

TABLE III

SUMMARY OF IONIZATION CONSTANT VALUES FOR N-CHLORO-*p*-TOLUENESULFONAMIDE OBTAINED BY TITRATION OF CHLORAMINE-T SOLUTIONS

Molar concn. of chloramine-T <sup>a</sup>	Section of titration curve and equation used	Average $K_2/f \times 10^5$	$-\log K_2/f$
0.01	A, equation 16	3.28	4.48
.01	C, equation 21	3.15	4.50
.02	A, equation 16	3.41	4.47
.02	C, equation 21	3.42	4.47
.04	A, equation 16	3.33	4.48
.04	C, equation 21	3.42	4.47
.08	A, equation 16	3.27	4.49
.08	C, equation 21	3.86	4.41

<sup>a</sup> This term also represents the ionic strength,  $\mu$ , at which the titration was carried out.

lated from the *pH* measurements by the equation  $pH = -\log(H^+)$  to hydrogen ion concentrations. The activity coefficients used for this purpose were taken from the chart of individual ion activities given by Chapin and Steiner.<sup>7</sup> The application of these corrections or the exact value of the activity coefficient used for them made very little difference over the greater part of the titration, but by including them it was possible to calculate consistent values for the ionization constant up to and even past the equivalence point.

In Fig. 2 a plot of the negative logarithms of  $K_2/f$ ,  $pK_2'$  values, obtained in the various experiments against the square roots of the ionic strengths at which the experiments were conducted is shown, the circles having been drawn with radii corresponding to an error of 0.02 unit in *pH* measurement. The extrapolation line drawn through the points has a slope of 0.5, corresponding to that given by the simple Debye-Hückel expression in the form  $pK_2 = pK_2' - 0.5\sqrt{\mu}$ .

(7) Chapin and Steiner, "Second Year College Chemistry," John Wiley and Sons, Inc., New York, N. Y., 5th edition, 1947, pp. 390-393.

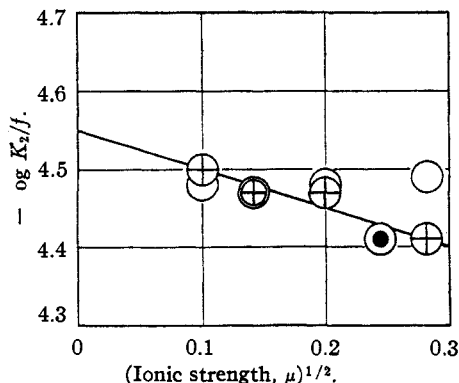


Fig. 2.—Variation of experimental ionization constants for  $C_7H_7SO_2NHCl$  with ionic strength: O, titration values for solutions unsaturated with Dichloramine-T; ⊕, titration values for solutions containing precipitate of Dichloramine-T; ⊙, value from solubility studies. Line corresponds to equation  $-\log f = 0.5\sqrt{\mu}$ .

The value of  $pK_2$  determined from the extrapolation is  $4.55 \pm 0.02$ . This leads to a value for  $K_2$ , the activity ionization constant of  $C_7H_7SO_2NHCl$ , of  $2.8 \pm 0.2 \times 10^{-5}$ .

### Summary

The ionization constant for N-chloro-*p*-toluenesulfonamide has been determined by potentiometric titration of solutions of Chloramine-T with acid and by measurement of the solubility of Dichloramine-T in solutions at *pH* 4.5 containing added quantities of *p*-toluenesulfonamide. Suitable mathematical equations have been developed to overcome the complications caused by the simultaneous occurrence of other equilibrium processes along with the ionization equilibrium.

The value obtained for the activity ionization constant of  $C_7H_7SO_2NHCl$  at 25° is  $K_2 = 2.8 \pm 0.2 \times 10^{-5}$ , corresponding to  $pK_2 = 4.55 \pm 0.002$ .

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

## Salts of an Aquoammonomolybdic Acid<sup>1,2</sup>

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In 1906, Rosenheim and Jacobsohn<sup>3</sup> prepared molybdenum(VI) oxide 3-ammonate by the interaction of the oxide and liquid ammonia. They considered the compound to be the diammonium salt of "imidomolybdic acid" and attempted to convert it to a lead(II) salt by reaction with lead(II) iodide in liquid ammonia at 108–109°, but their results were inconclusive.

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(2) Presented at the first Southwestern Regional Meeting of The American Chemical Society, Austin, Texas, December 7, 1945.

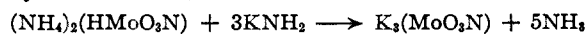
(3) Rosenheim and Jacobsohn, *Z. anorg. allgem. Chem.*, **50**, 297 (1906).

In terms of Franklin's nitrogen system of compounds,<sup>4</sup> molybdenum(VI) oxide 3-ammonate may be looked upon as a salt of a mixed aquoammonomolybdic acid. As such, this acid salt should be unreactive toward liquid ammonia solutions of ammonium salts (acids in liquid ammonia), but in the same medium should react, for example, with potassium amide (a base in liquid ammonia) to form a tripotassium salt which in turn should be convertible by metathesis to other

(4) Franklin, "The Nitrogen System of Compounds," A. C. S. Monograph No. 68, Reinhold Publishing Corporation, New York, N. Y., 1935, pp. 86-199.

metal salts. These properties have been demonstrated by the work described below.

The formation of the yellow tripotassium salt by the reaction,



goes to completion only very slowly even in the presence of a large excess of potassium amide. A red-brown dipotassium salt appears to be formed as an intermediate. Conversion by metathesis to the silver salt,  $\text{Ag}_3(\text{MoO}_3\text{N})$ , or the lead salt,  $\text{Pb}_3(\text{MoO}_3\text{N})_2$ , is more rapid and apparently quantitative.

### Experimental

**Materials.**—With the exceptions noted below, all chemicals employed were of analytical reagent grade and of purity demonstrated by analyses prior to use.

**Molybdenum(VI) Oxide.**—A Schering-Kahlbaum product was dried for six hours at  $110^\circ$ , stored *in vacuo* over concentrated sulfuric acid, and used without further purification.

*Anal.* Calcd. for  $\text{MoO}_3$ : Mo, 66.65. Found: Mo, 66.60.

This oxide was also prepared by partial evaporation of a solution of sodium molybdate in concentrated nitric acid.

*Anal.* Calcd. for  $\text{MoO}_3$ : Mo, 66.65. Found: Mo, 66.35.

**Experimental Methods.**—Unless otherwise specified, all reactions in liquid ammonia employed the familiar faraday tube technique<sup>5,6</sup> and were effected at or near  $25^\circ$ . It is important here only to recognize that these techniques permit one to conduct reactions out of contact with the atmosphere under strictly anhydrous conditions and to form, purify, and isolate ammonia-insoluble reaction products.

**Diammonium Aquoammonomolybdate.**—Molybdenum(VI) oxide (0.6842 g.) was treated with about 15 ml. of liquid ammonia and agitated frequently over a period of one hour. The insoluble product was washed five times with liquid ammonia. Following evaporation of the solvent, the tube was evacuated by means of an oil pump for a period of two hours, filled with dry nitrogen and samples of the white crystalline solid ( $d^{25}_4$  4.04) were removed for analysis.

*Anal.* Calcd. for  $\text{MoO}_3 \cdot 3\text{NH}_3$ : Mo, 49.98; N, 21.87. Found: Mo, 49.78; N, 21.65.

This compound loses ammonia slowly when exposed to the atmosphere and is rapidly and completely deammonated when heated to  $110^\circ$ .

Attempts to demonstrate the presence of ammonium ions in terms of hydrogen liberated upon treatment with liquid ammonia solutions of potassium led to results that were inconclusive.

**Treatment of Diammonium Aquoammonomolybdate with Ammonium Salts.**—To the diammonium salt produced (as above) from 0.2918 g. of molybdenum(VI) oxide and about 10 ml. of liquid ammonia was added an eight-fold excess (2.3738 g.) of ammonium chloride dissolved in liquid ammonia. After frequent agitation at  $25^\circ$  over a period of eighteen hours, the white solid was washed and removed for analysis in the manner indicated above.

*Anal.* Calcd. for  $\text{MoO}_3 \cdot 3\text{NH}_3$ : Mo, 49.98; N, 21.87. Found: Mo, 49.80; N, 21.75.

Substantially identical results were obtained using an excess of ammonium nitrate at  $25^\circ$  and ammonium chloride or ammonium nitrate at  $100^\circ$ . The experiments at  $100^\circ$  employed a modified Faraday tube<sup>7</sup> so constructed that it

could be heated in an autoclave identical with that described by Bergstrom.<sup>8</sup>

**Tripotassium Aquoammonomolybdate.**—Preliminary experiments showed that the reaction between diammonium aquoammonomolybdate and potassium amide in liquid ammonia at  $25^\circ$  is slow and leads initially to mixtures of products. Accordingly, known weights of molybdenum(VI) oxide and potassium were placed in separate legs of a faraday tube, ammonia was condensed in the tube and the oxide and potassium were converted, respectively, to diammonium aquoammonomolybdate and potassium amide. The amide solution was then added to the suspension of the ammonium salt and the reaction mixture agitated intermittently prior to decantation of the supernatant solution and washing of the insoluble product preparatory to opening the tube for analysis. In a series of experiments of this type, the reaction ratio and time of contact were varied in an effort to obtain a product of reproducible composition. The resulting data are given in Table I. The tripotassium salt ( $d^{25}_4$  4.59) hydrolyzes slowly upon exposure to the atmosphere. When treated with water, the salt hydrolyzes rapidly and yields an alkaline solution containing molybdate ion.

TABLE I

PREPARATION OF TRIPOTASSIUM AQUOAMMONOMOLYBDATE

MoO <sub>3</sub> , g.	K		Time, hr.	Color	Insoluble product <sup>a,b</sup>	
	g.	equiv.			Mo, %	N, %
0.6317	0.5878	3.42	0.5	Red-brown	39.12	6.15
.3986	.3575	3.60	0.5	Red-brown	38.48	5.77
.5172	.4671	3.32	2.0	Slate-gray	34.50	5.32
.8590	.9402	4.07	12	Yellow	34.79	5.25
.5620	.9313	6.10	12 <sup>c</sup>	Yellow	34.71	5.22

<sup>a</sup> Calcd. for  $\text{K}_3\text{HMoO}_3\text{N}$ : Mo, 40.46; N, 5.90. <sup>b</sup> Calcd. for  $\text{K}_3\text{MoO}_3\text{N}$ : Mo, 34.86; N, 5.09. <sup>c</sup> Reaction times as long as twenty-six hours (using four to six equivalents of potassium amide) were employed without substantial change in the character of the results.

**Silver(I) Aquoammonomolybdate.**—The tripotassium aquoammonomolybdate equivalent to 0.7160 g. of molybdenum(VI) oxide was prepared and purified as described above. Thereafter, it was agitated (in the faraday tube in which the tripotassium salt was prepared) with a liquid ammonia solution containing excess silver(I) nitrate (3.1612 g.) until there was no further evidence of reaction (*ca.* one hour). Excess silver(I) nitrate and by-product potassium nitrate were separated from the black insoluble solid product by repeated washing with liquid ammonia.

*Anal.* Calcd. for  $\text{Ag}_3\text{MoO}_3\text{N}$ : Ag, 67.20; Mo, 19.95; N, 2.91. Found: Ag, 67.03; Mo, 19.73; N, 3.18.

This salt ( $d^{25}_4$  7.64) underwent no change in appearance or composition during exposure to the atmosphere for twenty-four hours.

**Lead(II) Aquoammonomolybdate.**—In an entirely analogous manner, the lead salt was formed by the reaction between a liquid ammonia solution containing excess lead(II) iodide (2.4200 g.) in the potassium salt derived from 0.4877 g. of molybdenum(VI) oxide. The purified product was a light brown ammonia-insoluble solid ( $d^{25}_4$  6.93) which is stable under ordinary atmospheric conditions.

*Anal.* Calcd. for  $\text{Pb}_3\text{Mo}_2\text{O}_6\text{N}_2$ : Pb, 66.25; Mo, 20.24; N, 2.86. Found: Pb, 65.98; Mo, 20.39; N, 2.82.

**X-Ray Diffraction Data.**—By the powder technique, X-ray diffraction patterns (Cu  $K_\alpha$  radiation) were obtained for the diammonium, tripotassium, and trisilver salts. The interplanar spacings ( $d$ ) in ångström units and the relative intensities ( $I/I_0$ ) of the lines are given in Table II. The pattern for the lead salt (twenty-four hour exposure) showed only one line ( $d = 2.010$ ).

(8) Bergstrom, *J. Org. Chem.*, **2**, 424 (1937).

(5) Reference 4, pages 319-330.

(6) Johnson and Fernelius, *J. Chem. Education*, **6**, 441-450 (1929).

(7) Holt and Watt, *This Journal*, **65**, 988 (1943); for full details see R. B. Holt, M. A. Thesis, The University of Texas, June, 1942.

TABLE II  
DATA FROM X-RAY DIFFRACTION PATTERNS

$(\text{NH}_4)_2(\text{HM}_2\text{O}_2\text{N})$ $d$ / $I/I_0$		$\text{K}_2(\text{MoO}_4\text{N})$ $d$ / $I/I_0$		$\text{Ag}_2(\text{MoO}_4\text{N})$ $d$ / $I/I_0$	
1.678	0.28	0.875	0.04	1.260	0.19
1.798	.85	0.941	.06	1.312	.21
1.891	.12	0.965	.07	1.665	.22
2.070	.09	1.001	.08	1.795	.31
2.167	.18	1.240	.09	1.920	.21
2.236	.20	1.453	.08	2.240	.49
2.458	.30	1.550	.08	2.615	.62
2.648	.10	1.711	.11	3.030	.19
3.218	.87	1.750	.13	3.340	1.00
3.319	.95	1.920	.19	4.320	0.76
3.594	.90	2.200	.10		
4.901	.52	2.220	.21		
6.315	.98	2.615	.16		
7.145	1.00	2.453	1.00		
		3.001	0.42		
		3.156	.48		
		3.251	.91		
		3.501	.62		
		5.011	.18		

The same result was obtained using a sample of the lead salt that had been maintained for three hours at 300° (without change in composition) in an atmosphere of dry oxygen-free nitrogen.

### Summary

1. The existence of a compound of molybdenum(VI) oxide and ammonia in a 1:3 mole ratio has been confirmed and the compound has been interpreted as the diammonium salt of an aquoammonomolybdc acid.

2. This salt has been shown to be unaffected by treatment with liquid ammonia solutions of ammonium chloride or ammonium nitrate at 25 and 100°.

3. By the use of excess potassium amide in liquid ammonia solution and long time of reaction, the diammonium acid salt has been converted to a yellow tripotassium salt.

4. By metathesis with solutions of silver(I) nitrate and lead(II) iodide in liquid ammonia, the tripotassium salt has been converted to the corresponding silver(I) and lead(II) salts.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## X-Ray Diffraction Studies of Systems Involved in the Preparation of Alkaline Earth Sulfide and Selenide Phosphors<sup>1</sup>

BY WILLIAM PRIMAK<sup>2a</sup> HERMAN KAUFMAN AND ROLAND WARD

The methods of preparation and some of the properties of the alkaline earth sulfide and selenide infrared phosphors have recently been described.<sup>2,3</sup> It has been shown<sup>4</sup> that in most cases their formation involves a complex interaction between solid phases and a fused salt, or flux, during which the composition of the phases alters. It is important to know the solubility limits of the different base materials which are used in the preparation of phosphors. A knowledge of the ways in which solid solutions may be formed is also useful. This paper presents the results of a study of the inter-solubility of some alkaline earth sulfides, selenides and oxides by means of X-ray analysis. The excellent back-reflection powder pictures given by the alkaline earth sulfides, selenides and oxides, all of which have the sodium chloride lattice, have permitted the determination of the lattice constant of these phases with high precision. Our results indicate that the simple Vegard law is

applicable over a wide range of composition of mixed sulfides and selenides so that changes in composition of the base material can be determined from the lattice constant measurement.

### Experimental

**Procedure.**—A symmetrical back-reflection focussing powder camera of 6 cm. radius was used for most of the pictures. Several were taken with a Philip's Straumanis type powder camera of 5.72 cm. radius, and these are indicated in footnotes. To obtain a precision lattice constant, the lattice constants computed from the back-reflection lines were plotted against the square of the sine of the Bragg angle and extrapolated to Bragg angle 90°.<sup>5</sup> The error in extrapolation was about 1/10,000, but the reproducibility in different samples of supposedly pure material was not better than 1/3000. Some of the chemical work did not warrant obtaining lattice constants of such precision. In these cases, lattice constants were computed from a single back-reflection line spacing. They were probably good to 1/500.

**Preparation of Materials.**—All chemicals used were purified as for the preparation of phosphors.<sup>6</sup> Strontium and calcium sulfide were prepared by reducing the sulfates with ammonia, hydrogen or hydrogen sulfide at 850–1050°. They were then treated with hydrogen sulfide at a temperature of 1000°. Strontium selenide was prepared by the reduction of the selenite with ammonia at about 850°. Several preparations of sulfides and selenides were made by the reaction of sulfur or selenium on

(1) The work described in this paper was carried out in whole under contract NObs 28370 between the Bureau of Ships and the Polytechnic Institute of Brooklyn.

(2a) Present address: Argonne National Laboratory, P. O. Box 5207, Chicago 80, Ill.

(2) Reports of B. O'Brien, F. Urbach and R. Ward, *J. Optical Soc. Am.*, **36**, 351 (1946).

(3) R. T. Ellickson, *ibid.*, **36**, 261 (1946); R. T. Ellickson and W. L. Parker, *Phys. Rev.*, **69**, 534 (1946).

(4) W. Primak, R. K. Osterheld and R. Ward, *THIS JOURNAL*, **69**, 1283 (1947).

(5) M. J. Buerger, "X-Ray Crystallography." John Wiley and Sons, Inc., New York, N. Y., 1942, p. 393.

(6) A. L. Smith, R. D. Rosenstein and R. Ward, *THIS JOURNAL*, **69**, 1725 (1947).