oxygen atom in many silicate structures while the positive ions like sodium and lithium will substitute for the hydrogen in the OH ion addition. Since all of the experiments result in the formation of a large amount of disintegrated and devitrified material, the inclusion of single OH ions in these structures would account for the decrease in *p*H, especially if a positive ion reacts with the included OH ion to displace the hydrogen. Such a proton displacement would reduce the *p*H. The positive test for sodium on volatilization of the devitrified material after being washed free of sodium ions gives support to this explanation.

The better fit of the lithium ion in silicate structures as shown by Newkirk and Tooley[21] through permeability measurements of alkali–silica glasses to metallic ions would account for the more rapid decrease in *p*H and smaller growth when lithium halide is used.

The ability of the halide ion to promote growth can be explained by referring to Table II which shows that the fluoride ion aids growth more than the other halides. The fluoride ion maintains a more constant *p*H by its ability to form the complex SiF_6^{--}. The replacement of OH or oxygen by fluoride ions in the silica or orthosilicate structures would replenish the solution. The presence of SiF_6^{--} when growth reactions involve fluoride ions has been shown.[3] Although not as well, the bromide and chloride ions could react in the same manner but not exist in the residues at room temperature and pressure.[22] Fluoride ion, Table VI, has the ability to extend the growth time by maintaining a growth *p*H longer while the other negative ions have not succeeded in doing the same thing.

Tables III, IV and V emphasize the fact that good growth depends upon optimum conditions of equilibrium between the rate of solution of the source and rate of deposition on the seed. With a constant surface area of seed, the relation between *p*H, halide concentration and number of water molecules is at *p*H 10, *N*/40 halide and 50% charge. A change in temperature under these conditions simply speeds up or slows down the reaction. Speeding up the reaction by increasing the density of the solution or amount of halide results in furnishing growth ions or molecules to the seed so fast that good crystalline growth is not possible.

(21) Newkirk and Tooley, *J. Am. Ceram. Soc.*, **32**, 272 (1949).

(22) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

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The Aqueous Solubility of Silver Molybdate and the Ternary Systems Ag_2MoO_4–$AgNO_3$–H_2O and Ag_2MoO_4–Na_2MoO_4–H_2O at 25°

BY JOHN E. RICCI AND WILLIAM F. LINKE

The 25° isotherms of the systems Ag_2MoO_4–$AgNO_3$–H_2O and Ag_2MoO_4–Na_2MoO_4–H_2O show that silver molybdate forms neither double compounds nor solid solutions with the salts from which it is usually prepared by precipitation. The aqueous solubility of silver molybdate is reported for the range 10 to 70°.

Silver molybdate is usually prepared by the interaction of solutions of silver nitrate and sodium molybdate, and it seems important to know whether or not the phase relations of the salts involved would lead one to expect any equilibrium contamination of the precipitate. In the analogous problem of the preparation of silver bromate from aqueous silver nitrate and aqueous sodium bromate, for example, the precipitate of silver bromate forms, with excess of sodium bromate, a solid solution (besides a double salt) with such relations that the precipitate is always contaminated with the sodium salt.[1] Although double salts of silver nitrate with other silver salts are rare,[2] it was decided to investigate the 25° isotherms of both the simple systems involved, Ag_2MoO_4–$AgNO_3$–H_2O and Ag_2MoO_4–Na_2MoO_4–H_2O, for information helpful in the preparation of pure Ag_2MoO_4. In both cases the salt pairs were found to form neither double salts nor solid solution, so that the precipitation method for the preparation of silver molybdate may be expected to give a pure product, except for mechanical contamination. At the same time, the solubility of silver molybdate over a range of temperature was also determined, to extend the available information on this salt.

Reagent grade silver nitrate was used; its purity was checked with various qualitative tests, and its consumption of KCNS was found to remain unchanged both after drying at 110° and after fusion. Sodium molybdate was used as the anhydrous salt obtained by heating the C.P. dihydrate at ~250° as discussed elsewhere.[3]

Silver molybdate was made by the simultaneous dropwise addition, with vigorous stirring, of solutions of silver nitrate and sodium molybdate to a large volume of hot water. The product so prepared, apparently amorphous, is white in color, with sometimes a very pale pink tint from photochemical or thermal decomposition. It was washed repeatedly with water by decantation until no significant flame test for sodium was obtained from either the precipitate or the wash water. The salt was air-dried and then stored in a vacuum desiccator over calcium chloride. The dry material was dissolved in nitric acid and analyzed for silver by titration with standard KCNS solution, and showed a purity of 99.9%. Heating in a drying

(1) J. E. Ricci and J. J. Aleshnick, THIS JOURNAL, **66**, 980 (1944).

(2) For those with AgI, AgBr, AgCN and AgCNS, see K. Hellwig, *Z. anorg. Chem.*, **25**, 157 (1900).

(3) J. E. Ricci and W. F. Linke, THIS JOURNAL, **69**, 1080 (1947).

oven, even at 85°, was sufficient to change the color of the product to a light purple, although no change was analytically detectable. Occasionally samples of the salt so prepared were deficient in silver by as much as one-half per cent. (relatively), and a flame test on these solids showed the presence of sodium. Since the ternary study shows silver molybdate to form no solid solution with sodium molybdate, this impurity was probably occluded sodium molybdate or sodium nitrate.

Crystalline silver molybdate was also prepared, although not used for solubility work. Evaporation of an ammoniacal solution of the salt[4] yielded colorless crystals turning pale gray-yellow upon standing. The pure salt is evidently colorless, although Donohue and Shand[4] reported the octahedral crystals to be "bright yellow."

Solubility of Silver Molydbate.—At 10° and 25° the salt was shaken with water in 250-ml. bottles immersed in large constant temperature water-baths. Approximately 100-ml. samples were removed by pipets fitted with filter paper tips, and delivered into weighed 250-ml. erlenmeyer flasks. Above 25° salt–water mixtures were stirred vigorously in an electrically heated one liter, 3-necked flask. Samples were withdrawn by a suction apparatus pulling the solution through a porous glass plate and then directly into the weighed receiving flask. It was not necessary to stop the agitation during this procedure. The receiving flask was cooled with ice to prevent loss of water by evaporation.

For analysis the 100-ml. sample was treated with 3–4 ml. of 6 *N* HNO_3 and evaporated to 1–2 ml. on a hot-plate. In tests on comparable amounts of silver nitrate the evaporation, carried out without boiling, to minimize mechanical loss, was found nevertheless to cause a reproducible apparent loss of silver of about 1.5%, which may have been the result of decomposition by light or heat. Such a relative correction was therefore applied in the analysis of the final solution, which was titrated, without transfer, with 0.004 *N* KCNS in a final volume of 10 ml. The concentrated solution was not transferred to a smaller container, more convenient for titration, since such transfer always led to still further loss.

Equilibrium was checked at all temperatures by reanalysis after further stirring. At 10° and 25° there was no change in samples rotating from one to five days. At the higher temperatures, with much more efficient stirring, 30 minutes sufficed for saturation, and stirring was continued for about two hours. Each value listed in Table I is the average of a number of independent samplings as indicated. In some of the runs at 25°, fresh water was added to the residual solid after each sampling. On the basis of deviations of individual values from the mean reported, and from the curve as plotted in Fig. 1, the uncertainty is estimated to be $\pm\sim 0.03(\times 10^{-3})\%$ for the lower temperatures and $\pm 0.1(\times 10^{-3})\%$ at 60 and 70°.

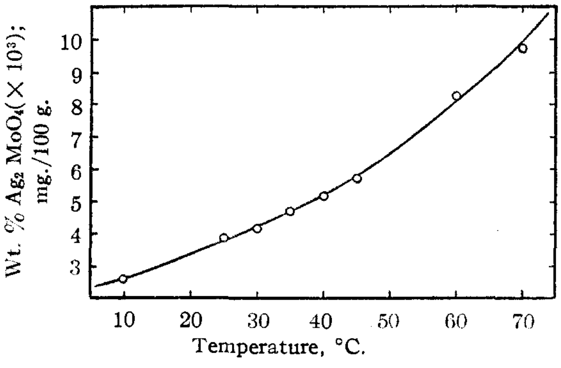

Fig. 1.—Aqueous solubility of Ag_2MoO_4.

TABLE I

AQUEOUS SOLUBILITY OF Ag_2MoO_4

Temp., °C.	No. of samples	Wt. % Ag_2MoO_4 ($\times 10^3$)
10	3	2.60
25	21	3.86
30	5	4.16
35	4	4.68
40	5	5.19
45	5	5.69
60	6	8.23
70	4	9.74

The value at 25°, 3.9 mg. per 100 g. solution, agrees fairly well with that of McCay,[5] who reported a solubility of 4.4 mg. per 100 ml. of water, but without stating how the determination was made. The solubility product at 18° was calculated by Britton and German[6] with neglect of the interaction of molybdate ion with water, from e.m.f. measurements of silver ion concentrations in solutions of silver nitrate treated with excess of sodium molybdate. With the same assumption, or with $K_{SP} = 4S^3$, their value of K_{SP} ($= 3.1 \times 10^{-11}$) gives a solubility of 7.4 mg. per 100 ml. solution, in serious disagreement with the value of 3.2 mg. at 18° read from Fig. 1. On the other hand the solubility 3.2 mg. per 100 ml. gives, with $K_{SP} = 4S^3$, a solubility product of $\sim 2.4 \times 10^{-12}$; this, however, is tentative only, since it neglects the unknown equilibrium constants relating the various possible ionic species of molybdic acid.

System Ag_2MoO_4–$AgNO_3$–H_2O **at 25°.**—Both ternary isotherms reported were investigated in the usual manner[3]; complexes of known composition were rotated at constant temperature and the filtered solution was analyzed at equilibrium. Because of the low solubility of Ag_2MoO_4 its concentration in presence of excess of either $AgNO_3$ or Na_2MoO_4 is practically zero, as was found by quantitative tests for molybdate and for silver ion, respectively. Evaporation to dryness therefore gave in each case the concentration of the second salt, $AgNO_3$ or Na_2MoO_4; the residue was brought to constant weight at 110° for $AgNO_3$ and at ~300° for Na_2MoO_4. For both systems the establishment of equilibrium was verified by reanalysis after further stirring, and although two days proved to be sufficient the actual time used varied from 5 to 21 days.

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[4] As suggested by M. H. Debray, *Compt. rend.*, **66**, 732 (1868); see also R. Wyckoff, THIS JOURNAL, **44**, 1994 (1922); and J. Donohue and W. Shand, *ibid.*, **69**, 222 (1947).

[5] L. W. McCay, THIS JOURNAL, **56**, 2548 (1934).

[6] H. T. Britton and W. L. German, *J. Chem. Soc.*, 1156 (1934).

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).

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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).