

STUDIES ON SOIL REACTION. I.

A RÉSUMÉ.

By E. A. FISHER, M.A., B.Sc. (OXON.).

Rothamsted Experimental Station (Lawes Agricultural Trust).

IMPORTANCE OF SOIL REACTION AS A FACTOR IN SOIL FERTILITY.

SOIL fertility is often spoken of as though it were an absolute property of the soil; in reality it is a particular relationship subsisting between *soil conditions* on the one hand and *crop growth* on the other. The conditions conducive to soil fertility are the resultant of two main groups of factors, the *intrinsic* properties of the soil which are dependent on its chemical, physical and biological nature, and those *extrinsic* properties impressed on the soil by topographical and climatic factors*. These two groups cannot be sharply distinguished from each other, nor can any hard and fast line be drawn between the various factors comprised in them, because few are at present susceptible of exact measurement. In other words, that particular group of conditions that make up the fertility of a soil is an equilibrium brought about by the interaction of numerous factors some of which however can be varied by the agriculturist by manurial and cultivation operations.

Among those soil factors that are most readily controllable are many that cannot vary beyond comparatively narrow limits without becoming limiting or controlling factors in crop production. In particular the growth of soil organisms, as well as that of the plant itself, is very sensitive to the reaction of the medium, and it may happen that the presence or absence of a base will act as a limiting factor in crop production, and not merely through the direct effect of acidity or alkalinity on the plant itself or on the soil organisms, but on account also of the varying displacements produced on many of the factors that go to make up the complex chain of soil equilibria.

The question of soil reaction is therefore of great importance and one aspect of it, *viz.* soil acidity, or "sourness" to use the farmers'

* For an interesting discussion of fertility from this point of view, see E. J. Russell, *Soil Conditions and Plant Growth* (Longmans), 3rd ed. 1917, especially chap. VII.

phrase, has attracted attention from very early times. The use of lime—as oxide, hydroxide or carbonate, the last named as chalk, limestone or marl—in correcting soil acidity, or adjusting soil reaction, is among the oldest of agricultural operations; while of late years the study of soil acidity has occupied an important place in agricultural research. It cannot be said, however, that the enormous amount of work done has either solved the practical problem or clarified our ideas as to what exactly soil acidity means; and matters are not simplified by the use of a multiplicity of such terms as “soil acidity,” “apparent acidity,” “real acidity,” “potential acidity,” “adsorption acidity,” “positive” and “negative” acidity, “lime requirements” of soils and of plants, “immediate” and “continuous” lime requirements, “active” and “latent” lime requirements, etc.

THEORIES OF SOIL ACIDITY.

Some soils are apparently so acid that when moist they will redden litmus paper almost immediately, but their aqueous extracts seldom redden litmus after boiling off the CO_2 . The comparatively few cases reported in which the CO_2 -free aqueous extracts were acid to litmus have invariably been the result of highly abnormal conditions*, and the immediate cause of the reaction is obvious. Most acid soils, however, yield so little soluble acid on extraction with water alone that it cannot usually be detected by litmus paper after boiling off CO_2 .

A. *Humic Acid Theory.*

Various theories have been put forward at different times to explain such acidity as this. Sprengel(69) in 1826 attributed the acidity to the accumulation of insoluble complex organic acids—the so-called humic acids—produced by the decomposition of plant residues left over from the crop. The dark alkaline solution obtained on treating an acid soil with ammonia was supposed to contain the soluble ammonium salts of these acids and the acids themselves could be precipitated on acidifying. Such acids were also supposed to occur in neutral and alkaline soils combined with calcium or magnesium and are then practically insoluble in alkalis, without a previous extraction with acid. This hypothesis long held the field. The compounds obtained from soils, however, were very indefinite and variable in composition and

* For examples of such see Blair and Macy (12); Abbott, Connor and Smalley (1); Ruprecht (62), and Ames and Schollenberger (4). The numerals refer to references collected at the end of the paper.

always contained mineral impurities that could not be eliminated. Doubts therefore arose as to whether these so-called humus acids really were definite chemical compounds.

B. *Selective Adsorption Theory.*

The first real advance was due to van Bemmelen^(10,11) (1888) who considered that these bodies were not definite chemical compounds but absorption complexes, *i.e.* mixtures of a base and of various colloidal substances held together by some sort of surface attraction. These ideas were further developed into a general theory of soil acidity by Baumann and Gully about 1910^(8,9). The acid reaction of peat moss and of peat soils was attributed by these authors to the colloidal matter in the coverings of the hyaline sphagnum cells. The original sphagnum was about as "acid" as the peat, hence it is unnecessary to assume that the "acid" is a decomposition product. Moreover, if an acid is really present it is very insoluble as an aqueous extract of peat is practically neutral to litmus: and this is generally true of most "acid" soils. These views were based on the work of Linder and Picton⁽⁴²⁾ who showed that when As_2S_3 is precipitated from colloidal solution by $BaCl_2$ a small amount of barium is carried down with it and a corresponding amount of HCl is set free. If Ca-, Sr-, or K-chloride is used the same amount of HCl is left behind showing that equivalent amounts of the base are absorbed in each case. The Ba thus carried down is held very firmly and cannot be removed by washing although it is easily removed by other bases by digesting with an appropriate salt in solution. The work of Whitney and Ober⁽⁸⁰⁾ concerning the electrical condition of colloidal solutions gave some theoretical basis to Baumann and Gully's views, and further support was accorded by the fact that acidity is developed on shaking an acid or a neutral soil with neutral salt solutions. This phenomenon was first noticed by Thompson⁽⁷³⁾ and was explained by Way⁽⁷⁸⁾ as due to an interchange of bases between the neutral salt and a constituent of clay—a hydrated alumino-silicate of an alkali or alkaline earth. Later when the general theory of surface adsorption had been put forward and developed by Willard Gibbs, J. J. Thomson, Freundlich⁽²³⁾ and Wo. Ostwald⁽⁵⁶⁾ it was extended and applied in a somewhat modified form and under the name of selective adsorption to soil interchanges by Cameron^(15,16) and later by E. G. Parker⁽⁵⁷⁾ and by Harris^(29,30). Parker found that when an acid soil is shaken with a solution of KCl, the potash was displaced by aluminium and other bases in nearly equivalent amounts, the Cl remaining unchanged. When NaOH was

also present with the KCl just as much potash was absorbed by the soil but no bases from the soil replaced it. Parker concluded that the base is adsorbed by the soil and a real acidity developed which then dissolves from the soil the bases found in the solution. This conclusion was supported by washing out the soluble bases from the soil with HCl, washing the soil free from HCl and treating with KNO_3 solution: a considerable amount of free HNO_3 was found in the solution besides the usual $\text{Al}(\text{NO}_3)_3$ etc. Further support is given to this view by the more recent work of Blum (13) and Knight (38).

C. *Basic Exchange Theory.*

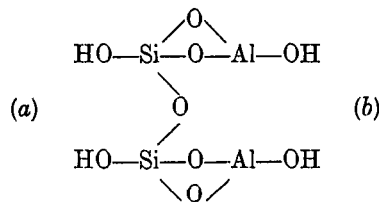
This adsorption view is not, however, universally held and many still hold that a real interchange of bases occurs not however with the insoluble organic acids of the soil but with the complex aluminosilicates of the clay fraction. This modern development of the classical work of Way (78) and that of Lemberg (40, 41) on the transformation of minerals by contact with salt solutions has much to support it. Sullivan (68) points out that CaCl_2 and an artificial Na-aluminosilicate may interact to form two slightly soluble substances, Na- and Ca-aluminosilicates. In such a case the reaction does not proceed to the formation of one of these two substances exclusively, but an equilibrium is reached in which both are present; a definite relationship prevails between the concentrations of the reacting substances in the solution: the amounts of different bases absorbed will vary with the solubility of their respective aluminosilicates, while change in temperature, by shifting the relative solubilities, may lead to readjustments in the equilibrium. Such an absorption is in general an exponential function of the concentration as also are the solubilities of the alkaline earth sulphates in acids of varying concentration (Ostwald (55)) and the action of K_2CO_3 on BaSO_4 (Meyerhoffer (51, 52, 53)). This form of curve is not therefore necessarily a proof of adsorption*. Such interchanges occur with many other silicates and aluminosilicates and sometimes Al is replaced by the base of a neutral salt: this accords with Veitch's (75) conclusion that an interchange of bases occurs between the neutral salt and the hydrated neutral silicates or aluminosilicates of the soil by which Al is brought into solution, the acidity developed being due to the hydrolysis of the Al salt. Daikuhara (21) and also Rice (60, 61) came to somewhat similar conclusions and this aspect has been further developed by the work of Spurway (70)

* This point cannot be too strongly emphasised; see Walker and Appleyard (76) and especially Moore (54).

on the "hydrolytic ratio" of soils, and that of Hartwell and Pember(31) on the part played by the Al⁺ ion in the toxicity of acid soils. This however is probably not the whole story and there is much evidence to show that both interchange of bases and true selective absorption may occur together in the same soil although possibly with different soil constituents. The work of Rice(60, 61) and of Knight(38) seems to support this conclusion and moreover the very complexity of the soil militates against any single factor being the sole cause of soil acidity.

D. Mineral Acid Theory.

A fourth theory proposed by O. Loew(46) attributes the acidity of certain Porto Rican clay soils deficient in humus to an aluminosilicic acid in the clay which he calls "argillic acid" and to which he gives the formula



By the neutralisation of the acid OH groups at (a) the acid would become neutral, while absorption of P₂O₅ is attributed to the basic OH groups at (b). By prolonged treatment of neutral clay, *i.e.* salts of argillic acid, with large quantities of water charged with CO₂ an acid clay may be produced. The reverse action should also take place, *i.e.* neutral salts should be decomposed by acid clay the base being absorbed and the acid set free; this was actually observed by Daikuhara(21). The work of Ashley(7), of Mellor(50) and of F. W. Clarke(19) on the constitution of pure clays supports at any rate the plausibility of the theory and Truog(74) also emphasises the importance of soil silicates in absorption phenomena. It has however never been shown that the phenomena cannot be explained equally well by selective absorption or by interchange of bases.

METHODS OF DETERMINING SOIL ACIDITY.

Whatever the cause or causes of "soil acidity" it is difficult to avoid the conclusion that a certain degree of real acidity is present which

should be capable of measurement. Many methods have been proposed at various times*. Among them are:

1. Inversion of cane sugar(61).
2. Saponification of ethyl acetate(20).
3. Liberation of iodine from a mixture of
 - (a) Potassium iodide and potassium iodate(8, 27, 28).
 - (b) Potassium iodide and potassium nitrate(45).
 - (c) Potassium iodide and potassium nitrite(21).
4. Basic exchange(60) with
 - (a) Neutral salts(21, 32, 33, 46), and
 - (b) Salts of weak acids(35, 36, 46).
5. Absorption of base from a solution of
 - (a) Basic hydroxide(1, 14, 47, 67, 75, 79), and
 - (b) Dye(37).

Table I. Comparison of various methods for determining
Lime Requirement.

CaCO₃ expressed as percentage of air-dried soil.

A. Hutchinson's (34) results.

Method used	Chelsea	Millbrook		Oundle	Woburn		Craibstone	
	CaCO ₃ %	CaCO ₃ %	Relative value	CaCO ₃ %	CaCO ₃ %	Relative value	CaCO ₃ %	Relative value
Jones ...	0.045	0.045	225.0	0.018	0.232	89.2	0.161	35.1
Hopkins ...	0.012	0.006	30.0	0.002	0.244	94.0	0.030	7.0
Lyon and Bizzell	—	—	—	—	0.226	87.0	0.436	101.4
Veitch ...	—	—	—	—	0.204	80.0	0.407	94.6
Hutchinson ...	Nil	0.020	100.0	Nil	0.260	100.0	0.430	100.0

B. Stephenson's (71) results.

Method used	Gray silt loam		Brown silt loam	
	CaCO ₃ %	Relative value	CaCO ₃ %	Relative value
Tacke	0.215	100.0	0.325	100.0
Hopkins	0.100	46.5	0.120	36.9
Jones	0.193	89.7	0.241	74.2
MacIntire	0.184	85.4	0.203	62.6
Veitch	0.232	108.1	0.316	97.4
Truog	0.610	283.7	0.797	245.2

* A short description of some of these methods is given by Hutchinson and MacLennan (34), a more critical examination of these methods, together with a résumé of all previous work on soil acidity, is given by Ames and Schollenberger (5) and by Frear (22).

Plot No.	1 None		2 Acid phosphate		29 Basic slag + mineral potash + NaNO ₃		18 Farmyard manure											
	a	b	a	b	a	b	a	b										
Fertiliser used	CaCO ₃ required	Compared with Hutchinson = 100	CaCO ₃ required	Compared with Hutchinson = 100	CaCO ₃ required	Compared with Hutchinson = 100	CaCO ₃ required	Compared with Hutchinson = 100										
Method																		
Hopkins	0.172	117.6	0.1320	97.8	0.004	8.2	0.181	142.7	0.006	9.6								
Veitch	0.100	68.4	0.100	74.1	Alk.	—	0.060	47.1	Alk.	—								
MacIntire	0.177	121.3	0.192	142.6	0.120	246.2	0.177	139.2	0.125	200.0								
Vacuum	0.365	249.6	0.387	288.9	0.190	389.7	0.310	243.1	0.211	338.0								
Hutchinson	0.146	100.0	0.135	100.0	0.049	100.0	0.127	100.0	0.062	100.0								
Plot No.	11	24	26	28	29	29	29	29	29	29								
Fertiliser used	Acid phosphate + mineral potash + NaNO ₃	Acid phosphate + mineral potash + Am ₂ SO ₄	Bone meal + mineral potash + NaNO ₃	Bone meal + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃	Basic slag + mineral potash + NaNO ₃							
Method																		
Hopkins	0.154	109.0	0.004	5.8	0.211	157.0	0.146	130.7	0.017	27.2	0.1275	113.8	0.0075	13.9	0.137	88.8	0.006	6.1
Veitch	0.090	63.7	Alk.	—	0.150	111.1	0.100	88.9	Alk.	—	0.060	53.3	Alk.	—	0.130	85.8	Alk.	—
MacIntire	0.192	134.7	0.125	181.8	0.200	148.1	0.185	164.4	0.145	218.9	0.180	160.0	0.105	195.3	0.110	135.5	0.1475	151.3
Vacuum	0.355	251.3	0.295	429.1	0.417	307.4	0.367	326.7	0.202	305.6	0.330	293.3	0.202	376.7	0.425	274.2	0.260	266.7
Hutchinson	0.141	100.0	0.066	100.0	0.135	100.0	0.112	100.0	0.066	100.0	0.112	100.0	0.051	100.0	0.155	100.0	0.0975	100.0

a = unlimed plots. b = limed in 1903 and 1909 to extent of 5,700 lbs. CaCO₃ per acre; lime requirements determined in 1912.

6. Decomposition of

(a) Insoluble(66, 72, 79, 82), and

(b) Soluble carbonates(34, 48).

7. Growth of *Azotobacter* in mannite(17) and of *B. mycoides* and *B. subtilis* in bouillon(43).

All these various methods give different results: the degree of acidity measured by some may be anything up to ten or twenty times that obtained by others. Examples are given in Table I, pp. 24, 25.

The conditions under which the various methods for estimating soil acidity are carried out vary so much among themselves and differ so enormously from the natural conditions in the field that the equilibrium approximately attained prior to the experiment would certainly be shifted in one direction or another during the determination. Thus Sharp and Hoagland(64) and Christensen(17) showed that the extraction of a soil with neutral salt solution, *e.g.* KCl or Ca-acetate, may actually change the reaction of the soil solution from distinctly alkaline to strongly acid, while in practically all cases extracts prepared with neutral salt solutions showed a higher hydrogen-ion concentration than extracts prepared with water alone. Moreover if a soil is extracted with Na-acetate solution of varying concentrations it has been found that the amount of acetic acid liberated increases while the actual hydrogen-ion concentration in the resulting solution diminishes as the concentration of the acetate increases. If the extraction is carried out with Na-acetate and NaCl solutions of equivalent strength then more titratable acid is liberated in the former case, but a higher hydrogen-ion concentration is attained in the latter.

SOIL ACIDITY A PHASE OF THE BROADER QUESTION OF SOIL REACTION.

In view of the above considerations it is permissible to ask of what value the usual laboratory methods can be as means of measuring soil acidity. At the best they can give some empirical information to the effect that certain soils examined will or will not be benefited by liming. They give—and can give—no quantitative information as to the degree of acidity in its strict, scientific and only possible meaning, *i.e.* the hydrogen-ion concentration of the nutrient solution bathing the soil particles. And yet the hydrogen-ion concentration of the soil solution, which is in equilibrium with the reserve of acidity bound up with the soil mass, is one of the few soil factors susceptible of investigation by really accurate methods. Until comparatively recently soil acidity has

been studied as though it were a thing apart and utterly unrelated to the ordinary physico-chemical concepts of acidity, the reason being, apparently, that the practical agricultural problem is complex involving colloid and physical factors as well as considerations of acidity in the physico-chemical sense,—*i.e.* as a function of the hydrogen-ion concentration. Soil acidity, in this narrower sense, thus becomes a phase of the broader question of soil reaction in general. Soil acidity is generally regarded as a pathological condition of the soil which may, and should, be removed by liming. This is not universally the case however. In potato growing an acid condition of the soil is beneficial, and is in fact generally preferred because it is not only not injurious to the potato crop but is inimical to the organism causing soft scab,—*Actinomyces scabies* (*chromogenus*)⁽²⁴⁾—one of the worst of potato pests. This disease never appears on a soil of a certain degree of acidity⁽²⁵⁾ and this work has met with some response in agricultural practice (Lipman⁽⁴⁴⁾)*.

SOIL ACIDITY CORRELATED WITH PHYSICO-CHEMICAL CONCEPTIONS OF ACIDITY.

A. Ionisation and dissociation constants of acids.

Acidity as a function of [H⁺].

At the outset soil acidity should be correlated with physico-chemical conceptions of acidity: all phenomena depending on acidity, whether in the soil or in any other medium, homogeneous or heterogeneous, are determined by the concentration of the hydrogen-ions in the continuous liquid phase. "Acidity," "alkalinity" and "neutrality" have a definite and quantitative meaning and refer to the ratio of the hydrogen-ion and hydroxyl-ion concentrations in the solution. All acids dissociate, or ionise, in aqueous solution thus— $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}'$; this ionisation is quantitative and balanced and for a given temperature

$$\frac{[\text{H}^+] \times [\text{A}']}{[\text{HA}]} = K_A, \text{ a constant} \dagger.$$

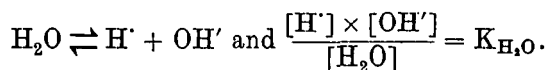
* The work of Coville (*U.S. Dept. of Agric. Bul.* 6, 1913) on acid land agriculture is also of interest in this connection.

† The square brackets indicate concentration terms in gm.-ions or gm.-molecules per litre. This equation applies strictly only to *weak acids*. The "anomaly of strong electrolytes," however, need not concern us here as (1) the above equation does hold strictly for weak electrolytes, and (2) on account of "buffer effects" the soil acids can be regarded as weak electrolytes regardless of their actual chemical composition.

K is called the *ionisation constant* of the acid. Similarly for a base $\text{BOH} \rightleftharpoons \text{B}' + \text{OH}'$; whence

$$\frac{[\text{B}'] \times [\text{OH}']}{[\text{BOH}]} = K_{\text{B}}, \text{ the ionisation constant of the base.}$$

The solvent—water—is regarded as being itself ionised to some small extent so that



The phenomena of hydrolysis are dependent on this ionisation of water which however is very small. In the case of water $[\text{H}'] = [\text{OH}']$ and the neutral reaction is due to the equivalent concentrations of the hydrogen- and hydroxyl-ions. In any solution “acidity” is due to a preponderance of H-ions over OH-ions and the degree, or intensity, of acidity can be quantitatively expressed by the ratio $[\text{H}']/[\text{OH}']$. Conversely the presence of OH-ions in greater concentration than the H-ions renders a solution alkaline and the degree or intensity of alkalinity can be quantitatively expressed by the ratio $[\text{OH}']/[\text{H}']$. This is the only interpretation that ought to be placed on the expression “acidity” or “alkalinity” or more generally the “reaction” of a medium. In pure water at 18° C. or in absolutely neutral aqueous salt solution $[\text{H}'] = [\text{OH}'] = 1 \times 10^{-7.07}$ g-ions per litre and $[\text{H}'] \times [\text{OH}'] = 1 \times 10^{-14.14}$. At constant temperature, then, the ionic product $[\text{H}'] \times [\text{OH}']$ of any aqueous solution is a constant; any solute, such as an acid, that increases $[\text{H}']$ will decrease $[\text{OH}']$ and any solute, such as a free base, that increases $[\text{OH}']$ will diminish $[\text{H}']$. But it is more convenient and much simpler, instead of expressing acidity in terms of $[\text{H}']$ and alkalinity in terms of $[\text{OH}']$, to express both in terms of $[\text{H}']$ alone. Neutrality would then correspond to a hydrogen-ion concentration of $1 \times 10^{-7.07}$ gms. per litre, acidity to a $[\text{H}']$ higher than and alkalinity to a $[\text{H}']$ less than $1 \times 10^{-7.07}$.

B. *Acidity as a function of* $-\log [\text{H}']$.

A further simplification is generally effected by regarding intensity of acidity as a function, not of the hydrogen-ion concentration, but of the reciprocal of the logarithm of the hydrogen-ion concentration. It is not easy at first sight to compare such a series of hydrogen-ion concentrations as

$$1 \times 10^{-10}; \quad 4.0 \times 10^{-10}; \quad 1.6 \times 10^{-11}; \quad 6.3 \times 10^{-12};$$

by a simple conversion, however, we get the following series

$$1.0 \times 10^{-10} = 10^{-10}; \quad 1.6 \times 10^{-11} = 10^{-10.8};$$

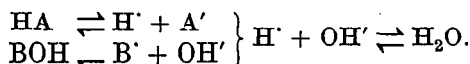
$$4.0 \times 10^{-10} = 10^{-9.4}; \quad 6.3 \times 10^{-12} = 10^{-11.2};$$

and the order of the acidities is at once apparent*. It thus becomes simpler to omit the 10, which is common to all, and to express the $[H']$ by means of the *minus* logarithms which are merely the reciprocals of the logarithms of the hydrogen-ion concentrations and are generally written $-\log [H']$ or $P_H \dagger$.

A further advantage of this mode of expression is found in expressing graphically on squared paper large variations in $[H']$. It is impossible for example to compare graphically on the same sheet of paper $[H'] = 10^{-0}$ and $[H'] = 10^{-14}$ gms. per litre or any really large variation between these limits; but it is perfectly easy to compare the minus logarithms of these values, viz. 0 and 14 and any variations of any magnitude between these values.

C. *Distinction between degree of acidity and titratable acidity.*

The degree of acidity as expressed by the hydrogen-ion concentration is of course not the same as that measured by titration. In the latter case hydrogen-ions are continuously removed by the alkali used in the titration, thus



The equilibrium is continually being shifted and as continually re-adjusted by the dissociation of more acid until all the acid has been

* When the $[H']$ is known the corresponding $[OH']$ can be easily found, when necessary, by dividing the former into the ionic product. Thus when $[H'] = 10^{-10.8}$ the corresponding $[OH']$ will equal $10^{-14.14}/10^{-10.8} = 10^{-3.34}$ g-ions per litre.

† This method of expressing $[H']$ was introduced by Sørensen (65) who substituted the term P_H for the older and more logical term $-\log [H']$. There would appear to be little justification for the introduction of the term P_H , although it has been adopted and widely used by many workers in agricultural science and in physiology. In pure physical chemistry the older term is in general use: its meaning is self-evident and perfectly unambiguous to any chemist while the term P_H requires explanation and may not always be quite free from ambiguity; thus in chemical kinetics p is the symbol generally employed to denote gaseous pressure and p_H would be the partial pressure due to hydrogen in a gaseous mixture. In the kinetic treatment of the theory of solutions gaseous pressure is replaced by osmotic pressure, the symbol for which is P . In this case P_H would denote the osmotic pressure due to hydrogen-ions which although a function of $[H']$ can hardly be regarded as identical with the minus logarithm of the same. In this paper the older term $-\log [H']$ will be used throughout.

dissociated and the hydrogen-ions removed by the alkali so that $[H^+] = 1 \times 10^{-7.07}$ which concentration corresponds roughly with the end-point of the titration. The "acidity" measured by titration methods refers to the total quantity of hydrogen-ions that can be produced from the acid when the ionic equilibrium is continually shifted by the introduction of hydroxyl-ions, and is often called *true* or *total* acidity, but would be more accurately described as *potential* or *titratable* acidity. The potential acidity of such a system as an acid soil may consist partly of undissociated acid dissolved in the soil water, or of acid derived from partly hydrolysed soluble salts such as $Al_2(SO_4)_3$, or possibly of a large excess of relatively insoluble or slightly soluble mineral acid or organic acid or even of "adsorbed" acid, such as phosphoric. The presence of "adsorptively unsaturated" compounds, however, such as colloids, in soils affects the hydrogen-ion concentration of the soil solution without necessarily affecting the titratable acidity and the apparently anomalous behaviour of soil extracts made with neutral salt solutions is often attributed to a "selective adsorption" of base.

D. *Nature of buffer action.*

All properties of a solution due to acidity depend really on the particular $[H^+]$ at the moment*. Many factors, however, may influence the actual $[H^+]$. Thus colloids, acid phosphates, salts of lime, etc. in the soil act as "buffers" or "reaction regulators" in presence of which the soil solution has a strong tendency to maintain its $[H^+]$ unchanged so that a given amount of acid or base would produce much less alteration in the $[H^+]$ in presence of a soil than it would in pure aqueous solution. Thus 1 c.c. of N/100 HCl added to one litre of water will decrease the $-\log [H^+]$ from 7 to 5, the resulting solution being strongly toxic to many bacteria. If on the other hand the same amount of acid be added to a like quantity of water containing 50 or 100 gms. of a soil of $-\log [H^+] = 7$ the resulting change in $-\log [H^+]$ is hardly appreciable. This effect is known as *buffer action*, the substances causing the condition being known as *buffers* and the solutions themselves as *buffer solutions*. In the case of pure aqueous solutions the mechanism of buffer action is clear. Thus suppose there is present a mixture of a weak acid,

* The so-called "neutral salt action" can be neglected in this connection as it in no way invalidates or conflicts with the point of view adopted here. The possibility that it may be a factor to be reckoned with in a consideration of the conditions involved in soil reaction should not however be overlooked. For an account of it of purely physico-chemical interest see Arrhenius (6), Lamble and Lewis (39), and McBain and Coleman (49).

e.g. acetic acid, and one of its salts, *e.g.* sodium acetate; the acetic acid is only slightly ionised, so that

$$\frac{[\text{H}'] \times [\text{Ac}']}{[\text{HAc}]} = K_A = 18.0 \times 10^{-6}.$$

The sodium acetate on the other hand is a strong electrolyte and a very large proportion of it is ionised. This involves an enormous increase in $[\text{Ac}']$ and in order to keep K_A of the acetic acid constant $[\text{H}']$ must be proportionately decreased, the result being that such a solution is by no means so sensitive to additions of acid or alkali as is pure water or pure aqueous acetic acid in the absence of the salt. This is clearly seen in the accompanying curve* (Fig. 1) which represents

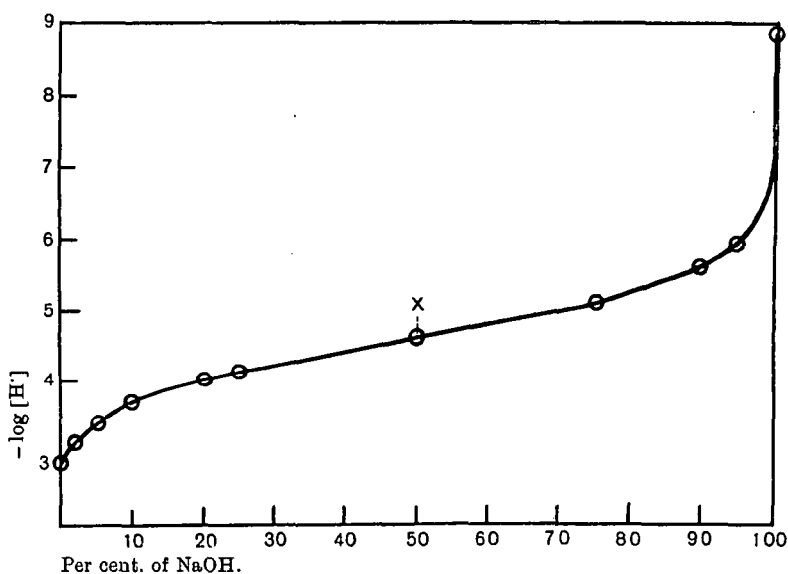


Fig. 1. Neutralisation curve of N/10 Acetic Acid.

the change in $-\log [\text{H}']$ of N/10 acetic acid when it is titrated with N/10 alkali. At either end of the curve when only acetic acid or NaAc is present the addition of ten per cent. of NaOH will cause a large alteration in $-\log [\text{H}']$. At the point X however where the acetate content of the solution consists of 50 per cent. acetic acid and 50 per cent. of Na-acetate the addition of 10 per cent. of NaOH or of HAc will produce only an insignificant effect on the $-\log [\text{H}']$.

Similar considerations apply to a weak base in the presence of one of its salts.

* Reproduced from Prideaux (58), p. 228.

The curves shown in Fig. 2* bring out some features of buffer action that are shown even more strikingly by soil-water mixtures. The curves represent the changes in $-\log [H^+]$ when 1 per cent. and 5 per cent. solutions of Witte's peptone are titrated with N/10 lactic acid and N/10 NaOH respectively. An examination of the two curves will show that the amount of buffer action is dependent upon a number of factors among which are:

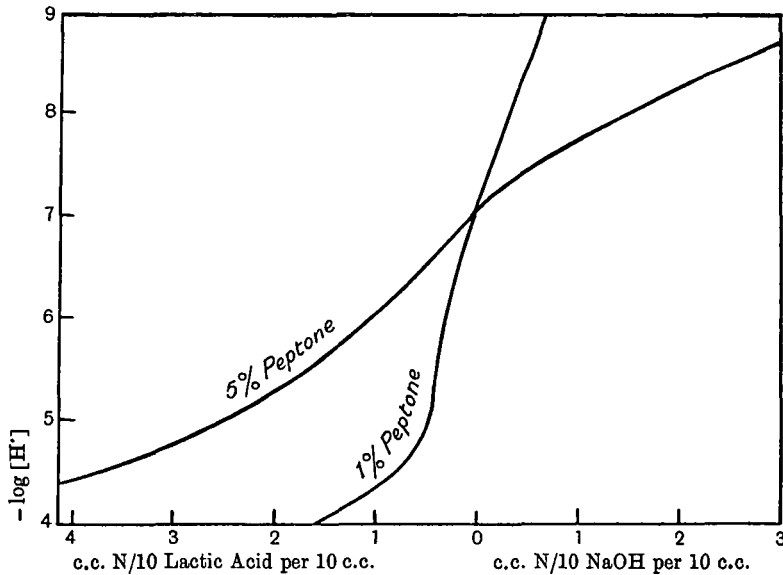


Fig. 2. Titration curves of Peptone Solutions.

1. The *nature* of the constituents as indicated by a comparison of the slopes of the curves in Fig. 2 with the slopes of that in Fig. 1:

2. The concentration of the constituents, the 5 per cent. solution being more resistant to change in $-\log [H^+]$, *i.e.* has greater buffer effect, than the 1 per cent. solution.

3. The buffer effect is not the same at all points of the curve but depends on the region of $-\log [H^+]$ at which the buffer action is measured. This last point is important and is brought out better in Fig. 3*, which is the titration curve of ortho-phosphoric acid. From this curve it will be noticed that there is practically no buffer action at $-\log [H^+]$ values of 4.4 and 9.3, but that there is very considerable buffer action in the region of $-\log [H^+]$ 7.4 to 6.2. This is the region

* Reproduced from Clark and Lubs' (18) paper.

between which the reaction of normally fertile soils varies, and the possibility that a part may be taken by acid phosphates as reaction regulators in soils has been very largely overlooked. Acid phosphates of course cannot be the only "buffers" in a soil—salts of lime may also act as such although not perhaps in the same region of $-\log [H^+]$. The soil colloids also act as powerful buffers but nothing is known as to the region of $-\log [H^+]$ in which they act best. Fig. 2 indicates that Witte's peptone exerts its greatest effect when $-\log [H^+]$ is less than 5 but the soil colloids from their very number and diversity may exert considerable effect in all regions of $-\log [H^+]$. Thus 1.67 c.c. N/10 H_2SO_4

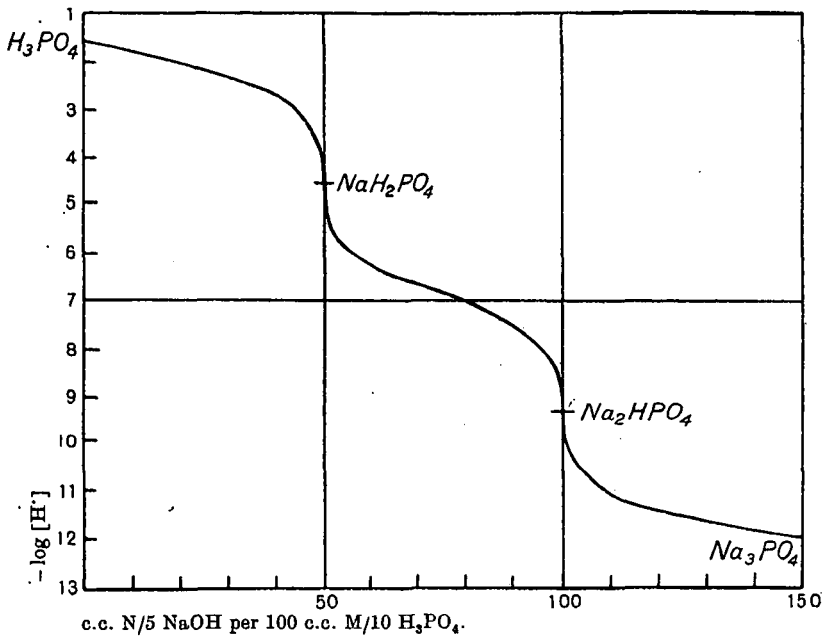


Fig. 3. Titration curve of O-Phosphoric Acid.

added to a mixture of 40 gms. of a slightly acid soil and 80 c.c. of water lowered the $-\log [H^+]$ from 6.6 to 5.6; the same amount of acid added to 80 c.c. pure water lowered the $-\log [H^+]$ from 6.8 to 2.5. It would appear therefore that the soil complex is well supplied with "buffers" which operate at all regions of $-\log [H^+]$. In view of these facts it is not surprising that although the lime requirements of different soils vary enormously yet the variations of $-\log [H^+]$ are confined within much narrower limits. The largest variations of $-\log [H^+]$ values of aqueous soil extracts are those given by Sharp and Hoagland (64), 3.7

to 9.7. These are relatively considerable and include extreme cases of acidity and alkalinity. These workers found however that the definitely fertile soils showed strikingly similar reactions: slightly alkaline as indicated by $-\log [H^+]$ values between 7.04 and 7.52. Such wide variations in $-\log [H^+]$ as 3.7 to 9.7 must correspond to abnormally large differences in titratable acidity. On the other hand identical or nearly identical values for $-\log [H^+]$ with different types of soil may exist along with widely different amounts of titratable acidity as found either by the ordinary lime requirement methods or by the colorimetric method described later. It is impossible at present to account completely for the buffer action in soils, and it can be expressed only by the slopes of titration curves.

METHODS OF MEASURING SOIL REACTION.

A. Failure of ordinary Titrimetric Methods.

The older titrimetric methods fail to investigate completely soil reaction, partly because they measure only titratable acidity, and partly because of "adsorptive" and other buffer effects. In all methods based upon extraction of a soil with solutions of salts of weak acids there is considerable obscuring or displacement of the end point of the titration by the buffer action of the salts (Knight(38)). It is well known that in mixtures containing weak acids with considerable buffer action near the change point of the indicator even the titratable acid cannot be determined by the ordinary titrimetric methods. With soil extracts the case may be even more complicated: soils have frequently been arranged in the order of their apparent acidities by the use of litmus paper, and Harris attempted to classify soils as "truly acid" and as what Ramann(59) called "adsorptively unsaturated" according to whether the extract alone or the moist soil itself were necessary to colour blue litmus paper. Walpole(77), and later Gillespie and Wise(26), showed that both buffer action and time of contact were potent factors in the behaviour of buffered solutions towards litmus paper: N/10,000 HCl in pure water has $-\log [H^+] = 4.8$ but will produce practically no effect on litmus paper apart from a certain amount of leaching of the dye from the paper after long contact. A standard buffer phosphate solution however of $-\log [H^+]$ as great as 6.8 reddens blue litmus paper almost instantaneously. The fact that moist soil itself reddens blue litmus paper when its aqueous extract does not implies no necessary difference between "truly acid" and "adsorptively unsaturated" soils, but merely

that the buffer action in aqueous soil extracts in the absence of the solid soil is not sufficient to maintain the $-\log [H^+]$ unchanged while the reaction of the paper itself was altering. The buffer action of soils is bound up with the solid phase and the reaction of the soil solution is maintained constant only when in contact with the solid phase. It follows therefore that the reaction of soil extracts bears no relation at all to the litmus test when litmus paper is used and both time and buffer factors are left out of account. No difficulty, on the other hand, is experienced in measuring with a fair degree of accuracy the reaction of an aqueous soil extract when suitable precautions are taken and the much more brilliant and sensitive sulphone-phthalein dyes are used in place of litmus.

B. *Study of the Hutchinson-MacLennan Method.*

In order to obtain further information as to the inadequacy of the older methods of determining lime requirements through neglect of possible "adsorptive" factors a study of the Hutchinson-MacLennan method was carried out.

Table II. *Lime requirements* of the Park Grass Plots as determined by*

Plot No.	(a) Hutchinson's method	(b) Colorimetric method	Ratio a/b
<i>A. Low Acidity Group.</i>			
3	0.020 %	0.0064 %	3.125
8	0.055	0.0084	6.55
4-1	0.060	0.0084	7.14
2	0.075	0.0067	11.19
16	0.115	0.0060	19.16
7	0.135	0.0062	21.77
<i>B. Medium Acidity Group.</i>			
1	0.260 %	0.029 %	8.96
13	0.335	0.056	5.98
4-2	0.520	0.129	4.03
<i>C. High Acidity Group.</i>			
10	0.625 %	0.129 %	4.84
11-2	0.705	0.207	3.40
11-1	0.735	0.244	3.01
9 (limed)	0.815	0.295	2.76
9 (unlimed)	0.900	0.317	2.84

* Expressed as % CaO of air-dried samples.

The lime requirements of many of the Rothamsted grass plots had been determined by this method in 1914, *i.e.* five years after liming and immediately before re-liming. The figures given below by the colorimetric method (see Part II) were obtained in 1919, *i.e.* five years after liming and immediately before re-liming. The figures are not therefore strictly comparable as they were not obtained on the same samples at the same time or by the same worker. It would appear, however, that they should show some sort of rough relationship as the samples were taken at the same point of the liming cycle, provided always that the same function is measured in the two methods. In Table II the two sets of figures are given for comparison.

There is no agreement between the two sets of figures: the results from the first are from three to twenty-two times as great as those from the second, the discrepancy being greatest in the case of the slightly acid plots. Among possible factors operative in causing the discrepancies are the "adsorptive" as distinct from the absorptive properties of the soil. The absorption of lime by an acid soil is probably a twofold process: part of the lime may be used up in neutralising the soil acids, and part may be adsorbed by the soil particles. However accurate therefore the colorimetric and electrometric methods of measuring the $-\log [H^+]$, *i.e.* the reaction, of soil-water mixtures may be neither they nor any other known method give exact information as to the actual amount of free acid present in a soil because whenever we attempt to neutralise this acid by adding a base some of the base is always "adsorbed" by the soil itself. We cannot therefore differentiate in practice between the "acidity" and the "lime requirements" of a particular soil: the latter is the more comprehensive term and may be defined as the percentage of lime required to bring the $-\log [H^+]$ of the soil to 7.07, always bearing in mind that this lime is utilised partly in neutralising soil acids and partly in being "adsorbed" by the soil itself. The amount of lime adsorbed can be expressed by the following general equation

$$\frac{y}{m} = kC^{\frac{1}{p}},$$

in which y is the amount of lime adsorbed by m gms. of soil, C is the final concentration of lime in the liquid phase, while k and p are constants.

When $-\log H = 7.07$, C is in the neighbourhood of zero, so that perfectly consistent and comparable results should be obtained by the colorimetric method provided the method is experimentally sound. In Hutchinson's method, however, C is always some positive quantity,

i.e. it is the amount of lime left in the solution after shaking with the soil and it should therefore follow that the amount of lime adsorbed is greater the greater C is. In other words since $N/50 \text{ CaH}_2(\text{CO}_3)_2$ is used for all soils, then the smaller the acidity the larger will C be and therefore the larger relatively will y/m be. It follows that the error inherent in this method for a given type of soil will be greater the smaller the acidity of the soil examined. This is supported by the fact already noted in Table V that the discrepancy between the two methods when applied to the same type of soil is greater the less the acidity. Moreover in no sense can the soil be said to have been neutralised by the lime absorbed from the bicarbonate solution even after equilibrium has been attained, because owing to the large excess of CO_2 the $-\log[\text{H}^+]$ of the resulting solution is in the neighbourhood of 6.0 and one cannot consider a soil to have been neutralised when in equilibrium with an acid solution. If these considerations are valid then it would follow that a neutral soil and, with heavier types of soil, even soils with a definite CaCO_3 content may show positive lime requirements with the Hutchinson method but none by the colorimetric method. This is denied by Hutchinson and MacLennan who say "The method possesses the advantage over several others suggested in that it indicates no absorption in the case of neutral soils." Yet elsewhere in a Table they give examples of soils possessing appreciable CaCO_3 contents and yet having considerable lime requirements*.

	Rothamsted	Chelsea	Devon	Mill-brook	Gees-croft	Metchley	Harpen Adams	Woburn	Craibstone	Leeds II
CaCO_3 present %	2.660	0.890	0.003	0.035	0.005	0.097	0.005	0.003	Nil	Nil
CaCO_3 required %	Nil	Nil	0.015	0.032	0.100	0.117	0.135	0.260	0.430	0.470

Wild (81) in a study of some New Zealand soils noticed similar phenomena. A soil containing 10 per cent. CaCO_3 showed a small, though positive, lime requirement by Hutchinson's method. Further, as indicated by the above general formula, the adsorption is of the nature of a balanced reaction; the quantity adsorbed is in equilibrium with the final concentration, C , of the surrounding solution. If the bicarbonate solution in equilibrium with the soil is replaced by one of a greater concentration than C the soil should give up lime to this solution until a fresh equilibrium is attained. Wild mentions a soil containing "a large excess of calcium carbonate" that gave up lime to the $N/50$ bicarbonate

* It is fair to point out that the authors suggest another explanation, an explanation that may hold in some cases. But they suggest it only and adduce no evidence to show that it applies to the examples given in the Table.

solution used: other instances are also recorded. Hutchinson and MacLennan realised the effect of the *initial* concentration of bicarbonate solution:

Initial concentration of solution	N/50	N/75	N/100
Absorption (as percentage of soil)	0.272	0.265	0.210

But they associate the initial concentration only with the time taken for attainment of equilibrium and do not discuss the effect of the final (equilibrium) concentration.

Table III.

y/m = mgs. CaO absorbed per 10 gms. soil	1.54	1.82	1.98	3.25	3.49	3.66	3.69	3.71	3.96	4.52	4.69
C = mgs. CaO left in 100 c.c. solution	10.37	14.16	11.06	6.02	6.805	16.40	21.80	6.10	7.39	28.57	13.58
y/m = mgs. CaO absorbed per 10 gms. soil	5.055	5.26	5.376	6.91	7.00	8.495	9.31	11.20	11.55	57.67	
C = mgs. CaO left in 100 c.c. solution	12.90	14.26	14.06	23.50	14.00	22.25	28.40	43.26	57.80	38.10	

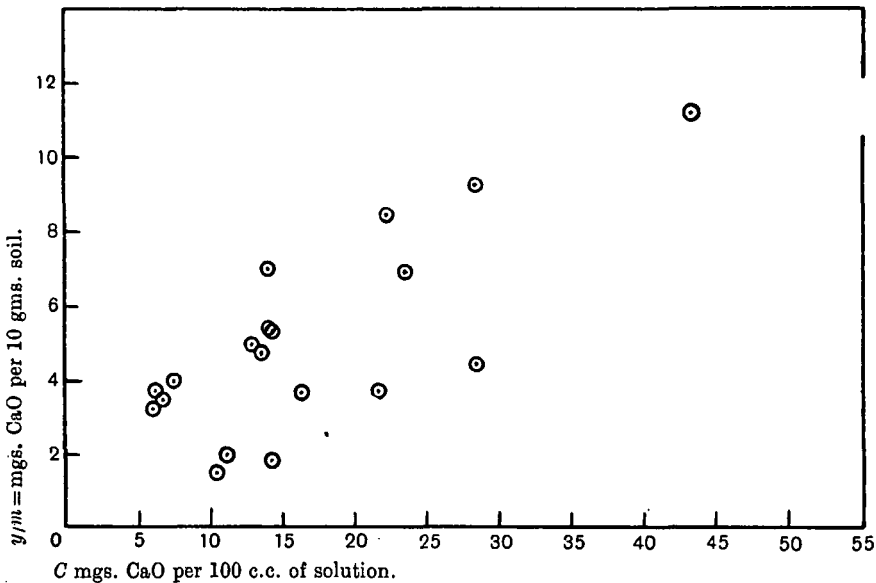


Fig. 4. Absorption of calcium bicarbonate by soil (3 mm. sample).

Wild found that the initial concentration of the bicarbonate solution affected not only the time required for apparent equilibrium to be attained but also the amount of lime absorbed.

If adsorption occurs then on plotting the amount of lime adsorbed by the soil against *final* equilibrium concentration of lime in the bicar-

bonate solution, *i.e.* plotting y/m of the general equation against C , a particular type of curve should be obtained expressible by the general equation when suitable values for the constants k and p are chosen. No such curve could be obtained from Wild's data as he gives only initial and not final concentrations. An attempt was therefore made to see whether the effect of C on y/m followed the usual adsorption equation. Approximately N/50 $\text{CaH}_2(\text{CO}_3)_2$ solution prepared in the usual way was diluted with distilled water to make a series of solutions of N/50, N/75, N/100, N/125, N/150, N/175, and N/200. Samples of soil (Grass Plot 19, air-dried 3 mm. sample) varying from 5 gms. to 30 gms. were shaken with varying volumes of the above solutions in an end-over-end shaker for three hours. Aliquot parts of the rapidly filtered extracts were then titrated with standard H_2SO_4 , N/10 acid being used for the stronger and N/50 acid for the more dilute extracts. The values of y/m (= mgs. CaO absorbed per 10 gms. of soil) and C (= mgs. CaO remaining per 100 c.c. of solution) are given in Table III and plotted in Fig. 4. These experimental points do not lie even approximately on a curve, but their very irregularity and the fact that some of the points were really duplicates and should therefore have coincided suggests some disturbing factor. The irregularities were traced to the unequal state of division of the soil samples. Adsorption is essentially a surface phenomenon and the amount of lime adsorbed should be in direct proportion to the amount of surface exposed. The 3 mm. sample would consist of particles of all sizes less than 3 mm. and not only is it certain to lack uniformity but the effective surface increases irregularly by the breaking up of the particles during the shaking. This would account for the anomalies suggested by Fig. 4 especially if the lime could only get at the interior surfaces within the larger crumbs by a slow process of diffusion. To test this point a series of determinations was carried out on soil from Grass Plot 18 which had been ground up in a mortar with a wooden pestle until practically the whole of it passed through a sieve with square meshes of 100 to the linear inch. The small percentage which would not pass through, consisting mainly of silica, was thoroughly mixed with the rest so as to avoid any effect due to fractionation. The determinations were carried out on this finely ground sample on the same day and the results are given in Table IV and Fig. 5.

In this series the points lie very fairly about a parabolic curve typical of adsorption isotherms and which is expressed quite well by the equation

$$y/m = kC^{1/p},$$

when $k = 5.13$ and $1/p = 0.475$,

i.e. $y/m = 5.13C^{0.475}$.

Moreover by a simple transformation we get

$$\log (y/m) = 1/p \log C + \log k,$$

Table IV.

$y/m =$ mgs. CaO absorbed per 10 gms. soil	33.60	* { 22.68 22.26	17.22	13.50	7.89	* { 4.09 4.525
$C =$ mgs. CaO remaining per 100 c.c. solution	50.96	* { 21.28 21.42	12.74	5.74	3.36	* { 0.980 0.420

* Duplicates.

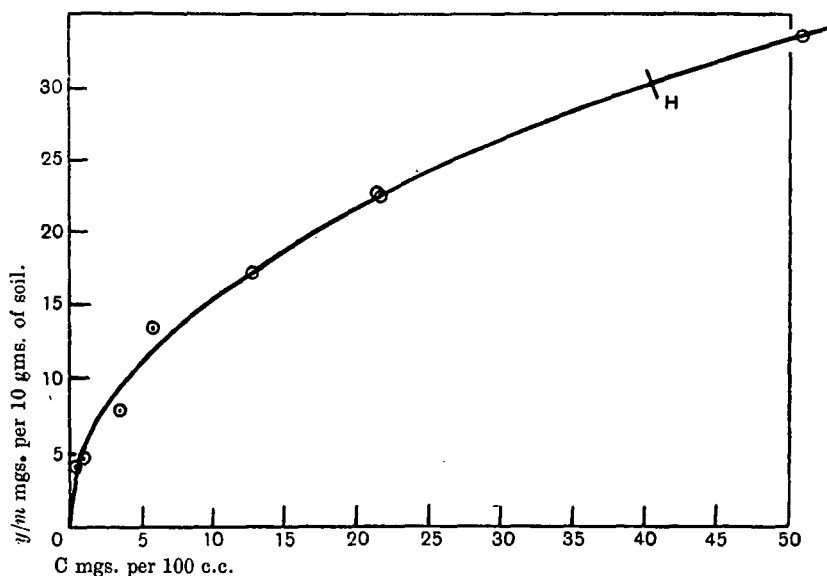


Fig. 5. Absorption of calcium bicarbonate by soil (finely ground sample).

and by plotting $\log (y/m)$ against $\log C$ the points obtained should lie approximately on a straight line. It will be seen from Fig. 6 that they lie distributed near a straight line with a very fair degree of approximation*. There would appear to be little doubt therefore that the lime requirement of a soil is the sum of two quantities: (1) the lime required to neutralise soil acids, and (2) the lime actually adsorbed by the soil complex and it is impossible at present to differentiate quantitatively

* It is from this approximately straight log. curve that we can obtain values for the constants k and $1/p$ with a very fair degree of approximation since when $\log C = 0$ the intercept cut off by the curve from the y axis will equal $\log k$ while the slope of the curve will equal $1/p$.

between these. It follows that equivalent quantities of different bases will not necessarily be equally effective in neutralising a soil unless we assume that they are equally adsorbed by the soil, which does not appear to be the case. Without further evidence therefore it is not legitimate to use baryta to neutralise a soil and then to calculate the result in terms of lime. (See Part II, p. 59.)

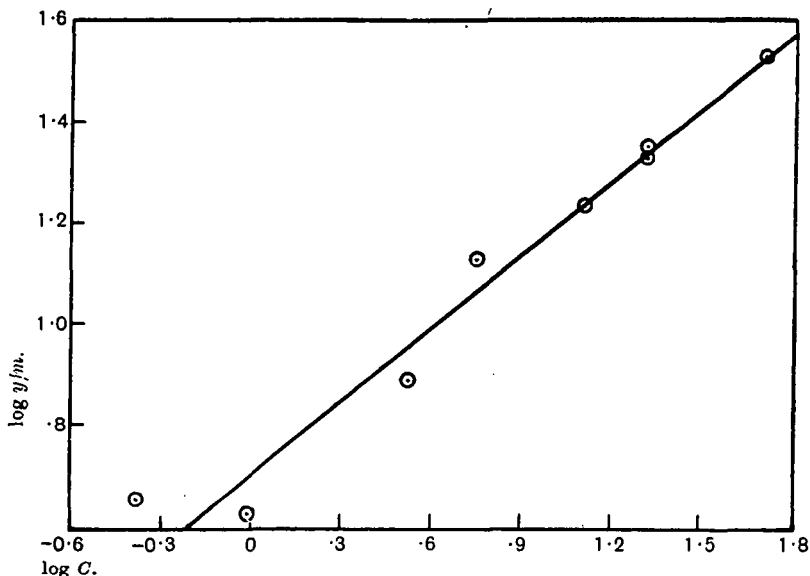


Fig. 6.

It is obvious that comparable results for the lime requirements of different soils cannot be obtained even approximately by the Hutchinson-MacLennan method as at present carried out. In the case of Plot 18 the lime requirement of the finely ground sample as determined by the Hutchinson method using 250 c.c. $N/50 \text{ CaH}_2(\text{CO}_3)_2$ and 15 gms. of the finely ground soil (the usual proportion) should be about 0.300 per cent. and is indicated on the curve (Fig. 5) by the point *H*; it was found actually to be 0.302 per cent. But, as the curve indicates, the apparent lime requirement increases with *C* and moreover the shape and slope of the curves are very different for different soils, the curve being very flat and close to the *C* axis for light sandy soils and very steep (much steeper than the one shown in Fig. 5) for heavy clay soils. To obtain comparable results therefore by Hutchinson's method an experimental curve of the type shown (or at any rate a considerable region of it round about the point *H*) should always be drawn. A lime requirement corre-

sponding to a fixed and constant final equilibrium concentration C could then always be obtained by interpolation and provided that the correct C was chosen as a reference point it is possible that fairly accurate and comparable results might be obtained*. The correct C could, however, be chosen only as the result of a large number of field trials on many different types of soil, and would not necessarily be the same with different soil types or with different systems of manuring. Moreover in carrying out the determinations finely ground samples should be employed owing to the impossibility otherwise of attaining equilibrium in a reasonable number of hours, and moreover because ground and unground soils possess different lime requirements. Thus two lots of 15 gms. each of the 3 mm. sample and two lots of 15 gms. each of the 100 mesh per inch sample from Plot 5-2, were shaken with 250 c.c. N/50 $\text{CaH}_2(\text{CO}_3)_2$ for three hours. They were then filtered and 100 c.c. of each titrated with N/10 H_2SO_4 . The results were as follows:

	Original N/50 $\text{CaH}_2(\text{CO}_3)_2$	Filtrate from 3 mm. sample	Filtrate from 100 mesh per in. sample
100 c.c. required c.c. N/10 H_2SO_4	(a) 21.98 } (b) 21.98 }	21.98 c.c.	18.33 } 17.01 } 17.67 c.c.
Lime requirement expressed as gm. CaO per 100 gms. air-dried soil		0.2016	0.2354

Thus in the case of the finely ground samples not only did the duplicates agree much better but the lime requirement was 16.7 per cent. higher than that of the 3 mm. sample.

REFERENCES.

- (1) ABBOTT, J. B., CONNOR, S. D. and SMALLEY, H. R. *Purdue Univ. (Ind.) Agric. Exp. Sta. Bul.* **170** (1913).
- (2) ALBERT, R. *Zeit. angew. Chem.* **22** (1909), p. 533.
- (3) AMES and SCHOLLENBERGER. *J. Ind. and Eng. Chem.* **8** (1916), p. 243.
- (4) ——— ——— *Soil Sci.* **1** (1916), p. 575.
- (5) ——— ——— *Ohio Agric. Exp. Sta. Bul.* **306** (1916).
- (6) ARRHENIUS, S. *Zeit. phys. Chem.* **31** (1899), p. 197.

* The above argument has been expressed in terms of the selective adsorption theory because this theory is widely accepted as satisfactory. Exactly similar results would be expected whether the lime is "adsorbed" on the surface of the soil particles or chemically precipitated by interaction with e.g. alumina to form calcium aluminate; the form of curve in the latter case would be determined by solubility and hydrolysis relationships. See above, p. 22 and also Meyerhoffer's (51, 52, 53) work on the solubility relationships in reciprocal salt pairs.

- (7) ASHLEY, H. E. *U.S. Bur. Standard, Tech. Paper* 23 (1913).
- (8) BAUMANN, A. and GULLY, E. *Naturw. Zeit. Land. u. Forst.* 6 (1908), p. 1; Abs. in *Exp. Sta. Rec.* 19 (1908), p. 1008.
- (9) ——— ——— *Mitt. der k. Bayr. Moorkultur-Anstalt.* (1910), p. 31.
- (10) BEMMELEN, J. H. VAN. *Landw. Vers. Sta.* 35 (1888), p. 113.
- (11) ——— *Die Absorption* (T. Steinkopff), Dresden, 1910.
- (12) BLAIR and MACY. *Flor. Agric. Exp. Sta. Bul.* 93 (1908).
- (13) BLUM. *J. Amer. Chem. Soc.* 38 (1916), p. 1282.
- (14) BOUYOUCOS, G. J. *Mich. Agr. Exp. Sta. Tech. Bul.* 27 (1916).
- (15) CAMERON, F. K. *J. Phys. Chem.* 14 (1910), pp. 320, 393.
- (16) ——— *The Soil Solution* (Easton, Pa.), 1911.
- (17) CHRISTENSEN, H. R. *Soil Sci.* 4 (1917), p. 115.
- (18) CLARK, W. M. and LUBS, H. A. *J. Bact.* 2 (1917), pp. 1, 109, 191.
- (19) CLARKE, F. W. *Data of Geochemistry, U.S. Geol. Survey Bul.* 330 (1908).
- (20) CONNOR, S. D. *J. Ind. and Eng. Chem.* 8 (1916), p. 35.
- (21) DAIKUHARA, G. *Bul. Imp. Cent. Agric. Exp. Sta. Japan*, 2 (1914), p. 1.
- (22) FREAR, W. *Pa. Dept. Agric. Bul.* 261 (1916).
- (23) FREUNDLICH, H. *Kapillarchemie*, 1909.
- (24) GILLESPIE, L. J. *Phytopathology*, 8 (1918), p. 257.
- (25) GILLESPIE, L. J. and HURST, L. A. *Soil Sci.* 6 (1918), p. 219.
- (26) GILLESPIE, L. J. and WISE, L. E. *J. Amer. Chem. Soc.* 40 (1918), p. 796.
- (27) GREGOIRE, A. *Bul. Soc. Chim. Belg.* 26 (1912), pp. 336, 362, 386; Abs. in *Chem. Zeitung* (5 Folge), 17 (1913), p. 647.
- (28) GREGOIRE, HENDRICK, CARPIAUX and GERMAIN. *Ann. Sta. Agron. Gembloux*, 2 (1913), p. 87.
- (29) HARRIS, J. E. *Mich. Exp. Sta. Tech. Bul.* 19 (1914).
- (30) ——— *J. Phys. Chem.* 18 (1914), p. 355; 21 (1917), p. 454.
- (31) HARTWELL, B. L. and PEMBER, F. R. *Soil Sci.* 6 (1918), p. 259.
- (32) HOPKINS, C. G. *Soil Fertility and Permanent Agriculture* (1910), p. 627.
- (33) HOPKINS, C. G., KNOX, W. H. and PETTIT, J. H. *U.S. Dept. Agric. Bur. Chem. Bul.* 73 (1903), p. 114.
- (34) HUTCHINSON, H. B. and MACLENNAN, K. *J. Agric. Sci.* 7 (1915), p. 75.
- (35) JONES, C. H. *Amer. Fert.* 39 (1913), p. 28.
- (36) ——— *J. Off. Assoc. Agric. Chem.* 1 (1915), p. 43.
- (37) KÖNIG, J., HASENBÄUMER, J. and HASSLER, C. *Landw. Vers. Sta.* 75 (1911), p. 377.
- (38) KNIGHT, H. G. *J. Ind. and Eng. Chem.* 12 (1920), pp. 340, 457, 559.
- (39) LAMBLE, A. and LEWIS, W. C. McC. *J.C.S.* 105 (1914), p. 2330; 107 (1915), p. 233.
- (40) LEMBERG, J. *Zeit. deutsch. geol. Ges.* 28 (1876), p. 519.
- (41) ——— *Bied. Centbl.* 8 (1877), p. 567.
- (42) LINDER, S. E. and PICTON, H. *J.C.S.* 67 (1895), p. 63.
- (43) LIPMAN, J. G. *U.S. Dept. Agric. Bur. Chem. Bul.* 152 (1912), p. 50.
- (44) ——— *Soil Sci.* 7 (1919), p. 121.
- (45) LOEW, O. *Zeitschr. Landw. Versuchs. Oesterr.* 12 (1909), p. 461; Abs. in *Chem. Abs.* 3 (1909), p. 2337.
- (46) ——— *Porto Rica Agric. Exp. Sta. Bul.* 13 (1913).

- (47) LYON and BIZZELL. *J. Ind. and Eng. Chem.* **5** (1913), p. 1011.
(48) MACINTIRE, W. H. *J. Ind. and Eng. Chem.* **7** (1915), pp. 227, 864.
(49) MCBAIN, J. W. and COLEMAN, F. C. *J.C.S.* **105** (1914), p. 1517.
(50) MELLOR, J. W. and HOLDCROFT. *Pot. Gaz.* **36** (1911), p. 680.
(51) MEYERHOFFER, W. *Monatsch.* **17** (1896), p. 13.
(52) MEYERHOFFER, W. and SAUNDERS, A. P. *Zeit. phys. Chem.* **28** (1899), p. 453;
31 (1899), p. 370.
(53) MEYERHOFFER, W. *Zeit. phys. Chem.* **38** (1901), p. 307; **53** (1905), p. 530.
(54) MOORE, B. and BIGLAND, A. D. *Biochem. J.* **5** (1911), p. 32.
(55) OSTWALD, W. *J. prakt. Chem.* [2], **29** (1884), p. 55.
(56) OSTWALD, W. *Colloid Chemistry*, tr. by M. H. Fischer (Churchill), 1919.
(57) PARKER, E. G. *J. Agric. Res.* **1** (1913), p. 179.
(58) PRIDEAUX, E. B. R. *The Theory and Use of Indicators* (Constable), 1917.
(59) RAMANN, E. *Bodenkunde* (J. Springer), Berlin, 1911.
(60) RICE, F. E. *J. Phys. Chem.* **18** (1914), p. 355; **20** (1916), p. 214.
(61) RICE, F. E. and OSUGI, S. *Soil Sci.* **5** (1918), p. 333.
(62) RUPRECHT, R. W. *Mass. Agric. Exp. Sta. Bul.* **161** (1915), p. 125.
(63) RUSSELL, E. J. *Soil Conditions and Plant Growth* (Longmans), 1917.
(64) SHARP, L. T. and HOAGLAND, D. R. *J. Agric. Res.* **7** (1916), p. 123.
(65) SÖRENSEN, S. P. L. *Ergeb. der Physiol.* **12** (1912), p. 393.
(66) SÜCHTING. *Zeitschr. angew. Chem.* **21** (1908), p. 1.
(67) SÜCHTING and ARNDT. *Zeitschr. angew. Chem.* **23** (1910), p. 103.
(68) SULLIVAN, E. C. C. *U.S. Geol. Survey Bul.* **312** (1907).
(69) SPRENGEL, C. *Archiv Gesamte Naturlehre*, **8** (1826), p. 145.
(70) SPURWAY, C. H. *J. Agric. Res.* **11** (1917), p. 659.
(71) STEPHENSON, R. E. *Soil Sci.* **6** (1918), p. 33.
(72) TACKE, B. *Chem. Ztg.* **22** (1897), p. 174.
(73) THOMPSON, H. S. *J. Roy. Agric. Soc. Eng.* **11** (1850), p. 68.
(74) TRUOG, E. *J. Phys. Chem.* **20** (1916), p. 457.
(75) VEITCH, F. P. *J. Amer. Chem. Soc.* **24** (1902), p. 1120.
(76) WALKER, J. and APPLEYARD, J. R. *J.C.S.* **69** (1896), p. 1334.
(77) WALPOLE, G. S. *Biochem. J.* **7** (1913), p. 260.
(78) WAY, J. T. *J. Roy. Agric. Soc. Eng.* **11** (1850), p. 313; **13** (1852), p. 123; **15**
(1854), p. 491.
(79) WHEELER, HARTWELL and SARGENT. *J. Amer. Chem. Soc.* **22** (1900), p. 153.
(80) WHITNEY and OBER. *J. Amer. Chem. Soc.* **23** (1901), p. 842.
(81) WILD, L. J. *J. Agric. Sci.* **8** (1916-17), p. 157.
(82) WILEY. *Agricultural Analysis*, **1** (1906), p. 373.

(Received July 16th, 1920.)