hydrate occurs at 12.7° it may be possible for all three hydrates (7, 5, 2) to occur as saturating solids at some temperature just below 12.7°.

Finally, the solubility curve for saturation with $MgMoO_4\cdot 5H_2O$, in Fig. 2, is interesting in that it passes through a maximum of water content somewhere near 5% $MgCl_2$. Although the analytical water concentration passes through this maximum, the vapor pressure of the solutions on this curve decreases steadily from point *b* to point *a*, since this is the direction of isothermal evaporation of the ternary solutions saturated with the pentahydrate.

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The Quaternary System $MgMoO_4$–Na_2SO_4–H_2O at 25° and its Related Ternary Systems

BY JOHN E. RICCI AND WILLIAM F. LINKE

The aqueous solubility relations of the reciprocal salt pair $MgMoO_4$–Na_2SO_4 at 25° are reported. Of the subsidiary ternary systems studied also at 25° that involving the pair $MgMoO_4$–$MgSO_4$, with $MgMoO_4\cdot 5H_2O$ and $MgSO_4\cdot 7H_2O$ as solid phases, appears to be simple, with neither double salt nor solid solution formation; but the presence of molybdate in the solid $MgSO_4\cdot 7H_2O$, which is isomorphous with $MgMoO_4\cdot 7H_2O$, may be merely beyond detection by the indirect means used. The system Na_2MoO_4–Na_2SO_4–H_2O is also simple, but the solid $Na_2SO_4\cdot 10H_2O$, isomorphous with $Na_2MoO_4\cdot 10H_2O$, does have some molybdate in solid solution. The system $MgMoO_4$–Na_2MoO_4–H_2O forms the hydrated double salt $MgMoO_4\cdot Na_2MoO_4\cdot 2H_2O$, incongruently soluble at 25°. The quaternary isotherm involves the solid phases $Na_2MoO_4\cdot 2H_2O$, $Na_2SO_4\cdot 10H_2O$, $MgSO_4\cdot Na_2SO_4\cdot 4H_2O$ (astracanite, congruently soluble), $MgSO_4\cdot 7H_2O$, $MgMoO_4\cdot 5H_2O$ and $MgMoO_4\cdot Na_2MoO_4\cdot 2H_2O$. The salts $MgMoO_4 + Na_2SO_4$ are incongruently soluble as the stable salt pair. Three of the quaternary invariants are congruently saturated drying-up points of the isotherm, and one is an incongruently saturated transition point with the phase reaction $MgMoO_4\cdot Na_2MoO_4\cdot 2H_2O + \text{liquid} \rightarrow MgMoO_4\cdot 5H_2O + Na_2SO_4\cdot 10H_2O + H_2O\nearrow$ for isothermal evaporation.

This is the report of a study of the 25° isotherm of the quaternary system of water and the reciprocal salt pair $MgMoO_4$–Na_2SO_4. As necessary parts of this system the 25° isotherms of the ternary systems Na_2MoO_4–Na_2SO_4–H_2O, $MgMoO_4$–$MgSO_4$–H_2O and $MgMoO_4$–Na_2MoO_4–H_2O were also studied. The system $MgSO_4$–Na_2SO_4–H_2O was available in the literature, and only a few points on its 25° isotherm were repeated for verification.

The solubility relations were investigated by the usual methods, as already described for systems involving some of these salts.

Sodium molybdate was used as the anhydrous salt prepared from the C.P. dihydrate. The sodium sulfate was anhydrous C.P. material, found 100.0% pure by precipitation of barium sulfate. Reagent grade $MgSO_4\cdot 7H_2O$ was analyzed by dehydration at dull red heat and gravimetrically for magnesium with 8-hydroxyquinoline. The results were 49.25 ± 0.03% $MgSO_4$ by dehydration and 49.32 ± 0.08% by magnesium determination, as compared with the theoretical value 48.84, indicating deficiency of water. Since the composition remained constant over a period of several weeks, the analytical salt content was used in calculations involving this material. Magnesium molybdate was used as the pentahydrate, prepared as previously described.[1]

The analytical methods used involved first of all the Volhard procedure applied to determination of molybdate in neutral solution. Tests on known amounts of sodium molybdate showed that the presence of magnesium and sulfate ions caused no significant interference with this determination.

For solutions containing both magnesium and molybdate it was necessary to remove the molybdate before the precipitation of magnesium with oxine. For this purpose the molybdate was precipitated with silver nitrate, used in small excess, and the silver molybdate was removed and washed in filter paper. The filtrate, diluted to 250 ml. and heated to ~80°, was treated with 3 g. of NH_4NO_3, 50 ml. of 6 *N* NH_3 and then the usual 5% oxine solution in excess. The precipitate was digested for half an hour, filtered, washed with 1 *N* NH_3 and then with water, and finally dried at 105° for weighing. This procedure differs slightly from the standard procedure,[2] to prevent interference on the part of silver ion, which also precipitates with oxine. If too great an excess of $AgNO_3$ is used in the removal of molybdate, a curdy, light yellow silver–oxine complex is precipitated, which redissolves too slowly upon addition of more ammonia. (Cyanide might prove more effective in preventing the interference by silver, but it was not tried.) It is not difficult, however, to control the excess of $AgNO_3$ in the precipitation of Ag_2MoO_4. The whole procedure was tested on magnesium sulfate in presence of varying amounts of sodium molybdate, and in each case the result was identical with that in absence of molybdate.

For determination of water, or of "total solids," the solutions were first evaporated to dryness at 85°. In absence of magnesium sulfate they were then heated to constant weight at ~300°. With magnesium sulfate present the residues were dried for a short time at 120° and then ignited to constant weight at dull red heat. Solutions requiring this treatment were transferred from the solubility tubes directly into porcelain crucibles, with rapid weighing. A test of the ignition procedure on known amounts of material showed a precision of 1/1000.

System Na_2MoO_4–Na_2SO_4–H_2O at 25°.—The complexes in this system were prepared from the anhydrous salts, and although the molybdate be-

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(1) J. E. Ricci and W. F. Linke, THIS JOURNAL, 73, 3601 (1951).

(2) I. M. Kolthoff and E. B. Sandell, "Text Book of Quantitative Analysis," The Macmillan Co., New York, N. Y., 1943, p. 374.

comes hydrated readily, it was always necessary to seed the solutions with the sulfate decahydrate. In order to detect any solid solution formation the tubes were rotated for long periods of time, some as long as 140 days. A few complexes were made up in larger tubes including marbles for better stirring, and many of the solutions were reanalyzed to verify equilibrium. The solutions were analyzed for molybdate and for total solids. On the molybdate solubility curve the approach to equilibrium may or may not have been from supersaturation because of the heat produced in the hydration of Na_2MoO_4; along the sulfate curve it was probably always from supersaturation because of the pronounced metastability of the anhydrous salt. The checks on equilibrium over long periods of time were good in every case. The densities were determined with delivery pipets.

The data are listed in Table I in terms of weight percentage, and the relations are plotted in Fig. 1. *Note:* The solid phases in this and succeeding tables and diagrams are labeled

A: $Na_2MoO_4 \cdot 2H_2O$	D: $MgMoO_4 \cdot 5H_2O$
B: $Na_2SO_4 \cdot 10H_2O$	E: $MgMoO_4 \cdot Na_2MoO_4 \cdot 2H_2O$
C: $MgSO_4 \cdot 7H_2O$	F: $MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$

TABLE I

SYSTEM Na_2MoO_4–Na_2SO_4–H_2O AT 25°

Complex		Saturated solution			
% Na_2MoO_4	% Na_2SO_4	% Na_2MoO_4	% Na_2SO_4	Density	Solid phase
0.00	...	0.00	21.55	1.201	B
5.04	23.08	6.16	18.50	1.238	B
5.03	23.10	6.18	18.50	1.236	B
9.40	22.39	12.40	15.53	1.273	B
15.00	20.05	19.31	13.11	1.328	B
19.00	17.11	23.34	12.28	1.360	B
16.06	23.66	25.32	11.54	1.375	B
22.52	15.96	26.19	11.29	1.380	B
24.00	16.02	28.31	10.89	1.415	B
24.74	16.04	29.50	10.57	1.426	B
26.88	15.08	30.67	10.59	1.447	B, A
38.40	10.02	30.05	10.99	1.444	B, A
(*c*) Average of six		30.33	10.75	1.446	B, A
41.00	8.51	30.45	10.57	1.444	A
40.71	7.00	32.37	8.27	1.441	A
36.38	5.81	34.19	6.09	1.435	A
...	0.00	39.38	0.00	1.432	A

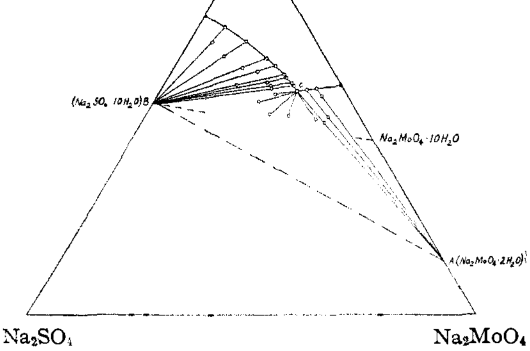

Fig. 1.—System Na_2MoO_4–Na_2SO_4–H_2O at 25°.

The only solid phases involved in Fig. 1 are seen to be $Na_2SO_4 \cdot 10H_2O$ and $Na_2MoO_4 \cdot 2H_2O$. The three tie-lines for saturation with $Na_2MoO_4 \cdot 2H_2O$ give errors of −0.09, +0.23 and −0.42% Na_2SO_4 respectively, when extrapolated to the line of 85.11% Na_2MoO_4, the theoretical percentage in the dihydrate. Since there is not corresponding dihydrate of Na_2SO_4, this solid phase, as expected, may be considered to be pure. The presence of molybdate in solid solution in the decahydrate, however, is to be expected, but the question is to what extent the phase relations at 25° would permit its detection. $Na_2SO_4 \cdot 10H_2O$ should be isomorphous with $Na_2MoO_4 \cdot 10H_2O$, which is stable below 10.27°, the transition point between the deca- and the dihydrates of sodium molybdate.[3,4] Solid solutions of corresponding hydrates are found in the systems Na_2MoO_4–Na_2CrO_4–H_2O[4] and Na_2CrO_4–Na_2SO_4–H_2O.[5] Similarly the two decahydrates of the present system do form solid solution, as indicated by the study of the ternary aqueous system at a few other temperatures. (This work is still incomplete, and will be reported later.) But the difference in transition temperatures is evidently so great that the position of sulfate-rich decahydrated crystals still stable as a saturating phase at 25°, which is 14° above the molybdate transition temperature, covers an almost negligible proportion of molybdate in its composition. Without this expectation of solid solution the 25° results here reported might be taken as indicating pure $Na_2SO_4 \cdot 10H_2O$ as solid phase, with deviations little beyond the order of the experimental error. The more significant tie-lines are those with high molybdate concentrations in the solutions. Extrapolated algebraically to the line connecting the compositions of the two decahydrates, the tie-lines for complexes 6–10 of Table I indicate, as saturating phase, a decahydrate solid solution containing 1.7, 2.2, 2.2, 2.5 and 2.5% $Na_2MoO_4 \cdot 10H_2O$, respectively.

System $MgMoO_4$–$MgSO_4$–H_2O at 25°.—Complexes were prepared from the actual hydrates and water, and were allowed to rotate for from 7 to 75 days. Equilibrium was approached from undersaturation. Several solutions were reanalyzed, with no significant change occurring in this period. The filtered samples were analyzed for molybdate and for total solid.

The data are given in Table II, in weight percentage. All the tie-lines on the two solubility curves extrapolate quite accurately to the pure salt hydrates, so that the system involves neither double salt nor measurable solid solution at this temperature. The average extrapolation error to the line 67.17% $MgMoO_4$ representing $MgMoO_4 \cdot 5H_2O$ is +0.02 or |0.33|% $MgSO_4$; for $MgSO_4 \cdot 7H_2O$ it is +0.09 or |0.28|% $MgMoO_4$ at the line 48.84% $MgSO_4$. According to Wyrouboff[6] the corresponding hydrates $MgMoO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 7H_2O$ are isomorphous. Formation of solid solu-

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[3] R. Funk, *Ber.*, **33**, 3696 (1900).

[4] W. E. Cadbury, THIS JOURNAL, **67**, 262 (1945).

[5] J. Takeuchi, *Mem. Coll. Sci.* (*Kyoto*), **1**, 249 (1915).

[6] G. Wyrouboff, *Bull. soc. franc. Min.*, **12**, 71 (1889); quoted in Gmelin, "Handbuch der anorganischen Chemie," Vol. 8, Molybdän, p. 288 (1935).

tion between them probably would be detected through solubility relations at some temperature at which the only solid phases are the heptahydrates. The absence of a measurable molybdate content in the $MgSO_4 \cdot 7H_2O$ at 25° may result from the wide differences in the solubilities and in the transition temperatures (wider than in the preceding system of the sodium salts): 12.7° for $MgMoO_7 \cdot 7H_2O \rightleftarrows MgMoO_4 \cdot 5H_2O$ and 48° for $MgSO_4 \cdot 7H_2O \rightleftarrows MgSO_4 \cdot 6H_2O$. An unusual feature of the isothermal relations, when plotted on the usual triangular diagram (not shown), is the practically linear decrease of the solubility of magnesium molybdate with increasing concentration of the sulfate up to the invariant point at 23.8% $MgSO_4$. The densities of these solutions saturated with $MgMoO_4 \cdot 5H_2O$ show a similar linearity when plotted against percentage of $MgSO_4$.

TABLE II

SYSTEM $MgMoO_4$–$MgSO_4$–H_2O AT 25°

Complex		Saturated solution			
% $MgMoO_4$	% $MgSO_4$	% $MgMoO_4$	% $MgSO_4$	Density	Solid phase
...	0.00	15.90	0.00	1.159	D
22.82	2.44	14.70	2.91	1.176	D
20.95	5.15	13.28	6.06	1.198	D
20.25	7.46	12.08	8.79	1.218	D
18.71	9.95	10.76	11.54	1.230	D
18.17	12.51	9.20	14.64	1.254	D
17.65	15.01	7.63	18.03	1.271	D
13.51	18.25	6.42	20.72	1.292	D
15.25	20.27	5.08	23.73	1.306	D, C
5.77	39.48	5.03	23.80	1.316	D, C
(*f*) Average of three		5.06	23.76	1.313	D, C
3.71	28.07	4.51	24.02	1.305	C
3.04	29.72	3.70	24.65	1.296	C
2.51	29.96	3.20	24.78	1.295	C
1.83	30.23	2.26	25.33	1.291	C
0.00	...	0.00	26.67	1.278	C

System $MgMoO_4$–Na_2MoO_4–H_2O at 25°.—In this system, as seen in the diagram of Fig. 2, the component salts combine to form the hydrated double salt $MgMoO_4 \cdot Na_2MoO_4 \cdot 2H_2O$. The compound is incongruently soluble with respect to $MgMoO_4 \cdot 5H_2O$, and its saturation curve is longer than that of either sample salt. The curve for saturation with $Na_2MoO_4 \cdot 2H_2O$ is very short (~0.1%), and only its ends were determined. The data are presented in Table III, in units of weight percentage.

The complexes were prepared from water, $MgMoO_4 \cdot 5H_2O$ and anhydrous Na_2MoO_4, so that some heat was evolved as the latter salt became hydrated. Only in the tubes containing the lower invariant solution *b*, with $Na_2MoO_4 \cdot 2H_2O$ as one of the solid phases at equilibrium, did any caking of the solids occur during mixing of the components; these complexes may have approached equilibrium from supersaturation since heating was necessary to break up the caked solids. The double salt did not form immediately, requiring in some cases several days after seeding. Some of the complexes with double salt as solid phase therefore also approached equilibrium from a metastable supersaturated level. Once the double salt had appeared equilibrium was readily attained, as was proved by reanalysis of a number of the solutions from initial periods of 3 days up to as long as 183 days.

TABLE III

SYSTEM $MgMoO_4$–Na_2MoO_4–H_2O AT 25°

Complex		Saturated solution			
% $MgMoO_4$	% Na_2MoO_4	% $MgMoO_4$	% Na_2MoO_4	Density	Solid phase
21.00	4.03	13.71	4.84	1.177	D
18.62	7.99	12.09	9.14	1.210	D
18.50	9.76	11.22	11.38	1.220	D
18.02	10.51	11.00	12.10	1.230	D
17.86	11.28	10.69	12.99	1.238	D
17.61	11.96	10.39	13.92	1.248	D
17.71	12.70	10.17	14.68	1.252	D
16.67	13.05	10.03	14.86	1.250	D
19.69	12.58	9.84	15.29	1.255	D
19.69	13.39	9.44	16.45	1.268	D
16.67	14.96	9.26	17.18	1.270	D
11.87	17.50	8.87	18.45	1.282	D^m
14.79	17.49	9.28	17.31	1.272	D, E
14.76	21.98	9.26	17.29	1.272	D, E
(*a*) Average of three		9.27	17.27	1.271	D, E
11.81	20.99	8.57	17.91	1.272	E
10.79	22.29	7.34	19.15	1.267	E
13.47	25.39	6.94	19.85	1.273	E
14.02	29.86	4.23	23.56	1.285	E
7.00	31.75	1.62	29.30	1.321	E
5.88	31.49	1.57	29.44	1.322	E
5.04	36.07	0.48	34.74	1.373	E
10.73	38.91	.39	35.79	1.387	E
8.02	39.41	.23	37.41	1.401	E
5.00	39.33	.10	38.26	1.419	E
8.84	41.97	.13	39.25	1.424	E, A
1.30	43.69	.12	39.32	1.429	E, A
(*b*) Average of four		.11	39.31	1.429	E, A

[m] Metastable.

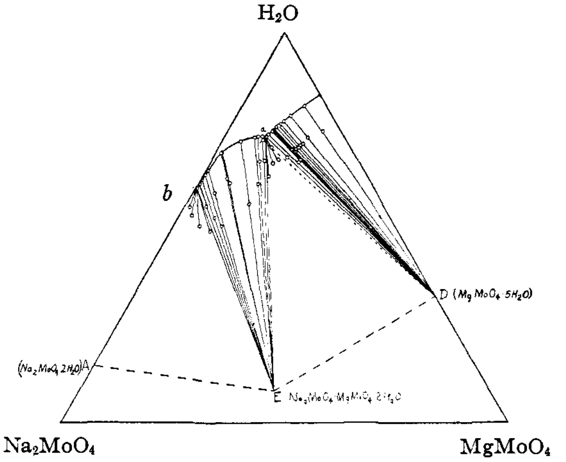

Fig. 2.—System $MgMoO_4$–Na_2MoO_4–H_2O at 25°.

The solutions were at first analyzed for magnesium by the oxine procedure and for total solid by evaporation. Consideration of the errors of extrapolation of tie-lines to the composition of the solid phase $MgMoO_4 \cdot 5H_2O$ along its saturation curve, however, indicated that there was a greater random error in the determination of total solid by evaporation than in the more laborious determination of total molybdate by the Volhard method. The error in either case reflects itself in terms of percentage of Na_2MoO_4, calculated by difference, and since this is the significant percentage in the use of the tie-lines for the indirect determination of the composition of the new double salt, the analyses were then made by the combination of the Volhard procedure for molybdate and the oxine precipitation for magnesium.

The composition of the double salt was determined by the point of intersection of the tie-lines. The diagram, Fig. 2, shows clearly that the compound is an equimolar combination of the salts, and the exact extrapolations of the tie-lines are required only to fix the degree of hydration. The graphical intersection indicates from one to three moles of H_2O in the formula. The only tie-lines which have value in fixing the water content, however, are those meeting the equimolar salt ratio line at an appreciable angle. The first three complexes of the double salt curve, as listed in Table III, are therefore ignored for this purpose. The tie-lines of the remaining seven complexes cross the line representing the equimolar ratio of the salts at the following percentages of water, calculated algebraically: 6.9, 8.7, 5.3, 11.3, 7.4, 8.3 and 10.0, respectively. The mean, 8.3% H_2O, with average deviation of 1.0, is to be compared with the theoretical percentages of H_2O in 1:1 double salts with 1, 2 and 3 moles H_2O, which are, respectively, 4.41, 8.45 and 12.17%. The result may therefore be taken as experimental evidence of the formula $MgMoO_4 \cdot Na_2MoO_4 \cdot 2H_2O$ for the double salt. Similar formulas, moreover, have been reported for two other double salts of magnesium molybdate, namely, $MgMoO_4 \cdot K_2MoO_4 \cdot 2H_2O$ and $MgMoO_4 \cdot (NH_4)_2MoO_4 \cdot 2H_2O$.[7]

The double salt is incongruently soluble at 25°, as may be seen from the diagram, but the relations suggest that it is possible that it may become congruently soluble at some temperature not far from 25°. It is not clear whether or not the stable section of the solubility curve of the double salt at 25° passes through a maximum of water content but from the curve the maximum, stable or metastable, must be near the invariant solution *a*, saturated with double salt and $MgMoO_4 \cdot 5H_2O$.

System $MgSO_4$–Na_2SO_4–H_2O **at 25°.**—This, the fourth aqueous ternary system of the quaternary system under consideration, has been studied extensively by several investigators. Only a few measurements, to check the invariant points at 25°, were made; these are listed in Table IV. The solutions were analyzed for magnesium and for total solid. The congruently soluble double salt astracanite, $MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$, always formed spontaneously after a few days, but seeding was again necessary for the formation of $Na_2SO_4 \cdot 10H_2O$. The agreement between the invariant compositions here obtained and those in the literature is not very close. The actual values found were used for the quaternary system; they agree most closely with those of Benrath.[8]

TABLE IV

SYSTEM $MgSO_4$–Na_2SO_4–H_2O; INVARIANTS AT 25°

Complex		Saturated solution				
% $MgSO_4$	% Na_2SO_4	% $MgSO_4$	% Na_2SO_4	Density	Solid phase	Point
15.05	22.24	15.96	18.36	1.354	B, F	*d*
16.10	26.78	16.05	18.46	1.353	B, F	*d*
24.38	20.59	20.55	13.32	1.360	F	
20.76	24.62	20.85	13.08	1.367	F	
27.23	12.74	21.66	12.20	1.349	F, C	*e*
26.13	15.74	21.59	12.20	1.349	F, C	*e*

Quaternary System $MgMoO_4$–Na_2SO_4–H_2O **at 25°.**—The complexes were prepared from water and the hydrated salts except for sodium sulfate, which was used in the anhydrous form; for $Na_2SO_4 \cdot 10H_2O$ as solid phase the mixture was seeded accordingly. For the quaternary curves of liquid saturated with two simple hydrates the complexes were made up with compositions calculated to leave some of each salt undissolved; enough of a third salt was then added to bring the solution composition as far into the quaternary diagram as desired. When the expected relations involved one of the double salts as solid phase the complex was usually brought to equilibrium in the pertinent ternary system before the third salt was added. Occasionally all the substances were mixed together and the complexes were then seeded with small amounts of the stable phases.

The analytical results, based on determination of magnesium, of molybdate, and of total solid,

TABLE V

SYSTEM $MgMoO_4$–Na_2SO_4–H_2O AT 25° (MOLES PER MOLE OF DISSOLVED SALTS)

Point or curve	$MgMoO_4$	$MgSO_4$	Na_2SO_4	Na_2MoO_4	H_2O	Density	Solid phases
b–1	0.0036		0.1258	0.8710	16.50	1.430	A, E
b–1	.0043		.2393	.7565	15.55	1.440	A, E
1	.0037		.3363	.6600	14.69	1.442	A, B, E
1–2	.0178		.3709	.6113	16.11	1.409	B, E
1–2	.0385		.4431	.5184	17.89	1.367	B, E
1–2	.1027		.5234	.3739	18.87	1.342	B, E
1–2	.1865		.6058	.2077	18.87	1.333	B, E
1–2	.2690		.6801	.0509	18.05	1.335	B, E
1–2	.2850		.7007	.0143	17.73	1.335	B, E
1–2	.2755	0.0357	.6893		17.52	...	B, E
1–2	.2637	.0669	.6703		17.20	1.349	B, E
1–2	.2435	.1131	.6432		16.77	1.346	B, E
1–2	.2258	.1524	.6218		16.36	1.347	B, E
1–2	.2113	.1861	.6027		15.99	1.349	B, E
1–2	.1951	.2194	.5856		15.64	1.348	B, E
2	.1793	.2529	.5678		15.26	1.358	B, D, E
a–2	.3773		.0703	.5524	29.33	1.281	D, E
a–2	.3895		.1222	.4883	28.49	1.283	D, E
a–2	.3960		.1845	.4196	27.19	1.290	D, E
a–2	.4183		.2993	.2824	25.80	1.289	D, E
a–2	.4044		.4190	.1766	23.51	1.303	D, E
a–2	.4073		.5416	.0510	20.98	1.311	D, E
a–2	.3333	.0904	.5762		18.60	1.332	D, E
2–3	.1558	.2910	.5532		14.74	...	B, D
2–3	.1351	.3328	.5321		14.31	1.370	B, D
2–3	.1220	.3639	.5140		14.01	1.369	B, D
3	.1133	.3781	.5086		13.74	1.376	B, D, F
d–3	.0315	.4670	.5016		13.88	1.358	B, F
d–3	.0760	.4270	.4792		13.82	1.365	B, F
d–3	.0934	.3946	.5120		13.82	1.369	B, F
3–4	.0974	.4726	.4300		13.62	1.368	D, F
3–4	.0926	.5127	.3945		13.79	1.366	D, F
3–4	.0851	.5664	.3485		13.75	1.374	D, F
3–4	.0779	.6056	.3167		13.73	1.365	D, F
4	.0759	.6164	.3077		13.63	1.375	C, D, F
e–4	.0357	.6478	.3166		13.77	1.356	C, F
e–4	.0503	.6404	.3093		13.70	1.362	C, F
f–4	.1101	.8052	.0846		16.57	1.330	C, D
f–4	.1021	.7521	.1456		15.78	1.342	C, D
f–4	.0892	.6908	.2198		14.82	1.361	C, D
f–4	.0775	.6221	.3004		13.87	1.376	C, D

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(7) F. Ullik, *Ann.*, **144**, 343 (1867).

(8) A. Benrath, *Z. anorg. Chem.*, **170**, 257 (1928).

are presented in Table V, expressed in terms of the number of moles of each component per mole of dissolved salt. The quaternary invariants *1–4* were each averaged from three or four independent determinations.

Complexes along curves *f–4*, *e–4*, *3–4*, *d–3* and *b–1* were rotated for 5 to 24 days before analysis, and representative solutions were reanalyzed to prove attainment of equilibrium. Complexes in which the double salt $MgMoO_4 \cdot Na_2MoO_4 \cdot 2H_2O$ was one of the saturating phases reached equilibrium much more slowly than the others. Of four complexes along curve *a–2*, prepared at the same time but not seeded with the double salt, this solid formed in two of them after four weeks, and in the other two after six weeks, of stirring. Along curve *1–2* equilibrium was reached in about two months with double salt initially present. In order to determine the course of this curve more expeditiously, large amounts of the salts and water were placed in a 250-ml. bottle fitted with a mercury-sealed motor-driven stirrer, and suspended in the 25° water-bath. Equilibrium was thus reached within a week, as proved analytically. When a point on the curve had been established, further amounts of salts were added to bring the complex deeper into the quaternary field. When point *2* was reached further addition of salt caused no change in the composition of the saturated solution.

Of the points on curve *2–3*, for saturation with solids B and D, one was obtained by addition of Na_2MoO_4 to point *3*, one by addition of $MgSO_4 \cdot 7H_2O$ to point *2*, and the third directly from a mixture of Na_2SO_4, $MgSO_4 \cdot 7H_2O$, $MgMoO_4 \cdot 5H_2O$, and water.

The salt proportions alone are plotted in the usual Jänecke diagram in Fig. 3, which gives vertically the total number of moles of molybdate salts and from left to right the total number of moles of magnesium salts, per mole of dissolved salts, as listed in Table V.

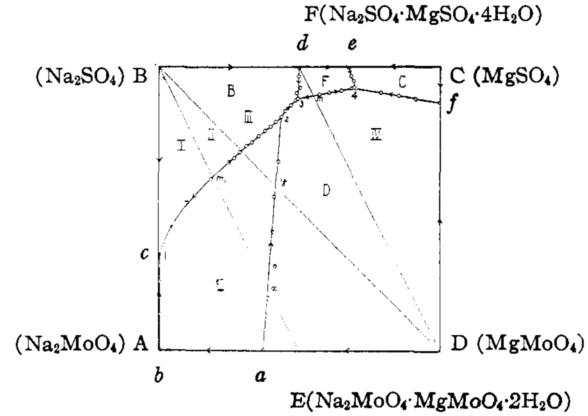

Fig. 3.—Jänecke diagram of system $MgMoO_4$–Na_2SO_4–H_2O at 25°.

The water content, in the units of Fig. 3, may be represented as a perpendicular ordinate on such a square as base. In Fig. 4, a "Jänecke elevation," the water content is then projected horizontally on the vertical section Na_2MoO_4–$MgSO_4$. In this figure one plots the number of moles of Na_2MoO_4 per mole of dissolved salts, to the left from the origin, for those solutions in Table V with compositions expressed in terms of $MgMoO_4$, Na_2SO_4 and Na_2MoO_4; for the others, the number of moles of $MgSO_4$ is plotted to the right from the origin.

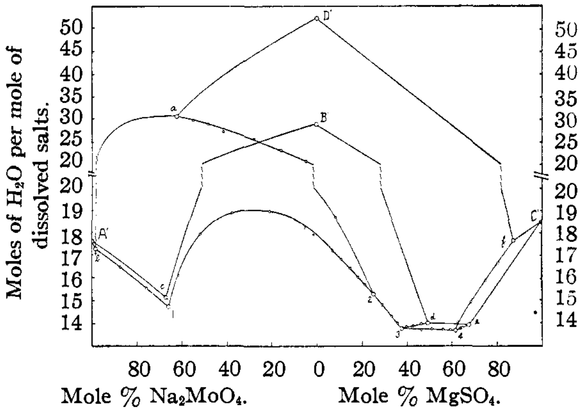

Fig. 4.—Water content of saturated solutions, projected on the section Na_2MoO_4–$MgSO_4$ (slightly distorted, or schematic).

The compositions of Table V may also be transformed into equivalent percentages of the components in the total of all four, including the water; mole percentages serve just as well in the present case. They may then be plotted in a regular square pyramid, its special vertical axis representing the equivalent (or mole) percentage of water. The radical or perspective projection of the relations from the water apex on the salt base again gives the Jänecke diagram of Fig. 3. Orthogonal projection on the base gives Fig. 5, the "orthogonal diagram." Here one plots (% $MgMoO_4$ − % Na_2SO_4), in moles per total moles, including water, to the right from the origin, and either % Na_2MoO_4

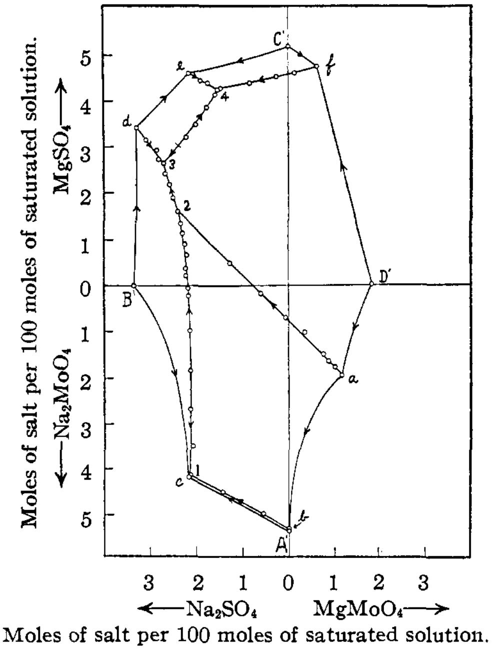

Fig. 5.—Orthogonal diagram of system $MgMoO_4$–Na_2SO_4–H_2O at 25°.

downward or % $MgSO_4$ upward from the origin, depending on which of these salts is represented as a positive quantity in Table V.

The general relations are more conveniently discussed on the basis of Figs. 3 and 4. The special points labeled in all the figures are summarized in Table VI. In Fig. 3 the peripheral points *a* to *f* represent the salt proportions in ternary solutions saturated with two adjacent solids; they may be identified from Figs. 1, 2 and Tables I–IV. Each is the origin of a curve of quaternary solution of twofold saturation. The compositions of solutions saturated with single solids (A′, B′, C′, D′, F′) are, of course, superimposed with the solid phases themselves in Fig. 3.

TABLE VI

SPECIAL POINTS OF FIG. 3 (MOLES PER MOLE OF DISSOLVED SALTS)

Point	$MgMoO_4$	$MgSO_4$	Na_2SO_4	Na_2MoO_4	H_2O	Density	Solids
A′				1.0000	17.60	1.432	A
c			0.3394	0.6606	14.67	1.446	A, B
B′			1.0000		28.70	1.201	B
d		0.4937	0.5063		13.87	1.345	B, F
F′		.5000	.5000		13.9	1.345	F
e		.6766	.3234		13.83	1.349	F, C
C′		1.0000			18.37	1.278	C
f	0.1222	0.8778			17.57	1.313	C, D
D′	1.0000				54.10	1.159	D
a	0.3750			.6250	30.39	1.271	D, E
b	.0031			.9969	17.56	1.429	E, A
1	.0037		.3363	.6600	14.69	1.442	A, B, E
m_1	.194		.612	.194	18.9	1.333	B, E
x	.391		.218	.391	27.3	1.290	D, E
y	.417		.583		20.2	1.320	D, E
2	.1793	.2529	.5678		15.26	1.358	B, D, E
3	.1133	.3781	.5086		13.74	1.376	B, D, F
m	.102	.449	.449		13.7	1.372	D, F
4	.0759	.6164	.3077		13.63	1.375	C, D, F

The course of isothermal evaporation for isothermally invariant solutions, both ternary and quaternary, is shown by the arrows on the curves and sides of Fig. 3. The directions on the three very short curves are A→*b*, *c*→*1*, F→*d*. Of the four isothermally invariant quaternary points, for solutions saturated with three solids, those numbered *1*, *3*, *4*, each lying within the triangle of its three solids (triangles I, III, IV), are congruent drying-up points for isothermal evaporation. Each of the points *1*, *3*, *4* is therefore a vapor pressure minimum of the isothermal saturation surfaces. In general, therefore, but not necessarily, they correspond to minima of water content, as may be seen in Fig. 4. The points *m* and m_1 are consequently "saddle points" of vapor pressure on their respective curves. The vapor pressure of saturated solutions falls, for example, to m_1 both from corner B and from point *x*, and falls away on the curve *1–2*, on either side of m_1. These saddle points therefore tend to be maxima of water content on their respective curves, Fig. 4.

The section F*m*D is seen to be a quasi-ternary isothermal section of the condensed system. The section *B*m_1E is not quasi-ternary since the double salt E is incongruently soluble. The salts $MgMoO_4$ and Na_2SO_4, as pentahydrate and decahydrate, respectively, constitute an incongruently soluble stable salt pair in the reciprocal aqueous system, curve *2–3* representing solutions saturated with the pair. They are not congruently soluble as a pair at this temperature, however, since the curve *2–3* does not fall across the diagonal BD.

The only transition curve of the diagram is that labeled *a–2*, for liquids in equilibrium with D and E, or the solids $MgMoO_4 \cdot 5H_2O$ and $MgMoO_4 \cdot Na_2MoO_4 \cdot 2H_2O$. Since the double salt E is incongruently soluble in water (Fig. 2), isothermal evaporation of the solution *a* involves a transition type of phase reaction, $D + \text{liquid} \rightarrow E + H_2O\nearrow$. This continues to be the reaction along the quaternary curve *a–2*, while the liquid becomes richer and richer in respect to sulfate until $Na_2SO_4 \cdot 10H_2O$, solid B, precipitates at point *2*. The liquid at point *2* is then isothermally invariant, with the transition reaction $E + \text{liquid} \rightarrow B + D + H_2O\nearrow$.

The quaternary transition point *2* is reached, in isothermal evaporation with complete heterogeneous equilibrium, only by solutions originating in the quadrangle B*2*DE. Those from triangle II dry up at point *2* to leave the solids B + D + E. For the rest, the solid E is consumed in the invariant reaction and the liquid, precipitating B and D, proceeds to point *3* when it dries up, as for all solutions in triangle III, to leave the solids B + F + D. For such an equilibrium process the transition curve *a–2* is reached by liquids from the region *a2*D carrying D as solid phase; the liquid then travels on the curve in the direction *a* → *2* while D is being transformed to E. The curve is crossed, into the E field *b1*m_1*2a*, however, by liquids originating in the region *ay*E, when all the solid D is consumed. Liquids from *ax*E, as for all compositions in triangle I, finally dry up at point *1*, to leave the solids A + B + E. Liquids from *xy*E proceed to the curve m_1*2* along which they travel to end finally at point *2*.

If complete equilibrium of solid phases is not maintained, all solutions below the line *x*D, like all those in triangle I, dry up at point *1* to leave four solids, A, B, D and E. Solutions reaching the transition curve in the section *x2*, as also those reaching the curve m_1*2*, dry up at point *3* to leave the solids B, F, D and E.

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