

develop this process, but especially to Mr. Herbert Eckweiler who carried out many of the experimental and technical operations necessary to this investigation.

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## SOIL ACIDITY—THE RESULTANT OF CHEMICAL PHENOMENA<sup>1</sup>

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That condition of soils known as acid is not confined to any one soil type. The major portion of the soils of the eastern half of the United States are acid in the sense that they will grow better crops when treated with agricultural lime. Many of these soils were acid in their virgin state and the majority have or are becoming more acid through the loss of metals in drainage waters and crops. The number of years required to bring about an acid condition varies with the soil. The composition, origin, natural fertility, system of cropping, and cultural practices followed all bear on the acidity. Nitrogen, phosphorus, and potassium have been the three elements considered essential in fertilization practices. Calcium (in agricultural lime), though not usually classed as a plant food, is occupying as important a place in soil fertility investigations as either nitrogen or potassium.

In an article entitled "Carbonic Acid Gas in Relation to Soil Acidity Changes," the writer made the following statement: "The changed reactions of this soil toward a neutral salt of a strong base and a strong acid ( $\text{KNO}_3$ ) after subjection to the varied conditions of the experiments at least suggests that soil acidity is largely the result of hydrolytic mass action phenomena." The present paper gives some of the reactions between water and soil constituents in relation to soil acidity results and additional experimental data in support of the statement just quoted.

Investigators have looked to the following substances and phenomena for the explanation of soil acidity: the presence of mineral acids, the presence of organic acids, free hydrogen ions, colloidal material, absorption and adsorption, and the presence of specific compounds.

The methods used and in use for making soil acidity determinations are many. The methods include the treatment of soils with substances of both low and high solubilities.

Salts of strong acids and strong bases, of strong

<sup>1</sup> The experimental work covered by this paper was done while the author was employed as research associate in chemistry and bacteriology at the Purdue University Agricultural Experiment Station.

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acids and weak bases, of weak acids and strong bases, of weak acids and weak bases, calcium hydroxide, the lowering of the freezing point of the soil, the catalysis of esters, and the hydrogen ion concentration have all been used in studying soil acidity. The results obtained by different methods have differed so widely with the same sample of soil that statements similar to the following are quite common: "Calcium acetate results are mainly due to 'organic' acidity, potassium nitrate results give mainly the 'inorganic' acidity, and the Veitch lime-water method gives the calcium-fixing power of the soil."

To point out some of the reasons for variations in results obtained by the different methods and to show the method of attack used in carrying out the investigations reported in this paper, the constitution of soils is considered in connection with some of the fundamental teachings of physical chemistry. The condition of a soil, at any time, can be considered as a stage in its progress towards a constantly changing equilibrium in accordance with the principle of LeChatelier.

Metals enter into reactions dependent on their places in the electromotive series, each one replacing (until an equilibrium is reached) any one occurring later in the series. The order of the metals in the electromotive series is *potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, zinc, chromium, cadmium, iron, cobalt, nickel, tin*, etc. Those italicized are present in arable soils and stand well up in the series. To avoid a rather common misconception, it must be noted that the electromotive series cannot be used to explain the tendency of one radical to dislodge another in double decompositions. The influences which determine decomposition are the solubilities and ionizations of the compounds concerned. The law of mass action states that the velocity of a chemical reaction is proportional to the masses of the substances reacting, or, in other words, is equal to the product of the masses of the reacting substances times a constant. This means that where the constituents of a slightly ionized substance are present, that substance will form at the expense of other substances that are more highly ionized.

Table I gives the solubilities of some of the salts of those metals regularly found in soils and shows that the inorganic sodium and potassium compounds that occur in soil are all more or less soluble, that calcium, magnesium, and manganese compounds are less soluble, and that iron and aluminum compounds are still less soluble.

The ionization theory makes it necessary to consider that chemical reactions take place between ions. If a sufficient quantity of any compound found in soils is put by itself with water and no reactions take place between it and the distilled water, there are present at equilibrium the following ions from the salt, the dissolved salt, and the crystalline undissolved salt. This condition is dependent on the laws of chemical and physical equilibrium and can be illustrated by sodium nitrate.

TABLE I—SOLUBILITIES OF DIFFERENT SALTS IN WATER

	POTASSIUM	SODIUM	CALCIUM	MAGNESIUM	MANGANESE	ALUMINUM	IRON
Acetate.....	188.0 <sup>20</sup>	26.0 <sup>20</sup>	39.2 <sup>20</sup>	Soluble	2.34	Soluble	Soluble
Carbonate.....	53.2 <sup>28</sup>	17.6 <sup>20</sup>	0.0003 <sup>18</sup>	0.097 <sup>12</sup>	0.013	.....	.....
Bicarbonate.....	24.9 <sup>20</sup>	8.8 <sup>20</sup>	.....	.....	.....	.....	.....
Chloride.....	25.5 <sup>20</sup>	26.4 <sup>20</sup>	42.7 <sup>20</sup>	35.2 <sup>20</sup>	43.6 <sup>28</sup>	41.1 <sup>15</sup>	47.9 <sup>20</sup>
Hydroxide.....	53.4 <sup>22-5</sup>	51.7 <sup>18</sup>	0.0003 <sup>25</sup>	0.0008 <sup>18</sup>	0.0002 <sup>18</sup>	Insol.	Insol.
Nitrate.....	24.0 <sup>20</sup>	46.8 <sup>20</sup>	54.8 <sup>18</sup>	43.1 <sup>18</sup>	62.4 <sup>28</sup>	V. soluble	V. soluble
Phosphate, Mono.....	25.0 <sup>40</sup>	V. soluble	1.8 <sup>18</sup>	.....	.....	.....	.....
Phosphate, Di.....	V. soluble	8.5 <sup>20</sup>	0.02 <sup>24</sup>	Sl. soluble	.....	.....	.....
Phosphate, Tri.....	Sl. soluble	11.3 <sup>18</sup>	0.004	0.02	.....	Insol.	Insol.
Sulfate.....	10.1 <sup>20</sup>	16.2 <sup>28</sup>	0.202 <sup>18</sup>	26.2 <sup>20</sup>	38.6 <sup>20</sup>	26.6 <sup>20</sup>	Sl. soluble

Those figures italicized are from Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, 1912 edition, and are percentages of anhydrous material in saturated solutions at the temperatures specified. Other notes are from Van Nostrand's "Chemical Annual for 1913," but calculated to anhydrous salt per 10 cc. water for saturated solutions.

By the law of physical equilibrium, we have

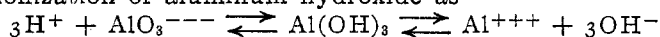
$$(1) \frac{\text{Concn. NaNO}_3 \text{ (diss.)}}{\text{Concn. NaNO}_3 \text{ (solid)}} = K$$

and by the law chemical equilibrium, we have

$$(2) \frac{\text{Concn. Na ions} \times \text{Concn. NO}_3 \text{ ions}}{\text{Concn. NaNO}_3 \text{ (diss.)}} = K^1$$

The numerator of (1) is the denominator of (2), so the denominator of (2) is a constant, therefore, the  $\text{Concn. Na}^+ \times \text{Concn. NO}_3^- = K$  times  $\text{Concn. solid NaNO}_3 \times K^1$ , for in a saturated solution of sodium nitrate the product of the concentration of the two ions is a constant number. Soils contain many compounds of different solubilities and the solubilities of many of these compounds are so low that the soil solution must always be approximately saturated with them. According to the law of chemical equilibrium, the concentration of the product of the ions of a substance divided by the amount of substance dissolved is a constant. This means that common ions affect the solubilities of other substances. From this it is easy to see that the whole system can be changed by the addition of an outside substance, which brings about the whole or partial precipitation of one kind of ion present in solution. The taking up of soil constituents by plants and the constant movement of soil moisture make it certain that the soil solution is constantly changing. Substances kept out of solution by other substances and substances in solution because of the presence of certain other substances are constantly being allowed to dissolve or are forced out of solution by the changing phenomena in connection with changes in soil moisture. Reversible reactions must play important rôles in the soil solution, for changes in soil moisture cause the active masses of the substances to change.<sup>1</sup>

Neutralization is the combining of a hydrogen ion with an hydroxyl ion to form undissociated water. Water, aluminum hydroxide, and certain other soil constituents are amphoteric, *i. e.*, they act as acids under specific conditions and as bases under other specific conditions. For example, we may express the ionization of aluminum hydroxide as

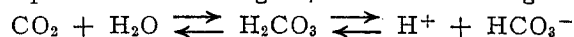


The mass action formula applied to water gives

$$\frac{\text{H}^+ \times \text{OH}^-}{\text{H}_2\text{O(sol.)}} = K$$

The denominator must be a constant; therefore the ionization constant for pure water is  $\text{Concn. H}^+ \times \text{Concn. OH}^- = K$ . Any substance which on reaction with water would remove either  $\text{H}^+$  or  $\text{OH}^-$  ions would make the solution either acid or alkaline, for

pure water is the standard for neutrality and a solution is only neutral when the concentration of the  $\text{H}^+$  ions is equal to the concentration of the  $\text{OH}^-$  ions. From the results of reaction between water and substances, we are led to conclude that water can act either as an acid or a base, depending on the conditions present. Water on reacting with metallic oxides may be considered a base, for in such cases the action depends on the formation of  $\text{OH}^-$  ions.  $\text{CaO} + \text{H}^+ + \text{OH}^- \rightarrow \text{Ca(OH)}_2$ . Water acts as an acid in that hydrogen is set free from water by potassium and sodium in the same manner that it is set free from hydrochloric acid by zinc. A type of reaction which takes place on extracting soils is the following:

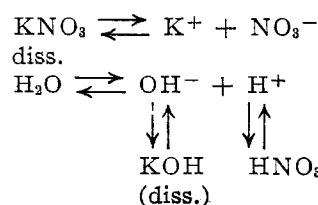


and  $\text{H}_2\text{CO}_3$  can be considered a hydrogen salt according to the same principle that  $\text{NaHCO}_3$  is a sodium salt.

The variations of the compounds present in soil as to quantities, solubilities, and their inter-reactions attendant upon variations in the moisture content and cropping phenomena show that water must play the important rôle in the constitution and reaction of soils. A recent investigation, as well as the present, gives evidence that the readily changing substances in the soil belong to those classes of compounds that hydrolyze readily. First, the work reported in this paper, and, second, the evidence obtained by Conner<sup>1</sup> show wide variations in soil acidity as the result of keeping soils at different moisture contents for one year. Silicates have also been found by Conner<sup>1</sup> to show increased reactions with normal potassium nitrate solutions in proportion as the water of constitution is increased.

The reactions between water and the salts commonly used for estimating so-called soil acidity illustrates the hydrolysis of all classes of salts but show that data so obtained are indicative of the nature of many substances that have to do with the reaction of soils.

Potassium nitrate in normal solution is the salt used in the Hopkins potassium nitrate method.<sup>2</sup> Potassium nitrate when dissolved in water is highly ionized, while water is only slightly ionized.

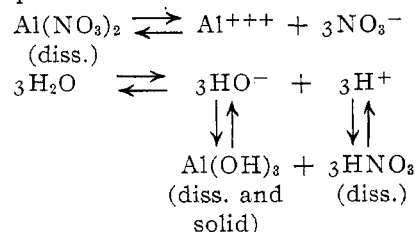


<sup>1</sup> S. I. Conner, *J. Agr. Res.*, **15** (1918), 321.

<sup>2</sup> THIS JOURNAL, **8**, (1916), 35.

<sup>3</sup> H. W. Wiley, Bureau of Chemistry, *Bulletin* **107**, p. 20.

Small amounts of molecular potassium hydroxide and nitric acid must be formed because potassium hydroxide and nitric acid have ionization constants. The net result is no appreciable hydrolysis, for both potassium hydroxide and nitric acid are almost completely ionized and the concentration of either  $H^+$  or  $OH^-$  ions is not appreciably affected. When soils that give an acid reaction by the potassium nitrate method are treated with the potassium nitrate solution, the results must be due to reactions between the potassium nitrate and weaker salts. Potassium forms soluble salts and stands at the head of the electromotive series of metals; thus at equilibrium any metal replaced by potassium will have a soluble nitrate ion to combine with, for all metallic nitrates are soluble. Many workers have shown that the potassium nitrate extract of acid soils contains considerable aluminum and some iron. That these results (the so-called acidity) were due to hydrolysis and attendant reactions is supported by the way aluminum nitrate and similar compounds react with water.

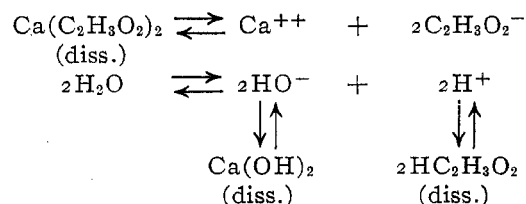


Aluminum hydroxide is a weak base and in addition is difficultly soluble. Nitric acid is highly ionized and the solution of aluminum nitrate in water is acid in reaction due to the  $OH^-$  ions of water being removed in molecular aluminum hydroxide. From the type of hydrolysis typified by the above and recognized in soils by Veitch<sup>1</sup> in 1904, it is evident that soil extracts may contain an excess of hydrogen ions when treated with normal potassium nitrate solution. The writer<sup>2</sup> has observed that the aluminum and iron present in the potassium nitrate extracts did not correlate with the titrations. This is to be expected, for through plant nutrition, draining, and chemical reactions the more soluble and stronger metals are being removed from the soil solution, thus allowing it to contain an excess of hydrogen ions under field conditions.

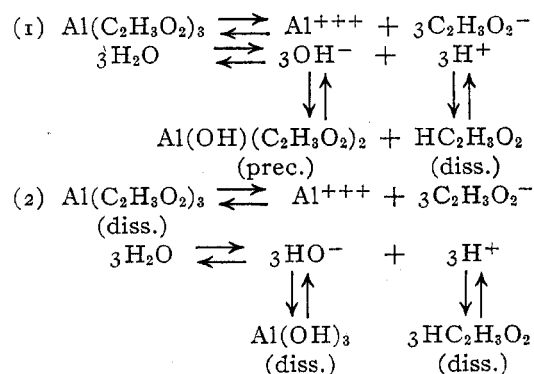
Gillespie<sup>3</sup> tested twenty-two soils of various types with the hydrogen electrode and found hydrogen ion exponents ranging from 4.6 to 8.6. No excess of hydrogen or hydroxyl ions would have given a hydrogen ion exponent of 7.0, and thus these soils under conditions tested ranged from acid to alkaline in reaction. Sharp and Hoagland,<sup>4</sup> as the result of quite extensive studies on soils with the hydrogen electrode, conclude that they have evidence "confirmatory of the view that soil acidity is fundamentally dependent on the equilibria of reactions yielding an excess of hydrogen ions." Conner,<sup>5</sup> through the hydrolysis of esters,

has also proved the presence of hydrogen ions in water and soil mixtures. The autocatalysis observed by Conner<sup>1</sup> shows that slight changes in the active masses of the soil constituents may have considerable effect on the rate of those reactions which have to do with soil acidity. The fact that autocatalysis increases the hydrolysis of an ester would indicate that autocatalysis may play an important part in increasing soil acidity. The part that catalyzers play in changing the velocity of soil reactions has been attributed to various things.<sup>2</sup>

Calcium acetate is the salt used in the C. H. Jones<sup>3</sup> acidity method. The reactions of calcium acetate with water illustrate the hydrolysis of the salt of a strong base and a weak acid and help in explaining the differences obtained for this and the potassium nitrate method.



Traces of molecular calcium hydroxide would be formed but this compound, though slightly soluble, is a strong base (highly ionized), and the hydroxyl-ion concentration of the system would not be appreciably changed until calcium hydroxide was precipitated. Molecular acetic acid would be formed, for acetic acid is not highly ionized and some hydrogen ions would thus be removed from the system. In contact with the soil, calcium acetate would cause the solution to become acid in reaction, since calcium (strong base) would tend to replace iron and aluminum in the soil constituents (silicates). The effect of water on aluminum acetate illustrates that the solutions titrated in the determination of acidity by the Jones method contain free acetic acid.



The chemical reagents used by Truog are calcium chloride (very similar in its reactions to potassium nitrate) and zinc sulfide, which illustrate another type of hydrolysis (that of a salt of a weak base and a weak acid).

<sup>1</sup> J. Am. Chem. Soc., 26 (1904), 637.

<sup>2</sup> H. A. Noyes and Lester Yoder, *Soil Science*, 5 (1918), 151.

<sup>3</sup> J. Wash. Acad. Sci., 6 (1916), 7.

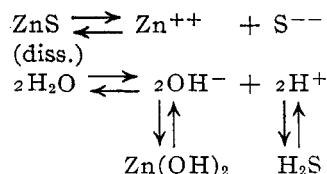
<sup>4</sup> J. Agr. Res., 7 (1916), 123.

<sup>5</sup> Loc. cit.

<sup>1</sup> Loc. cit.

<sup>2</sup> G. Bertrand, *Ann. inst. Pasteur*, 26, 852.

<sup>3</sup> *Proc. Assoc. Off. Agr. Chem.*, 1914.



Zinc hydroxide is a very weak base and difficultly soluble. Hydrogen sulfide is a very weak acid, largely un-ionized, and a gas. The hydrolysis of the zinc sulfide will be almost complete but the solution will be neither strongly basic nor acid, due to the zinc sulfide, because of the weakness of the resultant products of hydrolysis. The results of the Truog test then are due to the calcium chloride. The acidity is the result of the replacement of aluminum, iron, etc., by calcium. The hydrolysis of the chlorides gives hydrogen ions which allow hydrogen sulfide to be boiled off.

Many organic compounds are present in soils. A study of the works of Gortner,<sup>1</sup> Jodidi and Wells,<sup>2</sup> Potter and Snyder,<sup>3</sup> and Robinson and Miller<sup>4</sup> shows that soil organic matter hydrolyzes readily. It has been found that calcium hydroxide will remove, by precipitation, much of the water-soluble organic matter in soil extracts, and it is well known that magnesium hydroxide will decompose soil organic matter yielding ammonia. The influence of double salts and the formation of complex ions must be considered in connection with the soil extract. The trivalency of the phosphate radical and especially the ability of sodium and potassium to enter into combination with other substances in forming soluble phosphates and silicates must have effects on the solubilities and dissociations of substances in the soil solution. Organic matter combines with metallic elements in such a way that the metallic elements are not readily precipitable. This probably has been one of the facts underlying much of the so-called absorption and adsorption data. To illustrate—many compounds such as sugar, glycerin, tartrates, and citrates are known to interfere with the precipitation of some metals. When a copper sulfate solution is mixed with glycerin, no precipitate of copper hydroxide is formed on the addition of sodium hydroxide. This behavior is made use of in Fehling's and Haines' solutions in testing for sugar.

A theory of how organic matter interferes with the tests for the metals is that it has in it hydroxyl groups with which the metallic hydroxides combine to form complex ions. Certain organic acids, which contain no hydroxyl groups, are capable of forming complexes with metallic ions. All of these complex ions are decomposed, rather readily, by the addition of strong acids whose hydrogen ion breaks up the complex ions by suppressing the anions of the weaker organic acids. In soil acidity determinations no opportunity is given for these complexes to be broken up. Acid as well as alkaline soils have an acid neutralizing

power which has to be considered in determining available phosphoric acid by the *N/5* hydrochloric acid method.<sup>1</sup>

Recent data of Gillespie and Wise<sup>2</sup> substantiate the statements made in the paragraph just previous concerning the hydrolysis of organic compounds. The following quotation from the contribution of Gillespie and Wise is given as showing that one can look to the regular working of fundamental physico-chemical laws rather than to the more hypothetical adsorption and colloidal activity theorems, as accounting for what is spoken of in the literature as soil acidity.

There seems to be no reason to doubt that the large decrease of potential seen when potassium chloride is added to humus is due to a large increase of hydrogen-ion concentration, which, in turn, is due mainly to a reaction between the potassium chloride and the humus. The action of salts on the hydrogen-ion activity of true solutions and the uncertainties due to diffusion potentials make it difficult to draw any conclusions as to the mechanism of the reaction between salts and humus.

The mechanism of the reaction between soils and neutral salts is in dispute. Harris maintains that when a portion of soil is repeatedly extracted with saline solution, the total acid substance yielded by sodium chloride or potassium nitrate is very much less than that yielded by sodium acetate.

He mentions a difference in the total acid yielded by potassium nitrate and sodium chloride (this difference is small compared with the difference seen by him in the action of ether and sodium acetate), and points out that it is difficult to account for the liberation of so much acid on the assumption that the reaction is purely chemical and insists that it is a case of adsorption, following the typical adsorption curve. It is fair to point out that the fact that sodium acetate reacts so much more extensively with soil than does potassium nitrate or sodium chloride (in a single treatment) may well be due to the buffer action of sodium acetate, which permits the liberation of a considerable quantity of acetic acid without too high a hydrogen-ion concentration resulting. We also appreciate the difficulty of accounting for the large apparent increase of hydrogen-ion concentration occurring when humus is treated with potassium chloride, on the assumption that the process is purely chemical, but we do not seek to draw a sharp line between chemical and adsorptive processes.

If instead of looking upon certain substances as colloids, we consider that specific conditions allow some substances to go into what is termed the colloidal state we have the following definition: "In the colloidal state a substance does not diffuse through parchment membranes; does not show more than slight osmotic pressures; and is non-crystalline." The solution and suspension theories of colloids have brought it about that we attribute the very marked differences in the physical properties of the various classes of solutions as being due to the differences in the size of the particles present. In considering the results to be obtained by any method of soil extraction, it is undoubtedly necessary to fully realize that soils contain ions ensuing from compounds of low conductivities which allow the presence of colloidal bodies. Methods for the preparation of colloids that would apply to those in soils are (1) that illustrated by the

<sup>1</sup> *Soil Science*, 2 (1916), 395.

<sup>2</sup> Iowa Experiment Station, *Research Bulletin* 3.

<sup>3</sup> *J. Am. Chem. Soc.*, 37 (1915), 2219.

<sup>4</sup> Michigan Agricultural Experiment Station, *Technical Bulletin* 35.

<sup>1</sup> Arthur Goss, in Wiley's "Principles and Practice of Agricultural Analysis," 1, 465.

<sup>2</sup> *J. Am. Chem. Soc.*, 40 (1918), 796.

preparation of colloidal ferric hydroxide and colloidal silicic acid, namely, dialysis, and (2) that illustrated by the production of colloidal matter from a normally difficultly soluble substance, in the absence of an electrolyte. Is it not reasonable to presume that carbon dioxide produced slowly through bacterial and root respirations might be the cause of the formation of some colloidal iron and aluminum compounds from dissolved salts of these metals present in a weak ionic solution in the soil interspaces to and from which water is continually moving? This reaction would apparently be quite similar to those taking place when ammonium carbonate is added to ferric chloride until a precipitate begins to form and then the mixture is dialyzed with water. A soil containing an excess of free carbon dioxide gas and water probably yields some colloidal silicic acid by forming soluble hydrated silicates in much the same way that colloidal silicic acid is prepared in the laboratory by adding a solution of sodium silicate to water containing a slight excess of hydrochloric acid. From the study of the action of water on various salts presented to illustrate hydrolysis, colloidal solutions may also be found in certain soils due to the formation of insoluble substances by soil reaction in the presence of small amounts of electrolytes. The formation of colloidal bodies in the soil solution is thus dependent on hydrolytic mass action phenomena, and any soil acidity which might be attributed to the presence of colloidal matter thus is primarily due to the workings of the mass law rather than to the presence of the colloidal bodies. The constancy of the soil moisture must determine largely the colloidal possibilities of the soil solution and the results already referred to, where Conner<sup>1</sup> got wide variations in soil acidity by several methods, due to keeping soils at different moisture content, rather goes against the belief that soil colloids could be more than slightly responsible for the acidity results obtained.

#### PLAN OF INVESTIGATIONS

Paraffined Wagner pots, filled with equal weights of soil to which the various applications of calcium carbonate and fertilizing materials had been added, were used for all experiments. The soil was kept one-half saturated with water throughout the investigation from February 4 to December 5, 1916. Each experiment except 5A (which contained only three pots) was made up of nine pots each carrying four plants of *Capsicum, annuum, abbreviatum* (*Celestial*). Three pots received no carbon dioxide gas additions, three received carbon dioxide gas at the rate of 650 cc. per pot per hr. from 8.00 A.M. to 4.00 P.M. each day commencing April 16, while the other three received the carbon dioxide gas treatment constantly from April 16 to the close of the experiments. The system of treatment, the description of the Wagner pot, and method of applying gas additions are given in the previous article.

#### THE SOIL USED

The soil used was a brown silt loam classified by the Bureau of Soils as Sioux Silt Loam. The acidity

<sup>1</sup> Loc. cit.

of this soil when taken from the field containing 18.0 per cent of moisture was 1540 parts calcium carbonate per million pounds of dry soil by the Veitch method and 233 parts by the Hopkins potassium nitrate method. The analysis of the soil is given in Table II.

TABLE II—ANALYSIS OF SOIL<sup>1</sup>

	Per cent
Insoluble residue <sup>2</sup> .....	82.05
K <sub>2</sub> O <sup>3</sup> .....	0.41
Na <sub>2</sub> O <sup>3</sup> .....	0.36
CaO <sup>3</sup> .....	0.44
MgO <sup>3</sup> .....	0.79
Fe <sub>2</sub> O <sub>3</sub> <sup>3</sup> .....	4.35
Al <sub>2</sub> O <sub>3</sub> <sup>3</sup> .....	3.65
P <sub>2</sub> O <sub>5</sub> <sup>3</sup> .....	0.13
Mn <sub>2</sub> O <sub>3</sub> <sup>3</sup> .....	0.18
SO <sub>3</sub> <sup>3</sup> .....	0.52
Water, hygroscopic <sup>4</sup> .....	2.31
Volatile matter <sup>4</sup> .....	5.76
Nitrogen <sup>5</sup> .....	0.19
Total carbon <sup>6</sup> .....	2.12
Inorganic carbon <sup>6</sup> .....	0.03

<sup>1</sup> From preliminary paper, *Loc. cit.*

<sup>2</sup> Solution and residue made by extracting soil on steam bath with hydrochloric acid (sp. gr. 1.115) for 10 hrs. Solution analyzed by usual procedures.

<sup>3</sup> Determined volumetrically from acid solution with hydrogen sulfide as reducing agent.

<sup>4</sup> Method of Goss.

<sup>5</sup> Five-gram aliquot used and both determinations made on same aliquots.

<sup>6</sup> Regular Kjeldahl.

<sup>7</sup> Method of Ames and Gaither as modified by Schollenberger.

<sup>8</sup> Method of Marr with dilute acid and vacuum as recommended by Ames of Ohio.

TABLE III—CHANGES IN ACIDITY DUE TO EXTRACTING VARIOUSLY TREATED ACID SOIL WITH CARBON DIOXIDE-FREE DISTILLED WATER

	CO <sub>2</sub> Treatment per Day Hours	CaCO <sub>3</sub> Added	Acidity at Close of Inversion	Acidity after Extraction <sup>1</sup>	Change Due to Extraction
Experiment 1					
Acid soil, with crop	0	0 <sup>1</sup> 592 <sup>1</sup>	534 <sup>1</sup>	—	58
	8	0 716	648	—	68
	24	0 881	791	—	90
Experiment 2					
Acid soil, with crop, and single application of CaCO <sub>3</sub>	0	770 362	378	+	16
	8	770 644	516	—	128
	24	770 736	585	—	151
Experiment 3					
Acid soil, with crop, and double application of CaCO <sub>3</sub>	0	1540 353	378	+	25
	8	1540 449	479	+	30
	24	1540 510	516	+	6
Experiment 4 <sup>2</sup>					
Acid soil, with crop, with triple application of CaCO <sub>3</sub> and single application of phosphorus, Banner bone <sup>3</sup> (dicalcium phosphate)	0	2310 242	265	+	23
	8	2310 350	365	+	15
	24	2310 333	302	—	31
Acid phosphate <sup>4</sup>	0	2310 324	234	—	90
	8	2310 456	353	—	103
	24	2310 416	315	—	101
Experiment 5 <sup>4</sup>					
Acid soil, with crop, with triple application of CaCO <sub>3</sub> and single application of nitrogen, Dried blood <sup>7</sup>	0	2310 315	232	—	83
	8	2310 397	275	—	122
	24	2310 454	338	—	116
Sodium nitrate <sup>7</sup>	0	2310 321	176	—	145
	8	2310 321	231	—	90
	24	2310 475	323	—	152
Experiment 5A <sup>8</sup>					
Acid soil, with crop, with triple application of CaCO <sub>3</sub> and approximately one-half application of nitrogen in form of sodium nitrate	0	2310 227	202	—	25
	8	2310 318	239	—	79
	24	2310 365	277	—	88

<sup>1</sup> Figures express parts per million parts of soil.

<sup>2</sup> Single application of lime equals 770 parts calcium carbonate per million of dry soil.

<sup>3</sup> Single application of phosphorus equals 501.5 parts per million of dry soil.

<sup>4</sup> Single application of nitrogen equals 235.6 parts per million of dry soil.

<sup>5</sup> In Expts. 4 and 5 comparisons were made between different carriers of phosphorus and nitrogen.

<sup>6</sup> Two pots in each set of three received Banner Bone and one acid phosphate in Expt. 4.

<sup>7</sup> Two pots in each set of three received dried blood and one sodium nitrate in Expt. 5.

<sup>8</sup> Carbon dioxide treatment started 20 wks. later in Expt. 5A than in other experiments.

<sup>9</sup> The extraction tube was weighed at the start and after the 500 cc. of extract had been obtained. The wet soil was removed and 62.5 cc. of 2 N potassium nitrate solution were added, together with enough water to make 125 cc. per 50 g. of dry soil. The figures for acidity after extraction were obtained in this manner in all cases.

At the close of the investigation the soil in each pot was emptied out in turn into a large pan and thoroughly

mixed. Samples of the mixed soil were taken to the laboratory, air-dried, and preserved for chemical analysis. Acidity determinations were made on these air-dry samples both before and after extraction with carbon dioxide-free distilled water by the Hopkins normal potassium nitrate method. The results are given in Table III.

#### EXTRACTION APPARATUS USED

Fig. 1 shows the extraction apparatus used. A graduated cylinder was fitted with a two-holed rubber stopper. One hole was used to make connections with the suction line and the other to connect with the extraction tube. The cylindrical part of the extraction tube was 12 in. long and had an internal diameter of about  $\frac{1}{2}$  in. The lower part of the extraction tube was drawn out and fused to a small glass tube. A perforated porcelain disc covered with a mat of pulped ashless filter paper forms the filter.

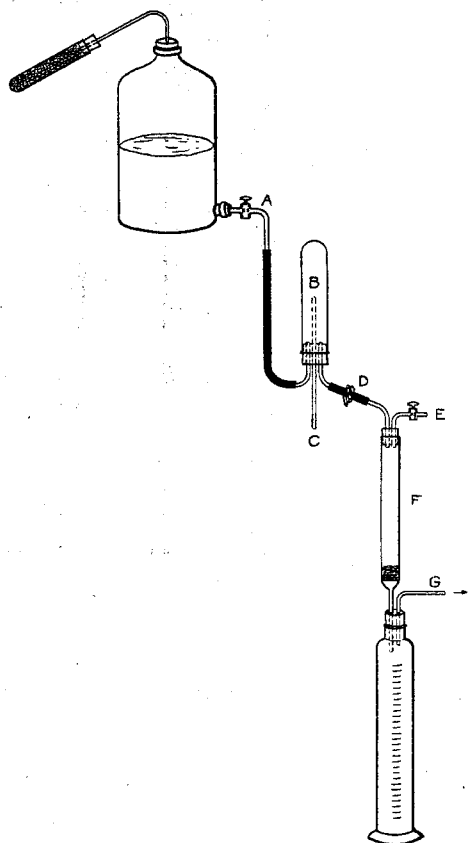


FIG. 1

The upper end of the extraction tube is closed with a two-holed rubber stopper carrying connections to the outside air and the overflow trap (which keeps water head constant). The properly protected supply of carbon dioxide-free distilled water and pinchcocks make the apparatus complete.

Fifty grams of the prepared air-dry soil are weighed out and slid into an extraction tube in which a filter has just been prepared. The soil is compacted slightly by tapping the extraction tube, held upright, on the bench a prescribed number of times. The extraction tube is put in place. The stopcock A is opened and the constant level tube B is filled; A is then closed

down until the water overflows slowly (drop by drop) at C. Pinchcock D is opened, and then pinchcock E is held open until a layer of water about 1 in. deep covers the surface of the soil in F. Stopcock A is adjusted to supply water as fast as it moves out of B into the extraction tube. When water begins to come through into the cylinder G the rate of flow is adjusted by raising or lowering B. In some cases it is advisable to apply suction at G rather than to increase the water head.

#### PRINCIPLE OF EXTRACTOR

In our extractions the following points were taken into consideration. Solubilities due to added carbonic acid in the water used for extraction were eliminated since the carbon dioxide factor was already included in the experiments. Carbon dioxide-free distilled water moving down slowly through the soil was expected to deplete the different soil layers successively of their water-soluble material and of the materials gradually brought into solution by changing the mass action relations. Substances having high solubility and high ionization (slightly hydrolyzed) constants were undoubtedly removed first. Each new layer of water bore a different relation to the soil it came in contact with and dissolved out substances under different conditions, since substances already removed gave possibilities of different solubilities and hydrolysis, and the active masses of the soil constituents were constantly changing. The effects of specific mineral radicals on the solubilities of other radicals changed constantly. The amount of solution (extract) obtained, 500 cc., and the rate at which it was obtained, 50 cc. per day, was such that the first 350 cc. removed most of the readily soluble material (the last three 50 cc. portions were found by test to contain little soluble material). Undoubtedly the greater portion of the dissolved material, the readily water-soluble material and material resulting from hydrolytic decompositions were in the extract. Small amounts (constant) of soluble material from substances of slight solubility and the soluble products of slow hydrolysis could have been obtained almost indefinitely.

The acidity determinations made on the soil both before and after extraction are given in Table III. The possibilities of hydrolysis of the reagent used in making acidities when it is dissolved in water made it seem advisable to use the potassium nitrate method for the determinations. The facts that the salts of potassium are soluble and that the nitrates of any metals replaced by potassium would be soluble were advantageous in studying whether the extraction of the soils with water had removed from them the substances responsible for the reactions obtained previous to extraction.

Table III brings out the following:

(1) Carbon dioxide gas, added to the soil, has, in every case, increased soil acidity as determined by the potassium nitrate method. The average results of all experiments expressed in terms of calcium carbonate follow. Before extraction, zero hours carbon dioxide treatment gave an acidity of 342 lbs. per

million; 8 hrs. carbon dioxide per day, 456 lbs. per million; and 24 hrs. carbon dioxide per day, 521 lbs. per million. After extraction, zero hours carbon dioxide treatment gave an acidity of 300 lbs. per million; 8 hrs. carbon dioxide per day, 388 lbs. per million; and 24 hrs. carbon dioxide per day, 431 lbs. per million.

(2) Carbon dioxide gas added to the soil has changed the constitution of the soil, in that the reactions of the soil with potassium nitrate were changed.

(3) Calcium carbonate additions to the soil decreased the acidity of the soil but not in proportion to the amounts added, showing that this compound has made other chemical combinations besides those which decrease the acidity measured by the potassium nitrate method.

(4) Calcium carbonate has also produced changes in the soil as shown by the differences in acidity before and after extraction with carbon dioxide-free water. There is a 58 lb. decrease due to extraction where no lime was added, an increase of 16 lbs. on extraction when a single application of lime was applied, and an increase of 25 lbs. with the double application of calcium carbonate.

(5) Carbon dioxide applications with calcium carbonate have generally effected changes in the soil shown in the differences between acidity determinations before and after extraction.

(6) Calcium from calcium carbonate has replaced acid-reacting substances soluble in normal potassium nitrate solution.

(7) The form in which the phosphorus was applied and both the form and the amounts in which the nitrogen was applied effected changes in the soil which are apparent when the soil is treated with a normal potassium nitrate solution.

(8) Acid phosphate when applied with calcium carbonate did not decrease the acidity of the unextracted soil to the same extent that dicalcium phosphate and an equal quantity of calcium carbonate did. This failure to decrease the acidity may be due to the fact that water-soluble calcium sulfate ( $\text{CaSO}_4$ ) reacted with the soluble phosphate to form aluminum compounds that were easily hydrolyzed by water.

Table IV gives the weights of material precipitated by ammonium hydroxide from potassium nitrate extracts of the variously treated soils. The differences are evidence that the results reported in Table III are due to changes in the substances making up the soil.

Table IV shows:

(1) Carbon dioxide gas additions to the soil have both increased and decreased the amount of substances precipitable by ammonium hydroxide which are extracted by a normal potassium nitrate solution.

(2) Calcium carbonate additions to the soil did not decrease the weights of ammonium hydroxide-precipitable material in proportion to the amount added. Calcium will replace aluminum and the results of such a reaction are apparent in the increased weight of precipitates from the potassium nitrate extract of the soil receiving double application of calcium carbonate.

(3) The form in which the phosphorus and nitrogen were applied was the cause of reactions which influenced the amount of material extracted by the normal potassium nitrate solution. The increased amounts of substances obtained after extraction are evidence that the fertilizing materials were the cause of soil solutions of different composition which in turn affected the solubility of aluminum-containing compounds in the soil. Acid phosphate and sodium nitrate (soluble materials) gave entirely different potassium nitrate extracts from the extracted soils than dicalcium phosphate and dried blood (insoluble materials).

TABLE IV—CHANGES IN WEIGHT OF MATERIAL PRECIPITATED BY AMMONIUM HYDROXIDE FROM POTASSIUM NITRATE EXTRACTS OF VARIOUSLY TREATED SOILS

TREATED SOILS				
	CO <sub>2</sub>	Normal Potassium Nitrate Extracts		
	Treat-	Wt. of Ppt. before	Wt. of Ppt. after	
	ment per	Extraction	Extraction	Change in
	Day	of Soil	of Soil	Grams
	Hours	Grams	Grams	
Experiment 1				
	0	0.0367 <sup>1</sup>	0.0348	—0.0019
	8	0.0399	0.0306	—0.0093
	24	0.0404	0.0382	—0.0022
Experiment 2				
	0	0.0375	0.0362	—0.0013
	8	0.0413	0.0316	—0.0097
	24	0.0437	0.0326	—0.0111
Experiment 3				
	0	0.0291	0.0328	+0.0037
	8	0.0338	0.0464	+0.0074
	24	0.0335	0.0524	+0.0189
Experiment 4				
	0	0.0284	0.0464	+0.0180
Banner bone.....	8	0.0269	0.0388	+0.0118
	24	0.0244	0.0424	+0.0180
Experiment 5				
	0	0.0231	0.0282	+0.0051
Acid phosphate.....	8	0.0248	0.0286	+0.0038
	24	0.0338	0.0256	+0.0018
Experiment 5A				
	0	0.0233	0.0490	+0.0257
Dried blood.....	8	0.0288	0.0458	+0.0170
	24	0.0276	0.0350	+0.0074
Experiment 6				
	0	0.0279	0.0260	—0.0019
Sodium nitrate.....	8	0.0226	0.0264	+0.0038
	24	0.0289	0.0298	+0.0009
Experiment 5A				
	0	0.0255	0.0264	+0.0009
	8	0.0251	0.0282	+0.0031
	24	0.0233	0.0264	+0.0031

<sup>1</sup> Figures are ignited precipitate from aliquot representing 50 g. of soil. The material was principally aluminum oxide ( $\text{Al}_2\text{O}_3$ ) but contained a little iron and some silica.

TABLE V—CONDUCTIVITY OF WATER EXTRACTS OF THE VARIOUSLY TREATED ACID SOIL

	CO <sub>2</sub> Treatment per Day Hours	Specific Conductivity
	Experiment 1	
	0	0.0914 <sup>10-3</sup>
	8	0.0911 <sup>10-3</sup>
	24	0.1001 <sup>10-3</sup>
	Experiment 2	
	0	0.0948 <sup>10-3</sup>
	8	0.0953 <sup>10-3</sup>
	24	0.1039 <sup>10-3</sup>
	Experiment 3	
	0	0.0856 <sup>10-3</sup>
	8	0.0965 <sup>10-3</sup>
	24	0.1001 <sup>10-3</sup>
	Experiment 4	
	0	0.1334 <sup>10-3</sup>
Banner bone.....	8	0.1362 <sup>10-3</sup>
	24	0.1414 <sup>10-3</sup>
	0	0.2799 <sup>10-3</sup>
Acid phosphate.....	8	0.2976 <sup>10-3</sup>
	24	0.3000 <sup>10-3</sup>
	Experiment 5	
	0	0.1757 <sup>10-3</sup>
Dried blood.....	8	0.2704 <sup>10-3</sup>
	24	0.2107 <sup>10-3</sup>
	0	0.3144 <sup>10-3</sup>
Sodium nitrate.....	8	0.3007 <sup>10-3</sup>
	24	0.1946 <sup>10-3</sup>
	Experiment 5A	
	0	0.2107 <sup>10-3</sup>
	8	0.1999 <sup>10-3</sup>
	24	0.2034 <sup>10-3</sup>

The specific conductivities of the extracts obtained with distilled water give indications of the nature



of the material removed by the extraction. The results are given in Table V.

The following may be deduced from the specific conductivities:

(1) Carbon dioxide gas additions to the soil have changed the constitution of the soil. This is shown by the differences in the conductivities of the water extracts.

(2) Calcium carbonate additions to the soil had comparatively little effect on the conductivities of the soil extracts. Two things undoubtedly account for this: the low solubility of the calcium carbonate, and the low solubilities and conductivities of the substances in the soil that the calcium replaced.

(3) Phosphorus and nitrogen applied in different forms were the cause of water extracts of very different specific conductivities. The extracts from the soils receiving dicalcium phosphate and calcium carbonate had low specific conductivities in comparison to the extracts from soil receiving sodium nitrate of acid phosphate (which contains sodium sulfate in addition to phosphate).

(4) The specific conductivities of extracts from the full application of sodium nitrate and acid phosphate are believed to show:

(a) The soluble sulfate ion from the calcium sulfate stayed in solution and kept up the specific conductivity.

(b) Where sodium nitrate was added the soluble sodium gave increased conductivity.

(c) The action of carbon dioxide gas on the soil constituents increased the ease with which sodium replaced substances in the insoluble compounds, and the conductivity would decrease due to the slight solubility and ionization constants of the replaced substances. The losses of nitrates from bacterial activities and plant absorption undoubtedly were also concerned.

(d) Evidently the one-half application of sodium nitrate did not furnish a large excess of sodium over that entering into the replacement reactions.

(e) The organic nature of the nitrogen in the dried blood and its constant conversion by bacterial agencies under the different conditions of aëration helps in explaining the conductivities of the extracts obtained.

#### DISCUSSION

Carbon dioxide gas added to this soil which does not have enough bases present to allow for the formation of carbonates gives increased acidity results by the potassium nitrate method.

Sharp and Hoagland<sup>1</sup> have found the hydrogen ion concentration of soils to be increased by the addition of potassium chloride, sodium chloride, and barium chloride. The increases were greater with barium chloride than they were with either potassium or sodium chloride, and it is to be noted that the salts of barium are more insoluble than those of sodium or potassium and thus the replacement of metals (such as aluminum) by barium would be more complete. Barium removed from solution would leave each chlorine ion offset by the ions of some metal or metals

further down in the electromotive series, and increased hydrolysis would result.

Bouyoucos has followed the changes in the freezing points of soil-water emulsions when treated with successive portions of calcium hydroxide and other dilute solutions. His results and those obtained in our investigations confirm the conclusion previously developed in the theoretical part of this paper, namely, that soil acidity is the resultant of the workings of physicochemical laws. The following paragraphs take up the work of Bouyoucos in connection with the present investigation.

Bouyoucos<sup>1</sup> has advanced as a method for the determination of the lime requirement of soils to replace or supplement the well-known Veitch lime-water method, the results obtained by adding successive portions of  $N/25$  calcium hydroxide to soil-water emulsions. On graphing his results, he gets three types of curves which he designates as (1) the acid curve, (2) the absorption curve, and (3) the alkaline or no lime curve. His acid curve is well illustrated by the changing freezing point depressions of acids and hydrolyzable salts, such as aluminum nitrate when treated with successive additions of calcium hydroxide solution. Example: When hydrochloric acid, which is highly ionized in dilute solution, is treated with  $N/25$  calcium hydroxide solution, the freezing point of the solution is raised, due to the neutralization of the hydrogen ions of the acid by the hydroxyl ions of the calcium hydroxide. When neutralization is complete, the freezing point depression increases again, due to the high ionization constants of both calcium chloride and calcium hydroxide. His absorption curve (2) is illustrated by soils which on the successive additions of calcium hydroxide undergo no change in the freezing point depression for a time and then depress it for each addition of the alkali. It is to be noted in this connection that organic matter combines with compounds such as calcium hydroxide and it is apparent that no change in freezing point depression would accompany a reaction of this kind. Further, it is well known that calcium is leached out of soils and that plant ash contains much more potassium and sodium than calcium and magnesium and but very little iron and aluminum. The increase in acidity of the limed soil in Expt. 3 after extraction in comparison to the decrease in acidity of the unlimed soil in Expt. 1 after extraction, in these investigations, shows that the addition of calcium is concerned with the replacement of iron and aluminum, which give titratable acidity because of the hydrolysis of aluminum and iron nitrates. This result and Bouyoucos' finding soils that give freezing point depression curves of the Type 2 show that both calcium and hydroxyl can be removed from solution by soil components. This is evidence *per se* that the freezing point depression is not going to be changed appreciably as long as both the calcium and the hydroxyl radicals are entering into chemical reactions with the soil. Bouyoucos' type 3 freezing point depression curve is a depression of the freezing point for each portion of calcium

<sup>1</sup> *Loc. cit.*

<sup>1</sup> Michigan Agricultural Experiment Station, Technical Bulletin 27.



hydroxide added. Soils of this type have no lime requirement.

The analysis of the soil used in the experiments reported in this paper has been given but this analysis gives little information concerning the constitution of the soil or the soil solution. The results obtained by Bouyoucos<sup>1</sup> on determining the freezing point depressions of soils under various conditions with different salts and acids throw some light on the reactions taking place between the soil and the soil solution. Quartz sand showed no lime requirement by the freezing point method except when treated with dipotassium phosphate ( $K_2HPO_4$ ) and monocalcium phosphate [ $CaH_4(PO_4)_2$ ]. These salts have lime requirements of their own, due to the way they ionize and the insolubility of the calcium phosphates which result. The addition of soluble salts to soils increased their lime requirements as shown by the freezing point method.

Bouyoucos' curves resulting from the lime requirement determination by the freezing point depression method when the soil is treated with a soluble salt are all of the acid type. This shows that in such cases the calcium hydroxide neutralizes hydrogen ions resulting from the hydrolysis of the soluble salt which in turn result from reactions between the soluble salt and the soil. This acid type curve is evidently the resultant of both the acid curve and the lime absorption curves. The broken curve from the soil treated with sodium nitrate, the more broken curve where calcium nitrate was used, and an almost horizontal section in the curve where monocalcium phosphate was used with the soil illustrate this.

In another article, Bouyoucos reports obtaining practically the same freezing point depressions on successive freezings of quartz sand, sands, and some sandy loams in comparison to changing depressions for successive freezings of loams, silty clays, and peats. This is rather conclusive that water enters into chemical combination with the soil constituents. The per cent of the original concentration of  $N/10$  acids and salts which goes to concentrate the soil solution, as measured by the changes in freezing point depression observed by Bouyoucos, depends quite regularly both on the solubilities of the salts of calcium, magnesium, iron, and aluminum, which can be formed from these compounds and the soils, and on the tendency of the salts formed to hydrolyze and form insoluble or hydrated compounds.

Some writers have said that no method will ever be devised by which the acidity of a soil can be determined. The changes in the soil used in these (Bouyoucos and Noyes) experiments make it quite certain that when the hydrogen ion concentration of the soil can be determined without the addition of water to the soil the result will give the hydrogen ion concentration of the soil at that instant. The addition of salts and changes in the water content of soil with attendant influences make it quite certain that the acidity of a soil is constantly changing and that recommendations for the application of agricultural lime have got to be

made, not specifically by the results of a chemical method, but by the results of chemical determinations in connection with extended knowledge of soil types and the crop results obtainable on these soil types.

#### SUMMARY

1—Soil acidity is discussed in relation to the place of the metals, ordinarily occurring in soils, in the electromotive series; the differences in the hydrolysis of the salts used in different soil acidity methods; and the conditions under which water may act as an acid or a base.

2—The presence of free hydrogen ions in the soil solution is accounted for on the basis of hydrolysis. Physicochemical explanations of the hydrolysis of silicates and of organic matter and the ability of organic matter to form complex ions with bases are held to be more satisfactory explanations of the rôle of organic matter than "adsorption" theories.

3—The active masses of substances normally present in soils and their tendencies to hydrolyze can account for the presence of substances in the colloidal state, and thus any soil acidity which might exist due to the peculiar properties of substances present in the colloidal condition is primarily due to the conditions which govern the formation of the colloidal solutions.

4—A special apparatus for extracting the water-soluble material in soils is described and the soils of all the experiments were extracted by this apparatus.

5—Carbon dioxide gas, added to the soil, has in every case increased soil acidity by the Hopkins potassium nitrate method. The average results for all experiments, expressed in terms of calcium carbonate, are as follows: Before extraction, no carbon dioxide treatment, 342 lbs. per million; 8 hrs. carbon dioxide treatment per day, 456 lbs. per million; and continuous carbon dioxide treatment, 521 lbs. per million. After extraction, no carbon dioxide treatment, 300 lbs. per million; 8 hrs. carbon dioxide treatment per day, 388 lbs. per million; and continuous carbon dioxide treatment, 431 lbs. per million.

6—Calcium carbonate decreased the acidity of the soil but not in proportion to the amounts added, showing that this compound has made other chemical combinations beside those which decrease the acidity measured by the Hopkins potassium nitrate method.

7—Calcium carbonate has also produced chemical changes in the soil that are shown by the differences in acidity before and after extraction with conductivity water. There was a 58 lb. decrease due to extraction where no lime was applied, an increase of 16 lbs. on extraction where the single application of lime was made, and an increase of 25 lbs. on extraction where the double application of calcium carbonate was made.

8—The form in which the phosphorus was applied and both the form and the amounts in which the nitrogen was applied effected changes in the soil, which are apparent when the soil is treated with normal potassium nitrate solution.

9—Carbon dioxide gas additions to the soil changed the amounts of substances precipitable by ammonium hydroxide, which are extracted by a normal potassium nitrate solution.

10—Calcium carbonate additions to the soil did not decrease the weights of ammonium hydroxide precipitable material in proportion as they decreased the acidity results. Calcium will replace aluminum, and the results of such a reaction are apparent in the increased weight of precipitates from the potassium nitrate extract of the soil receiving double application of calcium carbonate.

11—The form in which the phosphorus and nitrogen were applied was the cause of reactions which influenced the amount of material extracted by the normal potassium nitrate solution. The increased amounts of substances obtained after extraction are evidence that the fertilizing materials were the causes of soil solutions of different composition, which in turn affected the solubility of aluminum-containing compounds in the soil. Acid phosphate and sodium nitrate (soluble materials) gave entirely different potassium nitrate extracts from the extracted soils than dicalcium phosphate and dried blood (insoluble materials).

12—Calcium carbonate additions to the soil had comparatively little effect on the conductivities of the soil extracts. Two things undoubtedly account for this, the low solubility of the calcium carbonate and the low solubilities, as well as conductivities, of the substances in the soil that the calcium replaced.

13—Phosphorus and nitrogen applied in different forms were the cause of water extracts of very different specific conductivities. The extracts from the soils which had received dicalcium phosphate and calcium carbonate had low specific conductivities in comparison to the extracts from soil which received sodium nitrate or acid phosphate.

14—The specific conductivities of extracts from the full application of sodium nitrate and acid phosphate are held to show: The soluble sulfate ion from the calcium sulfate in the acid phosphate stayed in solution and kept up the specific conductivity; carbon dioxide gas augmented the increased conductivities; where sodium nitrate was applied, the sodium ions gave increased conductivity; the action of carbon dioxide gas on the soil constituents increased the ease with which sodium replaced substances in the soil; the conductivity decreased due to the slight solubilities and ionization constants of the new substances formed; the loss of nitrates through bacterial activities and plant "absorption" were also concerned.

15—Chemical reactions are held to be the causes of, and known laws of chemistry offer satisfactory explanations for soil acidity.

16—In conclusion, the reaction of a soil at any time is dependent both on the nature of and the proportions in which its constituents are present with water. Changing the water content, removing substances from solution, and the addition of other substances change the reaction in accord with the working of the law of mass action. The solubilities of sub-

stances in, the possibilities of combination, and the rate at which reactions take place in soil vary so that the condition of a soil at any time can be considered but a stage in its progress towards a constantly shifting equilibrium in accordance with the principle of LeChatelier.

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### A FURTHER STUDY OF THE DEROODE METHOD FOR DETERMINING POTASH

By T. E. KEITT AND H. E. SHIVER

Received March 31, 1919

We have proved<sup>1</sup> that the Lindo-Gladding method for determining potash gives low results in the presence of certain constituents normally present in mixed fertilizers and present in some sources of domestic potash. As a substitute<sup>2</sup> for the Lindo-Gladding method we have offered a modification of a method suggested by DeRoode,<sup>3</sup> and we have presented much concordant analytical data to prove its accuracy.

With potash selling at the present high prices it is but just that the producers of domestic potash shall have a fair valuation of their product, which will no doubt soon come in competition with foreign sources of potash. Treater dust is a case in point: this material shows about 0.6 per cent more water-soluble potash by the DeRoode method than it does by the Lindo-Gladding method. That this potash is actually present in water-soluble form will be shown in this article. With water-soluble potash selling for \$4.50 per unit, this means a loss of \$2.70 on each ton of this material due to an inaccurate method of analysis. When \$2.70 is multiplied by the total tonnage produced annually, we readily see that the aggregate loss is large.

The high degree of accuracy obtained through the use of the DeRoode method, the lessened number of operations, and the elimination of platinum apparatus make the method highly desirable.

Since the publication of our former article certain chemists have expressed doubt as to the accuracy of the method in the presence of nitrate of soda, ammonium salts, high content of phosphates, and large amounts of organic matter. We had already tested the samples used in the former work for ammonia and had established its presence in most of them. We have since estimated quantitatively the percentage of ammonia present as ammonium salts, by distilling over magnesium oxide. Table I shows that the ammonia content ran as high as 1.87 per cent in these samples.

An inspection of the following table shows that eleven of the twenty samples contained less than  $\frac{1}{2}$  per cent of ammonia, with an average plus difference for the DeRoode method of 0.081 per cent. Three samples contained between  $\frac{1}{2}$  and 1 per cent of ammonia with an average plus difference of 0.11 per cent. Six samples contained between 1 and 2

<sup>1</sup> THIS JOURNAL, 10 (1918), 994.

<sup>2</sup> *Ibid.*, 10 (1918), 219.

<sup>3</sup> J. Am. Chem. Soc., 17 (1895), 85.