Short Communications

The Formulae of Sodium and Ammonium Paramolybdate

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In a recent critical review on the polymolybdates, Carpéni[1] reports two possible mole ratios $M_2O:MoO_3$ for the paramolybdates without deciding in favour of either. In the following these mole ratios are given the symbols (5 : 12) and (3 : 7). In connection with an X-ray investigation of the polymolybdates, polytungstates and polyvanadates, which has been started in this institute, it was found necessary to take up the problem of the mole ratio of the paramolybdates.

Our efforts were confined to the sodium and ammonium paramolybdates, which possess very different amounts of water of crystallization. These compounds were discovered in 1853 by Zenker[2] and in 1848 by Svanberg and Struve[3] and were by them given the mole ratios (4 : 9) and (2 : 5). Later the (3 : 7) formulae $3Na_2O \cdot 7MoO_3 \cdot 22H_2O$ and $3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O$ were ascribed to these salts by Delafontaine[4,5] and Ullik[6]. In 1916, however, Rosenheim[7] carried out analyses leading to the (5 : 12) formulae $5Na_2O \cdot 12MoO_3 \cdot 38H_2O$ and $5(NH_4)_2O \cdot 12MoO_3 \cdot 7H_2O$, which were then widely accepted (*cf.* Gmelin[8]). In a review, Jander[9] supported these later formulae, obviously because they were required by his theory of the ion aggregation in molybdate solutions. No analyses were carried out by Jander. In recent years Byé[10] and Guiter[11,12], have

again reported (3 : 7) formulae, but none of them has tried to make a complete analysis with modern and well established methods. As a consequence of these diverging results Carpéni[1] has not decided in favour of either formula. He does not, however, mention the important X-ray investigation on the ammonium paramolybdate by Sturdivant[13], which seems to us quite deciding in this question. As the corresponding paratungstates are generally given (5 : 12) formulae, one can easily understand the actual confusion in this field. Under these circumstances we have found a thorough analysis desirable.

*Sodium paramolybdate.** This compound was formed by isothermal evaporation at 20° from a solution of 9.68 g $Na_2MoO_4 \cdot 2H_2O$ in 21.5 ml 1.98—C HCl and 20 ml H_2O. We obtained well defined crystals which were shown to be free from chloride ions. These crystals were quickly dried between filter papers, weighed, and heated in a platinum crucible in order to determine the water content. The residue was weighed and then dissolved in water. Part of the solution was poured through a cadmium reducer and molybdenum was determined[14] by titration with $KMnO_4$. Another part was drawn through a column of »Amberlite IR 100 Ion Exchanger», which had previously been saturated with ammonium ions[15]. The solution containing the molybdate ions was discarded. The ion exchanger was then washed with 5 % HCl until we did not get any sodium flame

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from the washing solution. In this solution, sodium was determined as $(UO_2)_3$ $NaMg(CH_3CO_2)_9 \cdot 8H_2O$ by a method given by Nydahl [16]**. This method was first established by analyses of solutions containing known amounts of sodium and molybdenum. The results are all given in Table 1.

Table 1. Sodium paramolybdate.

1. *Check on the method.*

Weighed amounts		Measured amounts	
Na$_2$O	MoO$_3$	Na$_2$O	MoO$_3$
15.44 mg	83.68 mg	15.51 mg	84.12 mg
9.380 »	86.40 »	9.428 »	86.78 »

2. *Analyses.*

	Weight percentages		
	Na$_2$O	MoO$_3$	H$_2$O
(5 : 12) calc.	11.39	63.47	25.14
(3 : 7) »	11.69	63.38	24.92
Analysis 1	11.77	63.40	24.84
» 2	11.78	63.23	25.01

Ammonium paramolybdate. This compound was recrystallized from solutions of commercial ammonium molybdate. Molybdenum was reduced as above and titrated with $KMnO_4$. NH_3 was determined by Kjeldahl-distillation into 0.1—C HCl and back titration with 0.1—C NaOH with methyl red as indicator. From the sum of NH_3 and H_2O lost by heating, H_2O could then be calculated. The results are given in Table 2.

Results. The (5 : 12) formulae can at once be excluded, but the compositions are in agreement with the (3 : 7) formulae. We hope that our X-ray investigations will make it possible for us to decide that the atomic arrangements give the formulae $3Na_2O \cdot 7MoO_3 \cdot 22H_2O$ and $3(NH_4)_2O \cdot 7MoO_3 \cdot$

** *Cf.* Schoorl *Rec. Trav. Chim. Pays-Bas* 59 (1940) 305—313.

Table 2. Ammonium paramolybdate.

Weight percentages

	(NH$_4$)$_2$O	MoO$_3$	H$_2$O
(5 : 12) calc.	12.32	81.72	5.96
(3 : 7) »	12.64	81.52	5.84
Analysis 1	12.55	81.43	5.89
» 2	12.55	81.40	5.80

$4H_2O$. Of course we are also going to investigate the formulae of paratungstates. In any case the formulae $5Na_2O \cdot 12MoO_3 \cdot 38H_2O$ and $5(NH_4)_2O \cdot 12MoO_3 \cdot 7H_2O$ are wrong and so are the theories of Jander as far as they are based on the existence of such compounds.

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