

the electrodes studied is doubtful. While gas is being evolved it is evidently not of the magnitude which has been claimed.

4. Evidence has been secured which indicates that the ordinary hydrogen overvoltage tables, obtained by using pure acid solutions as the electrolyte, do not show the current densities necessary for the deposition from acid solutions of metals having a greater electromotive force than hydrogen.

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THE SOLUBILITY OF ALUMINUM NITRATE CRYSTALS IN SOLUTIONS OF NITRIC ACID OF VARIOUS STRENGTHS AT VARIOUS TEMPERATURES

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In connection with other work which was in progress, it was necessary to determine the solubility of aluminum nitrate crystals, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, in solutions of nitric acid of various strengths, at various temperatures. The results obtained seem to be of sufficient general interest to warrant publication.

The literature fails to reveal any quantitative data on the solubility of this substance $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Seidell¹ gives no data whatsoever. Comey² states: "Deliquescent. Very soluble in H_2O , HNO_3 + Aq, or alcohol. (Berzelius)." Probably the best bibliography on aluminum nitrates is found in Friend's "A Text Book of Inorganic Chemistry"³ In addition to the references there, Inamura⁴ has made a phase rule study of the system aluminum nitrate:water:nitric acid, at 25° and finds that the nonhydrate is the stable hydrate in the presence of nitric acid of less than 73% strength.

Preliminary experiments showed that the sirupy filtered liquor resulting from digestion of nitric acid with an excess of aluminum hydroxide was slow to crystallize, and the crystals formed from it were very small and difficult to filter. Because of this behavior of solutions containing no free nitric acid, it is perfectly possible to obtain a sirupy liquor which is more or less stable at room temperature with respect to aluminum nitrate nonhydrate and contains less water than the crystals of this hydrate. On standing for a few days such a liquor will become cloudy and deposit a white substance which is probably a basic salt. When, however, nitric

¹ Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., 1919.

² Comey, "A Dictionary of Chemical Solubilities," MacMillan and Co., 1896, p. 243.

³ "A Textbook of Inorganic Chemistry," Ed. J. N. Friend, Chas. Griffin and Co., Ltd., 1917, vol. IV, p. 88.

⁴ Inamura, *J. Tokyo Chem. Soc.*, **41**, 1 (1920), through *C. A.*, **14**, 2451 (1920).

acid is added to this liquor, rapid crystallization takes place with the formation of colorless coarsely-granular crystals of the nonhydrate. The following study of the solubility of these crystals in solutions of nitric acid of various strengths, at various temperatures, was made to obtain quantitative data on this phenomenon.

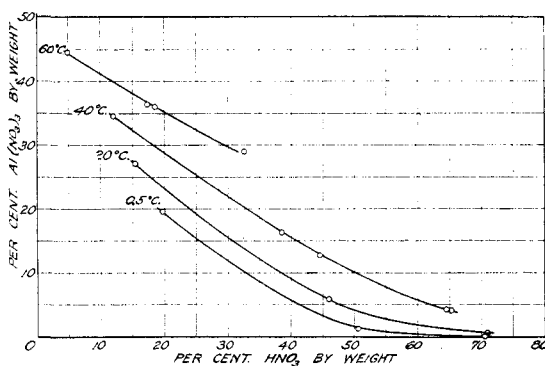


Fig. 1.—The solubility of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in nitric acid of various strengths, at various temperatures.

Aluminum nitrate crystals were prepared by dissolving pure washed aluminum hydroxide, obtained by cooling a hot conc. solution of sodium aluminate, in c. p. nitric acid. The resulting solution, which contained an excess of nitric acid, was cooled and the crystals which separated were centrifuged until dry, and then bottled and analyzed.

ANALYSES^a

	Found %	Calc. for $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ %
Al_2O_3	13.45	13.61
NO_3 (titration).....	49.4	49.57
SiO_2	None
TiO_2	None
Fe_2O_3	0.012

^a The sodium in these crystals was not determined, but it must have been very low because the aluminum hydroxide from which the original solution was made contained only 0.05% of Na_2O .

An excess of these crystals was put in a large test-tube and covered with nitric acid of the desired strength. The tube, which was fitted with a rapidly rotating stirrer, was then placed in a thermostat. After about 30 minutes the stirring was stopped for about 5 minutes and a sample of the clear liquor rapidly pipetted into a weighing bottle which was stoppered and weighed when it had reached room temperature. The sample was diluted to a given volume and aliquots were analyzed gravimetrically for alumina by precipitation with ammonia, and volumetrically for total nitrate by titration in a boiling solution with standard

sodium hydroxide solution and phenolphthalein as indicator.⁵ The alumina was calculated to aluminum nitrate $\text{Al}(\text{NO}_3)_3$, and the residual nitrate over that required to combine with the aluminum, to nitric acid HNO_3 . These constituents were expressed as grams per 100 grams of the original solution.

TABLE I
THE SOLUBILITY OF $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ IN NITRIC ACID OF VARIOUS STRENGTHS, AT
VARIOUS TEMPERATURES

No.	Temp. ° C.	Approximate Sp. Gr. of Soln. Indicated temp./20°	HNO_3 % by wt.	$\text{Al}(\text{NO}_3)_3$ % by wt.
1-a	0.4	1.311	20.6	19.1
b	0.4	1.311	18.9	20.2
2-a	0.5	1.335	51.3	1.54
b	0.5	1.336	50.0	1.46
3-a	0.5	1.433	72.4	0.25
b	0.5	1.431	68.9	0.21
4-a	19.8	1.351	15.4	27.2
b	19.8	1.349	15.5	27.0
5-a	20.0	1.339	46.8	5.88
b	20.0	1.341	45.3	5.83
6-a	20.0	1.415	71.4	0.67
b	20.0	1.415	71.3	0.79
7-a	40.0	1.400	11.6	34.6
b	40.0	1.398	12.3	34.6
8-a	40.0	1.374	38.6	16.3
b	40.0	1.367	38.4	16.3
9-a	40.0	1.375	44.7	12.9
b	40.0	1.373	44.9	13.2
10-a	40.0	1.410	64.7	4.17
b	40.0	1.408	64.3	4.13
11-a	40.0	1.398	65.4	4.09
b	40.0	1.401	65.3	4.18
12-a	60.0	1.457	4.98	44.3
b	60.0	1.460	4.88	44.4
13-a	60.0	1.457	16.7	37.0
b	60.0	1.461	17.6	35.8
14-a	60.0	18.8	36.2
b	60.0	1.450	19.0	35.8
15-a	60.0	1.461	32.8	29.3
b	60.0	1.462	32.5	28.9

After the first sample had been taken, the stirrer was started again, and in a few minutes another sample of the solution was withdrawn and the analysis averaged with that of the first sample to give a point on the solubility curve. The results of these experiments are given in Table I, and the averages have been plotted as curves in Fig. 1. A 10cc. pipet was used to measure out the liquid, and consequently it was an easy

⁵ See Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., 1920, p. 11. The method is there described for $\text{Al}_2(\text{SO}_4)_3$.

matter to compute the approximate specific gravity of the liquor samples at the indicated temperature of the experiment compared with water at 20°; this information is given in the third column of the table.

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THE FACTORS DETERMINING THE HYGROSCOPIC PROPERTIES OF SOLUBLE SUBSTANCES. I. THE VAPOR PRESSURES OF SATURATED SOLUTIONS

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Introduction

A dry, crystalline, water-soluble solid, not forming a crystalline hydrate, will, when exposed to air containing water vapor, tend to absorb moisture, with the formation of a saturated solution. If we neglect for the moment pure surface adsorption, such absorption can occur only when the vapor pressure of the saturated solution is lower than the partial pressure of water vapor in the atmosphere to which the solid is exposed. Since the vapor pressure of any aqueous solution is lower than that of pure water, any solid will absorb moisture when exposed to *saturated* aqueous vapor, and is therefore to some extent "hygroscopic." This term, however, is commonly applied only to such substances as absorb moisture readily from air under normal atmospheric conditions.

Although the hygroscopic properties of commercial solids which are to be sold in other than sealed containers (for example, fertilizer salts) play an important part in limiting the commercial applications of such solids, no careful scientific study seems to have been made of the factors involved in determining the extent or rate of their absorption of moisture.

As indicated above, the vapor pressure of the saturated aqueous solution determines the partial pressure of water vapor with which the solid (and its saturated solution) may be in equilibrium; a solid may be expected to absorb moisture when exposed to an atmosphere containing more water vapor than this, and conversely the moist solid will lose water when exposed to an atmosphere containing a lower partial pressure of water vapor. The *rate* at which the moisture will be absorbed will depend upon a number of factors. We can predict from *a priori* considerations that the rate of moisture absorption will be affected by (1) the difference between the partial pressure of water vapor in the atmosphere and the

¹ Certain preliminary measurements were made by N. E. Oglesby