

# Hydrates of Aluminium Nitrate.

BY

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Of aluminium nitrate, the hydrate with 18 molecules of water,  $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$ , is most well known, but, in addition, the hydrates with less molecules of water have also been described. Recently, Z. Jovitschitsch<sup>1</sup> obtained a new hydrate in snow-white prisms by heating ignited alumina with concentrated nitric acid (sp. gr. 1.4) and he gave it the formula,  $\text{Al}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$ , from the analysis of a single sample. Then, R. Seligman and P. Williams obtained three hydrates under different conditions, and their conclusions were as follows:<sup>2</sup>

“Aluminium nitrate may crystallise in at least three forms, and the compositions of two of these have been determined as  $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$  and  $\text{Al}_2(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$ . The third hydrate probably crystallises with 15 or 16 molecules of water. The hydrate containing  $12\text{H}_2\text{O}$  does not appear to have been discovered hitherto.

“The hydrate containing  $18\text{H}_2\text{O}$  is the most stable form at  $20^\circ$  in nitric acid having  $D_{1.42}$  and is the least soluble.

“In acid having  $D_{1.5}$  at  $20^\circ$  the hydrate containing  $12\text{H}_2\text{O}$  is alone stable.

“The hydrate containing 15 or  $16\text{H}_2\text{O}$  is stable in an acid of intermediate strength.”

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<sup>1</sup> Monatsh. Chem., **33**, 16 (1912).

<sup>2</sup> J. Chem. Soc., **109**, 612 (1916).

The authors could not definitely determine the composition of the intermediate hydrate on account of the difficulty of drying it.

Now the writer, on the suggestion of Prof. Y. Osaka, took up the systematic study of the hydrates of aluminium nitrate from the standpoint of the phase rule, taking aluminium nitrate, nitric acid, and water as the components.

The materials used in the investigation were prepared in the following way :

*Aluminium nitrate.* Aluminium hydroxide was precipitated from a solution of purified alum with ammonia, washed well with water until it was free from sulphuric acid radical. It was dissolved in excess of nitric acid of sp. gr. 1.375 and the solution was evaporated. Crystals of the hydrate with  $18\text{H}_2\text{O}$  were obtained and were re-crystallised from nitric acid.

*Nitric acid.* Nitric acid of sp. gr. 1.375 of the Jap. Pharm. was mixed with about an equal volume of concentrated sulphuric acid and distilled under atmospheric pressure. The acid thus obtained was somewhat coloured with nitrous fumes, which were removed by passing dry air through it under slight warming. To obtain a more concentrated acid, concentrated sulphuric acid was added again to about an equal volume of the prepared acid and the mixture was distilled under a reduced pressure of about 30 mm. mercury. This was almost colourless. To remove traces of the sulphuric acid which happened to contaminate it by accident, it was redistilled with some barium nitrate under reduced pressure as before.

*Water.* The ordinary distilled water was used.

The experiments were carried out in the following way : The three components were mixed in different proportions in an Erlenmeyer flask with a well ground stopper, of a capacity of about 50 cc. The flask was made to rotate in a thermostat of  $25.0^\circ$  for one or two days. When equilibrium was attained, the solution and the residue were separated by filtration through asbestos. During the process a loss of a minute quantity of nitric acid was unavoidable. The residue was pressed between folded filter paper to remove the mother liquor as much as possible.

For experiments when more concentrated acid was required, the hydrate with  $18\text{H}_2\text{O}$  was dehydrated before use. For this purpose,

it was fused on a water-bath and gave a white mass. It was powdered and dried in a steam-bath for about 10 hours. On analysis it was found to have lost some nitric acid and had the composition corresponding to the formula,  $\text{Al}_2\text{O}_3 \cdot 2(\text{N}_2\text{O}_5) \cdot 9\text{H}_2\text{O}$ . Thus, although the acid was concentrated as much as 96 per cent., it was impossible to study the equilibrium in an acid solution more concentrated than 90.51 per cent.

The solutions and residues were analysed in the following way:

Aluminium was determined as alumina by igniting aluminium nitrate to a constant weight.

Nitric acid was determined according to the method of Schlösing and Grandeau, improved by Tiemann and Schulze,<sup>1</sup> by estimating the volume of nitric oxide produced by decomposing nitrate with ferrous chloride and hydrochloric acid.

Water was estimated by difference.

The results of the analyses are reproduced in Table 1, from which Table 2 was prepared.

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<sup>1</sup> Treadwell—Hall, *Analyt. Chem.*, II, 456 (1914).

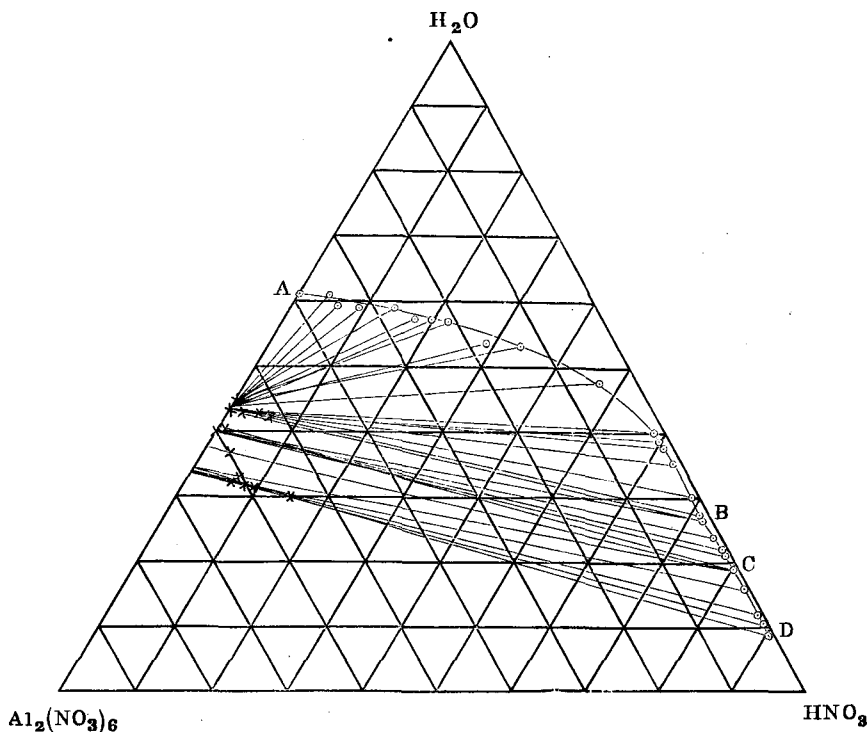
TABLE I.

No.	Solution.			Residue wet with some solution.		
	Al <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O
	(in gram percentages.)			(in gram percentages.)		
1	9.32	29.27	61.41	13.57	41.79	44.64
2	9.36	29.81	60.83	13.63	41.15	45.22
3	8.32	29.99	61.69	13.58	41.97	44.45
4	8.21	31.30	60.49	13.61	42.05	45.34
5	7.71	32.29	60.00	13.54	42.80	45.61
6	6.53	32.41	61.06	13.12	41.70	45.18
7	6.06	33.95	59.98	13.41	42.83	43.76
8	5.44	34.37	60.19	13.47	42.85	43.68
9	4.98	34.53	60.49	13.23	42.36	44.41
10	4.21	37.91	57.88	13.34	42.78	43.38
11	3.16	38.72	58.12	13.25	42.80	43.95
12	1.21	44.19	54.60	13.05	42.67	44.28
13	0.44	51.33	48.23	13.20	43.49	43.31
14	0.38	52.40	47.22	12.76	43.98	43.26
15	0.34	52.87	46.79	12.73	43.22	44.05
16	0.32	55.16	44.52	13.14	43.62	43.24
17	0.23	59.73	40.04	12.79	43.51	43.70
18	0.30	61.93	37.77	12.53	44.89	42.58
19	0.26	62.28	37.46	13.39	43.62	42.99
20	0.30	62.66	37.04	12.80	45.03	42.17
21	0.30	62.70	37.00	13.31	43.73	42.96
22	0.22	62.81	36.97	14.44	45.25	40.31
23	0.17	65.10	34.73	14.31	45.62	40.07
24	0.11	66.26	33.63	14.25	45.13	40.62
25	0.11	67.02	32.87	14.32	45.44	40.24
26	0.07	67.32	32.61	14.48	45.89	39.63
27	0.06	68.97	30.97	14.13	46.23	39.64
28	0.06	69.42	30.52	14.30	48.51	37.19
29	0.04	69.61	30.35	14.49	51.41	34.10
30	0.02	71.49	28.49	14.78	52.03	33.19
31	0.04	75.46	24.50	14.20	53.20	32.60
32	0.04	75.78	24.18	14.15	53.23	32.62
33	0.05	76.31	23.64	14.39	52.50	33.11
34	0.06	76.47	23.47	14.21	52.16	33.63
35	0.08	76.99	22.93	14.07	52.89	31.04
36	0.10	77.75	22.33	13.25	54.51	32.24

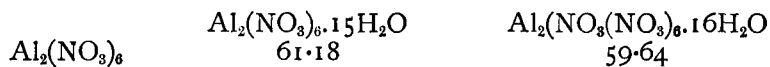
TABLE 2.

No.	Solution.			Residue wet with some solution.		
	Al <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> (in gram percentages.)	HNO <sub>3</sub>	H <sub>2</sub> O	Al <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> (in gram percentages.)	HNO <sub>3</sub>	H <sub>2</sub> O
A 1	38.87	—0.33	—	56.60	—1.45	—
2	39.04	0.15	60.81	56.85	—2.42	—
3	34.70	4.21	61.09	56.64	—1.27	—
4	34.24	6.15	59.61	56.77	—1.30	—
5	32.16	9.15	58.69	56.47	—0.15	—
6	27.23	13.67	59.10	54.72	0.12	45.16
7	25.32	17.15	57.53	55.93	0.36	43.71
8	22.69	19.97	57.34	56.18	0.16	43.66
9	20.77	21.86	57.37	55.19	0.47	44.34
10	17.57	28.65	53.78	55.65	0.06	44.29
11	13.18	33.49	53.33	55.27	0.91	43.82
12	5.05	47.08	47.87	54.42	1.52	44.06
13	1.84	58.26	39.90	55.06	1.90	43.04
14	1.59	59.73	38.68	53.23	4.10	42.67
15	1.42	60.43	38.15	53.09	3.34	43.57
16	1.34	63.17	35.49	54.81	2.28	42.91
17	0.97	68.84	30.19	53.35	3.44	43.21
18	1.25	71.15	27.60	52.26	6.02	41.72
19	1.08	71.71	27.21	55.85	1.35	42.80
20	1.25	72.01	26.74	53.29	5.30	41.41
B 21	1.25	72.06	26.69	55.52	1.77	42.71
22	0.92	72.47	26.61	60.24	—0.64	—
23	0.71	75.34	23.95	59.68	0.29	40.03
24	0.45	76.91	22.64	59.44	—0.07	—
25	0.46	77.80	21.74	59.72	0.05	40.23
26	0.28	78.31	21.41	60.38	—0.01	—
27	0.24	80.28	19.48	58.93	1.67	41.07
C 28	0.24	80.58	19.18	59.64	3.70	36.66
29	0.17	81.08	18.75	60.44	6.37	33.19
30	0.08	83.35	16.57	61.65	6.02	32.33
31	0.17	87.66	12.17	59.23	9.53	31.24
32	0.18	88.26	11.56	59.01	9.77	31.22
33	0.21	88.86	10.93	60.01	8.03	31.96
34	0.25	89.02	10.73	59.27	8.29	32.44
35	0.34	89.54	10.12	58.68	9.66	31.66
D 36	0.43	90.12	9.45	55.27	14.57	30.16

FIG. 1.

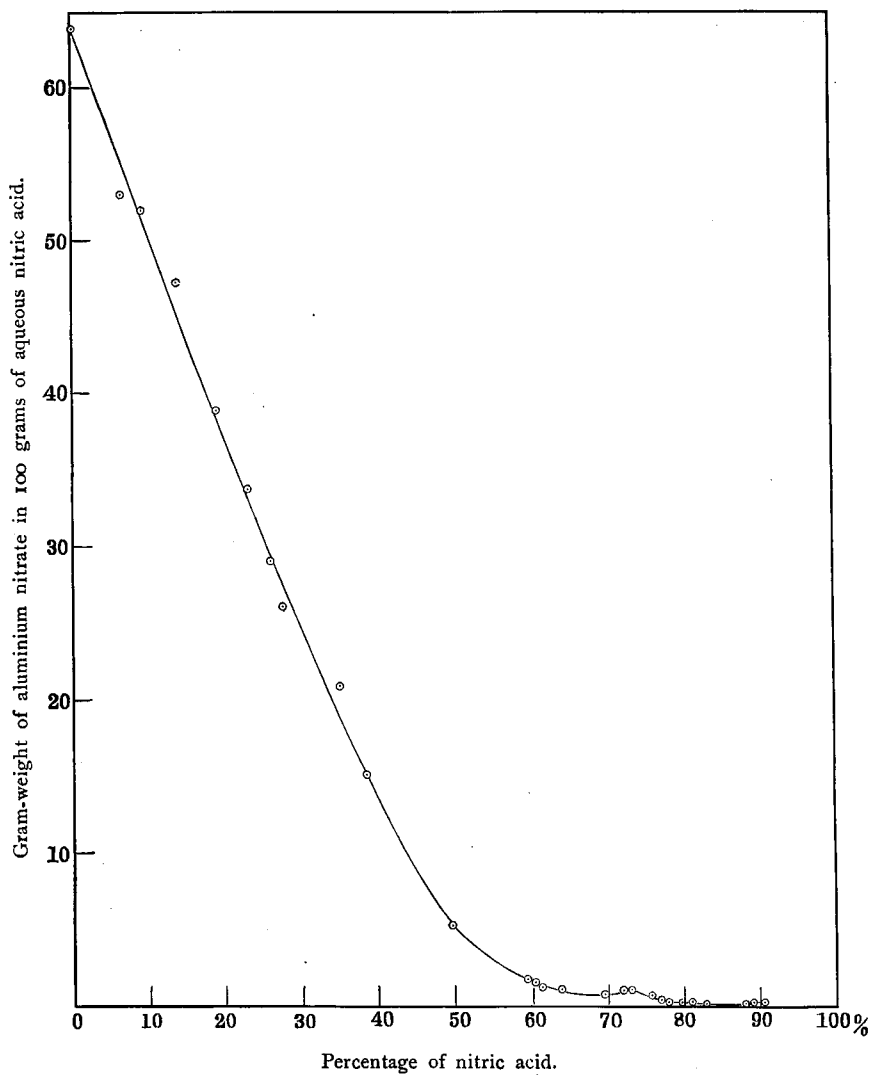


The data in Table 2 are graphically represented in Fig. 1, referring to a triangular coordinate. The point A represents the saturated solution of aluminium nitrate with  $18\text{H}_2\text{O}$  in water. In the solutions from A to B the residue is  $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$  [ $(\text{Al}_2(\text{NO}_3)_6:\text{H}_2\text{O} = 56.78:43.23)$ ]. At the point B the concentration of the acid is about 73 per cent. (sp. gr. 1.435 at  $15^\circ$ ). In the solution from B to C, the residue seems to have  $16\text{H}_2\text{O}$  rather than  $15\text{H}_2\text{O}$ , as the percentages of aluminium nitrate in them are as follows:



In the solution from C to D, the residue is  $\text{Al}_2(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$  [ $(\text{Al}_2(\text{NO}_3)_6:\text{H}_2\text{O} = 66.33:33.67)$ ]. At the point D the percentage of the acid is 90.51 (sp. gr. 1.497 at  $15^\circ$ ).

FIG. 2.



The hydrate with  $16\text{H}_2\text{O}$  was obtained as very fine needles, but that with  $12\text{H}_2\text{O}$  as a fine powder only.

Solubilities of aluminium nitrate in nitric acid of different concentrations are shown in Fig. 2, the percentage of nitric acid and gram-weight of aluminium nitrate in 100 grams of aqueous nitric acid being taken as coordinates. Naturally the curve consists of three parts, each corresponding to a particular hydrate. As clearly seen from the

figure, the solubility of aluminium nitrate decreases very rapidly when the concentration of the acid is increased until the acid is about 60 per cent. Thenceforward, the solubility is only slightly changed with the concentration of the acid.

#### CONCLUSION.

At 25.0° three kinds of hydrates of aluminium nitrate may crystallise out stably from nitric acid of proper concentrations.

The hydrate with 18H<sub>2</sub>O is stable in acid solution below 73 per cent. (sp. gr. 1.435 at 15°).

The hydrate with 16H<sub>2</sub>O is stable in acid between 73 and 81 per cent. (sp. gr. 1.435—1.463 at 15°).

The hydrate with 12H<sub>2</sub>O is stable in acid above 81 per cent.

The writer wishes to express his thanks to Professor Osaka for his suggestion of the work and for the kind interest he has taken in the experiment throughout.

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