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The System $MgCl_2$–KCl–$MgSO_4$–K_2SO_4–H_2O at 100°

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Introduction

The system named is one of four components, since the four salts are connected by the equation

$$MgCl_2 + K_2SO_4 \rightleftharpoons 2KCl + MgSO_4$$

In addition to the simple salts, several double salts occur, depending on the temperature of investigation. The system is at all temperatures of considerable scientific and industrial importance, because of its connection with the formation of natural salt deposits by evaporation, for example, the Stassfurt deposits. Extended investigations of this system, its component ternary systems, and allied systems, have been carried out by van't Hoff and his school[1,2,3] 1908.

Somewhat similar studies on the direct evaporation of sea water bittern have been carried out by Hildebrand,[4] with a view to the possible exploitation of the potash content of sea water. The complete solubility relations of the above four component system have been investigated by Loewenherz,[5] but only for the temperature 25°. A complete investigation of the fused melts (water absent) has been made by Jänecke;[6] the lowest temperature of any point on his diagram is above 400°. While nothing new could be expected to develop, after the exhaustive work of van't Hoff and others, from an investigation of the ternary system $MgCl_2$–KCl–H_2O, the system K_2SO_4–$MgSO_4$–H_2O had not been so carefully worked out; and in addition, while the compound kainite was known to decompose at 83°, anhydrokainite appeared in the fused salts, suggesting the possible existence of a compound of the composition of kainite but containing less water, between the temperature 83° and the melting point of the salts. (It should be said at once that we have not found any such salt to exist at 100°.) It was therefore decided to investigate the full four-component system, as well as the associated three-component systems, at the commercially important temperature of 100°.

The associated three-component systems are

(a) $MgSO_4$–$MgCl_2$–H_2O (b) $MgSO_4$–K_2SO_4–H_2O
(c) $MgCl_2$–KCl–H_2O (d) K_2SO_4–KCl–H_2O

The investigation of the three-component systems was carried out by the Schreinemackers method, which always, in theory at least, yields exact knowledge as to the composition of the solid phase in equilibrium with any given solution. A knowledge of the nature of the solid phase in quaternary systems is not always so easily obtained. However, the solid phases were analyzed here too, and, owing to a segregation of solid phases into two layers over a large

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(1) "Vorlesungen über Bildung und Spaltung von Doppelsalzen," Leipzig, 1897.

(2) "Zur Bildung der ozeanischen Salzlagerungen," Braunschweig, 1908.

(3) "Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen, insbesondere des Stassfurter Salzlagers," Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1912.

(4) Hildebrand, *J. Ind. Eng. Chem.*, **10**, 96 (1918).

(5) Loewenherz, *Z. physik. Chem.*, **13**, 459 (1894).

(6) Jänecke, *ibid.*, **80**, 1 (1912).

part of the diagram, a double analysis was possible and the interpretation an easy matter in these cases. In addition, the boundary lines of the quaternary diagram were checked by the method of isothermal evaporation.

Experimental Details

All solutions for solubility determinations were stirred overnight. Filtration from excess solid phase was carried out in the thermostat, below the surface of the thermostatic liquid, by means of compressed air and a sintered glass filter. The isothermal evaporations were carried out by forcing a gentle stream of air through a solution, originally unsaturated, maintained at a temperature of 100°. The solutions were stirred vigorously. After solid commenced to separate, portions of liquid phase were removed from time to time and analyzed. The solid phase was never removed.

Methods of Analysis

The radicals to be determined in this investigation were magnesium, potassium, sulfate and chloride.

(a) **Chloride.**—Volhard's method was used.[7]

(b) **Sulfate.**—The method of Wildenstein[8] was used, the solutions being quarter normal. It was found convenient to carry out the estimations in a test-tube, boiling the mixture after every addition, to hasten the settling of the solids, so that the supernatant liquid could be examined for the presence of potassium chromate. Performed in this way, the method is rapid and accurate.

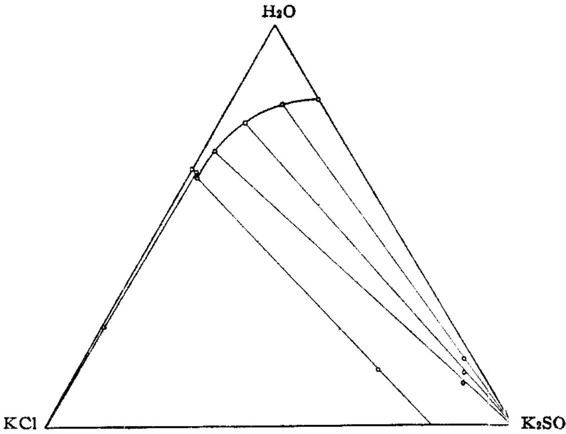

Fig. 1.

(c) **Magnesium.**—The volumetric method of Meade[9] was used.

(d) **Potassium.**—Where the quantity of potassium was considerable, it was estimated by difference, but in the determination of the points of the carnallite curve in the system $MgCl_2$–KCl–H_2O, the determination of potassium simply by difference was found impossible, as the experimental error in the determination of magnesium is greater than the amount of potassium present (carnallite solutions are never congruently saturated). This difficulty is also mentioned by Loewenherz.[5]

In the present work the difficulty was avoided by precipitating most of the magnesium as oxalate. The ratio of potassium to magnesium was thereby much increased, and the potassium could then be estimated accurately, by difference, from a determination of the residual magnesium content.

Purity of Materials

Mallinckrodt U. S. P. magnesium sulfate was used. The magnesium chloride was either B. D. H. certified chemical or J. T. Baker purified crystals. The potassium sulfate was Mallinckrodt powdered potassium sulfate which was recrystallized. Mallinckrodt potassium chloride was used throughout this work. One recrystallization of this salt was considered to yield a product sufficiently pure.

The System Potassium Chloride–Potassium Sulfate–Water at 100°.—Our results for this system are contained in Table I.

TABLE I

SOLUBILITIES OF POTASSIUM CHLORIDE AND OF POTASSIUM SULFATE IN THE PRESENCE OF EACH OTHER AT 100°

	Liquid phase composition		Solid phase composition of wet residue	
	% KCl	% K_2SO_4	% KCl	% K_2SO_4
	...	18.76	...	...
	8.58	11.00	1.88	81.81
	18.63	5.54	3.87	83.15
	28.58	2.46	5.05	84.67
Invariant point —	35.96	1.63	21.16	64.85
	34.64	1.56	74.75	.289
	35.60	...	...	...

The results are represented graphically by the method of Schreinemackers in Fig. 1.

Further discussion of the isothermal is unnecessary in view of the essential agreement with the work of Hildebrand,[4] who has discussed and interpreted it fully.

The System Potassium Chloride–Magnesium Chloride–Water at 100°.—Our results for this system are contained in Table II.

TABLE II

	Liquid phase composition		Solid phase composition of wet residue	
	% KCl	% $MgCl_2$	% KCl	% $MgCl_2$
	29.80	4.35	75.10	1.84
	23.59	9.93	67.96	4.39
	17.50	16.35	67.45	6.19
	13.45	20.15	52.20	11.30
	9.60	24.80	50.60	13.50
Invariant point —	5.15	29.89	44.45	26.00
	1.88	40.00	14.31	37.80
	1.64	40.20	26.80	34.20
Invariant point —	0.73	41.10	44.45	2.18

These results are represented graphically by the method of Schreinemackers in Fig. 2. The more important considerations of this well-known isothermal have been discussed frequently and

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[7] Volhard, *Z. anal. Chem.*, **14**, 321 (1875).

[8] Sutton, "Volumetric Analysis," 11th ed., p. 337.

[9] Meade, THIS JOURNAL, **21**, 746 (1899).

need not be raised again here. Owing to the fact that carnallite solutions are never congruently saturated, or, in other words, that the carnallite branch of the curve is displaced to one side, it is not easy to determine points on it.

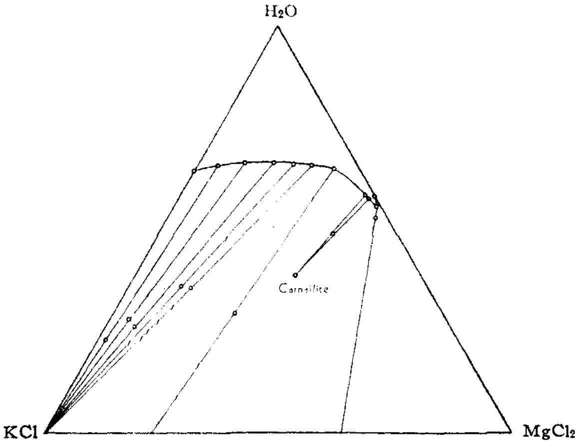

Fig. 2.

The second invariant point is so close to the short $MgCl_2$ curve that it is particularly difficult to determine. Owing to its shortness, points on the $MgCl_2$ curve could not be obtained, but work on the associated system $MgCl_2$–$MgSO_4$–H_2O shows the solid phase to be $MgCl_2 \cdot 6H_2O$.

The System Magnesium Chloride–Magnesium Sulfate–Water at 100°.—Our results for this system are comprised in Table III.

TABLE III

SOLUBILITIES OF MAGNESIUM CHLORIDE AND OF MAGNESIUM SULFATE IN PRESENCE OF EACH OTHER AT 100°

	Percentage solubility		Percentage solid phase analysis	
	% $MgCl_2$	% $MgSO_4$	% $MgSO_4$	% $MgCl_2$
	41.20	1.08	47.03	21.05
	41.50	1.23	0.56	45.00
	40.25	0.87	42.50	23.00
	40.60	.60	51.25	19.30
	29.00	.99	43.00	22.50
	37.60	2.12	30.30	27.05
	37.00	2.83	42.80	19.02
	36.80	2.81	43.00	20.85
Invariant point—	37.35	2.82	42.65	20.88
	31.00	3.30	49.05	14.00
	20.85	9.05	51.40	9.35
	19.85	8.65	51.50	9.98
	12.50	16.30	50.60	6.52
	8.42	21.20	60.00	3.50
	2.88	29.50	67.00	1.01
	33.10	0.37	45.00	0.17

These results, when plotted by the method of Schreinemackers yield the triangular diagram of Fig. 3.

No double salt formation takes place, but the solubility isothermal at this temperature consists of three intersecting curves, representing isothermally univariant equilibria between the solution and one solid phase. The third branch of the isothermal is due to the appearance of a new solid phase, anhydrous $MgSO_4$, produced by the dehydrating action of the magnesium chloride solution. We met with this dehydrating action of magnesium chloride solution frequently in our work. It was found to be very marked on this isothermal. Robson[10] found varying results when determining the solubility of $MgSO_4 \cdot H_2O$, due to the presence in the metastable condition of penta and tetrahydrates. We also found this difficulty in obtaining the solubility of $MgSO_4 \cdot H_2O$ in water, but, on addition of the smallest quantity of magnesium chloride, the dehydrating effect at once became apparent and equilibrium with the monohydrate was established at once. This dehydrating action increases as the $MgCl_2$ content increases, and finally results in the dehydration of the monohydrate. The solubility of $MgSO_4 \cdot H_2O$ in water was found to agree with Robson's value of 50.5 g. per 100 g. of water or 33.5%.

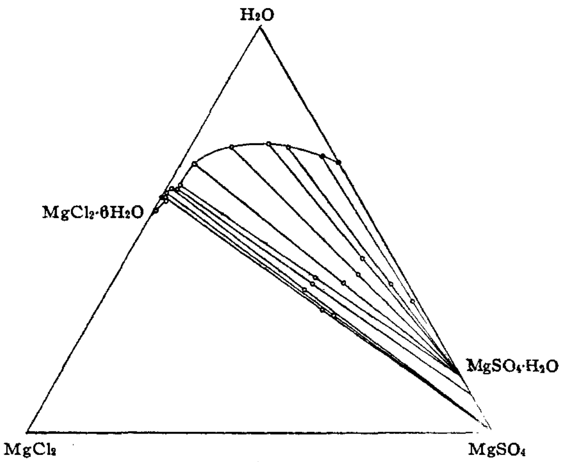

Fig. 3.

The System Magnesium Sulfate–Potassium Sulfate–Water at 100°.—Starr and Storch[11] investigated this system at 85 and 100°. The solid phases were examined chemically and with a petrographic microscope. No analytical figures for the solid phases are given nor are triangular diagrams determined.

We conducted a complete investigation of the system at 100°, the numerical results of which are given in Table IV.

(10) Robson, THIS JOURNAL, **49**, 2772 (1927).

(11) Starr and Storch, *J. Phys. Chem.*, **34**, 2368 (1930).

Table IV

Solubilities of Magnesium Sulfate and Potassium Sulfate in the Presence of Each Other

	Liquid phase percentage solubility		Solid phase composition of wet residue	
	% $MgSO_4$	% K_2SO_4	% $MgSO_4$	% K_2SO_4
	9.25	17.70	2.2	80.2
	13.90	15.40	3.9	80.0
Invariant point—	21.90	14.00	37.0	35.1
	24.00	11.70	44.5	30.0
	27.60	8.00	44.8	25.2
	28.50	6.75	44.5	25.5
Invarient point—	34.00	3.40	61.5	7.0
	...	19.00	...	...
	33.50	...	...	...

These results are expressed graphically in Fig. 4.

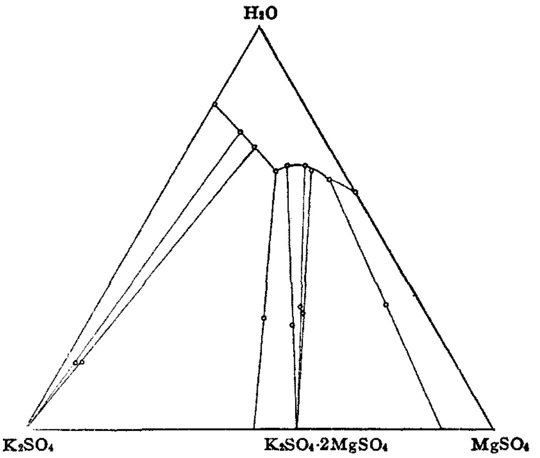

Fig. 4.

The extreme right-hand branch of the curve is questionable. The conditions represented in this graph were obtained by using heptahydrated magnesium sulfate and allowing the solution to come to equilibrium, but it was found by Robson[10] and also by us that it is very difficult to obtain $MgSO_4 \cdot H_2O$ in equilibrium with solution at 100°, owing to the presence of the metastable penta- and tetrahydrates. This results in a high solubility for $MgSO_4 \cdot H_2O$.

The invariant point $MgSO_4 \cdot H_2O$—langbeinite—was determined using $MgSO_4 \cdot H_2O$ as one solid phase. It is presumably, therefore, though not necessarily, free from error.

The solubility curve joining the two invariant points represents a solution in equilibrium with double salt, and the tie-lines from this curve intersect at 42% K_2SO_4, and 58% $MgSO_4$ which corresponds to anhydrous $K_2SO_4 \cdot 2MgSO_4$, the double salt known as langbeinite. This double salt appears as fine white tetrahedral crystals, which form a very distinct powder that can be separated readily from magnesium sulfate or potassium sulfate. This was of importance in dealing with the quaternary system. The coördinates of the invariant point langbeinite–$MgSO_4 \cdot H_2O$ differ somewhat from those found by Starr and Storch[11] for the same point.

The System Magnesium Sulfate–Potassium Chloride–Potassium Sulfate–Magnesium Chloride–Water at 100°.—Following the work of Van der Heide,[12] and Precht,[13] Loewenherz carried out a complete investigation of this system at 25°.[5] On the K_2SO_4–$MgSO_4$ curve, Loewenherz found invariant points, due to the formation of the double salt schoenite. The dehydrating action of magnesium chloride is shown in the conversion of magnesium sulfate heptahydrate to hexahydrate, at a certain concentration of magnesium chloride. The KCl–$MgCl_2$ curve shows the formation of carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$. His diagram for 25° plotted on Jänecke's coördinates is reproduced along with our own for 100°, so that the two isothermals may be compared. It will be observed that there are five ternary invariant points, as follows

(1) Carnallite, $MgSO_4 \cdot 6H_2O$, $MgCl_4 \cdot 6H_2O$
(2) Carnallite, $MgSO_4 \cdot 6H_2O$, KCl
(3) $MgSO_4 \cdot 7H_2O$, $MgSO_4$, $6H_2O$, KCl
(4) $MgSO_4 \cdot 7H_2O$, schoenite, KCl
(5) K_2SO_4, schoenite, KCl

Loewenherz obtained the invariant points by saturating with two of the desired phases and then adding excess of the third. The fields were determined by joining the invariant points by straight lines.

Jänecke[6] investigated the molten system $MgSO_4$–K_2Cl_2–$MgCl_2$–K_2SO_4. The results showed that together with the previously known double salts, $K_2Mg_2(SO_4)_3$ a third compound, $KMgClSO_4$, separated from the melt. The latter compound may be considered as being anhydrous kainite, and hence Jänecke termed it anhydrokainite.

According to van't Hoff[2,3] kainite disappears at 83° as a solid phase in contact with solution. A complete investigation of the 100° isothermal was therefore of interest in this connection, since the natural supposition is that the disappearance of kainite at 83° should immediately give rise to its anhydrous form. Our work shows conclusively that anhydrokainite does not separate under any circumstances from the above system at 100°. It is strange that the salt should come

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(12) Van der Heide, *Ber.*, **26**, 873 (1893).

(13) Precht, *Z. physik. Chem.*, **12**, 124 (1893).

into existence again in its anhydrous form between 100° and, say, 500°.

The experimental method used by us consisted in starting from the invariant points of the ternary systems forming the boundaries of the diagram. Taking excess of the salts in the proportions in which they are present in solution at the invariant point, we added a little of the third salt and thus proceeded along a line which has become univariant in virtue of the added component. Eventually ternary invariant points were reached at which the composition of the solution became independent of further (small) additions of the third salt.

In all cases where langbeinite was one of the solid phases it was readily possible, owing to its difference in density and crystalline form, to separate it from the other solid forms and analyze each. This was done in six cases. The results were plotted on the diagram and the points joined to the plot of the solution by tie-lines.[14] These tie-lines meet the boundary line at points approximating to the composition of the four solids as nearly as can be expected when the adhering mother liquid and crude method of separation are considered. This procedure defined the large langbeinite area with considerable exactness. In the case of other boundary lines this procedure could not be adopted because the heterogeneous solids are too intimately mixed. Frequent analyses showed, however, that the solid phase was heterogeneous. The small areas and invariant points in the top right-hand corner of the diagram are conjectural, but on account of the smallness of the three areas involved, the error cannot be great. In one case the invariant point has been determined, *viz.*, the invariant for $MgSO_4 \cdot H_2O$–carnallite–KCl.

The results are expressed numerically in Table V, and graphically in Fig. 5, using Jänecke's method of representation.[15]

TABLE V

THE SYSTEM $MgSO_4$–K_2SO_4–$MgCl_2$–KCl–H_2O AT 100°

SOLUBILITY DATA[a]

Percentage composition				
Mg	K_2	SO_4	Cl_2	H_2O
7.10	3.01	1.31	22.50	66.25
6.82	4.89	1.88	22.95	63.50
6.71	5.44	2.08	21.50	64.27
7.09	3.51	2.09	22.40	64.90
8.78	1.74	1.02	26.08	62.50
7.75	5.50	1.99	21.60	63.21
6.66	2.24	5.69	17.30	68.11
5.58	8.90	1.44	23.42	60.65
9.70	1.10	0.22	20.20	60.00
10.50	0.35	.29	30.70	58.15
9.25	.76	.57	27.20	62.20
1.88	14.00	3.07	16.14	64.91
0.64	16.95	1.53	16.35	64.98
5.87	9.04	7.25	13.70	64.12
7.73	1.53	2.77	20.85	67.52
6.15	1.73	14.70	8.70	68.70
6.12	1.43	9.20	12.39	70.00
3.81	7.65	22.62	1.46	64.50
2.21	13.02	13.95	5.93	64.75
3.44	7.10	21.12	8.82	67.30
2.16	10.90	7.00	11.07	68.70
3.19	10.70	17.00	3.14	65.90
7.35	1.50	28.20	1.96	61.00
6.54	2.50	16.31	8.73	65.80
6.70	2.13	26.80	1.68	63.00
7.03	1.27	25.95	2.30	63.50
6.96	1.62	28.30	0.82	62.50
7.45	0.81	27.09	2.48	62.50
7.05	1.76	21.25	6.41	63.40
6.35	1.71	26.35	0.66	65.00
7.03	1.95	28.42	1.2	61.50
6.64	1.88	26.25	1.64	63.50
7.25	1.53	28.25	1.96	61.00
6.72	1.76	26.40	1.69	63.40
3.87	7.72	21.40	2.47	65.20
3.32	10.45	18.39	6.62	62.50
3.22	9.10	14.52	6.93	66.20
3.76	7.95	21.05	2.56	64.50
3.39	7.28	20.70	1.19	65.70
3.74	7.92	22.80	2.13	64.80

[a] Liquid phase in contact with two solid phases throughout.

Experiments on Isothermal Evaporation.—The field of the quaternary diagram having been outlined by the method just described, it was decided to check the boundaries by the method of isothermal evaporation. The composition of the solution in equilibrium with the first trace of solid separating defines a point on one of the boundaries of the diagram. Further evaporation causes the composition of the solution to change along a boundary line in the direction of an invariant point. In this way the contours of the boundary line were determined. The experimental results are not reproduced as being of minor importance, but the crystallization paths are indicated in Fig. 5.

Discussion

In work of this kind but little discussion is necessary since the diagrams summarize all the results. In the ternary systems nothing new has resulted, except that the contours of the boundary line have been determined experimentally, whereas they were previously for the most part ob-

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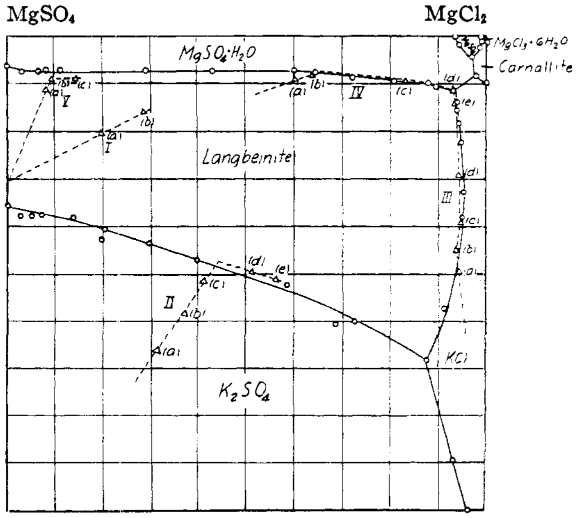
[14] Not shown in Fig. 5.

[15] Jänecke, *Z. physik. Chem.*, **51**, 132 (1908); **71**, 1 (1911).

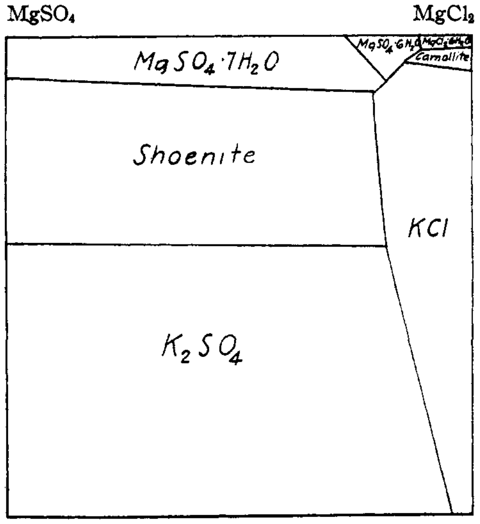
tained merely by joining invariant points with straight lines.



100° Isothermal.

Fig. 5a.

The 100° isothermal for the quaternary system is of considerable importance, since it does not appear to have been investigated at all, previously. A comparison with the 25° isothermal of Loewenherz for the same system shows that: (1) The field of $MgSO_4 \cdot 7H_2O$ has altered to that of $MgSO_4 \cdot H_2O$, without changing greatly in area. (2) The field of $MgSO_4 \cdot 6H_2O$ has become that of $MgSO_4$ anhydrous, and decreased in area. (3) The field of $MgCl_2 \cdot 6H_2O$ has decreased considerably in area. (4) The carnallite field alters in contour but not much in area. (5) The KCl field has shrunk a little. (6) The schoenite field has given place to that of langbeinite, with a somewhat increased area. (7) The K_2SO_4 field remains large. (8) Kainite is not formed.



25° Isothermal.

Fig. 5b.

Summary

1. The following isothermals have been investigated at 100°: (a) $KCl-K_2SO_4-H_2O$; (b) $KCl-MgCl_2-H_2O$; (c) $MgCl_2-MgSO_4-H_2O$; (d) $MgSO_4-K_2SO_4-H_2O$; (e) $K_2Cl_2-MgCl_2-K_2SO_4-MgSO_4-H_2O$.

2. The ternary isothermals exhibit nothing new.

3. The quaternary isothermal (e) has not previously been investigated. Its areas have been determined both from solubility determinations in presence of known solid phases, and from isothermal evaporations. The stable double salt is langbeinite, which occupies a large area on the diagram. Kainite does not occur.

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