test with the diphenylamine reagent as prepared by us is conducted as follows: Place 1 cc. of the liquid to be tested in a clean test tube; add 1 drop of the diphenylamine reagent and mix thoroughly by shaking. From a pipe is added 2 cc. of concentrated sulfuric acid, while the tube is held at an angle so as to form two layers of the liquids. The tube is gently agitated so as to cause a slight mixing of the liquids at the plane of contact, and it is then placed in a bath at the temperature of 40° and left for 15 or 20 minutes. This method will reveal the presence of one part of nitrite nitrogen in 25 million or one part of nitrate nitrogen in 35 million. By heating for one hour instead of 15 or 20 minutes the test will show one part of nitrite nitrogen in 32 million or one part of nitrate nitrogen in 44 million.

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PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS CONTAINING AMMONIA AND CITRIC ACID.

BY ROBERT A. HALL AND JAMES M. BELL.

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In the analysis of commercial fertilizers for the so-called "available" phosphoric acid, it is usual to employ a solution of "exactly neutral" ammonium citrate,[1] having a specific gravity of 1.09 at 20°. After extraction of the fertilizer with water, the residue is treated with the citrate solution and the phosphoric acid which remains undissolved is termed insoluble, or non-available; that which the water dissolves is the water-soluble; and that dissolved in the citrate solution is the reverted or citrate-soluble. The sum of the water-soluble and the citrate-soluble phosphoric acid constitutes the available. Upon the results of these analyses depend the valuation of the fertilizer material, and, if the guarantee accompanying the fertilizer claims a higher percentage of phosphoric acid than is shown in the analysis by the state chemist, the manufacturer is liable to a fine.

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[1] Bureau of Chemistry, *Bull.* 107 (revised), 1.

In the preparation of the "exactly neutral" ammonium citrate solution, however, great difficulty is encountered, due to the lack of sensitiveness of every color indicator. This lack of sensitiveness in the color indicator is general in the neutralization of a weak base, such as ammonium hydroxide, by a weak acid, such as citric acid.

The Association of Official Agricultural Chemists prescribes[1] the use of a saturated alcoholic solution of corallin as indicator in testing for the neutrality of the citrate solution; also an "optional method" wherein the citrate is precipitated by an alcoholic solution of calcium chloride, and the filtrate tested for acidity or alkalinity with cochineal as indicator. This method is employed apparently with the object of avoiding the difficulty experienced in determining the end point in the former method. That both methods are unreliable and unsatisfactory is evidenced by the fact that at almost every meeting of chemists engaged in fertilizer analyses there is animated discussion of, and general protest against, both the "official method" and the "optional method" on account of the difficulty in getting a sharp end point with corallin, or any other color indicator.

In the absence of any satisfactory color indicator of the end point in the neutralization of a weak acid by a weak base, several physical properties of mixtures of ammonia and citric acid have been investigated with a view of applying these to the determination of the end point. The use of conductivity as an indicator of neutrality has been demonstrated by Küster and Grüters[2] in the titration of weak acids by strong bases, the conductivity being measured after each addition of the base to the solution. By plotting the quantity of alkali against the conductivity, a decided break was found in the curve just at the neutral point. The solution consisted of a mixture of the acid and salt in varying proportions up to the neutral point, after which it was composed of the alkali and salt. The method of conductance has also been employed to determin the acidity of colored liquids,[3] such as wines, where the color of the liquid would mask the color change of the indicator.

Another physical measurement has been used by Ostwald, *viz.*, density, as an indicator of the neutral point, a sharp break in the composition-density curve being found at this point of neutrality.

The present paper contains the results of measurements of conductivity and of density of a series of solutions containing constant amounts of citric acid and varying amounts of ammonia in a fixed volume of solution. The conductivity measurements were made with the usual Wheatstone apparatus, the conductivity cell used being of the H. C. Jones type, designed for concentrated solutions. In making up the solutions standardized

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[1] Bur. of Chem., *Bull.* 107 (revised), 1.

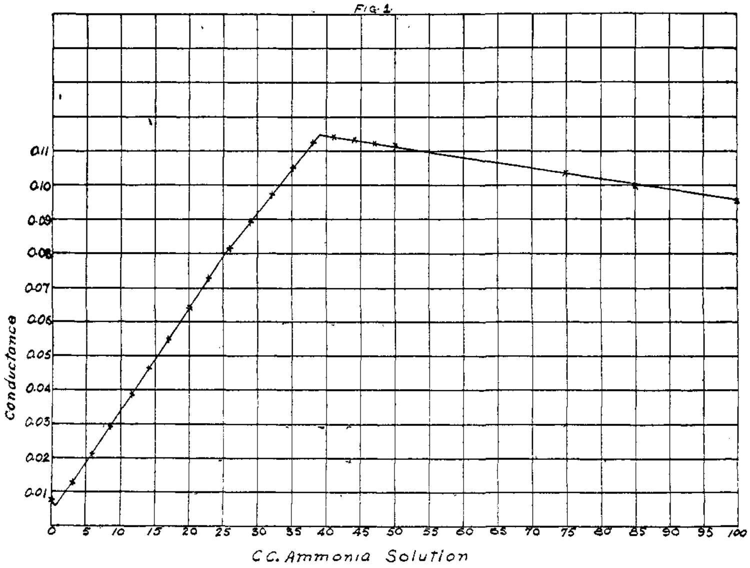
[2] *Z. anorg. Chem.*, 35, 454 (1903).

[3] Küster and Grüters, *Loc. cit.;* Geibel, *Z. anorg. Chem.*, 42, 231 (1905).

(D. & R.) pipets, burets, and flasks were used, and also, as a check, the flask and contents were weighed after each addition. This was deemed advizable on account of the very concentrated solutions used and on account of the volatility of the ammonia. In order to minimize the loss of ammonia by evaporation, the stock solution was siphoned from a bottle protected with a capillary opening. The flow of liquid into the buret was controlled by a glass stopcock, and the top of the buret was closed except for a capillary opening. The outflow from the buret was made through a small tube, drawn to a capillary opening, of sufficient length to pass nearly to the bottom of the flask in which the solutions were mixed. This capillary tube was coated on the outside with a high-melting paraffin to prevent the solution in the flask clinging to the tube when the ammonia solution was led into the body of the citric acid solution. The escape of ammonia was thus minimized or prevented entirely, no ammonia being noticeable by odor or by a change of color of moist neutral litmus paper.

Each solution in the first series of conductivity measurements had a total volume of 200 cc. This contained 100 cc. of a solution of pure citric acid (Kahlbaum's), 370 grams per liter, thus approximating the citrate content of the solution employed in fertilizer analysis.[1] To these solutions were added in the way described above varying amounts of the ammonia solution, whose exact strength was determined both by titration against standardized acid and also by density determinations. The 200 cc. measuring flask was then cooled and filled up to the mark with dis-

Fig. 1.



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[1] *Loc. cit.*

tilled water. After thorough mixing, the solutions were transferred to glass-stoppered bottles and placed in the thermostat which was electrically heated and controlled. The temperature was maintained at 25°, within 0.01°. This temperature was chosen rather than 20°, at which the fertilizer chemist makes this specific gravity determination, because of the inconveniences of running a thermostat at a temperature below that frequently existing in this neighborhood.

In another series of measurements the above solutions were diluted one-half, 100 cc. to 200 cc., and the conductivities ascertained.

In Table I are given the results of the conductivity measurements of the concentrated solutions, made as described above. The quantity of citric acid solution used was always 100 cc., weighing 113.00 ± 0.02 grams. In Figure I the conductivities are plotted against the cc. of ammonia.

TABLE I.

Solution no.	Ammonia solution. cc.	Conductivity.
1	0.00	0.007791
2	3.00	0.01292
3	5.75	0.02113
4	8.60	0.02943
5	11.55	0.03901
6	14.31	0.04629
7	17.15	0.05500
8	20.00	0.06401
9	23.00	0.07271
10	26.00	0.08187
11	29.00	0.08984
12	32.00	0.09731
13	35.00	0.1052
14	38.00	0.1124
15	41.00	0.1145
16	44.00	0.1132
17	47.00	0.1124
18	50.00	0.1116
19	75.00	0.1032
20	85.00	0.09990
21	100.00	0.09523

It will be seen in Figure 1 that there is a sharp break in the curve at the point representing 39 cc. of the ammonia solution. The strength of the ammonia solution used in these experiments was determined by density measurements and also by titration against hydrochloric acid of known strength. This acid was compared with a solution of caustic soda, which was standardized by comparison with a normal solution of oxalic acid made by weighing the exact amount of oxalic acid. The titrations with oxalic acid were made with phenolphthalein, and those with ammonia with methyl orange as indicator. By this method the ammonia was found to be 13.51 normal. Therefore, the 39 cc. of ammonia solution contain 0.5268 mols. NH_3. Of citric acid in 100 cc. of acid solution there are 37 grams, equal to 0.156 mols. Now, 0.5268/0.176 = 2.993; that is, the neutral solution, as determined by this method is at triammonium citrate.[1] This suggests the applicability of the conductivity method for determining the neutral point of ammonium citrate solution.

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[1] Van Itallie, *Z. anorg. Chem.*, 60, 358 (1908).

Some of the above solutions were diluted one-half; that is, 100 cc. of the solution were diluted to 200 cc., and the conductivities ascertained. In Table II the measurements are given, and in Fig. 2 the conductivities are plotted against the cc. of ammonia solution as before. The break in the conductivity curve of the diluted solutions agrees with that found for the more concentrated ones, showing that a dilution of one-half has no influence on the neutral point as found by this method.

FIG. 2.

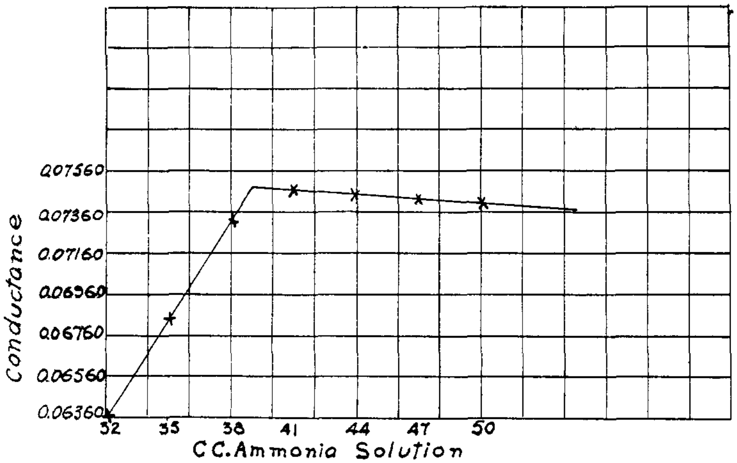


TABLE II.

Solution no.	Ammonia solution, cc.	Conductivity.
12........	32.00	0.06360
13........	35.00	0.06841
14........	38.00	0.07330
15........	41.00	0.07471
16........	44.00	0.07440
17........	47.00	0.07418
18........	50.00	0.07402

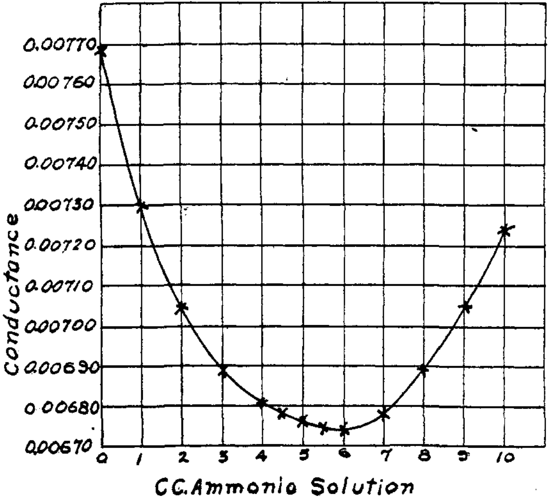
It will be noticed further in the curve of Fig. 1 that the first point of the curve does not fall in the smooth curve with the other points up to the neutral point. To investigate the failure of this point to fall on the regular curve there was made a further series of measurements in which the quantities of ammonia solution added differed by smaller increments (0.5 cc.). This showed that the curve has a minimum. In a further series of measurements having a still smaller increment of ammonia solution (0.1 or 0.2 cc.) the region of this minimum was more carefully investigated. In this series the original ammonia solution was diluted ten times, and so 0.1 or 0.2 cc. of the original solution correspond to 1 or 2 cc. of the diluted solution. In Table III the measurements are given and in Fig. 3 the conductivities are plotted against the number of cc. of the diluted ammonia solution.

TABLE III.

Solution no.	Ammonia. cc.	Conductivity.
1	0.00	0.00768
2	1.00	0.00730
3	2.00	0.00704
4	3.00	0.00689
5	4.00	0.00681
6	4.50	0.00678
7	5.00	0.00676
8	5.50	0.00674
9	6.00	0.00674
10	7.00	0.00678
11	8.00	0.00689
12	9.00	0.00705
13	10.00	0.00724

With a strong acid at great dilution successive additions of ammonia (or any other base) would lower the conductivity, due to the displacement of the exceedingly mobil hydrogen ion by the slower moving ammonium ion. With a weak acid, however, two opposing factors enter, the hydrogen ion being replaced, as before, by the ammonium ion, and also the salt having a far higher degree of dissociation than the acid. The second factor is probably the predominant one and slight additions of ammonia would increase the conductivity. Should the citric acid contain a minute amount of a strong acid, the strong acid would be neutralized first, and thus give a minimum conductance. Whether this minimum be due to impurities, or whether other weak bases and weak acids exhibit the same phenomenon is still under investigation in this laboratory.

FIG. 3.



Another method of determining the neutral point of ammonium citrate solution was suggested by the fact that chloroform dissolves free ammonia[1]

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[1] Hantzsch and Sebaldt, *Z. physik. Chem.*, 30, 266 (1899); Abbott and Bray, THIS JOURNAL, 31, 729 (1909).

but does not dissolve citric acid or ammonium citrate and therefore may be used as an agency for removing NH_3 from its salts, if ammonia be present in excess. A series of nine solutions, containing 35, 36, 37 ..... 43 cc. of ammonia solution, respectively, was prepared, and each solution shaken with chloroform. The chloroform extracts from the solutions containing 35 to 39 cc. of ammonia solution showed no free ammonia on titration with dilute sulfuric acid, methyl orange being used as indicator. The extracts from solutions containing 40 to 43 cc. of ammonia solution contained increasing amounts of free ammonia. Thus the presence of free ammonia in the citrate solution may be detected by shaking out with chloroform and testing the chloroform layer for free ammonia. This offers another method for establishing the end point when citric acid is being neutralized by ammonia.

A series of measurements of the densities of solutions containing citric acid and ammonia offer further confirmation of the position of the neutral point. In preparing these solutions 50 cc. of citric acid solution were placed in a 100 cc. measuring flask and ammonia was added. Water was then added to the mark and the flask and contents weighed and the density computed in the usual way. In Table IV the data thus obtained are given, and in Fig. 4, the number of cc. of ammonia solution is plotted against the densities. It is seen that the neutral solution has the maximum density and that this solution is the same as that indicated by the break in the curve obtained by the conductivity method,

FIG. 4.

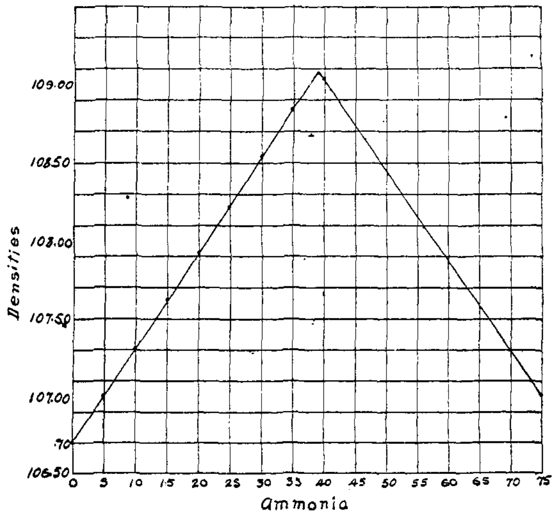

TABLE IV.

Solution no.	Ammonia solution. cc.	Density.	Solution no.	Ammonia solution. cc.	Density.
1	0	1.0670	7	30	1.0853
2	5	1.0700	8	35	1.0883
3	10	1.0731	9	40	1.0903
4	15	1.0762	10	45	1.0874
5	20	1.0792	11	50	1.0846
6	25	1.0822	12	75	1.0702

Summary.

In this paper it has been shown that the neutral point for a weak acid and a weak base, such as citric acid and ammonia, may be accurately determined by conductivity measurements; that the presence of an excess of ammonia in the ammonium citrate solution may be ascertained by shaking out with an immiscible solvent, as chloroform, which dissolves a part of the excess of the base but neither the free acid nor the salt; and that the neutral point of the ammonium citrate solution may also be established by density determinations.

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APPLICATION OF THE "GLOW REACTION" TO THE QUALITATIVE DETECTION OF THE PLATINUM METALS.[1]

BY L. J. CURTMAN AND P. ROTHBERG.

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For a long time it has been known that the platinum metals present the rather remarkable phenomenon of condensing relatively large volumes of gases upon their surfaces at room temperatures, and also, that this property is especially pronounced if the metals are in that finely divided state obtained by the reduction of their salts. In 1823 Döbereiner[2] showed that the occlusion of gases by platinum sponge, particularly in the case of a mixture of hydrogen and air, was accompanied by the oxidation of hydrogen to water and it was noted that this reaction took place so rapidly and energetically as to cause the platinum sponge to glow intensely. From the early investigations of Döbereiner to the present day, this occlusion of gases by platinum has been the subject of much research,[3] and among other things, it has been shown that hydrogen in the occluded state acts in the same manner as nascent hydrogen[4] and that,

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[1] Presented at the March meeting of the New York Section of the American Chemical Society.

[2] Schweigger, *J. für. Chem.*, 39, 159 (1823).

[3] J. L. Howe, "Bibliography of the Platinum Metals" in *Smithsonian Inst. Misc. Collections*, Vol. 38.

[4] T. Graham, *Proc. Roy. Soc.*, 16, 422 (1868).