Knight

Acidity and Acidimetry of Soils

# ACIDITY AND ACIDIMETRY OF SOILS

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B. A. University of Washington, 1902.
M. A. University of Washington, 1904.

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1917

# UNIVERSITY OF ILLINOIS

## THE GRADUATE SCHOOL

May, 1917

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY HENRY GRANGER KNIGHT

ENTITLED ACIDITY AND ACIDIMETY OF SOILS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

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9 Feb. 18 Colley

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# ACIDITY AND ACIDIMETRY OF SOILS

## Introduction.

### (Review of Literature)

It has been long known that for the production of certain crops, it is advisable to have the land "sweet". The Roman writers upon agriculture, Cato, Columella, Virgil, Palladius, and Pliny[1] emphasize this fact and suggest a method of testing for sour soils by taste, but there is question whether they contrasted "sweet" with "sour" or with "bitter" for the fact that "sour" soils very seldom give an acid flavor, while lands impregnated with sea water would have a bitter flavor due to the magnesium salts present and undoubtedly the early Romans were familar with the latter conditions.

In much of the later writings, in the use of the term "sour" there is some doubt whether reference is made to the soil or to the character of the vegetation.[2] The latter interpretation finds further support in the fact that the first chemical test (litmus paper test) seems to have been first suggested by Voelcker[3] in 1865, who states regarding the action of soil upon litmus, "--if the blue color of the test paper turns rapidly red

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[1] Dickson, 1788, Husbandry of the Ancients, Edinburg, Vol.1, Chap.11
[2] Donaldson, 1860, British Agriculture, London, p. 315.
[3] Voelcker, 1865, Jr. Roy. Ag.Soc., England, p. 115.

the soil is certain to contain something injurious to plant life. All good and fertile soils either have no effect upon red or blue litmus paper, or show a slight alkaline reaction, that is to say, in a wet condition they restore the blue color to reddened litmus paper."

Lime was well known to the ancients but does not seem to have been used for correcting "sour" soils until the time of Pliny[1] who writes of it as being used by the Gauls[2] and was found to be beneficial to vines and olives in Italy; and that marl was used by the Britons.[3]

## General Occurrence of Acid Soils

Although the term "sour" as applied to soils is entrenched in popular speech and writings, a search of the literature seems to indicate that there was no knowledge of the general occurrence of acid soils except of those which contained a high percentage of organic matter as soils of peat bogs and moors. Hilgard,[4] in a private communication to Roberts stated that "Saurer Sand boden" is an expression he had heard applied in Berlin to the Uplands of that region, but in his publication[5] he follows in the main example of the early writers, and briefly states that "the peaty soils of woodlands, notably in the United States of the soils of the long leaf pine region of the cotton states both upland and lowland as well as of many deciduous forests in northern climates

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1. Dickison, 1788, Husbandry of the Ancients, Edinburg VI,p.330.
2. Ibid, p. 340
3. Ibid, p. 345
4. Hilgard, 1907,Roberts' Fertility of the Sand,p. 315.
5. Hilgard, Soils, 1906, Macmillan Company,New York,pp.122-123.

as being characteristically acid." The subject received, however, very little consideration until Wheeler and his Co-workers[1] called attention to the acidity of the uplands and naturally well-drained soils of Rhode Island. Subsequent work reported would seem to indicate that acid soils are the rule rather than the exception in humid regions.

Blair and Macy[1a] report that two-thirds of the surface soils and one-half of the subsoils tested from Florida are acid.

Conner and Abbott[2] show that some of the black soils of northern Indiana are acid.

Kinsley[3] reports all but ten per-cent of the soils examined from the state of Oregon as being acid.

Hopkins[4] and his associates have reported the analysis of the soils for a number of counties which may be summarized with respect to the subject under discussion as follows: - The soils of Clay County[5] are, in general, acid to the depth of forty inches with the exception of deep peat[6]. The upland timber and terrace soils of Moultrie County[7] are acid, while all the other types have limestone present with the exception of the upland prairie brown silt loam. All of the upland timber soils of Hardin County[8]

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[1] Wheeler, 1895, Rhode Island Agr. Exp. Sta., 8th Ann. Rep.
[1a] Blair and Macy, Florida Agr. Exp. Sta. Bul. 90, pp. 45-69.
[2] Indiana Agr. Exp. Sta. Bul. 157, pp. 35-264.
[3] Oregon Agr. Exp. Sta. Bul. 90.
[4] University of Illinois, Agr. Exp. Sta. Soil Reports.
[5] Ibid, No. 1, 1911.
[6] Ibid, No. 1, p. 8.
[7] Ibid, No. 2, 1911.
[8] Ibid, No. 3, 1912.

are acid with the exception of the type fine sandy loam, of the terrace soils the type gray silt loam on tight clay is acid, and all of the upland soils show marked acidity in the subsurface and subsoil samples. The upland timber soils of Sangamon County[1] are acid. The terrace and upland timber soils of LaSalle County[2] are in the main acid. All of the uplands of Knox County[3] and McDonough Counties[4] are acid. All of the upland soils of Bond County[5] are acid. All of the upland soils of Lake County[6] with the exception of two types and much of the bottom lands are acid. Most of the soils of McLean County[7] are acid. All of the types in Pike County[8] are acid. All of the upland prairie, and timber types and the terraces types of soil with few exceptions in Winnebago County[9] are acid.

Frear[10] reports that from private samples submitted to him, many types of soil in Pennsylvania suffer from this defect.

King[11] states that the cultivated soils of Japan are nearly all acid to litmus.

The work reported indicates that cultivated soils of humid regions are almost universally acid in character. This fact and its importance should not be underestimated.

Since such legumes, as the clovers and alfalfa, upon which,

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[1] Ibid, 1912, No. 4.
[2] Ibid, 1913, No. 5.
[3] Ibid, 1913, No. 6.
[4] Ibid, 1913, No. 7.
[5] Ibid, 1913, No. 8.
[6] Ibid, 1915, No. 9.
[7] Ibid, 1915, No. 10.
[8] Ibid, 1915, No. 11.
[9] Ibid, 1916, No. 12.

[10] Penn. Dept. of Agr., Bul. No. 261, p. 108, 1915.
[11] Farmers of Forty Centuries, p. 424.

in the best systems of agricultural practice, dependence is placed for the gathering of nitrogen from the atmosphere for soil enrichment, do not thrive upon soils which are acid in character, no opportunity for soil improvement by growing these valuable plants may be accomplished without first correcting the acidity.

This is accomplished by applications of limestone or of lime in some form. The expenses involved are considerable, and when we consider ~~that~~ the great percentage of soils which will be benefit~~t~~ed by liming in the United States, it can readily be understood that the problem is not local in character but is of national, and even of world-wide, importance. Our knowledge of such a subject should be very thorough.

SOILS TEND TO BECOME ACID.

A study of the composition of drainage waters from normal soils show that the fixed bases such as lime, magnesia, sodium and potassium are present in larger equivalent amounts than are the fixed acid constituents as silicic, phosphoric, sulphuric and hydrochloric acids. The basic elements tend to be leached from the soil in excess of the acid constituents.

Voelcker[1] reports an average of 98.1 parts of lime, 5.1 parts of magnesia, 1.7 parts of potash, 6 parts of soda, and 5.7 parts of peroxide of iron for the basic materials, as against 24.7 parts of sulphuric acid, 0.63 parts of phosphoric acid, 10.7 parts of chlorine, and 10.9 parts of soluble silica for the fixed acid constituents, per million parts of drainage waters from plots Nos. 3 and 4 of Broadbalk field, which were the unfertilized plots. The excess bases were combined with carbonic and nitric acids. The loss of lime alone from plot 3 in the drainage is at the rate of 800 pounds per acre per annum calculated as calcium carbonate.[2]

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1. Hall, Rothamstead Experiments, London, (1905), p. 237.
2. Hopkins, Soil Fertility and Permanent Agriculture, 1910, p.174.

Lyon and Bizell[1] show that the loss of fixed bases is much greater than the loss of fixed acids from both cropped and uncropped soils.

Bartow[2] reports 90 analyses of Illinois well waters drawn from glacial sands, gravel and till, which show a similar loss of basic elements from the soils of Illinois.

Besides the loss from drainage there is an appreciable loss of basic elements over the fixed acids through cropping.[3]

## THEORIES CONCERNING SOIL ACIDITY

It may be inferred that prior to 1805 burned lime was applied to soils in the belief that it combined with the acids of the soil neutralizing them[4] but undoubtedly it was used primarily in the belief that it was a fertilizer. As late as 1855, Norton[5] in discussing liming of peat soils states that the common belief is that the lime acts upon the vegetable matter converting it into a condition more readily assimilated by plants, but he later states[6] that lime is supposed to act upon peat soils "by neutralizing the acid properties which are believed to be inimical to vegetation."

Lowdon[7] questions the presence of acids in soil and states that "it would have been a wise practice to have previously ascertained the certainty of this existence of acid, and to have determined its nature, in order that it might be effectively removed.

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[1] Journ. Ind. Eng. Chem. 3, 1911, p. 734.
[2] Illinois Water Survey Bulletin, No. 4, 1908.
[3] Hopkins, ibid, pp. 75 and 154.
[4] Dickson, 1805, Practical Agriculture, London, p. 226.
[5] Norton Encyclopedia of Agriculture, 1855,London,Vol.II,p.254.
[6] Ibid, p. 266.
[7] Encyclopedia of Agriculture, 1857, London, p. 345.

The fact really is that no soil was ever yet found to contain any notable quantity of uncombined acid."

Voelcker[1] from his researches comes to the conclusion that the acid reaction which some barren or unproductive soils exhibit it caused either by an excess of organic acids (humic acids) or by the presence of small quantities of sulphate of iron.

Hopkins, Knox and Pettit[2] claim that the acidity is due to acids or acid salts, and that by treatment with a neutral salt solution a double decomposition takes place carrying acidity into solution.

This view is supported by Truog[3] who discriminates between active and latent soil acidity.

Baumaum and Gully[4] conclude that the apparent acid properties of sphagnum moss and its derived peat is due to colloidal adsorption and not to acids.

Rindell[5] has checked the work of Baumaum and Gully in detail and has reached the conclusion that the reaction is chemical rather than physical i,e. is due to the presence of acids.

Tacke and Lüchting[6] after considerable investigation of moor soils also reject Baumaum and Gully's theory.

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1. Jr. Royal Agr. Soc. 1865, 26, p. 115.
2. 19th Ann. Proceedings O.A.C., Bul. No. 73,Bureau of Chem.,U.S. Dept. of Agr., 1902, p. 114.
3. Jr. Ind. Eng. Chem., 1916, 8, p. 341.
4. Mittheil K. Bayer, Moorkulturanstalt,1910, No. 4,pp.31-156; Exp. Sta. Rec., 1910, 23, p. 715.
5. Internat. Mittheil Boden kunde, 1911, 1, p. 67-80.
6. Lander. Jahrbucher, 1911, 41, pp. 752-3.

Gully[1] defends the previous contention of Baumaum and Gully that the acid reaction of peat moss and peat soils is due to the colloidal matter of the covering of the hyalin sphagnum cells.

Fraps[2] claims that acid soils contain free inorganic or organic acids or acid salts.

Ames and Gaither[3] state that the nature of soil acidity or the cause is not the same for all soils.

Loew[4] in discussing the acidity of the red clay soils of Porto Rico considers it to be due to a clay acid, a hydrated aluminium silicate to which he assigns a definite formula and gives the name argillic acid. The formation of this clay acid according to Loew seems to be especially favored by heavy rains and a high summer temperature.

Harris[5] concludes from his experiments with soils of a sandy loam type that the acidity is due to absorption by silicate colloids and not to organic acids.

MacIntire[6] states that absorption of magnesium by soils from magnesium carbonate is chemical rather than physical and that both calcium and magnesium go into the form of silicates.

Conner[7] shows that the acidity of silicates and of clay soils is effected by the amount of water of constitution. Igniting acid silicates and clay reduce the acidity while acid peat

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1. Int. Mitteil.f. Bodl.,1913, 3, p. 529.
2. Penn.,Principals of Agricultural Chemistry, 1913, p.250.
3. Ohio Agr. Exp. Sta., 1913, Bul. No. 261.
4. Porto Rico Agr. Exp. Sta.,1913, Bul. No. 13, p. 6.
5. Jour. Phy. Chem.,1914, 18, p. 355.
6. Tenn. Exp. Sta., 1914, Bul. No. 107, p. 192.
7. Jour. Ind. Eng. Chem., 1916, 8, p. 39.

and peaty sand soils were rendered alkaline.

Veitch[1] had already noted the phenomena discussed by Conner.

Gaws[2] in investigation of the hydrochloric acid soluble silicates of the soil concludes that, acid alumino-silicates are caused by weathering and give an acid reaction to the soil.

Bouyoucus[3] from freezing point studies concludes that the acidity or lime requirement of soils is due mainly to the insoluble acids of the soil, the silicic acid, silica, acid alumino-silicates and perhaps the insoluble organic acids.

Wiegner[4] observed that the exchange of bases between soil silicates and neutral salt solutions conformed closely to the law or formula of adsorption, and hence concludes it to be a case of adsorption.

Truog[5] brings arguments to sustain his contention (loco cite) that soil acidity is due to true acids and not to colloidal absorption.

Brown and Johnson[6] notes a decrease in acidity due to grinding the soil, while Cook[8] notes an increase.

Asch and Asch[7] show that, by the hexite-pentite theory developed by them, clays must have the properties of acids. Further proof is claimed by their mode of formation in nature.

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1. Jr. Am. Chem. Soc.,1904, 26, p. 637.
2. Int. Mitteil f. Bodl., 1913, 3, p. 529.
3. Mich. Tech. Bul., 1916, No. 27, p. 56.
4. Jr. f. Landw., 1912, 60, p. 111.
5. Jr. Phys. Chem., 1916, 20, p. 457.
6. Jr. Ind. Eng. Chem.,1915, 7, p. 776.
8. The Silicates in Chemistry and Commerce, New York, 1914, p.106, English translation by Searle.
7. Soil Science, 1916, 1, p. 95.

Vernadsky[1] shows that halogen salts such as potassium iodide and potassium bromide decompose clays at moderate temperatures with separation of halogen salt.

Mellor and Holdcroft[2] consider kaolin to be alumino-silicic acid.

Dalkuhara[3] examined various hydro-silicates which were acid to litmus and observed that notwithstanding repeated washing, these silicates completely retained their acidity. If, however, a neutral salt is added to the clay, a soluble acid is immediately produced. He also established the fact that finely divided feldspar, which he regarded as neutralized kaolin, upon prolonged treatment with aqueous solutions of carbon dioxide produces an acid reacting silicate which behaves in a manner similar to the clays just mentioned.

Köhler[4] treated kaolin with solutions of magnesium and sodium chlorides and found the resulting solutions slightly but distinctly acid to litmus.

Sullivan[5] repeated the experiments of Köhler and obtained the same results, accounting for them by an exchange of the sodium and magnesium of these salts in part for the iron and aluminum of the kaolin, the salts of the latter undergoing hydrolysis.

Van Bemmelen[6] treated 100 grams of soil with 200 c.c. portions containing 8 and 40 milligrams, equivalents of potassium chloride. After filtration the solutions were analyzed, and it was found that

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[1] Zeits. f. Kryst. U. Mineral, 1901, 34, p. 37.
[2] Trans. Eng. Cer. Soc., 1910, 10, p. 94.
[3] Dalkuhara, Chem. Zeit., 1908, 32, p. 1187
[4] Zeit. Prakt. Geol. Jahrg., 1903, 11, p. 49.
[5] U. S. Geol. Survey Bul. No.312, 1907.
[6] Landw. Vers. Sta., 1877, 21, p. 135.

an almost complete change of potassium for sodium, calcium and magnesium had taken place. Chlorine was determined in one experiment and had not changed in amount.

Sullivan[1] found that by treating kaolin and various other silicates with salt solutions a quantity of bases almost equivalent to the loss of base from the salt was dissolved in each case.

Wiegner[2] found on treating an artificial amorphorous, water-containing so-called double silicate with a neutral salt solution, the cation of the neutral salt was taken in part from the solution, and in its place the cations of the silicates-gel in nearly equivalent amounts entered the solution. The anion of the neutral salt remained unchanged provided secondary reactions did not take place.

Parker[3] concludes from analysis of extracts prepared by treating soils with potassium chloride and potassium acetate, that the base was absorbed to a little greater extent than it was liberated by the soil and that the excess of anion should be accounted for by the presence of the corresponding acid.

That, when a portion of soil is shaken with a neutral salt solution, much of the cation of the salt is removed by the soil and often bases are given up by the soil to the solution, has long been known.[4]

Many investigators have noted the presence of aluminum and iron in such extracts and have attributed the acidity to this

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[1] Loc. cit.
[2] Jour. Lander., 1912, 60, pp. 111-150, 197-222.
[3] Jr. Ind. Eng. Cham., 1914, 6, p. 831.
[4] Thompson: Jr. Rcy. Agr. Soc., 1850, 11, pp. 68-74
Way, Jr. Rcy. Agr. Soc., 1850, 11, pp. 313-379:
1852, 13, pp. 123-143.

cause[1].

Cameron[2] and Harris[3] attribute the acidity of the extracts prepared by shaking soils with neutral salt solutions to the predominant removal of the base from the solution leaving the soil acid, which phenomena they explain upon the theory of colloidal adsorption.

Rice[4] concludes from hydrogen ion concentration studies upon thirty-one soils by means of the indicator method of Sŏrensen[5] that when so-called acid soils are shaken with salt solutions, part of the cation of the salt is absorbed and an equivalent quantity of the base from the soil is given up to the solution, and that the extracts obtained show greater acidity than that of the salt solutions themselves, which is accounted for by the fact that one of the bases is aluminum which does not securely hold its schare of the acid, but through hydrolysis hydrated aluminum oxide is formed along with equivalent quantities of free acid.

## METHODS PROPOSED FOR DETERMINING SOIL ACIDITY.

Voelcker[6] suggests the use of litmus paper for determining

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[1] Veitch, Vour. Am. Chem. Soc., 1904, 26, p. 637; Sullivan, U. S. Geo. Survey Bu., No. 312, 1907; Morse F. Curry, N. H. Agr. Sta. Rep., 1906-08, pp. 271-293; abbott, Conner, and Smalley, Ind. Agr. Exp. Sta. Bul., 1913, No. 170; Ruprecht, Mass. Agr. Exp. Sta., 1915, Bul. No. 161.

[2] The Soil Solution

[3] Mich. Agr. Coll. Tech. Bull., No. 19, 1914.

[4] Jr. Phys. Chem., 1916, 20, p.. 214.

[5] Bio-Chem. Zeit., 1909, 21, pp. 131-304.

[6] Jr. Roy. Agr. Soc., 1865, p. 115.

qualitatively whether a soil is acid.

Müntz[1] proposes extracting with ammonium hydroxide. If the soil is acid a black color is imparted to the alkaline extract.

Holleman[2] extracts the soil with a saturated solution of carbon dioxide and from data obtained concluded that soils which gave up less than a specified percentage of calcium oxide would be benifited by liming.

Tacke[3] expells carbon dioxide from calcium carbonate brought in contact with the soil at ordinary room temperature. Hydrogen is passed over the soil for some time, then an excess of finely divided calcium carbonate in water is introduced and allowed to act two and one half hours or longer, and the lime requirement calculated from a determination of the carbon dioxide evolved.

Wheeler, Hartwell and Sargent[4] discuss in detail the above methods and conclude from carefully planned research that a modification of Tacke's method whereby the soil and calcium carbonate are heated together at the boiling point in the presence of water gave promise of good results if the period of heating be made uniform and is very brief.

Albert[5] treats the soil with an excess of standard barium hydroxide and immediately adds ammonium chloride in solid form and distills off the ammonia set free into standard acid. A blank containing no soil is run and the difference is taken as the measure of the acidity of the soil.

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1. Encyclopedia Chemique, 4, pt. 4, p. 18.
2. Die Land. Versuchs. Stationen, 41, 1892, p. 38.
3. Chem. Ztg., 1897, 20, p. 174.
4. Jr. Am. Chem. Soc., 1900, 22, p. 153.
5. Zeit. Angew. Chem., 1887, 1, p. 533.

Bezzell and Lyon[1] modify Albert's method by digesting the soil with barium hydroxide at the temperature of boiling water for one hour before adding the ammonium chloride, upon the assumption that Albert does not give time for the soil and alkali to react completely.

Veitch[2] treats soil with various amounts of calcium hydroxide, dries on a steam bath, adds water, filters and boils the filtrate with phenolphthalein until a pink color shows or to 5 c.c. Being a "cut-and-try" method it is rather slow and tedious.

Süchting[3] modifies Tacke's method by agitating the soil and an excess of calcium carbonate two hours, discarding the liberated carbon dioxide. The residual calcium carbonate is calculated from determinations of carbon dioxide evolved with hydrochloric acid.

Hopkins, Pettit, and Knox[4] recommend shaking the soil with 5% commercial common salt solution as follows: 100g. of soil are placed in a 400 c.c. shaking bottle with 250c.c. 5% NaCl solution, closing the bottle with a rubber stopper and shaking for three hours in a mechanical shaker or every half hour for twelve hours by hand, centrifuge or let stand until 125 c.c. clear liquid may be obtained. Heat the liquid to boiling to expell traces of carbon dioxide and titrate with standard fixed alkali using phenolphthalein as an indicator. The result is multiplied by 3 to calculate the total acidity of the soil. Later[5] a normal solution of potassium nitrate is substituted for the 5% solution of common salt and the factor

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1. Jr. Ind. Eng. Chem.,1913, 12, p. 1011.
2. Jr. Am. Chem. Soc., 1902, 24, p. 1120.
3. Chem. Ztg., 1897, 21, p. 174.
4. 19th An. Proceedings O.A.C. U.S. Dep. Agr. Bureau of Chem., Bul. No. 73, p. 114.
5. U. S. Dep. Agr. Bureau of Chem., Bul., No. 107, p. 20.

2.5 is used instead of 3 in making the calculations.

Loew[1] suggests treating the soil with a one percent solution of potassium iodide in water; heating for 5-10 minutes on a boiling water bath, adding a few drops of potassium nitrate and cooling quickly. If the soil is acid a dark blue color will be given to the liquid upon the addition of starch, owing to the liberation of iodine by the potassium iodide and its subsequent union with the starch, with the formation of starch iodide.

Christensen and Larsen[2] conclude from a comparison of laboratory and plat experiments that the latter are more reliable for estimating the lime requirements.

Lipman[3] suggests a bacteriological method based upon the fact that certain types of organisms will not grow in bouillon in which the acidity exceeds 2%. The addition of a soil to a neutral medium will retard growth in proportion to the acidity.

Gregoiri[4] proposes a method which is based upon the liberation of iodine from a mixture containing an iodide and iodate.

Jones[5] mixes the soil in a mortar with calcium acetate and water to a paste, makes up to standard volume, filters and titrates an aliquot part with a fixed alkali using phenolphthalein as an indicator.

Hutchinson and MacLennan[6] propose treating the soil with an excess of calcium carbonate in water solution, shaking for three hours and determining the calcium remaining in an aliquot part of

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[1] Zeitschrift Lander. Versuchsn. Oesterr., 1909, 12, p. 461
[2] Exp. Sta. Rec., 1911, 24, p. 527.
[3] U. S. Dep. of Agr.,Bureau of Chem.,Bul. 152, 1912, p. 50.
[4] Exp. Sta. Rec., 1913, 28, p.708.
[5] American Fertilizer, 1913, 39, No. 11, p. 28.
[6] Chemical News, 1914, 110, p. 61.

the solution. The loss represents the amount of calcium absorbed.

MacIntire[1] proposes a method which is practically the Hutchinson and MacLennan method above, which he uses for determining the immediate requirements of soils.

Truog[2] suggests a qualitative method based upon the liberation of hydrogen sulphide from zinc sulphide in the presence of calcium chloride. The hydrogen sulphide is tested for with lead acetate paper.

Hanley[3] notes that on boiling a neutral or alkaline soil with a 1.25 percent sugar solution for two hours, the sugar remains comparatively unchanged, but, with an acid soil, a marked inversion of the sugar occurs. He suggests that this difference in behavior may be useful as a test for acidity.

Connor[4] proposes the determination of the speed of hydrolysis of ethyl acetate as a measure of soil acidity.

Ames and Schollenberger[5] make comparisons of a number of methods including the vacuum method which is essentially a modification of the method of Tacke, but instead of boiling the mixture of soil and calcium carbonate at 100°C. the soil is heated in contact with finely divided calcium carbonate under reduced pressure as in the Marr[6] method for determination of soil carbonates.

Truog[7] proposes adding an excess of barium hydroxide to the soil and allowing it to act just one minute, then adding carbon

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1. Jr. Ind. Eng. Chem., 1915, 7, p. 864.
2. Wis. Agr. Exp. Sta., 1915, Bul. No. 249.
3. Jr. Agr. Sc., 1916, 6, p. 63.
4. Jr. Ind. Eng. Chem., 1916, 8, p. 35.
5. Jr. Ind. Eng. Chem., 1916, 8, p. 243.
6. Jour. Agr. Science, 3, pt. 2, p. 155.
7. Jr. Ind. Eng. Chem., 1916, 8, p. 341.

dioxide to precipitate all of the excess barium. After evaporating to dryness, the amount of barium absorbed is calculated from a determination of the carbon dioxide evolved with acid. This he calls active acidity. By evaporating the barium hydroxide mixture at the temperature of a boiling water bath, adding water, and passing in carbon dioxide and making a determination of the carbon dioxide absorbed, he obtains a figure which he calls total acidity. The difference between total acidity and active acidity he calls latent acidity. He shows that it makes little difference what base is used to determine the acidity. ¶ Bonyoucus[1] suggests a freezing point method as a means of determining both the nature of the acidity and the lime requirement of soils.

## DISCUSSION OF METHODS

The litmus paper method proposed by Voelcker[2] is not a quantitative method and it has been shown by Barlow[3] that there is no correlation between the time required for the color change and the degree of acidity except possibly in the case of soils whose lime requirement is two tons or more to the acre. The litmus paper must be placed in contact with the soil as it is rare that the soil solution will have an effect upon the color of the paper. The fact that the soil will, while the soil solution will not, affect the color of litmus paper is explained by Cameron[4] by the selective absorption theory. Certain soil constituents have se-

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1. Mich. Tech. Bul., 1916, No. 27.
2. Loco. cite.
3. Jr. Am. Soc. of Agron., 1916, 8, p. 29.
4. The Soil Solution, Easton, Pa., 1911, p. 66.

lective absorption powers taking up the base of the litmus leaving the red dye upon the paper. The litmus paper test is without question a valuable qualitative method, because of its reliability and convenience.

The method proposed by Müntz[1] was investigated by Wheeler, Hartwell, and Sargent[2] who demonstrated that there is not necessarily any relation between the color of the ammoniacal extract and acidity of the soil.

Holleman's method[3] at best is qualitative only and since it is much slower and tedious than the litmus paper test, there can be no advantage claimed for its use.

Tacke's method[4] has not come into general use, but that it has promise is shown by the number of suggested modifications.

Bezzell and Lyon[5] object to the Albert method[6] as proposed by him upon the ground that the reaction between barium hydroxide and the soil is not immediate.

Moulton and Trowbridge[7] from their investigations conclude that the Bézzell and Lyon modification of the Albert method gives a lime requirement which is proportional to the strength of the barium hydroxide used, the period over which the distillation is carried, and the volume of the distillate. They find the method as difficult of manipulation as the Veitch.[8]

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1.Loc. cit.
2.Loc. cit.
3.Loc. cit.
4.Loc. cit.
5.Loc. cit.
6.Loc. cit.
7.Jr. Ind. Eng. Chem, 1914, 6, p. 835.
8.Loc. cit.

It would appear that the Albert method and the Bezzell and Lyon modification are very unsatisfactory.

The Veitch method is probably the method most generally used for quantitative determinations of soil acidity, but has the objection that it is slow and at best gives only an approximation. Truog[1] claims that the method of Veitch gives a lime requirement which is much too low because of the hydrolysis effect at the temperature at which the test is made.

The Hopkins[2] method has been criticized by Cameron,[3] Harris,[4] Freer[5] and others upon the ground that it is not a measure of the acidity of the soil or of the lime requirement, but represents the selective ion adsorption by the colloidal bodies present, under the conditions to which the soil is subjected in making the test. Cameron[6] compares the absorption of a base from solutions of neutral salts by cotton, paper, and soils, considering it to be due to the same cause in each case. He also states[7] that from potassium chloride solutions free hydrochloric acid is left in solution. Hopkins[8] states that it developes that bleached cotton may retain sufficient acid used in the bleaching process to change the color of litmus.

Truog[9] in a recent article combats the selective adsorption

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1. Jour. Ind. Eng. Chem., 1916, 8, p. 35.
2. Loc. cit.
3. U.S. Dep. of Agr. Bureau of Soils, 1905, Bul. No. 30, p. 34.
4. Jr. Phys. Chem., 1914, 18, p. 355; Mich.Agr.Exp.Sta.Bul.No.19
5. Dep. of Agr. Penn., 1915, Bul. No. 261, p. 106.
6. The Soil Solution, 1911, p. 62
7, Ibid.
8. Soil Fertility and Permanent Agriculture,1910, p. 566.
9. Jour. Phys. Chem., 1916, 20, p. 457.

theory of Cameron[1] and Harris[1] and brings evidence to show that soil acidity is due to true acids present in the soil. From his experiments[1] he finds that absorbent cotton shows much greater absorbtive powers for cations than raw cotton, and points to the fact that a consideration of the method of preparation of absorbent cotton will give chemical reasons for its acid character.

Harris[2] shows that the acidity is dependent upon the character of the salt solution used and uses it as an argument to support his views that the difference is due to selective ionic adsorption. It may be inferred that this was noted by the authors of the Hopkins method, since in changing from sodium chloride to potassium nitrate the factor for calculating the acidity is also changed, but they attribute it to a different cause.

The objection to Gregoirie's method is that other compounds in the soil besides weak organic acids will set free iodine.

Ames and Schollenberger[3] in a recent article compare the results obtained by the Hopkins, Hutchinson-MacLennan, MacIntire, Veitch and Vacuum methods upon soils from a number of variously treated plots from one of the fertility sections of the Wooster farm, located on silt loam soil which is largely derived from sandstones and shale. A great variation for the lime requirement was obtained by the different methods. Attention is called to the fact that all of these methods are emperical in nature, and comparatively slight variations in the procedure affect the results obtained markedly.

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1. Journal. Phys. Chem.,1916, 20, p. 457.
2. Journal. Phys. Chem, 1914, 18, p. 346.
3. Journal. Ind. Eng. Chem., 1916, 8, p. 243.

Veitch[1] had previously noted a great difference in lime requirements as determined by the Hopkins and Veitch methods. The greatest difference was shown[2] by soils containing large quantities of organic matter.

MacIntire[3] shows that the loss of carbon dioxide from an excessive application of magnesium carbonate is more rapid and complete than where an equivalent quantity of calcium carbonate was applied. The soil decomposes from three-fourths to more than four times the Veitch requirement of calcium carbonate in a year. As an explanation between the speed of decomposition of magnesium and calcium carbonate he suggests that there is greater activity of acid silicates for magnesium than for calcium. A further suggestion is made[4] that a soil may be alkaline from the presence of magnesium silicates, but would still require remedial lime treatment.

The variation obtained for the lime requirement upon the same soil by different methods is so great that unless the method used is specified results cannot be compared.

## WHAT IS AN ACID SOIL?

Voelcker[5] really defines an acid soil upon the basis of the litmus paper test, and it is evident that this is the determining test in the minds of investigators, but Frear[6] states that in his experience not all soils acid to litmus show acidity by the

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1. Jour. Am. Chem. Soc., 1904, 26, p. 637.
2. Ibid, p. 654.
3. Tenn. Exp. Sta. 1914, Bul. No. 107, p. 157. 4. Ibid, p. 197.
5. Jour. Agr. Soc., 1865, p. 115.
6. Dep. of Agr. Pa., 1915, Bul. No. 261, p. 104.

Hopkins' reagent, and Ames and Schollenberger[1] show that soils acid to litmus do not all show a lime requirement by the Veitch test, but instead may even be alkaline.

The methods proposed for testing for soil acidity or for determining the lime requirement may lead to other definitions which may or may not produce the same end result when put into practical use. The wide difference in results reported upon the same soil by the use of different methods makes it quite evident that a slight variation in procedure may effect enormously the end result. Further, the work of MacIntire[2] and Truog[3] indicates quite clearly that the reactions which take place in soil are of such an order that time becomes an important factor.

## SOME PROPERTIES OF COLLOIDS.

Bancroft[4] defines a colloid in the following words, "We now call a phase colloidal when it is sufficiently subdivided, not committing ourselves definitely as to what degree of subdivision; Colloidal Chemistry is, therefore, the Chemistry of bubbles, drops, grains, films, and filaments."

Cameron[5] states that soil chemistry may be considered a branch of colloidal chemistry provided a colloid is defined as a phase sufficiently divided so that the surface phenomena are predominant.

Ostwald[6] emphasizes the fact that colloidal chemistry is

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1. Jr. Ind. Eng. Chem., 1916, 8, p. 243.
2. Loc. cit.
3. Loc. Cit.
4. Jr. Phys. Chem., 1894, 18, p. 549.
5. Jour. Phys. Chem., 1915, 19, p. 1.
6. Handbook of Colloidal Chem., Eng. Translation 3" German edition, 1915, p. 3.

not a study of colloidal substances but a study of the colloidal state and makes the following significant statements regarding colloidal phenomena[1]: "As is well known the surfaces of solid and liquid bodies of ordinary dimensions exhibit a whole series of peculiar phenomena, the intensity of which increases in direct proportion with the absolute and specific surfaces of the bodies. As examples, might be mentioned the condensation of gases on solid surfaces, the many effects of surface tension and the fact that the majority of electrical phenomena appear at surfaces. We are driven to conclude that all these phenomena observed at ordinary surfaces increase enormously in intensity and that they may even change qualitatively when we come to deal with surfaces." And[2] "The difficulty of washing out the last traces of electrolytes from precipitates, especially such as are gelatinous, like aluminum and ferric hydroxides, compels one to conclude that colloids tend to concentrate electrolytes upon themselves."

## 1. Adsorption.

Way[3] in his several papers noted that soils showed a marked absorptive power for a number of substances and concludes that clay is the active substance retaining manure. He[4] found that there was a progressive absorption of lime by soil which depended upon the time of contact. The greater portion of the lime being absorbed immediately but further absorption takes place slowly for some time (Compare MacIntire[5] and Truog[5]) and the amount ab-

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[1] Handbook of Colloidal Chem., Eng. Translation 3" German edition, 1915, p. 28.
[2] Ibid, p. 234.
[3] Jr. Roy. Agr. Soc., 1850, 11, p. 313, ibid, 1852, 13, p. 123.
[4] Ibid, 1854, 15, p. 491.
[5] Loc. cit.

sorbed depended upon the strength of solution.

The work of Bodlander[1], Hardy[2], Bechhold[3] and Freundlich[4] show that different concentrations of various electrolytes are required to precipitate colloids from solutions, but Whitney and Ober[5] observed that from neutral salt solutions equivalent amounts of cations were carried slowly by the precipitation of colloidal arsenious sulphide.

Picton and Linder[6] showed that when colloidal arsenious sulphide solutions were precipitated by barium chloride solutions a small part of the barium was held in the precipitate which could not be washed out with water, but could be displaced by another base.

Duclaux[7] found that when a colloidal solution of arsenious sulphide was precipitated by the addition of barium chloride a quantity of arsenic remained in solution corresponding closely to the barium taken up.

Linder and Picton[8] observed that colloidal arsenious sulphide migrates to the anode and colloidal ferric hydroxide toward the cathode under the influence of an electric field. The behavior of many colloidal substances has been investigated since.

A calculation of the charges on a single particle of col-

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[1] Jahrb. Mineral., 1893, 2, p. 147.
[2] Zeitsch. Phys. Chem., 1900, 37, p. 385.
[3] Zeitsch. Phys. Chem., 1904, 48, p. 385.
[4] Zeitsch. Phys. Chem., 1903, 44, p. 144.
[5] Jour. Am. Chem. Soc., 1901, 23, p. 842.
[6] Jour. Chem. Soc., 1895, 67, p. 63
[7] Jour. Chem. Phys., 1908, 6, p. 592.
[8] Chem. Soc. Jour., 1892, 61, p. 148.

loidal silver and gold has been made by Burton[1] on the assumption that in the precipitation of these colloids by aluminum chloride the amount of aluminum ion which just precipitates the silver or gold is such that the positive electric charges upon it just equals the negative electric charges on the particles precipitated. The charge on one gram ion equivalent of silver is four per cent of the charge of one gram equivalent of silver ions and the charge upon a colloidal particle of gold is twelve per cent of the charge on one gram ion equivalent of univalent ions. The assumption is made in the above calculations that all the aluminum ions took part in the discharge of the colloids.

Lewis[2] believes that only a fraction of the aluminum ions are available; therefore, the results calculated by Burton[1] are much too high.

Van Bemmelen's[3] work shows that the absorption by silicic acid is proportional to the concentration of the solution and the quantity of weakly held hydrated water in silicic acid.

The origin of the electrical charges upon the colloidal particles was at first obscure. At present, two theories have been advanced.

Noyes[4] suggests that the aggregates of a substance collect around negative or positive ions forming negative or positive colloids respectively. From this theory the assumption may be made that the colloidal particles could collect around the ions produced from the ionization of water. Suppose that the colloid

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1. Phil. Mag., 12, Su. 6, 1906, p. 477.
2. Zeitsch. Kolloide, 1909, 4, p. 209.
3. Jr. Prackt. Chem., (2), 1881, 23, p. 324-349.
4. A Textbook of Chemistry, New York, 1913, p. 262.

collects around the negative hydroxyl ions. When an electrolyte is added such as a neutral salt the positive ions of the salt combine with the negatively charged colloidal particle neutralizing it while the positive hydrogen would be left in solution, and the solution remains electrically neutral, but the solution would remain acid in exact proportion to the amount of positive ions carried down by the precipitated colloid.

Suppose that a colloidal solution was filtered; upon the basis of the theory the filtrate should be neutral otherwise an electro static condition would develop.

Electrically, or Chemical?

It has been suggested that colloidal particles may acquire their charges like any other ions by the process of electrolytic dissociation. This process is well illustrated by Mathews[1]. This theory assumes an electrical double layer next the colloidal particles.

That many soils in contact with water give an acid reaction which may be measured has been shown by Gillespie[2] although usually water filtered from an acid soil does not give an acid reaction by the ordinary chemical methods as used, nor would this be expected if either of the above theories may be applied, assuming that soil acidity is due to soil colloids.

Gibbs[3] from purely theorectical considerations derived the theorum that substances which lower the surface tension of a pure disperse medium, tend to collect in its surfaces. This has been experimentally demonstrated by Zawidski[4] and later by Miss Benson.[5]

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[1] Physiological Chemistry, New York, 1915, pp. 219-221.
[2] Jr. Wash. Academy of Sciences, 1916, 6, p. 7.
[3] Trans. Conn. Academy, 1876, 3, p. 439.
[4] Zeitsch. Phys. Chem., 1900, 35, p. 77.
[5] Am. Jr. Phys. Chem., 1903, 7, p. 532.

Freundlich and Seal[1] by the capillary tube method show that potassium chloride increases the surface tension of water.[2]

Truog[3] in comparing the work of Picton and Linder[4] and Whitney and Ober[5] upon the absorption of barium from barium chloride by colloidal arsenic trioxide with his own findings with respect to the amount of lime absorbed by acid soils, shows that the latter is far too great to be accounted for by any theory of colloidal adsorption.

## DIVISION OF INVESTIGATIONS

For convenience, the studies reported in this paper are divided into four parts. Part I is a study of acid soils by means of the hydrogen electrode. Part II is an investigation of the Hopkins and Pettit[6] method for the determination of soil acidity. Part III is a comparison of various methods for determining lime requirement of soils with the hydrogen electrode. Part IV is a discussion of a proposed method for determining the lime requirement of soils.

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[1] Z. Chem. Ind. Koll., 11, p. 259.

[2] See Castell-Evans Physical Chemical Tables Vol. II, 1911, London, for data for other salts.

[3] Jr. Phys. Chem., 1916, 20, p. 470.

[4] Jr. Chem. Soc., 1901, 67, p. 842.

[5] Jr. Am. Chem. Soc., 1901, 23, p. 842.

[6] Loc. cit.

# PART I.

## INVESTIGATIONS OF ACID SOILS BY MEANS OF THE HYDROGEN ELECTRODE.

Although the literature upon the subject of soil acidity is rather voluminous, so far as the writer is aware, no attempt has been made to follow the change in hydrogen ion concentration of soil solution in contact with the soil under various conditions.

As the hydrogen electrode is becoming quite generally used for determining hydrogen ion concentration of solutions, especially by chemists and biologists, it was believed that it could be modified to serve the purpose of these investigations.

Gillespie[1] has already made use of it for determining the hydrogen ion concentration of a mixture of soil with pure water, however, for reasons which will develop, no attempt was made by him to investigate the hydrogen ion concentration of a soil and water without the presence of a conducting medium.

The principal studies made by the writer are: speeds of reaction between neutral salt solutions and soils, speed of reaction in the presence of a base, change in hydrogen ion concentration with change of amount of base and with time, and change in conductivity.

## THEORY OF THE HYDROGEN ELECTRODE.

When a metal is placed in a solution of its salt, there is developed an electrical potential between the solution and metal

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[1] Loc. cit.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

due to a reaction which may be expressed by the equation $M = M^{+} + {}^{\ominus}$ The E. M. F. may be expressed mathematically by the Nernst[1] equation $E = E_o + \frac{RT}{NF} \text{Log}_e C$ when E is the potential at an ion concentration C, $E_o$ is the potential when the ion concentration is one gram equivalent per liter, R is the gas constant 8.316 joules, T. the temperature on the absolute scale, N is the number of charges carried by each ion, and F is Farraday's number, about 96500 coulombs.

To determine the potential of a metal dipped in a solution of ions of the metal which we shall call a half cell, it is necessary to measure it through another half cell thus,

$$M_x \mid \text{Salt}_x \parallel \text{Salt}_y \mid M_y$$

the chain taking the form of a galvanic cell. The total potential of the chain neglecting the slight potential differences at the contact of the two salts x and y is the algebraic difference of the two half cells and may be expressed as follows,

$$E = E_{ox} + \frac{RT}{NF} \log_e C_x - E_{oy} - \frac{RT}{NF} \log_e C_y$$

where E is the observed voltage of the chain.

Should one of the half cells be a gas concentration cell, the pressure of the gas will exert an influence upon the potential of the gas and the equation becomes[2]

$$E = E_{ox} + \frac{RT}{NF} \log_e C_x - E_{oy} - \frac{RT}{NF} \log_e C_y + \frac{RT}{2F} \log_e \frac{P}{P_o}$$

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[1] Zeit. Phys. Chem., 1889, 4, p. 129.

[2] MacInnes, Trans. Am. Elect. Chem. Soc., 1916, 29, p. 317.

for a diatomic gas where $P_0$ is the standard pressure 760 m.m. and P is pressure at which readings are taken.

As ordinarily used in practice for determining hydrogen ion concentration a calomel half cell constitutes the fixed portion of the chain and in the work reported in this paper the complete chain is as follows:

$$Hg \mid HgCL \text{ in } N\ KCl \parallel .5\ N\ KCl \mid H \quad H_2$$

The best values for the calomel half cell upon the scale of $E_0$ for hydrogen $+0.00$ is $+0.275$ volts[1] and this value was used in all calculations. The equation may be simplified as follows:

$$E = 0.275 - \frac{RT}{F} \log_e C_H$$

$$\text{or} \quad \log_e \bar{H} = \frac{F(0.275-E)}{RT}$$

$$\log_{10} H = \frac{F(0.275-E)}{2.303\ RT}$$

$$= \frac{5038.7(0.275-E)}{T}$$

from which the hydrogen ion concentration may be readily calculated from the electro motive force of the chain.

## DESCRIPTION OF APPARATUS.

Preliminary experiments were conducted with an apparatus similar to that described by Hildebrand[2] and some experiments described elsewhere with soil solutions were carried out, but for use with solutions in contact with the soil it was found to be very unsatisfactory. For all the work reported unless otherwise

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[1] Abegg, Anerbach & Luther, Abhandel. Deutsch. Bunsen Ges., No.8 1915, p. 46.

[2] Jr. Am. Chem. Soc., 1913, 35, p. 847.

stated, a high grade potentiometer[1] was used with a gas cell especially designed for the work.

## The Gas Cell

The gas cell shown in Plate I was designed for this work. It is cylindrical in shape, 3.3 Cm. in diameter, and 16 cm. in length, the ends being rounded off. An opening at one end is provided of a size to carry a No. 4 rubber stopper, through which pass the connection (a) to the platinum plate (b) to serve as the hydrogen electrode, the tube (d) for the ingress of hydrogen gas and tube (e) for the outlet. Tubes (b) and (e) have capillary tubes sealed into the ends to regulate the flow of hydrogen. To make connections with the calomel half cell a glass tube (g) is provided at the further end of the gas cell provided with a stop cock (e) and a restricted tip (f). This tube reached to within a few mm. of the bottom of the gas cell and as it did not readily clog with soil was found to be very satisfactory. The gas cell was designed to be of 100 cm. capacity and to be filled half full of liquid leaving room for 50 c. cm. of gas. The reasons for this arrangement will develop later.

The hydrogen electrode (b) is a rectangular piece of sheet platinum 1.2 x 2.4 cm. with pieces of platinum wire welded to each end. The wires were sealed into the glass tube at each extremity as shown making connections with the mercury in the tube and at the same time supporting the electrode rigidly. The de-

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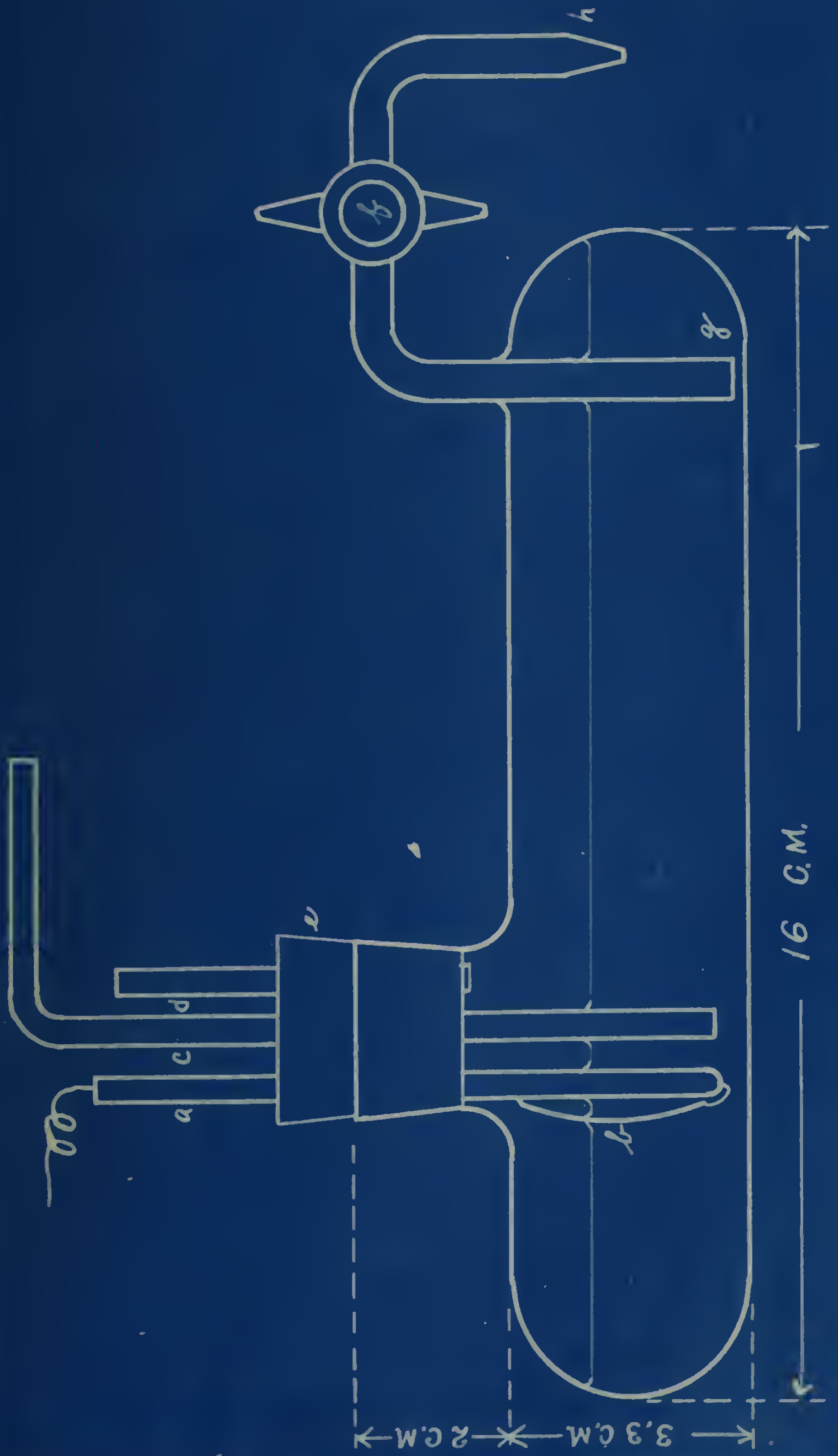
[1] Leeds of Northrup No. 28952.

PLATE I.



sign of the electrode is similar to that used by Gillespie[1] in his researches.

Since most soils would tend to settle out of solution, it was necessary to provide some agitating arrangement to keep the soil and solution thoroughly mixed at all times.

Plate II shows diagramatically the method of agitating the cell and the connections as measurements were being made. (a) is the calomel electrode provided with a stop cock (b), and (c) is a U tube filled with normal potassium chloride making connection with the hydrogen gas cell by the tube (d). All are placed upon a tilting table hinged at the point (o) to the base (p). The table is rocked by means of the adjustable arm (k) and crank (l) attached to suitable gears and pullies to a constant source of power.

It was found by experiment that by giving the table 72 complete oscillations per minute through a total angle of 6° and 7° the liquid was thoroughly agitated, that the rubber stopper carrying the electrode and gas tube was not wetted, but that the soil was kept thoroughly mixed with the solution while the coarser particles of sand in the soil would tend to collect in a nodal point (s) in the bottom of the cell. At this speed the hydrogen bubbles rose to about the point (r) before they broke so that the cell was quickly and well scavanged of air. Except for very light peat soils there was no tendency for the soil mixtures to ascend into the tube (d).

The arrangement of the different parts of the apparatus as used in making measurements is shown diagramatically in Plate

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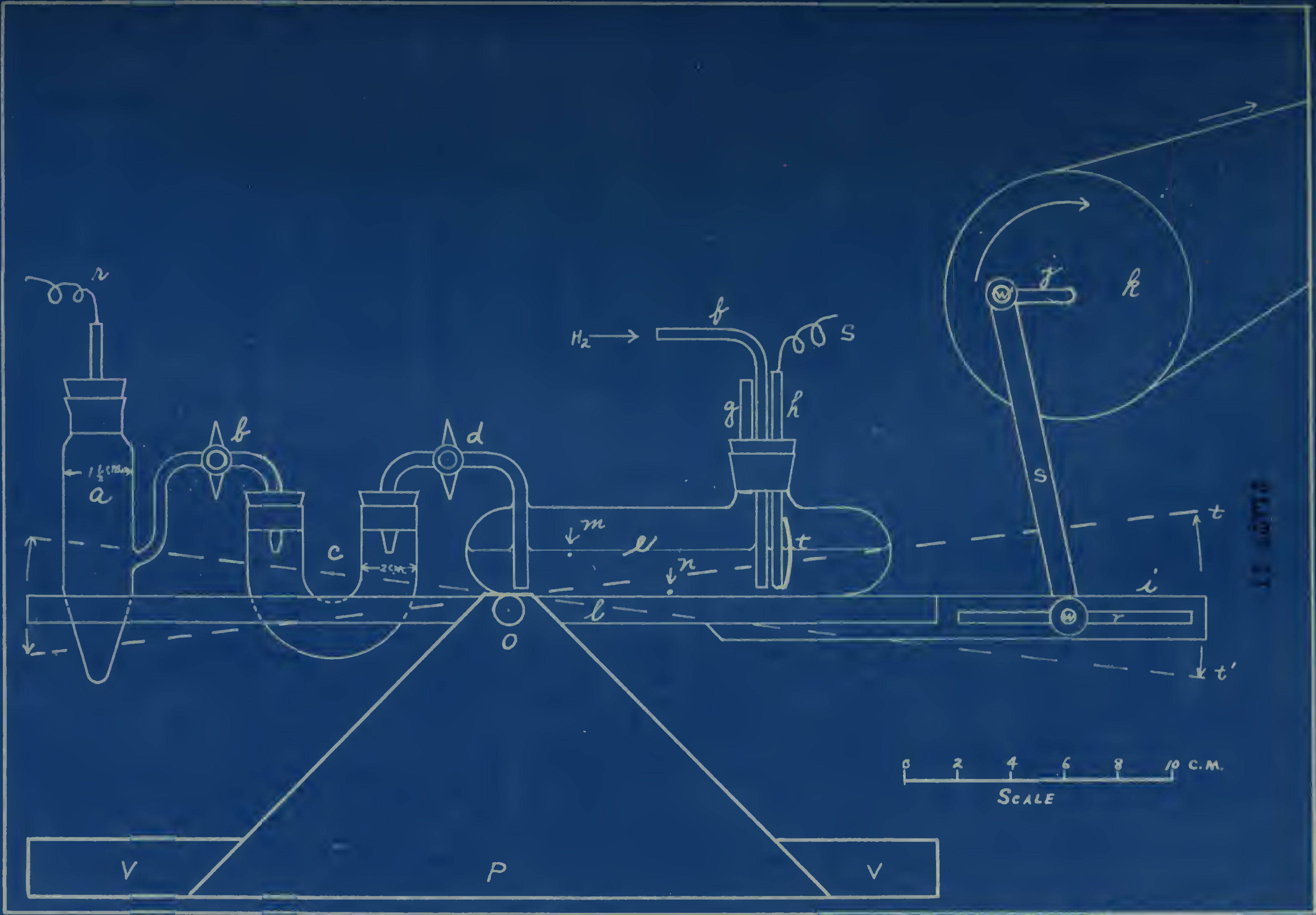
[1] Wash. Academy, 1916, 6, p. 7.

PLATE II



III. As will be noted the apparatus is designed to carry two gas cells marked E. M. F., that duplicate measurements may be made without changing cells.

The use of a U tube for making connection between the gas cell and calomel electrode was found to be a most satisfactory arrangement. The resistance of the chain is increased slightly but has the very desirable advantage of reducing diffusion markedly. During several weeks continuous use the calomel electrode changed less than .0005 volt.

The gas cell was designed to meet the following conditions: (a) large capacity, (b) absence of dead air spaces, (c) ease of cleaning, (d) all glass contact with liquid, (e) freedom from clogging, (f) ease of manipulation, (g) adaptability to agitation, (h) minimum diffusion; all of which seem to have been met in this form of cell.

## The Calomel Electrode.

Calomel was prepared by treating pure mercury with dilute nitric acid, precipitating with hydrochloric acid, washing with distilled water until free from acid, washing twenty times with normal potassium chloride and finally shaking up with normal potassium chloride and pure mercury as recommended by Ellis[1] for obtaining an electrode of constant potential. The electrodes were prepared with this gray mixture of mercury and calomel and normal potassium chloride by first putting into the bottom of the carefully cleaned electrode cell a small amount of pure mercury

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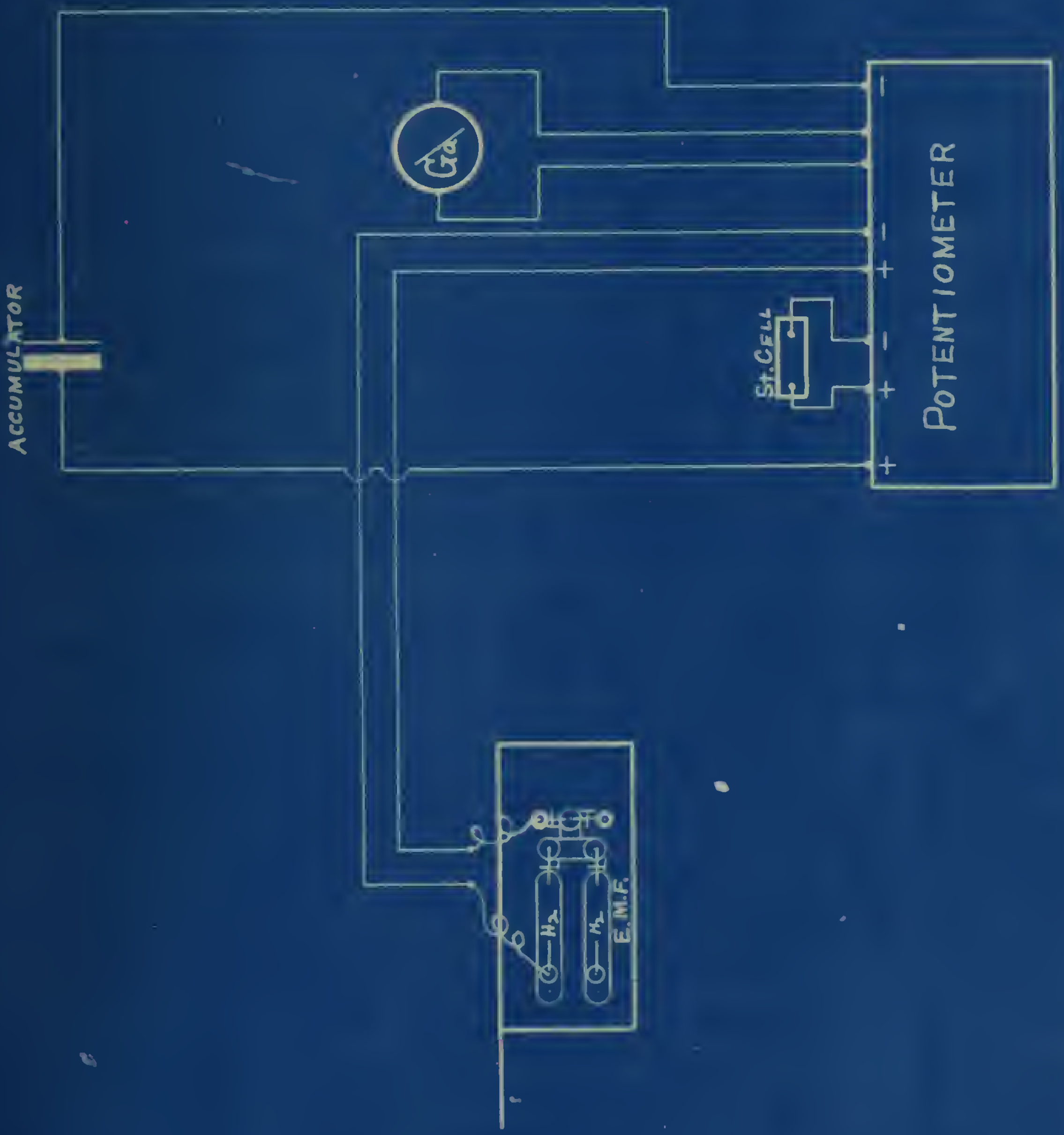
[1] Jr. Am. Chem. Soc., 1916, 28, p. 737.

PLATE III.



to cover the platinum connection. No difficulty was experienced in getting electrodes to check within .0005 volt.

The stop cocks upon the tubes leading from the calomel electrodes were well greased and were opened only when readings were being taken. Connection was made to the U tube (c), Plate II, through a rubber stopper well driven home, making this side of the system practically gas tight.

## Setting up the Apparatus.

### The Gas Cell

To fill the tube (g), Plate I, of the gas cell, one of two methods was used. Either the cell was partially filled with one-half normal salt (KCl), a stopper inserted in the opening (h) and pressure exerted, so that, when the stop cock (e) was opened, the liquid would fill the tube (g) and flow out at (f), the excess salt solution being poured out; or the material in the tube, upon which measurement was to be made was forced out by pressure as indicated above. In either case, care was taken to thoroughly wet the stop cock (e) by loosening and turning. All measurements were made with this stop cock closed.

### Hydrogen Electrode.

The platinum electrode was prepared by plating the cathode in a 1% solution of platinum chloride containing a small amount (about .05%) of lead acetate to cause the platinum black to adhere. Attempts were made to use pure platinic chloride as recommended by Ellis[1] but this proved unsatisfactory as the platinum black in-

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[1] Jr. Am. Chem. Soc., 1916, 28, p. 737.

variably washed off within a few minutes after being placed in the cell.

In plating a platinum anode was used. The strength of the current used for plating was varied from time to time but no variation in the potentials of the electrode or in the time required to become saturated with hydrogen was noted from this cause. If the evolution of hydrogen was too lively some of the platinum black was loosened. The plating was continued from one to two hours. The electrodes were placed in distilled water and given a final wash just before using.

## Source of Hydrogen.

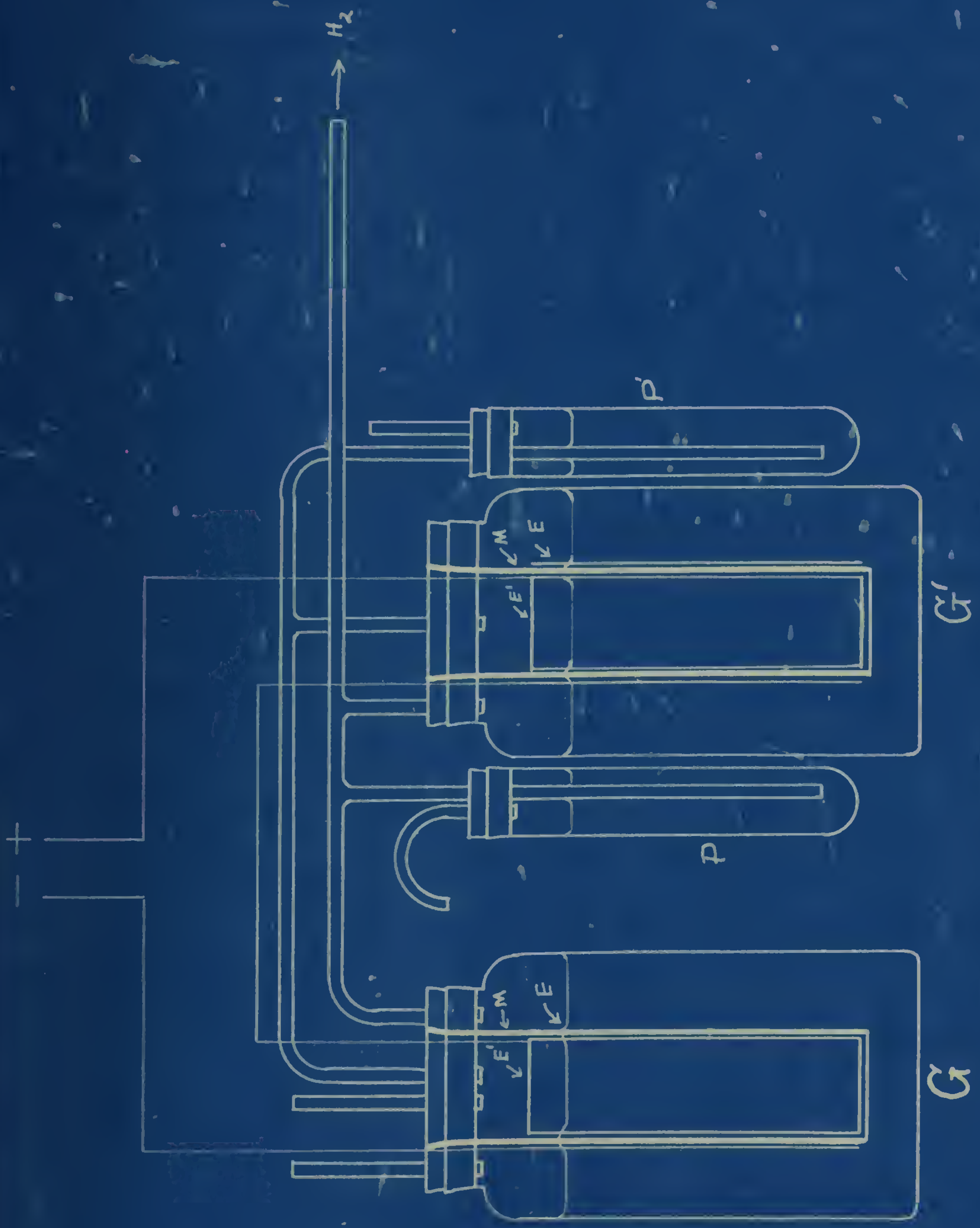
Hydrogen was prepared electrolytically as needed, using potassium hydroxide for the electrolyte and nickel electrodes, Plate IV.

To separate the electrode and reduce diffusion of the gas to a minimum the electrode compartments were separated by a glass tube M running to within a few centimeters of the bottom of the cell. Two cells were used in parallel and electrolyzed with a current of 10 amperes giving a total of 150 c.c. of hydrogen per minute. General precautions were taken in washing and purifying the gas.

## Procedure.

After the gas cell was filled with soil and solution and placed as shown in Plate II, the table was oscillated and hydrogen run in at (f) for four or five minutes; the tube (g) was then closed with a pinch cock and the rocking continued for four minutes; hydrogen was again run in for four minutes to drive out the

PLATE IV.



last traces of air; pinch cock on (g) was again closed; the tube (b) opened and readings were taken immediately.

The procedure varied somewhat with the number of readings to be taken, type of experiment, etc. If readings were to cover a period of half an hour or more, after the first large volume was run in, it was found advisable to allow a small amount to bubble through to over come any diffusion which might take place through the rubber connections.

## Descriptions of Soils Investigated.

Yellow-gray silt loam. An acid subsoil collected from the southern part of the state of Illinois. On the basis of two million pounds, this soil gave a lime requirement by the Hopkins method of 4.2 tons and by the Veitch method of 5.6 tons, calculated as calcium carbonate. No carbonates were present as determined by the Marr method.

Black peaty loam. Sample No. 1-281 collected by C. G. Hopkins near Bolton, N. C. The limestone requirement by the Hopkins method was 6,890 pounds.

Black clay loam. Sample No. 1-284 collected by C. G.Hopkins near Bolton, N. C. Some leaf mold was present. Limestone requirement by the Hopkins method was 9,964 pounds.

Peat. Sample No. 1-241, labeled deep peat or muck, collected near Titusville, Fla., by C. G. Hopkins. Limestone required by the Hopkins method was 6,535 pounds.

Black Muck. Sample No. 1-242 collected from Wauchula, Fla., b C. G. Hopkins. Limestone requirement by the Hopkins method was 8112 pounds.

Yellow silty clay. Sample No. 2660 collected from Clay County, Illinois. A sticky clay stiff and plastic. A subsoil sample. Limestone required by the Hopkins method was 5.08 tons.

Gray clayey silt. Sample No. 2968 collected from Jackson County, Illinois. A compact, almost impervious subsoil containing iron blotches and concretions. Limestone required by the Hopkins method was 7.92 tons.

Gray plastic clay. Sample No. 3957 collected from Winebago County, Illinois. A subsoil sample containing clayey sand. Limestone required by the Hopkins method was 2.6 tons.

Yellow plastic clayey silt. Sample No. 3559 collected from Clay County, Illinois. A subsoil sample. Limestone required by the Hopkins method was 4.67 tons.

Yellow silt loam. Sample No. 4068 collected from LaSalle County, Illinois. A subsurface sample, having a lime requirement by the Hopkins method of 2.89 tons.

Brown sandy loam. Sample No. 6316. A subsurface sample having a limestone requirement by the Hopkins method of 1.65 tons.

## EXPERIMENT I.

### Speed of Reaction between an acid soil and a neutral salt.

This experiment was planned to observe the speed of change in hydrogen ion concentration of a neutral salt solution when shaken together with an acid soil.

The gas cell was filled with 50 c.c. of 0.5 N. salt solution and after the potential had become constant, which was usually within ten minutes, 5 grams of soil (2½ grams in the case of peat soil) were quickly introduced and readings were taken at stated intervals.

## Table I.
## SPEED OF REACTION BETWEEN ACID SOIL AND NEUTRAL SALT.
Results are given in volts.

| | Yellow-Grey Silt Loam | | | Brown Sandy Loam | Yellow Plastic Clay Silt | Peat |
|---|---|---|---|---|---|---|
| Time minutes | .5 N. KCl | $\frac{1}{4}$ Mol. $CaCl_2$ | .5 N. $KC_2H_3O_2$ | .5 N. KCl | .5 N. KCl | .5 N. KCl |
| 0 | 0.6969 | 0.6823 | 0.7295 | 0.6966 | 0.6967 | 0.6967 |
| 5 | 0.4843 | 0.4947 | 0.6715 | 0.5658 | 0.4944 | 0.5706 |
| 10 | 0.4843 | 0.4950 | 0.6707 | 0.5660 | 0.4944 | 0.5691 |
| 15 | 0.4848 | 0.4950 | 0.6706 | 0.5660 | 0.4944 | 0.5687 |
| 20 | 0.4854 | 0.4950 | | | 0.4944 | 0.5687 |
| 25 | 0.4860 | | 0.6693 | | 0.4946 | 0.5688 |
| 30 | 0.4865 | 0.4950 | | 0.5660 | 0.4946 | 0.5690 |
| 40 | 0.4871 | | 0.6693 | | 0.4950 | 0.5692 |
| 60 | 0.4878 | 0.4957 | 0.6693 | 0.5664 | | 0.5696 |
| 90 | 0.4890 | 0.4963 | | | | |
| 120 | | | | 0.5670 | 0.4969 | |
| 180 | 0.4895 | 0.4972 | 0.6688 | | 0.4984 | |
| 240 | | | | | 0.5010 | |
| | 0.4963* | | | 0.5733# | 0.5063" | |

* After 24 hours.
\# After 48 hours.
" After standing over night.

It will be noted that the lowest voltages are read within five minutes which corresponds to the highest concentration of hydrogen ions. The only exceptions noted are (1) with the peat, which may be accounted for by the fact that the peat did not wet readily with the solution, (2) with the yellow-gray silt loam with potassium acetate, which will be discussed in connection with the next experiment.

After the lowest point is reached there is a gradual increase in voltage corresponding to a decrease in the hydrogen ion concentration.

It is quite evident that the main reaction between the salt solution and the soil reaches an equilibrium very quickly. Secondary reactions are indicated by an increase in the voltage after a lapse of considerable time except in the case when potassium acetate was used. In this case there are apparently only slight secondary reactions.*

## EXPERIMENT II.

### Speed of Reaction in the presence of a base.

This experiment was conducted similarly to Experiment I. 50cc of .5 N KCl solution containing the quantities of $Ca(OH)_2$ calculated as calcium carbonate was used.

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* An attempt was made to use potassium nitrate but it was noted that even in a neutral solution reduction took place to an extent which could be noted with organic indicators.

## Table II.

Speed of Reaction in presence of a base.

Results are recorded in volts.

|  | Brown Sandy Loam | Yellow-Gray Silt Loam. |  | Yellow Plastic Clayey Silt. | Peat. |
|---|---|---|---|---|---|
| Time minutes | 2 T. $CaCO_3$ | 4 T. $CaCO_3$ | 10 T. $CaCO_3$ | 5 T. $CaCO_3$ | 10 T. $CaCO_3$ |
| 0 | 0.9543 | 0.9715 | 0.9961 | 0.9803 | 0.9961 |
| 5 | 0.7783 | 0.7483 | 0.8505 | 0.6562 | 0.8345 |
| 10 | 0.7565 | 0.6923 | 0.8410 | 0.6302 | 0.7642 |
| 15 | 0.7440 | 0.6467 | 0.8363 | 0.6228 | 0.7370 |
| 20 | 0.7313 | 0.6161 | 0.8356 | 0.6199 | 0.7173 |
| 25 | 0.7269 | 0.6037 | 0.8337 | 0.6170 | 0.7053 |
| 30 | 0.7232 | 0.5978 | 0.8326 | 0.6148 | 0.6951 |
| 40 | 0.7165 | 0.5935 | 0.8298 | 0.6111 | 0.6809 |
| 60 | 0.7113 | 0.5897 | 0.8273 | 0.6072 | 0.6672 |
| 90 |  | 0.5855 | 0.8262 |  |  |
| 120 | 0.7066 |  |  | 0.5987 | 0.6499 |
| 180 |  | 0.5820 | 0.8206 | 0.5951 | 0.6432 |
|  | 0.7022* |  | 0.8186# | 0.5933" | 0.6394" |

*After 48 hours.

#After 5 hours.

"After 4 hours.

The change in the hydrogen ion concentration is very rapid at first, but continually rises for as long as the experiments were conducted. The plotted curves are all similar in character and of the general type shown in Figure 1, which is for the yellow-gray silt loam with four tons of lime.

Although equilibrium is not reached for a considerable period the greater portion of the reaction takes place within a few minutes under the conditions of the experiments. After the neutral point is reached the hydrogen ion concentration continues to increase at the same relative rate without change. This phenomena would seem to substantiate the work of MacIntire[1], who distinguishes between immediate and continued lime requirements, and Truog[2], who makes the division into active and latent soil acidity, altho there seems to be no good reason for making the division. Both investigators added an excess of lime to the soil, while in certain of the above experiments the lime requirements were not satisfied. Apparently the reaction is in each case an equilibrium reaction, such being the case any division as above is an arbitrary one, and the results will not bear, necessarily, any relation to the total lime requirements.

This experiment would seem to throw some light upon the action of soil with potassium acetate in Experiment I. Potassium acetate is basic in character and even at the end of 180 hours the mixture with soil contained only a slight excess of hydrogen ions.

It would seem from an inspection of the curve that the relation may be expressed imperically by the equation,

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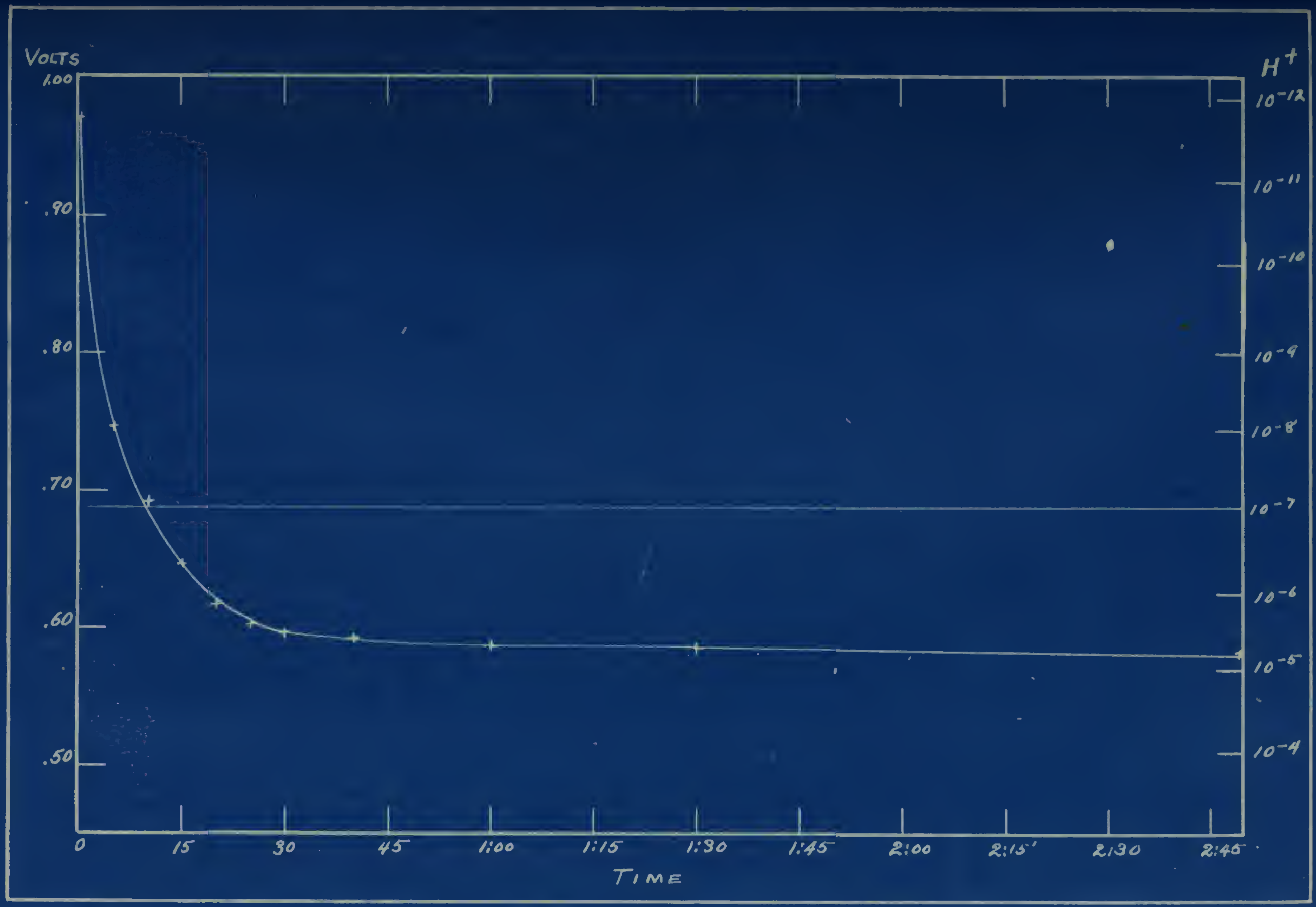
1.Tenn. Exp. Sta. Bul., 1914, No. 107, p. 193.
2.Jr. Ind. Eng. Chem.,1916, 8, p. 341.



Volts
1.00
.90
.80
.70
.60
.50
H⁺
10⁻¹²
10⁻¹¹
10⁻¹⁰
10⁻⁹
10⁻⁸
10⁻⁷
10⁻⁶
10⁻⁵
10⁻⁴
0
15
30
45
1:00
1:15
1:30
1:45
2:00
2:15'
2:30
2:45
Time

Fig 1

$$\frac{dx}{dt} = K\,(A-x)$$

when x is the hydrogen ion concentration with time t, A is the total change in hydrogen ion concentration, and K is a characteristic constant for the system under consideration. It would appear that the longer the interval chosen the more nearly would the results approach the true lime requirement, provided side reactions are not considered. It is quite probable that under field conditions the reactions will be far slower than the above experiment would indicate. In the field conditions are not maintained for rapid reaction while the reverse is true in the laboratory. Here a salt solution has been used with calcium hydroxide, a condition certainly where reaction may take place with the utmost speed.

## EXPERIMENT III.

### Study of the change in hydrogen ion concentration of a Neutral Salt solution to which various amounts of base have been added.

Procedure. 50 c.c. of a .5 N neutral salt solution containing the desired amount of base was placed in the gas cell and readings were taken at the end of 20 minutes. The gas cell was rocked continually as in the former experiments.

In the light of Experiment II it can be readily understood that duplicates are somewhat difficult to obtain unless the manipulation is identically the same and the time factor eliminated. The speed of the reaction should depend somewhat upon the base used and the neutral salt with which it is combined. Considering these facts it is rather remarkable that the results obtained as shown

in Table III should be of the same order. The experiments were all conducted upon yellow gray silt loam.

## TABLE III.

### Effects of various amounts of a base.

Results recorded in volts.

| Base Equivalent to T $CaCO_3$ | .5N KCl $Ca(OH)_2$ | .5N NaCl $Ca(OH)_2$ | .5N $CaCl_2$ $Ca(OH)_2$ | .5N $K_2SO_4$ $Ca(OH)_2$ | .5N KCl KOH |
|---|---|---|---|---|---|
| 0.0 | 0.4843 | 0.4995 | 0.4966 | 0.5245 | 0.4843 |
| 1.0 | 0.5099 | 0.5118 | 0.5105 | 0.5345 | 0.5119 |
| 2.0 | 0.5247 | 0.5180 | 0.5259 | 0.5527 | 0.5269 |
| 2.5 | | | | | |
| 3.0 | 0.5428 | 0.5575 | 0.5475 | 0.5679 | 0.5505 |
| 4.0 | 0.6019 | 0.6125 | 0.6216 | 0.6169 | 0.6136 |
| 4.2 | 0.6187 | | | | |
| 4.4 | 0.6342 | | | | |
| 4.6 | 0.6405 | | | | |
| 4.8 | 0.6651 | | | | |
| 5.0 | 0.6868 | 0.6890 | 0.6694 | 0.6700 | 0.6888 |
| 5.2 | 0.6943 | | | | |
| 5.4 | 0.7059 | | | | |
| 5.6 | 0.7211 | | | | |
| 5.8 | 0.7232 | | | | |
| 6.0 | 0.7387 | 0.7414 | 0.7070 | 0.7330 | 0.7391 |
| 7.0 | 0.7726 | | | | 0.7743 |
| 8.0 | 0.7942 | | | | |
| 9.0 | | | | | |
| 10.0 | 0.8529 | 0.8335 | 0.7990 | 0.8443 | 0.8819 |

The salt solutions in contact with the soil (series 0.0 T. $CaCO_3$) show considerable differences in potential, but all show about the same neutral point, 5.0 T. $CaCO_3$. From this point the variation in the readings becomes rather wide.

The general form of the curves is shown by the type curve Figure 2. Two points regarding this curve may be discussed. It will be noted that the curve changes in slope inclining more toward the vertical as the neutral point is reached and after this point is passed the slope inclines away from the vertical, approaching the slope at the lower end of the curve.

There is no abrupt change in hydrogen ion concentration as was noted by Hildebrand[1] when a strong acid is neutralized by a base, but rather the curve approaches a straight line, i.e. for each addition of base there is a corresponding nearly equal change in hydrogen ion concentration. Roughly one may represent the change in the hydrogen ion concentration by an equation as follows,

$$C = KB \quad K'$$

where C is the hydrogen ion concentration, B the base added, and K and $K_1$ are characteristic constants.

The systems investigated above have all the characteristics of mixtures having a high reserve acidity,[2] i.e. the hydrogen ion concentration suffers very little change with comparatively large additions of base.

Referring again to Table III it will be noted that after the

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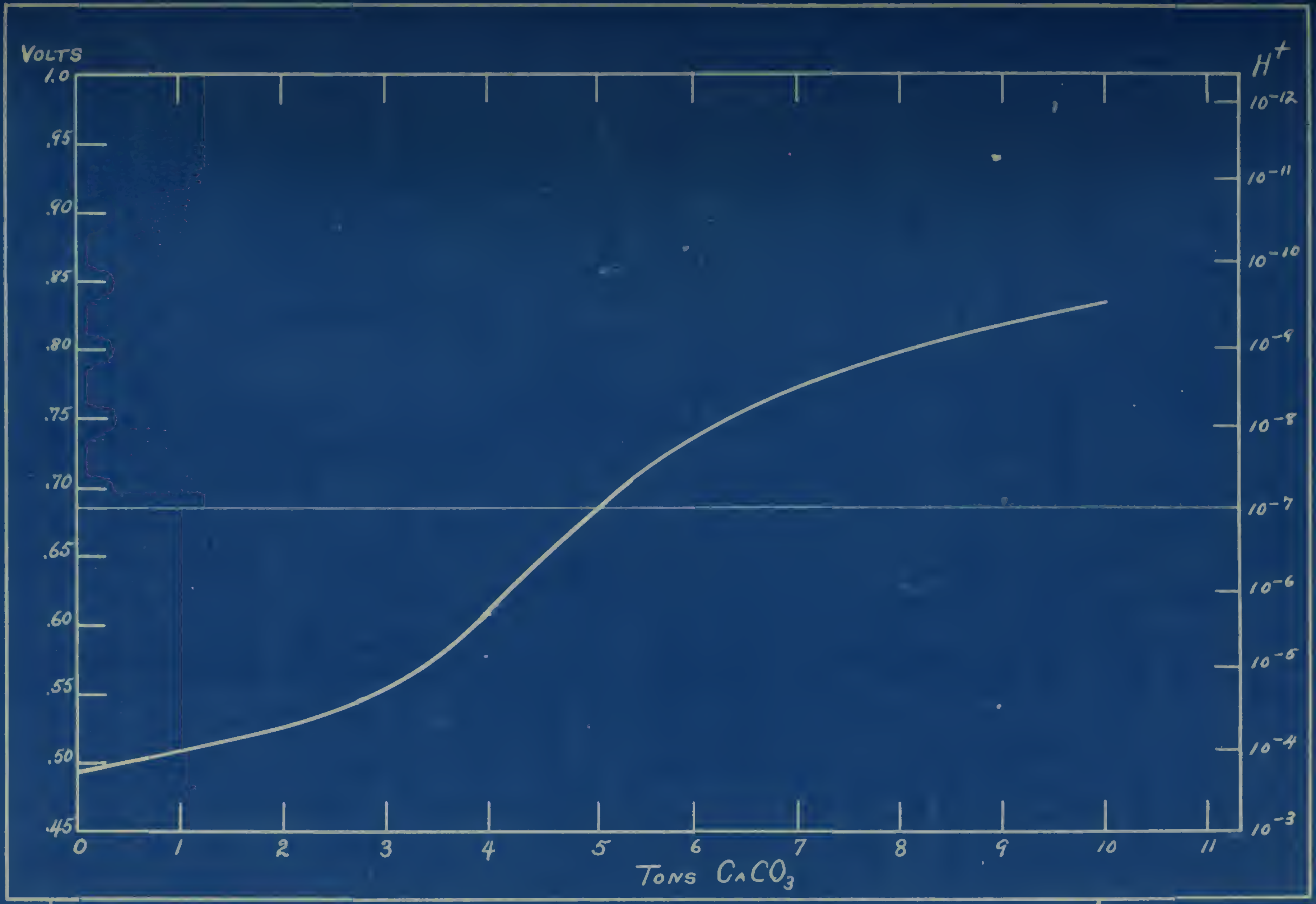
1. Jr. Am. Chem. Soc., 1913, 35, p. 847.

2. Washburn, Jour. Am. Chem. Soc., 1908, 30, p. 37.


VOLTS
1.0
.95
.90
.85
.80
.75
.70
.65
.60
.55
.50
.45
$H^+$
$10^{-12}$
$10^{-11}$
$10^{-10}$
$10^{-9}$
$10^{-8}$
$10^{-7}$
$10^{-6}$
$10^{-5}$
$10^{-4}$
$10^{-3}$
0
1
2
3
4
5
6
7
8
9
10
11
TONS $CaCO_3$

neutral point is reached the hydrogen ion concentration for the system, $CaCl_2$ $Ca(OH)_2$ Soil, shows a higher hydrogen concentration than the system, KCl KOH Soil, for the same equivalents of base. This may be accounted for by the precipitating action of calcium hydroxide when added in excess.

## EFFECT OF TIME

If the base is allowed to act for a longer time there is a tendency for the hydrogen ion curve to become more nearly a straight line, as is indicated by Table IV and Figure 3 which is the graph of the system, .5N KCl, $Ca(OH)_2$ Soil; time three and one-half hours, during which period the mixtures were shaken in a machine.

Table IV.

Effect of Time

Results recorded in volts.

| Base Equivalent to T $CaCO_3$ | .5N KCl $Ca(OH)_2$ | .5N KCl KOH |
|---|---|---|
| 0.0 | 0.4963 | 0.4997 |
| 1.0 | 0.5120 | 0.5157 |
| 2.0 | 0.5249 | 0.5276 |
| 3.0 | 0.5418 | 0.5445 |
| 4.0 | 0.5820 | 0.5959 |
| 5.0 | 0.6397 | 0.6488 |
| 6.0 | 0.6797 | 0.6702 |
| 7.0 | 0.7217 | 0.7268 |

It will be noted that for the same amount of base there is a higher hydrogen ion concentration than shown in Table III. Hydrogen ion concentration increases with time in the presence

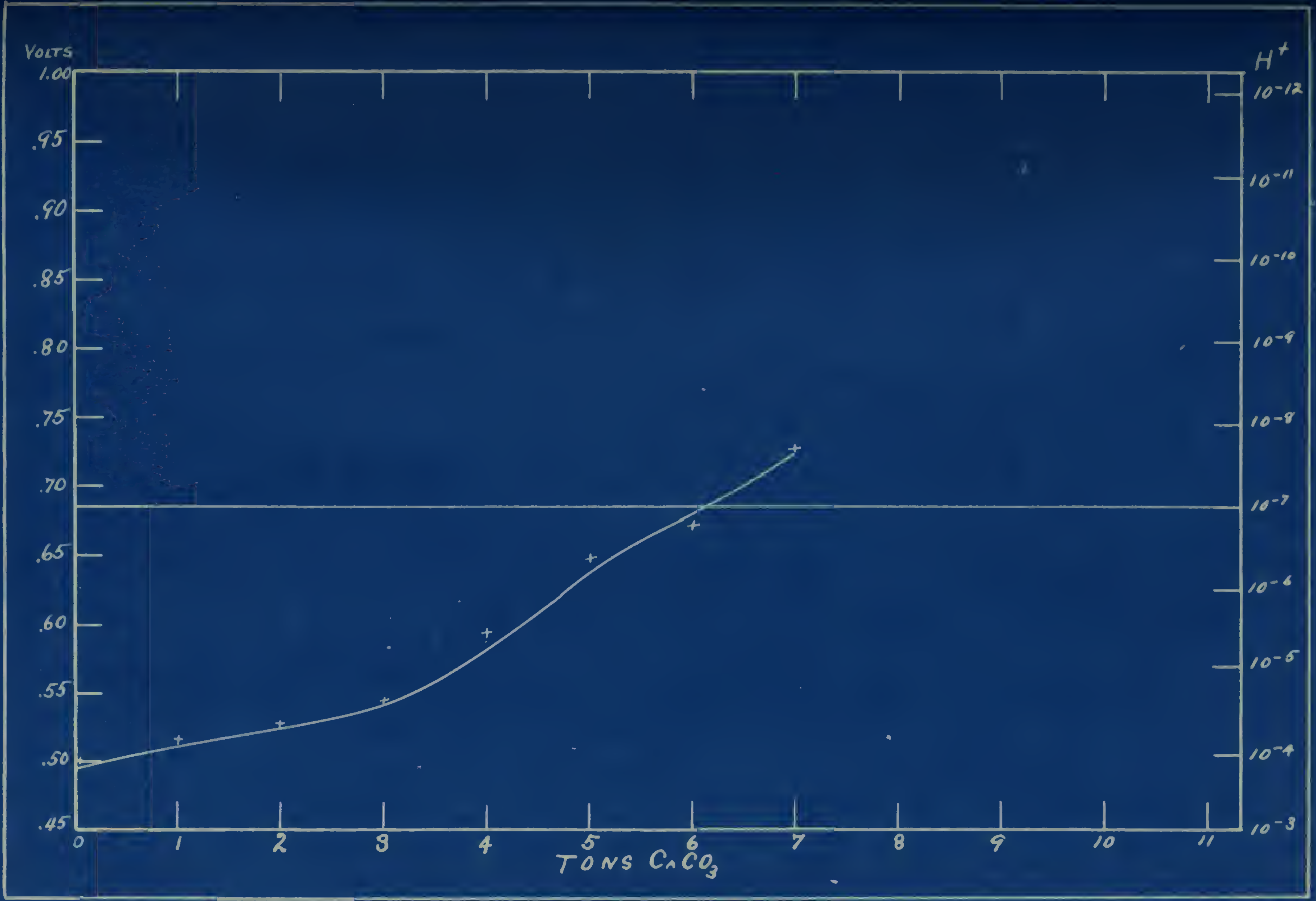

VOLTS
1.00
.95
.90
.85
.80
.75
.70
.65
.60
.55
.50
.45
$H^+$
$10^{-12}$
$10^{-11}$
$10^{-10}$
$10^{-9}$
$10^{-8}$
$10^{-7}$
$10^{-6}$
$10^{-5}$
$10^{-4}$
$10^{-3}$
0
1
2
3
4
5
6
7
8
9
10
11
TONS $CaCO_3$

Fig 4

of a soluble base.

## HYDROGEN ION CONCENTRATION OF VARIOUS SOILS.

For some comparison between the changes of the hydrogen ion concentration of salt solutions in contact with different soils a number of soils were chosen and similar determinations made as with the yellow-gray silt loam above. All the soils were shaken for three hours with 50 c.c. of .5N KCl solution containing the required amount of lime. In each case 5 grams of soil were used except in the case of the peat soils, of which 2.5 grams were taken.

Table V.

Comparison of hydrogen ion concentration of various soils.

Results are recorded in volts.

| T CaCO$_3$ | (1) Black Peaty Loam. | (2) Black Clay Loam. | (3) Peat | (4) Black Muck. | (5) Yellow Silty Clay. | (6) Gray Claying Silt. | (7) Gray Plastic Clay. |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.5290 | 0.5089 | 0.5654 | 0.4995 | 0.4979 | 0.4707 | 0.5072 |
| 1.0 | 0.5396 | 0.5171 | 0.5699 |  | 0.5184 | 0.4831 | 0.5271 |
| 2.0 | 0.5487 | 0.5257 | 0.5757 |  | 0.5199 | 0.4922 | 0.5526 |
| 3.0 | 0.5629 | 0.5352 | 0.5828 |  | 0.5311 | 0.5001 | 0.6077 |
| 4.0 |  | 0.5463 | 0.5705 |  | 0.5485 | 0.5076 | 0.6408 |
| 5.0 | 0.5953 | 0.5571 | 0.5948 | 0.5413 | 0.5942 | 0.5178 | 0.6974 |
| 6.0 |  | 0.5679 | 0.6006 |  | 0.6338 | 0.5206 | 0.7485 |
| 7.0 |  |  |  |  | 0.6755 |  |  |
| 8.0 |  |  |  |  | 0.7164 |  |  |
| 9.0 |  |  |  |  | 0.7372 |  |  |
| 10.0 | 0.6391 | 0.6105 | 0.6373 | 0.5822 | 0.7770 | 0.5820 | 0.8483 |
| 15.0 | 0.6783 | 0.6470 | 0.6699 | 0.6198 |  |  |  |
| 20.0 | 0.7267 | 0.7006 | 0.7153 | 0.6684 |  |  |  |

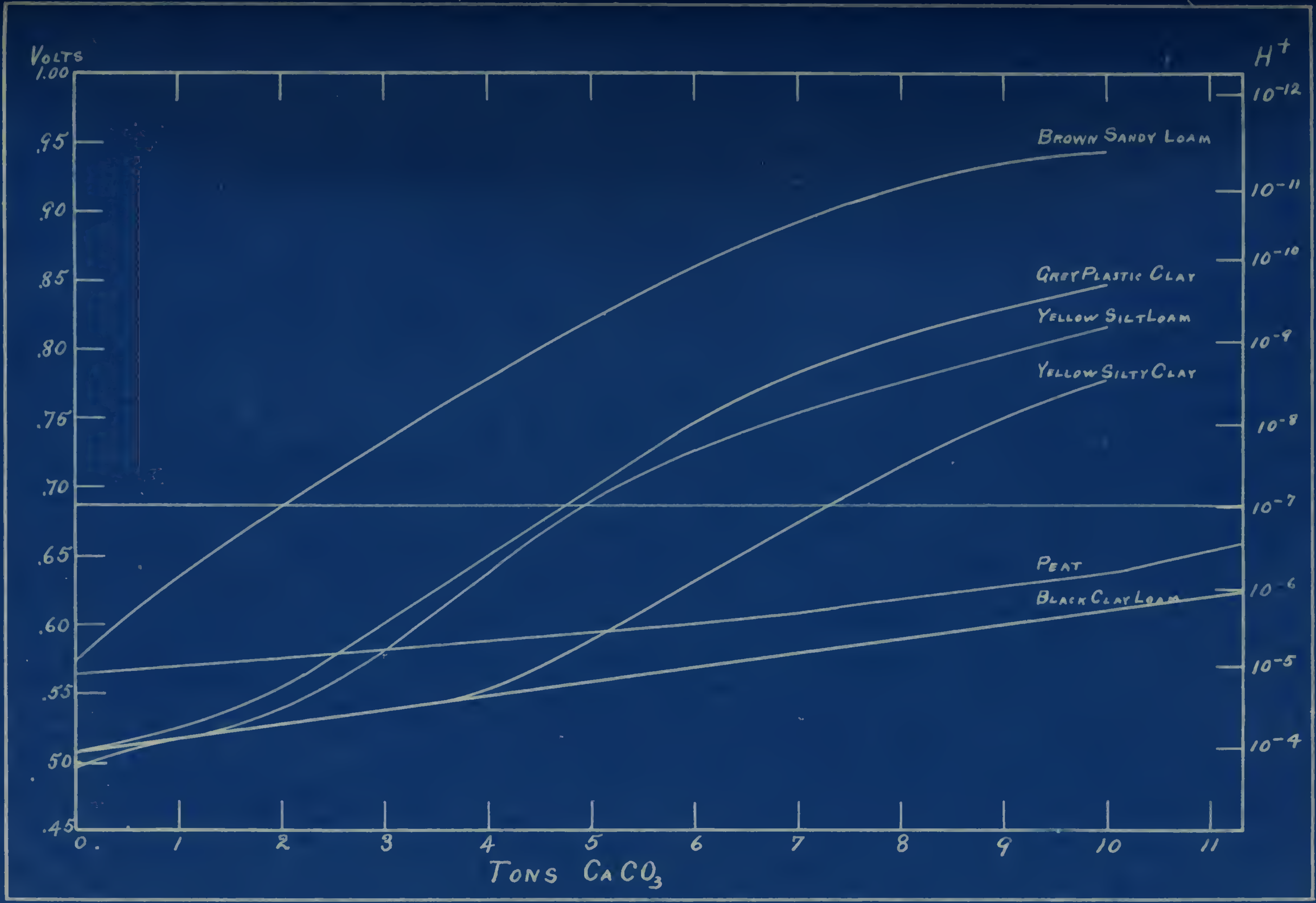

VOLTS
1.00
.95
.90
.85
.80
.75
.70
.65
.60
.55
.50
.45
H+
$10^{-12}$
$10^{-11}$
$10^{-10}$
$10^{-9}$
$10^{-8}$
$10^{-7}$
$10^{-6}$
$10^{-5}$
$10^{-4}$
BROWN SANDY LOAM
GREY PLASTIC CLAY
YELLOW SILT LOAM
YELLOW SILTY CLAY
PEAT
BLACK CLAY LOAM
0.
1
2
3
4
5
6
7
8
9
10
11
TONS $CaCO_3$

Fig 5

Table V (continued)

| T. $CaCO_3$ | (8) Yellow Plastic Clay Silt. | (9) Grayish Yellow Clay Silt | (10) Yellow Silt Loam. | (11) Brown Sandy Loam. |
|---|---|---|---|---|
| 0.0 | 0.4997 | 0.5034 | 0.4984 | 0.5753 |
| 1.0 | 0.5065 | 0.5126 | 0.5177 | 0.6366 |
| 2.0 |  | 0.5227 | 0.5386 | 0.6887 |
| 3.0 | 0.5275 | 0.5338 | 0.5780 | 0.7340 |
| 4.0 |  | 0.5538 | 0.6364 | 0.7796 |
| 5.0 | 0.5719 |  | 0.6955 | 0.8240 |
| 6.0 | 0.6233 | 0.6502 | 0.7297 | 0.8596 |
| 7.0 | 0.6748 |  |  |  |
| 8.0 | 0.7216 |  |  |  |
| 9.0 |  |  |  |  |
| 10.0 | 0.7658 | 0.7737 | 0.8178 | 0.9446 |

Graphs of the above readings (Figure 4) will show nearly straight line functions. Certain of the soils tested show straight line function for all measurements taken, Soils No. 1, 2, 3, 4, 6, and 11, while the others show more or less distinct changes in slope at two points, one being on the acid side, i.e. where the H concentration is greater than $10^{-7}$ and the other on the basic side. The same is true of the yellow-gray silt loam (Figure IV). At no point in these graphs is there an abrupt change in slope, as would be expected if we were neutralizing a strong acid, but instead the neutral point is reached at an angle depending upon the character of the soil. It requires comparatively large additions of base to produce a marked change in hydrogen ion concen-

tration.

It may be readily understood that the indicators which change color at different hydrogen ion concentration will show marked differences in the lime requirements because of the slow change in hydrogen ion concentration with the addition of lime. With the sandy loam soil a change in hydrogen ion concentration of the indicator from $10^{-5}$ (corresponding to the color change of methyl orange) to $10^{-8}$ (corresponding to the color change of phenolphlthalein) would correspond to a change in the lime requirement for peat from about 1 T. to more than 20 T. of calcium carbonate. Soils solution may be distinctly acid to litmus while alkaline to methyl orange.

The slow change in hydrogen ion concentration with additions of base will account for the great variation in results obtained for the lime requirement of soils by the different methods proposed. The greater the slope of the curve the less will be the differences observed. With sandy soils it would be expected that the results obtained by various methods would approach each other; greater variations would be observed with other inorganic soils; while soils high in organic matter would be expected to show the widest differences.

The time factor becomes rather important as is shown in Experiments I and II. The longer the base acts the higher is the hydrogen ion concentration at all initial concentrations of base. The temperature undoubtedly should receive consideration. The speed of reaction is increased and salts are hydrolyzed to a greater extent[1] and water of hydration may be decreased with in-

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[1] Landoldt and Bornstein, Phys. Chem. Tab.

crease in temperature. We should expect that an acid soil would take up larger quantities of calcium from calcium carbonate than from calcium chloride, or sodium from sodium acetate than from sodium chloride as has been repeatedly shown to be the case, which may be explained at least partially by differences in hydrolysis of the salts and the differences in the ionization of the acid. With a carbonate as the reagent, since the point of equilibrium depends also upon the partial pressure of carbon dioxide, it may be understood that the apparent lime requirement may be changed by simply changing the partial pressure of carbon dioxide. The results reported by Ames and Shollenberger[1], by the Hutchinson-MacLennan[2] and the vacuum methods are in line with this argument.

The placing of the soil under artificial conditions with respect to temperature and the use of such powerful reagents in solution, or in an extremely finely divided condition as is done in most of the methods suggested, will certainly not only effect the speed of the reaction but without doubt the equilibrium reached is a metastable one. The present researches may not be said to be free from these faults.

In soils in contact with solutions we have to deal with solid phases whose reaction velocities are necessarily very slow. The substances which produce the acid phenomena when salt solutions are added to acid soils are undoubtedly little soluble, and the products formed pass into similar solid phases. Even substances which are assumed to be soluble, may be held rather in the colloidal condition. Kahlenburg and Lincoln[3] claim that

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1. Jr. Ind. Eng. Jr., 1916, 8, p. 243.
2. Chem. News, 1914, 110, No. 2854.
3. Jr. Phys. Chem., 1898, 2, p. 88.

the silicic acid of spring waters is present in the colloidal condition, and the fact that aluminum salts are hydrolyzed to a marked extent while the solubility of aluminum hydroxide is very slight may be taken as an indicator that it is held in solution in part as a peptized colloid. The work of Mahin, Ingrahen, and Stewart[1] seems to be evidence that the above statement is true relative to the aluminates, although Hildebrand[2] comes to the opposite conclusion.

## Conductivity of Soil Solutions.

To test the hypothesis of the insolubility of the products formed when a base is added to an acid soil, some conductivity experiments were planned as given below.

5 grams of soil were shaken with 75 c.c. of distilled water containing the required amount of base, and conductivity measurements were made upon the recently shaken mixture of soil and solution with a plunge electrode having a constant of .0305. All readings were taken at 25° ± 1°.

1√

2√

## Table VI.

## Conductivity of the Soil Treated with Varying Quantities of a Base.

Soil - Yellow-Gray Silt Loam.

Base - $Ca(OH)_2$ calculated as T $CaCO_3$ per acre.

| Base T $CaCO_3$ | Sp. CondX$10^5$ | Increase over No base Sp. Condx$10^5$ | Equivalent conductivity | Corrected equivalent conductivity |
|---|---|---|---|---|
| 0.0 | 1.016 | | | |
| 1.0 | 1.089 | 0.073 | 8.18 | 0.55 |
| 2.0 | 1.220 | 0.204 | 4.59 | 0.77 |
| 3.0 | 1.638 | 0.622 | 4.11 | 1.56 |
| 4.0 | 1.906 | 0.890 | 3.58 | 1.68 |
| 4.4 | 2.033 | 1.017 | 3.49 | 1.75 |
| 4.8 | 2.226 | 1.210 | 3.49 | 1.89 |
| 5.2 | 2.226 | 1.210 | 3.22 | 1.75 |
| 5.6 | 2.346 | 1.330 | 3.15 | 1.78 |
| 6.0 | 2.480 | 1.464 | 3.11 | 1.84 |
| 7.0 | 3.390 | 2.374 | 3.64 | 2.55 |
| 10.0 | 10.170 | 9.154 | 7.64 | 6.88 |
| | | Same as above after standing 18 hours. | | |
| 0.0 | 1.016 | | | |
| 1.0 | 1.129 | 0.113 | 8.48 | 0.85 |
| 2.0 | 1.129 | 0.113 | 4.24 | 0.42 |
| 3.0 | 1.464 | 0.448 | 3.67 | 1.12 |
| 4.0 | 1.980 | 0.964 | 3.72 | 1.81 |
| 4.4 | 2.120 | 1.104 | 3.62 | 1.89 |
| 4.8 | 2.248 | 1.232 | 3.52 | 1.93 |
| 5.2 | 2.276 | 1.260 | 3.30 | 1.82 |
| 5.6 | 2.365 | 1.349 | 3.16 | 1.81 |

| Base T. $CaCO_3$ | Sp. Condx$10^5$ | Increase over No Base Sp. Condx$10^5$ | Equivalent conductivity | Corrected equivalent conductivity |
|---|---|---|---|---|
| 6.0 | 2.352 | 1.336 | 2.95 | 1.68 |
| 7.0 | 2.799 | 1.783 | 3.00 | 1.92 |
| 10.0 | 4.842 | 3.826 | 3.64 | 2.87 |

Base Used KOH.

Measurements after 1 hour.

| | | | | |
|---|---|---|---|---|
| 0.0 | .982 | | | |
| 1.0 | 1.276 | 0.298 | 9.59 | 2.24 |
| 2.0 | 1.733 | 0.751 | 6.51 | 2.82 |
| 3.0 | 2.520 | 1.638 | 6.32 | 4.10 |
| 4.0 | 3.748 | 2.766 | 7.04 | 5.21 |
| 4.4 | 4.637 | 3.655 | 7.90 | 6.24 |
| 4.8 | 5.100 | 4.118 | 7.99 | 6.44 |
| 5.2 | 5.864 | 4.882 | 8.49 | 7.66 |
| 5.6 | 7.318 | 6.336 | 9.84 | 9.17 |
| 6.0 | 9.300 | 8.318 | 16.66 | 10.42 |
| 7.0 | 14.250 | 13.270 | 15.30 | 14.26 |
| 10.0 | 43.580 | 42.500 | 32.76 | 31.95 |

Same as above after standing 18 hours.

| | | | | |
|---|---|---|---|---|
| 0.0 | .874 | | | |
| 1.0 | 1.203 | 0.329 | 9.05 | 2.47 |
| 2.0 | 1.618 | 0.744 | 6.08 | 2.80 |
| 3.0 | 2.376 | 1.502 | 5.95 | 3.77 |
| 4.0 | 3.245 | 2.369 | 6.09 | 4.45 |
| 4.4 | 3.748 | 2.874 | 6.41 | 4.92 |
| 4.8 | 4.122 | 3.248 | 6.46 | 5.09 |
| 5.2 | 4.620 | 3.746 | 6.68 | 5.42 |

| Base T. $CaCO_3$ | Sp. Condx$10^5$ | Increase over No base Sp. Condx$10^5$ | Equivalent conductivity | Corrected equivalent conductivity |
|---|---|---|---|---|
| 5.6 | 5.352 | 4.487 | 7.18 | 6.01 |
| 6.0 | 5.978 | 5.104 | 7.48 | 6.40 |
| 7.0 | 8.718 | 7.844 | 9.33 | 8.44 |
| 10.0 | 29.330 | 28.460 | 22.05 | 21.39 |

Same as above after standing 48 hours.

| | | | | |
|---|---|---|---|---|
| 0.0 | .959 | | | |
| 1.0 | 1.201 | .242 | 9.04 | 1.82 |
| 2.0 | 1.562 | .603 | 5.87 | 2.26 |
| 3.0 | 2.111 | 1.152 | 5.29 | 2.89 |
| 4.0 | 2.998 | 2.039 | 5.63 | 3.83 |
| 4.4 | 3.427 | 2.468 | 5.86 | 4.22 |
| 4.8 | 3.785 | 2.826 | 5.93 | 4.42 |
| 5.2 | 4.295 | 3.336 | 6.21 | 4.83 |
| 5.6 | 4.896 | 3.937 | 6.13 | 5.28 |
| 6.0 | 5.170 | 4.211 | 6.48 | 5.28 |
| 7.0 | 6.719 | 5.760 | 7.21 | 6.19 |
| 10.0 | 20.740 | 19.781 | 15.60 | 14.87 |

Base used $Ca(OH)_2$, Shook 3 hours.

| | | | | |
|---|---|---|---|---|
| 0.0 | 0.913 | | | |
| 1.0 | 0.916 | 0.003 | 6.89 | 0.02 |
| 2.0 | 0.994 | 0.081 | 3.73 | 0.31 |
| 3.0 | 1.146 | 0.233 | 2.87 | 0.59 |
| 4.0 | 1.495 | 0.582 | 2.81 | 1.09 |
| 4.4 | 1.691 | 0.778 | 2.89 | 1.33 |
| 4.8 | 1.826 | 0.913 | 2.87 | 1.43 |
| 5.2 | 1.980 | 1.067 | 2.87 | 1.54 |

| Base T. $CaCO_3$ | Sp. Condx$10^5$ | Increase over No Base Sp. Condx$10^5$ | Equivalent conductivity | Corrected equivalent conductivity |
|---|---|---|---|---|
| 5.6 | 2.048 | 1.135 | 2.75 | 1.53 |
| 6.0 | 2.074 | 1.161 | 2.59 | 1.46 |
| 7.0 | 2.310 | 1.397 | 2.48 | 1.57 |
| 10.0 | 3.427 | 2.514 | 2.58 | 1.89 |

Base used KOH, Shook 3 hours.

| | | | | |
|---|---|---|---|---|
| 0.0 | .913 | | | |
| 1.0 | 2.132 | 1.218 | 16.04 | 9.15 |
| 3.0 | 1.968 | 1.055 | 4.93 | 2.65 |
| 4.0 | 2.402 | 1.489 | 4.51 | 2.80 |
| 6.0 | 4.888 | 3.975 | 6.12 | 4.96 |
| 10.0 | 25.420 | 24.507 | 19.12 | 18.42 |

Soil. Black Peaty Loam.

Base used $Ca(OH)_2$, Measurements after 1 hour.

| | | | | |
|---|---|---|---|---|
| 0.0 | 2.341 | | | |
| 1.0 | 2.825 | 0.484 | 21.24 | 2.07 |
| 2.0 | 3.050 | 0.709 | 11.48 | 2.67 |
| 3.0 | 3.468 | 1.127 | 8.68 | 2.82 |
| 4.0 | 3.744 | 1.403 | 7.04 | 2.64 |
| 5.0 | 3.916 | 1.375 | 5.89 | 2.07 |
| 6.0 | 4.140 | 1.799 | 5.19 | 2.25 |
| 7.0 | 4.440 | 2.099 | 4.77 | 2.25 |
| 8.0 | 4.880 | 2.359 | 4.59 | 2.21 |
| 9.0 | 5.528 | 3.187 | 4.62 | 2.66 |
| 10.0 | 6.055 | 3.714 | 4.55 | 2.79 |

| Base T. $CaCO_3$ | Sp. Condx$10^5$ | Increase over No Base Sp. Condx$10^5$ | Equivalent conductivity | Corrected equivalent conductivity |
|---|---|---|---|---|
| Soil, Black Peaty Loam | | | | |
| Base used $Ca(OH)_2$ | | Measurements after 3 hours. | | |
| 0.0 | 2.837 | | | |
| 1.0 | 3.388 | 0.551 | 25.48 | 4.14 |
| 2.0 | 3.720 | 0.883 | 13,98 | 3.31 |
| 3.0 | 4.013 | 1.176 | 10.06 | 2.95 |
| 4.0 | 4.296 | 1.456 | 8.02 | 2.74 |
| 5.0 | 4.554 | 1.717 | 6.85 | 2.58 |
| 6.0 | 4.767 | 1.930 | 5.98 | 2.42 |
| 7.0 | 4.968 | 2.131 | 5.33 | 2.29 |
| 8.0 | 5.197 | 2.360 | 4.88 | 2.22 |
| 9.0 | 5.322 | 2.485 | 4.47 | 2.07 |
| 10.0 | 5.457 | 2.640 | 4.10 | 1.99 |
| Black Clay Loam, $Ca(OH)_2$, after 1 hour. | | | | |
| 0.0 | 3.813 | | | |
| 1.0 | 4.015 | 0.202 | 30.19 | 1.52 |
| 3.0 | 4.498 | 0.685 | 11.27 | 1.71 |
| 5.0 | 4.905 | 1.092 | 7.37 | 1.64 |
| 7.0 | 5.408 | 1.595 | 5.82 | 1.71 |
| 10.0 | 5.820 | 2.007 | 4.38 | 1.51 |

The figures in the third column headed, "Increase Sp. Cond. X $10^5$ are obtained by subtracting the first figure in the second

column from all the others upon the assumption that the changes in conductivity are due to the base alone which may or may not be true.

The equivalent conductivity is obtained directly from the figures in the second column upon the basis of change in concentration of the base.

Corrected Equivalent Conductivity is the calculated[#] equivalent conductivity from the results tabulated in the third column upon the basis of change in concentration of the base, upon assumption that the conductivity of the water solution is a constant factor. This assumption is probably not warranted.

From an inspection of the table, the following deductions may be made.

(1) The specific conductance increases with each addition of base, but the increase is much greater with potassium hydroxide than with calcium hydroxide. The difference is far too great to be accounted for by the difference in conductivity of potassium and calcium salts.[#] Either the calcium salts formed are less soluble or they must ionize to a far less extent. The former view is substantiated by the difference noted in the soluble base left in solution when a soil is treated with water containing an excess base. From the standpoint of adsorption theory it may be argued that calcium hydroxide is absorbed to a greater extent than potassium hydroxide, but this theory can hardly be substantiated in

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[#] For method of calculation for calcium and potassium ions, see Bates (Jr. Am. Chem. Soc., 1913, 35, p. 534); and Washburn (Principles of Physical Chemistry, New York, 1915, p. 214) for calculated values, the equivalent constant of calcium and potassium ions at infinite dilution being 51 and 63.3 respectively.

face of the fact that potassium and calcium hydroxide seem to have practically equivalent power to neutralize the acid of the soil as noted elsewhere in this paper.

(2) The specific conductivity decreases with time. This is true in every case except with the black peaty loam. This may be accounted for by the increase in soluble material brought into solution. It will be noted that the water solution in contact with the soil showed a higher conductivity after shaking. Equilibrium evidently had not been reached. If this is taken into account, the conductivity of the solution in contact with this soil also shows the above characteristic with time. It would seem that the reactions are progressive and that equilibrium is not reached for a considerable period. This is directly in line with the change in hydrogen ion concentration determination discussed elsewhere in this paper.

The equivalent conductances apparently decrease with the addition of base and then increase rapidly, the changes being much accentuated in the cases where potassium displaces calcium hydroxide as the base, but when the equivalent conductivities are corrected for the conductance of the soluble material brought into solution from the soil, there is, in general, an increase in equivalent conductance with addition of base which is very marked when potassium hydroxide is used.

As the acid-producing substances present in the soils are extremely insoluble, shown by the fact that the pure-water extract shows no acidity by ordinary indicators, it would be expected that reactions would be exceedingly slow, especially as the equilibrium point is approached. It will be noted in line with this that

there was a much more marked change in conductivity with time at the higher base concentrations.

The rather slow increase in conductivity would point to precipitation effects which are more marked in the case where calcium is used as the base. Acid substances which are highly insoluble would show high reserve acidity, a condition which is quite evident in the soils investigated.

In anticipitation of criticism from the use of neutral salt solution in the potential readings throughout these investigations the following experiment was planned:-

It may be reasoned that if insoluble acids are present in acid soils it should be possible to measure the hydrogen ion concentration from such a water solution if the acid ionizes at all, by means of the hydrogen electrode and other indicators. This has been done by Gillespie (loco cite), but no attempts have been made to follow the change in hydrogen ion concentration upon the addition of base. In repeating Gillespie's experiment,using the yellow-gray silt loam, it was found that after shaking 5 grams of the soil with 50 c.c. of distilled water for one-half hour the potential reading of the mixture was suppressed to 0.565 volt, but there is question whether equilibrium had yet been attained considering the evidence given below of the fact that neutral salts suppress the reading to about 0.5 volt.

The above described experiment was modified by using 50 c.c. of distilled water containing the equivalent of 4 tons per acre of calcium hydroxide calculated as calcium carbonate; after the readings had become constant 5 grams of yellow-gray silt loam was added and readings taken at stated intervals. The results are tabulated below:

| Time | Volts |
|---|---|
| 0 minutes | 0.9723 |
| 20 " | 0.7056 |
| 60 " | 0.6772 |
| 90 " | 0.6580 |
| 240 " | 0.6529 |
| 420 " | 0.6416 |

Equilibrium evidently had not been reached after seven hours of continuous shaking. In performing the experiment some difficulty was encountered because of the high resistance of the chain, but the readings are typical. It will be noted that the reaction is much slower than in the presence of a neutral salt, as may be expected from a consideration of the number of ions present in each case.

The salt solutions used throughout this research unless otherwise stated were .5 N strength, while the calcium hydroxide solution used above was .008 N, or an approximate ratio of 500 to 8 at the beginning of the reaction. While the neutral salt concentration remained practically unchanged the calcium hydroxide concentration and consequently the hydroxyl ion concentration became progressively less.

In the presence of neutral salt solutions the following reactions are possible.

(1) $KCl + HX = KX + HCl$.

(2) $2\ HCl + Ca(OH)_2 = CaCl_2 + 2\ H_2O$.

(3) $Ca(OH)_2 + 2KX = CaX_2 + 2\ KOH$

(4) $Ca(OH)_2 + 2HX = CaX_2 + 2\ H_2O$

Reaction (1) may take place almost instantly because of the larger number of K present, and the extent to which the reaction takes place will depend upon the speed of removal of H, reaction (2). Reactions (3) and (4) may be considered as side reactions, but (4) becomes the principal reaction if lime in water alone is used.

The above experiment brings out another fact of importance. After the base has been neutralized the hydrogen ion concentration continues to rise slowly. The substances producing the action comes to an equilibrium very slowly with water; six hours after the lime was neutralized hydrogen ions were still being thrown into the solution.

## Migration of Suspensoids.

Preliminary experiments were made with yellow-gray silt loam to determine if there was any migration of the suspensoids under the influence of the electric current. The soil was shaken with distilled water and electrolyzed in a U tube under an electrical potential gradient of about two volts per centimeter. The suspended matter migrated toward the positive poll at the rate roughly of two centimeters per hour. Reversing the current caused the suspended matter to travel in the opposite direction against gravity. After reversing the current several times a noticeable separation occurred, the top layer of which resembled very much a precipitate of aluminum hydroxide. No attempt was made however to verify this. The cathode portion became distinctly alkaline to phenolphthalein, which was proof of the presence of soluble bases even though the amount was in all probability very slight. There

was marked evidence of precipitation of suspensoids as they came in contact with the positive electrode.

The above is proof without question that when the soil is shaken with water negatively charged suspended matter is present which may account in part for the acid condition of the soil, but the extent to which this is the cause was not determined. However, if one is to judge by the speed of precipitation of the suspended matter, taking into consideration the small amount of electricity passing, it is only a fraction of the total acidity.

## Comparison of change in hydrogen ion concentration with conductivity.

It may be of interest to make a rough comparison of the change in conductivity with change in hydrogen ion concentration. The change in the hydrogen ion concentration by progressive additions of a base conforms roughly to the general formula $C = \log H_c + K$ when C is the concentration of the base, $H_c$ the hydrogen ion concentration and K a characteristic constant for the system under consideration. If C and $\log H_c$ are plotted as ordinates the curve is almost a straight line for some distance each side of the neutral point while no such functions are shown for the change in conductivity. However this could hardly be expected considering the fact that as already pointed out reactions under the conditions in which the conductivity experiment were carried out are exceedingly slow and there was no attempt made to follow the changes in conductivity due to changes in concentration of substance other than the base. Without doubt the electrically charged suspended material is precipitated, which factor would

effect the conductance, and the most that may be hoped for in the preliminary experiment is the direction of the reaction.

## PART II.

## Studies of the Hopkins and Pettit Method for Determining Soil Acidity.

This method proposed in 1902[1] is essentially as follows: 100 g. of soil is shaken in a bottle of 400 c.c. capacity with 250 c.c. of 5% common salt solution for three hours. 125 c.c. of the clear liquid is taken off, boiled to expel carbon dioxide and titrated using phenolphthalein as an indicator. The results are multiplied by 3 as a factor to determine the total amount of base required. Later[2], a normal solution of potassium nitrate is substituted for the 5% solution of common salt and the factor 2.5 is recommended.

The method as modified is still the provisional method of the A. O. A. C. for determining the acidity of soils.

Veitch[3] criticizes the Hopkins method upon the grounds that it gives only the apparent need for lime or the most urgent need, and claims further that the acidity shown by this method is largely due to aluminates. He also notes[4] that there is a great dis-

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[1] 19th Ann. Proceedings O.A.C.,U.S.Dept. of Agr. Bureau of Chem. Bul., No. 73, 1902, p. 114.

[2] U.S. Dep. of Agr., Bureau of Chem. Bul. No. 107, 1908, p. 20, and Hopkins "Soil Fertility and Permanent Agriculture", 1910 p. 566.

[3] Jr. Am. Chem. Soc., 1904, 26, p. 637.

[4] ibid.

crepancy between the Hopkins and the method proposed by Veitch[1] upon soils high in organic matter.

Harris[2] claims that the acidity shown by this method is due to selective ion adsorption by the soil colloids, basing his views upon the fact that the acidity shown by the extract is dependent upon the character of the salts used. Frear[3] also holds to this view.

Truog[4] strenuously combats the theory of colloidal adsorption and brings evidence to support the view held by Hopkins[5] that the reaction is one of double decomposition between the acids or acid salts in the soil and the neutral salt solution.

Parker[6] concluded from analysis of extracts prepared by treating soils with KCl and KAc, that the base was absorbed to a little greater extent than it was liberated by the soil and that the excess of the anion should be accounted for by the presence of the corresponding acid.

Bogue[7] states "It has been repeatedly proven that the base liberated by the soil is usually not nearly equivalent to the base absorbed from the solution."

Many investigators have noted the presence of aluminum and iron in salt extracts from acid soils;[8] Morse and Curry[9] Abbott, Conn

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[1] Jr. Am. Chem. Soc., 1902, 24, p. 1120.
[2] Mich. Agr. Coll. and Stat. Bul., 1914, No. 19.
[3] Penn. Dep. Agr. Bul., 1915, Bul. No. 261, p. 106.
[4] Jr. Phys. Chem., 1916, 20, p. 157.
[5] Ibid.
[6] Jr. Ind. Eng. Chem., 1914, 6, p.831.
[7] Jr. Phys. Chem. 1915, 19, p. 665.
[8] Sullivan, U. S. Geo. Survey, 1907, Bul. No. 312.
[9] New Hamp. Agr. Sta. Rep., 1906-08, p. 271.

and Smalley[1]; Conner[2]; Ruprecht[3] and others.

Rice[4] concludes from hydrogen ion concentration studies upon thirty-one soils using the indicator method of Sörensen[5] that when so called acid soils are shaken with salt solutions part of the cation of the salt is absorbed and an equivalent quantity of the base from the soil is given up to the solution.

It was to test the above criticisms and points upon which there is controversy that the following investigations were made.

## Experimental.

Harris[6] obtained different lime requirements for soils by repeated shaking with different salt solutions. These experiments were repeated in this laboratory using yellow-gray silt loam and similar differences were obtained as was reported by Harris for different salts. As Hopkins[7] claims that the reaction between the neutral salt solution and the soil is one of equilibrium, the end reaction would be practically impossible to realize by such a treatment. To overcome the objections which would arise from the above method provisions were made for forcing the salt solutions through the soil, so that the soil particles would be continually bathed by fresh solutions.

Twenty grams of soil were placed upon a dry filter paper and the salt solution was allowed to perculate through. The perculate

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1. Ind. Agr. Exp. Sta. Bul. No. 170, 1913.
2. ibid., 1916, 8, p. 36.
3. Mass. Agr. Exp. Sta., 1915, Bul., No. 161.
4. Jr. Phys. Chem, 1916, 20, p. 214.
5. Bio. Chem. Zeit., 1909, 21, p. 131-304.(See also Walpole Bio. Chem., 1911, 5, pp. 207-214; 8 (1914) pp, 628-640.
6. ibid.
7. ibid.

was boiled and treated with .04 N KOH at room temperature using phenolphthlein as an indicator.

Amount filtering through

| Salt Used | Percolate and titration | | | | c.c. KOH | T. $CaCO_3$ |
|---|---|---|---|---|---|---|
| | 100cc | 250c.c. | 250c.c. | 250c.c. | Total | equiv. |
| N. $KNO_3$ | 36.40 | 2.8 | 1.2 | 0.5 | 40.5 | 4.05 |
| N. KCl | 35.95 | 4.3 | 2.1 | 0.5 | 39.95 | 3.99 |
| N. $NaNO_3$ | 26.50 | 9.2 | 1.8 | 1.4 | 38.9 | 3.89 |
| N.NaCl | 31.20 | 6.4 | 1.4 | | 39.0 | 3.90 |
| $\frac{N}{2}$. $CaCl_2$ | 31.40 | 5.4 | 1.3 | 0.5 | 38.6 | 3.86 |

The greatest difference shown is .19 T, calculated as calcium carbonate, which may be accounted for by several factors.

It will be noted that the acidity of the sodium nitrate extract was quite marked even after 600 c.c. had passed through, while the first 100 c.c. showed the lowest acidity of the salt solutions.

That none of the extractions were carried to completion is evident, but all with the possible exception of extraction with sodium nitrate, were carried to a point beyond which it was impossible to measure the acidity with any degree of accuracy by the ordinary indicator methods.

The calcium salt extract would be expected to show a slower reaction after the first surface reaction because of the greater insolubility of calcium compounds, which would be formed upon the surface of the soil grains.

A precipitate was always formed in considerable quantities

in the first two series of extracts which was found to have a rather marked effect upon the indicator used. The pink color produced by the addition of a slight excess of base dissappeared after a time even when the titrating flask was tightly stopped. By the addition of base the second time the color could be brought back.

The end point is markedly influenced by the amount of indicator present. It is quite apparent that the indicator is absorbed to some extent by the precipitate. Instead of having the simple equilibrium

$$\begin{array}{ccc} \text{H In} & \longrightarrow & \text{In}^- + \text{H}^+ \\ \text{Colorless} & \longleftarrow & \text{Colored} \end{array}$$

there must be taken into consideration the equilibrium with the absorbed indicator.

$$\begin{array}{ccccc} \text{H In} & \longrightarrow & \text{H In} & \longrightarrow & \text{In}^- + \text{H}^+ \\ \text{Absorbed} & \longleftarrow & \text{colorless} & \longleftarrow & \text{colored} \end{array}$$

Two equal quantities of potassium nitrate extract of an acid soil gave the following readings with different amounts of indicator.

| Phenolphthalein Used | .04 N KOH Required to give same change in color. |
|---|---|
| 4 drops | 62.7 |
| 10 drops | 61.1 |

which clearly shows the difference which may be caused by different amounts of indicator. In several instances a point was reached which showed no visible color change with four or five drops of indicator while upon the addition of larger quantities a marked color change was observed.

To overcome so far as possible the variation due to the indicator the same quantity was used in each case unless otherwise stated.

[illegible]

$$[illegible]$$

[illegible]

$$[illegible]$$

[illegible]

[illegible]

[illegible]

The temperature, at which the titration is carried out, was found to produce an effect which is shown by the following experiment. Two equal quantities of potassium nitrate extract were titrated with .04 N potassium hydroxide using the same quantity of phenolpnthalein as an indicator. The only difference between the duplicates was that of temperature.

| Temp. C. | c.c. KOH |
|---|---|
| 22° | 16.7 |
| 85° | 19.2 |

## Effect of Temperature Upon the Determination by The Hopkins Method.

If the Hopkins method is a measure of the colloidal adsorption for the base by a soil as maintained by Harris[1] there should be a temperature effect which could be measured.

Travers[2] showed that the adsorption of carbon dioxide by charcoal decreases markedly with rise in temperature, and we may expect a similar change to be shown by soils in contact with neutral salt solutions.

To test this theory an apparatus shown in Plate V was arranged in a constant temperature electrical oven of the Freas type. The apparatus was arranged in duplicate; (a) is the recepticle for the neutral salt solution, (b) a stop cock for regulating the flow of the neutral salt through tube (d) which passes through the ventil-

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[1] loco.cite

[2] Proc. Roy. Soc., 1904, 74, p. 126.

lating openings (c) provided by the manufactures in the stock oven. The bulb (e) serves to bring the salt solution to the temperature of the oven before it runs into the recepticle (f) which contains the soil under investigation. The filtrate passes out of the apparatus through tube (g) through ventillating openings in the oven at (c') and is caught in measuring flasks (not shown). (i) is a thermometer placed in the center of the oven for noting the temperature.

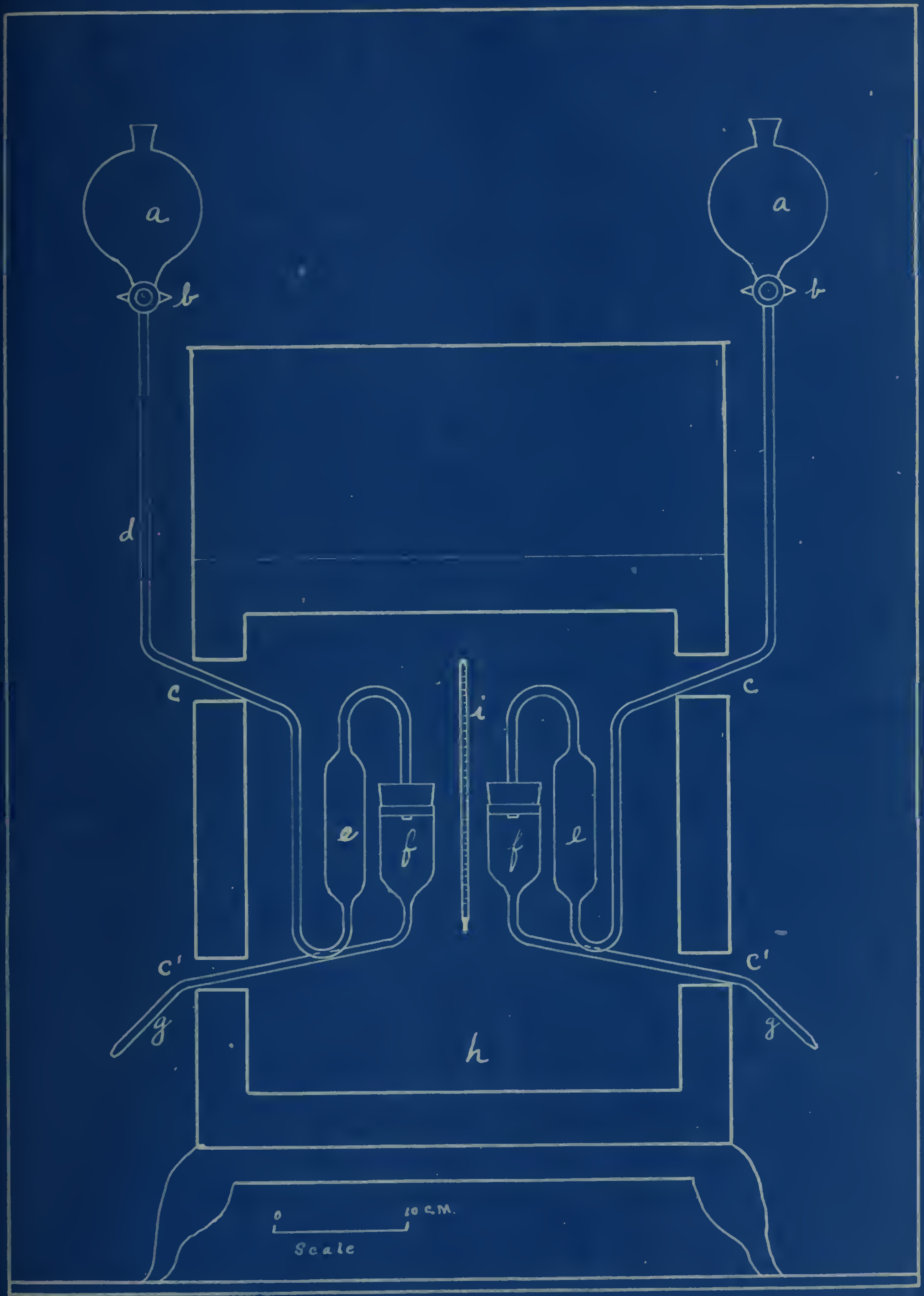
Twenty grams of soil were placed in the receptacle (f) and Normal potassium nitrate solution allowed to perculate through. The perculate was titrated at room temperature.

| C.C. Percolate | C.C. .04 N KOH Temp. 90° ± 1° | T. $CaCO_3$ | C.C. .04 N KOH Temp. 25° ± 1° | T. $CaCO_3$ |
|---|---|---|---|---|
| 100 | 37.85 | 3.785 | 36.4 | 3.64 |
| 400 | 3.15 | 0.315 | 3.0 | 0.30 |
| Total 500 | 41.00 | 4.1 | 39.4 | 3.94 |

If there is any temperature effect it is very slight, and is in the direction indicating a chemical action rather than adsorption.

## Effect of Rate of Filtering

To determine the effect of rate of filtering, 20 grams samples of yellow-gray silt loam were spread out upon a filter paper place in a Büchner funnel and a normal solution of potassium nitrate was filtered through by suction. This was compared with ordinary gravity filtration previously described. The average time for 300 c.c. of solution to filter through was 2 hours and 40 minutes with the forced filtration and 7 hours by gravity.


a
a
b
b
d
c
c
i
e
f
f
e
c'
c'
g
g
h
0
10 C.M.
Scale

| Am't filtered | Hours | Suction, Acidity | Hours | Gravity, Acidity |
|---|---|---|---|---|
| 300 c.c. | 2 2/3 | 3.91 | 7 | 3.97 |

There is no appreciable difference. The reaction evidently comes to an equilibrium rather quickly when the solution is constantly changed.

## EFFECT OF STRENGTH OF SALT SOLUTION

Potassium nitrate solutions of different strengths were filtered through 20 g. samples of yellow-gray silt loam and the filtrate titrated with .04 N KOH using phenolphthalein as an indicator with the following results:

C.C. .04 N KOH required.

|  | N $KNO_3$ | .5 N $KNO_3$ | .1 N $KNO_3$ |
|---|---|---|---|
| 1st 100 c.c. | 35 | 33.3 | 18.3 |
| 2nd 100 c.c. | 3.5 | 4.7 | 7.6 |
| 3rd 100 c.c. | 1.2 | 1.5 | 4.3 |
| 4th 100 c.c. | 0.8 | 0.9 | 3.7 |
| 5th 100 c.c. | 0.5 | 0.6 | 3.3 |
| 6th 100 c.c. |  |  | 1.6 |
| Total | 40.8 | 41.0 | 38.8 |
| As T. $CaCO_3$ | 4.08 | 4.10 | 3.88 |

It will be noted that with the stronger salt solutions the larger is the amount of acidity shown in the first 100 c.c. but the amount rapidly falls, while the weaker solutions show a higher acidity in succeeding fractions. Evidently end extractions would lead to the same end results regardless of the strength of the salt solutions.

Fig.     shows the change in acid concentration. A further study of this reaction was made by extracting 10 g. samples of the same soil with various strengths of potassium nitrate solution and titrating the acid in the first 100 c.c. of the perculate. The results are tabulated below.

| Normality $KNO_3$ | c.c. .04 N KOH Required | Calculated as T $CaCO_3$ |
|---|---|---|
| 1.00 | 15.2 | 3.04 |
| .50 | 15.3 | 3.06 |
| .25 | 15.2 | 3.04 |
| .125 | 13.25 | 2.65 |
| .0625 | 8.00 | 1.60 |
| .0312 | 4.10 | 0.82 |
| .0156 | 1.95 | 0.39 |
| .0078 | 1.17 | 0.23 |

The acidity of the first portion of the extract increases with increase in concentration of the neutral salt solution up to about one-fourth normal.

## Examples of Colloidal Adsorption.

As examples, of what are usually considered colloidal phenomena the following experiments are submitted.

### Experiment I.

20 g. of yellow-gray silt loam were shaken with various amounts of lime contained in 200 c.c. of solution for 12 hours and an aliquot part of the clear liquid was titrated with the following results.

| Lime added calculated as | Absorbed by soil | Left in Solution | Normality Solution at end. |
|---|---|---|---|
| T. $CaCO_3$ | | | |
| 12 | 11.71 | .29 | 0.000285 |
| 14 | 13.36 | .64 | 0.00064 |
| 16 | 14.59 | 1.41 | 0.0014 |
| 20 | 16.75 | 3.25 | 0.0032 |
| 30 | 20.93 | 9.07 | 0.009 |
| 40 | 24.96 | 15.04 | 0.015 |

The greater proportion of the lime is absorbed from the dilute solutions than from the more concentrated. Apparently this follows the colloidal adsorption law.

## Experiment II.

20 g. of soil were placed in an extracting apparatus (b) Plate VI and a .04 N $Ca(OH)_2$ solution allowed to percolate through. In the diagram (a) is the receptacle for the base, (e) a stop cock for regulating the flow of the base into (b). (E) is a graduated receiver connected with tube (d) which serves to equalize the pressure. The apparatus is a closed system and duplicate results were easily obtained. 237.2 c.c. of filtrate passed through before a pink color could be detected when phenolphthalein was used as an indicator, representing a lime adsorption at this point of 23.7 T. as calcium carbonate. At the close of the experiment 537.6 c.c. of filtrate had perculated through, the last 50 c.c. being .0285 N base while the soil had absorbed a total of 35.28 T. of calcium carbonate equivalent. 15.82 T. of calcium carbonate equivalent were washed out by the first 700 c.c. of distilled


a
e
d
b
c
0
10 CM.
SCALE

water, the end fraction passing through .00242 N alkali. 19.46 T. of lime were still left in the soil.

The details are tabulated below, while Fig. gives the general course of the experiment. A and B are duplicate determinations.

A.

| c.c. Percolated | T. $CaCO_3$ absorbed | % absorbed | T. $CaCO_3$ Percolate |
|---|---|---|---|
| 236.5 | 23.65 | 100 | 0.00 |
| 27.0 | 2.50 | 92.6 | 0.20 |
| 28.5 | 1.95 | 68.4 | 0.90 |
| 45.0 | 1.97 | 43.7 | 2.53 |
| 51.4 | 1.61 | 31.3 | 3.53 |
| 48.6 | .93 | 19.1 | 3.93 |
| 50.0 | 1.04 | 20.8 | 3.96 |
| 50.5 | 1.45 | 28.7 | 3.60 |
| Total 537.5 | 35.10 | | |

B.

| c.c. Percolated | T. $CaCO_3$ absorbed | % absorbed | T. $CaCO_3$ Percolate |
|---|---|---|---|
| 238. | 23.80 | 100. | 0.00 |
| 43.2 | 4.17 | 96.6 | 0.15 |
| 58.0 | 3.04 | 52.2 | 2.76 |
| 50.5 | 1.24 | 24.5 | 3.81 |
| 50.0 | 1.08 | 20.2 | 3.92 |
| 50.0 | 1.15 | 23.0 | 3.85 |
| 50.0 | .99 | 19.8 | 4.01 |
| Total 539.7 | 35.47 | | |

A.

| Water added C.C. percolated | T. Lime left in soil. | T. $CaCO_3$ in percolate. |
|---|---|---|
| 51.5 | 31.36 | 3.74 |
| 49.0 | 29.16 | 2.20 |
| 51.5 | 27.52 | 1.64 |
| 53.5 | 26.19 | 1.33 |
| 48.5 | 25.21 | 0.98 |
| 51.5 | 24.27 | 0.94 |
| 49.0 | 23.48 | 0.79 |
| 49.0 | 22.77 | 0.71 |
| 47.0 | 22.19 | 0.58 |
| 53.5 | 21.61 | 0.58 |
| 50.5 | 21.15 | 0.46 |
| 49.5 | 20.74 | 0.41 |
| 74.0 | 19.18 | 0.56 |
| 27.5 | 19.00 | 0.18 |

B.

| | | |
|---|---|---|
| 56.5 | 31.02 | 4.45 |
| 44.0 | 28.84 | 2.18 |
| 46.0 | 27.31 | 1.53 |
| 48.0 | 26.12 | 1.19 |
| 51.0 | 24.51 | 1.61 |
| 55.0 | 23.07 | 1.44 |
| 96.0 | 21.60 | 1.47 |
| 47.0 | 21.04 | 0.56 |
| 49.0 | 20.52 | 0.52 |
| 45.0 | 20.10 | 0.42 |
| 58.5 | 19.66 | 0.44 |
| 79.5 | 19.05 | 0.61 |
| 21.5 | 18.93 | 0.12 |

## Experiment III.

20-gram samples of yellow-gray silt loam were shaken 3 hours with 200c.c. of .04 N Calcium hydroxide and of potassium hydroxide. Since the solution containing the potassium hydroxide would not settle, 25 c.c. of N. $KNO_3$ was added to both the calcium and potassium hydroxide solutions and filtered. Titrations gave the following figures for 100 c.c.

| | .04 N. HCl required. |
|---|---|
| $Ca(OH)_2$ solution | 7.7 c.c. |
| K(OH) " | 31.9 c.c. |

As the potassium hydroxide solution was neutralized a copious precipitate was formed apparently of aluminum hydroxide, while no precipitate was noted upon neutralizing the calcium hydroxide solution.

It would appear from this experiment that the soil has a greater absorption power for calcium than for potassium which is not apparent from other experiments. It would appear that a chemical difference in the action of the two bases is the more simple explanation. Potassium aluminate is soluble while calcium aluminate is not. Both are unstable except in the presence of a base. Since the potassium aluminate passes into solution it is titrated while the calcium aluminate is precipitated around the soil particles.

This it seems throws doubt upon the magnitude of the colloidal adsorption effects which may be assumed from Experiments I and II above. The probable cause would seem to be precipitation effects. When water is added in Experiment II hydrolysis will account for the lime rapidly washing out.

## BASIC EXCHANGE

There is considerable doubt as to whether, when an acid soil is shaken up with a neutral salt, there is a complete exchange of base. Rice[1] in a recent paper comes to the conclusion that there is an equivalent exchange and that the acidity is due to the aluminum salts. He further claims that the ordinary methods of analysis are too crude to determine this accurately. Analyses however were made of the potassium nitrate extract of yellow-gray silt loam with the following results.

| | |
|---|---|
| Acidity | 627 c.c. of .04 N acid |
| $SiO_2$ | 0.04741 g. |
| $P_2O_5$ | 0.00576 |
| $Al_2O_3$ | 0.38822 |
| $Fe_2O_3$ | Trace |
| CaO | 0.06025 |
| $Mn_3O_4$ | 0.04839 |
| MgO | 0.19901 |

The acid combined with the alumina would be equivalent to 570 c.c. of .04 N leaving an excess of 57 c.c. to be accounted for in other ways.

Since, as has been shown by Blum[2], alumina is completely precipitated before the hydrogen ion concentration drops to a value of $10^{-7}$, and since, conversely, alumina will not pass into solution until the hydrogen ion concentration reaches a value higher than

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[1] ibid.

[2] Jr.Am. Chem. Soc., 1916, 7, p. 1282.

$10^{-7}$, it is reasonable to conclude that there must be some absorption of base before the alumina will pass into solution. If this is true we must assume that the solution of alumina is a secondary reaction. The above analysis certainly points in this direction.

It was noted that, upon making strong acid extracts of this soil, the extracts were highly colored with iron. The question arose why it was that if alumina is brought into solution by a secondary reaction as suggested above, iron is not also taken out in larger quantities. To test this point 100 g. samples of yellow-gray silt loam were shaken with 250 c.c. of .04 N strength acids and a partial analysis made of 125 c.c. of the filtered extracts.

| | $Al_2O_3$ | $Fe_2O_3$ |
|---|---|---|
| Acetic | 0.00383 g. | Trace |
| Nitric | 0.06913 | Trace |
| Hydrochloric | 0.07049 | Trace |

The solutions were still acid and upon neutralization white precipitates of aluminum hydroxide were formed in the hydrochloric and nitric acid extracts but none was noted in the acetic acid extract until after the neutralized extract was boiled. It seems that we have a parallel case to the one above.

The conclusions which may be drawn are:

(1) There is an exchange of base between the soil and the solution.

(2) The alumina does not account for the total acidity of the extract although it does account for the major portion of it.

## DYALISIS

Normal potassium nitrate solution was shaken with yellow-gray silt loam and allowed to settle. The supernatant liquid was taken off into a collodion bottle and subjected to dialysis with the following results:

| | .04 N KOH |
|---|---|
| 1. Liquid | 35.1 c.c. |
| 2. " | 12.06 |
| 3. " | 24.9 |
| Left in flask | 24.9 |
| Total Titrated | 96.96 c.c. |

74% of the titratable acid had passed through the membrane. As the liquid left in the dialyzing flask was being titrated a heavy precipitate formed, while that which passed through remained clear upon neutralization. It was evident that the acid passed through while the aluminum hydroxide did not, which however was to be expected as this is one of the recognized methods for the preparation of colloidal aluminum hydroxide.[1]

## DISTILLATION OF EXTRACT

Attempts were made to distill off acid from potassium nitrate and chloride extracts by prolonged distillation with steam but without success. Better success followed the distillation of the potassium acetate extract of the yellow-gray silt loam.

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[1] Graham, Leibig Ann., 1866, 121, p. 41.

### Acidity in terms of .04 N Base

| Potassium acetate Extract | | Stock Solution Potassium acetate. | |
|---|---|---|---|
| Distillate | Residue | Distillate | Residue |
| 72.9 c.c. | 21.9 c.c. | 8.6 c.c. | 1.95 c.c. |

Phenolphthalein was used as an indicator. This experiment shows the presence of appreciable quantities of acetic acid in the soil extract. About three-fourths of the acidity shown by the extract was distilled over.

Walter Crum[1] prepared colloidal aluminum hydroxide by separating the acetic acid by heating, but as there was only a trace of aluminum salts carried by the potassium acetate extract(see above)[2] it can hardly be conceived that the phenomena may be accounted for by the presence of these salts. Rather there is an excess of acid.

## CATION AND ANION ABSORPTION COMPARED.

To compare the cation and anion absorption of the yellow-gray silt loam from neutral salt solutions, a solution of calcium chloride .0358 N was made up and allowed to percolate through 20 g. of the soil in the apparatus shown in Plate VI. The extract was analyzed for calcium and chlorine. The calcium was determined in an aliquot portion of the extract which had been freed from iron and aluminum by first precipitating as the oxalate and titrating the precipitate with standard potassium permanganate in the presence of dilute sulphuric acid. The chlorine was determined by the Volhard method[3] using solutions of .04 N strength.

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[1] Lûbig, Ann., 1854, 89, p. 168.
[2] Compare also Conner, Jr. Eng. Ind. Chem., 1916, 8, p. 35.
[3] Lûbig Ann., De Chem., 190, p. 1.

| Extract | N Ca | N Cl | N Acidity |
|---|---|---|---|
| 1st 50 c.c. | 0.0180 | 0.0348 | 0.0046 |
| 2nd 50 c.c. | 0.0314 | 0.0358 | 0.0037 |
| 3d 50 c.c. | 0.0332 | 0.0358 | 0.0028 |
| 4th 50 c.c. | 0.0335 | 0.0358 | 0.0022 |

The cation is absorbed to a measurable extent while the acidity lacks considerably of accounting for the withdrawal of calcium, so there must have been an exchange of base which confirms the fact that there is a basic exchange regardless of the neutral salt used.[1] The anion is absorbed but little or not at all. The slight absorption shown in the first 50 c.c. of extract is probably due to the wetting of the particles and, as air-dried soil was used, to a slight dilution of the extract. A small amount of precipitate was formed upon neutralizing the extract in each case.

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1. See analysis of potassium nitrate extract.

# PART III.

## COMPARISON OF VARIOUS METHODS FOR DETERMINING LIME REQUIREMENT OF SOILS WITH THE HYDROGEN ELECTRODE.

Through the courtesy of Professor J. W.Ames of the Ohio Agricultural Experiment Station fifteen samples of soil were obtained from a number of variously treated plots from one of the fertility sections of the Wooster farm located on silt loam soil which is derived from sandstones and shales. Ames and Schollenberger[1] had made determinations of the lime requirement upon these soils by the Veitch, Hopkins, Hutchinson-MacLennan, MacIntire and Vacuum Methods and all were tested with litmus paper and found to give a decided reaction. "The west half of the plots had been treated with 1875 pounds per acre of calcium oxide in 1903 and 2000 pounds of limestone in 1909. The composition of the lime materials applied was such that the equivalent of 5700 pounds of calcium carbonate had been applied to the limed halves of the plots previous to the time samples were taken from the plots, which was three years after the last treatment with lime"[2] The amount of lime left was neglegible. All samples gave a decided acid reaction to litmus and when a mixture of the soils with recently boiled distilled water were tested with the hydrogen electrode all showed a hydrogen ion concentration greater than $10^{-7}$.

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1. Jr. Ind. and Eng. Chem., 1916, 8, p. 243.
2. Jr. Ind. and Eng. Chem., 1916, 8,p244.

Hydrogen electrode determinations upon these soils, after mixing with ½ N $KCl + Ca(OH)_2$ gave the following potential readings after three hours shaking.

| Plot | Fertilizer | 0 Lime | 1T Lime | 2T Lime | 3T Lime | 4T Lime |
|---|---|---|---|---|---|---|
| 0 | None | 0.5174 | 0.5684 | 0.6300 | 0.6739 | 0.7450 |
| # | None + lime | 0.5670 | 0.6406 | 0.6850 | 0.7393 | |
| 2 | Acid phosphate | 0.5209 | 0.5725 | 0.6392 | 0.7000 | |
| | Acid phosphate + lime | 0.5760 | 0.6561 | 0.6974 | 0.7473 | |
| 5 | Sodium nitrate | 0.5184 | 0.5671 | 0.6317 | 0.6862 | 0.7482 |
| | Sodium nitrate + lime | 0.5803 | 0.6511 | 0.7103 | 0.7540 | |
| 11 | Acid phos. + Mur. Pot. + Sod. Nitr. | 0.5164 | 0.5657 | 0.6308 | 0.6920 | |
| | Acid phos. + Mur. Pot. + Sod. Nitr. + lime | 0.5626 | 0.6398 | 0.6865 | 0.7421 | |
| 24 | Acid Phos. + Mur. Pot. + Amm. Sulf. + lime | 0.5445 | 0.6230 | 0.6612 | 0.7260 | |
| 26 | Bone Meal + Mur. Pot. + Sod. Nitr. | 0.5209 | 0.5731 | 0.6375 | 0.6774 | 0.7394 |
| | Bone Meal + Mur. Pot. + Sod. Nitr. + lime | 0.5516 | 0.6265 | 0.6841 | 0.7312 | |
| 29 | Basic Slag + Mur. Pot. + Sod. Nitr. | 0.5220 | 0.5794 | 0.6271 | 0.6826 | 0.7339 |
| | Basic Slag + Mur. Pot. + Sod. Nitr. + lime | 0.5668 | 0.6424 | 0.7074 | 0.7467 | |
| 18 | Manure | 0.5202 | 0.5659 | 0.6164 | 0.6622 | 0.6938 |
| | Manure + lime | 0.5574 | 0.6163 | 0.6708 | 0.7218 | |

Interpolating the above results as straight line functions to determine the amount of lime necessary to lower the hydrogen ion concentration to $10^{-7}$ normal using .69 volts as the potential at this concentration, a comparison may be made directly with the results given by Ames and Schollenberger.[1]

POUNDS OF $CaCO_3$ EQUIVALENT TO ACIDITY IN 2 MILLION POUNDS.

| Plot | Fertilizer | Hopkins | Veitch | MacIntire | Hutchinson | Vacuum | Hydrogen Electrode# |
|---|---|---|---|---|---|---|---|
| 0 | None | 3440 | 2000 | 3550 | 2925 | 7300 | 6456 |
| | None + lime | 100 | alk | 2250 | 1700 | 4900 | 4225 |
| 2 | Acid Phos. | 2640 | 2000 | 3850 | 2700 | 7800 | 5670 |
| | Acid Phos. + lime | 80 | alk | 2400 | 975 | 3800 | 3640 |
| 5 | Sodium Nitr. | 3640 | 1200 | 3550 | 2550 | 6200 | 6122 |
| | Sodium Nitr + lime | 120 | alk | 2500 | 1250 | 4225 | 3310 |
| 11 | Acid Phos. + Mur. Pot. + Sod. Nitr. | 3080 | 1800 | 3850 | 2825 | 7100 | 5960 |
| | Acid Phos. + Mur. Pot + Sod. Nitr. + lime | 80 | alk | 2500 | 1375 | 5900 | 4126 |
| 24 | Acid Phos. + Mur. Pot + Amm. Sulf. + lime | 4240 | 3000 | 4000 | 2700 | 8300 | 4889 |
| 26 | Bone Meal + Mur. Pot + Sod. Nitr. | 2940 | 2000 | 3700 | 2250 | 7350 | 6407 |
| | Bone Meal + Mur. Pot + Sod. Nitr. + lime | 360 | alk | 2900 | 1325 | 4050 | 4250 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 29 Basic Slag + Mur. Pot. + Sod. Nitr. | 2560 | 1200 | 3600 | 2250 | 6600 | 6288 |
| Basic Slag + Mur. Pot. + Sod. Nitr. + lime | 150 | alk | 2100 | 1075 | 4050 | 3460 |
| 18 Manure | 2760 | 2600 | 4200 | 3100 | 8500 | 7760 |
| Manure + lime | 120 | alk | 2950 | 1950 | 5200 | 4937 |

The Vacuum method approaches nearer to the lime requirement as shown by the hydrogen electrode than do any of the other methods given above, but with this method the results are uniformally higher. It may be assumed that if the soils had been shaken with the lime for a longer period than three hours the lime requirement as shown by the hydrogen electrode would have approached that given by the vacuum method.

With the exception of the Veitch, all of the quantitative methods, including the hydrogen electrode, as well as the qualitative test with litmus, agree in showing acidity in all of the soils used for the comparison of these methods. The Veitch method not only shows alkalinity in soils which by all other tests show acidity, but it also shows the lowest acidity in all other soils.

It is quite evident that the methods above with the possible exception of the vacuum method do not indicate the amount of lime necessary to satisfy the soils requirements, especially in the presence of neutral, salts except for a limited period.

## ~~PART IV.~~

## PROPOSED METHOD FOR DETERMINING THE LIME REQUIREMENT OF SOILS.

The use of the hydrogen electrode for the determination of the lime requirement would be out of the question, except as it may be valuable for checking other methods, for the following reasons. (1) It is difficult to manipulate even by one who has had considerable experience in using it. (2) The process is rather slow, in fact slower than **any** other method so far proposed. (3) Expensive and delicate apparatus is required if satisfactory results are to be obtained.

Although it will be found valuable for standardizing other methods, and approximate lime requirement values may be obtained by making two determinations and calculating the lime requirement as a linear function, the method may not be taken seriously as an analytical laboratory method.

As the time element is an important factor automatic titration would not be highly satisfactory.

Considering the difficulties enumerated above other lines were investigated in the hope that a practical, rapid method for the determination of the lime requirement of a soil could be worked out.

Tacke's method[1] would appear to have a logical foundation but it is difficult to conceive in the light of the present investigations how it could be expected to yield concordant results, and it is doubtful if it or any of the proposed modifications would approach the true lime requirement of a soil for a period of a year because of the slow action of calcium carbonate even in finely di-

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[1] loco.cite

vided condition upon most soils.

An attempt was made to determine the lime requirement by mixing a weighed quantity of soil with precipitated calcium carbonate, adding recently boiled distilled water, boiling for a fixed period and determining the evolved carbon dioxide by the Parr Method[1] as modified by Pettit[2], but concordant results could not be obtained; however, by adding a neutral salt rather close results were obtained.

The method used for the results obtained in the table below was to take a weighed sample of soil, usually 5 or 10 grams, add an excess of precipitated calcium carbonate in a 125 c.c. Erlenmeyer flask, attach to the Parr apparatus and run in about 25 c.c. of normal salt solution,[3] and boil for a definite period[4], fill flask and condenser with distilled water to a mark upon the capillary tube connecting the condenser with the Endiometer. Readings were taken as instructed by Pettit.[5]

The results are calculated in pounds of calcium carbonate to 2,000,000 pounds of soil except in case of peat soils where 1,000,000 pounds were used.

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[1] Jr. Am. Chem. Soc., 1904, 26, p. 294.

[2] Jr. Am. Chem. Soc., 1904, 26, p. 1640.

[3] Preliminary experiments showed that it made little difference what neutral salt was used. Experiments were made with definite quantities of KCl, NaCl and $KNO_3$; also by varying the amount of calcium carbonate and KCl with duplicate results, provided there was an excess of calcium carbonate and not enough KCl to change materially the boiling point of the solution.

[4] If the boiling was attended with frothing a few drops of a neutral oil were added.

[5] loco. cite.

Pounds of $CaCO_3$ equivalent to Acidity in 2 million of Soil.

| Ohio Soils<br>Plot No. | Fertilizer | Methods Employed<br>Hopkins | Veitch | MacIntire | Hutchinson | Vacuum | Hydrogen electrode | Modified Tacke<br>5 min. | 10 min. |
|---|---|---|---|---|---|---|---|---|---|
| 0 | None | 3440 | 2000 | 3550 | 2925 | 7300 | 6456 | 6941 | 7783 |
| | None+lime | 100 | alk. | 2250 | 1700 | 4900 | 4225 | | 6908 |
| | Difference | 3340 | — | 1300 | 1225 | 2400 | 2231 | | 875 |
| 2 | Acid phos. | 2640 | 2000 | 3850 | 2700 | 7800 | 5670 | 6737 | 7809 |
| | Acid phos.+lime | 80 | alk. | 2400 | 975 | 3800 | 3640 | 5123 | 6599 |
| | Difference | 2560 | — | 1450 | 1725 | 4000 | 2030 | 1614 | 1210 |
| 5 | Sodium Nitrate | 3640 | 1200 | 3550 | 2550 | 6200 | 6122 | 7264 | 7924 |
| | Sodium Nitr. + lime | 120 | alk. | 2500 | 1250 | 4225 | 3310 | | 5431 |
| | Difference | 3520 | — | 1050 | 1300 | 1975 | 2812 | | 2493 |
| 11 | Acid phos.+Mur. Pot.+ Sod. Nitr. | 3080 | 1800 | 3850 | 2825 | 7100 | 5960 | 7042 | 7493 |
| | Acid.Phos. Mur. Pot.+ Sod. Nitr.+lime | 80 | alk. | 2500 | 1375 | 5900 | 4126 | | 6184 |
| | Difference | 3000 | — | 1350 | 1450 | 1200 | 1834 | | 1309 |
| 24 | Acid phos.+Mur. Pot.+ Sod. Nitr.+Amm.Sulf.+ lime | 4240 | 3000 | 4000 | 2700 | 8300 | 4989 | | 6547 |
| 26 | Bone Meal + Mur. Pot.+ Sod. Nitr. | 2940 | 2000 | 3700 | 2250 | 7350 | 6407 | 6973 | 7530 |
| | Bone Meal + Mur. Pot.+ Sod. Nitr.+lime | 360 | alk. | 2900 | 1325 | 4050 | 4250 | | 6951 |
| | Difference | 2580 | — | 800 | 925 | 3300 | 2157 | | 579 |
| 29 | Basic Slag+Mur. Pot.+ Sod. Nitr. | 2560 | 1200 | 3600 | 2250 | 6600 | 6288 | | 7822 |
| | Basic Slag+Mus. Pot.+ Sod. Nitr.+lime | 150 | alk. | 2100 | 1075 | 4060 | 3460 | | 6233 |
| | Difference | 2410 | — | 1500 | 1175 | 2540 | 2828 | | 1589 |
| 18 | Manure | 2760 | 2600 | 4200 | 3100 | 8500 | 7760 | 8327 | 8776 |
| | Manure+lime | 120 | alk. | 2950 | 1950 | 5200 | 4937 | | 7206 |
| | Difference | 2640 | — | 1250 | 1150 | 3300 | 2823 | | 1570 |

Other soils investigated are given below.

| | Hopkins | Hydrogen Electrode | Modified Tacke 5 min. | 10 min. | 30 min. |
|---|---|---|---|---|---|
| Yellow-Gray Silt Loam | 8400 | 12490 | 14847 | 15822 | |
| Black Peaty Loam | 6890 | 32420 | | | |
| Black Clay Loam | 9964 | 38026 | | 34718 | |
| Peat | 6536 | 34260 | 11011 | 20772 | |
| Black Muck | 8122 | # | | 31342 | |
| Yellow Silty Clay | 10160 | 14708 | | | |
| Grey Claying Silt | 15840 | ♭ | 28803 | 30640 | 33624 |
| Grey Plastic Clay | 5200 | 10000 | | 11094 | |
| Yellow Plastic Claying Silt | 9340 | 14650 | 18173 | 19611 | |
| Yellow Silt Loam | 5780 | 14578 | 13453 | 14954 | 17250 |
| Brown Sandy Loam | 3300 | 4574 | | 5792 | |

It will be noted that the proposed modification of Tacke's method gives varying results which depend upon the time of boiling, and in every case except for peat and yellow silt loam the five minute boiling period showed a higher lime requirement than the hydrogen electrode, A ten-minute boiling period showed a higher lime requirement in every case except one (Ohio plot No. 24 limed) than by the Vacuum method proposed by Ames and Schollenber[1]; That the reaction is not complete even at the end of the ten minutes period is shown by the increase at the end of a thirty minute boiling period.

The proposed method has the advantage over most of the others in that it gives a figure which represents the "Power of a soil to decompose calcium carbonate" (which is a measure of the eventual lime requirements), is rapid, and approximates the results obtained with the hydrogen electrode.

It is suggested that ten minutes be fixed as the time for boiling.

It is quite apparent that the interaction at room temperature

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#more than 40000#
♭more than 20000#
1.loc.cit.

between a soil and a caustic lime solution containing a neutral salt is not complete within three hours (which was the period at which the hydrogen ion concentrations were determined with the hydrogen electrode), as shown by both the vacuum and the modified Tacke methods. The period required to cause an interaction at room temperature between a soil and calcium carbonate may be assumed to be a considerable period. MacIntire[1] has shown that calcium slowly passes into the form of silicates.

It is quite evident that any of the proposed methods give comparative results only. The true lime requirements must be determined by field experiments.

### MEASURING THE REDUCTION OF ACIDITY

By substracting the acidity values found in limed soils from those found in unlimed soils from the corresponding half plots at the Ohio Station (see page 86), differences are obtained which measure the residual reduction in acidity due to previous applications equivalent to 5700 pounds of calcium carbonate. As an average of the results from the seven plots which afford data for this measurement, the reduction in acidity is 2864 pounds by the Hopkins method, 2674 by the vacuum method, and 2388 by the hydrogen electrode, while the MacIntire, Hutchinson, and modified Tacke methods show reductions of 1243, 1279, and 1375 pounds, respectively. That any method will show a greater reduction in acidity than actually occurs and remains at the time of sampling seems very doubtful.

As suggested above, the vacuum method appears to furnish the most trustworthy measure of the total lime requirement, and it also seems safe to assume that the hydrogen electrode will give results

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[1] Tenn. Exp. Sta. Bul., 1914, No. 107.

in substantial agreement with the vacuum method if sufficient time is allowed. If these methods are accepted as standards, then the Hopkins method seems to give correct results when used to measure the reduction in soil acidity by applications of lime. It may also measure with accuracy the most immediate lime requirement, altho it does not measure the total power of a soil to decompose carbonates. If we assume that the reduction in acidity should be approximately the same for all limed plots, then the Hopkins method and the hydrogen electrode show the highest percentage consistency.

# SUMMARY AND CONCLUSIONS

## PART I.

1. A new hydrogen electrode cell has been designed which has proven satisfactory for certain types of soil investigation.

2. When an acid soil is added to a neutral salt solution the hydrogen ion concentration of the solution reaches a maximum almost immediately if the soil is wet thoroughly by the solution, but secondary reactions later cause a decrease in hydrogen ion concentration of the solution.

3. When an acid soil is added to a neutral salt solution containing a free base the base is neutralized rapidly as indicated by the change in hydrogen ion concentration of the solution following closely the law for equilibrium reactions, but the hydrogen ion concentration of the solution continues to rise for an unknown period.

4. There is no sharp break in the progress of base absorption by an acid soil which will warrant the arbitrary division such as active and latent acidity, or immediate and eventual lime requirement.

5. The changes in Log $C_H$ approach nearly straight line functions with time, with progressive additions of base in the presence of a neutral salt solution.

6. Different indicators will give differences in lime requirement for soils depending upon the slope of the Log $C_H$ curve. The greatest difference may be expected with soils high in organic matter.

7. A general explanation is given for the different results obtained by different methods for determining soil acidity, and why

slight changes may markedly effect these results.

8. When a base is added to an acid soil comparatively insoluble products are formed. Calcium produces a product less soluble than does potassium.

9. The specific conductance of a water solution of an acid soil to which a base has been added increases with each addition of base, but the increase is greater with potassium than with calcium hydroxide, which is far too great to be accounted for by the difference in conductivity of potassium and calcium.

10. Calcium hydroxide and potassium hydroxide have practically equivalent power to neutralize the acid of an acid soil.

11. The specific conductivity of a pure water solution containing a base in contact with an acid soil decreases with time.

12. An acid soil shows high reserve acidity.

13. The reaction between a water solution of a base and an acid soil is much slower than in the presence of a neutral salt.

14. The suspensoids of an acid soil will migrate under the influence of an electrical potential toward the positive pole, proving that they are charged negatively.

## PART II.

15. Potassium nitrate, potassium chloride, sodium nitrate, sodium chloride (normal solutions) and calcium chloride (one half normal) when percolated through an acid soil all gave the same end titrations using phenolphthalein as an indicator, which coroberates Hopkins' teachings.

16. The precipitate found in titrating the soil extract obtained

by the Hopkins' Method absorbs to some extent the indicator used. The end result depends upon the temperature, time, and amount of indicator.

17. The acidity of the salt extract of an acid soil is independent of the temperature (25° to 90°).

18. The acidity of the salt extract of an acid soil is independent of the rate of extraction.

19. The acidity of the salt extract of an acid soil is a function of the strength of the salt solution, but end extractions show the same total acidity.

20. The adsorption of bases by acid soils may be accounted for by other theories than colloidal absorption, which are more nearly in accord with the facts.

21. The acidity as determined by the Hopkins method may not all be accounted for by the presence of aluminum salts.

22. An acid soil absorbs from a neutral salt solution the cation to a measurable extent. The anion is absorbed little or not at all.

23. When an acid soil is brought in contact with a neutral salt solution an exchange of base takes place.

NOTE. Since this thesis was written Sharp and Hoagland (Jr. Ag. Res., 1916, 7, p. 123) have published an article entitled "Acidity and Adsorption in Soils as measured by the Hydrogen Electrode" wherein they show that soil acidity is due to an excess of hydrogen ions, and that the acidity is increased by the presence of certain neutral salts. The first contention is supported by the work given in this paper, but I have accounted for the differences noted in the latter by the difference in the speeds of reaction.

They (ibid, p. 142) also suggest the use of the hydrogen electrode for determining the lime requirement of soils, while I objected to its use for a number of reasons, the principal one being the difficulty of manipulation and the slowness of the de-determinations.

# NOTE.

Henry Granger Knight was born at Bennington, Ottawa Co., Kansas, July 21, 1878. He secured his common school education in the public schools of Kansas and Washington. The first two years of high school work was pursued at Leland, Washington; the third year was completed at the Port Townsend High School, from which institution he received a diploma in 1896. In the fall of 1897 he entered the University of Washington at Seattle as a conditioned freshman. He graduated from this institution in June 1902 with the degree of Bachelor of Arts with honors in Chemistry. During the years 1898-1899, 1900, 1901-1902, he held the position of Assistant in Chemistry at the University of Washington.

He entered the University of Chicago in July, 1902 as a member of the Graduate School where he studied chemistry under the direction of Dr. McCoy until August 1903, at which time he left to accept a position of Assistant Professor of Chemistry at the University of Washington. In January 1904 he was elected Professor of Chemistry of the University of Wyoming. He was granted the degree of Master of Arts by the University of Washington in 1904 upon work at the University of Washington, the University of Chicago and a thesis completed at the University of Wyoming. While holding this position in the summer of 1906 he attended the summer school of the University of Chicago. In June 1910, he was appointed Director of the University of Wyoming Agricultural Experiment Station and Agricultural Chemist of the Agricultural College and one year later also appointed Dean of the Agricultural College. In September 1915, he was granted a leave of absence to carry on graduate work at the University of Illinois.

He is the senior author of Bulletin No. 62, "Some Food Products and their Adulteration"; Bulletin No. 65, "Wyoming Forage Plants and their chemical Composition- Studies No. 1"; Bulletin No. 69, "Digestion Experiments with Wethers"; Bulletin No. 70, "Wyoming Forage Plants and their Chemical Composition- Studies No. 2"; Bulletin No. 76, "Wyoming Forage Plants and their Chemical Composition- Studies No. 3"; Bulletin No. 78, "Digestion Experiments II"; Bulletin No. 82, "Soil Nitrogen"; Bulletin No. 87, "Wyoming Forage Plants and their Chemical Composition- Studies No. 4"; Bulletin No. 97, "The Identification of the Woody Aster"; Bulletin No. 100, "Meteorology for Twenty Years"; and "Alkali VI", Sixteenth Annual Report; all of which have been published by the University of Wyoming Agricultural Experiment Station. He is the junior author of "Notes on Qualitative Analysis", published by John Wiley and Sons, and Bulletin No. 94, "The Chemical Examination of Death Camas" published by the University of Wyoming Agricultural Experiment Station.

In 1903 he was Fellow elect at Chicago. He is a member of the Washington Chapter of Sigma Xi and of Phi Beta Kappa, and of the Illinois Chapter of Sigma Upsilon, The American Chemical Society, National Geographic Society, the Society for the Promotion of Agricultural Science, et cetera.