value for the specific heat and a lower value of heat of vaporization than those measured by previous investigators.

An analysis of the various factors entering into the calculations of the specific heat and heat of vaporization leads to the conclusion that the probable accuracy of the present results is within about 1% in each case. By far the greatest factor entering into this uncertainty is that caused by the lag in the temperature measurement.

Further work is being carried out with a calorimeter of the same type as the one described in this investigation. It has been redesigned to permit the use of a platinum thermometer of the flat type, which the work of the present investigation indicated was very necessary in such a calorimeter, several other improvements being also incorporated.

Summary

A new type of calorimeter for the determination of the specific heats and heats of vaporization of liquids is described. It can also be used for the determination of the specific heats of compressed gases. This calorimeter can be used over wide ranges of temperature and is especially suited for use in the range under room temperature.

The heat of vaporization and specific heat of liquid ethyl ether were determined for the temperatures 0° and 12°, with an accuracy within about 1%.

The main factor in reducing the accuracy of the results was determined, and the method of avoiding it given. Work is proceeding with the calorimeter in its improved form.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE SYSTEM MAGNESIUM SULFATE-SODIUM SULFATE-WATER AND A METHOD FOR THE SEPARATION OF THE SALTS

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In order that a method might be devised for the separation by fractional crystallization of sodium sulfate from magnesium sulfate or *vice versa* it was necessary to know the solubility relationships of these salts over the entire range of temperature from the freezing points to the boiling points of their solutions. The data given by Roozeboom,[1] van't Hoff,[2] Hildebrand,[3] Blasdale,[4] D'Ans,[5] and Seidell[6] apply to only a few temperatures.

[1] Roozeboom, *Rec. trav. chim.*, **6**, 333 (1888).

[2] van't Hoff, "Über die Bildungsverhältnisse der ozeanischen Salzablagerungen," Leipzig, **1912.**

[3] Hildebrand, *J. Ind. Eng. Chem.*, **10**, 96 (1918).

[4] Blasdale, *ibid.*, **10**, 344 (1918); *ibid.*, **12**, 164 (1920).

[5] D'Ans, *Kali*, **9**, 177 (1915).

[6] Seidell, "Dictionary of Chemical Solubilities," D. Van Nostrand Co., **1920.**

It was necessary, therefore, to make a great many determinations of the solubility over a considerable range of temperature. These measurements with the results obtained are described below. Finally, a method of procedure is suggested by which the sulfates can be separated, the one from the other, as comparatively pure products.

Previous Investigations Bearing on this Problem

The solubility relationships of the double salt, astrakanite or blödite ($MgSO_4.Na_2SO_4.4H_2O$) were studied by Roozeboom. He found the transition point for the reaction $MgSO_4.7H_2O + Na_2SO_4.10H_2O = MgSO_4.Na_2SO_4.4H_2O + 13H_2O$ to be 22.0° at which temperature 100 moles of water dissolve 2.85 moles of sodium sulfate and 4.63 moles of magnesium sulfate. This corresponds to a solution containing 14.6% of sodium sulfate and 20.2% of magnesium sulfate. Roozeboom also showed that the solubility of astrakanite varies but little with temperature.

Between the years 1897 and 1908 van't Hoff and his co-workers published a great many papers dealing with the conditions of formation of oceanic salt deposits.[2] The portion of this work that has a direct bearing upon the present problem is the determination of the solubility relationships of the system, magnesium sulfate-sodium sulfate-magnesium chloride-sodium chloride-potassium chloride, for the temperatures 25° and 83°.

From data given by Roozeboom,[1] van't Hoff[2] and Seidell,[6] Hildebrand[3] constructed an equilibrium diagram for the system, magnesium sulfate-magnesium chloride-sodium sulfate-sodium chloride at 25°. He proposed to precipitate sodium chloride and kieserite, $MgSO_4H_2O$, by evaporation at higher temperatures, leaving a mother liquor that would be treated by the carnallite process for the recovery of the potassium chloride and the remaining magnesium sulfate.

He pointed out that magnesium chloride had apparently a dehydrating influence, allowing kieserite to be stable in contact with the solution at a lower temperature. By taking advantage of the relatively low solubility of kieserite, the sodium chloride might be dissolved out of the precipitated solid by a cold solution of magnesium chloride. It was recognized, however, that the formation of astrakanite at ordinary temperatures and of löweite ($MgSO_4.Na_2SO_4.5/2H_2O$) and vanthoffite ($MgSO_4.3Na_2SO_4$) at higher temperatures might render this scheme useless. From the works of van't Hoff it appears that löweite forms above 43° and vanthoffite above 46° while they can co-exist at about 60°.

Isothermal relations for the system sodium sulfate-sodium chloride-potassium sulfate-potassium chloride, have been investigated for several temperatures by Blasdale.[4] He applied the information obtained to the separation of each pair of salts. With the chlorides satisfactory results were apparently obtained. Here the process consisted in the alternate evaporation, with the separation of sodium chloride, and the cooling, with crystallization of potassium chloride. Blasdale also pointed out that kieserite does not form a part of this system at 25°; it could not be precipitated even by inoculation.

D'Ans[5] gives the results of quite a number of his own measurements for the system sodium sulfate-magnesium sulfate-water together with values from Roozeboom and van't Hoff. The temperatures of quintuple points were obtained by producing the boundary lines of saturation surfaces on a model.

Materials and Method of Procedure

The sulfates used in this work were Baker's Analyzed chemicals which were found to contain 0.005% of chlorides but were free from other impurities, except a trace of iron. Various mixtures of sodium sulfate decahydrate, $Na_2SO_4.10H_2O$, and magnesium sulfate heptahydrate, $MgSO_4.7H_2O$, were vigorously agitated with small amounts of distilled water in test-tubes immersed in a bath kept at the desired temperature. Two tubes were operated concurrently. After agitation for some six hours the tubes were stoppered, the solid allowed to settle and portions withdrawn through cotton wool filters by means of a warmed pipet. These portions were weighed in stoppered bottles, then analyzed for magnesium and total sulfate, using a separate sample in each case. Difficulties due to supersaturation were overcome as far as possible by inoculation with small amounts of partially dehydrated mixtures. It was not considered necessary to redetermine the solubilities of single salts. Free use has been made of the results from other investigations; for such results, in Table I under "Expt." the name of the observer is given.

Thermometers were compared with instruments standardized by the United States Bureau of Standards.

All values are expressed on the basis of percentage by weight, as the information appears to be more useful in this form.

SOLUBILITY DATA. ABBREVIATIONS USED TO INDICATE SOLID PHASES

Mg-12	$MgSO_4$, $12H_2O$	Na-10	Na_2SO_4, $10H_2O$ (Glauber's salt)
Mg-7	$MgSO_4$, $7H_2O$ (Epsom salt)	Ast.	$MgSO_4$, Na_2, SO_4, $4H_2O$ (astrakanite)
Mg-6	$MgSO_4$, $6H_2O$	Löw.	$MgSO_4$, Na_2SO_4 $5/2H_2O$ (löweite)
Mg-1	$MgSO_4$, H_2O (kieserite)	Vant.	$MgSO_4$, $3Na_2SO_4$, (vanthoffite)

TABLE I

EQUILIBRIUM DATA FOR VARIOUS ISOTHERMS

ISOTHERM AT 0°

Expt.	$MgSO_4$ %	Na_2SO_4 %	H_2O %	Solid phase[a]
Mulder[7]	0.0	4.58	95.42	Na-10
62	9.65	4.89	85.46	..
63	11.25	4.69	84.06	..
64	20.0	4.63	75.37	Na-10, Mg-7
D'Ans[5]	19.9	4.35	75.75	..
65	20.0	4.3	75.7	Mg-12 (?)
Interp.	20.0	0.0	80.0	..
Mulder[7]	21.2	0.0	78.8	Mg-7
Diacon[9]	19.75	3.97	76.28	(Not stated)
		ISOTHERM AT 10°		
Mulder[7]	0.0	8.3	91.7	Na-10
13	0.75	8.3	90.95	..
14	19.4	7.4	73.2	..
34	20.9	7.46	71.64	Na-10, Mg-7
Mulder[7]	23.9	0.0	76.1	Mg-7
		ISOTHERM AT 18.7°		
i.	0.0	15.05	84.95	Na-10
1	1.48	14.68	83.84	..

TABLE I (*Continued*)

Expt.	$MgSO_4$ %	Na_2SO_4 %	H_2O %	Solid phase *a*
3	8.92	13.90	77.18	..
6	11.30	13.50	75.20	..
7	15.35	12.30	72.35	..
8	15.70	12.30	71.90	..
9	20.57	11.80	67.63	Na-10, Mg-7
10	20.60	11.48	67.92	Mg-7
11	24.4	3.4	72.2	..
12	25.7	0.5	73.8	..
i.	26.2	0.0	73.8	..
i. Interpolated from Mulder.				
ISOTHERM AT 25°				
Mulder[7]	0.0	21.8	78.2	Na-10
16	0.25	21.2	78.55	..
Blasdale[4]	16.6	17.8	65.2	Na-10, Ast.
..	21.15	13.0	65.85	Ast., Mg-7
21	19.8	16.9	63.3	(Na-10, Mg-7)
22	22.6	10.8	66.6	Mg-7
Mulder[7]	27.8	0.0	72.2	..
ISOTHERM AT 30°				
Mulder[7]	0.0	29.0	71.0	Na-10
18	6.48	26.08	67.44	..
Roozeboom[1]	12.3	23.25	64.45	Na-10, Ast.
..	15.8	18.6	65.6	Ast.
23	23.25	12.35	64.4	Ast., Mg-7
26	24.5	9.27	66.23	Mg-7
25	24.55	8.75	66.7	..
Mulder[7]	29.0	0.0	71.0	..
ISOTHERM AT 40°				
Mulder[7]	0.0	32.8	67.2	Na_2SO_4
60	2.54	30.70	66.76	..
61	3.61	30.70	66.99	..
51	11.0	24.7	64.3	..
52	11.6	24.5	63.9	Na_2SO_4, Ast.
68	12.2	23.2	64.6	Ast.
53	12.4	23.8	63.8	..
50	15.35	19.15	65.5	..
54	20.95	13.8	65.25	..
56	24.8	10.35	64.85	..
77	25.1	9.6	65.3	..
78	28.0	8.5	63.5	Ast., Mg-7
Mulder[7]	31.3	0.0	68.7	Mg-7
ISOTHERM AT 50°				
Mulder[7]	0.0	31.8	68.2	Na_2SO_4
58	2.58	30.7	66.72	..
59	2.6	30.0	67.4	..
66	9.4	26.3	63.3	..

TABLE I (*Continued*)

Expt.	$MgSO_4$ %	Na_2SO_4 %	H_2O %	Solid phase[a]
48	9.65	26.85	63.5	Na_2SO_4
82	12.7	25.0	62.3	Na_2SO_4, Ast.
143	13.7	23.8	62.5	Vant., Ast.
39	14.1	21.8	64.1	Ast.
47	16.0	19.0	65.0	..
41	16.35	18.7	64.95	..
75	16.4	18.3	65.3	..
43	18.4	16.05	65.55	..
76	18.4	16.1	65.5	..
81	24.4	11.1	64.5	..
149	27.8	9.75	62.45	..
44	28.3	7.1	64.6	..
40	30.45	6.15	63.4	..
69	31.3	5.7	63.0	Ast., Mg-6
70	31.1	6.06	62.84	Mg-6
42	31.3	5.0	63.7	..
Smith[8]	33.5	0.0	66.5	..
ISOTHERM AT 60°				
(Mulder)	0.0	31.2	68.8	Na_2SO_4
32	5.04	28.0	66.96	..
87	6.05	27.85	66.1	..
86	8.8	25.6	65.6	..
84	9.9	24.85	65.25	..
71	14.0	21.8	64.2	Ast.
72	15.6	19.6	64.8	..
36	18.2	15.8	66.0	..
29	23.1	12.0	64.9	Ast.
30	25.9	9.6	64.5	..
37	30.0	6.5	63.5	..
31	33.8	4.6	61.5	Ast., Mg-6
35	33.8	3.55	62.65	Mg-6
38	34.5	1.92	63.58	..
Mulder[7]	35.5	0.0	64.5	..
ISOTHERM AT 80°				
Mulder[7]	0.0	30.4	69.6	Na_2SO_4
89	4.29	28.1	67.61	Na_2SO_4, Vant. (?)
103	13.9	22.4	63.7	Vant.
102	14.2	22.25	63.55	..
73	14.55	22.3	63.15	Vant., Löw.
74	14.7	22.0	63.3	Löw.
104	15.4	21.4	63.2	..
105	16.4	19.7	63.9	..
107	18.1	17.85	64.05	..
108	24.06	12.6	63.34	..
161	33.25	6.25	60.4	..
122	36.3	4.9	58.8	..
123	38.4	2.8	58.8	Mg-1
Smith[8]	38.6	0.0	61.4	..

Table I (*Concluded*)

Isotherm at 100°

Expt.	$MgSO_4$ %	Na_2SO_4 %	H_2O %	Solid phase [a]
Mulder[7]	0.0	29.8	70.2	Na_2SO_4
126	13.7	20.5	65.8	Vant.
163	13.75	20.6	65.65	..
119	16.9	19.4	63.7	Vant., Löw. (?)
118	23.2	12.55	64.25	Löw.
124	31.1	6.5	62.4	..
125	32.0	6.07	61.93	..
Seidell[6]	40.6	0.0	59.4	Mg-1
Mulder[7]	42.5	0.0	57.5	(Mg-6)

Miscellaneous Data

Ref. no.	Temp., °C.	$MgSO_4$	Na_2SO_4 %	Solid phase
10	−2.9	13.9	0.0	Ice
11	−3.9	19.0	0.0	Ice, Mg-12
12	−6.0	19.0	0.0	(Ice, Mg-7)
11	1.8	21.1	0.0	Mg-12, Mg-7
13	32.383	0.0	(33.61)	Na-10, Na_2SO_4
14	48.4	(33.0)	0.0	Mg-7, Mg-6
15	68.0	37.0	0.0	Mg-6, Mg-1
5	55.0	22.45	14.35	Ast., Na_2SO_4
5	55.0	31.7	5.2	Mg-6, Ast.
5	65.0	13.4	23.0	Na_2SO_4, Vant.
5	65.0	26.8	9.4	Ast., Löw.
5	65.0	34.3	5.2	Mg-1, Löw.
5	90.0	31.5	6.65	Mg-1, Löw.
5	90.0	19.6	16.3	Löw., Vant.

[a] In most cases the solid phase was assumed from the position on the isotherm.

Isotherms

The percentages of sodium sulfate were plotted against percentages of magnesium sulfate to give solubility isotherms which are shown in Figs. 1 and 2. A break in a curve indicates a change in the solid phase in equilibrium with the solution at that point. As the change of direction was very slight in some cases, a certain amount of doubt exists as to the transition points, particularly between the double salt portions, and between

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[7] Mulder, "Schiekundige Verhandelungen en Ouderzockingen," **1864,** vol. 3, part 2, pp. 52, 123.

[8] Smith, in Landolt and Börnstein's "Tabellen," 4th ed., Julius Springer, Berlin, **1912,** p. 481.

[9] Diacon, "Jahresber. Fortschr. Chem.," **1866,** p. 61.

[10] de Coppet, *Ann. chim. phys.*, [4] **25,** 528 (1872).

[11] Cottrell and others, *Sitzber. k. Akad. Wiss.*, Berlin, **1902,** p. 276.

[12] Weston, *J. Chem. Soc.*, **121,** 1223 (1922).

[13] Richards and Wells, *Z. physik. Chem.*, **43,** 471 (1903). Dickinson and Mueller, This Journal, **29,** 1381 (1907).

[14] Carpenter and Jette, *ibid.*, **45,** 578 (1923).

[15] van't Hoff, *Sitzber. k. Akad. Wiss.*, Berlin, **1902,** p. 370.

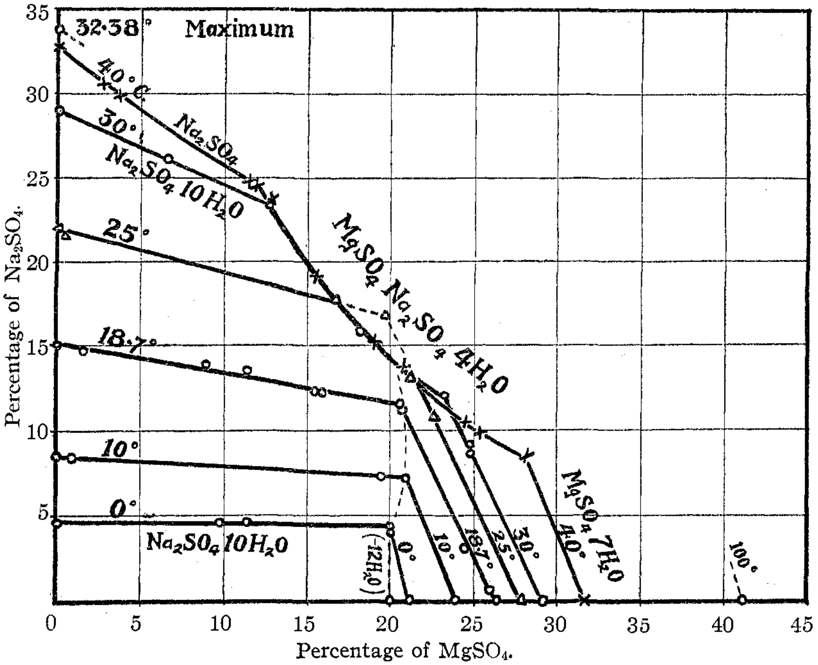

Fig. 1.—Solubility isotherms from 0° to 40°.

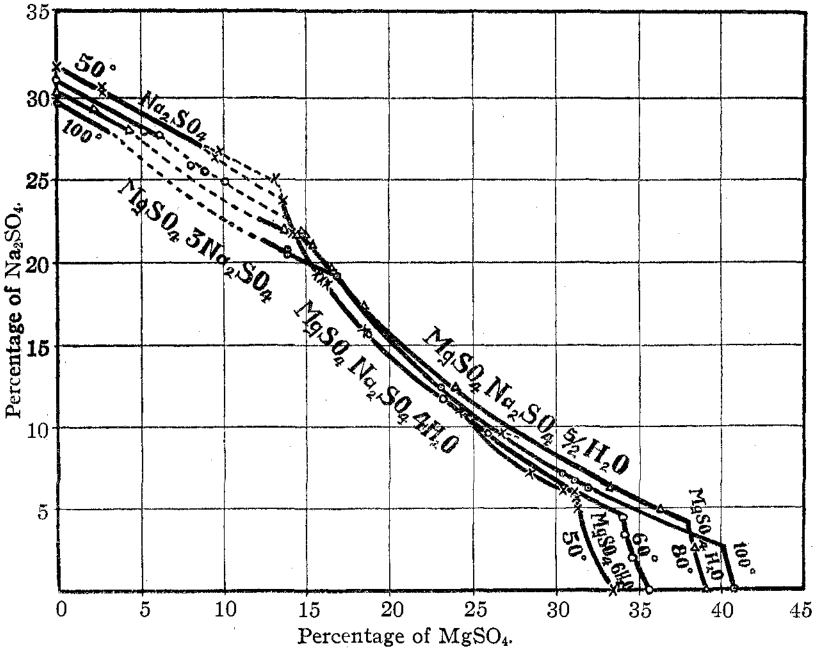

Fig. 2.—Solubility isotherms from 50° to 100°.

vanthoffite and sodium sulfate. The magnesium sulfate portion of the isotherm at 0° is also uncertain since it is doubtful as to which hydrate was present. However, these cases are of little importance from a practical standpoint, as they do not affect the general shape of the isotherms.

Temperatures were then plotted along a third axis at right angles to give a solid model (Fig. 3), which shows the saturation areas of the stable solid phases. The extent of the vanthoffite field is at present uncertain. Dilatometer methods might here yield definite results, by taking advantage of changes in volume on passing from one solid phase to another. Such variations would, no doubt, be fairly distinct, since R. Görgey[16] states that density determinations may readily be used to differentiate between these double salts.

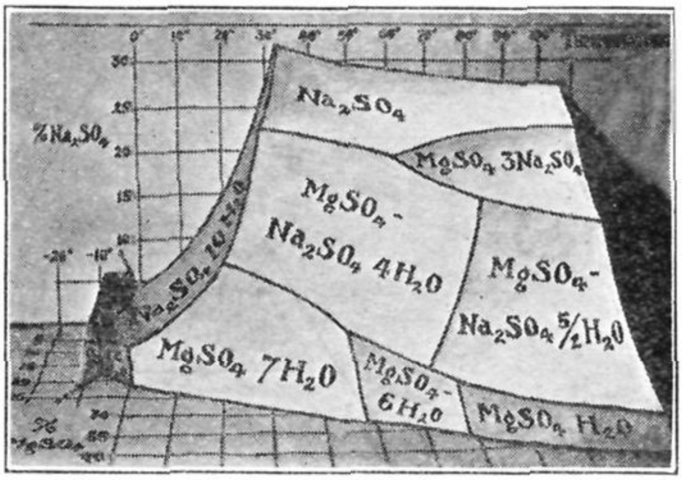

Fig. 3.—The phase relationships of $MgSO_4$ and Na_2SO_4 in contact with their water solutions.

Determination of Solid Phase

Schreinemakers' "residue" method was frequently made use of in determining the solid phase present. This method is based on the fact that if the composition of the solid with adhering mother liquor is plotted on a triangular diagram, this point must lie on the straight line joining the points representing the compositions of the liquid and solid phases. Thus, when at least two different solutions are analyzed together with their wet residues, the composition of the pure solid may be found by extrapolation. It must be remembered, however, that this method is only applicable when the solid consists of one phase of constant composition.

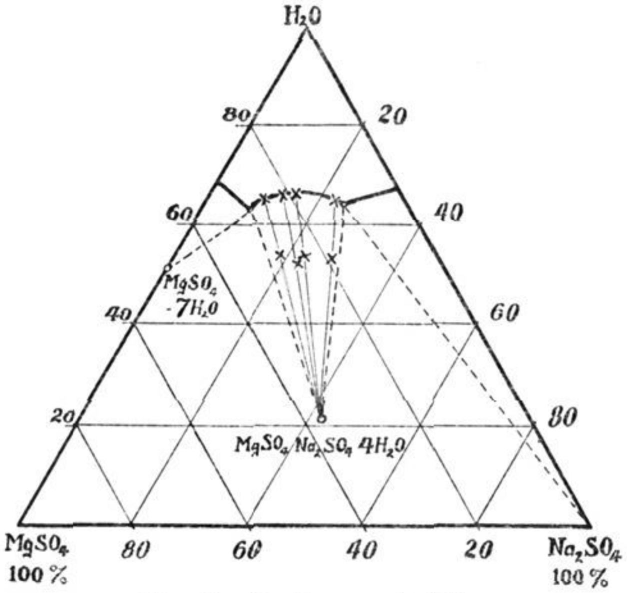

Fig. 4.—Isotherm at 40°.

Mixtures were made up so as to obtain points at intervals along that portion of the isotherm under investigation. Analyses were made both of

[16] Görgey, *Min. petro. Mitt.*, **28,** 334 (1910); *C. A.*, **4,** 1281 (1910).

the saturated solutions and of the solid residues with adherent mother liquor, and the results plotted on triangular diagrams. The straight lines joining each pair of values were produced to intersection, this point representing the composition of the pure solid.

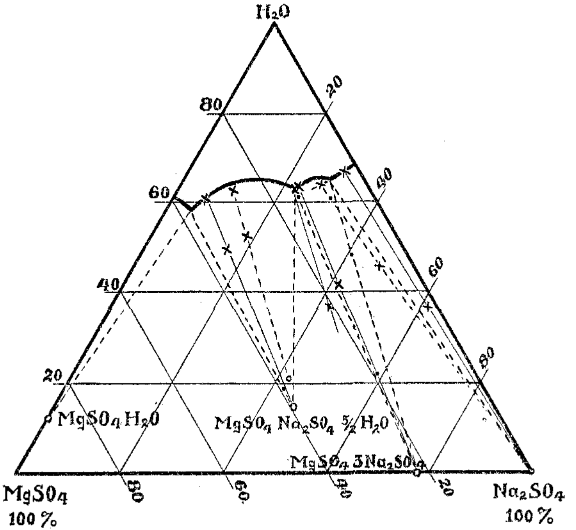

Fig. 5.—Isotherm at 50°.

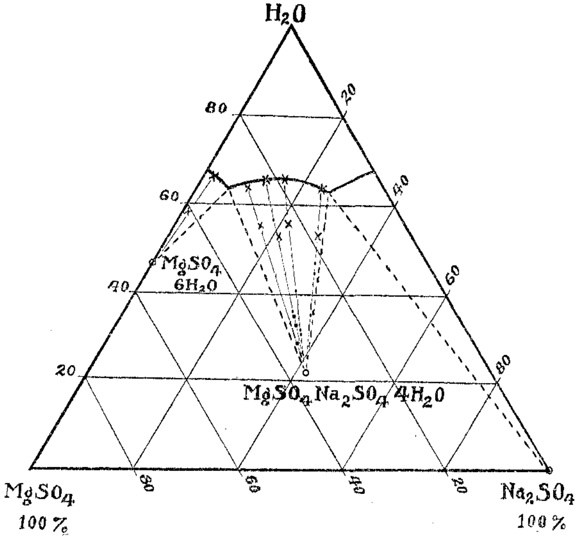

Fig. 6.—Isotherm at 80°.

The results obtained from these experiments are contained in Table II, while the triangular diagrams illustrating the graphical determinations of the solid phases at 40°, 50° and 80° are shown in Figs. 4, 5 and 6.

It is to be regretted that time did not permit the completion of this branch of the work. However, sufficient determinations were made to identify the double salts in their proper order along several of the isotherms.

TABLE II

RESULTS ACCORDING TO SCHREINEMAKERS' METHOD

	Solution			Wet residue			
Temp. °C.	$MgSO_4$ %	Na_2SO_4 %	H_2O %	$MgSO_4$ %	Na_2SO_4 %	H_2O %	Solid phase
40	13.15	22.80	64.05	19.3	27.2	53.5	Astrakanite
	21.60	13.45	64.95	25.2	22.6	52.2	......
	24.10	10.80	65.10	27.6	18.3	54.1	......
	19.20	15.00	65.80	23.8	23.07	53.13	......
50	13.3	23.0	63.7	18.8	28.2	53.0	......
	18.2	16.0	65.8	22.2	21.9	55.9	......
	21.3	13.5	65.2	25.2	21.7	53.1	......
	27.8	9.75	62.45	29.5	16.3	54.2	Astrakanite
	32.8	2.51	64.69	40.0	2.2	57.8	$MgSO_4.6H_2O$
80	13.85	22.55	63.60	17.6	40.7	38.3	Vanthoffite
	33.25	6.35	60.40	34.0	15.8	50.2	Löweite
100	13.75	20.60	65.65	17.40	42.75	39.85	Vanthoffite

Scheme of Separation

A method for the separation of these two sulfates was suggested from a study of their isothermal relations at lower temperatures. This scheme depends on the fact that below 22° the two solids, $MgSO_4.7H_2O$ and $Na_2SO_4.10H_2O$, can co-exist in equilibrium only with solutions whose compositions fall along the line AB in Fig. 7, such a system being monovariant. This line represents the boundary between the Epsom and Glauber's salt areas in the solid model.

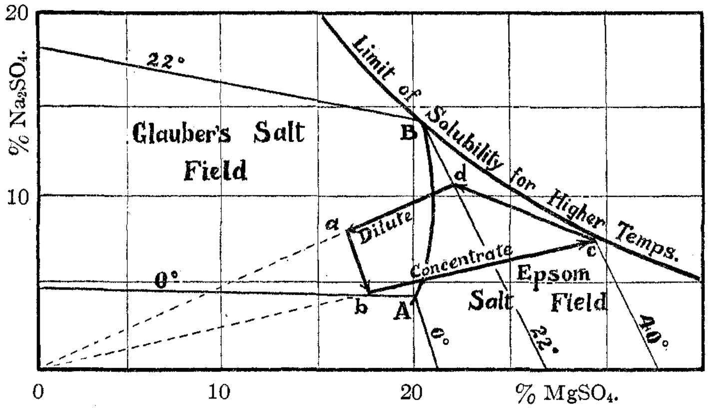

Fig. 7.—Scheme of separation.

Thus on cooling a solution of original composition "a" below its saturation temperature, Glauber's salt will separate along the line "ab."

This may be removed by rapid filtration or centrifuging, while the mother liquor of composition "b" is then concentrated at higher temperatures to point "c" which would give a saturated solution at say 40°. When the solution is cooled to about 22°, Epsom salt separates along the line "cd." The mother liquor may then be diluted so as to bring the concentration well within the Glauber's salt field before being cooled further for the separation of more sodium sulfate. Similar cycles of operations may be repeated until the solution has been reduced to a very small volume.

The process may be commenced from any point on either side of the line AB, and the composition of the solution may be brought into the cycle by dilution, concentration, or partial separation of one of the salts. Concentration might also be brought about by the addition of a mixture high in magnesium sulfate.

This method was tested on a laboratory scale with several mixtures and gave results which were quite satisfactory. Fractions of salt of a high degree of purity were obtained in each case.

The following results of Test 1 and Test 2 will serve to illustrate the method.

Results of Separation Test 1

Sample	$MgSO_4$ %	Na_2SO_4 %	H_2O %	Excess H_2O %	Separation %
A (salt)	4.62	36.10	59.28	13.58	88.7
B (M. L.)	18.55	5.40	76.05		
C (salt)	45.25	0.89	53.86	6.51	98.0
D (M. L.)	21.70	10.40	67.90		
E (salt)	3.70	39.40	56.90	7.00	91.5
F (M. L.)	17.60	5.40	77.00		

In this test a solution having the original composition 17.1% of magnesium sulfate and 9.2% of sodium sulfate was cooled to 2° and frequently stirred. The solid that separated was sucked dry on a Büchner filter, but not washed. A above shows the results of the analysis of this solid; B represents the mother liquor. The "Excess H_2O" is the difference between the total water and that necessary for the crystallization of the major salt; while the "% Separation" shows the amount of the major salt contained in the total anhydrous material.

The mother liquor B was evaporated to two-thirds of its volume (to a concentration of 27.8% of magnesium sulfate and 8.1% of sodium sulfate) and then cooled to 20°. The solid C was removed as before without washing. D represents the composition of the mother liquor. This mother liquor was diluted with one-fourth its volume of water giving a solution of about 16.5% of magnesium sulfate and 13.9% of sodium sulfate. This was cooled to 2° and the solid E separated as before. The final mother liquor is shown as F which is very close in composition to mother liquor B.

In controlling the process during operations, as the composition of the original solution is known, changes in concentration during evaporation and dilution can be followed by observing the volume changes. These are plotted on a chart showing isotherms for each alternate degree between 0° and 22° together with sets of lines along which the salts would separate on cooling. Samples were taken at various points and analyzed.

Results of Separation Test II

Sample		$MgSO_4$ %	Na_2SO_4 %	H_2O %	Separation %
Original solution		26.75	7.80	65.45	
cooled to 20°	salt	48.00	0.74	51.26	98.5
	M. L.	22.00	9.90	68.10	
Diluted $^1/_6$ and cooled to 0°	salt	3.76	37.60	58.64	91.0
	M. L.	20.40	4.40	75.20	
Evaporated $^1/_3$ and cooled to 20°	salt	44.40	2.20	53.40	95.3
	M. L.	23.00	7.62	69.38	
Diluted $^1/_6$ and cooled to 0°	salt	5.70	37.80	56.50	87.0
	M. L.	19.95	4.80	75.25	

This test was made with a mixture of approximately 25% of Glauber's salt and 75% of Epsom salt, as this is a rough average of certain natural deposits; 200 g. of the mixed hydrates was dissolved in sufficient water to give a saturated solution at 40°. The process was followed through two complete cycles and the solids separating out were treated as before.

The high percentages of magnesium sulfate in the Glauber's salt fractions of Test II may in part be due to insufficient dilution previous to their separation. This is shown by the fact that the compositions of the mother liquors are almost identical with the values found for the quadruple point at 0° at which both the solid hydrates can precipitate on cooling.

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Summary

1. A study has been made of the solubility relations of mixtures of magnesium and sodium sulfates at the following temperatures: 0°, 18.7°, 25°, 30°, 40°, 50°, 60°, 80° and 100°.

2. The solid phases were determined in a few doubtful cases, and a solid model was constructed to show the saturation fields of all stable solids in contact with solutions.

3. A scheme for the separation of sodium and magnesium sulfates was evolved, and tests made on a laboratory scale proved quite satisfactory, giving fractions of salt as high as 98.5% pure without washing.

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