

**A Study of the Reciprocal Salt Pairs :**  
 **$\text{Na}_2\text{Cl}_2 + \text{MgSO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$**   
**at 25°C.**

By

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Various heterogeneous equilibria in systems consisting of water and almost all possible combinations of the chlorides and sulphates of sodium, potassium, magnesium, and calcium were studied by J. H. van't Hoff<sup>1)</sup> and his co-workers during the years 1897-1908. Their work had in view the explanation of the genesis of the oceanic salt deposits in Stussfurt and other places. Up to this present, however, there has been no systematic study of those reciprocal salt pairs above-named. We have some data for some parts of this system, but some of them are not sufficiently exact. Therefore the author, on the suggestion of Prof. Y. Osaka, took up the study of the equilibrium of the system at 25°C. from the standpoint of the phase rule.

About two months ago when the present work was nearly completed, an article on the same subject by W. C. Blasdale<sup>2)</sup> came to the author's notice, but since his results are not in agreement with the author's at several points, he continued his work, which seemed not to be superfluous. The results are given in this article.

**Materials:** Sodium sulphate, magnesium sulphate, and magnesium chloride were purified by thrice recrystallisation from commercial pure salts, as  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  respect-

<sup>1</sup> J. H. van't Hoff: Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen. Leipzig Akademische Verlagsgesellschaft, 1912; J. Chem. Soc. Abst. (1898), ii, 564, ff. from Sitzungsber. K. Akad. Wiss. Berlin.

<sup>2</sup> J. Ind. Eng. Chem. **2**, 164 (1920).

ively, and sodium chloride was prepared by precipitation from a saturated solution of commercial pure salt by hydrochloric acid gas.

Methods of experiments: All the experiments were divided into three parts, namely,

1. Measurement of solubilities of four single salts.
2. Study of equilibria between two salts which have a common ion.
3. Study of the equilibria among three salts, namely, that of the reciprocal salt pairs.

The experiments were carried out in the following way: Mixtures of salts in different proportions were put each in an Erlenmeyer flask of a capacity of about 30 c.c. which was made to rotate in a thermostat at 25.0°C. for at least twenty-four hours. When equilibrium was attained, the flask was allowed to stand for a while in the same thermostat until the suspended matter had settled. Then about 10 c.c. of the solution were sacked up by a pipette through a cotton filter into a weighing bottle, and subjected to analysis. The residue which had been pressed between a porous plate and folded filter paper, was redissolved in water to a definite volume, for analysis. The residue taken for analysis was sometimes still wet with some mother liquor, but naturally it had no influence over the determination of the nature of the residue.

Magnesium and sulphate radicals were determined as magnesium pyrophosphate and barium sulphate respectively, and chlorine by titration with a 1/20-normal silver nitrate solution. Sodium was estimated by difference.

1. *The solubilities of single salts*: The solubilities of single salts, found in the present investigation, are given together with the data found in literature as follows (Grams anhydrous salt per 100 grams of solution):<sup>1)</sup>

a. *Sodium chloride*.

1. 26.52	}	26.49 (Takegami)
2. 26.46		
		26.47 (Osaka) <sup>2)</sup>
		26.52 (Mulder) <sup>3)</sup>
		26.30 (Kopp) <sup>3)</sup>

<sup>1</sup> Here and in the following pages, the data quoted from the literature were recalculated, when necessary, to make them comparable with the author's.

<sup>2</sup> J. Tokyo Chem. Soc., 29, 116 (1908).

<sup>3</sup> Landolt, Bernstein, Meyerhoffer's Tabellen, p. 556.

b. *Sodium sulphate.*

1. 21.33  
 2. 21.55 } 21.54 (Takegami)  
 3. 21.53 }  
 21.9 (Mulder)<sup>1)</sup>

c. *Magnesium chloride.*

1. 35.90 } 35.86 (Takegami)  
 2. 35.81 }  
 36.1 (Löwenherz)<sup>2)</sup>  
 36.2 (van't Hoff and Meyerhoffer)<sup>3)</sup>

d. *Magnesium sulphate.*

1. 26.59 } 26.68 (Takegami)  
 2. 26.77 }  
 28.2 (Mulder)<sup>4)</sup>  
 25.9 (Löwenherz)<sup>2)</sup>  
 27.9 (van't Hoff)<sup>3)</sup>

2. *Equilibria between two salts which have a common ion.*

a. *Sodium chloride and sodium sulphate.*

The results of the determination of solubility are given in the following table:—

TABLE I.

No.	Composition of solution in gram percentages.			Composition of residue in gram percentages.		
	Na <sub>2</sub> Cl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	Na <sub>2</sub> Cl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O
1	26.49	...	73.51	...	...	...
2	24.57	3.00	72.43	90.92	0.14	8.94
3	22.98	6.80	70.22	49.54	35.90	14.56
4	20.47	8.60	70.93	5.04	79.65	15.31
5	18.95	10.12	70.93	3.65	81.05	15.30
6	13.06	15.60	71.34	4.13	78.59	17.28
7	13.07	15.60	71.33	1.54	90.61	7.85
8	13.61	15.18	71.21	2.64	45.63	51.73
9	9.74	15.65	74.61	3.68	33.37	62.95
10	4.21	18.25	77.54	1.12	37.51	61.37
11	...	21.54	78.46	...	...	...

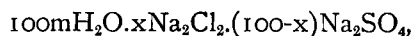
<sup>1</sup> Seidell: Solubilities of inorganic and organic substances, p. 311.

<sup>2</sup> Zs. physik. Chem., 13, 459 (1894).

<sup>3</sup> Ozeanische Salzablagerungen, p. 42.

<sup>4</sup> Loc. cit.

The following table was recalculated from the last one by representing the compositions of solutions and residues by the formula :



where  $x$  denotes the molar percentage of  $\text{Na}_2\text{Cl}_2$  and  $m$  the number of moles of water to one mole of salt.

TABLE 2.

No.	Solution		Residue		
	x	m	x	m	Solid phase
1	100.00	18.02	...	...	$\text{Na}_2\text{Cl}_2$
2	90.88	17.40	99.87	0.64	"
3	80.40	15.96	62.65	1.20	$\text{Na}_2\text{Cl}_2$ ; $\text{Na}_2\text{SO}_4$
4	74.32	16.73	7.14	1.40	$\text{Na}_2\text{SO}_4$
5	69.42	16.89	5.19	1.41	"
6	50.44	17.90	6.00	1.63	"
7	50.44	17.90	2.02	0.67	"
8	51.31	18.03	6.57	8.38	$\text{Na}_2\text{SO}_4$ ; $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$
9	43.06	21.42	11.82	13.13	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$
10	21.91	26.20	3.50	12.46	"
11	0.00	28.51	...	...	"

From the data on this table, we obtain Fig. 1.

From Fig. 1, it may be seen that the decahydrate of sodium sulphate is dehydrated to the anhydrous form when the amount of sodium chloride in the saturated solution of sodium sulphate is increased to some definite degree. And there is no formation of any double salt between them.

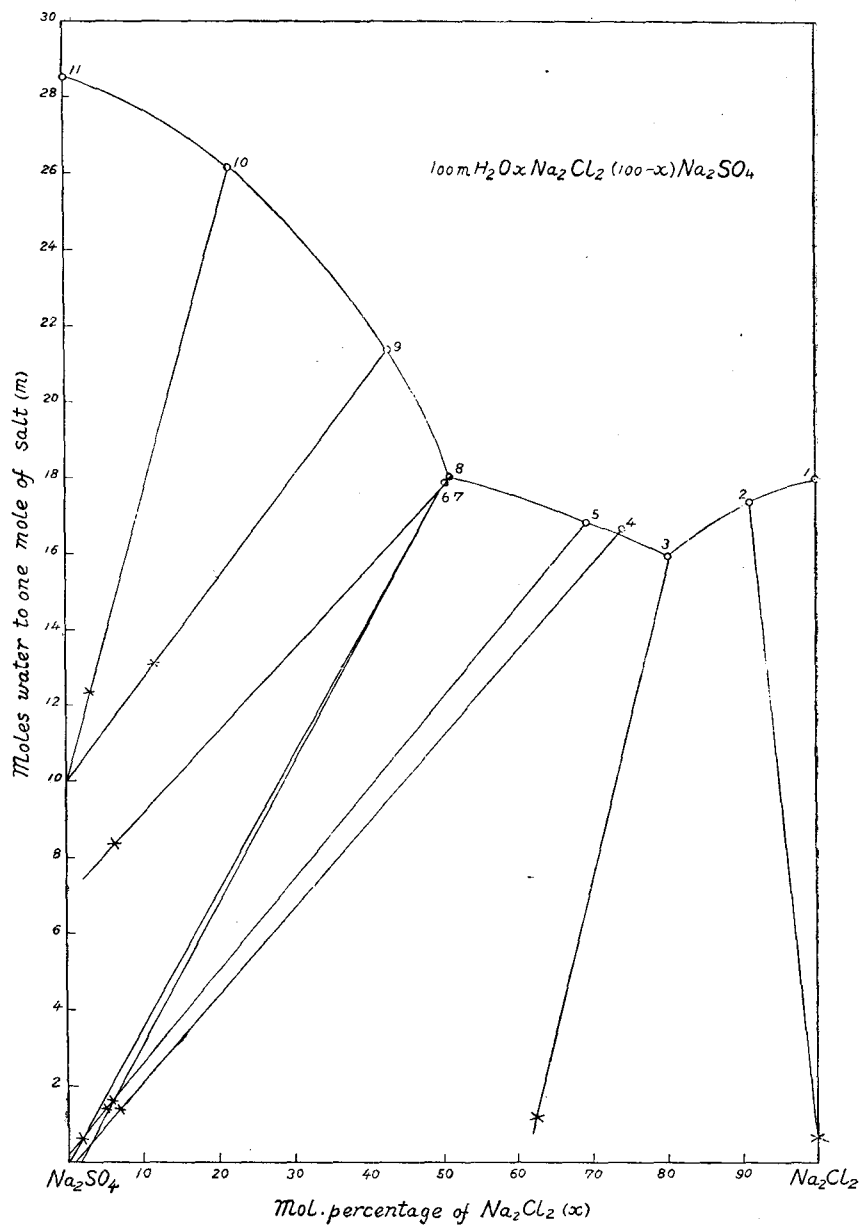
About this equilibrium, though a part of it has been reported by van't Hoff,<sup>1)</sup> it seems, there has been no complete investigation except the most recent studies of Blasdale.<sup>2)</sup> The values found by these two authors are in fair agreement with those found in the present investigation.

The solution, saturated with sodium chloride and sodium sulphate, corresponds to the point 3, of which

<sup>1</sup> van't Hoff: Ozeanische Salzablagerungen, p. 73.

<sup>2</sup> Loc. cit.

Fig. 1.



$$m=15.96 \text{ and } x=80.40,$$

while according to the previous investigations, they are

$$m=16.0, \quad x=81.6 \quad (\text{van't Hoff})$$

$$m=16.12, \quad x=79.93 \quad (\text{Blasdale})$$

The coordinates of the points 8, which represents the solution saturated with anhydrous and decahydrated sodium sulphate are

$$m=18.03, \quad x=51.31$$

while those found by Blasdale are

$$m=17.70, \quad x=51.34$$

*b. Sodium chloride and magnesium chloride.*

The equilibrium of this system is very simple as shown in Fig. 2, Tables 3, and 4, as there is no formation of any double salt nor change of water of crystallisation in the salts.

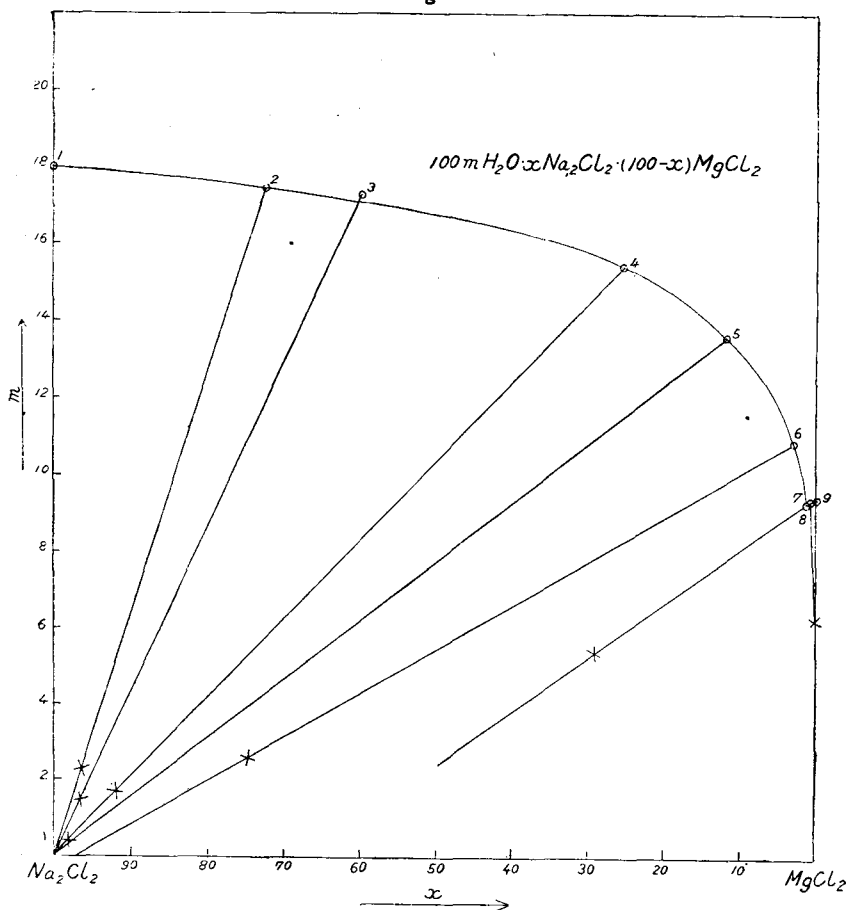
TABLE 3.

No.	Composition of solution in gram percentages			Composition of residue in gram percentages		
	Na <sub>2</sub> Cl <sub>2</sub>	MgCl <sub>2</sub>	H <sub>2</sub> O	Na <sub>2</sub> Cl <sub>2</sub>	MgCl <sub>2</sub>	H <sub>2</sub> O
1	26.49	...	73.51	...	...	...
2	19.77	6.24	73.99	71.44	2.24	26.32
3	16.62	9.15	74.23	78.41	2.52	19.07
4	7.80	18.79	73.41	73.15	5.48	21.37
5	4.11	24.40	71.49	82.53	11.73	5.74
6	1.12	31.65	67.23	55.20	15.27	29.53
7	0.48	35.68	63.84	16.28	35.16	48.56
8	0.21	35.73	64.06	0.00	45.55	54.45
9	...	35.86	64.14	...	...	...

TABLE 4.

100mH <sub>2</sub> O·xNa <sub>2</sub> Cl <sub>2</sub> ·(100-x)MgCl <sub>2</sub>					
No.	Solution		Residue		
	x	m	x	m	Solid phase
1	100.00	18.02	...	...	Na <sub>2</sub> Cl <sub>2</sub>
2	71.95	17.49	96.11	2.30	"
3	59.50	17.26	96.19	1.52	"
4	25.15	15.38	91.56	1.72	"
5	12.00	13.59	98.27	0.44	"
6	2.79	10.86	74.54	2.59	"
7	1.08	9.32	27.95	5.42	Na <sub>2</sub> Cl <sub>2</sub> ; MgCl <sub>2</sub> ·6H <sub>2</sub> O
8	0.27	9.40	0.00	6.29	MgCl <sub>2</sub> ·6H <sub>2</sub> O
9	0.00	9.41	...	...	"

Fig. 2.



The composition of the solution saturated with the two salts, represented by the point 7 in Fig. 2 is

$$x=1.08 \quad \text{and} \quad m=9.32.$$

The corresponding values found by van't Hoff are

$$x=2.3 \quad \text{and} \quad m=9.4.$$

According to Blasdale, however, the solubility of sodium chloride in the saturated solution of magnesium chloride is negligibly slight, so that it may be represented by

$$x=0.00 \quad \text{and} \quad m=9.63$$

As seen from the above statement, the solubility of sodium chloride in the saturated solution of magnesium chloride is much less than that found by van't Hoff but not so trifling as Blasdale has observed.

*c. Magnesium sulphate and sodium sulphate.*

Into the only double salt, astrakanite,  $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , which these two sulphates form, there are many investigations,<sup>1</sup> but no systematic study of the equilibrium of this system at 25°C. seems to have been published until the work of Blasdale appeared. The results of the author are represented in Table 5, 6, and Fig 3.

TABLE 5.

No.	Composition of solution in gram percentages			Composition of residue in gram percentages		
	MgSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	MgSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O
1	26.68	...	73.32	...	...	...
2	23.77	6.69	69.54	39.35	2.52	58.13
3	20.06	10.80	67.14	37.85	3.18	58.97
4	19.84	26.54	63.62	36.29	7.08	56.63
5	21.60	12.45	65.95	33.59	24.91	41.50
6	19.46	14.13	66.41	30.96	32.75	36.29
7	18.28	15.89	65.83	29.40	26.58	44.02

<sup>1</sup> J. H. van't Hoff and Ch. M. van Deventer; Zs. physik. Chem., **1**, 170 (1887); **3**, 337 (1889); Ber., **19**, 2144; H. W. B. Roozeboom: Zs. physik. Chem., **2**, 518 (1888).



8	16.31	18.22	65.47	28.25	31.28	40.47
9	16.14	18.16	65.70	28.68	32.21	39.11
10	14.14	20.50	65.36	27.85	34.00	38.15
11	15.63	18.63	65.74	12.56	37.59	49.85
12	17.67	18.16	64.17	6.32	34.68	59.00
13	10.93	19.17	69.90	3.75	35.97	60.31
14	10.78	18.85	70.37	4.54	33.28	62.18
15	3.34	20.88	75.78	0.55	41.40	58.05
16	...	21.54	78.46	...	...	...

TABLE 6.

100mH <sub>2</sub> O·xMgSO <sub>4</sub> ·(100-x)Na <sub>2</sub> SO <sub>4</sub>					
No.	Solution		Residue		
	x	m	x	m	Solid phase
1	100.00	18.31	...	...	MgSO <sub>4</sub> ·7H <sub>2</sub> O
2	81.79	15.74	94.80	9.32	"
3	70.68	14.35	93.38	9.69	"
4	58.70	12.54	85.86	8.93	"
5	67.28	13.69	61.51	5.06	MgSO <sub>4</sub> ·7H <sub>2</sub> O; Astrakanite
6	62.01	14.09	52.83	4.13	Astrakanite
7	57.70	13.84	51.73	5.71	"
8	51.49	13.77	51.70	4.93	"
9	51.30	13.91	51.30	4.66	"
10	44.98	13.85	49.26	4.49	"
11	49.86	13.97	28.35	7.00	Astrakanite; Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O
12	53.55	12.95	17.76	11.05	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O
13	40.31	17.18	11.00	11.79	"
14	40.41	17.57	13.92	12.70	"
15	15.95	24.08	1.55	10.90	"
16	0.00	28.51	...	...	"

The transition points, 5 and 11, as found by Blasdale, are respectively :

$$x=65.77, \quad m=13.71 \quad \text{and}$$

$$x=52.48, \quad m=13.83$$

against the author's values

$$x=67.28, \quad m=13.69;$$

$$x=49.86, \quad m=13.97.$$



*d. Magnesium chloride and magnesium sulphate.*

Of the equilibria of the four systems each of two salts with a common iron, those of the three already mentioned do not much differ in essential points from those found by previous investigators.

Now, as to the fourth system, the opinions of the previous observers are divided; and as the equilibrium state of this system has a great influence upon that of the reciprocal salt pairs, it is the most important and the most interesting of the four ternary systems.

According to Löwenherz,<sup>1)</sup> the first systematic investigator of this system, the solubility curve in this system consists of three branches in consequence of the change of water of crystallisation of magnesium sulphate from hepta to hexa. He determined the compositions of the solutions which have the two salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , as residue respectively to be

$$x=83, \quad m=11.3 \quad \text{and} \quad x=88, \quad m=8.5.$$

According to van't Hoff,<sup>2)</sup> however, there exist two more hydrates, namely, penta and tetra, and his results are as follows:

x	m	Residue.
83.0	11.4	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ .
90.4	10.7	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ; $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ .
92.2	10.4	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ; $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ .
94.9	9.4	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

The Blasdale's results are very near to those of Löwenherz, and no investigations have been undertaken about the penta and tetra hydrates of magnesium sulphate. His data are as follows:

x	m	Residue.
88.98	11.55	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ .
93.65	9.30	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ;

The author's results are represented in Tables 7, 8, and Figs. 4 and 5.

<sup>1</sup> Zs. physik. Chem., **13**, 459, (1894).

<sup>2</sup> van't Hoff: Ozeanische Salzablagerungen p. 71, Ber. Berl. Akad., 1898, 487.

TABLE 7.

No.	Composition of solution in gram percentages			Composition of residue in gram percentages		
	MgCl <sub>2</sub>	MgSO <sub>4</sub>	H <sub>2</sub> O	MgCl <sub>2</sub>	MgSO <sub>4</sub>	H <sub>2</sub> O
1	...	26.68	70.32	...	...	...
2	1.62	24.43	73.95	0.52	40.38	59.10
3	5.31	19.63	70.06	—	—	—
4	9.42	14.89	75.69	3.13	36.81	60.06
5	10.51	14.02	75.47	3.18	37.89	58.93
6	14.05	10.68	75.27	4.78	35.77	59.45
7	14.77	11.08	74.15	4.60	37.35	58.05
8	16.22	10.14	73.64	4.76	37.17	58.07
9	23.53	5.44	71.03	5.11	39.21	55.68
10	26.06	5.02	68.92	7.44	37.83	54.73
11	26.36	4.90	68.74	9.22	35.80	54.98
12	27.84	4.29	67.87	3.35	45.66	50.99
13	28.21	4.35	67.44	11.55	32.59	55.86
14	28.72	4.14	67.14	10.63	34.26	55.11
15	30.08	3.80	66.12	9.41	37.10	53.49
16	30.91	3.76	65.33	9.82	37.16	53.02
17	31.39	3.75	64.86	8.60	38.87	52.60
18	32.14	3.77	64.09	9.41	38.11	52.48
19	32.36	3.85	63.79	10.89	36.10	53.01
20	30.79	3.87	65.34	19.16	24.78	56.06
21	32.48	3.04	64.48	11.68	37.60	50.72
22	32.97	2.91	64.12	11.30	39.60	49.10
23	33.09	2.82	64.09	12.27	44.02	45.71
24	33.56	2.81	63.63	17.20	31.44	51.36
25	34.03	2.96	63.01	36.52	10.58	52.90
26	33.89	2.99	63.12	44.39	0.91	54.70
27	34.80	1.45	63.75	43.24	0.65	56.11
28	35.86	...	64.14	...	...	...

TABLE 8.

$100mH_2O \cdot xMgCl_2 \cdot (100-x)MgSO_4$					
No.	Solution		Residue		
	x	m	x	m	Solid phase
1	0.00	18.31	...	...	MgSO <sub>4</sub> ·7H <sub>2</sub> O
2	7.75	18.61	1.60	9.59	"
3	25.51	18.97	—	—	"
4	44.46	18.80	9.72	9.82	"
5	48.72	18.39	9.60	9.37	"
6	62.48	17.60	14.48	9.47	"
7	62.80	16.48	13.48	8.96	"
8	66.95	15.99	13.94	8.96	"
9	84.57	13.43	14.47	8.12	"
10	86.81	12.08	19.94	7.72	MgSO <sub>4</sub> ·7H <sub>2</sub> O; MgSO <sub>4</sub> ·6H <sub>2</sub> O
11	87.20	11.96	24.59	7.72	MgSO <sub>4</sub> ·6H <sub>2</sub> O
12	89.16	11.43	8.50	6.81	"
13	89.13	11.21	30.94	7.88	"
14	89.80	11.04	28.21	7.69	"
15	90.92	10.51	24.32	7.27	"
16	91.22	10.14	25.08	7.12	"
17	91.38	9.93	21.89	7.04	"
18	91.54	9.60	23.82	6.99	"
19	91.40	9.48	27.65	7.08	"
20	90.97	10.15	49.48	7.62	MgHO <sub>4</sub> ·5H <sub>2</sub> O
21	93.11	9.72	28.24	6.45	"
22	93.49	9.56	25.34	6.17	"
23	93.70	9.55	22.81	5.34	MgSO <sub>4</sub> ·4H <sub>2</sub> O
24	93.80	9.36	40.94	6.43	"
25	93.58	9.11	81.39	6.20	MgSO <sub>4</sub> ·4H <sub>2</sub> O; MgCl <sub>2</sub> ·6H <sub>2</sub> O
26	93.46	9.16	98.39	6.38	MgCl <sub>2</sub> ·6H <sub>2</sub> O
27	96.82	9.33	98.84	6.75	"
28	100.00	9.41	...	...	"

Fig. 4.

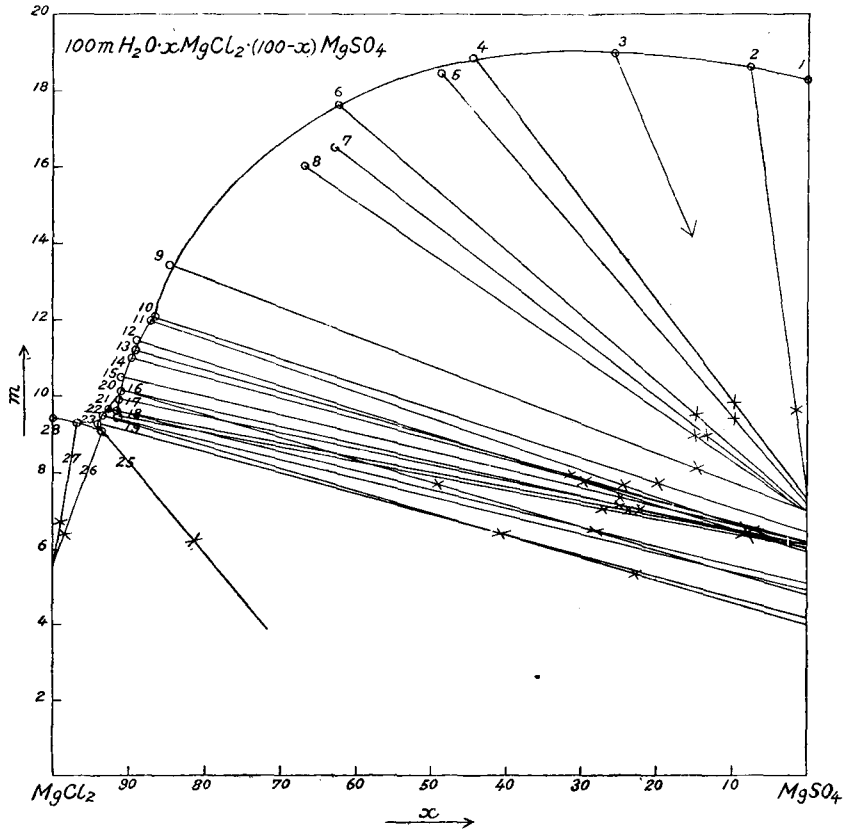
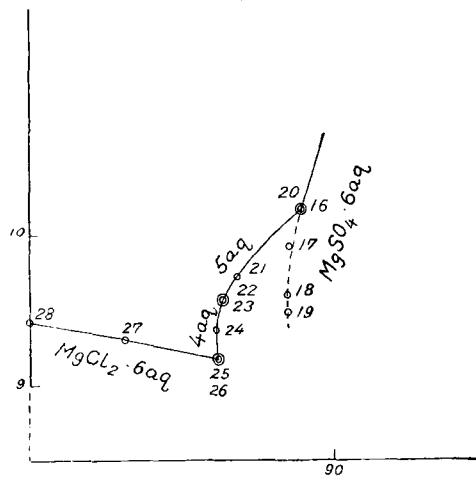


Fig. 5.



It may be clearly seen from Fig. 4 that the solid phases of this system are  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Thus van't Hoff's observation was confirmed qualitatively, but quantitatively there are some differences.

That part of the diagram where the opinions of previous investigators are not in agreement, was studied with special care in the present work. Fig. 5 is drawn to expose this part on a greater scale. It may be seen from Fig. 5 that the hexahydrate has the transition point to the pentahydrate at the point 16, but the curve for the hexahydrate might be further continued as represented by the points 17, 18, and 19. From the relative position of the curves for the hexa and penta hydrates, it is beyond doubt that the three latter points represent metastable equilibria.

The compositions of solutions, represented by points 16 and 20 in Fig. 5, and having the hexa- and penta-hydrates as residue respectively, are almost the same, and it may be permitted to take the average values of them as the composition of a solution saturated with these two hydrates. They are

$$x = 91.10, \quad m = 10.15.$$

In a similar way, the composition of the solution saturated with the penta- and tetra-hydrates of magnesium sulphate, is determined at the points 22 and 23 as follows:

$$x = 93.60, \quad m = 9.56.$$

Thus the existence of the penta- and tetra-hydrates of magnesium sulphate was confirmed. Though Löwenherz and also Blasdale believe that they had obtained a solution saturated with the hexahydrates of magnesium sulphate and of magnesium chloride, it is evident from the present investigation that the hydrate of magnesium sulphate which coexists with the hexahydrate of magnesium chloride in stable equilibrium is the tetra- and not the hexahydrate.

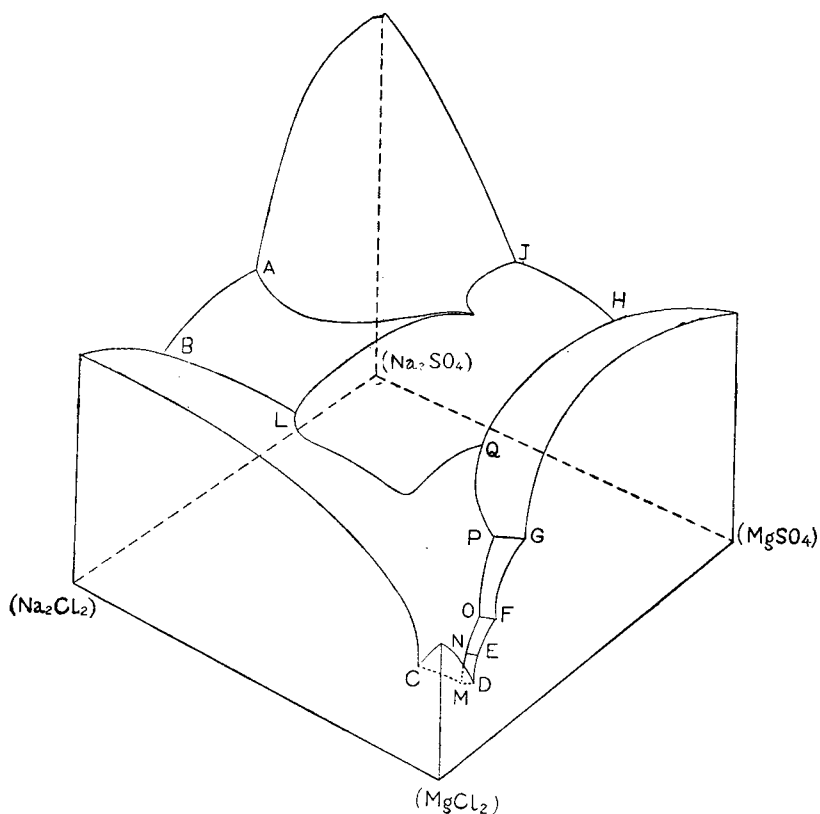
The following observation may be added as an evidence of the existence of the lower hydrates of magnesium sulphate. The crystals of the hexahydrate in equilibrium flasks were somewhat translucent, but as soon as they changed into the lower hydrates, they became opaque.

3. *The reciprocal salt pairs of sodium chloride and magnesium sulphate, and sodium sulphate and magnesium chloride at 25°C.*

There are two methods for the graphical representation of the equilibrium of reciprocal salt pairs, one referring to octahedral coordinates first used by R. Löwenherz<sup>1)</sup> and the other referring to the quadratic prism proposed by E. Jänecke.<sup>2)</sup> Since the second mode of representation is simpler and more convenient, it is adopted here to reproduce the results of the work.

Fig. 6 represents a model of the system, Fig. 7 is its horizontal projection, and in Fig. 8, a portion of it is reproduced in a larger

Fig. 6.



<sup>1</sup> Zs. physik. Chem., 13, 459 (1894).

<sup>2</sup> Zs. anorg. Chem., 15, 132 (1906).



scale. The vertices of the square represents the four single salts respectively as indicated in the figure. The sides represent the equilibria of the systems of two salts, with a common ion, and water, and they are nothing but the projections of the rectangle diagram of those ternary systems on the horizontal side, which have been already described.

Fig. 7.

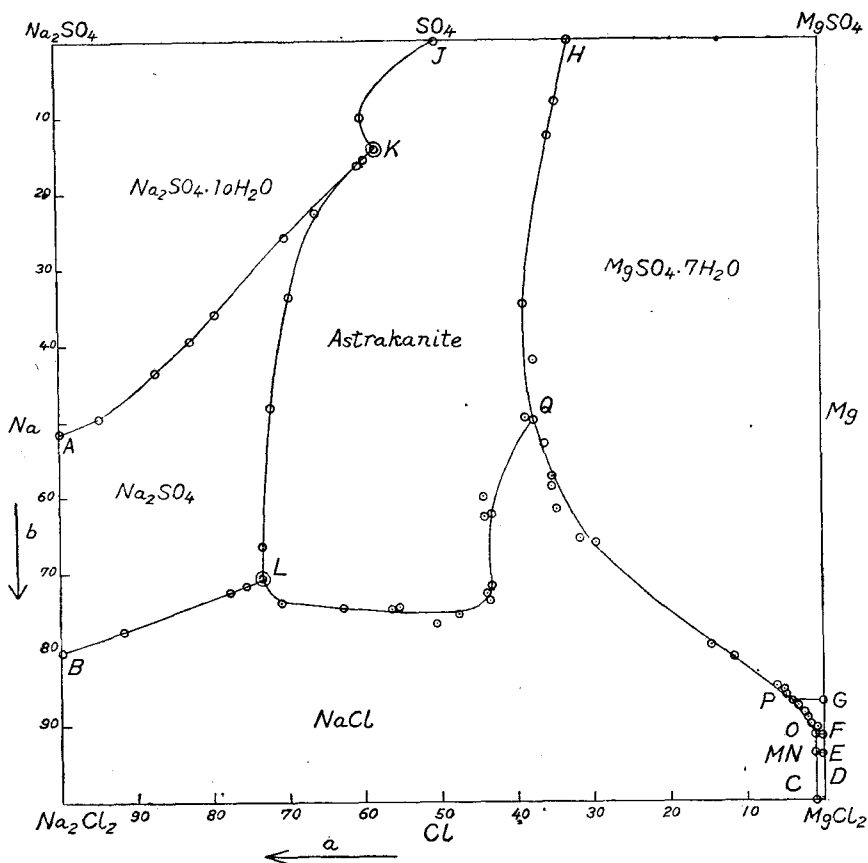
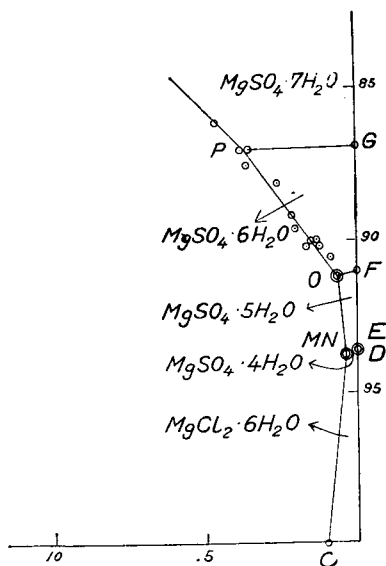


Fig. 8



Now, the experimental method, by which the data necessary for the construction of the model and Fig. 7 were sought, and the results thus obtained will be described.

The experiments were carried out in the following way: Into a solution saturated with two salts having the common ion, another salt was added in different proportions, and it was so arranged that, when equilibrium was attained, two or three salts remained as residue. Then the solution was analyzed.

The composition of the solution was represented by the formula:

$$100\text{mH}_2\text{O} \cdot a\text{Na}_2 \cdot (100-a)\text{Mg} \cdot b\text{Cl}_2 \cdot (100-b)\text{SO}_4$$

and by the values of  $a$  and  $b$ , the position of the points representing the solution in the diagram was determined. Fig 7 was obtained as the results of such determinations and some details about the diagram will be given in the following pages.

*The curve: AK.*

The solutions, represented by the points on this curve, have always  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  as the residue, and they change

from A to K along this curve when the concentration of magnesium salts increases. When K is reached, a new solid phase, astrakanite, comes into existence. The data for some points on the curve are given in the following table.

TABLE 9.

No.	a	b	m
A	100.00	51.31	18.03
1	94.55	49.40	17.07
2	87.33	43.49	16.33
3	82.84	39.10	16.21
4	79.03	35.94	15.89
5	69.89	25.77	14.74
7	59.77	15.71	13.94
7	59.63	15.58	13.81
K	57.92	14.05	13.71

The curve: JK.

The solutions, represented by the points on the curve, have always astrakanite and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  as the residue and when K is reached, a new solid phase,  $\text{Na}_2\text{SO}_4$ , separates out.

TABLE 10.

No.	a	b	m
J	49.86	0.00	13.97
	60.00	9.96	13.68
K	57.98	13.70	13.64

The values for the point K in table 9 is in good agreement with those in table 10, and the means are taken as the values for K as follows:

K:  $a = 57.95$ ,  $b = 13.88$ ,  $m = 13.66$ .

The corresponding values found by Blasdale are

$a = 80.47$ ,  $b = 40.42$ ,  $m = 16.92$ .

There is a great discrepancy between the two sets of values. In the author's experiments for the points on the curve AK, the residue in every equilibrium flask was examined for magnesium and first, when the composition of solution reached the point K, a noticeable amount of magnesium was found in the residue. Moreover the fact that the data for K found along the curve AK is in fair agreement with those found along the curve JK makes it very probable that the values now found are the true ones for the solution having  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and astrakanite as the residue.

*The curve : BL.*

The solutions, represented by the points on this curve, have always  $\text{Na}_2\text{SO}_4$  and NaCl as the residue and when L is reached, a new solid phase, astrakanite, comes to appearance.

TABLE I I.

No.	a	b	m
B	100.00	80.40	15.96
1	91.70	77.63	15.67
2	77.57	72.40	15.10
3	75.55	71.55	15.10
L	73.35	70.70	15.06

*The curve : KL.*

The solutions, represented by the points on this curve, have always  $\text{Na}_2\text{SO}_4$  and astrakanite as the residue, and when the curve reaches K or L, a new residue,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  or NaCl comes to existence in addition respectively.

TABLE I 2.

No.	a	b	m
K	57.95	13.88	13.66
1	66.15	22.45	14.67
2	69.32	33.51	15.02
3	72.10	48.09	15.64
4	73.65	66.52	15.47
L	73.40	70.61	15.06

The data for L in Tables 11 and 12 are in fair agreement with each other, so the respective mean values of them are taken as the correct ones, namely :

$$L: \quad a=73.38, \quad b=70.66, \quad m=15.06.$$

The corresponding data found in the literature are as follows :

$$a=71.38, \quad b=72.71, \quad m=15.19 \text{ (Blasdale)}$$

$$a=74.8, \quad b=70.3, \quad m=15.3 \text{ (van't Hoff)}$$

*The curve: QL.*

The solutions, represented by the points on this curve, have always NaCl and astrakanite as the residue; and when the point Q is reached, a new solid phase,  $MgSO_4 \cdot 7H_2O$ , comes into existence.

TABLE 13.

No.	a	b	m
L	73.38	70.66	15.06
1	70.98	73.84	15.40
2	62.86	74.62	15.34
3	56.18	74.70	15.14
4	55.29	74.53	15.12
5	50.75	76.29	15.16
6	47.62	75.10	15.11
7	43.32	73.73	15.38
8	43.78	72.72	15.32
9	43.26	72.05	15.14
10	43.77	63.74	13.92
11	43.46	62.67	13.98
12	44.39	60.01	13.95
Q	38.52	49.55	13.94

*The curve: HQ.*

The solutions, represented by the points on this curve, have always  $MgSO_4 \cdot 7H_2O$  and astrakanite as the residue; and when the point Q is reached, a new solid salt, NaCl separates out.

TABLE 14.

No.	a	b	m
H	32.72	0.00	13.69
1	34.44	8.02	13.97
2	35.75	12.28	14.00
3	38.64	34.67	14.15
4	37.66	41.88	14.04
Q	37.42	49.87	13.98

As the data for Q in Tables 13 and 14 are practically the same, the respective mean values of them are taken as the correct ones for Q, namely:

$$Q: \quad a=37.97, \quad b=49.71, \quad m=13.96.$$

The corresponding data found in the literature are as follows:

$$a=21.00, \quad b=74.94, \quad m=13.93 \text{ (Blasdale)}$$

$$a=38.8, \quad b=49.3, \quad m=14.9 \text{ (van't Hoff)}$$

The author's data are very near to van't Hoff's and greatly different from Blasdale's. When the curve was followed from the point H by increasing the amount of chloride radical gradually, very fine crystals of astrakanite, difficult to settle, were always observed in the interval between H and Q, but as soon as the solution passed over Q, such a phenomenon could be recognized no more. Moreover, a noticeable amount of chloride radical was first found in the residue at Q. Thus, it will not be unreasonable to take the data, above obtained, as the correct composition of the solution saturated with those three salts.

*The point: M.*

The point, representing the solution saturated with  $MgCl_2 \cdot 6H_2O$ , NaCl, and  $MgSO_4 \cdot 4H_2O$  was determined as follows:

	a	b	m
	0.29	93.79	9.29
	0.18	93.75	9.25
M:	0.24	93.77	9.27

van't Hoff's data, corresponding to this, are

$$a=0.9, \quad b=95.3, \quad m=9.3.$$

The space, enclosed by C, M, and D, is the field of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and the point D corresponds to a solution saturated with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ .

*The point: N.*

In the ternary system, magnesium chloride, magnesium sulphate, and water, the solution saturated with  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and that saturated with  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$  contain the two salts almost in the same ratio, as seen in Fig. 5. So in Figs. 7 and 8, the points D and E representing the respective solutions can not be distinguished.

A great deal of trouble was taken to obtain such a solution saturated with NaCl,  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , which is represented by an assumed point N, but it was in vain, as the solution represented by the point O which is saturated with  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and NaCl always resulted. Van't Hoff assigned the following composition to that point N:

$$a=1.1, \quad b=91.6, \quad m=10.5.$$

But in the present investigation, taking the data for the curves DM and OP, and the point D in consideration, it may be estimated as

$$N: \quad a=0.25, \quad b=93.7, \quad m=9.5$$

*The point: O.*

The point representing the solution saturated with  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , NaCl, and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  was determined as follows:

	a	b	m
	0.75	91.21	9.91
	0.64	91.14	10.08
	0.64	91.01	10.11
	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
O:	0.68	91.12	10.03

van't Hoff's data for it are as follows:

$$a=2.1, \quad b=99.4, \quad m=10.6$$

*The curve: OP.*

The solutions, represented by the points on this curve, have always  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{NaCl}$  as the residue; and when the point P is reached, a new residue,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , comes also into existence.

TABLE 15.

No.	a	b	m
O	0.68	91.12	10.03
1	0.89	90.49	10.64
2	1.70	90.17	10.81
3	1.37	90.00	10.75
4	1.34	90.15	10.76
5	1.57	90.00	10.95
6	2.10	89.70	10.93
7	2.04	89.31	11.17
8	2.61	88.11	11.57
9	3.55	87.49	11.77
	3.92	87.08	11.90
	3.62	87.00	11.94
P	3.77	87.04	11.92

But van't Hoff's data for the solution corresponding to the point P are as follows:

$$a = 13.4, \quad b = 80.8, \quad m = 12.7.$$

As may be seen, the difference between the two observations is very considerable.

*The curve: PQ.*

The solutions, represented by the points on this curve, have always  $\text{NaCl}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  as the residue.



TABLE 16.

No.	a	b	m
P	3.77	87.04	11.92
1	4.63	86.21	12.18
2	4.98	85.62	12.41
3	6.13	85.04	12.62
4	11.63	80.93	13.41
5	14.26	79.35	13.58
6	29.58	66.02	13.94
7	31.83	65.21	13.98
8	34.61	61.88	13.81
9	35.15	58.40	13.93
10	35.14	57.20	14.00
11	36.10	53.11	14.04
Q	37.97	49.71	13.96

**SUMMARY.**

There exist nine kinds of solid phases in the system of equilibrium of the reciprocal salt pairs of sodium chloride and magnesium sulphate, and sodium sulphate and magnesium chloride at 25°C., namely,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , astrakanite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

The special points representing the saturated solutions of a single, two, or three salts are summarized in the following table.

TABLE 17.

	Solid phase	a	b	m
	NaCl	100	100	18.02
	MgSO <sub>4</sub> ·7H <sub>2</sub> O	0	0	18.31
	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	100	0	28.51
	MgCl <sub>2</sub> ·6H <sub>2</sub> O	0	100	9.41
B	NaCl; Na <sub>2</sub> SO <sub>4</sub>	100	80.40	15.96
A	Na <sub>2</sub> SO <sub>4</sub> ; Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	100	51.31	18.03
C	NaCl; MgCl <sub>2</sub> ·6H <sub>2</sub> O	1.08	100	9.32
H	MgSO <sub>4</sub> ·7H <sub>2</sub> O; Astrakanite	32.72	0	13.69
J	Astrakanite; Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	50.14	0	13.97
G	MgSO <sub>4</sub> ·7H <sub>2</sub> O; MgSO <sub>4</sub> ·6H <sub>2</sub> O	0	86.81	12.08
F	MgSO <sub>4</sub> ·6H <sub>2</sub> O; MgSO <sub>4</sub> ·5H <sub>2</sub> O	0	91.10	10.15
E	MgSO <sub>4</sub> ·5H <sub>2</sub> O; MgSO <sub>4</sub> ·4H <sub>2</sub> O	0	93.60	9.56
D	MgSO <sub>4</sub> ·4H <sub>2</sub> O; MgCl <sub>2</sub> ·6H <sub>2</sub> O	0	93.58	9.11
K	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O; Na <sub>2</sub> SO <sub>4</sub> ; Astrakanite	57.95	13.88	13.66
L	Na <sub>2</sub> SO <sub>4</sub> ; NaCl; Astrakanite	73.38	70.66	15.06
Q	NaCl; Astrakanite; MgSO <sub>4</sub> ·7H <sub>2</sub> O	37.97	49.71	13.96
P	NaCl; MgSO <sub>4</sub> ·7H <sub>2</sub> O; MgSO <sub>4</sub> ·6H <sub>2</sub> O	3.77	87.04	11.92
O	NaCl; MgSO <sub>4</sub> ·6H <sub>2</sub> O; MgSO <sub>4</sub> ·5H <sub>2</sub> O	0.68	91.12	10.03
N	NaCl; MgSO <sub>4</sub> ·5H <sub>2</sub> O; MgSO <sub>4</sub> ·4H <sub>2</sub> O	0.25	93.7	9.5
M	NaCl; MgSO <sub>4</sub> ·4H <sub>2</sub> O; MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.24	93.77	9.27

In conclusion the author wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instructions.