

which might produce a partial efflorescence of the exposed hydrate. The point is left unsettled at this time.

It is our purpose to compare oxalic acid prepared in this manner with other standards used in acidimetry, and to test the same method of preparation in the study of other hydrated compounds used as standards, including Mohr's salt and copper sulfate.¹¹

Summary

1. Crystals of hydrated oxalic acid as usually prepared from aqueous solution contain several tenths of a per cent. of included water, which is not wholly lost by 4 months' exposure to atmospheres of the same aqueous tension as the crystals or higher.

2. Crystals superficially dry will lose this included water in about 24 hours' time if ground to pass a 100-mesh sieve and set in an atmosphere of an aqueous tension in equilibrium with the hydrate.

3. A mixture of hydrated and anhydrous oxalic acid is the only desiccating agent giving an aqueous tension in equilibrium with the hydrate at all temperatures.

4. The powdered hydrate can be dried in about 1 hour's time in a current of air passed over this desiccating mixture, so that its oxidimetric value agrees with that of sodium oxalate within 0.025%.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

THE MEASUREMENT OF OVERVOLTAGE

By HERMAN V. TARTAR AND HARMON E. KEYES

Received December 8, 1921

Introduction

It is now generally agreed that overvoltage is an electromotive force which acts counter to the applied e.m.f. during electrolysis. For the purpose of this paper hydrogen overvoltage is defined as an e.m.f. which is the difference of potential between a reversible hydrogen electrode and an electrode surface at which hydrogen gas is being formed from hydrogen ions by electrolysis, both potential measurements being referred to the same electrolyte.

Opinion has been divided as to the proper method of determining overvoltage, especially when high and varied current densities are used. Two distinct methods of measurement have been employed; (1) the commu-

¹¹ The possible use of a mixture of hydrate and anhydrous compound as a drying agent came to the attention of one of us in conversation some 20 years ago with Prof. Robert W. Hall, then professor of analytical chemistry at New York University. It is not remembered that Professor Hall claimed originality for the idea, and we have not been able either to find its origin or to hear that it has ever been tested.

tator method in which the current is periodically interrupted with a rapidly rotating commutator; (2) the direct method, in which the electrode potential is determined while the current is flowing. The latter method always gives the higher result. In either case the measurements are made with a hydrogen electrode or indirectly with any standard electrode. It is unnecessary here to give any review of the quite voluminous literature reporting the results obtained by these methods. The methods themselves will be presented more fully in a later part of this paper.

Any correct method of measurement must fulfil the first two and, if the current is interrupted, all of the following requirements: (1) neither the size nor shape of the containing vessel nor the distance between anode and cathode should exert any influence; (2) by definition, the value found must represent an e.m.f. and not a resistance; this entails the elimination of appreciable potential drops due to resistance of electrolyte or any resistance of whatever nature at the surface of the electrode; (3) if measurement be made while the current is interrupted the counter e.m.f. must be instantaneously constant and have the same value as when the exciting current is flowing; there must be no fall of potential during the period of interruption.

The aim of the work here presented was to compare simultaneously the two methods of measurement by obtaining, at a certain point in the procedure, a potential of known value. To secure this condition advantage was taken of the fact that a metal, such as zinc, which is above hydrogen in the electromotive series, may be deposited electrolytically from a strongly acid solution of its salts, upon a cathode of a metal of lower overvoltage, as for example copper or nickel, by simply raising the current density until a transition point is reached when zinc is deposited instead of hydrogen. The deposition of zinc occurs, of course, when the cathode surface has reached the potential of zinc in the electrolyte.

By way of acknowledgment, the writers wish to state that they were led to this method of attack through the work of U. C. Tainton¹ in which he sought to ascertain the critical current densities necessary for the deposition of zinc upon metals of lower overvoltage.

Experimental Part

Apparatus and Materials.—The apparatus consisted of a Leeds and Northrup potentiometer of the smaller type, a Leeds and Northrup galvanometer of the portable lamp and scale type, a rotating commutator driven by an electric motor, lead storage cells, resistances, normal calomel electrode, hydrogen electrode and experimental cell. The arrangement of the apparatus is shown in Fig. 1.

The electrodes of the experimental cell were circular discs 1 cm. in diameter, soldered on one side to copper wires which were sealed into glass tubes. This side of the electrode

¹ Unpublished work now being presented to the American Electrochemical Society. Mr. Tainton was assisted by one of us, Keyes.

and any exposed copper wire were completely covered with sealing wax. Cathodes of copper, nickel, lead, iron and bright and platinized platinum were used with a lead anode. Previous to each test the electrodes were cleaned with nitric acid, if necessary, and then rubbed with No. 00 sandpaper to give a surface as nearly uniform as possible.

The commutator used was carefully tested for short circuits and mechanical deficiencies, to avoid any errors due to faulty construction or improper manipulation.

The electrolytes used were made of distilled water and "C. P. Analyzed" sulfuric acid and zinc sulfate. Further purification of these chemicals was found not to modify the experimental results.

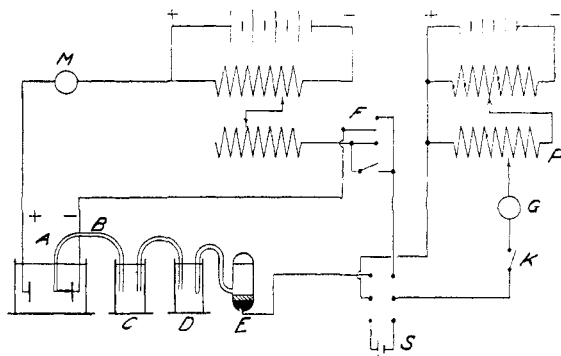


FIG. 1.

- | | |
|----------------------------------------|---------------------------------|
| <i>A</i> , Exp. cell | <i>G</i> , Galvanometer |
| <i>B</i> , Capillary connection | <i>K</i> , Key |
| <i>C</i> , Cell electrolyte | <i>P</i> , Potentiometer |
| <i>D</i> , Sat. KCl solution | <i>S</i> , Standard Weston cell |
| <i>E</i> , <i>N</i> -Calomel electrode | <i>M</i> , Milli-ammeter |
| <i>F</i> , Commutator | |

Results of duplicate tests confirmed the observations of previous workers that overvoltage varies with the nature of the electrode surface, and also with time. For this reason it was difficult, after cleaning an electrode, to obtain results closely agreeing with former values obtained with the same electrode under similar conditions of time and current density. Since the main purpose of these experiments was to determine overvoltage by the two methods of measurement, at a given time, and to compare the two values with a known potential, any change of overvoltage by altering the degree of smoothness of the electrode surface was considered immaterial.

Throughout the paper reference is made to the value of the zinc potential. This was obtained in the following manner.

A lead electrode and a zinc electrode, upon which a new surface of zinc had been deposited electrolytically, were placed in the solution of sulfuric acid and zinc sulfate. A current was passed for a moment through this cell at a sufficient e.m.f. to deposit zinc. The circuit was then opened and the potential of the zinc cathode taken when it had reached a fairly constant value using a normal calomel electrode. The values secured from separate trials agreed within 2 millivolts. When the circuit was opened the potential quickly dropped a small amount and then remained constant for a time before appreciable action of the acid upon the metal took place; the potential during this

period of constancy was taken to be that of zinc in the solution in question. The value obtained was found to equal the back e.m.f. as shown by the commutator method, when zinc was being deposited at *very low current densities*. While the determination cannot be regarded as very exact, it was found to be sufficiently accurate for the work herein reported. In presenting the data which follow it has been found convenient in each case to express the zinc potential in terms of the hydrogen overvoltage corresponding to the same; *i. e.*, the difference in volts between the potential of the zinc and that of the reversible hydrogen electrode.

It was found convenient, throughout the experiments, to employ a normal calomel electrode instead of a hydrogen electrode for measuring the cathode potentials, and separately to determine the hydrogen potential for the solution. The latter was accomplished with the use of the same calomel electrode; 2 hydrogen electrodes were used which gave identical results. From the data secured the difference between the various cathode potentials and that of the reversible hydrogen electrode (the overvoltage) was easily calculated. In all cases a saturated potassium chloride solution was employed to connect the 2 electrodes, to minimize any liquid-liquid potential. The unavoidable variations caused by changes in the electrode surface, time, etc., are, with both methods, of sufficient magnitude to overshadow completely corrections for liquid-liquid potential or small changes of temperature. The measurements were made at approximately 20°.

In the direct method, great care must be taken to ascertain the potential between the cathode surface and the electrolyte in immediate contact with it. To effect this, the solution connecting the standard electrode was connected with the experimental electrode by means of a capillary tube of about 1 mm. in diameter, the end of the capillary being not more than 0.2 mm. from the surface of the cathode. See B, Fig. 1.

To determine whether the direct method satisfies Requirement 1 mentioned above, an experiment was carried out using bright platinum electrodes in dil. sulfuric acid and measuring the cathode potential at constant current density but varying the distance between the electrodes. The results obtained are given in Table I.

TABLE I
EFFECT OF ELECTRODE SPACING ON POTENTIAL MEASUREMENTS BY THE DIRECT METHOD
Solution: dil. sulfuric acid

Current Amp.	Electrode spacing Cm.	Cathode potential, calomel electrode being taken as +0.56 volt Volts	Current Amp.	Electrode spacing Cm.	Cathode potential, calomel electrode being taken as +0.56 volt Volts
0.200	0.5	-0.654	0.200	15.0	-0.650
	15.0	-0.656		10.0	-0.371
	0.5	-0.656	0.800	8.0	-0.371
	15.0	-0.657		0.5	-0.3704
	0.5	-0.651			

The results show that changes as great as 30 times the cathode-anode

spacing did not appreciably alter the cathode potential, the current density remaining constant. However, moving the capillary away from the electrode surface greatly increased the potential reading. The size or shape of the containing vessel was found not to influence the results.

It appeared obvious that results obtained by the commutator method would be independent of the relative distances of the anode and cathode as well as of the position of the bridge connecting the cathode with the standard electrode, but this was verified by experiment.

Both methods of measurement having fulfilled the requirements of Requirement 1, the next step was to investigate the commutator method with a view of ascertaining its meeting Requirement 2. If the fall of potential is appreciable during the period of interruption, a variation in the value of the back e.m.f. with speed of rotation would naturally result. Approximately ten tests were made, all of which gave similar results, of which the following is a typical example.

Sulfuric acid, 0.527 *N*, containing 15 g. per liter of zinc as zinc sulfate, was electrolyzed, using an iron cathode. The current was gradually raised at intervals and the cathode potential determined by both methods. The speed of the commutator was varied from about 8 to 40 revolutions per second. The data are reported in Table II.

TABLE II
EFFECT OF SPEED OF ROTATION OF COMMUTATOR ON OVERVOLTAGE READINGS
Solution: 0.527 *N* sulfuric acid, containing 15 g. per liter of zinc as zinc sulfate
Speed of commutator: 8 to 40 revolutions per second

Current density Amps. per sq. dcm.	Hydrogen overvoltage		
	Commutator method Volts	Direct method Volts	Valuation with speed Volts
0.13	0.255 to 0.256	0.321	0.001
0.63	0.210 to 0.365	0.433	0.155
2.55	0.765	0.870	None

At the highest potential given, zinc was being deposited instead of hydrogen. There was little or no variation in potential with speed of rotation of the commutator just prior to the first evolution of hydrogen or after the transition point was reached when the cathode had changed to a zinc surface. In the intervening period, however, when hydrogen gas was being given off, the variation was from 0.100 to 0.200 volts, the potential reading increasing with the commutator speed. This shows that in a circuit where molecular hydrogen is being formed the fall of potential at the electrode surface, during the period of interruption of the current, is considerable between the speeds given. When gas is being evolved, the difference between the two methods is greater than before the evolution of hydrogen or after the deposition of zinc, the direct method always giving the higher result.

Experiments were next made to ascertain the effect of current density on the divergence of the two methods. The electrolyte used was 0.5 *N* sulfuric acid. In each experiment the applied e.m.f. was gradually raised until the first continuous current was noted from the milli-ammeter. The current density was gradually raised at intervals of about 2 minutes and measurements made by both methods. The current was interrupted by the commutator only long enough to make the readings for this method. The average speed of rotation of the commutator was about 30 revolutions per second. The overvoltage data will be found in Table III. The greater the current density the greater is the difference in the values by the two methods, the commutator method always giving the lower result.

TABLE III
COMPARISON OF OVERVOLTAGES BY THE TWO METHODS WITH INCREASING CURRENT DENSITIES

Current density Amps. per sq. dcm.	Solution: 0.5 <i>N</i> sulfuric acid							
	Platinized platinum		Nickel		Cathode Metal Copper		Iron	
	Commu- tator method Volts	Direct method Volts	Commu- tator method Volts	Direct method Volts	Commu- tator method Volts	Direct method Volts	Commu- tator method Volts	Direct method Volts
0.13	0.204	0.235	0.440	0.518
0.26	0.011	0.011	0.238	0.312	0.456	0.563	0.248	0.290
0.39	0.010	0.015	0.235	0.324	0.454	0.619	0.297	0.431
0.51	0.239	0.346	0.463	0.664	0.312	0.494
0.64	0.015	0.020	0.240	0.356	0.475	0.690	0.354	0.584
0.77	0.254	0.373	0.460	0.719	0.330	0.643
0.89	0.261	0.387	0.485	0.770	0.351	0.698
1.02	0.259	0.413	0.475	0.775	0.325	0.751
1.27	0.018	0.022	0.275	0.432	0.475	0.832
2.55	0.020	0.028	0.314	0.519	0.475	0.912
3.82	0.327	0.560
5.10	0.018	0.035	0.332	0.607	0.440	1.066
10.20	0.021	0.047	0.330	0.691	0.440	1.145
19.10	0.026	0.067	0.345	0.940	0.430	1.213

Experiments were next conducted using a solution of the same hydrogen concentration as 0.5 *N* sulfuric acid but containing 15 g. per liter of zinc in the form of zinc sulfate. The solution was 0.527 *N* with respect to the acid. Measurements were made similarly with increasing current density and the potentials noted as the transition point from hydrogen to zinc was reached. The zinc potential corresponded to an overvoltage of 0.758 volts. The values are recorded in Table IV.

The overvoltages for low current densities given in Table IV correspond to those of Table III. With time and increase of current density, however, the rise of cathode potential is more rapid in the case of the electrolyte containing zinc. A possible explanation of this result is that during the

TABLE IV
COMPARISON OF OVERVOLTAGES BY THE TWO METHODS USING SOLUTION CONTAINING
SULFURIC ACID AND ZINC SULFATE

Solution: 0.527 *N* sulfuric acid, containing 15 g. per liter of zinc as zinc sulfate
Zinc potential corresponds to overvoltage of 0.758 volts

Nickel			Copper			Iron		
Current density Amps. per sq. dcm.	Commu- tator method	Direct method	Current density Amps. per sq. dcm.	Commu- tator method	Direct method	Current density Amps. per sq. dcm.	Commu- tator method	Direct method
	Volts	Volts		Volts	Volts		Volts	Volts
0.13	0.224	0.278	0.13	0.425	0.471	0.13	0.245	0.321
0.26	0.235	0.305	0.13	0.505	0.563	0.26	0.253	0.361
0.51	0.249	0.355	0.20	0.529	0.628	0.64	0.365	0.433
0.76	0.256	0.393	0.26	0.693	0.745	1.27	0.295	0.512
1.53	0.345	0.565	0.26	0.685	0.775	2.29	0.311-0.429	0.623
1.53	0.357	0.620	0.26	0.748	0.808	2.29	0.740	0.900
1.53	0.720	0.875	0.38	0.757	0.810	2.55	0.765	0.870
1.53	0.761	0.880	0.51	0.758	0.800	5.10	0.755	0.845
1.91	0.765	0.843	1.28	0.759	0.802
3.82	0.771	0.875	5.10	0.758	0.802
10.30	0.777	0.920	10.30	0.763	0.827
19.10	0.775	0.950	19.10	0.668	0.854

electrolysis there is an increase in the concentration of the zinc sulfate and a decrease of sulfuric acid at the cathode. This would be accompanied by a change in hydrogen-ion concentration and consequently of the hydrogen potential. The cathode potential in an acid solution containing zinc sulfate would therefore not be the same at a given current density as that in an acid solution having the same initial hydrogen-ion concentration.

The results indicate that the ordinary overvoltage tables, obtained with the use of 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.

The data of Table IV also show that the potential values obtained by the two methods of measurement became more and more divergent with increase in current density until, according to the direct method, the zinc potential was reached and zinc deposited. At this point the values obtained by the two methods approach each other closely, the values of the commutator method suddenly rising to practically that of the zinc potential. Upon reaching this critical point, the potential as measured by the direct method suddenly rose to a slightly higher value. This rise was only temporary, however, and gradually disappeared as the coating of zinc on the cathode became more uniform. In all cases it was found that at the critical potential for the deposition of metal there was a very abrupt change in the values obtained by the commutator method.

A further series of experiments was tried with the object in view of controlling any sudden rise in potential. To accomplish this the applied

e.m.f. was gradually decreased as the point for metal deposition was reached. Readings were made by both methods in quick succession at time intervals of about 1 minute. In the commutator method the current is flowing only intermittently and the time factor is therefore not parallel to that of the direct method. To avoid any influence of time on the overvoltage, the potential was read according to the direct method, then the potentiometer was set at the approximate value for the commutator reading, the commutator was suddenly connected in the circuit and the final reading taken as quickly as possible. This was done in order to obtain the readings by the two methods under conditions as nearly identical as was possible. Two electrolytes and two different metals were used; in one case, a nickel cathode was tried with the same solution as that referred to in Table IV; in the other case, bright platinum with a solution which was 0.204 *N* with respect to sulfuric acid and containing sufficient zinc sulfate to give 120 g. of zinc per liter, as zinc sulfate. The zinc potential with the latter solution was equivalent to an overvoltage of 0.708 volts. Representative results will be found in Table V. Only the last part of each series of readings is given; those of the first part correspond to the values given in Table IV.

TABLE V

COMPARISON OF OVERVOLTAGES BY THE TWO METHODS WITH GRADUAL POTENTIAL RISE
Solution used with nickel cathode: 0.527 *N* sulfuric acid containing 15 g. per liter of zinc as zinc sulfate

Zinc potential: overvoltage of 0.758 volts

Solution used with bright platinum cathode: 0.204 *N* sulfuric acid, containing 120 g. per liter of zinc as zinc sulfate

Zinc potential: overvoltage of 0.708 volts.

Current density Amps. per sq. dcm.	Nickel		Bright Platinum		
	Commutator method Volts	Direct method Volts	Current density Amps. per sq. dcm.	Commutator method Volts	Direct method Volts
0.64	0.338	0.675	0.38	0.247	0.697
0.13	0.323	0.705	0.38	0.250	0.712
0.26	0.320	0.735	0.26	0.682	0.737
0.13	0.322	0.755	0.13	0.695	0.747
0.07	0.675	0.765	0.13	0.693	0.777
0.07	0.700	0.765	0.33	0.702	0.797
..	0.77	0.719	0.817

The direct method shows a *gradual increase* in potential without any sudden changes or fluctuations, and zinc was deposited upon reaching the zinc potential. When the zinc potential was registered by the direct method, there was a sudden and abrupt rise in the commutator readings. This sudden break is shown with both solutions although these had distinctly different zinc potentials.

Attempts were also made using the commutator arrangement by itself

to increase the potential *gradually* to the point for metal deposition without any sudden change in the magnitude of the readings. The commutator rotated at the rate of 30 revolutions per second. The electrolyte was the same as that used for obtaining the results given in Table IV. Using an iron cathode, as soon as the potential had been raised by steps to an overvoltage of 0.460, the readings immediately rose to 0.758, the value of the zinc potential, and zinc began to deposit. By lowering the applied e.m.f. until the thin coating of zinc dissolved, the overvoltage remained at 0.745 and then suddenly became less than 0.375. There was no point between 0.460 and 0.758 at which the potential could be held, in spite of numerous trials. Similar results were obtained with cathodes of bright platinum and nickel. The phenomenon of the abrupt change in readings is typical of the commutator method using cathodes of metal of low overvoltage in acid solutions of zinc sulfate.

The preceding tabulated data were secured with a limited number of solutions. Analogous results have been obtained with other solutions in which the concentrations of both sulfuric acid and zinc sulfate were varied, thus giving different values for the hydrogen and zinc potentials. *The sudden break in the commutator readings has been found to be not characteristic of a given potential nor of the nature of the cathode metal, but is determined by the zinc potential.*

Discussion of Results

The experimental data presented above show that more consistent results are obtained by the direct method. The sudden and abrupt changes in the readings with the commutator method given in Tables IV and V furnish practically decisive evidence that this method cannot be relied upon to give the true overvoltage. There is no experimental evidence reported in the literature to show that the counter e.m.f. is instantaneously constant when the current is interrupted and has the same value as when the exciting current is flowing. The foregoing data furnish strong evidence to the contrary. The hydrogen overvoltage must be sufficient for the cathode to reach the zinc potential before zinc is deposited. Evidently this point would be reached gradually. A method for determining overvoltage must show this gradual change of potential and at the critical point for metal deposition must closely coincide with the zinc potential. The direct method meets this requirement.

The data of Table III show that there was no abrupt rise in the overvoltages by the commutator method even when the values by the direct method were greater than those at which this sudden change was found in the experiments of Table IV. The values in Table III by the commutator method would indicate that, at the current densities used, it would be impossible with the metals employed to reach a cathode potential at which

zinc would be deposited. Nevertheless, it is an experimental fact that zinc can be deposited from an acid solution of the same hydrogen-ion concentration and within the same range of current density (See Table IV).

Consideration will now be given to Requirement 2 mentioned previously. While overvoltage is generally accepted to represent a potential, the difference in the results by the two methods of measurement has been taken to be due to a resistance, commonly designated as "transfer resistance."² The experimental work here presented shows the commutator method to be in error and consequently the so-called transfer resistance cannot be of the magnitude which has been claimed.² The data also show that the measurements made by the direct method do not vary in any case from the zinc potential at the point of zinc deposition by more than 0.05 volts. With a smooth electrode surface such as that afforded by bright platinum and with careful control of the rise in potential, zinc was deposited at 0.029 volts above the zinc potential, when the current density was 0.0026 amperes per sq. cm. This would represent a transfer resistance of approximately 11 ohms. By further refinement of the method of procedure it might be possible to show the non-existence of a resistance of even this magnitude. These results, considered with the comments recently made by MacInnes,³ based upon more precise measurements, show that the probable error in the direct method due to the presence of a resistance at the electrode surface is of small proportion, if it exists at all.

In conclusion the writers wish to express their sincere thanks to Dr. D. A. MacInnes, of the Massachusetts Institute of Technology, who has read this paper in manuscript and given useful suggestions.

Summary

1. The findings of former investigators that overvoltage increases with time and current density and varies with the nature of the electrode surface has been confirmed.

2. A comparison, based upon the transition point for hydrogen-zinc deposition from solutions containing sulfuric acid and zinc sulfate, has been made of the two methods used for overvoltage measurement. The data obtained show that the commutator method gives erroneous results; when gas is being evolved at the experimental electrode the error is large and varies with the speed of rotation of the commutator. The direct method has been found to give more consistent results and to be the more accurate method; the criticism that it is subject to variation due to electrode spacing and size and shape of containing vessel has been shown to be invalid.

3. The existence of an appreciable transfer resistance at the surface of

² Newbery, *Trans. Faraday Soc.*, **19**, 126 (1919).

³ MacInnes, *THIS JOURNAL*, **42**, 2233 (1920).

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

BY LOWELL H. MILLIGAN

Received December 20, 1921

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 , $\text{HNO}_3 + \text{Aq}$, 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).