On the Octahydrate of Magnesium Sulphate

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By

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Of magnesium sulphate, there are various hydrates. Besides the well known hydrates with 1, 4, 5, 6, 7, and 12 molecules of the water of crystallisation, the hydrates with 5/4, 2, and 3 molecules of water also exist.

Among these hydrates, the hydrates with 1, 6, 7, and 12 molecules of water are stable in contact with the pure solution of magnesium sulphate each within certain limits of temperature, but the others are obtained chiefly from a solution containing magnesium chloride in addition to it. The hexa- and hepta- hydrates exist each in two modifications.

The transition temperatures between two successive ones among the four kinds of the hydrates which are stable in contact with the pure solution, are as follows:

$$\text{Dodeca.} \overset{1{\cdot}8^\circ}{\rightleftarrows} \text{Hepta.} \overset{42{\cdot}2^\circ}{\rightleftarrows} \text{Hexa.} \overset{68{\cdot}0^\circ}{\rightleftarrows} \text{Mono.}$$

This is a general outline of the results[1] obtained by the previous investigators.

On the author's previous investigation[2] of the reciprocal salt pairs: $Na_2Cl_2 + MgSO_4 \rightleftarrows Na_2SO_4 + MgCl_2$ at 25°C., there was one special

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[1] Abegg: Handbuch der anorg. Chem. II. **2**, p. 56; Gmelin-Kraut-Friedheim: Handbuch der anorg. Chem. II. **2**, p. 405; Seidell: Solubilities of Inorganic and Organic Compounds. 2d. ed., p. 396.

[2] Journ. Tokyo Chem. Soc., **41**, 831 (1920); These Memoirs, **4**, 317 (1921).

case in the system of magnesium sulphate and sodium sulphate, in which the magnesium sulphate as the residue formed the octahydrate. In the literature, however, there was no mention of the octahydrate of magnesium sulphate, and moreover, in the other two cases the residue was the heptahydrate, it was attributed to an experimental error, and the author arrived at the conclusion that the magnesium sulphate which forms the residue in the system of magnesium sulphate and sodium sulphate at 25°C., was the heptahydrate.

But during the investigations which were made afterwards to ascertain whether the above conclusion were true or not, the existence of the octahydrate of magnesium sulphate became very probable. Therefore, on the suggestion of Prof. Y. Osaka, the study of the equilibrium of the system of magnesium sulphate, sodium sulphate, and water was again undertaken.

The experiments were carried out in the same way as in the case of the reciprocal salt pairs. But, in order to have magnesium sulphate as the only residue, a very large excess of magnesium sulphate was used and to secure the complete equilibrium, the equilibrium flask was warmed previously to dissolve the salts completely, and then rotated in a thermostat.

I. *The system of magnesium sulphate, sodium sulphate, and water at 25° C.*

The results are represented in Table 1, 2, and Fig. 1.

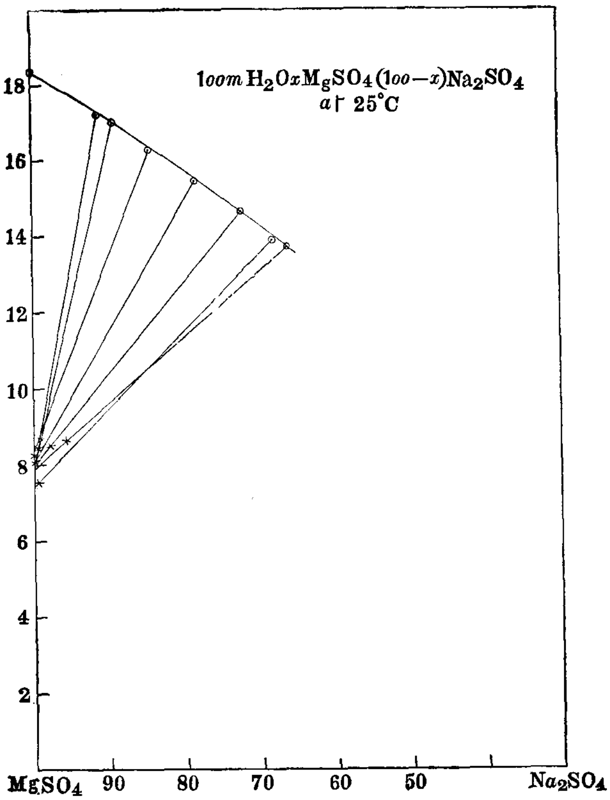
TABLE 1.

No.	Composition of solution in gram percentages.			Composition of residue in gram percentages.		
	$MgSO_4$	Na_2SO_4	H_2O	$MgSO_4$	Na_2SO_4	H_2O
1.	26·68	......	73·32	......	......	......
2.	25·48	2·73	71·79	43·99	0·25	55·76
3.	25·04	3·54	71·42	43·01	0·53	56·46
4.	24·49	5·20	70·31	44·63	0·00	55·37
5.	23·49	7·50	69·01	45·17	0·15	54·68
6.	22·32	10·10	67·58	42·91	1·21	55·88
7.	21·79	11·90	66·31	46·69	0·30	53·01
8.	21·27	12·76	65·97	41·65	2·25	56·10

TABLE 2.

$100mH_2O.xMgSO_4(100\text{-}x)Na_2SO_4$					
No.	Solution.		Residue.		
	x	m	x	m	Solid phase.
1.	100·00	18·31	......	......	$MgSO_4.8H_2O$
2.	91·30	17·20	99·50	8·44	"
3.	89·30	17·03	98·95	8·69	"
4.	84·75	16·28	100·00	8·30	"
5.	78·70	15·47	99·75	808	"
6.	72·27	14·64	97·67	8·51	"
7.	68·36	13·92	99·46	7·55	"
8.	66·30	13·75	95·60	8.61	"

Fig. 1.



It may be clearly seen from Fig. 1 that whenever it was considered to have attained the complete equilibrium, the residue was always the octahydrate. The reason why the heptahydrate was obtained in the author's previous work, is perhaps due to the fact that the heptahydrate was shaken with the solution and was analysed before it reached equilibrium.

If the proportion of sodium sulphate was increased to some definite point, a transition point of the octahydrate to the heptahydrate might have been found as in the case at 30°C. in the next section, but the formation of astrakanite prevented the further experiment.

2. *The system of magnesium sulphate, sodium sulphate, and water at 30° C.*

The results are represented in Tables 3, 4, and Fig. 2.

TABLE 3.

No.	Composition of solution in gram percentages.			Composition of residue in gram percentages.		
	$MgSO_4$	Na_2SO_4	H_2O	$MgSO_4$	Na_2SO_4	H_2O
*	29·0	......	71·0	......	......	......
1.	26·35	3·96	69·69	42·28	0·79	56 93
2.	24·35	8·43	67·22	43·14	1·27	55·59
3.	22·89	11·80	65·31	42·95	1·76	55·29
4.	22·82	12·56	64·62	42·99	2·06	54·95
5.	23·00	12·49	64·51	45·91	1·04	53·05
6.	22·33	13·71	63·96	45·77	1·26	52·97
7.	21·92	14·47	63·61	46·58	0·84	52·58

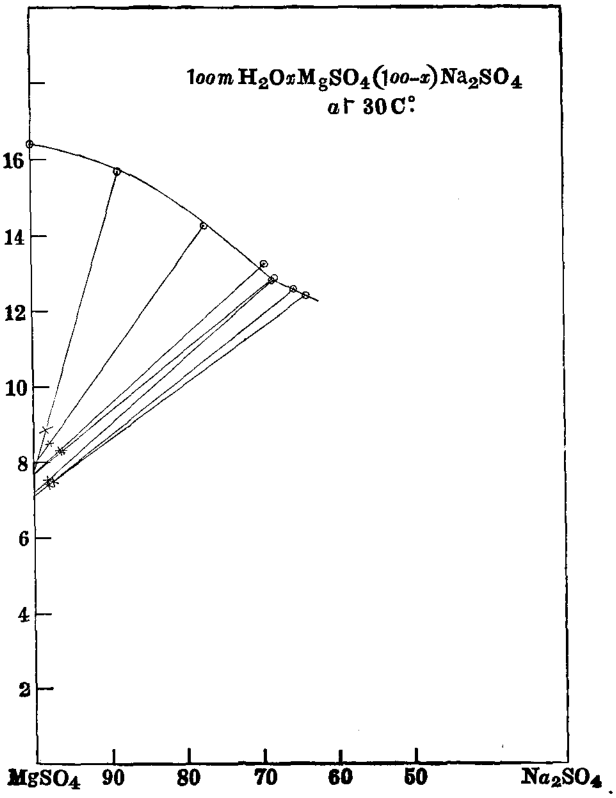
TABLE 4.

$100mH_2O.xMgSO_4\ (100\text{-}x)\ Na_2SO_4$

No.	Solution.		Residue.		
	x	m	x	m	Solid phase.
*	100·0	16·4	......	......	
1.	88·67	15·69	98·43	8·86	$MgSO_4.8H_2O$
2.	77·33	14·28	98·05	8·45	,,
3.	69·60	13·28	96·64	8·32	,,
4.	68·19	12·91	96.11	8·22	,,
5.	68·49	12·85	98·11	7·58	$MgSO_4.8H_2O$; $MgSO_4.7H_2O$
6.	65·78	12·60	97·70	7·56	$MgSO_4.7H_2O$
7.	64·13	12·45	98·25	7·42	,,

* Determination by Mulder (Seidell, *loc. cit.*).

Fig. 2.



As may be seen from Fig. 2, when the molar fraction of sodium sulphate in a solution reaches 0·32 or more of the whole sulphate, the octahydrate of magnesium sulphate as the residue is transformed into the heptahydrate, and there is a marked difference in solubility between the octa- and hepta- hydrate. Accordingly it is evident that the octahydrate is more stable than the heptahydrate under the solution where the molar fraction of sodium sulphate in the solution is less than 0·32.

It must be here remarked that the residue, which was proved to be the octahydrate on its analysis in a state still wet with the mother liquor, was converted into the heptahydrate, when it was pressed between folded filter papers and dried.

What we can infer from the present investigation of the ternary system, is as follows: According to the literature, the crystals of magnesium sulphate which is stable in contact with its pure solution at 25°C. and 30°C., is the heptahydrate, but it has become clear from the present investigation that at these temperatures, magnesium sulphate which exists in contact with a solution containing sodium sulphate is the octahydrate until the concentration of sodium sulphate reaches a certain limit. It may also be inferred from the figure that crystals of magnesium sulphate in contact with its pure solution at those temperatures are the octahydrate. It may be presumed that the data for the solubility of magnesium sulphate at 30°C., determined by Mulder, is a solubility of the octahydrate.

3. *Some further experiments*

To make the relation between the octa- and hepta- hydrates more clear, a measurement of vapour pressure of these salts and solutions was undertaken, but, as various difficulties occurred, it was given up. Then a transition cell was constructed, and the thermometer method was tried to determine the transition temperature, but no satisfactory result could be obtained.

Thus the original method was again adopted, namely, an equilibrium system in which the solution, containing always 7–9% of sodium sulphate, was studied at various temperatures to see their influence upon the water of crystallisation of the residue at different temperatures.

The results are shown in Tables 5, 6, and Fig. 3.

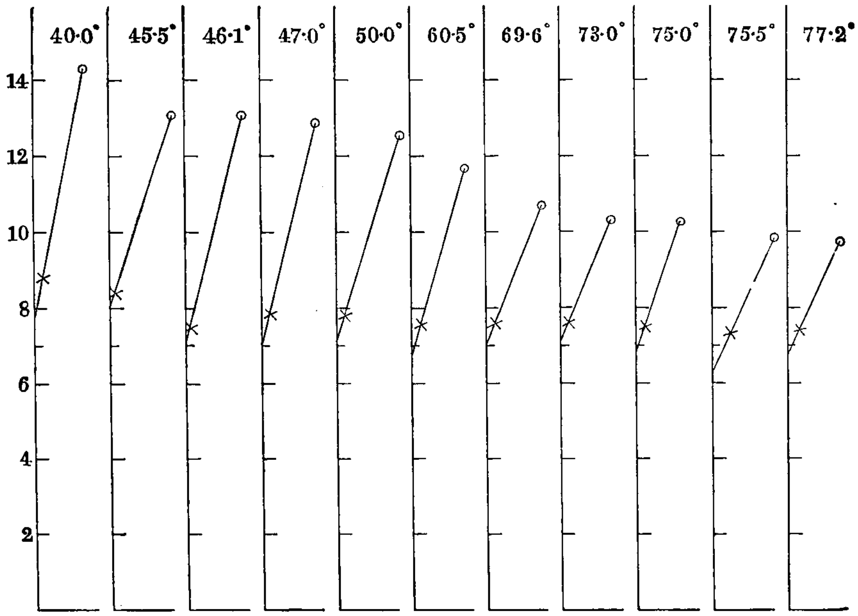
TABLE 5.

Temp.	Composition of solution in gram percentages.			Composition of residue in gram percentages.		
	$MgSO_4$	Na_2SO_4	H_2O	$MgSO_4$	Na_2SO_4	H_2O
40·0	29·58	2·47	67·95	42·57	0·61	56·82
45·5	30·96	3·24	65·80	43·97	0·40	55·63
46·1	31·22	2·97	65·81	46·39	0·33	52·78
47·0	31·56	2·88	65·56	45·42	0·55	54·03
50·0	31·68	3·40	64·92	45·60	0·62	50·78
60·5	33·69	3·03	63·28	46·30	0·68	53·02
69·6	35·48	3·34	61·18	46·24	0·65	53·11
73·0	36 40	3·14	60·46	46·29	0·55	53·16
75·0	36·92	2·77	60·31	46·45	0·67	52·88
75·5	36·81	3·98	59·21	46·32	1·39	52·29
77·2	37·53	3·39	59·08	46·60	0·87	52·53

TABLE 6.

$100mH_2O \cdot xMgSO_4 \cdot (100-x) Na_2SO_4$					
Temp.	Solution.		Residue.		
	x	m	x	m	Solid phase.
40 0	93·37	14·35	98·79	8·82	$MgSO_4.8H_2O$
45·5	91·86	13·06	99·23	8·40	„
46·1	92·54	13·05	99·42	7·49	$MgSO_4.7H_2O$
47·0	92·80	12·89	98·97	7·84	„
50·0	91·67	12·57	98·85	7·80	„
60·5	92 92	11·68	98·76	7·56	„
69·6	92·61	10·68	98·82	7·59	„
73·0	93·20	10·35	98·99	7·60	„
75·0	94·01	10·27	98·79	7·52	„
75·5	91·61	9 86	97·51	7·36	$MgSO_4$ $6H_2O$(?)
77·2	92·91	9·78	98·46	7·42	$MgSO_4.7H_2O$

Fig. 3.



The hydrates of magnesium sulphate in contact with a solution containing 7–9% of sodium sulphate, have a transition point of the octa- to the hepta- hydrate at the temperature of 45·5°–46·1°C.

The system in which a hydrate of magnesium sulphate is the residue and is in equilibrium with a solution containing sodium sulphate in addition to magnesium sulphate, is a bivariant system, so the transition temperature of the octa- to the hepta- hydrate varies when the concentration of sodium sulphate increases. Therefore the temperature of 48·2°C. which is determined as the transition temperature of the hepta- to the hexa- hydrate by means of the dilatometer by van der Heide,[1] seems to correspond to that of the octa- to the hepta-hydrate in the present investigation. Next, it was naturally suspected that the temperature of 68°C. which is known as the transition temperature of the hexa- to the mono- hydrate, might correspond to the transition temperature of the hepta- to the hexa- hydrate in the present case, but no hexahydrate could be obtained up to 77·2°C., except one case at 75·5°C., where the residue was rather the hexa-hydrate. Accordingly within the limit of the present investigation, a special temperature corresponding to 68°C., could not be found.

As the existence of octahydrate of magnesium sulphate seems to be unquestionable, the number of solid phases which exist in the equilibrium system of the reciprocal salt pairs, in question, is not nine but ten with the addition of $MgSO_4.8H_2O$.

Summary

The system of equilibrium of magnesium sulphate, sodium sulphate, and water at 25°C. and 30°C. was studied; and the existence of the octahydrate of magnesium sulphate was ascertained.

Magnesium sulphate which is the residue in this system at 25°C. is always the octahydrate.

At 30°C., when the amount of sodium sulphate in the solution reaches 32% or more, the octahydrate is transformed into the hepta-hydrate.

In the system containing 7–9% of sodium sulphate in the solution, the octahydrate is stable under 45·5°C. and the heptahydrate is stable above 46·1°C. and to at least 77·2°C.

1 Z. physik. Chem., **12**, 417 (1893)

Lastly it may be concluded that the transition temperatures of the hydrates of magnesium sulphate as inferred from the case in which sodium sulphate coexists, as follows:

$$\text{Octa.} \overset{48\cdot2^\circ}{\rightleftarrows} \text{Hepta.} \overset{\text{over } 77\cdot2^\circ}{\rightleftarrows} \text{Hexa.}$$

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