ART. LIV. — *On Ethylidenamine Silver Sulphate*; by W. G. MIXTER. Contributions from the Sheffield Laboratory of Yale College, No. LVI.

ALDEHYDE AMMONIA precipitates metallic silver from many of its salts almost as readily as from the nitrate. A mixture of solutions of silver sulphate and aldehyde ammonia produces a mirror when warmed, and at common temperatures evaporates to dryness, with but slight decomposition. The fact that a sulphate solution decomposed less readily than the nitrate led to the hope that an investigation of the sulphate compound would throw more light on the constitution of silver amines. The first experiments were made with ammoniacal aqueous solutions of silver sulphate and aldehyde ammonia. Analyses proved the crystalline product to be a mixture. Alcoholic ammonia was next used as a solvent, and the analysis of the first crop of crystals showed nearly pure $\text{Ag}_2\text{SO}_4(\text{NH}_3)_4$, 0.6 per cent of carbon was found and a solution of the crystals reacted for aldehyde. Aqueous solutions of silver sulphate and a large excess of aldehyde ammonia, over four molecules of the latter to one of the former, yielded either mixtures or ammonio silver sulphate. When, however, aldehyde ammonia is dissolved in a small quantity of water, and silver sulphate, in the proportion of one molecule of the latter to four molecules of the former, is slowly added with constant agitation; and after some hours the small black residue filtered off and the solution left to spontaneous evaporation, few or no crystals of the ammonio sulphate form, but colorless transparent crystals separate, which react strongly for aldehyde. At summer temperatures tabular crystals, and at from 10° to 15° C. elongated crystals, predominate.

The following analyses were made of carefully selected and well-defined tabular crystals, which were from 2 to 5^{mm} in diameter, and which were freed as much as possible from the mother liquor by blotting paper, then washed with alcohol and finally with ether. They were considered dry when they did not lose weight on the balance in five or ten minutes.

Calculated for $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_5\text{NH})_4$						Calculated for $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_5\text{NH})_3$ NH_3		
S	6.61	6.68	II.			III.	2	47.10
Ag	44.64	44.55	2	48.60	2	46.03	2	47.10
C	19.83	18.13	7.4	15.90	5.9	16.27	6.2	15.72
H	4.13	4.62		4.14		4.31		3.95
N	11.57	11.28						12.20
**	**	**	**	**	**	**	**	**
$3\text{H}_2\text{O}$	10.04	10.24		10.50		10.39		10.15

Calculated for $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_3\text{NH}_3\cdot 3\text{H}_2\text{O}$							
				IV.		V.	
Ag	42.20	42.08	2	41.08	2	41.07	2
C	14.06	13.92	5.9	14.73	6.4	14.77	6.4
H	4.69	4.91		4.88			
N	10.90	10.64					
**	***	***	**	***	**	***	**
$3\text{H}_2\text{O}$	10.15					10.20	

The following results were obtained from crystals of an entirely different habit from those used in the preceding analyses, many of the crystals were one or two centimeters long, 4 or 5mm wide, and 1 to 3mm in thickness. They were freed from the mother liquor in the manner already described.

Calculated for $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_4\cdot 6\text{H}_2\text{O}$			Calculated for $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_4$			VII.		
VI.								
S	5.40	5.26	1					
Ag	36.48	36.12	2	44.64		44.70	2	43.89 2
C	16.21	15.66	7.8	19.83		18.72	7.6	18.79 7.6
H	5.41	5.6		4.13		4.43		4.52
**	** *	** *	** *	** *		** *	** *	
N	9.46	9.06	3.9					
$6\text{H}_2\text{O}$	18.24	17.29						17.67

The atomic relations between the silver and carbon found are expressed by the figures following the percentages. The combustion for I was with lead chromate, and this carbon result may be too low, as subsequent duplicate combustions on another lot of crystals gave variations of 1 per cent of carbon. All the other combustions were made with oxygen, copper oxide, lead chromate and metallic copper. The silver in I and VI was weighed as chloride, and the other silver estimations were from weighing the residue left in the tray after the combustions, a method necessitated by the small quantity of material available. The duplicate VII shows the possibility of a mechanical loss. An error of 1 per cent in the silver found makes but a small difference in the atomic ratio between the silver and carbon, since the atomic weight of the former is high. The sulphur was precipitated as barium sulphate, and the nitrogen as ammonium platonic chloride, after separating the silver with hydrochloric acid. The water was determined by drying over oil of vitriol or caustic potash. A drop of sulphuric acid on a watch glass in the potash desiccator showed that there was a slight loss of ammonia on drying. The weights of substance for VI from one crop of crystals were made rapidly. 0.7395 gram was at once placed in the combustion tube whose anterior half was red hot; 0.438 gram was next put into water for the nitrogen estimation, and finally 0.533 gram of crystals, which

had become opaque white on edge, were dried to a constant weight for the water determination, and then used to find the sulphur content. The 17.67 per cent of water in VII was from drying 2.37 grams of crystals which had also become opaque while on edges.

Analysis VI corresponds with the theory, and the anhydrous material used in VII was from the same kind of crystals. The deficiency in the amount of carbon found may be ascribed either to impurities or a slight decomposition. I after losing water of crystallization, has essentially the same composition as VII. Both I and VI are hydrates of a compound analogous to ammonio silver sulphate, thus,

The name ethylidenamine silver sulphate is proposed for the present.

Analysis IV was made with hydrous crystals, and II with anhydrous substance from the same crop of crystals which were apparently of the same form as the crystals which gave results I. II and IV, give the formula,

Leaving out the $3\text{H}_2\text{O}$ we see that the substance has the same composition as a mixture of 3 molecules of $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_4$ and one molecule $\text{Ag}_2\text{SO}_4(\text{NH}_3)_4$. But if we suppose it a mixture of $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_4$, $3\text{H}_2\text{O}$ and $\text{Ag}_2\text{SO}_4(\text{NH}_3)_4$ we find that the water is 8.1 per cent and does not accord with the water found, and the conclusion is that the substance analyzed was not a mixture, but a compound containing three ethyliden groups, and answering to the formula already given. III and V of two different crops of crystals appear to be mixtures of $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_4$, $3\text{H}_2\text{O}$ and $\text{Ag}_2\text{SO}_4(\text{C}_2\text{H}_4\text{NH})_3\text{NH}_3$, $3\text{H}_2\text{O}$. Ethylidenamine silver sulphate is soluble in water and yields aldehyde when treated with acids. The hex-hydrated salt loses water more readily in dry air than the trihy-drated.