A Partial Solubility Isotherm of the System NH_3–MoO_3–H_2O at 25°

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The complex ammonium or alkali metal molybdates may be conveniently regarded as addition products of a normal molybdate and molybdenum trioxide. They are usually hydrated. In the literature at least seven such complex ammonium molybdates have been described. With one exception, all of them usually form very fine-grained precipitates and the evidence as to whether these are compounds, mixtures or possibly solid solutions is very inconclusive. The exception mentioned above is the so-called para compound which can be obtained in largec lear bluish-green crystals having the composition $3(NH_4)_2MoO_4$·$4MoO_3$·$4H_2O$.[1]

An obvious method of determining at least the stable compounds at a given temperature is by means of the usual isothermal solubility diagram of the three components which make up all the compounds. This method, however, has certain inherent difficulties. It becomes unreliable if equilibrium is reached too slowly. It also practically becomes unreliable when the solubility of two of the components in the solution becomes very slight. This condition not only slows down the attainment of equilibrium but also makes it difficult or impossible to interpret the solubility results correctly. Finally there is the difficulty of identifying a finely-divided solid phase in equilibrium with concentrated solutions, due to contamination with the latter. The identification of such solid phases by the analysis of wet residues by the well-known Schreinemakers method becomes unreliable when complex compounds like the molybdates are present.

All these difficulties are present to a certain extent in the case of the ammonium molybdates, which perhaps accounts for the lack of reliable solubility data in the system. Preliminary experiments convinced us, however, that true equilibrium could be reached over a considerable portion of the system. At the molybdic acid end, solubilities become so low that the results are not conclusive, and at the other end, the colloidal

character of the solids and the high concentrations of solutions have prohibited the use of phase rule methods.

Experimental

As sources of the molybdic acid component, we used both molybdenum trioxide and ammonium paramolybdate, $3(NH_4)_2MoO_4$·$4MoO_3$·$4H_2O$. The former was prepared by igniting the para salt. The latter was obtained by recrystallizing an excellent C. P. product under suitable conditions. The average of closely agreeing determinations on the para salt used gave 81.67% MoO_3 and 8.08% NH_3 (calcd.: 81.53% MoO_3 and 8.27% NH_3). At 25° this salt decomposes very slowly in contact with its solution yielding a more acid solid phase, so that it is only stable at this temperature in contact with a solution containing a slight excess of ammonia. This decomposition was observed repeatedly and is also indicated by the solubility data given below.

The mixtures for the solubility determinations were made from suitable proportions of water, the para salt and either ammonia or molybdenum trioxide. As we anticipated difficulty in reaching equilibrium, the mixtures were in all cases rotated at 25° for periods ranging from several weeks to several months. The para salt was purposely used in a coarsely crystalline condition and in the cases where it decomposed in reaching equilibrium, the process could be followed by examining the samples at intervals. The decomposition product was white and finely divided and the original crystals coarser and distinctly colored. The complete decomposition of the salt required several days in the thermostat.

For analysis, the clear solution was drawn off without difficulty after allowing sufficient time for the solids to settle. The solids for analysis were separated from the liquid by pressing rapidly between filter papers until they appeared dry. When the para salt was the solid phase, this offered no difficulty whatever, due to its coarsely crystalline condition. The other residues were more finely divided and offered more difficulty in freeing them from the mother liquor. Fortunately, these residues were relatively insoluble so that contamination from the mother-liquor was not serious. Ammonia was determined in all samples by distilling with sodium hydroxide into standard acid and determining the excess with standard alkali. Molybdenum trioxide was determined by gentle ignition to constant weight. Molybdenum trioxide is appreciably volatile at high temperatures but under the conditions used, the weights after repeated ignitions remained constant within very narrow limits. Duplicate determinations of ammonia were made in all cases but one. The determination of ammonia is probably slightly less accurate than that of molybdenum trioxide. Water was determined by difference.

The results obtained are given in the table. Duplicate determinations are averaged. All re-

(1) The formula of this compound is often written $5(NH_4)_2MoO_4$·$7MoO_3$·$7H_2O$, or its equivalent. The calculated percentages of the components in both formulas are so nearly identical that it is hardly possible to determine by analysis which is correct. We have therefore used the simpler formula.

sults are given which were obtained within the solubility limits shown. From solutions containing a somewhat higher proportion of ammonia than No. 1, another solid phase separated but it was extremely colloidal in character and its composition was not determined.

TABLE I

SHOWING THE COMPOSITION OF THE SOLUTIONS AND THE SOLIDS IN EQUILIBRIUM WITH THEM, TOGETHER WITH THE MOLECULAR RATIOS OF THE COMPONENTS IN THE SOLIDS

$T, 25°$

No.	Solution % NH₃	% MoO₃	Solid % NH₃	% MoO₃	% H₂O	Molec. ratio NH₃	MoO₃	H₂O
1	5.72	26.94	8.21	81.52	10.27	5.97	7.00	7.05
2	4.40	21.97	8.09	81.48	10.43	5.88	7.00	7.16
3	4.09	20.86	8.20	81.54	10.26	5.95	7.00	7.04
4	3.60	19.45	8.46	81.66	9.88	6.13	7.00	6.77
5	3.44	19.03	8.17	81.58	10.25	5.93	7.00	7.03
6	3.56	18.87	7.86	82.06	10.08	Mixture		
7	3.39	17.54	7.45	83.38	9.17	6.04	8.00	7.03
8	3.56	17.06	7.38	83.43	9.19	5.98	8.00	7.04
9	3.02	14.75	7.36	83.28	9.36	5.98	8.00	7.18
10	2.56	12.71	7.52	83.32	9.16	6.10	8.00	7.03
11	2.27	11.25	7.32	83.40	9.28	5.94	8.00	7.11
12	1.86	9.54	7.34	83.43	9.23	5.95	8.00	7.07
13	1.35	7.00	7.39	83.47	9.14	5.99	8.00	7.00

Within the solubility limits given in the table, the results show there are two solid compounds. The para compound, $3(NH_4)_2MoO_4·4MoO_3·4H_2O$, is the solid present in nos. 1–5. The calculated percentages of NH_3 and MoO_3 in this compound are 8.27 and 81.53, respectively, and the averages of the five corresponding determinations are 8.23 and 81.56. The averages of the molecular ratios derived from these analyses are 5.97:7.00:7.01 instead of 6:7:7.

No. 6 in the table is the univariant point, with two salts present. Both salts could be seen in the residue, corroborating the results of the analysis.

A second solid is present in nos. 7–13 in which the molecular ratio is $6NH_3·8MoO_3·7H_2O$, or $3(NH_4)_2MoO_4·5MoO_3·4H_2O$. The calculated percentages of NH_3 and MoO_3 in this compound are 7.40 and 83.46, respectively, and the averages of the six determinations are 7.39 and 83.39. The individual analyses of the seven samples agree so closely with the average that there can hardly be a doubt that this compound exists. The solubility results show that it forms under a fairly wide range of conditions. It has not previously been described.

The solubility results, if plotted, lie not far from a straight line with a slight break at the univariant point. No. 8 lies farthest from the solubility curve, indicating an error of about 0.3% of ammonia if the molybdenum trioxide is correct.

It seems worth while to point out that five ammonium molybdates are mentioned in the literature which contain a larger proportion of molybdenum trioxide than is present in either of the salts obtained by us. It seems very unlikely that all these can exist in stable equilibrium at 25°, for in that case they would necessarily form, in succession, along the very short portion of the curve left undetermined at the molybdic acid end of the system. Unfortunately, solubility methods can hardly be expected to settle the matter.

Summary

A partial solubility isotherm of the system NH_3–MoO_3–H_2O at 25° has shown conditions for the existence of the two complex ammonium molybdates $3(NH_4)_2MoO_4·4MoO_3·4H_2O$ and $3-(NH_4)_2MoO_4·5MoO_3·4H_2O$. The former is the well-known para molybdate and the latter a compound which has not been described previously.

STERLING CHEMISTRY LABORATORY
NEW HAVEN, CONN.   RECEIVED APRIL 21, 1936