The measurements for the system Ag_2MoO_4–$AgNO_3$–H_2O, listed in Table II in terms of weight percentage, show that the only solid phases are pure Ag_2MoO_4 and, presumably, pure $AgNO_3$.

TABLE II

SYSTEM Ag_2MoO_4–$AgNO_3$–H_2O AT 25°

($A = Ag_2MoO_4$; $B = AgNO_3$)

Original complex % A	Original complex % B	Saturated solution % B	% B in solid, by extrapolation	Solid phase
5.16	11.68	12.32	−0.08	A
5.11	22.37	23.54	+ .66	A
5.09	33.14	34.87	+ .71	A
5.47	47.82	50.56	+ .52	A
6.68	53.98	57.84	+ .05	A
5.21	64.59	68.14	+ .05	A
5.31	69.88	71.81		A, B
3.17	72.59	71.80		A, B
0.00	...	71.82		B

The tie-lines fixed by the compositions of solution and total complex were extrapolated algebraically[7] to the line 100% Ag_2MoO_4, and the errors so calculated, in terms of % $AgNO_3$, are shown in column 4 of the table. To ensure easy attainment of solid phase equilibrium in case of solid solution formation, the proportion of solid Ag_2MoO_4 used in the complexes was kept small, and hence the errors of analysis and synthesis, which are probably quite small, are greatly multiplied by the extrapolation. It is clear, however, that the silver molybdate is free of silver nitrate.

System Ag_2MoO_4–Na_2MoO_4–H_2O **at 25°.**—From the data, presented in Table III in terms of weight percentage, we see that here too there is neither compound formation nor solid solution between the salts. The algebraic extrapolations of tie-lines show the silver molybdate to be pure. The other solid phase of the isotherm is $Na_2MoO_4 \cdot 2\ H_2O$, the solubility of which has already been reported.[3]

TABLE III

SYSTEM Ag_2MoO_4–Na_2MoO_4–H_2O AT 25°

($A = Ag_2MoO_4$; $B = Na_2MoO_4$; $C = Na_2MoO_4 \cdot 2\ H_2O$)

Original complex % A	Original complex % B	Saturated solution % B	% B in solid, by extrapolation	Solid phase
5.18	4.95	5.21	+0.09	A
5.01	12.77	13.49	− .32	A
4.98	20.45	21.52	+ .05	A
5.13	28.66	30.22	− .19	A
5.00	35.81	37.71	− .29	A
2.93	40.66	39.37		A, C
1.99	45.56	39.36		A, C
0.00	...	39.38		C

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[7] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The System Magnesium Molybdate–Water and the 25° Isotherm of the System $MgMoO_4$–$MgCl_2$–H_2O

BY JOHN E. RICCI AND WILLIAM F. LINKE

A new hydrate of magnesium molybdate, $MgMoO_4 \cdot 2H_2O$, is reported. From solubility–temperature curves the transition points between the hepta- and the pentahydrates and between the penta- and the dihydrates have been determined, as 12.7 and 60.8°, respectively. The eutectic of the system is at −1.67° and 11.55% $MgMoO_4$, with $MgMoO_4 \cdot 7H_2O$ and ice as solids. The formula of the new hydrate was established by direct analysis and further confirmed through the solubility relations in the ternary system $MgMoO_4$–$MgCl_2$–H_2O at 25°, in which the solid phases are $MgMoO_4 \cdot 5H_2O$, $MgMoO_4 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$.

Although two hydrates of magnesium molybdate, namely, $MgMoO_4 \cdot 7H_2O$ and $MgMoO_4 \cdot 5H_2O$, have long been known,[1] the literature has apparently no information on the transition points and solubilities of the hydrates of this salt. As an aid in the characterization of the salt and in the comparison of its properties with those of related substances, the system $MgMoO_4$–H_2O was studied from the eutectic (−1.67°) to 95°. The transition point between the two known hydrates was thus determined as 12.7°, and at a second transition point at 60.8° the pentahydrate was found to decompose to the dihydrate, a compound not previously reported.[2] To confirm further the composition of this lowest hydrate it was decided to study the 25° isotherm of the ternary system $MgMoO_4$–$MgCl_2$–H_2O, chosen because the high solubility of $MgCl_2$ causes both the penta- and the dihydrates of $MgMoO_4$ to appear as stable saturating phases at room temperature.

Preparation of Hydrates of $MgMoO_4$.—One procedure described[3] for the preparation of magnesium molybdate is the reaction of magnesium oxide with a hot suspension of molybdic oxide. This method was tried, but possibly because of impurities in the reagents causing some reduction of the molybdic oxide at high temperature, the product was slightly green, giving pure magnesium molybdate (pentahydrate) only after two recrystallizations. The pure pentahydrate was therefore made directly as follows. To a large quantity (~200 g.) of pure silver molybdate[4] suspended in a liter of water at 60° a solution of pure magnesium chloride was added, with stirring, until nearly an equivalent amount was present. The silver molybdate was rapidly converted to silver chloride, and

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[1] For original references, see Gmelin, "Handbuch der anorganischen Chemie," Vol. 8, Molybdän, 1935, p. 288.

[2] Although the dihydrate as such is apparently not mentioned, the loss of three moles of H_2O from the pentahydrate at elevated temperatures has been reported by several observers (see Gmelin, ref. 1).

[3] For example, by F. Ullik, *Ann. Chem.*, **144**, 212 (1867).

[4] For its preparation, see J. E. Ricci and W. F. Linke, THIS JOURNAL, **73**, 3601 (1951).

with excess of solid silver molybdate present, the solution contained, in effect, only magnesium molybdate. When the solution gave no test for chloride, the mixed residue of AgCl and Ag_2MoO_4 was removed by suction filtration.

The pentahydrate was then obtained from the filtrate in either of two ways. (1) The solution was concentrated by boiling until some solid appeared. This solid redissolved upon cooling, and the evaporation was continued until the solution remained saturated at room temperature, with a small amount of undissolved solid. The solution was then evaporated *in vacuo* over sodium hydroxide, with formation of the coarsely crystalline $MgMoO_4 \cdot 5H_2O$, which was then ground to powder before use. (2) The solution was evaporated to a small volume on the steam-bath or hot-plate, with vigorous stirring to prevent excessive bumping during the precipitation of the solid dihydrate. When only a little liquid was left the mixture was allowed to cool and it was then stirred for 2 or 3 days at room temperature. Analysis of the solid at the end of this time showed that it had been completely converted to the pentahydrate, which was then pulverized and air-dried before use. This method of evaporation is faster than the first, which is essentially an isothermal removal of water, with crystals forming large masses clinging tenaciously to the walls of the beaker.

The amount of combined water varied slightly from lot to lot, but the ratio of magnesium to molybdate was always 1:1. No noticeable change in composition occurred at room temperature in the open air, and the actual water content was considered when the salt was used in synthetic complexes. A typical analysis gave 67.13 ± 0.04% $MgMoO_4$ by Volhard determination of molybdate,[5] and 67.10 ± 0.12% gravimetrically by oxine precipitation of magnesium[6]; the theoretical value is 67.17% for the pentahydrate.

Magnesium molybdate heptahydrate, $MgMoO_4 \cdot 7H_2O$ was prepared by evaporation of a solution of the pentahydrate at 4°. The evaporation was carried out over sodium hydroxide in a refrigerated vacuum desiccator. The crystals were pressed between filter papers and dried with acetone. Analysis gave 40.73% H_2O by dehydration at dull red heat, and 59.44% $MgMoO_4$ by molybdate determination; theoretical values are 40.63 and 59.37%, respectively.

Magnesium molybdate dihydrate was prepared by the evaporation of a solution of the pentahydrate on the steam-bath. The product was dried between filter papers and stored at 85°. Analysis gave 15.97% H_2O by dehydration at red heat and 84.01% $MgMoO_4$ by molybdate determination, as compared to 16.36 and 83.64%, respectively, for the theoretical composition $MgMoO_4 \cdot 2H_2O$. The results account for all the material present and indicate merely deficiency in water.

The three hydrates differ considerably in appearance. The heptahydrate is rather fluffy and cottony in nature, while the pentahydrate is coarsely crystalline, the crystals increasing noticeably in size when digested in their saturated solution in pure water. The dihydrate is very light and finely divided, settling quite slowly. It becomes more granular upon digestion, but the individual particles remain very small. The salts are pure white, and stable to light and heat. They are not hygroscopic and they readily become anhydrous at dull red heat.

System $MgMoO_4$–H_2O.—For the solubility determinations the salt was stirred with water in a 200-ml. flask clamped in a small water-bath capable of maintaining temperatures from 0 to 100° within 0.1°. The results are listed in Table I and are plotted in Fig. 1. The temperatures (corrected) are uncertain by about 0.02–0.03° at lower temperatures and by ~0.1° for 75–95°. Equilibrium was checked in all reported solubility values. The initial sampling, after about one hour of stirring, was followed by additional samplings at one-half to one hour intervals until constant results indicated attainment of equilibrium. Some of the points were verified by approaching equilibrium both from undersaturation and from supersaturation, and the agreement for the two directions was always good. Samples were removed in calibrated 2-ml. delivery pipets, and, after weighing, they were analyzed for molybdate by the Volhard procedure. The solubilities reported are probably correct to 1 or 2/1000, but the densities are not as reliable. For sampling above room temperature, the pipets were preheated and insulated. Because of its retrograde solubility curve there was no danger of precipitation of the dihydrate upon cooling.

Both the heptahydrate and the pentahydrate are seen to be incongruently melting compounds. While the solubility of the heptahydrate increases with temperature at a moderate rate, the slope for the pentahydrate is still positive but much smaller. The dihydrate exhibits retrograde solubility throughout the range of temperature studied. The transition points were estimated graphically from the intersections of the solubility curves. The heptahydrate–pentahydrate transition occurs at 12.7°(± 0.2°) and 15.15(± 0.05)% $MgMoO_4$, while the pentahydrate–dihydrate transition is at 60.8° (± 0.2°) and 19.85 (± 0.05)% $MgMoO_4$.

Only the heptahydrate reached equilibrium from both directions fairly rapidly. The pentahydrate dissolves readily but requires more than an hour of vigorous stirring to reach the saturation concentration at any temperature. The approach from supersaturation is very slow; in one case the temperature was changed rapidly from 58 to 43°, and although excess of the pure solid pentahydrate was always present and the mixture was stirred continuously, 15 hours were required to reach the new equilibrium concentration. The dihydrate dissolves very slowly in cold, more rapidly in hot water. When the temperature of a solution saturated with this solid was changed by 5°, from 1 to 3 hours of rapid stirring were needed to reach equilibrium again. The anhydrous or partially anhydrous material forms suspensions in water which

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(5) J. E. Ricci and L. Doppelt, This Journal, 66, 1985 (1944).

(6) For this determination molybdate was first removed as silver molybdate, as described in the succeeding article, J. E. Ricci and W. F. Linke, *ibid.*, 73, 3607 (1951).

TABLE I

EQUILIBRIA IN SYSTEM $MgMoO_4$–H_2O

^{m} metastable, ^{s} from supersaturation (all others from undersaturation), ^{g} determined graphically.

Temp., °C.	Wt. % $MgMoO_4$	Density
	Ice	
−0.45	3.94	...
−0.75	6.28	...
−1.25	9.38	...
	Ice + $MgMoO_4 \cdot 7H_2O$	
−1.67	11.55^{g}	1.111^{g}
	$MgMoO_4 \cdot 7H_2O$	
5	12.94	1.127
7	13.50	1.134
	13.50^{s}	1.135
10	14.31	1.143
11	14.61	1.145
	$MgMoO_4 \cdot 7H_2O$ + $MgMoO_4 \cdot 5H_2O$	
12.7^{g}	15.15^{g}	1.151^{g}
	$MgMoO_4 \cdot 5H_2O$	
5	14.43^{m}	1.143
10	14.85^{m}	1.147
15	15.26	1.151
20	15.59	1.150
25	15.89	1.159
	15.92^{s}	1.159
30	16.29	1.161
36	16.88	1.164
	16.90^{s}	1.157
43	17.62	1.160
	17.63^{s}	1.160
45	17.74	1.178
50	18.40	1.180
55	19.00	1.185
58	19.48	1.184
59	19.55	1.192
62	19.90^{m}	1.195
	$MgMoO_4 \cdot 5H_2O$ + $MgMoO_4 \cdot 2H_2O$	
60.8^{g}	19.85^{g}	1.192^{g}
	$MgMoO_4 \cdot 2H_2O$	
60	19.96^{m}	1.196
63	19.12	1.182
64	18.83	1.177
71	16.51	1.149
72	16.13	1.147
75	15.30	
	15.30^{s}	1.141
80	13.70^{s}	1.121
85	12.09	1.096
90	10.79	1.084
	10.76^{s}	1.090
95	9.38^{s}	1.072

may remain undissolved for many days; heating and vigorous stirring are necessary to effect complete solution. Correspondingly, phase changes near the transition points are not rapid. A solution in equilibrium with the pentahydrate was stirred for several hours at 5° with no evident conversion to the heptahydrate. At 0°, analysis showed a steady decrease in concentration with time during stirring, which must indicate conversion to the heptahydrate although no change was visible.

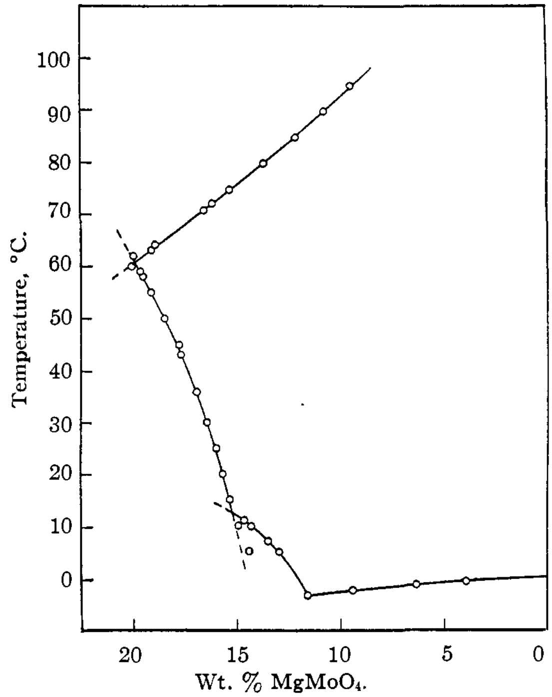

Fig. 1.—System $MgMoO_4$–H_2O.

Points on the ice curve were determined from heating curves on internally stirred samples of known composition. For the eutectic, with $MgMoO_4 \cdot 7H_2O$ and ice as solid phases, the temperature of −1.67° was averaged from several independent determinations, while the composition (11.55% $MgMoO_4$) and density (1.151) were obtained graphically from the intersection of the curves.

System $MgMoO_4$–$MgCl_2$–H_2O.—The general procedure for the ternary isotherm was that usually described for similar systems; the results, in terms of weight percentage, are listed in Table II, and plotted in Fig. 2. This figure is only part of the equilateral composition triangle of the system $MgMoO_4$–$MgCl_2$–H_2O, described by the points $MgMoO_4 \cdot 2H_2O$, H_2O and $MgCl_2 \cdot 6H_2O$.

Complexes of definite composition were made up from solid $MgMoO_4 \cdot 5H_2O$, water and weight aliquots of a solution of $MgCl_2$ prepared from the C.P. hexahydrate, since the water content of this solid is not dependable. The stock solution used for the first seven complexes listed in Table II was analyzed for chloride by the Volhard method and for magnesium gravimetrically by precipitation with oxine according to standard procedure, with the results 24.65 ± 0.03 and 24.63 ± 0.01% $MgCl_2$, respectively, so that the salt was considered pure. A saturated solution of the hexahydrate, kept in the thermostated bath at 25°, was used for the remaining complexes, requiring higher concentrations of $MgCl_2$. This solution was analyzed at the same time that portions were withdrawn for use. For complexes requiring excess of solid $MgCl_2 \cdot 6H_2O$ the slightly moist solid was used; for these the "complex" compositions were calculated with neglect of this excess of water since their precise compositions are not important.

The saturated solution was analyzed volumetrically both for the molybdate and for the total num-

TABLE II

SYSTEM $MgMoO_4$–$MgCl_2$–H_2O AT 25°

A = $MgMoO_4$; B = $MgCl_2$; C = $MgMoO_4 \cdot 5H_2O$; D = $MgMoO_4 \cdot 2H_2O$; E = $MgCl_2 \cdot 6H_2O$; *a* = approximate composition

Original complex		Saturated solution			Error in extra-polation	Solid phase
% A	% B	% A	% B	Density		
...	0.00	15.90	0.00	1.159		C
24.45	1.57	12.84	2.03	1.143	−0.12	C
24.85	3.22	10.07	4.29	1.128	+ .16	C
21.07	5.79	7.14	7.54	1.131	+ .01	C
14.41	9.77	4.06	11.58	1.141	+ .55	C
18.93	11.57	2.75	15.36	1.156	+ .29	C
11.7^a	16.5^a	1.55	19.30	1.179		C
17.76	18.11	0.91	24.20	1.216	+ .28	C
13.26	19.78	.83	24.25	...	+ .42	C
12.96	20.93	.78	25.63	1.231	+ .04	C
13.02	21.50	.67	26.34	1.229	+ .30	C
13.03	21.98	.53	26.96	1.231		C, D
12.95	22.43	.58	26.73	1.238		C, D
12.97	22.93	.61	26.80	1.233		C, D
12.99	23.03	.60	26.82	1.238		C, D
Average		.58	26.83	1.235		C, D
12.95	23.60	.63	27.52	1.234	+1.11	D
17.55	22.52	.52	28.03	...	+1.14	D
15.07	24.12	.39	29.29	1.258	−0.03	D
5.93	28.29	.31	30.37	...	− .47	D
5.98	29.08	.30	31.25	1.278	− .58	D
17.69	25.51	(.08?)	32.29	1.293	+ .12	D
18.04	26.18	.26	33.34	1.297	− .24	D
10.06	30.45	.12	34.53	1.312	+ .25	D
8.68	31.57	.10	35.32	...	−1.19	D
5.30	35.2^a	.14	35.47	1.325		D, E
5.06	35.5^a	.09	35.56	...		D, E
2.90	36.5^a	.17	35.53	1.323		D, E
1.05	37.1^a	.16	35.54	...		D, E
1.06	37.6^a	.17	35.53	...		D, E
Average		.15	35.53	1.324		D, E
0.00	...	0.00	35.71	1.323		E

ber of equivalents of chloride and molybdate. Both determinations, applying the Volhard method, were made on the same sample. Silver nitrate was added to a neutral solution of the two salts until precipitation was complete, and the mixture was boiled for complete coagulation of the mixed precipitate. After filtration through paper the excess of silver in the solution was determined with KCNS. The mixed precipitate itself was shaken with 3 *N* HNO_3 to separate the molybdate from the chloride. The mixture was again filtered, and the dissolved silver (of the molybdate) was determined with KCNS. Some care was taken to avoid exposure of the mixed precipitate to light, lest the silver formed by decomposition of the chloride (the molybdate is relatively stable and was in any case to be dissolved) be later dissolved in the nitric acid and cause high results for molybdate. The method was convenient for the system being studied especially because only a small amount of molybdate was usually involved. The procedure was checked by analysis of the same solution both by this method and by the use of independent samples, one for chloride alone (in which nitric acid is added before silver nitrate to prevent precipitation of Ag_2MoO_4) and one for the total precipitation in neutral solution. The agreement between the two methods was good: 15.36% $MgCl_2$ and 2.75% $MgMoO_4$ by the combined method, compared with 15.35 and 2.75%, respectively, with the use of separate samples.

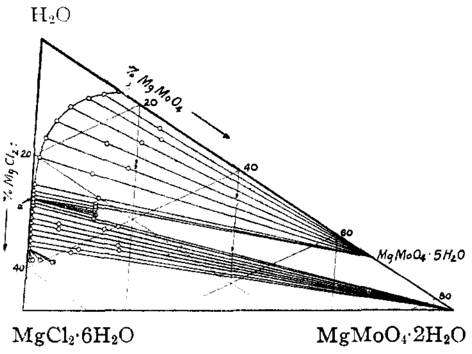

Fig. 2.—System $MgMoO_4 \cdot 2H_2O$–$MgCl_2 \cdot 6H_2O$–H_2O at 25°.

Complexes with $MgMoO_4 \cdot 5H_2O$ as solid phase came to equilibrium within a week, as indicated by reanalysis after an additional month of stirring. For solutions containing more than 26.83% $MgCl_2$, $MgMoO_4 \cdot 2H_2O$ is the saturating phase. These complexes took longer, in general, to reach equilibrium since the original solid had to change composition. In some cases seeding was necessary to hasten the transition. When the dihydrate did appear it was unmistakable, since the precipitate was voluminous and the mixture had a milky appearance. The solid nevertheless settled easily to give a clear supernatant liquid.

Although the direct analyses of the solid penta- and dihydrates of magnesium molybdate were close to the theoretical values, both formulas may be confirmed further by the extrapolation of the tie-lines of this ternary isotherm. The "errors in extrapolation" listed in Table II are in units of percentage of $MgCl_2$ at the line representing the theoretical percentage of $MgMoO_4$ in each hydrate. These "errors" represent operational errors multiplied by the relative lever arms of the segments of the tie-lines passing through the total complex composition. In the case of the pentahydrate the average error is small, being only +0.21%, thus distinguishing the hydrate from its possible neighbors, the hexa- and the tetrahydrates, for which the average "extrapolation error" would be +1.20 and −0.88%, respectively. The error for the dihydrate is larger, for several possible reasons, such as incomplete transformation of the original pentahydrate, incomplete attainment of equilibrium, in every case from supersaturation, and somewhat longer lever arms multiplying the effect. Nevertheless the results are sufficient to establish the formula as the dihydrate. The (algebraic) average error is +0.01%, while the average absolute error is 0.57%; for the extrapolation to the compositions of the possible tri- and monohydrates, the (algebraic) average errors would be +2.34 and −2.84%, respectively.

A concentration of 26.8% $MgCl_2$ lowers the transition temperature of the equilibrium $MgMoO_4 \cdot 5H_2O$ + $MgMoO_4 \cdot 2H_2O$ + solution + vapor by 35.8°. Since the transition to the heptahydrate 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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

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.