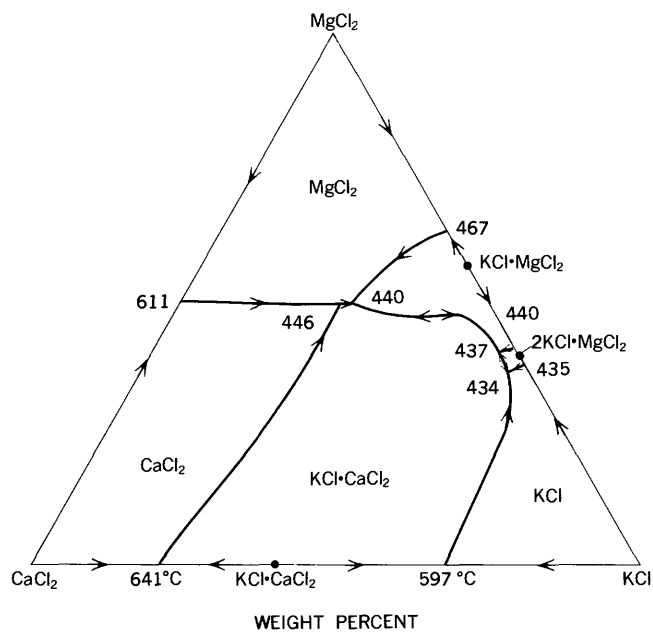


FIGURE 52.—The ternary system $KCl-MgCl_2-CaCl_2$ (from Ivanov, 1952).

tems and the two ternary systems comprising this quaternary reciprocal salt system. The $2KCl \cdot MgCl_2$ compound reported by Ivanov (1952) and Klemm, Beyersdorfer, and Oryschkewitsch (1948) was not

shown by Jänecke (1912) in the $K, Mg/Cl, SO_4$ system which was used for this compilation; however it will be included in the following discussion. It is not known how far into the composition prism the phase volumes of $CaSO_4 \cdot 3MgSO_4$, $K_2SO_4 \cdot 2MgSO_4$ (langbeinite), $K_2SO_4 \cdot 2CaSO_4$ (calcium langbeinite), solid solution of langbeinite-calcium langbeinite, $KCl \cdot CaCl_2$, $KCl \cdot MgCl_2$, $2KCl \cdot MgCl_2$, $CaSO_4$, $MgSO_4$, K_2SO_4 , $CaCl_2$, $MgCl_2$, and KCl will extend. Since KCl is found in the system $NaCl-K_2SO_4-MgSO_4-CaSO_4$, the effects and interactions of KCl with $K_2SO_4-MgSO_4-CaSO_4$ should be considered in the overall evaluation of the entire so-called quaternary system. It is not possible to predict the behavior of this quaternary reciprocal salt system without considerable experimental data, which is not available at present. Nevertheless, the quaternary reciprocal salt system is shown with the $Ca, Mg/Cl, SO_4$ system and the internal plane $KCl-MgSO_4-CaSO_4$ left incomplete.

A composition on a join from KCl to 22.5 percent $CaSO_4$, 36.5 percent $MgSO_4$, and 41.0 percent K_2SO_4 (in the ternary base), containing 50 percent KCl , was prepared and studied. The cooled melt showed KCl and langbeinite solid solution as the only phases. We can assume that the phase volume for

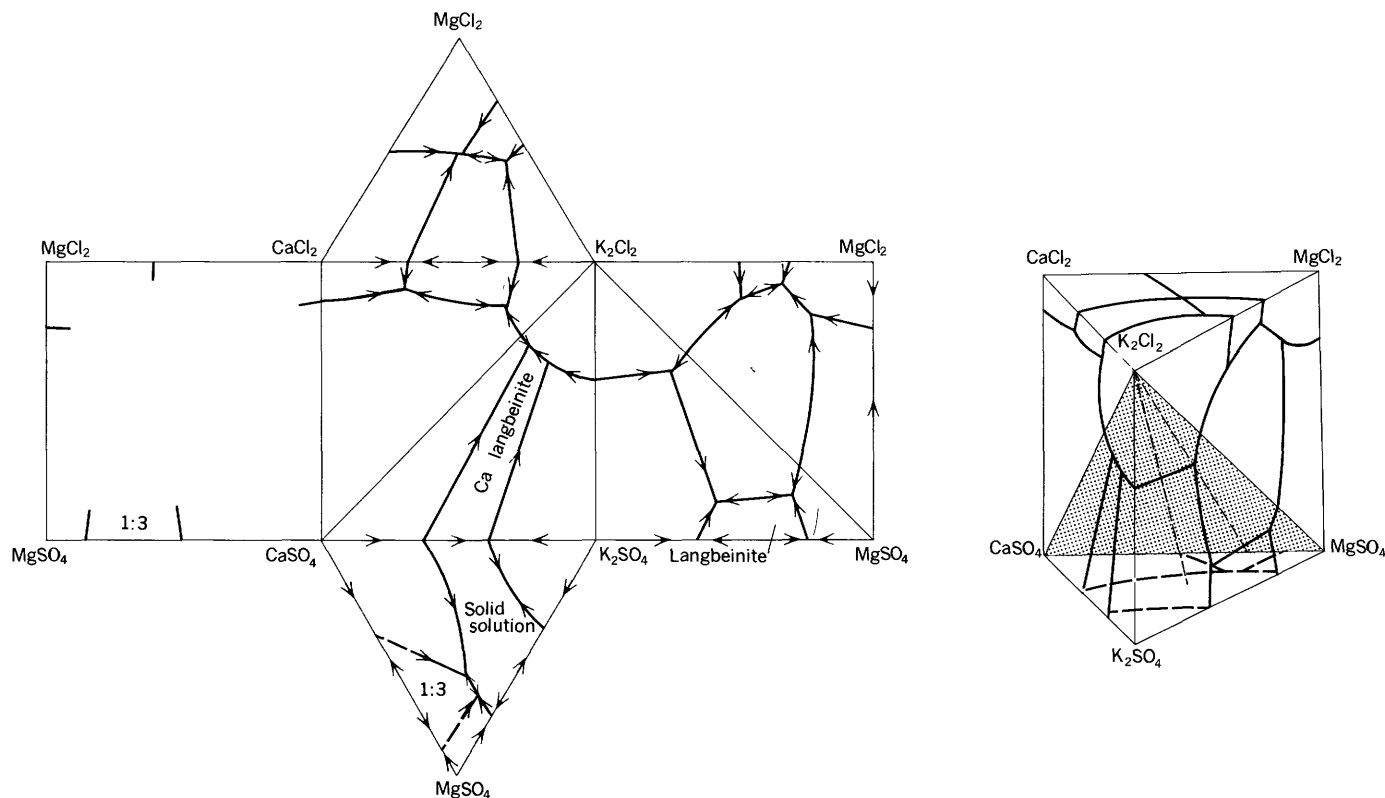


FIGURE 53.—The $K, Mg, Ca/Cl, SO_4$ quaternary reciprocal salt system.

langbeinite–calcium langbeinite solid solution occupies a considerable portion of the prism.

X-ray examination of a melt of composition 50 percent KCl on a join from KCl to $\text{CaSO}_4 \cdot 3\text{MgSO}_4$ showed the presence of KCl, MgCl_2 , and langbeinite solid solution. It must be concluded that the phase volume of langbeinite solid solution extends up into the composition prism to intersect the plane $\text{KCl-MgSO}_4\text{-CaSO}_4$. Therefore, the plane $\text{KCl-MgSO}_4\text{-CaSO}_4$ is pseudoternary.

Additional study should be done on the Ca,Mg/Cl,SO_4 ternary reciprocal salt system and on planes in the K,Mg,Ca/Cl,SO_4 quaternary reciprocal salt system to properly define this system.

$\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$

The system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ is the part of the quinary system $\text{Na,K,Mg,Ca/Cl,SO}_4$ which has direct application to the crystallization of the Gnome melt. It is a pseudoquaternary system in that fields are found for KCl and Na_2SO_4 . Hence its complete graphical representation is not quantitatively possible. To study parts of the system, we investigated the plane $\text{NaCl-langbeinite-calcium langbeinite}$ and a section containing 40 percent NaCl.

$\text{NaCl-K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (LANGBEINITE)— $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ (CALCIUM LANGBEINITE) PLANE

This is the plane from NaCl through langbeinite and calcium langbeinite across the tetrahedron (fig. 1) representing compositions in the system $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$. The liquidus on the join NaCl to $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (langbeinite) exhibits a minimum at 632°C and 47 percent NaCl (table 3, fig. 29). The liquidus on the join NaCl to $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ (calcium

langbeinite) shows a minimum at 630°C and 42 percent NaCl (table 4, fig. 47).

We prepared several compositions on the join NaCl to 70 percent langbeinite : 30 percent calcium langbeinite. Heating-cooling, quenching, and hot-stage microscope studies were made to determine thermal effects, liquidus, and primary phases. Results are shown in table 6 and figure 54. The liquidus minimum on this join is at 615°C and 37 percent NaCl. Langbeinite is the primary phase to this point; NaCl or $(\text{Na,K})\text{Cl}$ solid solution is the primary phase for compositions richer in NaCl than 37 percent.

Three compositions were prepared on the join from NaCl to 50 percent langbeinite on the langbeinite–calcium langbeinite join in the $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ system. These were studied to determine the extent of the primary phase volume of CaSO_4 (see table 6 and fig. 55). From quenching experiments, CaSO_4 was found to be the primary phase for the compositions containing 30 percent NaCl. It can be assumed that the langbeinite solid solution, on this join, decomposes to CaSO_4 plus liquid as was found in the ternary system $\text{K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$. The phase volume for CaSO_4 intersects the plane of this section and the NaCl becomes $(\text{Na,K})\text{Cl}$ within the system; hence, it is a pseudoternary system.

40-PERCENT NaCl PLANE IN THE $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ SYSTEM

The compositions we prepared on this plane are shown in table 7 and figure 56. The final cooled melts of compositions on this section show the presence of NaCl, KCl, Na_2SO_4 , MgSO_4 , CaSO_4 , langbeinite solid solution, and $\text{CaSO}_4 \cdot 3\text{MgSO}_4$.

TABLE 6.—Compositions in the $\text{NaCl-langbeinite-calcium langbeinite}$ plane in the $\text{NaCl-K}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$ system

[Lgss = langbeinite solid solution; ss = solid solution]

NaCl (wt percent)	K_2SO_4 (wt percent)	MgSO_4 (wt percent)	CaSO_4 (wt percent)	Phases present	Liquidus temperature ($^\circ\text{C}$)	Temperature of other thermal effects ($^\circ\text{C}$)	Primary phase
Compositions on the join NaCl to 70 percent langbeinite : 30 percent calcium langbeinite							
0	41.95	40.60	17.45	Lgss	900	----	Lgss
10	37.75	36.55	15.7	Lgss + $(\text{Na,K})\text{Clss}$	820	610, 515	Lgss
20	33.6	32.5	13.9	Lgss + $(\text{Na,K})\text{Clss}$	729	610, 515	Lgss
30	29.36	28.42	12.22	Lgss + $(\text{Na,K})\text{Clss}$	640	610, 515	Lgss
40	25.2	24.4	10.4	Lgss + $(\text{Na,K})\text{Clss}$	630	610, 565, 515	$(\text{Na,K})\text{Clss}$
50	20.98	20.3	8.72	Lgss + $(\text{Na,K})\text{Clss}$	705	615, 515	$(\text{Na,K})\text{Clss}$
Compositions on the join NaCl to 50 percent langbeinite : 50 percent calcium langbeinite							
30	28.4	20.6	21	$(\text{Na,K})\text{Clss} + \text{Lgss}$	> 620	610	CaSO_4
50	20.3	14.7	15	$(\text{Na,K})\text{Clss} + \text{Lgss}$	650	610, 515	$(\text{Na,K})\text{Clss}$
70	12.2	8.8	9	$(\text{Na,K})\text{Clss} + \text{Lgss}$	----	----	$(\text{Na,K})\text{Clss}$

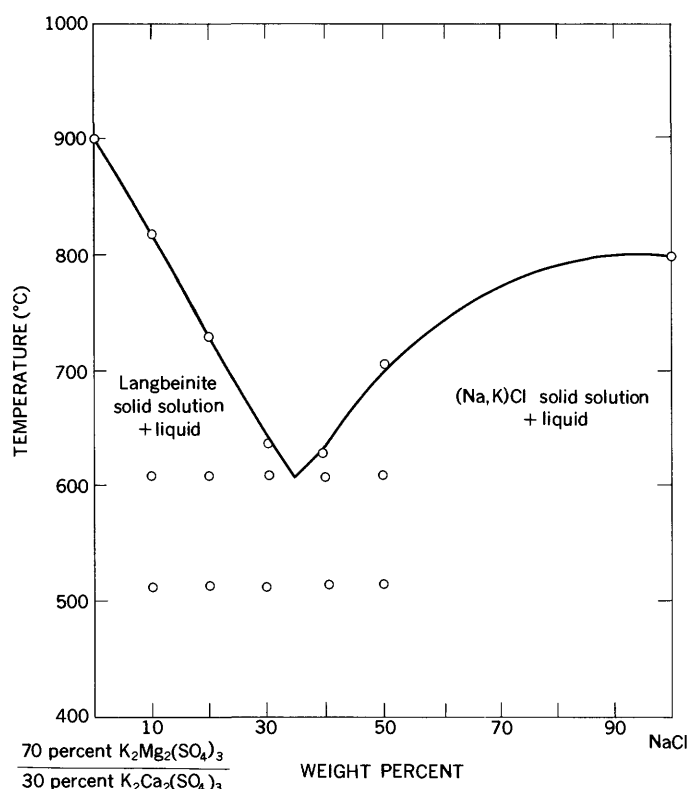


FIGURE 54.—The join NaCl to 70 percent langbeinite : 30 percent calcium langbeinite.

On the 40-percent NaCl plane, we have what appears to be a stable quaternary system in the area bounded by the langbeinite-calcium langbeinite join and the CaSO₄-MgSO₄ binary system. For compositions richer in K₂SO₄ than those on the langbeinite-calcium langbeinite join, the system is made complex by the formation of Na₂SO₄ (below the liquidus)

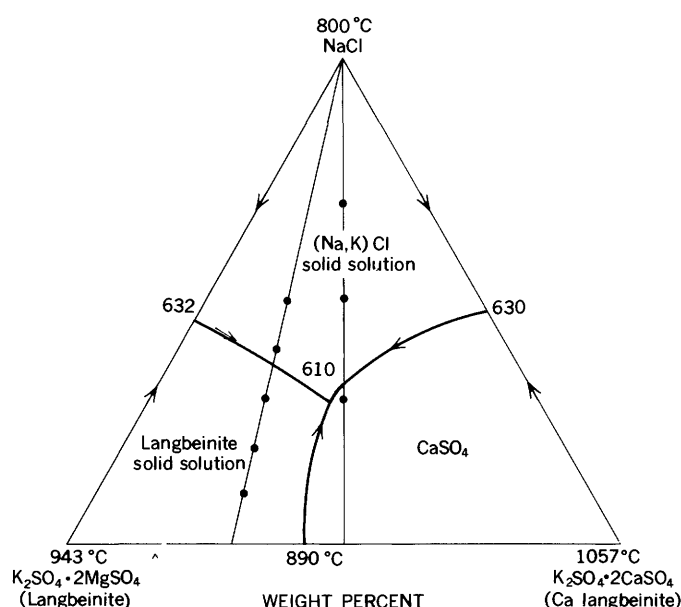


FIGURE 55.—The plane NaCl-langbeinite (K₂SO₄ · 2MgSO₄)-calcium langbeinite (K₂SO₄ · 2CaSO₄).

and KCl and is no longer quaternary but of higher order, containing five components; hence, all the phase composition cannot be graphically represented.

DISCUSSION

The four ternary systems which make up this so-called quaternary system are shown in figure 57. The phase relations were derived from the data of our incomplete study and the data from previous studies supplemented by limited experimental checking. The difficulty in representing a system of this complexity has been discussed earlier in this report.

TABLE 7.—Compositions on the 40-percent NaCl plane in the NaCl-K₂SO₄-MgSO₄-CaSO₄ system

[Lg = langbeinite, K₂SO₄ · 2MgSO₄; Lgss = langbeinite solid solution, (K,Mg,Ca)SO₄]

K ₂ SO ₄ (wt percent)	MgSO ₄ (wt percent)	CaSO ₄ (wt percent)	Phases present	Liquidus temperature (°C)	Temperature of other thermal effects (°C)	Primary phase
10	80	10	NaCl + CaSO ₄ · 3MgSO ₄ + MgSO ₄ + Lg	885	--	MgSO ₄
15	58.3	26.7	NaCl + CaSO ₄ · 3MgSO ₄ + CaSO ₄ + Lg	890	620	CaSO ₄ · 3MgSO ₄
15	43.4	41.6	NaCl + CaSO ₄ · 3MgSO ₄ + CaSO ₄ + Lg	773	548	CaSO ₄
16.6	50	33.4	NaCl + CaSO ₄ · 3MgSO ₄ + CaSO ₄ + Lg	660	616	CaSO ₄
20	20	60	NaCl + CaSO ₄ + Lgss	1020	--	CaSO ₄
25	60	15	NaCl + CaSO ₄ + Lgss + CaSO ₄ · 3MgSO ₄	625	555	Lgss
33.3	33.3	33.3	NaCl + CaSO ₄ + Lgss	620	490	CaSO ₄
35	20	45	NaCl + CaSO ₄ + Lgss	745	610	CaSO ₄
35.5	38.7	25.8	NaCl + CaSO ₄ + Lgss	654	--	Lg
38.3	41.7	20	NaCl + CaSO ₄ + Lgss	630	608	NaCl
41.6	41.6	16.8	NaCl + Lgss + KCl + Na ₂ SO ₄	625	510	NaCl
50	35	15	NaCl + Lgss + KCl + Na ₂ SO ₄	600	510	NaCl
50	25	25	NaCl + Lgss + KCl + Na ₂ SO ₄	700	590, 540, 485	NaCl
59	20	21	NaCl + Lgss + KCl + Na ₂ SO ₄	572	--	NaCl
66.6	16.7	16.7	NaCl + Lgss + KCl + Na ₂ SO ₄	578	562	NaCl

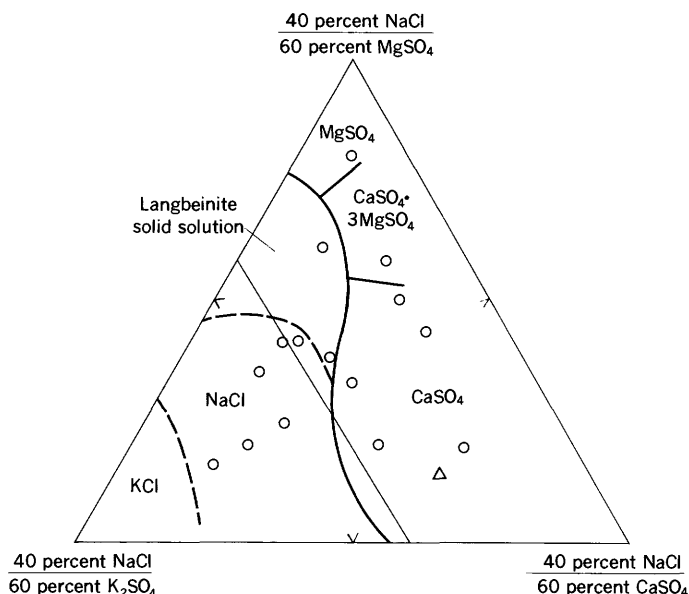


FIGURE 56.—The 40-percent NaCl plane in the NaCl-K₂SO₄-MgSO₄-CaSO₄ system. ○, compositions studied; Δ, intersection of the Gnome composition with this plane.

The tetrahedron representing the NaCl-K₂SO₄-MgSO₄-CaSO₄ system can be subdivided by planes joining the compounds in the system. The Gnome composition, shown as a triangle in figures 56 and 57, lies in a subtetrahedron bounded by NaCl-CaSO₄-K₂SO₄·2MgSO₄-K₂SO₄·2CaSO₄. Compositions on the 40-percent NaCl plane adjacent to the Gnome composition showed NaCl plus CaSO₄ plus langbeinite-

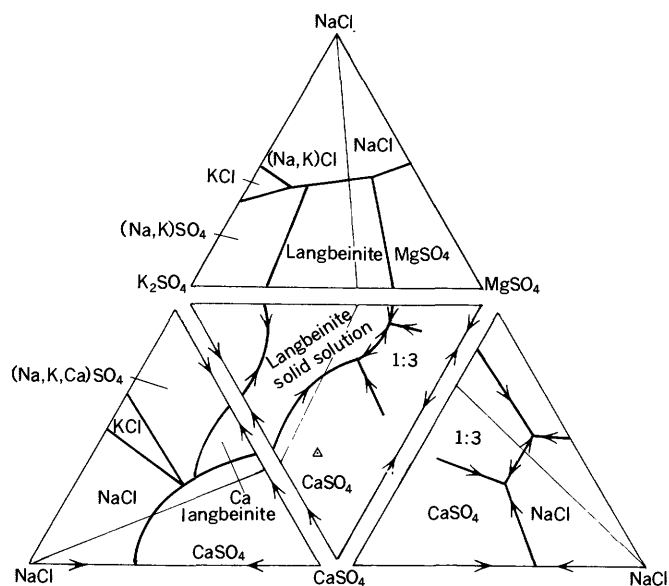
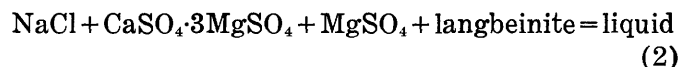
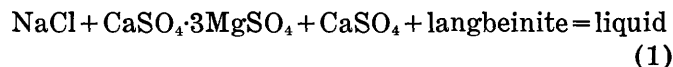


FIGURE 57.—The sides and base of the tetrahedron representing the NaCl-K₂SO₄-MgSO₄-CaSO₄ system. Δ, Gnome composition.

ite solid solution as the final phases in the cooled melt. Compositions in the tetrahedron bounded by NaCl-K₂SO₄·2MgSO₄-CaSO₄-CaSO₄·3MgSO₄ showed NaCl plus CaSO₄ plus langbeinite plus CaSO₄·3MgSO₄. The composition in the tetrahedron NaCl-CaSO₄·3MgSO₄-K₂SO₄·2MgSO₄-MgSO₄ gave NaCl plus MgSO₄ plus CaSO₄·3MgSO₄ plus langbeinite as the final phases.

The following quaternary isobaric invariant points will be considered in the discussion of the crystallization of the Gnome melt:



The NaCl in both 1 and 2 probably contains some KCl in solid solution, but the system will be nearly quaternary. Thus, these points may actually be isobarically univariant with the assemblages stable over a small temperature range. In other parts of the system, it has not been possible to determine invariant points because of the complexity.

CRYSTALLIZATION-DIFFERENTIATION IN THE GNOME MELT

From the limited work done in the various complex systems composing the NaCl-K₂SO₄-MgSO₄-CaSO₄ system, we can develop a theory for the probable course of crystallization of the melt after the Gnome event. We will assume that the melt consists of 5,000 tons of material with a composition of 80.7 percent NaCl, 4 percent K₂SO₄, 2.8 percent MgSO₄, and 12.5 percent CaSO₄ excluding silt, clay, and water. The impurities of silt, clay, and water occur as separate beds interlayered in the halite and account for less than 10 percent of the original material.

The first phase to crystallize will be NaCl (fig. 58) at about 760°C. It will crystallize along the tieline from NaCl through the original composition, until the liquid composition reaches the surface of the phase volume of CaSO₄. The composition of the melt will have passed through the phase volume of NaCl, and about 2,900 tons of NaCl will have crystallized. The composition of the remaining 2,100 tons of liquid will then be 55 percent NaCl (1,135 tons), 9.5 percent K₂SO₄ (200 tons), 7.0 percent MgSO₄ (140 tons), and 28.5 percent CaSO₄ (650 tons).

After the liquid composition meets the surface of the CaSO₄ phase volume, NaCl and CaSO₄ will simultaneously crystallize and the composition of the liquid will trace a path on the CaSO₄ phase volume

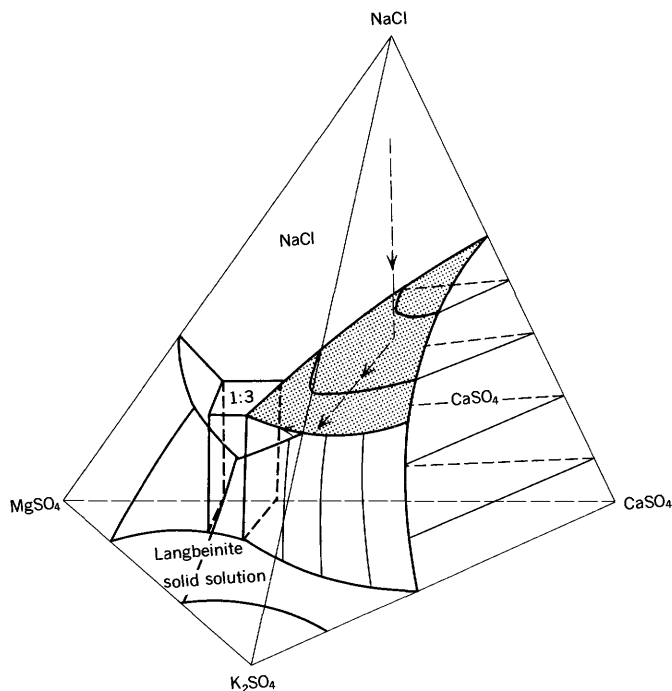


FIGURE 58.—Path of crystallization of the Gnome melt.

surface determined by a plane through the NaCl–CaSO₄ edge of the tetrahedron and the composition of the aforementioned liquid. The liquid will reach the phase volume of the langbeinite–calcium langbeinite solid solution at about 640°C. Then langbeinite solid solution will start to crystallize along with CaSO₄ and NaCl. The liquid composition will proceed along the boundary of the phase volumes as determined by the formation of solid solution. For the composition with which we are concerned the final crystallization should be langbeinite solid solution (figs. 6, 7). Hence the crystallization will end, not at a eutectic, but at a point determined by the properties of the solid solution. At this point, estimated to be 610°C, the composition of the liquid will be about 22.5 percent K₂SO₄, 30 percent MgSO₄, 17.5 percent CaSO₄, and 30 percent NaCl. Langbeinite solid solution, NaCl, and CaSO₄ will all continue to crystallize to completion.

In the preceding discussion, it was assumed that the system contained only the salts NaCl, K₂SO₄, MgSO₄, and CaSO₄. If other constituents are present in minor amounts, they will remain in solution until after the quadruple point is reached, provided that they are soluble in the melt. These impurities would include bomb materials and silicates which may further depress the final freezing point. The process of crystallization-differentiation should result in the

accumulation of all minor components soluble in the melt and complete solidification at a temperature below the quadruple point.

Kahn and Smith (1966) in a study of the actual Gnome melt, found that the radioactivity was concentrated in the portions which were not water soluble. The water soluble portion did not exhibit any radioactivity. Of the radioactive insoluble material, they found considerable CaSO₄ as gypsum and anhydrite, in addition to minor amounts of olivine (Fe,Mg)₂SiO₄ and kirschsteinite (CaFeSiO₄). Although they assumed that the gypsum and anhydrite crystallized early in the cooling process, we feel that they were among the last to crystallize from the residual liquid after most of the NaCl had crystallized.

We had planned to study the effects of SiO₂ as another component, with the possible formation of feldspars and olivines during cooling of the melt, but this would have enormously increased the complexity of our study. Hence the work was limited to the quinary reciprocal salt system Na,K,Mg,Ca/Cl,SO₄ to develop a theory for the crystallization of the salt mass.

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