THE REACTION BETWEEN DILUTE ACIDS AND THE PHOSPHORUS COMPOUNDS OF THE SOIL.

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FEW reactions are more important to the soil chemist than that involved in the action of dilute acids on the phosphorus compounds of the soil, but, owing to its complex nature, little has been definitely ascertained about it. The importance of the reaction lies in the fact that it affords a distinction between those phosphorus compounds which are fairly easily soluble, and may therefore be expected to enter the plant root without much difficulty, and the less soluble compounds which are of less value in the nutrition of plants.

The necessity for such a distinction was emphasised in a classical memoir published in 1845 by Daubeny[1], who used the terms "active" and "dormant" to express the more and less soluble constituents respectively. He suggested that a solution of carbonic acid might be used to discriminate between them, but the manipulative difficulties proved considerable, and the suggestion was gradually forgotten, and along with it the distinction it was intended to emphasise. It was not till 1894 that general attention was once more directed to the need for the distinction by the publication of Dyer's important paper[2] in which he uses the terms "available" and "unavailable" for these groups,— terms which have since been generally adopted in this country. From the circumstance that the earlier analyses were expressed not only in percentages but also in pounds per acre, the idea gradually arose that the "available" and "unavailable" compounds were sharply distinct.

[1] Daubeny, C. G. B., "On the rotation of crops and on the quantity of Inorganic Matters abstracted from the soil by various plants under different circumstances." *Phil. Trans.* 1845, 179–253.

[2] Dyer, B., "On the analytical determination of probable available mineral plant food in soils." *Trans. Chem. Soc.* 1894, **65**, 115–67; also *Phil. Trans.* 1901, **194**B, 235–90.

Hall and Plymen[1], however, argued from their numerous analyses that there was no evidence of two definite groups, but that all the facts could be explained on the view that a considerable number of compounds occur of different degrees of solubility which, however, merge gradually one into the other.

Dyer used 1 % citric acid as a solvent, and found that it brought out amounts of phosphorus comparable with those which might be expected from a knowledge of the crop producing properties of the soil. This particular solvent had already been recommended by Tollens[2], and used by Stutzer[3] for the examination of phosphatic manures, but it was finally selected by Dyer on theoretical grounds. At that time plant roots were supposed to excrete acids that dissolved the soil phosphates and other mineral substances which then passed into the roots by osmosis. Now Dyer found that 1 % citric acid had approximately the same degree of acidity as cell sap, and argued that it must therefore exert approximately the same solvent action on the soil phosphates as the plant excretions, and would therefore give the most faithful picture of the phosphatic material available for plant nutrition.

The conception of the plant root as a special excreting and dissolving agent is now generally abandoned, as no satisfactory evidence can be obtained that any acid other than carbonic acid is excreted, or that any action beyond respiration is concerned. With this conception the theoretical basis underlying the selection of 1 % citric acid has gone too, and the method becomes purely empirical, and justifiable only by the extent to which its results are of value in soil analysis.

Judged by this empirical standard 1 % citric acid has proved fully satisfactory, and in Great Britain it is very generally adopted. Wood[4] and also Hall and Plymen[5] found that it gave results which accorded with the agricultural history of the soil. But it has not found acceptance elsewhere. N/200 hydrochloric acid has been recommended in the United States, and 2 % HCl (about N/1·82) in Sweden. Mitscherlich[6] adopts a saturated solution of carbonic acid, again, in order to simulate the action of the plant roots, and has carried out extended observations

[1] *Trans. Chem. Soc.* 1902, **81**, 117–44.

[2] A. Grupe and B. Tollens, *Ber. d. deutsch. Chem. Gesell.* 1880, **13**, 1267; v Ollech and Tollens, *Journ. f. Landw.* 1882, **30**, 519.

[3] *Chem. Ind.* 1884, **7**, 37.

[4] Wood, T. B., *Trans. Chem. Soc.* 1896, **69**, 287, also Wood and Berry, This *Journal*, 1905, **1**, 114–21.

[5] *Trans. Chem. Soc.* 1902, **81**, 117–44.

[6] *Landw. Jahrb.* 1907, **36**, 309–369.

to show that it gives results in agreement with those of pot experiments. Aspartic acid, acetic acid, and others have also been used.

From the fact that so many dilute solvents remain in use by analysts, it may be inferred that almost any acid can be made to give satisfactory results provided sufficient trouble is taken to ascertain suitable conditions of extraction. Direct experimental verification of this view was obtained by Hall and Plymen, who found that all the dilute acids gave the same kind of results, although there were considerable differences in the amount of phosphoric acid brought out; but citric acid proved to be on the whole at least as convenient as any other, and, as it had already been in use for some years, there was no advantage in giving it up. It is on this basis that the analytical side of the problem has solved itself, and in any country where considerable experience has been gained with a particular solvent there is probably little to be said in favour of making any change. The extensive literature that has grown up round this branch of soil analysis is largely concerned with the accumulation and record of experience of the particular solvent adopted, and need not therefore be discussed by us at this stage.

There is, however, a wider problem of more fundamental significance. By studying the reaction under definite conditions in the light of the well established laws of chemical dynamics it ought to be possible to discover the type of the reaction, and thus to obtain information as to the nature of the phosphorus compounds in the soil. The first attempts in this direction were made by Hall and Amos[1]. Soil was extracted with successive doses of citric acid and the P_2O_5 determined: the results were plotted in the usual way. The curves, however, could not be fitted by any of the ordinary equations. Similar negative results were obtained by de Sigmund[2] in an interesting series of investigations with nitric acid. Our own experiments also yield the same results. It may be taken as established that the reaction is not of the simple type presented by the familiar mono-, di-, or tri-molecular reactions of the text-books.

Hall and Amos considered that their results could be explained on the supposition that soil contains several phosphorus compounds of varying degrees of solubility. This may be so, but it cannot be the only factor. We shall show that citric acid extracts considerably more phosphorus from the soil than equivalent concentrations of nitric acid,

[1] *Trans. Chem. Soc.* 1906, **89**, 205–22.
[2] *J. Amer. Chem. Soc.* 1907, **29**, 929–36.

a fact which indicates that something more is concerned than a mere mixture of phosphates.   One of us has shown, also, that Hall and Amos's results are better explained on the view developed in this paper[1].

Schloesing[2] states that the amount of phosphorus dissolved from soils is constant whatever the concentration of the acid between certain limits and de Sigmund[3] supported this claim.   As his paper is not generally accessible to agricultural chemists his curve is reproduced here (Fig. 1).   With very dilute acids the action is only slight: as the concentration increases more phosphate comes into solution.   Then for a period the action is constant whatever the strength of the acid; finally, with stronger acid the action again increases, and goes on increasing with each addition to the strength of the acid.   These results, if correct, would afford strong indication of the presence of an easily soluble phosphate which was being dissolved out during the period of constant action (the horizontal part of the curve), and of less soluble phosphates, which are only brought out by the stronger acids.
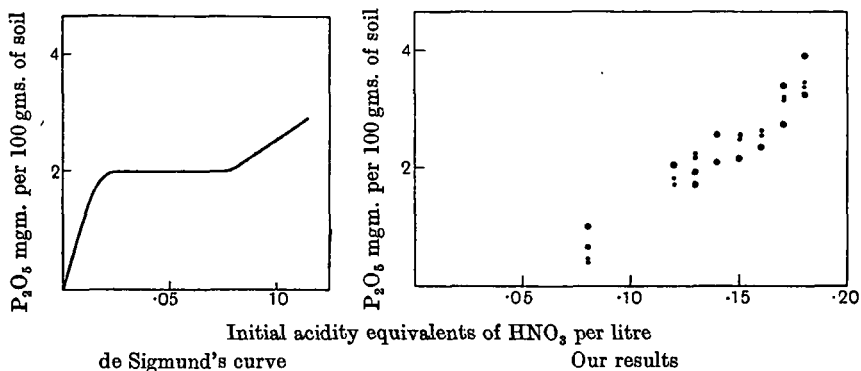

Initial acidity equivalents of HNO_3 per litre

de Sigmund's curve   Our results

Fig. 1.   Amounts of P_2O_5 extracted from soil by HNO_3 of varying concentration.
Laboratory temperature.

We have carefully repeated these experiments but failed to obtain the same results.   Both Schloesing and de Sigmund seem to have carried out their extractions at laboratory temperature, which in practice is somewhat variable.   The improved method now available for estimating phosphoric oxide in solution enables us to plot the results on a larger scale than was possible for the earlier investigators.   Working under their conditions the results are very variable, and fit neither a curve nor a straight line (Fig. 1, Table II), although if one reduced the scale

[1] J. A. Prescott, *Proc. Chem. Soc.* 1914, **30**, 137–8.

[2] *Compt. Rend.* **128**, 1004.

[3] *J. Amer. Chem. Soc.* 1907, **29**, 929–36.

of plotting they might be made to fit a curve of the Schloesing and de Sigmund type, or, for that matter, almost any other. Arrangements were therefore made for shaking at constant temperature. Under these conditions uniform results are obtained, but the figures show no constancy over any period (Fig. 2, Table III). Thus the evidence of constant action disappears, and with it the evidence for the view that the action of dilute acids on soil is a simple solvent action, an easily soluble phosphate being first attacked, and then more difficultly soluble phosphates. We have just seen also that the action is not of the ordinary mono-, di-, or tri-molecular type.

The significance of these conclusions is very considerable. The soil was for a long time regarded as a collection of insoluble inert mineral fragments admixed with small quantities of more soluble substances some of which arose by weathering or other decomposition processes. This view had the advantage of simplicity, and it allowed of the application of simple and chemical and physical laws to soil processes. But unfortunately it leads to inaccurate conclusions. If soil is simply a mixture of insoluble inert minerals with phosphates, etc., there is no reason why it should behave abnormally towards dilute acids. In like manner the view leads to wrong conclusions as to the phenomena of evaporation of water from the soil[1].
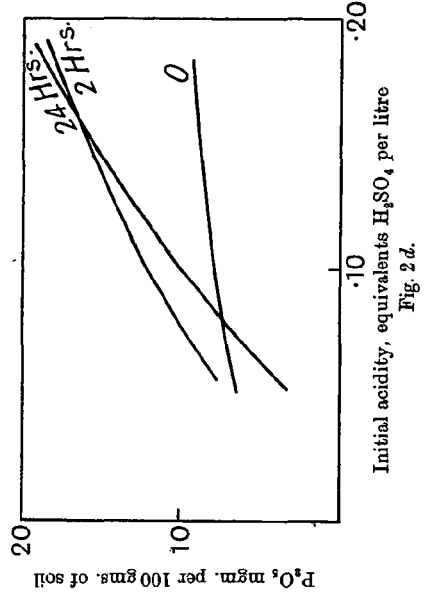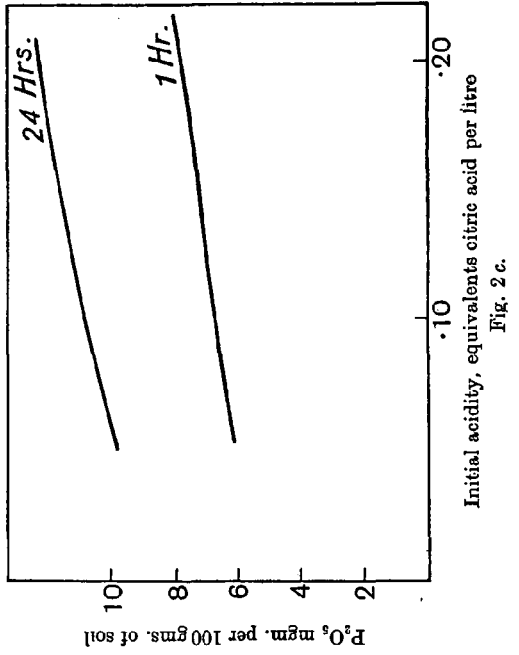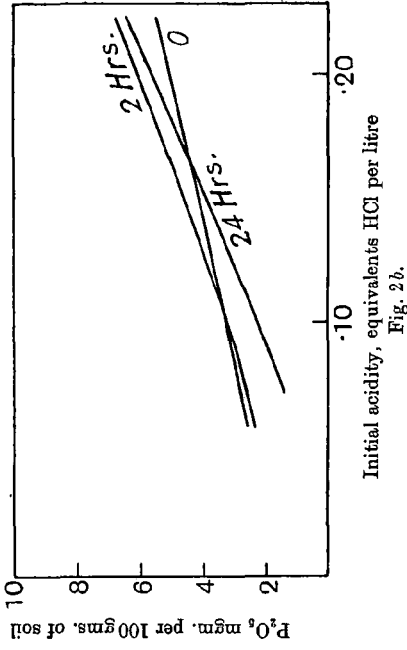
It thus appears that this simple conception of the constitution of the soil is inaccurate, and must be discarded. We have been able to show that another conception is more in accordance with the facts.

The most convenient method of studying the reaction between dilute acids and the phosphorus compounds of the soil is to shake a definite weight of the soil,—we used 50 or 100 gms.,—with a uniform volume, —1 litre in our experiments,—of the acid at constant temperature (23° C.) for a definite time, and then to estimate the amount of phosphorus compounds in the solution. Thus all the factors are under control and can be varied one at a time, all the others remaining constant. The results obtained are briefly summarised below.

1. When a soil is shaken for a definite period at constant temperature with a dilute acid the amount of action is found to increase continuously with the concentration of the acid. The increase is nearly proportional to the concentration of the acid, but not quite, and on plotting the results they are seen to fall on perfectly smooth curves

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[1] This *Journal*, 1914, **6**, 456–475; also *Annual Report of the Rothamsted Experimental Station*, 1914, p. 6.

Agdell Soil.
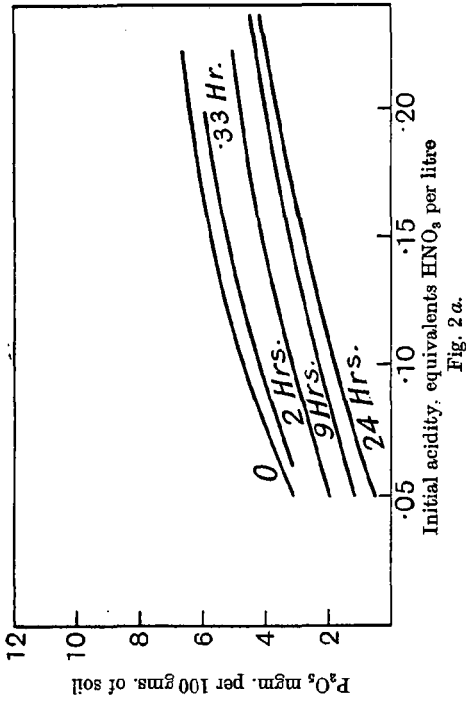
Fig. 2 b.

Initial acidity, equivalents HCl per litre

P₂O₅ mgm. per 100 gms. of soil

Fig. 2 d.

Initial acidity, equivalents H₂SO₄ per litre

P₂O₅ mgm. per 100 gms. of soil

Fig. 2 a.

Initial acidity, equivalents HNO₃ per litre

P₂O₅ mgm. per 100 gms. of soil

Fig. 2 c.

Initial acidity, equivalents citric acid per litre

P₂O₅ mgm. per 100 gms. of soil

MANURING FOR HIGHER CROP PRODUCTION

BY

E. J. RUSSELL, D.Sc. (LOND.)

DIRECTOR OF THE ROTHAMSTED EXPERIMENTAL STATION

PREFACE

IN the following pages I have collected information about manures and soil management which will I hope prove helpful to farmers in drawing up their schemes for cropping. Conditions are changing so quickly, and labour and transport difficulties react in such complex ways, that no general advice could hold good all round. All farmers ought to increase the produce of their land, and most of them are trying to do so. I have aimed at giving them facts from which they can draw conclusions suited to their own conditions and bearing on their own problems. In agriculture the judgment of the man on the spot has usually to be final, and the more clearly he has the facts before him the sounder the judgment is likely to be. Fortunately the system of County Expert Advisers is in working order, so that no farmer need have any difficulty in getting information on which to base his plan of action.

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which though very flat do not appear over any part of their course to be straight lines.   There is no sign of any break in the curves, and nothing to indicate any definite stages in the reaction (Fig. 2, Table III).

Hoos 2 C Soil
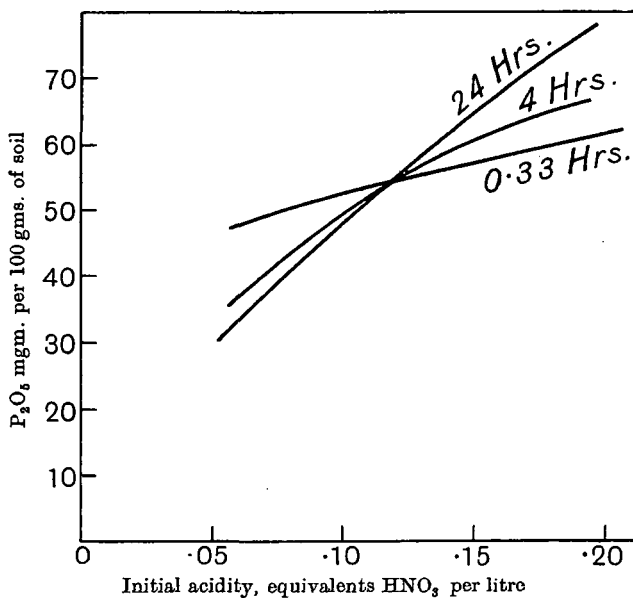
Fig. 2 e.

2.   All dilute acids, as far as they have been examined, give curves of the same type.   The amount of action, however, varies in a remarkable manner, the strong acids such as hydrochloric and nitric being less potent than equivalent concentrations of the weaker citric and oxalic acids.   At $N/10$ concentration hydrochloric and nitric acids behave very similarly and bring out less phosphate than $N/10$ sulphuric acid: this in turn brings out less than $N/10$ citric acid, while $N/10$ oxalic acid gives the highest results of any.

3.   When curves obtained for different periods of time are plotted together they are seen to be very much alike, but they do not all lie parallel to one another: there is a certain amount of crossing, *i.e.* the amount of action is not proportional to the time.   At the beginning of the curve, where the concentration of the acid is nearly $N/20$, the action usually shows the remarkable peculiarity that it is *less* after 24 hours than after 10 minutes.   Beyond certain concentrations,

however, the curves cross one another, and the action finally increases with the time.

4.   Thus if acid of sufficiently low concentration (N/20 to N/10) is allowed to act on soil for different periods of time the amount of phosphorus compound extracted does not increase with the time but decreases, so that less is extracted after 24 hours than after 10 minutes.

This result indicates that a reverse reaction is coming into play removing the phosphorus compounds from the solution, but that it operates more slowly than the direct action of the acid in dissolving the phosphorus compounds from the soil. Thus in the 10 minutes experiment the net result is mainly determined by the direct action; after 24 hours the reverse reaction has become more pronounced and reduced the amount of phosphorus left in the solution.

5.   The reverse reaction does not appear to be due to any precipitating out of the phosphorus compounds from the solution by any substance slowly extracted from the soil. For no precipitation of phosphorus compound occurs when an extract obtained by shaking soil with nitric acid for 10 minutes, and therefore rich in phosphorus, is mixed with one obtained after 24 hours' shaking, and therefore rich in any phosphorus-precipitating compound, if such is present. The seat of the reverse action, therefore, is not in the solution, but in the soil.

6.   The phenomena can be reproduced by adding sodium phosphate to the mixture of soil and acid. Some of the phosphate is absorbed by the soil, notwithstanding the presence of excess of acid. The absorption is found to take place in presence of both N/10 and N/5 acid, though it fell off at the higher concentration (Table VII). Thus, the reverse reaction of § 4 is not confined to acids of low concentration, but is general: with acids of low concentration the absorption is great relative to the extraction of the phosphoric oxide; with acids of higher concentration it is small relative to the amount of P_2O_5 extracted.

7.   The absorption of the P_2O_5 ion from solution in presence of acid is found to follow precisely the ordinary lines of adsorption by colloids, and is completely expressed by the ordinary adsorption formula $\frac{y}{m} = Kc^{\frac{1}{p}}$, where $y =$ the amount adsorbed by a quantity m of the soil, $c =$ the concentration of P_2O_5 in the solution when equilibrium is established, and K and p are constants (Figs. 3, 4 and 5). In one respect only is there any notable difference: adsorption by colloids is usually an instantaneous process, whilst the reverse reaction observed

in the soil becomes more marked after 24 hours than after shorter periods. It is shown later, however (§ 15), that the discrepancy is not real. We are therefore justified in speaking of the absorption as an *adsorption*.

8. The different acids have markedly different effects on the adsorption of phosphates from solutions of sodium phosphate. Adsorption goes on readily in the presence of hydrochloric and nitric acids, but is notably smaller in presence of citric acid in equivalent concentration. It may be inferred, therefore, that the greater net action of citric acid in comparison with hydrochloric or nitric acids is not due so much to a greater solvent power, but to a greater power of reducing adsorption. Thus we should expect the actual solvent action of these acids to be more nearly alike than is indicated by the net action.
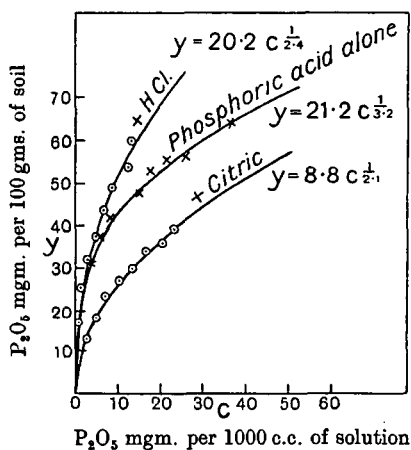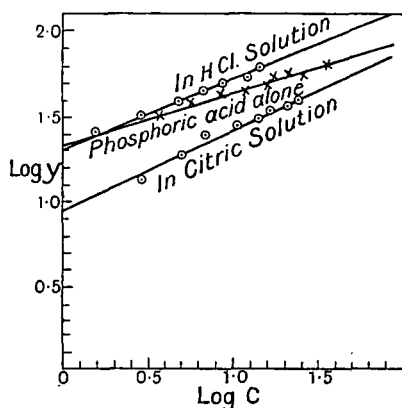
Fig. 3 a.   Fig. 3 b.

Fig. 3 a.   Amounts of P_2O_5 adsorbed by soil Agdell B in presence of different acids. The log. curves are given in Fig. 3 b (see p. 95).

9. This expectation turns out to be correct. Adsorption can be eliminated almost entirely by arranging the experiment so that the phosphorus compound is removed from the soil as soon as it is dissolved. This is readily accomplished by diffusion. The practical difficulties are overcome by shaking the soil with 2 % agar solution, and pouring the suspension quickly into glass tubes so as to cast it into sticks. These are then placed upright in beakers containing the various acids: diffusion of acid into the stick, and of dissolved P_2O_5 out of it, rapidly takes place, and after some ten or more changes the diffusate is practically free from phosphate. Under these circumstances the amounts of phosphorus compound dissolved out from the soil are substantially

the same for hydrochloric, nitric, and citric acids (Table VIII). Sulphuric acid, however, brings out rather higher quantities.

10. Thus the reaction of the soil phosphorus compounds with dilute acids may be resolved into two separate actions: a direct action of the acid on the phosphorus compound, and an adsorption of the dissolved P_2O_5 by the soil. In high acid concentrations the former action predominates, but both actions always go on. The solvent action is practically the same for nitric, hydrochloric, and citric acids of equivalent strengths, and appears to be the normal action of an acid on a phosphate. The reverse reaction is the typical adsorption shown by colloids, and can be expressed by the equation which has been found to fit so many of them. It is considerably influenced by the acid, being greater in the presence of the mineral acids than of the organic acids. The amount of phosphorus compound actually brought out is the difference between the direct and the reverse action. Thus hydrochloric acid dissolves out a certain amount of phosphate, but considerable adsorption takes place, so that the net amount left in solution becomes small. Citric acid dissolves out the same amount of phosphate, but there is much less adsorption, and therefore the amount left in solution is markedly greater. The difference between the various dilute acids lies, therefore, not so much in their solvent power, which is very similar for all, but in their influence on the adsorption process.

11. Since all these dilute acids behave similarly in their direct action, and differ only in the extent to which they influence the adsorption process, the observed net effect of the acid on the soil is expressed by the ordinary adsorption curve, *i.e.* parabolic curves of the general type:

$$y = Kx^{\frac{1}{p}},$$

where K and p are constants for each set of conditions, and do not include the variables x and y. But the numerical values of K and p depend on the nature and concentration of the acid, the time and temperature of the action, etc. A complete expression of the action of a given acid at varying concentrations for a given time therefore requires a series of curves, one for each concentration: or, in other words, a surface; the three variables being: P_2O_5 left in the soil, P_2O_5 left in solution, concentration of acid. The surface only expresses the action for the given time and temperature, and a series of surfaces is required to express the action at varying times but constant temperature, while with varying temperatures the case becomes more complex still. A very

pretty problem thus opens out, with which, however, we do not at present propose to deal.

The adsorption process.

12. Adsorption is not confined to phosphoric acid. Both oxalic and citric acids are adsorbed even in presence of nitric acid. Adsorption curves closely agreeing with the equation can be obtained for oxalic acid (p. 124) but not readily for citric acid, owing to the difficulty of the analytical process. On the other hand hydrochloric and nitric acids are not perceptibly adsorbed.

As a general rule adsorption of phosphoric acid is less in presence of those acids which are themselves adsorbed, than of those which are not.

We may infer that acids such as citric and oxalic satisfy the adsorption capacity of the soil and leave it with little power to take up phosphoric acid: nitric and hydrochloric acids, however, do not, and thus leave the soil free to take up phosphoric acid.

13. The order in which acids are adsorbed by soil is as follows:

$$\left.\begin{array}{l}\text{Oxalic} \\ \text{Citric}\end{array}\right\} \text{most}$$

Phosphoric
Sulphuric

$$\left.\begin{array}{l}\text{Hydrochloric} \\ \text{Nitric}\end{array}\right\} \text{least}$$

It must not be supposed that adsorption is exclusive, *i.e.* that citric acid is wholly taken in preference to phosphoric. Both are adsorbed simultaneously, but citric acid displaces some of the phosphoric.

This order appears to be determined by the nature of the acid, and not by the soil, for it is practically identical with that given by Skraup[1] for the adsorption of acids by filter paper, viz.:

Phosphoric
Sulphuric
Nitric
Hydrochloric
Acetic

When an acid is adsorbed by soil it not only displaces some of the acids below it, but also other adsorbed material. Thus, citric and oxalic

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[1] Vienna, 1909, quoted in *Jour. Phys. Chem.* 1914, p. 387.

acids yield dark coloured solutions containing organic matter previously adsorbed by the soil; sulphuric acid yields lighter coloured solutions containing less; hydrochloric and nitric acids, on the other hand, displace very little organic matter, and yield almost colourless solutions. Citric acid brings out more iron than either hydrochloric or nitric acids.

14.   There is not, however, a rigid parallelism between the displacement of adsorbed organic matter and that of adsorbed phosphate. Thus, of all acids and salts investigated, ammonium oxalate gave the darkest coloured solutions, but it did not dissolve most phosphate. Again, sodium fluoride gave a dark coloured solution, but dissolved only little phosphate.

The change in adsorption with the time.

15.   The amount of adsorption depends not only on the acid but on the time.   Figs. 4 and 5 show that the continued action of N/10 nitric acid causes increased adsorption both by Hoos and Agdell soils. At first sight N/5 acid appears to show the contrary behaviour, but on closer inspection it becomes clear that the curves will cross, so that the 24 hour will ultimately come above the one hour as in the N/10 curve.   And in point of fact the N/10 curves themselves also show this relationship in the early part of their course.

Citric acid, however, behaves differently: the adsorption after one hour is greater than after 24 hours, and it is not obvious from inspection that the curves will ever cross.

It might be supposed from the N/10 nitric acid curve that adsorption was a slow business.   This does not appear to be the case, however. After any given interval a definite equilibrium is attained expressed by an equation with definite constants.   The phenomena are entirely consistent with the view that the adsorption itself is instantaneous (as is almost invariably the rule with the other adsorbents), but that the constants change with the time.   In the curves of Figs. 4a and 5, p tends to fall as the time increases, so that the curve opens out.

16.   The changes in the amount of adsorption occur simultaneously with a change in the soil and in the solution.   The acid causes continuous decomposition of the soil, the extent of which may be seen from the reduction in strength of the acid.   Table III shows the amounts of nitric acid neutralised by soil after different intervals: these are considerably greater than corresponds with the calcium carbonate, phosphates, etc., present.   Much silica is liberated during the action.

Agdell soil.

$y=9.4 c^{\frac{1}{1\cdot3}}$

24 Hrs.

1 Hr.

$y=11.3 c^{\frac{1}{2\cdot5}}$

Time = 0

$y=11.5 c^{\frac{1}{3\cdot1}}$

P_2O_5 mgm. per 100 gms. of soil

P_2O_5 mgm. per 1000 c.c. of solution
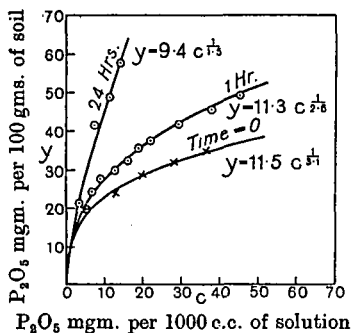
Fig. 4 a.

Agdell soil, log. curves.

24 Hrs.

1 Hr.

Log y

Log C

Fig. 4 b.

Saxmundham soils.

Unmanured

$y=6.3 c^{\frac{1}{2\cdot0}}$

Superphosphates

$y=7.9 c^{\frac{1}{3\cdot1}}$

P_2O_5 mgm. per 100 gms. of soil

P_2O_5 mgm. per 1000 c.c. of solution
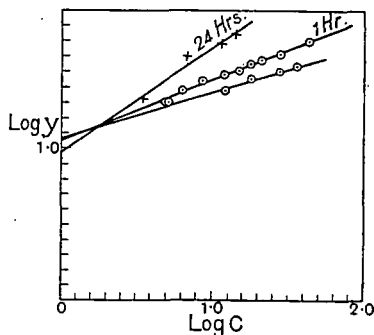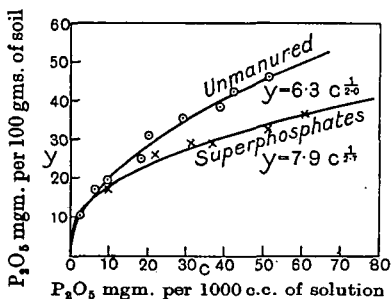
Fig. 4 c.

Saxmundham soils, log. curves.

Unmanured

Superphosphate

Log y

Log C

Fig. 4 d.

Light soils.

Woburn

$y=30.7 c^{\frac{1}{5\cdot2}}$

Bramford

$y=2.7 c^{\frac{1}{1\cdot8}}$

P_2O_5 mgm. per 100 gms. of soil

P_2O_5 mgm. per 1000 c.c. of solution
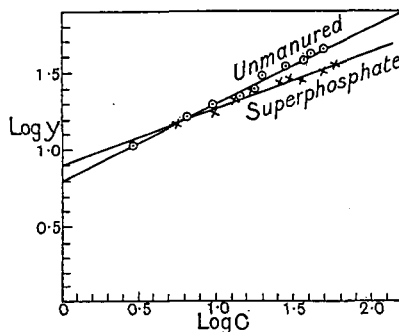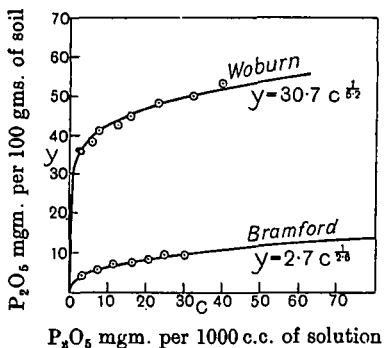
Fig. 4 e.

Light soils, log. curves.

Woburn

Bramford

Log y
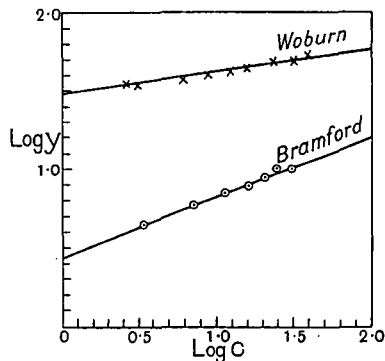
Log C

Fig. 4 f.

Fig. 4 a, c and e. Amounts of P_2O_5 adsorbed by various soils in presence of N/10 HNO_3.
Fig. 4 b, d and f. The log. curves.

Hoos 2C Soil.
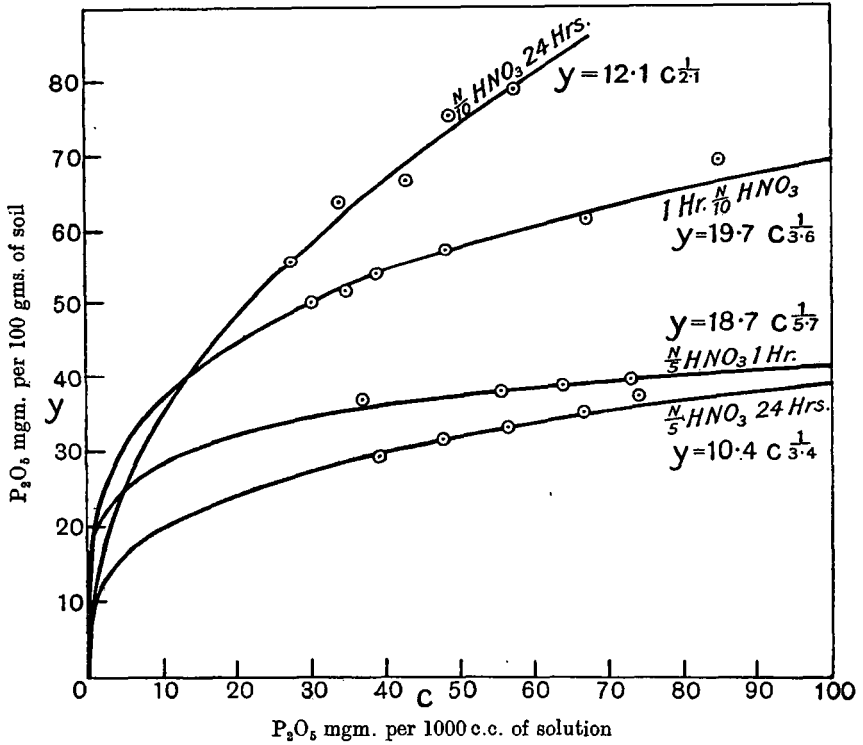
Fig. 5 a.
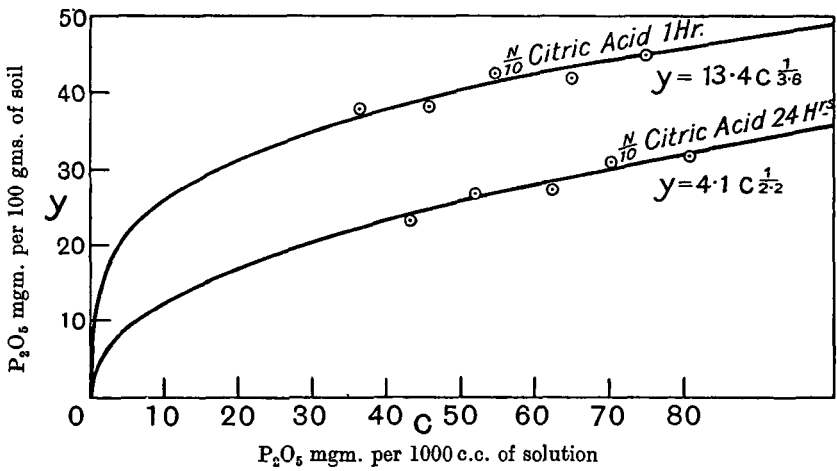
Fig. 5 b.

Fig. 5.   The effect of time, and of strength of acid, on the adsorption phenomena.

17. It does not appear, however, that treatment with acid affects the adsorptive capacity of the soil: the curve obtained after preliminary treatment of the soil with acid coincides with that for the untreated soil (Fig. 6).

Agdell Soil.
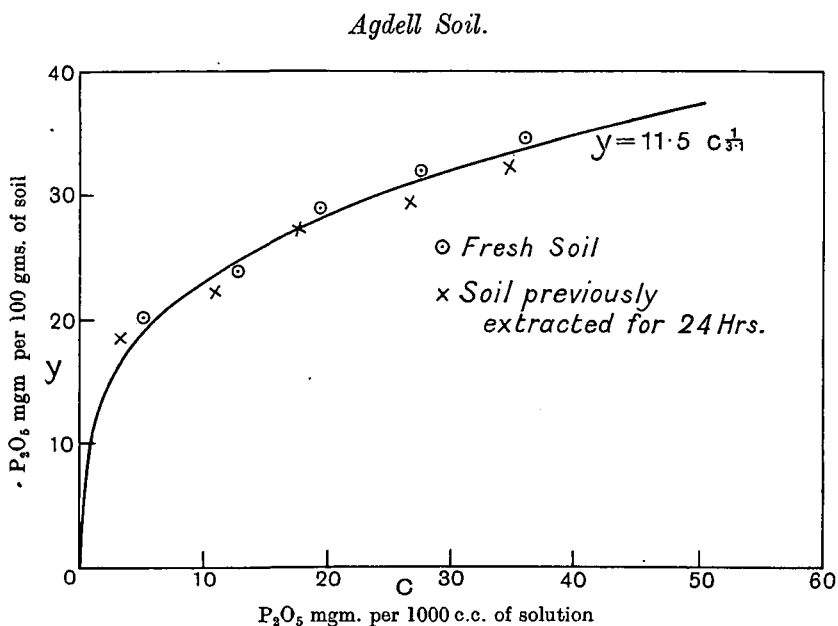
Fig. 6. Adsorption of P_2O_5 in presence of $N/10$ HNO_3 from (a) fresh soil, (b) soil previously extracted for 24 hours by $N/10$ HNO_3.

The change in the constants with the time appears to be determined by the changes in the solution. Some soil was divided into two parts: one was treated with acid which had been in contact with soil for 24 hours, and the other with an equivalent amount of fresh acid. The adsorption curves were entirely different: that obtained with the fresh acid falling below the other, and being related to it in the same manner as the "Time = 0" curves are to the "Time = 24 hour" curves (Fig. 7).

It follows that the simplest results are obtained when the time is reduced to a minimum, because here the composition of the liquid has suffered minimum change by interaction with the soil.

Hoos 2C Soil.
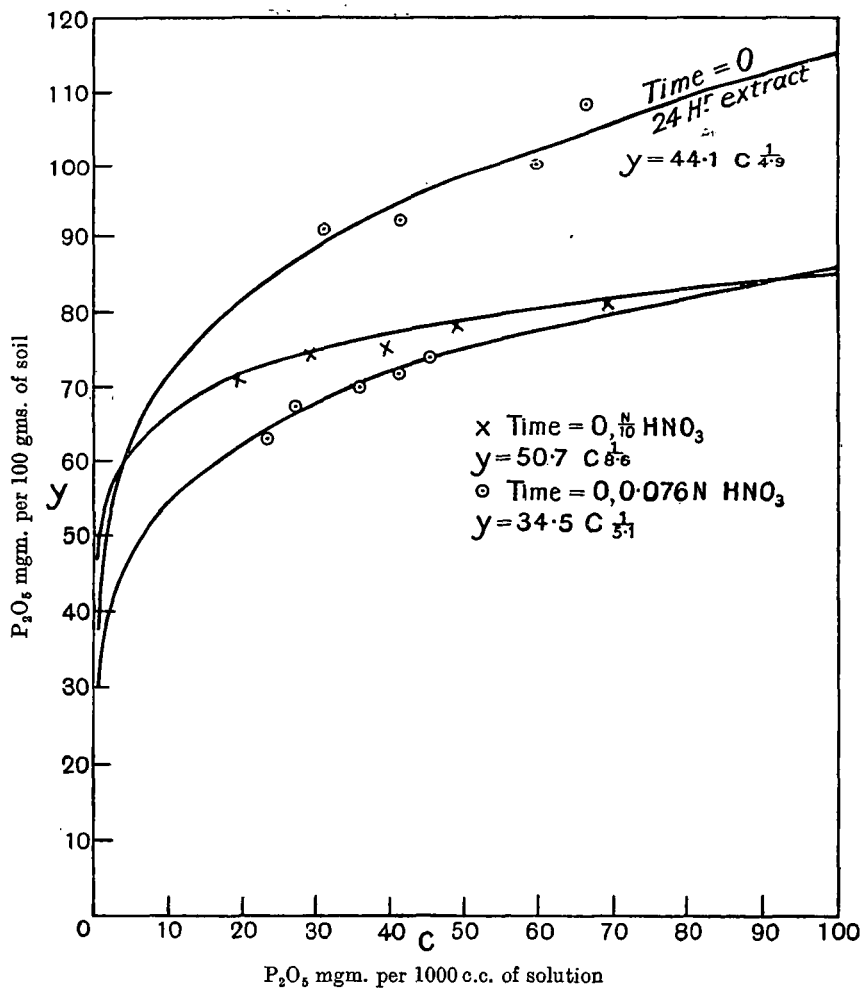
Fig. 7.   Adsorption of P_2O_5 in presence of (*a*) N/10 HNO_3 which has already been in contact with soil for 24 hours, (*b*) fresh HNO_3 of equivalent concentration. Two experiments were made, one with N/10 acid (equivalent initial concentration), the other with 0·076 N HNO_3 (equivalent final concentration).

The equations obtained and the meaning of the constants.

18. The following equations have been obtained expressing the equilibrium obtained in the adsorption of P_2O_5 by soils in the presence of various acids:

Heavy soils. Rothamsted.

General equation $y = KC^{\frac{1}{p}}$.

N/10 HNO₃	Time = 0	Time = 1 hr.	Time = 24 hrs.
Hoos 2 C (Superphosphate)		$y = 19 \cdot 7\, C^{\frac{1}{3 \cdot 6}}$	$y = 12 \cdot 0\, C^{\frac{1}{2 \cdot 1}}$
Agdell (unmanured)	$y = 11 \cdot 5\, C^{\frac{1}{3 \cdot 1}}$	$y = 11 \cdot 3\, C^{\frac{1}{2 \cdot 6}}$	$y = 9 \cdot 4\, C^{\frac{1}{1 \cdot 5}}$
,, ,, *		$y = 16 \cdot 1\, C^{\frac{1}{5 \cdot 0}}$	
,, ,, extracted†	$y = 11 \cdot 5\, C^{\frac{1}{3 \cdot 1}}$		
N/5 HNO₃			
Hoos 2 C		$y = 18 \cdot 7\, C^{\frac{1}{5 \cdot 7}}$	$y = 10 \cdot 4\, C^{\frac{1}{3 \cdot 4}}$
N/10 HCl			
Agdell B (extracted)‡			$y = 20 \cdot 2\, C^{\frac{1}{2 \cdot 4}}$
N/10 citric acid			
Hoos 2 C		$y = 13 \cdot 4\, C^{\frac{1}{3 \cdot 6}}$	$y = 4 \cdot 1\, C^{\frac{1}{2 \cdot 2}}$
Agdell B (extracted)‡			$y = 8 \cdot 8\, C^{\frac{1}{2 \cdot 1}}$

Lighter soils. Saxmundham.

N/10 HNO₃. Time = 2 hours

Plot 4 (2 cwt. superphosphate annually) ...   . $y = 7 \cdot 9\, C^{\frac{1}{2 \cdot 7}}$

Plot 6 (unmanured) ...   . $y = 6 \cdot 3\, C^{\frac{1}{2 \cdot 0}}$

Woburn.

N/10 HNO₃. Time = 1 hour

Stackyard wheat plots (unmanured)   ...   . $y = 30 \cdot 7\, C^{\frac{1}{6 \cdot 2}}$

Lightest soil. Bramford§.

N/10 HNO₃. Time = 1 hour

...   . $y = 2 \cdot 7\, C^{\frac{1}{2 \cdot 6}}$

* Na₂HPO₄ added after 50 minutes' shaking. See p. 106.

† With N/10 HNO₃ which removed 3·60 mgms. P_2O_5 per 100 gms. soil. See p. 108.

‡ With H_2SO_4 and then NaOH. See p. 94.

§ Owing to the richness of this soil in phosphates it had to be subjected to a preliminary extraction with N/5 nitric acid.

With the exception of the Woburn soil these all fall into a series, K varying from 19·7 in the heavy Hoos field soil, down to 2·7 in the light Bramford soil, while y shows much less change and at equal times has actually the same value for the heavy as for the light soils.

The question naturally arises: what do these constants mean? and are they connected with any of the other properties of the soil?

At the outset it must be observed that these "constants" have no absolute value: they are not constant for the soil but only for the special conditions under which the experiment was carried out. Thus, for Hoos $2C$: K varies from 4·1 to 19·7, and no doubt wider variations could be obtained. The figures, therefore, cannot be regarded as absolute measures of any soil property.

Nor can they be used indiscriminately even for purposes of comparison when different soils are being studied under the same experimental conditions. For however nearly alike the conditions may be at the beginning of the experiment they soon begin to diverge as the experiment proceeds. It is shown on p. 109 that the substances dissolved out from the soil considerably affect the values of the constant.

But by exercising due caution it is possible to learn something from them.

The meaning of K may be arrived at by inspection of the equation. It is the amount of P_2O_5 that will remain in the soil when $C = 1$, *i.e.* when unit quantity of P_2O_5 is present in the solution; it therefore represents *the tenacity with which the soil keeps its P_2O_5*, or in other words, the reluctance with which the soil parts with its P_2O_5, under the conditions of the experiment.

It is high for heavy soils, low for light ones (except Woburn): it falls off under the continued action of the acid, so that it is less after 24 hours than after one hour; it is greater in presence of nitric and hydrochloric acids than of citric acid.

The meaning of p is less obvious. The equation shows that it is more complex than K, being the ratio of the logarithms of c and y. Inspection of the curves, and especially of Fig. 4 *a*, shows that where p is large the curve bends over to the axis of X, *i.e.* the soil soon ceases to adsorb P_2O_5, so that large amounts remain in the solution. Where p is small the curve opens out, and more P_2O_5 is taken up by the soil, while less remains in the solution. p, therefore, is connected with *the manner in which the adsorptive capacity of the soil is satisfied*, or in which *the soil takes P_2O_5 out of the solution* under the conditions of the experiment.

It is not much affected by the soil, but it falls off with the time of action.

It has been pointed out that the heavy soils show a high value for K, i.e. a high reluctance to part with their P_2O_5, while the light Bramford soil only shows a small reluctance and parts with it fairly easily. We are unable to explain why the Woburn soil behaves otherwise. The immediate reason is that the diffusion process does not come to an end as speedily as in other cases,—a phenomenon which would be readily explained if small nodules of coprolite were present,—as indeed they are known to be elsewhere in the district.

Whatever the explanation of the behaviour of the Woburn soil there is evidence that this distinction holds generally: it is difficult to get clean cut illustrations, but as a rule sandy soils respond less to phosphates than clay soils, not only because there is often more there, but also because plants can make more use of what is actually present, in other words, the sandy soils part with their phosphates more readily than heavier soils would do. This is clearly a promising field for enquiry, and we hope that fresh data will be obtained so that a fuller discussion may become possible.

It is less easy to say much about p because it varies so little with changes in the soil, and so much with changes in the solution. It is apparently less directly connected with the properties of the soil than K, and is therefore of less interest to us. And as physicists themselves have not come to any agreement as to its meaning in spite of a vast amount of work, we may safely leave it alone for the present.

The bearing of the results on soil analysis.

Since the action between dilute acids and soil consists of two parts: a direct and a reverse reaction, it follows that the amounts of P_2O_5 brought out by the ordinary treatment with dilute acids do not represent any definite extractable material in the soil, but only the difference between the quantity dissolved by the acid and that adsorbed by the soil, which varies with the acid and the conditions of the experiment.

Thus it is incorrect to call the net amount brought out the "available P_2O_5" as if it were something real in the soil: it is simply an analytical result, which will vary when the conditions of treatment are varied. If two soils have widely different adsorptive capacities they may give different analytical results even when they contain similar amounts of phosphate. Of all the acids examined citric suffers least complication from adsorption, a fact which shows the wisdom of Dyer's choice in

1894. But all acids are affected. The only way to get precise determinations of the easily soluble phosphate in the soils is to adopt a diffusion method whereby the reverse reaction becomes eliminated.

This is perfectly feasible. But so long as the conditions of the experiment are constant and the soils are of the same character, possessing similar adsorptive capacities, dilute acids may be expected to give comparable results. Not otherwise, however.

Comparable results may be of great value to soil analysts. Obviously they can be obtained only by first selecting typical soils and determining the data for them as fully as can be. This involves a soil survey, and is one of the many justifications that can be urged in favour of surveys. When typical soils have been studied it is not difficult to compare any soil *of the same kind* with them, and to give information of value to the farmer; but our results show the hopelessness of trying to compare two dissimilar soils.

Absolute results could be obtained by the diffusion method, but until we have had more experience with it we are not prepared to say what sort of value they would have for the analyst.

EXPERIMENTAL.

The soils and methods used.

Heavy soils. Rothamsted. Heavy soil, Clay-with-Flints formation.

Agdell field. This is under a rotation,—clover, wheat, swedes, and barley, and has been for many years. The soil was taken from the space between the plots unmanured since 1843, and has neither carried crops nor received manure.

Hoos field. Continuous barley plots. 1.0.—Unmanured since 1852. 2C.—This has received 1000 lbs. of rape cake, and $3\frac{1}{2}$ cwts. superphosphate each year since 1852.

Lighter soils. Saxmundham. A Boulder Clay from the Experimental field of the East Suffolk County Council.

Rotation I. Plot 6.—Unmanured since 1900. Plot 4.—This has received 2 cwts. superphosphate each year since 1900.

Woburn. Lower greensand formation. From the continuous wheat plots in Stackyard field of the Royal Agricultural Society's farm. This plot has been unmanured since 1872.

Lightest soil. Bramford. A light gravel soil from the farm on which the East Suffolk County Council experiments were carried out during the years 1893 to 1910.

The mechanical and chemical analyses of these soils are given in Table I.

TABLE I. *Mechanical analyses of soils.*

	Heavy soils, Rothamsted		Lighter soils			Lightest soils
	Agdell	Hoos Field	Saxmundham		Woburn	Bramford
		Plot 2 *C*	Plot 6	Plot 4		
Fine gravel	0·4	0·7	2·1	0·7	0·4	1·0
Coarse sand	6·4	11·3	41·5	38·6	58·0	50·3
Fine sand	29·1	22·5	15·9	18·1	13·4	23·6
Silt	21·6	24·2	4·5	5·5	7·0	2·2
Fine silt	11·8	12·8	7·1	6·6	6·9	5·5
Clay	15·4	14·0	15·7	16·0	5·7	3·9

Chemical analysis of the soils.

	Agdell	Hoos 2 *C*	Saxmundham		Woburn	Bramford
			6	4		
Phosphoric acid (P_2O_5) soluble in strong HCl	0·110	0·255	0·096	0·096	0·121	0·17
Phosphoric acid (P_2O_5) soluble in 1 % citric acid	0·012	0·083	0·009	0·014	0·011	0·11
Potash (K_2O) soluble in strong HCl	0·520	0·503	0·568	0·575	0·24	—
Potash (K_2O) soluble in 1 % citric acid........................	0·012	0·014	0·008	0·009	0·021	—
Calcium carbonate	0·04	0·14	0·31	0·37	nil	—
Loss on ignition	4·9	5·0	5·1	—	3·5	4·1

The method of extraction of the soil with the acid. A special feature of our experiments is that the extraction was carried out at constant temperature. The apparatus is shown in Fig. 8. A bicycle wheel is mounted at the apex of a triangular wooden stand, which can either rest on the floor, holding the wheel upwards, or else on the top rim of the thermostat, holding the wheel downwards in the water. The wheel is fitted with stout wooden clips enabling it to carry eight Winchester pint bottles. As a preliminary to each experiment 100 gms. of soil and a volume of distilled water sufficient to make one litre of dilute acid are placed in each bottle, which is then closed with a rubber stopper; the bottles are fixed on the wheel, put into the thermostat, and rotated by means of a hot air motor for an hour, by which time the contents have attained the temperature of the thermostat (23° C.). Then the bottles are lifted out, the requisite quantity of strong acid (2 N) is added
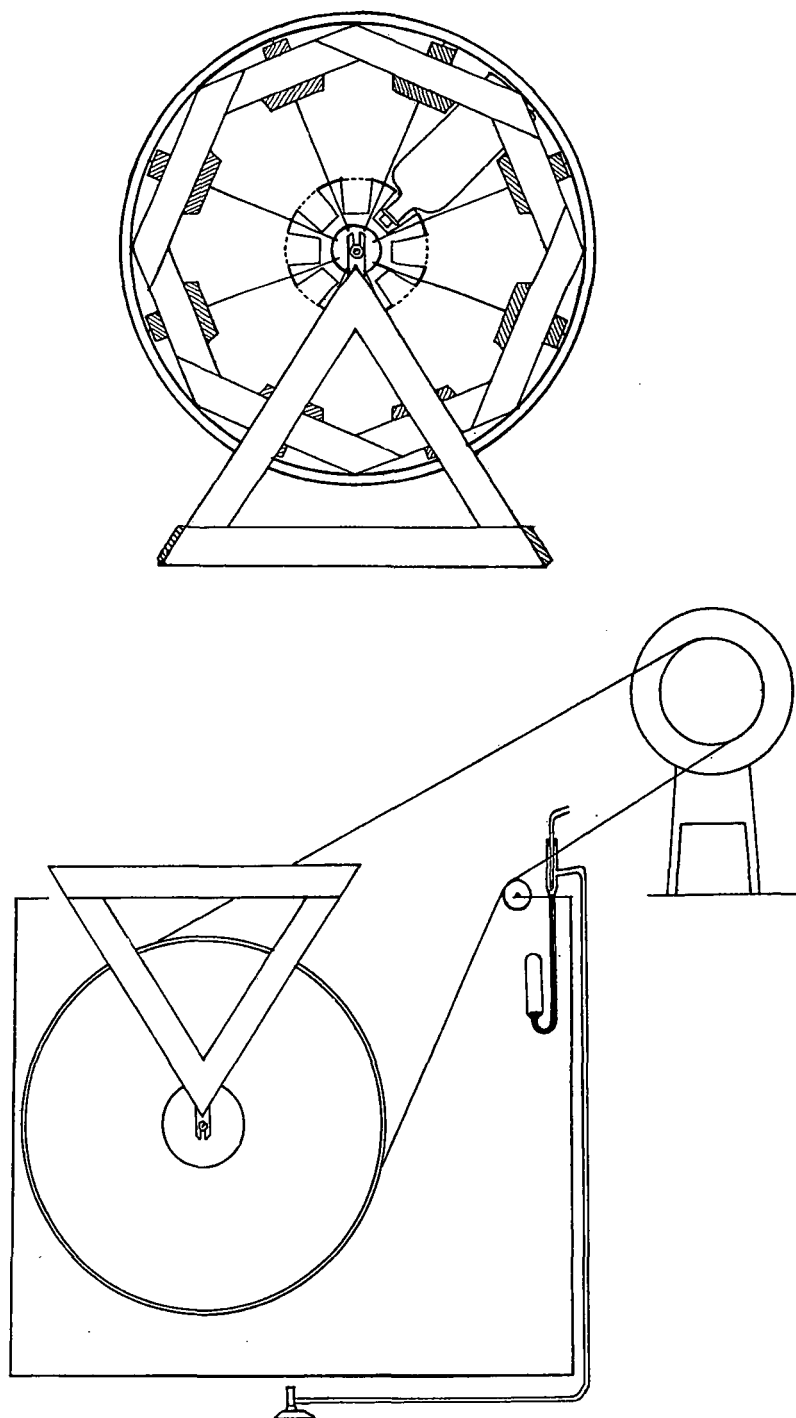
Fig. 8.   Apparatus used for shaking soil with acid at constant temperature.

to each, and they are rapidly replaced in the thermostat and shaken for the proper time. In the case of the so-called "Time = 0" experiments the bottles were not put back, but were vigorously shaken for a few seconds and allowed to stand a further few seconds for settling.

The estimation of the phosphate.

The liquid is rapidly filtered through asbestos packed on a Buchner funnel; 250 c.c., or if necessary 500 c.c., of the filtrate are evaporated to dryness, and the residue treated as already described by one of us[1].

The action of dilute acids on soils. Relation between the concentration of the acid and the amount of P_2O_5 extracted.

Schloesing and de Sigmund have both stated that the amount of P_2O_5 extracted from a soil by acids of increasing concentration is constant over part of the curve, but we failed to find evidence of this. Working exactly as they did, viz. at laboratory temperature, we obtained the results given in Table II, and plotted in Fig. 1, which certainly might be made to fit a curve like theirs, but could equally fit any other. Under the more precise conditions of the thermostat we obtained the smoother results given in Table III, and plotted in Fig. 2.

In all cases there was a considerable excess of acid left after the experiment, though the amount that had been neutralised was considerably more than corresponds with the calcium carbonate (which in this case was only small) and the P_2O_5 extracted.

The action is complex: aluminium and silica are both found in solution and in increasing quantities as the action is prolonged. But the final solution is always strongly acid, and readily dissolves calcium phosphate and attacks fresh soil dissolving out more phosphate: the variations in amount of P_2O_5 dissolved cannot therefore be attributed to exhaustion of the acid.

The amounts of P_2O_5 extracted by sulphuric, citric, and hydrochloric acids are given in Table III, and plotted in Fig. 2. They increase with the concentration of the acid, but not quite proportionately, and the curves are apparently not straight lines over their whole course, although they usually are nearly so. There is no sign of a break anywhere, and in particular no indication of the horizontal run shown in de Sigmund's

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[1] Prescott, This *Journal*, 1914, 6, 110. Extended experience with this method has demonstrated its great accuracy for small amounts of P_2O_5 such as occur in soil extracts.

curve, on which was based the evidence for simple dissolution of a simple phosphate.

TABLE II.   *Amounts of P_2O_5 extracted by dilute nitric acid of varying concentration from soil (Barnfield Subsoil) in 24 hours at room temperature ; 100 gms. of soil to 1000 c.c. of acid.*

Initial acidity Equivalents HNO_3 per litre	Mgms. P_2O_5 dissolved per 100 gms. of soil			
	(1)	(2)	(3)	(4)
·08	0·5	1·1	0·7	0·4
·12	2·2	2·0	1·9	—
·13	2·3	2·1	2·4	1·9
·14	2·8	—	2·3	—
·15	2·7	2·3	—	2·7
·16	3·1	2·5	2·8	2·8
·17	3·4	3·4	2·9	3·7
·18	3·6	4·2	3·5	3·7

In 1 hour at room temperature.

Initial acidity Equivalents HNO_3 per litre	Mgms. P_2O_5 dissolved per 100 gms. of soil	
	(1)	(2)
·06	2·0	1·9
·08	3·1	3·2
·10	4·0	3·7
·12	4·4	3·8
·14	5·7	4·9
·16	6·1	4·9
·18	5·8	6·3
·20	7·2	—

The effect of time on the process.   This is shown both in the Tables and the Curves.   Nitric acid gives the most remarkable result of all. The shorter the time of extraction the more P_2O_5 is dissolved: in a few seconds more is brought out than in 20 minutes, and considerably more than after 24 hours.   This holds for all strengths of acids up to N/5, and beyond with poor soil, though with the richer Hoos 2C soil the curves cross at N/8 (Fig. 2 e).   The result can only mean that P_2O_5 is being taken back from the solution by the soil.

Hydrochloric acid shows the same behaviour up to N/10, but at greater concentrations the curves cross; at N/5 the 24 hour curve lies

Table III. *Amounts of P_2O_5 extracted from soil by 1000 c.c. of acids of different strength at constant temperature.*

Agdell Soil.   *Temperature 23° C.*

	Sulphuric acid			Citric acid		
Initial acidity Equivalents H_2SO_4 per 1000 c.c.	Mgms. P_2O_5 per 100 gms. of soil		Initial acidity Equivalents citric acid per litre		Mgms. P_2O_5 per 100 gms. of soil	
	(a)	(b)			(a)	(b)
Time = 0			Time = 1 hour			
·057	7·1	6·6	·06		6·2	5·9
·114	7·8	8·4	·12		6·9	6·7
·170	8·5	9·7	·16		7·0	7·4
Time = 2 hours			·20		7·6	8·0
·06	8·0	8·1	Time = 24 hours			
·10	—	12·1	·06		9·7	10·1
·14	15·1	14·9	·12		11·0	11·3
·18	17·1	17·9	·16		11·3	11·7
Time = 24 hours			·20		12·1	12·3
·057	4·2	4·2				
·114	11·8	11·4				
·170	17·2	17·4				

Note.—Extractions were also made with acetic acid, but the amounts of P_2O_5 were too small to be estimated.

Hydrochloric acid

Initial acidity Equivalents HCl per litre	Mgms. P_2O_5	
	(a)	(b)
Time = 0		
·06	2·5	2·6
·12	3·8	3·5
·18	4·6	4·6
Time = 2 hours		
·06	2·5	—
·10	3·2	3·0
·14	4·1	4·7
·18	5·4	5·4
Time = 24 hours		
·075	1·3	1·7
·149	3·7	4·0
·224	6·5	6·4

TABLE III (*continued*).   *Amounts of P_2O_5 extracted from Soils by* dilute Nitric Acid *of varying strength acting for different periods of time.*

Agdell Soil, 100 *gms. to* 1000 *c.c. of acid.*   *Temperature* 23° C.

Initial acidity Equivalents HNO_3 per litre	Mgms. P_2O_5 extracted								
	0		0·33 hrs.		2 hrs.	9 hrs.		24 hrs.	
	(a)	(b)	(a)	(b)	(a)	(a)	(b)	(a)	(b)
·06	3·7	—	3·0	3·6	2·3	1·5	1·6	0·7	1·0
·08	4·3	—	3·5	4·1	2·9	2·0	2·1	2·1	1·4
·10	5·2	—	3·8	5·1	3·5	2·5	—	1·2	2·6
·12	5·5	6·2	4·9	5·0	3·8	3·0	3·0	2·5	2·3
·14	6·0	6·1	5·6	5·6	4·0	3·6	3·5	3·3	3·2
·16	6·0	6·2	6·0	—	4·8	3·6	4·0	3·4	2·7
·18	6·5	6·1	6·4	—	4·6	—	4·9	4·1	4·5
·20	6·9	6·3	6·8	—	5·7	—	4·9	4·6	3·9

Equivalents of acid neutralised *in the above experiments.*

Initial acidity Equivalents HNO_3 per litre	Amount of acid neutralised by soil after				
	0	0·33 hrs.	2 hrs.	9 hrs.	24 hrs.
·06	·0160	·0182	·0206	·0236	·0270
·08	·0156	·0196	·0224	·0252	·0286
·10	·0166	·0206	·0242	·0280	·0304
·12	·0174	·0216	·0244	·0304	·0330
·14	·0182	·0218	·0262	·0324	·0338
·16	·0182	·0232	·0276	·0326	·0352
·18	·0194	·0240	·0284	·0246	·0368
·20	·0196	·0252	·0288	·0356	·0376

Hoos 2 C (50 *gms. used per* 1000 *c.c. of acid but results calculated to* 100 *gms.*).

Initial acidity Equivalents HNO_3 per litre	Mgms. P_2O_5 per 100 grams of soil	Initial acidity Equivalents HNO_3 per litre	Mgms. P_2O_5 per 100 grams of soil
Time = 0·33 hours		Time = 4 hours	
·06	47·6	·14	59·2
·10	46·7	·18	64·1
·12	55·1	Time = 24 hours	
·14	55·6	·06	33·0
·18	59·2	·10	44·9
Time = 4 hours		·12	55·8
·06	35·8	·14	60·1
·10	56·2	·18	72·8
·12	54·0		

above the Time = 0 curve, and is approaching, and shows signs of soon crossing, the 2 hour curve. Sulphuric acid behaves in the same way, but the points of crossing occur at still lower concentrations; the 2 hour curve has already crossed the Time = 0 curve at concentrations lower than those we used, while the 24 hour curve crosses it just before N/10. At higher concentrations the 24 hour curve crosses the 2 hour curve, and at N/5 the longer the time of action the greater the amount of P_2O_5 extracted. Citric acid always gives this result at all of the times and concentrations used by us, but we have not tried extremely dilute acids.

In comparing the various acids, therefore, a steady gradation can be detected: nitric acid shows the remarkable falling off in net action, and therefore an increase in the reverse action with the time at all concentrations up to N/5 and apparently beyond; hydrochloric acid shows it nearly up to N/5; sulphuric acid only up to N/10; while citric acid either does not show it, or if it does, only at concentrations below N/20.

This marked difference in behaviour between citric and nitric acids is not due to any special decomposition effected by citric and not by nitric acid, for after the soil has been treated 24 hours with citric acid it behaves in the same way towards nitric acid.

A quanitty (300 gms.) of Agdell soil was extracted for 24 hours with N/10 citric acid. It was then divided into three lots: one was extracted with HNO_3 for half an hour; the second for 24 hours; the third with N/10 citric acid for 24 hours. The results were as follows:

1st extraction, N/10 citric acid 10.4 mgms. P_2O_5 per 100 gms. of soil		
2nd extraction		
N/10 HNO_3 Half-an-hour	N/10 HNO_3 24 hours	N/10 citric acid 24 hours
3.5	1.7	3.8 mgms. P_2O_5 per 100 gms. of soil

The half-hour treatment with nitric acid still brings out more P_2O_5 than the 24 hours' treatment.

The falling off in solvent action with the time is not peculiar to our soil. Surprisingly few out of the vast number of soil analyses bear on

the point: we have, however, found a paper by Lemmermann[1] in which similar results were obtained: dilute nitric acid dissolving out more P_2O_5 from the soil in $1\frac{1}{2}$ hours than in 72 hours.

His results are:

Soil from	Mgms. P_2O_5 dissolved per 100 gms. of soil in		Ratio $\frac{1\frac{1}{2} \text{ hrs.}}{72 \text{ hrs.}}$	Clay in soil * per cent.
	$1\frac{1}{2}$ hours	72 hours		
Dahlem	7·3	7·3	1·00	3·7
Boche.........	1·4	1·2	1·17	4·3
Prüfer	12·3	8·4	1·46	11·1
Marsch	8·4	5·0	1·68	18·1
Rettgau......	3·6	0·9	4·00	31·3

* Ascertained by J. A. Prescott in 1913.

The effect varies in the different soils. The Rettgau soil is very heavy, and the Dahlem soil very light. One of us ascertained the percentage of clay in the soils, and, it will be observed that the falling off of the solvent action with the time,—in other words the extent of the reverse reaction,—varies with the percentage of clay in the soil.

The effect of different dilute acids. The results given in the different parts of Table III are all comparable, and lead to the following conclusions:

Nitric acid shows the least net solvent effect, and the greatest reverse effect.

Hydrochloric shows more net solvent effect, and less of the reverse effect.

Sulphuric shows still more of the net solvent effect, and still less of the reverse effect.

Citric acid shows the most net solvent effect, and the least reverse effect, the acids being all in equivalent concentrations.

Beyond certain concentrations and times, however, sulphuric acid has a greater net solvent effect than citric acid.

The extent of the net reaction therefore varies inversely with that of the reverse reaction.

The nature of the reverse reaction. The reverse action by which P_2O_5 is removed from the solution is not a precipitation caused by a change in composition of the liquid. This was proved by adding the

[1] *Landw. Versuchs-Stat.* 1913, **83**, 357.

24 hour extract to the instantaneous nitric acid extract, which contained a high amount of P_2O_5; no precipitation occurred. That the soil and not the extract was responsible for the removal of the P_2O_5 was demonstrated by adding sodium phosphate to the mixture of soil and nitric acid; in spite of the excess of acid some of the added P_2O_5 was withdrawn from the solution by the soil (Table IV).

TABLE IV. *Amounts of P_2O_5 removed by soil from sodium and calcium phosphates in free $N/10$ nitric acid*

Mgms. of P_2O_5 added in Na_2HPO_4	Mgms. of P_2O_5 found in the nitric acid extract	Mgms. of added P_2O_5 recovered	Percentage of P_2O_5 recovered
0	2·9	—	—
6·6	6·7	3·8	57·0
22·0	18·3	15·4	69·6
49·6	39·2	36·2	73·1
66·2	51·8	48·9	73·8

	P_2O_5 added, mgms.	P_2O_5 recovered, mgms.	Percentage of P_2O_5 recovered
Soil + 0·1 gms. apatite	41·3	20·6	49·9
Soil + 0·1 gms. tricalcic phosphate	41·1	22·2	54·0
Soil + 0·1 gms. dicalcic phosphate	53·7	28·2	52·5

In all cases excess of acid remained at the end of the experiment.

In view of the excess of acid invariably present the removal of the P_2O_5 from the solution cannot be regarded as simple chemical precipitation.

There remained the possibility that the action might belong to the remarkable physical effects classed vaguely as absorptions in the older days, and now called by the more definite name of adsorptions.

It is well known that charcoal has the power of withdrawing certain dissolved substances from their solutions. There is no evidence of any chemical change in the ordinary sense of the term, and indeed the quantitative relationships are quite different from those of any ordinary reaction. A considerable amount of experimental work has shown that the quantity of substance adsorbed by a given amount of the adsorbent is not proportional to the actual amount present in the solution, but to some power of this quantity: so that if

$y =$ amount of substance adsorbed,

$c =$ concentration of the substance in the solution when equilibrium is reached,

$m =$ amount of adsorbent,

then $\dfrac{y}{m} = Kc^{\frac{1}{p}}$, where K and p are both constants.

This curve is parabolic: it becomes the ordinary parabola in the special case where $p = 2$.

This curve has been found to hold for the most diverse cases; for blood charcoal and various acids, chlorine, bromine, etc.; for wool and dyes; for filter paper and acids; and numerous others. It does not hold invariably, however, which indicates that there may be various types of adsorption, but it stands for the most usual type.

In applying this equation to the case in hand we are confronted with the difficulty of determining y,—the amount of P_2O_5 adsorbed. It is, of course, easy to find out what proportion of added P_2O_5 is adsorbed (as shown in Table IV) but this takes no account of the adsorption of the P_2O_5 given up by the soil to the solution.

Two methods were therefore adopted.

1. The extractable P_2O_5 was carefully removed from a sample of Agdell field soil by extracting it twice with $N/5$ H_2SO_4, and then seven times with 2 % caustic soda in the cold. The resulting material gives up no P_2O_5 when treated with dilute acids. It was shaken with a mixture of HCl ($0 \cdot 06$ N) and sodium phosphate for 24 hours at $23°$ C.

Direct analysis of the resulting solution gives c in the above equation: subtraction from the amount originally added gives y: there is here no complication from the amount initially present in the soil because all this was removed in the preliminary treatment. The results are given in Table V. When these values are substituted in the equation it is found that

$$K = 20 \cdot 2; \quad p = 2 \cdot 4 \text{ for the hydrochloric acid experiment}$$

and $\quad K = 8 \cdot 8; \quad p = 2 \cdot 1$ for the citric acid experiment.

Thus the two equations become

$$y = 20 \cdot 2\, C^{\frac{1}{2 \cdot 4}}$$

and $$y = 8 \cdot 8\, C^{\frac{1}{2 \cdot 1}} \text{ respectively.}$$

The curves are drawn on Fig. 3: it is clear that they fit the experimental points very well.

A simpler and more accurate method of checking the results and observing the agreement is to take out the logarithms of y and c.

If the equation is true:

$$\log y = \frac{1}{2\cdot 4} \log C + 1\cdot 3,$$

i.e.
$$\log y - \frac{1}{2\cdot 4} \log C = 1\cdot 3.$$

TABLE V. *Adsorption of P_2O_5 by soil,—Agdell B,—from which all phosphate has been removed by extraction with H_2SO_4 followed by NaOH (p. 94).*

Time 24 hours. *Temperature 23° C.*

50 gms. of soil to 1000 c.c. of solution.

Phosphoric acid alone.

P_2O_5 added (mgs. per 1000 c.c.)	19·6	24·7	29·6	34·5	39·5	44·4	49·3	54·3	69·1
P_2O_5 found in solution (C) (mgs. per 1000 c.c.)	3·7	5·6	8·4	12·0	15·5	17·8	21·4	25·9	36·6
P_2O_5 left in soil (y) (mgs. per 100 gms. of soil)	31·8	38·2	42·4	45·1	48·0	53·2	55·9	56·7	65·0

Equation obtained: $y = 21\cdot 2\, C^{\frac{1}{3\cdot 2}}$.

In presence of HCl ·06 N.

P_2O_5 added (mgs. per 1000 c.c.)	9·7	14·5	19·3	24·1	29·0	33·8	39·6	43·4
P_2O_5 found in solution (C) (mgs. per 1000 c.c.)	0·8	1·6	2·9	4·8	6·7	8·9	12·4	13·1
P_2O_5 left in soil (y) (mgs. per 100 gms. of soil)	17·8	25·8	32·8	38·7	44·5	49·9	54·4	60·7

Equation obtained: $y = 20\cdot 2\, C^{\frac{1}{2\cdot 4}}$.

In presence of Citric acid N/10.

P_2O_5 added (mgs. per 1000 c.c.)	9·7	14·5	19·3	24·1	29·0	33·8	38·6	43·7
P_2O_5 found in solution (C) (mgs. per 1000 c.c.)	2·9	5·0	7·1	10·3	13·6	16·4	20·2	23·6
P_2O_5 left in soil (y) (mgs. per 100 gms. of soil)	13·4	19·0	24·4	27·7	30·8	34·9	36·8	40·1

Equation obtained: $y = 8\cdot 8\, C^{\frac{1}{2\cdot 1}}$.

The amount of P_2O_5 left in the soil is calculated to mgms. per 100 gms. of soil so as to facilitate comparison with the other results. The amount of soil actually used was 50 gms.; the experimental values for y were therefore one half of the figures here given.

This is the equation of a straight line.   If, therefore, $\log y$ is plotted against $\log C$ all the points ought to lie on a line.   The figures show that they do so.

2.   Sodium phosphate was added but the soil was not subjected to any preliminary treatment; instead the amount of extractable P_2O_5 was determined.   This value *plus* the amount of added P_2O_5 gives the total $y + C$. C being determined by analysis, y is known by simple subtraction.

TABLE VI. P_2O_5 *contained in successive* 24 *hour periods of diffusion in* $N/10$ *HCl.   The results are calculated as a percentage of the soil.*

Soils	1	2	3	4	5	6–9	10–13
Hoos 1 O	→	→	→	→	·001	·003	·004
Hoos 2 C	·027	·0132	·0075	→	·0097	·0195	·0128
Agdell	·003	·0018	→	→	·0021	·0054	·0048
Teynham	·054	·0192	·0081	→	·0112	·0144	·0087
Saxmundham*	·0027	·0015	→	→	·0015	·0043	·003
„ †	·0045	·0021	→	→	·0013	·0060	·0043
Woburn	·0064	·0045	·0042	→	·0078	·0108	·0067

Soils	14–17	18–21	Total	HClsoluble ("Total")	Citric soluble ("available")
Hoos 1 O	trace	trace	·008	·101	·0053
Hoos 2 C	·0126	·009	·111	·255	·083
Agdell	·0048	·0030	·025	·110	·012
Teynham	·0067	·0042	·126	·172	·084
Saxmundham*	·002	·002	·017	·096	·009
„ †	·0043	·003	·026	·096	·014
Woburn	·0055	trace	·046	·159	·023

* Plot 6 (unmanured).   † Plot 4 (superphosphate).

In determining the total extractable P_2O_5 it is obviously necessary to eliminate the reverse reaction.   This is done by a diffusion process. The ordinary diffusion thimble is not satisfactory for soil, and no muslin is fine enough to hold it together and keep it out of the diffusion liquid.   The soil was therefore shaken with 2 % agar solution, and then cast into solid sticks by pouring into a glass tube of 10 mm. diameter and 100 mm. in length; these sticks can be placed in dilute acids, and they allow of rapid diffusion without disintegration.   In carrying out the experiment 5 to 10 gms. of soil and 30 c.c. of agar

are convenient quantities; this makes three sticks, which for better protection are put into a muslin bag; this is then suspended from a glass rod into a 250 c.c. bottle containing the acid. Twice in each 24 hours the liquid is changed, and the whole is evaporated to dryness.

The results given in Table VI show how the P_2O_5 comes out from the soil; the experiment was continued for 21 periods each of 24 hours. For comparison the "Total P_2O_5" (*i.e.* the amount soluble in boiling concentrated HCl) and the "available P_2O_5" (*i.e.* the amount soluble in 1 % citric acid) are also given.

In practice it is unnecessary to pour off more than 10 times for citric acid, or 20 times for hydrochloric or nitric acid. There is, of course, no need to make separate determinations: it is easier and more accurate to continue the evaporations in the same basins till the process has gone sufficiently far.

When the total extractable P_2O_5 has been determined the value is used as above for determining y, and the equation is then easily completed.

The results obtained with five different soils are given in Table VII, and plotted in Figs. 4 and 5. The logarithms of y are also plotted against those of c, giving straight lines, showing that the equation holds both for rich and for poor soils. In the rich Hoos $2C$ soil (Fig. 5) the experimental numbers all lie on the same side of the bend so that the curves cannot be verified as completely as we would like, but in the poorer soils there is no difficulty on this score (Fig. 4).

TABLE VII. *Values for y and C for different soils treated with $N/10$ or $N/5$ acid containing varying quantities of Na_2HPO_4.*

Agdell soil. Time $= 1$ hour. $N/10\ HNO_3$. Temperature 23° C.

100 gms. of soil to 1000 c.c. of solution.

P_2O_5 brought out by diffusion $= 0.025\ \% = 25$ mgms. per 100 gms. of soil.

P_2O_5 added (mgms. per 1000 c.c.)	0	5·7	11·4	17·1	22·9	28·6	34·3	45·7	57·2	68·6
P_2O_5 found in solution (C) (mgms. per 1000 cc.)	5·2	6·6	8·9	12·3	15·4	18·1	21·5	29·0	37·2	44·5
P_2O_5 left in soil (y) (mgms. per 100 gms.)	19·8	24·1	27·6	29·8	32·4	35·5	37·8	41·7	45·0	49·1

Equation obtained: $y = 11\cdot3\ C^{\frac{1}{2\cdot6}}$.

TABLE VII (*continued*).

Saxmundham.   Plot 6 (*unmanured*).

> *Time* = 2 *hours.*   *N*/10 HNO_3.   *Temperature* 23° *C.*

50 gms. of soil to 1000 c.c. of solution.

P_2O_5 brought out by diffusion = 17 mgms. per 100 gms. of soil.

P_2O_5 added (mgms. per 1000 c.c.)	0	6·6	11·0	16·6	22·1	27·6	38·6	49·7	55·2	66·2
P_2O_5 found in solution (*C*) (mgms. per 1000 c.c.) ...	2·9	6·7	9·8	14·1	18·3	20·8	29·5	39·2	42·6	51·8
P_2O_5 left in soil (*y*) (mgms. per 100 gms.)...............	10·9	17·2	19·9	22·3	25·0	31·1	35·6	38·4	42·6	46·2

Equation obtained: $y = 6 \cdot 3\, C^{\frac{1}{2 \cdot 0}}$.

Saxmundham.   Plot 4 (*superphosphate*).

> *Time* = 2 *hours.*   *N*/10 HNO_3.   *Temperature* 23° *C.*

50 gms. of soil to 1000 c.c. of solution.

P_2O_5 brought out by diffusion = 26 mgms. per 100 gms. of soil.

P_2O_5 added (mgms. per 1000 c.c.)	0	5·5	11·0	16·5	22·1	27·6	33·1	38·6	55·2	66·2
P_2O_5 found in solution (*C*) (mgms. per 1000 c.c.)......	5·6	9·7	13·6	17·3	22·0	27·1	31·6	37·2	51·8	61·1
P_2O_5 left in soil (*y*) (mgms. per 100 gms.)	14·8	17·6	20·9	24·5	26·0	27·5	29·1	28·9	32·7	36·3

Equation obtained: $y = 7 \cdot 9\, C^{\frac{1}{2 \cdot 7}}$.

Agdell soil.   *N*/10 HNO_3.   *Time* = 0.

100 gms. of soil to 1000 c.c. of solution.

P_2O_5 brought out by diffusion = 25 mgms. per 100 gms. of soil.

P_2O_5 added (mgms. per 1000 c.c.)	0	11·4	22·9	34·3	45·7
P_2O_5 found in solution (*C*) (mgms. per 1000 c.c.)......	5·0	12·7	19·1	27·4	36·1
P_2O_5 left in soil (*y*) (mgms. per 100 gms.)...............	20·0	23·8	28·8	31·9	34·7

Equation obtained: $y = 11 \cdot 5\, C^{\frac{1}{3 \cdot 1}}$.

TABLE VII (*continued*).

$N/10\ HNO_3$.   *Time* = 24 *hours.*

P₂O₅ added (mgms. per 1000 c.c.)	0	22·9	34·3	45·7
P_2O_5 added (mgms. per 1000 c.c.)	0	22·9	34·3	45·7
P_2O_5 found in solution (C) (mgms. per 1000 c.c.)......	3·6	7·0	11·2	13·7
P_2O_5 left in soil (y) (mgms. per 100 gms.)...............	21·4	40·9	48·1	57·0

Equation obtained : $y = 9 \cdot 4\, C^{\frac{1}{1 \cdot 5}}$.

Hoos 2C soil. $N/10\ HNO_3$.   *Time* = 1 *hour.*   *Temperature* 23° *C.*

50 gms. of soil to 1000 c.c. of solution.

P_2O_5 brought out by diffusion = 110 mgms. per 100 gms. of soil.

P_2O_5 added (mgms. per 1000 c.c.)	0	5·5	10·9	21·8	43·7	65·5
P_2O_5 found in solution (C) (mgms. per 1000 c.c.)......	29·6	34·3	38·3	47·6	66·5	84·1
P_2O_5 left in soil (y) (mgms. per 100 gms.)...............	50·7	52·4	54·7	58·4	62·7	70·8

Equation obtained : $y = 19 \cdot 7\, C^{\frac{1}{3 \cdot 6}}$.

Time = 24 *hours.* $N/10\ HNO_3$.

P_2O_5 added (mgms. per 1000 c.c.)	0	10·6	21·1	31·6	42·1
P_2O_5 found in solution (C) (mgms. per 1000 c.c.)......	26·8	33·3	42·2	48·4	57·0
P_2O_5 left in soil (y) (mgms. per 100 gms.)...............	56·4	64·7	67·8	76·6	80·3

Equation obtained : $y = 12 \cdot 0\, C^{\frac{1}{2 \cdot 1}}$.

Woburn wheat (unmanured).

Time = 1 *hour.* $N/10\ HNO_3$.   *Temperature* 23° *C.*

100 gms. of soil to 1000 c.c. of solution.

P_2O_5 brought out by diffusion = 39 mgms. per 100 gms. of soil.

P_2O_5 added (mgms. per 1000 c.c.)	0	0	5	11·0	16·6	22·1	33·1	44·2	55·2
P_2O_5 found in solution (C) (mgms. per 1000 c.c.) ...	2·7	3·2	6·2	8·8	12·6	16·1	23·6	32·8	40·3
P_2O_5 left in soil (y) (mgms. per 100 gms.)	36·3	35·8	38·3	41·2	43·0	45·0	48·5	50·4	53·9

Equation obtained : $y = 30 \cdot 7\, C^{\frac{1}{6 \cdot 2}}$.

TABLE VII (*continued*).

Bramford subsoil (extracted).*

Time = 1 *hour*. $N/10\ HNO_3$.   *Temperature* 23° *C*.

100 grms. of soil to 1000 c.c. of solution.

P_2O_5 by diffusion = 90·9 mgms. per 100 gms. of soil.
P_2O_5 removed   = 83·0 ,,   ,,   ,,   ,,
∴ P_2O_5 left in soil   = 7·9 ,,   ,,   ,,   ,,

P_2O_5 added (mgms. per 1000 c.c.)	0	5·5	10·9	16·4	21·9	27·3	32·8
P_2O_5 found in solution (C) (mgms. per 1000 c.c.) ...	3·5	7·4	11·7	16·5	21·0	25·2	30·6
P_2O_5 left in soil (y) (mgms. per 100 gms.)	4·4	5·9	7·1	7·8	8·8	10·0	10·1

Equation obtained: $y = 2\cdot7\,C^{\frac{1}{2\cdot6}}$.

* The Bramford soil contained so much P_2O_5 that it hardly showed the ordinary adsorption phenomena: instead therefore of working with the surface soil we used the subsoil, and treated it with $N/5\ HNO_3$ to remove part of the P_2O_5.

Time = 1 *hour*. Hoos 2 *C*. $N/5\ HNO_3$.

P_2O_5 added (mgms. per 1000 c.c.)	0	19·0	28·5	38·0
P_2O_5 found in solution (C) (mgms. per 1000 c.c.) ...	36·2	55·0	63·7	72·6
P_2O_5 left in soil (y) (mgms. per 100 gms.)	37·6	37·9	39·5	40·8

Equation obtained: $y = 18\cdot7\,C^{\frac{1}{5\cdot7}}$.

Time = 24 *hours*. $N/5\ HNO_3$.

P_2O_5 added (mgms. per 1000 c.c.)	0	9·5	19·0	28·5	38·0
P_2O_5 found in solution (C) (mgms. per 1000 c.c.) ...	39·4	48·1	57·1	66·4	73·8
P_2O_5 left in soil (y) (mgms. per 100 gms.)	31·1	32·7	33·7	36·1	38·4

Equation obtained: $y = 10\cdot4\,C^{\frac{1}{3\cdot4}}$.

TABLE VII (continued)

Time = 1 *hour.*   *N*/10 *citric acid.*

P$_2$O$_5$ added (mgms. per 1000 c.c.)	0	10·5	21·0	31·5	42·0
P$_2$O$_5$ found in solution (C) (mgms. per 1000 c.c.) ...	36·1	46·7	55·0	65·8	75·6
P$_2$O$_5$ left in soil (y) (mgms. per 100 gms.)	37·8	37·8	42·1	41·5	44·7

Equation obtained: $y = 13 \cdot 4\, C^{\frac{1}{3 \cdot 6}}$.

Time = 24 *hours.*   *N*/10 *citric acid.*

P$_2$O$_5$ added (mgms. per 1000 c.c.)	0	10·5	21·0	31·5	42·0
P$_2$O$_5$ found in solution (C) (mgms. per 1000 c.c.) ...	43·4	52·4	62·2	71·1	81·3
P$_2$O$_5$ left in soil (y) (mgms. per 100 gms.)	23·2	26·1	27·5	30·8	31·3

Equation obtained: $y = 4 \cdot 1\, C^{\frac{1}{2 \cdot 2}}$.

It is thus clear that the reverse reaction, *i.e.* the removal of the P$_2$O$_5$ from the solution by the soil is an ordinary adsorption, and conforms to the general law expressed by the equation already given.

Turning now to the direct reaction, this must obviously be studied by eliminating the reverse reaction, which as we have seen can be done by the diffusion method. The results for citric, nitric and hydrochloric acids are given in Table VIII and are remarkably alike: considerably more so than when the experiment is carried out by the usual extraction method. Sulphuric acid, however, brings out more P$_2$O$_5$ than any of these.

Reference to Table III and Fig. 3 shows that the *net* solvent action of these three acids is very different, citric acid dissolving most, hydrochloric acid next, and nitric acid least.

It follows, therefore, that the reverse reaction, *i.e.* the adsorption of P$_2$O$_5$ from the solution is greatest in presence of nitric acid, next of hydrochloric, and least in presence of citric acid.

TABLE VIII. *Quantities of P_2O_5 brought out by diffusion, in comparison with the amounts brought out by ordinary extraction methods. Results calculated as percentage of the soil.*

Soil, Hoos 2C.

	N/10 citric acid	N/10 HNO$_3$	N/10 HCl	N/10 H$_2$SO$_4$	N/10 ammonium citrate
Diffusion	·109	·108	·111	·146	—
Ordinary extraction, 24 hrs.	·084	·054	·045	·077	—

Soil, Agdell.

	N/10 citric acid	N/10 HNO$_3$	N/10 HCl	N/10 H$_2$SO$_4$	N/10 ammonium citrate
Diffusion	·031	—	·032	—	·031
Ordinary extraction, 24 hrs.	·0104	—	·0017	—	·013

Soil, Woburn Stackyard Field, unmanured wheat.

	N/10 citric acid	N/10 HNO$_3$	N/10 H$_2$SO$_4$
Diffusion	·041	·037	·048
Ordinary extraction	·013	·004	·016

The striking result brought out by this experiment is that *the direct solvent action of dilute citric, hydrochloric, and nitric acids on the soil phosphates is the same for all three acids.*

The characteristics of the adsorption.

The fixation of P_2O_5 in soil has been variously attributed to calcium carbonate, to oxides of iron or aluminium, or to humus. None of these, however, is the potent agent in the soils used in our experiments. The fact that adsorption goes on in the presence of acids rules out the carbonates and oxides: the Agdell *B* experiments (Table V, Fig. 3) rule out soluble humus, because this material has already been removed. Subsoils show the phenomena just as freely as surface soils. Moreover extraction of the soil with toluene has no measurable effect on its adsorbing powers; nor does heating the soil till it is charred cause

them to go entirely: not till the soil is ignited is the property lost altogether, and the whole of the added P_2O_5 recovered:

	Ignited soil		Charred soil
	Agdell Surface	Rothamsted Deep subsoil	Rothamsted Garden soil
P_2O_5 obtainable from soil, mgms....	12·2	7·4	83·7
P_2O_5 added, mgms.	10·0	10·0	10·0
Total..............	22·2	17·4	93·7
P_2O_5 found by HNO_3 extraction ...	22·3	16·1	86·6
P_2O_5 adsorbed, mgms....................	Nil	1·3	7·1 mgms. P_2O_5
Percentage	Nil	12·8	71 per 100 gms. of soil

The acids adsorbed. Although we have confined ourselves hitherto to P_2O_5 we have evidence that the phenomena are general and that other acids are adsorbed in the same manner, though in varying degrees. Thus oxalic acid is adsorbed in the presence of nitric acid, giving a curve of exactly the same nature as that for phosphoric acid. (See p. 124.)

Citric acid is also adsorbed but the analytical difficulties proved so considerable that we have been unable to obtain sufficiently reliable results to allow of the drawing of a curve.

On the other hand, we could find no evidence that either hydrochloric or nitric acid is adsorbed to any notable extent.

Thus, it appears that the acids most diminishing the adsorption of phosphoric acid, viz. citric and oxalic acids, are themselves freely adsorbed: while the acids which do not so greatly diminish the adsorption, viz. hydrochloric and nitric acids are not adsorbed.

We have examined various possibilities, but the simplest and most in accordance with the facts is that citric and oxalic acids satisfy the adsorption capacity of the soil better than P_2O_5 and thus displace some of it into the solution, while dilute hydrochloric and nitric acids will not, so that much of the P_2O_5 still remains adsorbed. We therefore enquired whether the addition to nitric or hydrochloric acids of substances known to be adsorbed by the soil would increase the net solvent action of these acids by displacing the adsorbed P_2O_5. The results of numerous trials are recorded in Table IX. None of them was successful.

TABLE IX. *Effect of added substances on the reaction between dilute acids and soil phosphorus compounds.*

P_2O_5 extracted in mgms. per 100 gms. of soil.

I. Organic substances: phenol, o-cresol, and pyrogallic acid.

Soil, Hoos 2C. Time = 0.

N/10 HNO_3 alone	N/10 HNO_3 + N/10 phenol	N/10 HNO_3 + N/10 cresol	N/10 HNO_3 + N/100 cresol	N/10 phenol alone	N/10 cresol
57	49	57	49	15	8·4

Soil, Hoos 2C. Time = 5½ hours.

N/10 HCl alone	N/10 HCl + N/10 phenol	N/10 HCl + N/100 phenol	N/10 phenol alone	N/100 phenol alone
63	55	54	8	9·6

Soil, Hoos 2C. Time = 0.

N/10 HCl alone	N/10 HCl + N/10 pyrogallic acid	N/10 HCl + N/100 pyrogallic acid	N/10 pyrogallic acid alone	N/100 pyrogallic acid alone	Distilled water
48	51·	48	17	10	7

II. Inorganic substances: potash-alum, Al_2O_3.

Soil, Hoos 2C. Time = 1 hour.

N/10 HNO_3 alone	N/10 HNO_3 + potash-alum (0·66 gms. Al_2O_3)	N/10 HNO_3 + Al_2O_3 (0·29 gms.)
50	78	26·2

Soil, Agdell. Time = 1 hour.

N/10 HNO_3 alone	N/10 HNO_3 + potash-alum (0·66 gms. Al_2O_3)	N/10 HNO_3 + Al_2O_3 (0·29 gms.)	N/10 HNO_3 + Al_2O_3 (0·58 gms.)	N/10 citric acid alone	N/10 citric acid + Al_2O_3 (0·29 gms.)
4·32	11·3	2·28	2·82	7·68	3·42

1000 c.c. N/10 HNO_3, the quantity used in the experiments, is equivalent to 1·7 gms. of Al_2O_3. The extracts made with N/10 HNO_3 and Al_2O_3 were very turbid.

TABLE IX (continued)

Soil, Agdell. Time = 3 hours.

N/10 HNO₃ alone	N/10 HNO₃ + 10 c.c. toluene	N/10 HNO₃ + NH₄NO₃*	N/10 HNO₃ + ammonium oxalate	N/10 ammonium oxalate alone	N/10 oxalic acid alone
7·7	6·7	8·2	24·7	7·9	29·8

N/10 HNO₃ + N/10 amm. citrate	N/10 ammonium citrate alone	N/10 citric acid alone	N/10 HNO₃ + N/10 NaF	N/10 NaF alone	N/5 HNO₃ alone	N/5 HNO₃ + 10 cc. toluene
9·6	11·5	10·4	11·0	7·1	9·4	8·2

* Sufficient to make the – NO₃ radicle up to N concentration.

Phenol, cresol, toluene and alumina, so far from increasing, actually reduce the amount of P_2O_5 brought out by nitric acid, and therefore check the direct solvent action or increase the adsorption. The following experiment shows that the adsorption is increased. 50 gms. of the soil Agdell A, which had been extracted with dilute sulphuric acid to remove most of the soluble phosphate, was treated with 1 litre of dilute HCl (·06 N) containing 25 % of ethyl alcohol, and a known amount of sodium phosphate was added. The following amounts of P_2O_5 were found: they are calculated as mgms. per 100 gms. of soil:

P_2O_5 added to solution	P_2O_5 found	P_2O_5 adsorbed
9·7	4·2	2·5 without alcohol
9·7	2·5	7·2 with alcohol

All substances do not behave like this however: Table X shows that pyrogallic acid is without effect, and that potash-alum and ammonium oxalate considerably increase the solvent action. These latter substances, however, give rise to sulphuric acid and oxalic acid respectively, both of which have greater net solvent power than nitric acid. In reducing the adsorption of P_2O_5 it is obvious that our only hope would be to light on something which is adsorbed in preference to P_2O_5, and for the moment we have nothing but chance to guide us in the search.

The change of adsorption with the time.

Reverting to Figs. 4 and 5, it is clear that adsorption in presence of nitric acid becomes more pronounced as the length of the action proceeds. Three times were studied: Time = 0, 1 hour, and 24 hours. The adsorption successively increases, and has become very marked after 24 hours.
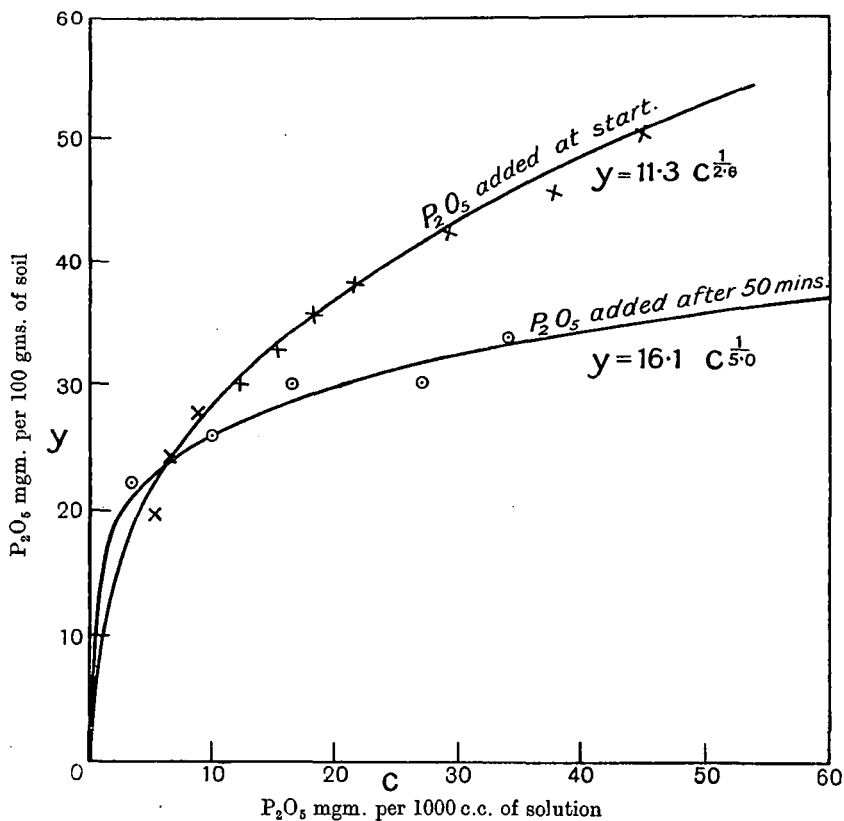
Agdell Soil.

Fig. 9. Effect of composition of the solution on adsorption phenomena.

The first explanation that occurs is that adsorption is a slow business and takes a long while to complete itself. Some support is given to this view by the following experiment:

One lot of soil was shaken for an hour with N/10 nitric acid and sodium phosphate in the usual way. Another lot was shaken with the acid for only 50 minutes, then the phosphate was added and the

shaking done for 10 minutes so as to complete the hour. The adsorption curves were quite different (Fig. 9).

P$_2$O$_5$ added, mgms.	0	10·50	21·00	31·50	42·00
P$_2$O$_5$ found in 1000 c.c. solution (C), mgms.	3·2	10·0	16·6	26·8	35·5
P$_2$O$_5$ left in 100 gms. soil (y), mgms.	21·8	25·5	29·4	29·7	33·5˙

Equation obtained: $y = 16 \cdot 1\, C^{\frac{1}{5 \cdot 0}}$.

This compares with the experiment recorded in Table VI, Fig. 4a, where the equation obtained is

$$y = 11 \cdot 3\, C^{\frac{1}{2 \cdot 6}}.$$

The experiment is not wholly free from criticism because we do not know exactly what other changes are produced by the acid, or how they are affected by the presence of the phosphate. Against the view that equilibrium is only slowly attained there seems to us to be an insuperable objection. The close agreement between the experimental and the calculated curves shows that a definite equilibrium is attained at each time. The Time $= 0$ curve, for example, indicates just as typical an adsorption as the 24 hour curve. Each adsorption is different, but each is complete in itself. We assume, therefore, until we have stronger evidence to the contrary, that equilibrium is attained instantaneously. This is also true of other cases, animal charcoal, etc.

The next possibility is that the adsorptive capacity of the soil may have increased in consequence of the action of the acid. Considerable change does take place: e.g. quantities of silica are dissolved, and it is possible that the total result of the action may be to increase the adsorptive capacity of the soil. Direct experiment, however, does not support this view. Some of the Agdell soil was treated for 24 hours with N/10 HNO$_3$, then filtered off, washed and dried. It was then treated for Time $= 0$ with HNO$_3$; and varying quantities of sodium phosphate. The results are as follows:

	Without preliminary treatment				
P$_2$O$_5$ added, mgms.	0	11·4	22·9	34·3	45·7
P$_2$O$_5$ found in solution (C), mgms.	5·0	12·7	19·1	27·4	36·1
P$_2$O$_5$ left in soil (y), mgms.	20·0	23·8	28·8	31·9	34·7

Equation obtained: $y = 11 \cdot 5\, C^{\frac{1}{3 \cdot 1}}$.

	After 24 hours' treatment with N/10 HNO$_3$				
P$_2$O$_5$ added, mgms.	0	11·4	22·9	34·3	45·7
P$_2$O$_5$ found in solution (C), mgms.	3·1	10·9	17·2	26·5	34·6
P$_2$O$_5$ left in soil (y), mgms......................	18·3	21·9	27·1	.29·2	32·2

Equation obtained: $y = 11 \cdot 5\, C^{\frac{1}{3 \cdot 1}}$.

TABLE X. *Effect of alteration of composition of extraction liquid on the adsorption equilibrium in soils.* Hoos 2C.

I. 50·2 gms. of soil treated with 1000 c.c. of an extract obtained by treating soil with N/10 HNO$_3$ for 24 hours and filtering off. 4 c.c. of phosphate solution was also added. Time = 0.

In extract after 24 hours there were 22·08 mgms. P$_2$O$_5$ per litre.

In soil there were 110 mgms. per 100 gms.

Acidity of original acid = 0·0956 equivs. HNO$_3$ per litre.

,, 24 hours' extract = 0·0760 ,, ,, ,,

,, final extract = 0·0660 ,, ,, ,,

P$_2$O$_5$ added	0	11·2	33·5	44·6
P$_2$O$_5$ in solution (1000 c.c.) (C) ...	31·4	41·9	60·2	67·1
P$_2$O$_5$ in soil (100 gms.) (y)	91·3	92·5	100·5	108·6

Equation is $y = 44 \cdot 1\, C^{\frac{1}{4 \cdot 9}}$.

II. Fresh acid. 50 gms. of soil to 1000 c.c. of 0·076 N HNO$_3$. Time = 0. In soil 110 mgms. P$_2$O$_5$ per 100 gms.

P$_2$O$_5$ added	0	5·5	16·4	21·8	27·3
P$_2$O$_5$ in solution (1000 c.c.) (C) ...	23·6	27·1	36·4	41·3	45·6
P$_2$O$_5$ in soil (100 gms.) (y)	62·7	66·7	69·9	71·0	73·4

Equation is $y = 34 \cdot 5\, C^{\frac{1}{5 \cdot 1}}$.

III. Fresh acid. 50 gms. soil to 1000 c.c. N/10 HNO$_3$. In soil 110 mgms. P$_2$O$_5$ per 100 gms.

P$_2$O$_5$ added	0	11·2	22·3	33·5	55·8
P$_2$O$_5$ in solution (1000 c.c.) (C) ...	19·9	29·4	39·9	49·5	70·0
P$_2$O$_5$ in soil (100 gms.) (y)	70·2	73·5	74·8	78·0	81·6

Equation is $y = 50 \cdot 7\, C^{\frac{1}{8 \cdot 6}}$.

These are plotted in Fig. 6, and the two curves superpose. The 24 hours' treatment then, much as it altered the soil, did not alter its adsorptive capacity.

There remains the possibility that the solution obtained at the end of 24 hours affects the equilibrium differently from that obtained after Time = 0. There is considerable à priori justification for such a view, inasmuch as the addition of alumina to the nitric acid depresses the amount of P_2O_5 extracted, and may therefore very well increase the amount of adsorption.

This was tested by treating two lots of the same soil (a) with N/10 HNO_3 that had already been in contact with the soil for 24 hours, and (b) with fresh HNO_3 of equivalent concentration. If the cause of the difference of adsorption lay in the changed condition of the liquid then adsorption from the 24 hours' liquid should be greater than that from the fresh acid.

Experiment showed that this actually happened. The curve obtained with fresh acid lay below that obtained with the 24 hours' extract, the two being related in the same way as those for Time = 0 and for Time = 24 hours (Table X, Fig. 7).

CONCLUSIONS.

The results enable us to explain what happens when a soil is shaken with a dilute acid in the ordinary process of soil analysis.

The acid dissolves out such phosphorus compounds as it can, and different acids have much the same effect at equivalent concentrations: nitric, hydrochloric and citric acids give the same results; sulphuric acid, however, gives a somewhat higher result.

A reverse reaction at once sets in, however. Some of the P_2O_5 is withdrawn from the solution in spite of the presence of excess of acid. The process is an ordinary adsorption and obeys the usual law expressed by the equation $y = Kc^{\frac{1}{p}}$. Its extent varies with the different acids; it is much more marked in the presence of nitric than of citric acid.

The amount of P_2O_5 actually determined by the analyst is, therefore, not the true amount dissolved, but the difference between these two wholly distinct actions.

It is now obvious why the amounts of "available P_2O_5" determined by extraction with dilute acids shows such great variations in different methods of analysis, and so little correlation with the actual quantities

obtainable by the crop. In no case do they stand for anything actual, but only for a difference between a direct action and an adsorption which varies with the nature of the acid and the conditions of the experiment.

So long as they are confined to the same type of soil, however, any of the acids investigated would have given useful results, but difficulties would arise directly an attempt was made to compare dissimilar soils. The proper way to use a soil analysis is in conjunction with a soil survey.

A diffusion method is described in which the reverse reaction is eliminated, and which therefore gives a true measure of the direct action. But until we have had more experience with it we are not prepared to say what value it has for soil analysis.