

# THE PHENOMENON OF ABSORPTION IN ITS RELATION TO SOILS.

A RÉSUMÉ OF THE SUBJECT.

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## *The facts of Absorption.*

It has been known from the earliest times that soils would remove salts and colouring matters from solution and the problems arising out of the observations made on this phenomenon were among the earliest to be attacked by agricultural chemists. It was known to Aristotle that sea water lost some of its taste by filtration through sand and this observation seems to have been confirmed and applied in many ways. Lord Bacon in his *Sylva Sylvarum*<sup>1</sup> discussed the question of making sea water potable by filtering through sand. Le Comte de Marsilli<sup>2</sup> made quantitative experiments. Sea water was filtered through fifteen successive vessels of garden soil and a diminution in the salt content was proved by evaporation and by the change in specific gravity. Similar results were obtained with sand. Boyle Godfrey<sup>3</sup> discussed the question of making sea water fit for use on ships and observed that if sea water be put into a stone straining cistern the first pint that runs through will be like pure water, having no taste of salt, but the next pint will be as salt as usual. Stephen Hales<sup>4</sup> in dealing with the same question refers to the use of a soft stone by the Dutch as a filtering material, but he points out that this method has no practical value as only the first portions of the filtrate are free from salt.

<sup>1</sup> §§ 1 and 882.

<sup>2</sup> *Histoire physique de la Mer*, 1725

<sup>3</sup> *Miscellaneous Experiments and Observations*, 1737.

<sup>4</sup> *Philosophical Experiments*, 1739.

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A more definitely agricultural observation was made by Gazzeri<sup>1</sup> who observed that soil and especially clay take up soluble substances which he considered an advantage inasmuch as they may become available later as the plants need them.

Lambruschini<sup>2</sup> suggests a special kind of combination (*incorporamento*) between plant nutrients and soil which was neither so weak as to allow them to be washed out nor yet so strong as to interfere with their absorption by the plant.

J. P. Bronner<sup>3</sup> observed that when river sand was shaken in a bottle with liquid manure both the smell and the colour were largely removed. This was confirmed independently by Huxtable in 1848. Liquid manure filtered through a loamy soil lost smell and colour<sup>4</sup>, "it went in manure and came out water."

The first quantitative experiments were made by H. S. Thompson in 1845<sup>5</sup>. Soils were mixed with a solution of ammonium sulphate and washed through with water. Analysis showed that considerable quantities of ammonia had disappeared from the solution while calcium and magnesium sulphates were present. The sulphuric acid radical was not absorbed.

### *Way's chemical hypothesis.*

J. T. Way followed up this work<sup>6</sup> and extended it to other bases: he showed that ammonia was absorbed from all its salts, so also were potassium, sodium and magnesium from their salts. Lime was also found to be absorbed from caustic lime and from bicarbonate solutions, but other salts were not tried because Way assumed that it was useless, there being no provision in the soil for the decomposition that would be first necessary. Burning a soil was found to diminish the absorption by about one-half and thoroughly ignited clays showed no absorption whatever. Absorption both of ammonia and potash increased with the strength of the solution but not proportionately. Way supposed the phenomena to be chemical. Matteucci<sup>7</sup> had already explained the absorption of salts by sand by assuming that the particles of sand have a greater attraction for salts than they have for water,

<sup>1</sup> 1819 *Text Book of Manuring*, quoted by A. Orth, *Landw. Versuchs-Stat.* 1873, 16, 56.

<sup>2</sup> *Atti dei Georgofili di Firenze.* 1830, 9, 330, quoted by F. Sestini, *Landw. Versuchs-Stat.* 1873, 16, 409.

<sup>3</sup> *Der Weinbau in Süddeutschland*, 1836.

<sup>4</sup> Quoted by Way.

<sup>5</sup> *Journ. Roy. Ag. Soc.* 1850, 11, 68.

<sup>6</sup> *Ibid.* 313.

<sup>7</sup> *Sur les phénomènes physiques des corps vivants*, 1847.

absorption being thus a manifestation of capillarity. Way pointed out that this physical action deals with the salt as a whole; in the type of soil absorption with which he was working, bases only were affected. This pointed to a chemical action. Again, while physically absorbed substances could be washed out with water, the chemically absorbed substances were completely insoluble.

In a following paper<sup>1</sup> Way develops the idea of absorption by precipitation of insoluble compounds in the soil. He assumed the presence in the soil of a small proportion of double silicates of lime and aluminium which by reaction with salts of ammonia or potassium gave rise to insoluble ammonium or potassium aluminium silicates and the corresponding calcium salts. He prepared double silicates by mixing solutions of alum and sodium silicate—a double silicate of sodium and aluminium was precipitated which by treatment with excess of calcium chloride gave the corresponding calcium compound.

The behaviour of this calcium compound towards salts was in every respect similar to that of soils and Way had “every certainty” that these double decompositions were “the efficient cause of the singular power.”

These experiments were subsequently confirmed by A. Voelcker<sup>2</sup> who attributed the beneficial effect of common salt as a manure to its action in setting free potassium from its combinations in the soil<sup>3</sup>.

R. Warington<sup>4</sup> also held that the phenomenon was to be explained on chemical grounds. He found that precipitates of aluminium and iron hydroxides were also efficient absorbents for both phosphates and bases; this he explained as due to the weak chemical affinity. He supposed that to these oxides was due at least to some extent the peculiar properties of soils, but he did not deny the possibility of the presence of Way's double silicates.

### *Liebig's physical hypothesis.*

J. v. Liebig<sup>5</sup> criticised Way's hypothesis. He compared the action of the soil with that of wood or animal charcoal, and regarded the attraction of soil for salts as being of a purely physical nature. He divided plant food constituents into two classes, one chemically and the other

<sup>1</sup> *Journ. Roy. Ag. Soc.* 1852, **13**, 123

<sup>2</sup> *Ibid.* 1860, **21**, 105; 1864, **25**, 333.

<sup>3</sup> *Ibid.* 1865, **26**, 298.

<sup>4</sup> *Trans. Chem. Soc.* 1868, **21**, 1.

<sup>5</sup> *Ann. Chem. Pharm.* 1853, **105**, 109; **106**, 185.

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physically combined in the soil, considering the latter only to be that immediately available to plants. "The power of the soil to nourish cultivated plants," he states, "is therefore in exact proportion to the quantity of nutritive substances which it contains in a state of physical saturation. The quantity of other elements in a state of chemical combination distributed through the ground is also highly important, as serving to restore the state of saturation, when the nutritive substances in physical combination have been withdrawn from the soil by a series of crops reaped from it<sup>1</sup>." "

### *Knop's compromise and analytical method.*

W. Knop<sup>2</sup> in reviewing the subject attempted to combine Way's chemical and Liebig's physical hypotheses. He explains the removal of bases from solution by surface attraction and by combination with silica or double aluminium silicates. The absorption of phosphates he attributed to the precipitation of calcium phosphates in the first instance and afterwards to the formation of iron and aluminium phosphates. Other acids were said to be held up also by iron and aluminium hydroxides with the formation of basic salts. Knop recognised that the chemical explanation was insufficient to account for the absorption of the bases, because an equilibrium was invariably established between the soil and the solution and the whole of the base could not be removed from its solution no matter how dilute this might be.

The chief facts concerning absorption by soils were accumulated by about 1880. Since then very little has been added except on the theoretical side. W. Henneberg and F. Stohmann<sup>3</sup> treated soils with different ammonium salts in varying amounts, and Peters<sup>4</sup> worked with potassium salts. Both obtained the same results as Way: as the concentration of the salt was increased the amount of base taken up by the soil increased also but was in lower proportion; *i.e.* the relative amount taken up decreased with the increase in concentration of the solution. A vast amount of subsequent work has shown that this is true of all absorption phenomena and the relationship has more recently been expressed mathematically. Two methods of investigation have been used: (1) the soil is brought into equilibrium with a definite

<sup>1</sup> *Natural Laws of Husbandry*, 1863, pp. 67-69.

<sup>2</sup> *Lehrbuch der Agriculturchemie*, Leipzig, 1868.

<sup>3</sup> *Journ. f. Landw.* 1859, 3, 25.

<sup>4</sup> *Landw. Versuchs-Stat.* 1860, 2, 113.

volume of solution, and (2) a solution is filtered through a column of soil. The first is by far the more accurate although there are occasions when the second is useful.

The effect of bringing a soil into equilibrium with a solution of potassium or ammonium salts is that some of the potassium or ammonium disappears from the solution, and other bases, chiefly calcium and magnesium, come in, which together are approximately equivalent to the potassium or ammonium absorbed. This was discovered by Way and has since been abundantly confirmed. E. G. Parker<sup>1</sup> states that the total quantities of Ca, Mg and Al in a solution of potassium chloride after treatment with a soil were not quite equivalent to the amount of potassium absorbed but that the difference was practically equivalent to the amount of free acid present in the solution.

The effect of the presence of other salts on the absorption of any particular base was studied by A. Frank<sup>2</sup>. A solution of potassium chloride was caused to percolate through a column of soil, the effluent was drawn off at various depths and the amount of potassium absorbed was determined. Sodium chloride was then added to the potassium chloride solution and a fresh percolation carried through; it was found that the presence of sodium salt lowered the absorption of the potassium which was consequently found in high concentrations even in the lower parts of the soil column.

The absorbed potassium or ammonium was found to be partially removed by a solution of a calcium salt but none of the early workers were able to obtain complete replacement<sup>3</sup>.

As pointed out above, Liebig considered that the absorbed bases of a soil were those immediately available to the plant. W. Knop<sup>4</sup> devised a method for determining the available plant food based on this assumption. He put the matter thus: "Soils of great fertility have a high absorptive power": "Soils of great fertility have a high content of easily replaceable bases" and on this account should show high absorption towards salt solutions. He therefore compared a series of 100 soils by determining the absorption of ammonia from a 0.5 % solution of ammonium chloride. The results obtained were in fair agreement with the agricultural history of the soils.

<sup>1</sup> *Journ. Agric. Research*, 1913, 1, 179.

<sup>2</sup> *Landw. Versuchs-Stat.* 1866, 8, 45.

<sup>3</sup> Way, Eichhorn, Dietrich, Peters, Schuhmacher. References are given elsewhere.

<sup>4</sup> *Bonitürung der Ackererde*, 1871.

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E. Biedermann<sup>1</sup> made a further comparison with 23 soils from various parts of Saxony and also obtained results in fair agreement with the assumption—exceptions were noted chiefly where the absorbed ammonia was replaced almost entirely by magnesium, the soils being then somewhat infertile. O. Kellner<sup>2</sup> varied the procedure somewhat, and determined the amount of available bases by boiling the soil with successive quantities of ammonium chloride solution. He states that the amounts of potassium and calcium thus removed are precisely equal to the quantities obtainable by plants. This he showed by the following experiment.

Twenty-two pea plants were grown for six weeks in 369.15 gms. of soil placed in a funnel plugged with asbestos and watered with a diluted solution of ammonium nitrate, 1 gm. of which was supplied during the whole period. The soil was analysed for available plant food by the above method. The amount of food material in the plants was also determined. The results are as follows:

	K <sub>2</sub> O	CaO		K <sub>2</sub> O	CaO
	gm.	gm.		gm.	gm.
Found in plants .....	0.1041	0.0417	In original soil.....	0.2208	1.1235
Originally in seed .....	0.0449	0.0060	After experiment.....	0.1612	1.0887
Removed from soil .....	0.0592	0.0357	Difference.....	0.0596	0.0348

This rather remarkable statement does not seem to have been since confirmed in spite of its obvious importance.

Recently E. Ramann has introduced a further modification: a 5% ammonium nitrate solution is allowed to percolate through the soil and the displaced potassium or other plant food is determined. He speaks of this as a "Base exchange" (*Basenaustausch*)<sup>3</sup>. A similar "Base exchange" was obtained by O. Kullenberg<sup>4</sup> with calcium, magnesium and sodium salts. Using these in various concentrations the final equilibrium resembles those already attained by Peters with potassium and Henneberg and Stohmann with ammonium salts.

<sup>1</sup> *Landw. Versuchs-Stat.* 1869, **11**, 1; 1872, **15**, 21.

<sup>2</sup> *Ibid.* 1886, **33**, 349 and 359.

<sup>3</sup> J. A. Hanley, *Nature*, 1914, **93**, 598. International Commission on the Chemical Analysis of Soils.

<sup>4</sup> *Jahresb. Agric. Chemie*, 1865, **8**, 15.

*Absorption of acid radicals.*

The absorption of acid radicals has not been much discussed, chiefly because the early workers invariably found as much Cl, SO<sub>4</sub>, or NO<sub>3</sub> in all their solutions after as before treatment with a soil. In the case of phosphoric acid the problem has been automatically removed from the discussion because most soils contain sufficient lime to precipitate soluble phosphates chemically. The soil phosphates have therefore been divided up into available or unavailable classes according to their solubility. Recent work however has shown that phosphoric acid can be physically absorbed by a soil in the presence of excess of acids like citric, nitric or hydrochloric acid. This absorption is discussed elsewhere<sup>1</sup>. The absorption of oxalic and citric acids (see p. 124) has been observed by the author to take place in the presence of nitric or hydrochloric acids. U. Pratolongo<sup>2</sup> has shown that there may be two distinct processes—with soils containing no lime, absorption of phosphoric acid from monocalcium phosphate solution is practically instantaneous, with a soil containing much calcium carbonate there is a further slow fixation of phosphoric acid after the initial absorption. The immediate process is regarded as an absorption, the second as precipitation. His results are as follows:

Time	Soil containing no lime	Soil containing 10·3 % of lime
5 mins.....	307 mgms.	774 mgms.
30 „ .....	315 „	903 „
1 hour .....	312 „	1101 „
6 hours.....	315 „	1774 „

The absorption of other acid radicals has not yet been observed in the case of soils.

*Effect of Temperature.*

Small changes in temperature seem to be without appreciable effect on absorption, but W. Schuhmacher<sup>3</sup> found that at high temperatures the absorption was usually less than at low temperatures.

<sup>1</sup> See *Proc. Chem. Soc.* 1914, 30, 123, and this *Journal*, p. 65

<sup>2</sup> *Le Stazioni Sperimentali Agrarie*, 1915, 48, 457.

<sup>3</sup> *Ann. der Landw.* 1867, 49, 322.

*Absorption by Humus.*

The part played by humus in the absorption processes in the soil has not been very fully worked out. J. M. Van Bemmelen<sup>1</sup> showed that humus is a typical colloid possessing absorbing powers similar to those of the gels.

A solution of humus in ammonia is precipitated by the addition of salts of metals such as copper, lead, calcium, magnesium—these so-called humates have been and still are in many quarters assumed to be true insoluble salts. Van Bemmelen showed that their composition was very variable and hence defined them as absorption complexes:

A. König<sup>2</sup> showed that a sphagnum moor soil consisting almost entirely of organic matter absorbed potassium from its salts with substitution of calcium and magnesium. Humus shows its greatest absorptive power with alkalis; its power of taking up ammonia is well known and is shown by the insoluble portion as well as by that soluble in alkalis. Peat which is almost entirely free from calcium and other bases still absorbs phosphoric acid. It also absorbs neutral salts as a whole. König also obtained negative absorption, *i.e.* the absorption of water instead of dissolved salt from the solution. A peat in contact with N/10 KCl solution absorbed water alone and left the solution more concentrated than before.

When an alkaline solution of humus is precipitated it carries down with it some of the substances present in the solution. W. Schuhmacher<sup>3</sup> using "humus" obtained by the action of sulphuric acid on sugar found an absorption of from 1.7 to 10 % from solutions of 0.5 % of sodium phosphate, potassium nitrate and calcium chloride. Humus is a very difficult substance to work with as there are so many fractions and so far no extensive attempts have been made to deal systematically with its absorptions.

In the author's experiments the amount of phosphoric acid absorbed by the humus was independent of the concentration of the phosphate solution. A strong solution of humus was made in ammonia the excess of which was then removed by a current of air. The solution was then made slightly acid with acetic acid and dialysed for three days. Considerable quantities of phosphate were removed, and finally the solution contained 15 mgms. of  $P_2O_5$  per 100 c.c. Portions of 25 c.c. of this

<sup>1</sup> *Landw. Versuchs-Stat.* 1888, 35, 67.

<sup>2</sup> *Landw. Jahrb.* 1882, 11, 1.

<sup>3</sup> *Ann. d. Landw.* 1867, 49, 322.

solution were made up to 100 c.c. with dilute nitric acid (making the acidity N/20) and varying amounts of sodium phosphate solution; after three hours' shaking, the precipitates were filtered and  $P_2O_5$  determined in 50 c.c. of the filtrate. The following results were obtained:

Mgms. per 25 c.c. humus solution		
$P_2O_5$ added + $P_2O_5$ in humus (3.75)	$P_2O_5$ found in solution	$P_2O_5$ fixed by humus
14.22	11.58	2.64
16.86	14.70	2.16
18.60	16.30	2.30
21.21	19.60	2.60

Much work remains to be done on the quantitative relationships in the absorption by the organic matter of soils.

*The introduction of the conception of colloids.*

Van Bemmelen was the first to introduce the conception of colloids into soil problems. The work of Thomas Graham (1861-1864) on colloidal solutions had led to the more precise definition of these bodies. He showed that solutions of gelatine, glue, gum arabic would not diffuse freely through organic membranes like parchment, whilst solutions of the ordinary crystalline substances would. He therefore divided substances into "crystalloids" and "colloids." This division is no longer sharply defined, as many substances can be obtained both in the crystalloid condition and in colloidal solution. Graham also found that certain solutions such as silicic acid, tungstic acid, aluminium and iron hydroxides would not diffuse through parchment; he therefore called these: "colloidal solutions" or "sols." These solutions however did not behave like true solutions in that they were radically changed by the addition of small quantities of electrolytes. The "sol" of silicic acid sets to a jelly in the presence of a trace of carbon dioxide, while a trace of sodium sulphate would precipitate a ferric hydroxide or aluminium hydroxide "sol." The precipitates or the jellies were termed "gels." Van Bemmelen investigated their properties, especially the rate at which they lost water by evaporation and their absorptive power for water and solutions. He further showed that these phenomena in gels resembled some of the known reactions of soils. It is interesting

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to trace the development of his ideas. In his first paper<sup>1</sup> he investigated the relationship between the amount of absorption and the easily decomposable silicates of the soil. Here he followed Way's earlier assumption as to the seat of the absorptive power of the soil and the later results that many natural "zeolotic" silicates, basalt, natrolite, etc., showed similar phenomena when brought into contact with salt solutions (Eichhorn<sup>2</sup>, Lemberg<sup>3</sup>). Heyden<sup>4</sup> had shown that a soil after treatment with hydrochloric acid gives up silica to a solution of caustic soda. Van Bemmelen regarded the amount of silica thus liberated as an indication of the quantity of easily decomposable silicates present. He generally found that soils which absorbed well also gave up much silica. After a soil had been boiled with hydrochloric acid, it took up only small quantities of potassium from a solution of neutral potassium salt but large quantities from the hydroxide or carbonate solutions. If such a soil were first treated with sodium hydroxide, then it would react normally with neutral potassium salts, potassium being taken up and sodium appearing in the solution. These reactions were attributed to the silica "gel" present in the soil after boiling with acid.

He concludes that soil absorption is a chemical and not a physical phenomenon, basing his conclusions chiefly on the fact that an exchange of bases always takes place.

In subsequent papers his opinions change. This later work is chiefly on absorption by simple gels, *e.g.* of silica, tin oxide, iron oxide and alumina. He found that neutral salts and acids were absorbed by silica in small quantities; in this case there could be no possibility of chemical reaction. He thus recognises the possibility of physical absorption of hydroxides and carbonates by silica and where substitution takes place he says that the substitution is not really chemical but only apparently so<sup>5</sup>. In 1900<sup>6</sup> he definitely stated that if any absorbent is in equilibrium with a solution of a substance  $C_1$  and a second substance  $C_2$  is brought into the solution, then partial substitution of  $C_1$  by  $C_2$  will take place. Van Bemmelen thus partially removed aluminium chloride from a silica gel, sulphuric acid from a manganese dioxide gel and calcium chloride from a chromium hydroxide gel by means of potassium chloride and potassium sulphate.

<sup>1</sup> *Ber. Deut. Chem. Ges.* 1878, **11**, 2228; also *Landw. Versuchs-Stat.* 1878, **23**, 265.

<sup>2</sup> H. Eichhorn, *Landw. Jahrb.* 1875, **4**, 1.

<sup>3</sup> J. Lemberg, *Zeits. d. deutschen geol. Ges.* 1883, **35**, 557.

<sup>4</sup> *Ann. d. Landw.* 1864, **43**, 310.

<sup>5</sup> *Die Absorption*, p. 100; *Landw. Versuchs-Stat.* 1888, **35**, 67.

<sup>6</sup> *Ibid.* p. 441; *Zeits. f. anorg. Chemie*, 1900, **23**, 321.

Similarly a silica gel was treated with calcium hydroxide and afterwards with potassium chloride solution. The potassium removed much of the calcium but the chloride radical remained in solution.

He concludes<sup>1</sup> that the phenomena of absorption in soils are of the same nature as in artificial calcium aluminium silicates brought into contact with the solutions of salts of the alkalies. Thus the soil absorptions fall into line with other absorption phenomena.

#### *Adsorption.*

Much of the recent work on the absorptive power of soils has been of a physico-chemical nature as it has been recognised that more definite knowledge as to the nature of the phenomena will be obtainable by this means. Before proceeding to the discussion of these developments it will be necessary to deal with the general phenomenon known as "adsorption." This subject has received considerable attention during the last ten years from the physical chemists and more recently from the physicists<sup>2</sup>. "Adsorption" is the concentration of any substance on the surface of another. The power of charcoal to absorb gases and to remove colouring matter from solution is perhaps the most familiar example.

Certain phenomena occur at the surface bounding any two phases of a system which are generally associated with the effect of Surface Tension. In the case of a liquid in contact with a gas this tension is a well defined and measurable constant. The surface energy of any system tends to become a minimum; in the case of a liquid in contact with a gas, the liquid tends to become a perfect sphere, which has the minimum surface and hence the minimum surface energy. Where the bulk of the liquid is too great and the force of gravity prevents the liquid becoming spherical the surface remains practically constant but the surface energy nevertheless falls if the opportunity occurs. The addition of soluble substances to a liquid usually changes the surface tension. If an increase of concentration decreases the surface tension, then a concentration of the solute occurs in the surface layer; in other words adsorption takes place. If however the addition of a solute increases the surface tension, the concentration of the solute in the surface layer diminishes, giving rise to "negative adsorption." These deductions from thermodynamical laws have been confirmed by experiments. Miss C. C. Benson<sup>3</sup> has shown that the froth obtained from a solution

<sup>1</sup> *Die Adsorption*, p. 433.

<sup>2</sup> See Trouton, *Brit. Assn. Report*, 1914.

<sup>3</sup> *Journ. Phys. Chem.* 1903, 7, 532.

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of amyl alcohol in water has a higher concentration of the alcohol than the original solution; amyl alcohol lowers the surface tension of water. J. v. Zawidzki<sup>1</sup> has obtained similar results with saponin.

It is extremely probable that the surface liquid-solid also shows surface tension phenomena, but so far no methods have been devised for determining its magnitude; but the above reasoning is still applied. The further discussion of the theoretical side of this subject leads into the realms of molecular physics and lies outside the scope of this paper. Negative absorption, *i.e.* the decrease in concentration at the surface of the solid, was first observed by C. Matteucci<sup>2</sup> who found that the density of a solution of sodium carbonate was increased by filtration through three metres of sand. G. Gore<sup>3</sup> investigated very fully the absorption of various salts by silica and obtained 13 cases of negative absorption, 97 cases with positive adsorption and 30 cases with no result. S. Lagergren<sup>4</sup> found negative adsorption in the cases of sodium, potassium and ammonium chlorides and animal charcoal. A. M. Williams<sup>5</sup> found that the adsorption of potassium chloride and magnesium sulphate by charcoal increases with the concentration to a maximum, then decreases, then passes through zero and finally becomes negative.

F. T. Trouton<sup>6</sup> has shown that a similar maximum of adsorption occurs at a definite concentration with certain sulphates and nitrates in contact with silica. The adsorption is not much influenced by small changes of temperature, but is diminished by a rise in temperature; below the critical concentration as given in the above experiments of Trouton an increase of adsorption follows a rise of temperature.

### *The adsorption isotherm.*

Generally speaking the adsorption increases with the concentration of the solution according to a simple relationship which can be expressed:

$$\frac{Y}{M} = KC^{\frac{1}{P}}, \text{ where } Y = \text{amount of substance adsorbed by } M \text{ of adsorbent,}$$

$C$  = concentration of solution in equilibrium with  $Y$ ,  
 $K$  and  $P$  are constants.

<sup>1</sup> *Zeits. phys. Chem.* 1903, **42**, 612.

<sup>2</sup> *Sur les phénomènes physiques des corps vivants*, 1847.

<sup>3</sup> *Birmingham Phil. Soc.* 1893, **9**, 1; see *Chem. News*, 1894, **69**, 22, 33, 43.

<sup>4</sup> *Bihang till K. Sv. Vet. Akad. Handl.* 1898, **24**, Afd. 11, No. 4.

<sup>5</sup> *Trans. Faraday Soc.* 1914, **10**, 155.

<sup>6</sup> *British Assn. Report*, 1914; *Nature*, 1914, **93**, 642.

This equation in various forms has been used for many years and was recognised by Van Bemmelen in 1878 as being applicable to one of his absorption results<sup>1</sup> but was not followed up by him. He only insisted that the ratio of the absorption to the equilibrium concentration was never constant.

It has been found to hold for the absorption of iodine by starch by F. W. Küster<sup>2</sup> and for picric acid and silk by J. Walker and J. R. Appleyard<sup>3</sup>. Freundlich and his co-workers have established the general applicability of this law since 1906<sup>4</sup>; the law holds in most cases of adsorption so far investigated using as solvents, water, alcohol and other organic solvents and as adsorbents, charcoal, silica and alumina, and various textile fibres.

A typical example of an adsorption curve is given in Fig. 1 from experimental data obtained by the author. This shows the adsorption of oxalic acid by a soil, in the presence of N/20 HNO<sub>3</sub> to prevent the chemical precipitation of insoluble oxalates. 25 gms. of a deep Rothamsted subsoil were shaken with 1000 c.c. of varying concentrations of oxalic acid in N/20 nitric acid in a thermostat at 23° C. for one hour. The oxalic acid was determined in the extracts by titration against potassium permanganate solution; the results obtained are given in Table I.

The experimental points are seen to lie fairly well on a curve expressed by the formula

$$\frac{Y}{M} = .28 C^{3.56},$$

which is of the usual adsorption type,  $\frac{Y}{M} = KC^{\frac{1}{P}}$ . The values for  $P$  usually lie between 2 and 10: there are some exceptions but in the majority of adsorptions so far investigated these are the limits. The value of  $K$  varies of course with the units employed to express the results and is proportional to the active surface of the adsorbent.

Other formulae have been proposed, notably by S. Arrhenius and by G. C. Schmidt, but at the present time the one given above is most generally used and it gives fair agreement so long as the concentrations of the solutions are not too high.

The rapidity with which the equilibrium is reached is very high; under favourable conditions the process may be said to be instantaneous.

<sup>1</sup> See W. Ostwald in editorial to *Die Absorption*.

<sup>2</sup> *Liebig Annalen*, 1894, **283**, 360.

<sup>3</sup> *Trans. Chem. Soc.* 1896, **69**, 1334.

<sup>4</sup> See *Kapillarchemie*, 1906.

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G. C. Schmidt<sup>1</sup> has found that adsorption is slowest if the adsorbent is placed directly into the solution. If the equilibrium is first established and the solution is then diluted the new equilibrium is attained almost immediately. Air films in the adsorbent are suggested as a cause for the slower rate with the fresh material.

TABLE I. *Absorption of oxalic acid by soil.*

Oxalic acid		
added	found in solution <i>C</i>	retained by soil $\frac{Y}{M}$
gms.	gms. per litre	gms. per 25 gms. of soil
0.094	0.017	0.077
0.157	0.046	0.111
0.220	0.078	0.143
0.283	0.121	0.163
0.315	0.148	0.166
0.441	0.253	0.188
0.567	0.356	0.211
0.756	0.526	0.230
0.945	0.702	0.243
1.260	0.980	0.280

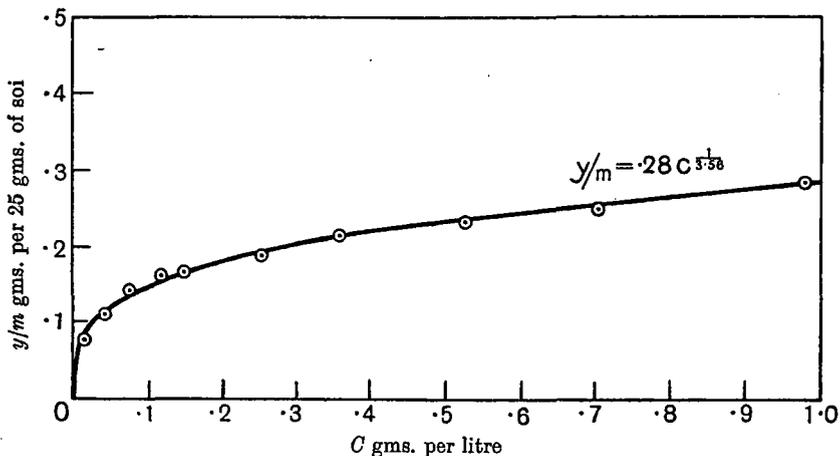


Fig. 1. Absorption of oxalic acid by soil in presence of excess nitric acid.

The simultaneous adsorption of two substances from solution is of much interest to the soil chemist. As already stated Van Bemmelen had shown that one adsorbed substance can be replaced by another

<sup>1</sup> *Zeits. phys. Chem.* 1910, 74, 689.

brought into the solution. Adsorption proceeds normally in the presence of a second substance but the constants of the isotherm are changed. Masius<sup>1</sup>, Michaelis and Rona<sup>2</sup> and Schmidt have shown that if two substances are adsorbed the adsorption of each one is diminished but it can still be expressed by the usual equation.

Van Bemmelen discusses the question whether absorption by gels is of the same nature as ordinary adsorption by charcoal, silica, etc. A web structure is attributed to the gelatinous precipitates and he points out that there is no essential difference in these cases between adsorption and absorption but he prefers to use the term "absorption" as being more general. In support of this view those precipitates which were supposed to have the largest "web" surface showed the highest adsorptive power and also those precipitates which after ignition were capable of becoming incandescent also showed very active adsorption. The gels used by Van Bemmelen must not be regarded as jellies in the usually accepted sense of the term. One of his silica gels is described as "a dry dusty powder" and most of his absorbents must have been in this form. They can only be described as colloids in that they possessed a structure in which the discontinuities were of colloidal dimensions, that is between  $0.1\mu$  and  $1\mu\mu$ . Adsorption is not a property peculiar to colloids although colloids show this property to a remarkable extent on account of the large surface they possess in proportion to the total mass.

#### *Applications to soils.*

Side by side with all this work, agricultural chemists have been trying to apply the above laws to the known phenomena of absorption by soils. The simplest type of absorption by a soil is shown by a dye-stuff. Here there is no chemical reaction but every probability that the phenomenon is purely physical. The adsorption of dyes by soils is found to follow the usual laws. H. E. Patten and F. K. Cameron<sup>3</sup> found a definite equilibrium with gentian violet, eosin and a manure extract which, when plotted as a curve, was seen to be of the usual adsorption type. Although they recognised the value of the adsorption equation for more simple cases, they did not attempt to express their soil curves by this equation as they considered the soil conditions were too complex. They concluded however that the distribution of solute

<sup>1</sup> *Dissertation*, Leipzig, 1908.

<sup>2</sup> *Biochem. Zeits.* 1908, **15**, 196.

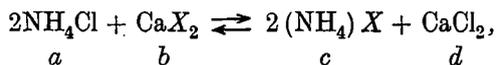
<sup>3</sup> *Journ. of Phys. Chemistry*, 1907, **11**, 581.

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between solvent and absorbent presents in general the same characteristics with soil as with other absorbents.

The difference between the absorption of a base from a neutral salt solution and of a dyestuff is that in the first case an equivalent of other bases is always found in the solution after equilibrium is established. This at first sight points to a chemical reaction in which two insoluble bodies are concerned.

As early as 1859 C. Boedeker<sup>1</sup> setting out from Henneberg and Stohmann's results formulated a mathematical expression for the relationship between the ammonia absorbed by a soil and the calcium turned out, which is substantially that obtained nearly 50 years afterwards by A. D. Hall and C. T. Gimmingham<sup>2</sup>. If we call the calcium complex in soil  $\text{Ca}(X)_2$ , then on treating with ammonium chloride the following reaction takes place:



where  $a$ ,  $b$ ,  $c$ ,  $d$  are the respective concentrations of the reacting substances, then  $\frac{a^2}{d} = K$ , the active masses of the insoluble substances being constant.

Hall and Gimmingham found this law to hold with fair accuracy for the reaction of china clay with ammonium chloride and they concluded that a simple chemical reaction was a sufficient explanation of the results obtained.

Adolf Mayer<sup>3</sup> had pointed out that Boedeker's equation does not apply to the potassium results of Peters. Moreover the active mass of the calcium represents also the amount of ammonia absorbed by the clay, and the equation  $\frac{a^2}{d} = K$  therefore becomes a special case of the usual adsorption isotherm where  $P = 2$ .

Attempts to explain the equilibrium results on physical lines have been made by Patten, Cameron and Parker in the United States and by Wiegner in Germany. Patten and Cameron in the paper quoted above worked out Peters' potassium results and found them to be of an adsorption type. E. G. Parker<sup>4</sup> working with potassium chloride and J. H. Aberson<sup>5</sup> working with ammonium chloride and soils obtained similar results.

<sup>1</sup> *Journ. f. Landw.* 1859, 48.

<sup>2</sup> *Trans. Chem. Soc.* 1907, 91, 677.

<sup>3</sup> *Lehrbuch der Agriculturchemie*, 1886.

<sup>4</sup> *J. Agric. Research*, 1913, 1, 179.

<sup>5</sup> *Kolloid Zeits.* 1912, 10, 13.

G. Wiegner has recently reviewed the whole subject<sup>1</sup> and shown that the absorption of ammonia by permutite (a technical calcium aluminium silicate) from a solution of ammonium chloride follows the absorption laws very completely; the equilibrium is instantaneous when reached from above and the absorptive power is dependent largely on the physical condition of the permutite. The Cl ion is not absorbed. The equilibrium attained was expressed by the formula

$$\frac{Y}{M} = 3.429 C^{0.398}$$

The following table is worked out by Wiegner from the results of various experiments and shows that the adsorption isotherm for soils is of the usual type:

Absorbent		Solute	K	$\frac{1}{P}$	Worker
Garden soil	... ..	NH <sub>4</sub> Cl	0.0948	0.039	} Henneberg and Stohmann
" "	... ..	NH <sub>4</sub> Cl	0.131	0.424	
Nile sediment	... ..	NH <sub>4</sub> Cl	0.489	0.399	Armsby
Permutite	} artificial	NH <sub>4</sub> Cl	2.823	0.398	Wiegner
Sodium zeolite		CaCl <sub>2</sub>	2.487	0.317	Armsby
Zeolite		LiCl	24.419	0.414	Campbell
Soil	... ..	NH <sub>4</sub> OH	0.0994	0.434	} Brustlein
"	... ..	NH <sub>4</sub> OH	0.147	0.461	
"	... ..	NH <sub>4</sub> OH	0.054	0.386	

In these experiments, the influence of temperature on the equilibrium was only small but the absorption decreased with the rise of temperature, as already shown by Schuhmacher. Equilibrium was very quickly attained. Wiegner concludes that the fixation of bases by soils is best explained as an adsorption phenomenon.

The explanation usually put forward is that the substance actually absorbed is the hydroxide. The OH can be replaced by other ions such as the HCO<sub>3</sub> but not usually by those of strong acids. The reaction taking place between the soil and the neutral salt solution consists in the establishment of an equilibrium between the various hydroxides and since the acid radical is not absorbed to any appreciable extent some of the hydroxides must be brought into solution.

Lachs and Michaelis<sup>2</sup> have shown that when charcoal is shaken with alkali, much adsorption takes place—the OH ion being strongly absorbed. If neutral salts are now brought into contact with the charcoal no

<sup>1</sup> *Journ. f. Landw.* 1912, 60, 111.

<sup>2</sup> *Zeits. f. Elektrochem.* 1911, 17, 1.

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adsorption of the anion takes place except in the case of phosphates but the cations are absorbed by exchange. If acid is brought into contact with the charcoal previously treated with alkali the H ion is strongly absorbed and afterwards the charcoal will no longer take up cations from neutral solutions.

These reactions are obviously parallel to those of Van Bemmelen described previously, and to the general type of absorption in soils by exchange of bases.

The reaction between the soil and phosphates has also been found to obey the adsorption equilibrium law—in this case the phosphates must be kept in solution by using another acid such as dilute hydrochloric or nitric acid as a medium for the reaction. The results<sup>1</sup> indicate that equilibrium obtained between soils and dilute acid solvents such as 1 % citric acid is of an adsorption type. In the case of citric acid there are further complications in that citric acid itself is absorbed by the soil and in this way influences the absorption of phosphate.

In the case of nitrates, sulphates, and chlorides, the absorption of the acid radical has not been noted, all the results obtained so far indicate that no absorption by soil takes place. Even in very dilute solution the author has not found any appreciable absorption of nitrate by soil.

100 gms. of the deep subsoil as used for the oxalic acid absorption (p. 123) were treated with 500 c.c. of a solution containing nitrate. Absorption if any was very small.

N added as nitrate	N found in solution as nitrate*
0 gm.	.00036 gm.
.010 gm.	.010 "
.020 "	.020 "

\* Determined colorimetrically.

Mention has been made of percolation experiments for the investigation of absorption phenomena. O. Schreiner and G. H. Failyer<sup>2</sup> obtained the leaching curves for monocalcium phosphate which had been added to a soil. Assuming that the rate of leaching, represented by the concentration of the percolate at any moment, is proportional to the amount of absorbed substance still to come out, then

$$\frac{dy}{dv} = K(A - Y),$$

<sup>1</sup> See this *Journal*, p. 65, and *Proc. Chem. Soc.* 1914, 30, 123.

<sup>2</sup> *Journ. Phys. Chem.* 1906, 10, 239.

where  $A$  = original amount of absorbed substance,  
 $Y$  = amount already removed,  
 $K$  = a constant.

Results were obtained in fair agreement with this assumption. From the adsorption isotherm the rate of removal of absorbed substances can also be worked out.

The concentration of the percolate at any moment must be related to the equilibrium existing between the percolate and the soil.

Using the same expressions as above:

$$\frac{dy}{dv} = K (A - Y)^{\frac{1}{p}}$$

is seen to be another form of the adsorption isotherm. This equation still requires experimental confirmation.

#### *Applications to soil problems.*

*The surface of soils.* The absorption of dyes by soils is a purely physical phenomenon and hence depends largely upon the surface of the soil. A number of workers, Sjollema, Endell, König, Hasenbäumer and Hassler, have suggested the use of this method as means of estimating the colloids of the soil, assuming that only the colloids in the soil take part in the absorption, which is hardly justifiable. J. A. Hanley<sup>1</sup> has reviewed this method and obtains equilibrium curves of the usual type. Where such an equilibrium is established it is obviously difficult to choose a suitable concentration of solution and Hanley points out that the final equilibrium concentration of the solution must be the same for every soil in order that the absorptions may be compared. T. Tadokoro<sup>2</sup> has obtained similar results and finds that the absorption of dyestuffs is closely related to the hygroscopicity—but has no regular relationship to the absorption of ammonia by the same soils.

#### *Soil acidity.*

The acidity of some soils has also recently been attributed to absorption phenomena—in the case of humus soils; on the one hand we have the view that the acidity is due to free acids, on the other hand that it is due to a physical absorption of bases by the humus itself leaving the acid free. Many soils give an acid reaction when brought into contact with moistened litmus paper—the suggestion has been made by Harris<sup>3</sup> and others<sup>4</sup> that this is due to the absorption

<sup>1</sup> This *Journal*, 1914, 6, 58.

<sup>2</sup> *Journ. Tohoku Imp. Univ. Sapporo, Japan*, 1914, 6, 27.

<sup>3</sup> *Journ. Phys. Chem.* 1914, 18, 355.

<sup>4</sup> See F. K. Cameron, *The Soil Solution*, p. 61.

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of the base of the litmus by the soil while the free acid is left on the paper. Many soils which give neutral solutions to water give acid extracts to neutral salt solutions and Veitch<sup>1</sup> shows that in some cases of sour soils, iron and alumina are present in the extract. Salts of these bases are easily hydrolysed, giving acid solutions; the acidity of the soil therefore is indicated by the circumstances that the iron and aluminium occur in a form easily turned out by another base. G. Dai-kuhara<sup>2</sup> has shown that in many cases the aluminium present is equivalent to the acidity. The acidity of the extract also varies with the concentration of the neutral salt solution used, there being a normal absorption equilibrium.

With most English soils showing acidity or sourness the defect can usually be remedied by the addition of lime or chalk to the soil; H. B. Hutchinson and K. MacLennan<sup>3</sup> have shown that such soils have a high absorptive power for calcium bicarbonate solution and they use the expression "lime requirement" to indicate the amount of bicarbonate necessary to saturate the soil.

It will be seen that there is a general tendency to associate all soil absorptions with the general phenomenon of adsorption, and indeed all the characteristics of adsorption are reproduced in most soil absorptions. Whitney and Cameron lay great emphasis on adsorption as the factor determining the composition of the soil solution although it may be doubted whether absorption suffices to keep the concentration of the soil solution within certain limits.

The actual portions of the soil which take part in the various types of absorption have yet to be determined—probably all of them play a certain part—even sand shows a measurable adsorption for dyestuffs. The absorption of bases by exchange—the *Basenaustausch* of the Germans—is more complicated, but the phenomenon is shown by most diverse absorbents.<sup>4</sup> In the soil there probably exists a complex of silica, alumina, possibly humus and iron oxide, which behaves like Van Bemmelen's gels or Way's complex silicates. Certainly combinations exist in soils which are easily decomposed in the cold by dilute acids with the appearance of aluminium and silica in the solution.

In another paper the influence of absorption on analytical methods is demonstrated and probably we are working towards a more precise definition of available plant foods based on our knowledge of how the soil absorbs them in the first instance.

<sup>1</sup> *J. Amer. Chem. Soc.* 1904, **26**, 637.

<sup>2</sup> *Bull. Imp. Cent. Ag. Expt. Stat. Japan*, **2**, 1.

<sup>3</sup> *This Journal*, 1915, **7**, 75.