THE RELATIONS EXISTING BETWEEN THE SOIL AND ITS WATER CONTENT.

A RÉSUMÉ OF THE SUBJECT.

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(A) INTRODUCTION.

IN any systematic account of the work done on the moisture in soil and its behaviour under varying conditions, it is necessary to keep constantly in mind that the underlying hypotheses have been profoundly modified in recent years. When physical methods were first applied to the examination of soils, the results were interpreted on the obvious hypothesis that the soil could be regarded as composed of mineral particles of varying shapes and sizes, over the surfaces of which the water was distributed in a thin film. The movements of the film water and its average thickness at any time, under the varying meteorological and soil influences, could be predicted more or less completely from known physical principles such as surface tension, etc. Similarly, the concentration of the plant nutrients in the soil moisture was considered mainly as a matter of solubility in, and diffusion within, this moisture. The foundation of the subject of soil physics was laid upon these lines in the early 19th century by Davy¹ and Schübler².

From 1850 onwards very few physical investigations were made on soil, and the subject became overshadowed by agricultural chemistry. Subsequently interest in soil physics revived and considerable developments were made in America and Germany. Of recent years further impetus has been given to the science by the recognition of the adsorptive and colloidal phenomena shown by soils. These effects have profoundly modified the older views on the relations existing between soil and its water content, and have revealed a much more intimate connection. It is no longer sufficient to imagine a mineral-grain framework covered with a film of water. Colloidal material exists in the soil, derived both

¹ Davy, H. *Elements of Agricultural Chemistry*, 1st ed. (1813). London.

² Schübler, G. *Gründsätze der Agrikultur-Chemie*, (1830). Leipzig.

from the humus and the clay fraction, and exerts in most cases a controlling influence on the water relationships. The constitution of this colloidal complex is by no means fully worked out, but a satisfactory provisional hypothesis for physical investigations is to assume that it coats more or less completely the soil-grains, especially those of smaller size.

The relations existing between soil and its moisture content are subject to so many variable factors that separation for purposes of discussion is only possible in a very general way. This difficulty did not exist to so great an extent with the original hypothesis, because the soil water could be conveniently classified as (1) hygroscopic moisture, (2) capillary water, (3) gravitation water¹. Gravitation water is defined as the water in excess of the amount the soil can retain under existing conditions and which can therefore drain away. The capillary water is that part retained in the capillary spaces under these conditions, and is capable of movement through capillary action. The hygroscopic water is the film on the surface of the grains, and is not capable of movement under gravitational or capillary forces. With this classification it was comparatively simple to treat any one aspect of soil moisture behaviour, such, for instance, as evaporation or percolation. But when similar treatment is attempted on the colloidal hypothesis, the more intimate relations postulated between the soil material and the water—relations which vary in a continuous manner over a wide range of moisture content—render the above divisions too empirical for a theoretical basis. The classification is undoubtedly convenient, especially in field studies, but its somewhat arbitrary nature should be kept in view.

These considerations are reflected both in the arrangement of the present paper and in the choice of material for discussion. A full treatment is given of the comparatively few recent papers in which the colloidal hypothesis is accepted, while the greater amount of work interpreted on the older theory is represented by typical papers; results which have a bearing upon the colloidal hypothesis, however, are especially noted. The section dealing with the hygroscopicity of soils is fully treated, because this phase of the subject is likely to help considerably in extending our knowledge of the colloidal nature of soil.

(B) SOIL MOISTURE IN GENERAL.

The amount of soil moisture may vary between wide limits for any one type of soil, ranging from a water-logged condition, when the pore space between the particles is practically filled with water, to almost

¹ Briggs, L. J. *U.S. Bureau of Soils, Bull.* 10 (1897).

complete dryness. A good proportion of the earlier work on soil physics was devoted to experiments on the amount of water held in the soil under varying conditions, and a broad series of divisions was worked out.

(a) *The maximum water capacity and pore space.*

King¹ did a considerable amount of work on the maximum water capacity, which is defined as the amount of water necessary completely to fill the interspaces between the particles. It is obvious that the mode of packing of the soil particles will directly affect this value. King therefore employed soils in their natural condition of consolidation, obtained by driving metal cylinders into the soil. When the desired depth was reached the surrounding soil was removed, and the cylinder, full of soil, taken for experiment. The results are given in Table I, and show the progressive diminution in the maximum water capacity, with increasing

Table I.

Maximum water capacity of different depths of soils (King).

Depth of sample inches	Weight when full of water lb.	Weight dry lb.	Weight of water lb.	Water expressed in inches	Per cent. of water
1-12	21.33	15.09	6.24	5.88	41.3
12-24	24.27	18.94	5.33	5.03	28.1
24-36	24.27	18.89	5.38	5.07	28.4
36-48	24.89	19.94	4.95	4.67	24.8
48-60	26.91	22.92	3.99	3.76	17.4

depth of soil. The water necessary for saturation was found to be greater in amount than the maximum values observed in the field when the soils were water-logged, owing to the more complete displacement of air in the laboratory experiments. The main value of experiments of this type lies in the information afforded on the pore space in soils. This is essentially a function of the size and mode of packing of the particles, but is also affected by the proportion of organic and colloidal matter present. These materials, besides having an important bearing on the formation of compound particles, and hence directly on the pore space—a phase discussed in more detail in the section below dealing with the hygroscopic coefficient—also imbibe large quantities of water and swell considerably, thus increasing the effective volume of a given weight of soil, and allowing it to take up more water than it would otherwise do.

(b) *The permeability of soil.*

The pore space in soils can also be studied by permeability methods. The permeability of a soil may be measured by that volume of liquid

¹ *Wisconsin Agric. Expt. Station 6th Rept.* (1889), p. 189.

which will pass per second through a soil column of 1 c.c. cross-sectional area, and 1 cm. in length under 1 cm. head of pressure. The liquid usually employed is water, but the permeability to gases can also be measured, and is defined in a similar manner.

By far the most exhaustive study on these lines has been done by King¹, who examined the permeability both for air and water of many porous rocks, and a large number of porous media. Various devices were used for the latter in an attempt to bridge the gulf between a capillary tube of uniform bore, in which the flow follows the well-known Poiseuille-Meyer Law, and a mass of particles, which gives in effect a number of irregular channels between the grains. These devices consisted of bundles of capillary tubes, bundles of knitting needles, brass tubes containing discs of wire-gauze, closely packed but haphazardly orientated, tubes of quartz sand of various grain size, and so on. King finds almost invariably a departure from the proportionality between flow and pressure which would be expected from Poiseuille's law, the flow increasing faster than the pressure. The reason for this is very difficult to understand. Röntgen², Warburg and Sachs³, and R. Cohen⁴, have all shown that the viscosity of water diminishes slightly with increasing pressure, but this diminution is not nearly sufficient to account for the observed increase of flow with pressure. The possibility that entrapped air in the materials was gradually washed out as the pressure head was increased is largely negatived by the careful technique used. A satisfactory explanation is, as yet, wanting. King's attempt to show that his observed increases are paralleled by similar results obtained in the classical experiments of Poiseuille and Meyer, on which the laws of capillary flow were based, is not completely convincing.

C. S. Slichter, in an appendix to King's work, has examined the mathematical conditions involved in the flow through porous media on the assumption that the particles are spheres of one size. Generally he confirms the experimental results, and is able to show that slight increases in the porosity of a soil due to the more open packing of the grains have an enormous influence on the flow of water or vapour through the soil. If two samples of the same sand are packed so that the pore space is 26 per cent. in one case and 47 per cent. in the other, the flow through the former is only one-seventh of that through the latter,

¹ King and Slichter. "Principles and conditions of the movements of ground water." 19th Annual Report, 1899 (Pt II), (U.S. Geol. Survey).

² *Wied. Ann.*, 22 (1884), p. 510.

³ *Wied. Ann.*, 22 (1884), p. 518.

⁴ *Wied. Ann.*, 45 (1892), p. 666.

while if the pore spaces are 30 per cent. and 40 per cent., the flow through the latter is 2.6 times that through the former.

Green and Ampt¹, in some ingenious experiments, have examined some of Slichter's results, both for "ideal" soils² and quartz sands. They obtain the paradoxical result that Slichter's permeability formula closely expresses the results for the irregular grains of quartz sand, but not for the spherical particles composing the "ideal" soil. They believe that the explanation of this is to be found in Slichter's method of treating each soil capillary as if it were a double triangular shaped pore with a partition down its centre, instead of an *undivided* approximately rhomboidal pore at its narrowest part. Reference to Fig. 1 taken from Green

Fig. 1. Arrangements of spheres in an ideal soil (Green and Ampt).

and Ampt's paper, will make this clear. It is not until the closest packing of the spheres is attained that the pore is divided into two. Extrapolation of the experimental results to the minimum pore space, which is reached when the spheres are packed as closely as possible, gives a value approximating to Slichter's theoretical value. For all the other systems of packing the rhomboidal pore will have a considerably greater permeability than Slichter's method of analysis would imply. On the other hand the angular shapes of the quartz sand have the effect of dividing the pore into triangular passages, and hence the agreement of experiment with theory is better in this case.

¹ *Journ. Agric. Science*, 5 (1912-13), p. 1.

² Green and Ampt state that the so-called "glistening dew" of the picture post-card artist is composed of almost perfectly spherical grains or beads of glass of diameter .25 mm. upwards, and is thus an invaluable material for experimental tests of theoretical deductions, such as those of Slichter.

(c) *Capillary effects and the "water retaining capacity."*

In earlier experiments on the same lines as those quoted in the preceding sub-section, Green and Ampt¹ found that the permeability of an actual soil when measured with water was less than with air as the experimental fluid, and that the ratio of these two values varied with the amount of colloidal matter present.

As noted above, the imbibition of water by the colloidal material means that a soil, draining under the influence of gravity, will hold up more water than it would otherwise do, and, in addition, the diminution in the diameter of the capillary pores as a result of the swelling of the gel-material will tend to increase this amount still further owing to the production of more effective interstices between the soil particles. It would therefore be expected that the permeability of the soil to water would decrease with increase in colloidal and organic matter.

The following values taken from Green and Ampt's paper illustrate this (Table II).

The actual permeability (P) of a soil can be shown to vary inversely as the viscosity (η) of the fluid used in the experiment. Hence if two different fluids are used, say air (a) and water (w), the value of the ratio $\frac{\eta_a P_a}{\eta_w P_w}$ should be unity, provided that the permeability is unaffected by any action of the fluid on the soil.

Table II.

Values of Ratio $\frac{\eta_a P_a}{\eta_w P_w}$ for three soils (Green and Ampt).

Canterbury Sand	...	2.0, 2.0
University Loam	...	3.5, 3.6, 3.1, 4.1, 6.0
Werribee Clay	...	14.2, 12.3, 14.2

It will be seen that the values increase rapidly with increasing percentage of clay. This is due to the imbibition of the water by the colloidal portion of the clay, and the resulting constriction of the capillary pores. Low values are thus obtained for P_w , and are reflected in the high values of the ratio $\frac{\eta_a P_a}{\eta_w P_w}$.

Crump² shows that the organic material has considerable influence on the total amount of water held. Working with extreme types of organic soils, such as moorlands and peats, he finds that a definite relationship

¹ *Journ. Agric. Science*, 4 (1911-12), p. 1.

² *New Phytologist*, 12 (1913), p. 125.

holds for any one type of moor or peat soil, between the amount of organic and colloidal material—collectively referred to as the humus content by Crump—and the water content. The latter was obtained by measuring the loss of water occurring when the peat was thoroughly air dried at about 15° C., and the former was determined by the difference in weight when the peat, previously heated at 100° C. to drive off hygroscopic moisture¹, was ignited to a dull red heat. Over the whole of the experiments it was found that the ratio $\left(\frac{\text{water content}}{\text{humus content}}\right)$ was very nearly a constant for any one type of soil. This constancy persisted when varying depths of the soil were separately examined, in spite of the considerable difference in actual moisture content. Crump proposes to call this ratio the “coefficient of humidity” and considers it is the best way of expressing the water content. The subjoined table is typical (Table III).

Table III.

Values of the coefficient of humidity (Crump).

Material		Water at 15° C.	Humus	$\frac{\text{Water}}{\text{Humus}}$
(i)	Humus at 1–2½ ins. ...	170.0 %	55.5 %	3.06 %
(ii)	Sandy soil below (i) ...	30.4	10.4	2.92
(i)	Black soil at ½–1½ ins. ...	67.4	33.4	2.01
(ii)	Same at 1½–2½ ins. ...	40.3	18.6	2.16

It will be seen that a close relationship holds in these extreme types of soil between the amount of humus and the moisture in excess of the hygroscopic moisture². Data are as yet lacking for similar determinations on ordinary soils, but some preliminary work of Crump in the paper mentioned seems to indicate that similar relationships will hold for the colloidal clay content in these soils as for the humus content in the peats.

Recent work of Alway and Neller³ on the influence of organic matter upon the water-holding-capacity of arable soils indicates that slight differences in moisture content between adjacent plots can be accounted for on the assumption that the organic matter has the same water-holding capacity as some of the most adsorbent peats. These retain, even when well drained, 300 to 400 parts of water to 100 parts of dry

¹ I.e. the moisture remaining in the 15° C. air-dried sample.

² The hygroscopic moisture is the amount of water held by an air-dried soil and should not be confused with the hygroscopic coefficient, which is the amount of water taken up by a dry soil when exposed to a saturated atmosphere of water vapour. There is, of course, a general parallelism between the two.

³ *Journ. Agric. Res.*, **16** (1919), p. 263.

peat. Alway and Neller found that a difference in manurial treatment on two adjacent plots had resulted in a difference of 1.37 per cent. in the organic matter, which gives a calculated difference in the water-holding capacity of about 5 per cent. The observed value was approximately equal to this. It should be noted that even if the whole of the organic matter present has the high water-holding capacity of 400 per cent., this will on the average account for only about 50 per cent. of the moisture content. Thus the plot containing 3.39 per cent. of organic matter varied in moisture content from 19.0 per cent. to 28.9 per cent., and the plot with 4.76 per cent. organic matter from 20.1 per cent. to 33.0 per cent. Other factors such as the colloidal property of the clay must therefore be included.

It is clear from the experiments of Crump, Green and Ampt, that the capillary effects in soils are very dependent upon the nature of the surface of the pore spaces. If these surfaces are mainly gel-like in character there is every reason to believe that the water relationships will be profoundly influenced.

The foregoing considerations indicate the main factors concerned in the "water-retaining-capacity" of a soil. This is defined as the amount of water a previously saturated soil retains when allowed to drain thoroughly into the subsoil under the action of capillary forces and gravity, while protected from evaporation. It is obviously of practical importance, because it gives some measure of the actual amount of water retained by soils under natural conditions, and closely corresponds to the sum of capillary and hygroscopic water in Briggs' classification of soil moisture¹. A large number of determinations have been made on this quantity, both under laboratory and field conditions, but the modes of procedure vary very considerably and there is, at present, no widely adopted standard method. It depends on the soil structure and texture, the water-retaining-capacity being greater the larger the number of interstices in a given volume of soil, and also, as mentioned above, on the nature of the soil particle surface, the water-retaining capacity increasing with the percentage of organic or colloidal water. Alway and fellow workers have recently done a considerable amount of work on the subject, and have endeavoured to correlate the values obtained with various physical "constants" of the soil. The results are discussed below in the appropriate section. It is of interest to note here some maximum and minimum limits of moisture content under various field conditions. Widtsoe and McLaughlin² working in Utah found that the maximum

¹ Ref. p. 45.

² *Utah Sta. Bull.*, No. 115 (1912), p. 195.

amount of water held by the soil against gravity under field conditions was about 24 per cent. (on dry weight) and the minimum amount about 8 per cent. except in the top foot, where it was less.

Determinations made by Russell¹ show how differences in organic content affect the amount of water held by the soil. The figures are expressed as volume percentages (Table IV).

Table IV.

Relation of water content to loss on ignition (Russell).

Rothamsted soils	Loss on ignition	Volume of water	
		In normal moist state	After period of drought (1909 and 1910)
Poor heavy loam ...	4.3 %	23.2	17.0
Heavily dunged arable soil	10.0	30.3	20.0

(d) *Capillary movement of soil water.*

The capillary movement of soil water may take place in all directions. The majority of the investigations deal with the upward movement of water, and less work has been done either on downward or lateral movement.

The general subject of the effect of capillary forces in causing movement of water in the soil is examined by Alway and McDole². Very diverse views on the subject have been expressed by different workers, some of whom consider that the water may come from very great depths. Mitscherlich³ as the result of an indirect calculation from experiments on the "heat of wetting" of soils finds the enormous value of 2 to 3 kilometres for heavy clay soils. He considers this value to be of no practical importance and his experimental values do not exceed 80 cms. over a period of three months. Leather⁴ from field studies in India during the dry period, concludes that the maximum distance over which water moves upward towards the surface is very limited and does not exceed a few feet. A series of determinations made by him of water present in varying depths of soil over a period of 9 months is given in Table V. The rapid loss of water from the third and fourth foot can hardly be attributed to belated drainage, because the soil below 4 feet is losing water at the same time. There is a small, but definite, loss from the fifth and sixth feet depths, while that from the seventh foot is scarcely perceptible.

¹ Russell, E. J. *Soil Conditions and Plant Growth*, 3rd ed. (1917), p. 140. Longmans.

² *Journ. Agric. Res.*, 9 (1917), p. 27.

³ *Landw. Jahrb.*, 30 (1901), p. 361.

⁴ *Mem. Dept. Agric. India*, Chem. Series I (1908), p. 79.

Table V.

Weight in lb. of water present at different times in varying depths of soil (Leather).

Depth	19th Sept.	20th Oct.	30th Nov.	8th Jan.	15th Feb.	27th Mar.	6th May	5th June	15th Jun
0-1 foot	18.97	15.78	14.21	12.15	12.10	14.18	10.83	13.87	10.41
1-2 feet	—	19.27	17.95	18.17	18.79	19.62	16.39	15.40	15.38
2-3 "	24.75	18.84	10.68	11.95	12.00	10.51	10.35	9.67	9.03
3-4 "	25.95	17.51	18.35	13.54	11.27	9.27	6.55	6.63	6.36
4-5 "	25.65	23.69	21.91	21.07	20.18	19.56	18.10	16.20	16.64
5-6 "	26.42	25.60	24.50	24.00	23.54	22.45	20.82	19.45	18.99
6-7 "	26.42	26.00	25.00	25.00	25.30	25.26	24.50	23.10	24.00
Total	169.12	146.69	133.00	125.88	123.18	120.85	107.57	104.32	100.81

The present writer¹ has shown that Slichter's² values for the dimensions of the triangular capillary tubes in an "ideal" soil, made up of spheres of one radius packed in the closest possible manner, may be employed to calculate the probable maximum capillary rise. The relation deduced is

$$h = \frac{.75}{R}$$

where h = height of liquid, R = radius of soil particle.

The average rise in feet for ideal soils of various grain size is shown in Table VI below:

Table VI.

Capillary rise in ideal soils of various grain size (Keen).

Soil fraction	Dia. in mm.		Average capillary rise in feet
	Max.	Min.	
Fine gravel ...	3	1	$\frac{1}{3}$
Coarse sand ...	1	.2	$1\frac{1}{2}$
Fine sand ...	.200	.040	$7\frac{1}{2}$
Silt ...	.040	.010	$31\frac{1}{4}$
Fine silt ...	.010	.002	150
Clay ...	.002	—	150 upwards

The possible height increases considerably with diminution in particle size and may theoretically be infinite. In actual soils there is no possibility of a high value for the capillary rise except in those containing a large amount of clay, and in this case the swelling of the colloidal portion due to the imbibition of water will close many of the capillary tubes and reduce others to such a small diameter that movement of water will be exceedingly slow. Hence in practice we should not expect to find the

¹ Keen, B. A. *Journ. Agric. Science*, 9 (1918-19), p. 396.

² King and Slichter, *loc. cit.*

values for the capillary rise in soils of different textures approaching the theoretical ones given in the table.

A further complication in soils is that the percentage of moisture in the column decreases with increasing distance from the source, i.e. the whole of the moist soil is not saturated. This may be due to one or both of two causes: at considerable distances from the source, water can ascend only through the finer channels in the soil, and thus the average water content in the layer will be short of the saturation value; the water may be present as a film over the surface of the soil particles and the capillary channels therefore not completely full. The motion of the water in this surface film would be very slow on either of the two hypotheses considered in this paper.

Although the capillary rise in fine grained soils exceeds that in coarse grained, the rate of rise is less, the equilibrium being reached more rapidly in the soils of open structure. The experiments of Loughridge¹ are typical of the many investigations. Less attention has been given to rate and amount of downward penetration of moisture. Alway and McDole² have studied the rate of both upward and downward movements of water in soils of varying original moisture contents and have compared the values obtained with the hygroscopic coefficients³ of the soils. Generally speaking their results are similar to those of Atterburg⁴ in that no consistent relationships could be discovered. The rate of downward penetration, while showing little dependence upon the hygroscopicity, increased with the amount of initial moisture content. The rate of capillary rise, on the other hand, was not so definitely connected with original moisture content, neither could any relation between it and the hygroscopic coefficient be traced.

In any attempt to correlate data of capillary rise and downward penetration with the soil conditions the use of the hygroscopic coefficient is not, by itself, sufficient. As shown in the section dealing with hygroscopicity, this is essentially a surface phenomenon, and although the capillary effects will vary with the nature of the soil grain surface, they will also directly depend on the extent and size of the pore spaces in the soil. Measurements of permeability, etc., on the lines of Green and Ampt quoted above, together with applications of the mathematical and experimental investigations of Buckingham⁵ are all needed for the satis-

¹ *California Expt. Sta. Rept.* (1892-4), p. 91.

² *Journ. Agric. Res.*, **10**, (1917), p. 391.

³ See footnote, p. 50.

⁴ *Landw. Vers. Stat.* **69** (1908), p. 93.

⁵ *U. S. Bureau of Soils, Bulls.* **25** (1904) and **38** (1907).

factory interpretation of data on capillary rise, or downward penetration, of water in soils.

King¹ did some experiments on lateral diffusion in surface soils, by maintaining a constant water level at one corner of a shallow square box of soil and determining the moisture content at intervals along the circumference of circles described with the corner as radius. He found that the lateral movement did not extend much beyond 3 feet in 31 days. No absolute value for the lateral movement can be obtained from these experiments, as evaporation into the air from the soil surface was not prevented. Some interesting work by Müntz and Gaudechon² on the diffusion of salts in the soil has a bearing on the present subject. They placed known amounts of various fertiliser salts in different positions in a box of soil, and determined the subsequent distribution of these salts. Surface evaporation was prevented and experiments were also done on the influence of rain—both natural and artificial—on the distribution of the salts. Diffusion was found to be very slow, especially in a lateral direction. Müntz and Gaudechon attribute this to the absence of a continuous medium for diffusion, in other words, the soil water is mainly present as a film over the particles, in which case both the diffusion of salts within it, and its own movement, would be very slow. Even under the influence of considerable amounts of rain the downward diffusion of the salts is slow, owing to the small value for downward percolation imposed on the soil water by the minute capillary spaces.

The whole question is extremely complicated, as a close relation exists between surface and capillary effects in soils, and any variation of one affects the other. Patten and Waggaman³ show that where the disturbing influences are not great, e.g. in quartz sands and similar materials, the time rate of absorption of dyes and various salts, and the distribution of these materials between solid and liquid can be expressed by the usual mathematical formulae applicable to such studies. But in practice the disturbing influences are important. A detailed study was made of one aspect—the change in the physical character of the soil itself consequent upon absorption of dissolved materials. The flocculated structure induced by acids and lime and the deflocculation with alkali, for instance, were shown directly to affect such physical factors as the drainage conditions, aeration, and the capacity of the soil to hold the soil solution and control its movement through the soil.

¹ *Wisconsin Agric. Expt. Station*, 7 (1890), p. 145.

² *Ann. Sci. Agron.* (3 sér.) 4, 1. (1909), p. 379.

³ *U.S. Bureau of Soils, Bull.* 52 (1908).

(e) The hygroscopic moisture in soils.

An excellent historical summary of work on hygroscopicity of soils is given in a paper by Alway¹ and again in conjunction with Kleine and McDole², and hence need not be repeated here. The principle underlying the method is that the large total surface of the soil grains will, in an atmosphere of water vapour, absorb on the surface a film of water, and this process will continue until the vapour pressure of the film so formed is equal to that of the vapour in which the soil is placed, when equilibrium will be reached. Various methods have been used to determine this hygroscopic coefficient. The practical difficulties are serious. It is difficult to maintain an atmosphere saturated with water vapour, and the effect of slight temperature and barometric changes is to cause additional condensation of moisture on the soil surface. Various methods have been devised, among which may be mentioned that of Rodewald and Mitscherlich³, in which the air-dried soil in a thin layer is placed over 10 per cent sulphuric acid in a vacuum desiccator, until equilibrium is attained, weighed, and then dried for 4 hours at 100° C. over P_2O_5 , to obtain the dry weight. The difference between these two weighings is considered to give a measure of the total soil surface for the given weight of dry soil. 10 per cent. sulphuric acid was selected because in experiments with varying strengths, it was found to prevent the formation of dew, and at the same time allowed of the absorption of almost as much hygroscopic moisture as from water. Mitscherlich, in subsequent papers, developed the method to give further information on the soil character. He considers⁴ that a determination of the soil surface by a hygroscopicity method gives a measure of the fineness of the soil type, without presupposing a definite form and the same specific gravity for the soil particles, and should therefore be superior to the ordinary mechanical analysis. He further develops his method to obtain information on the compound particles existing in soil of good tilth, which are of course broken down to their ultimate grains in a mechanical analysis. The 10 per cent. sulphuric acid is replaced by an organic liquid of high molecular weight, which is supposed to condense only on the *outer* surface of a compound particle, whereas water vapour condenses on the *inner* surface as well. Mitscherlich considers that the value given by the organic liquid experiments relates to the mechanical state of the

¹ *Nebraska Agric. Expt. Station Res., Bull.* 3 (1913).

² *Journ. Agric. Res.*, 11 (1917), p. 147.

³ *Landw. Vers. Stat.*, 59 (1904), p. 433.

⁴ *Ztsch. Angew. Chem.*, 23 (1910), p. 1840.

soil and ease of working, while the sulphuric acid determination can be regarded as a measure of the soil productiveness. His earlier views have apparently changed, because he previously states¹ that the hygroscopicity is of no importance from the standpoint of plant growth, but later on he asserts that hygroscopicity and the yield are related by the law of minimum (ref. 4, p. 56). These experiments were made with mustard plants grown in sand with varying additions of peat. The cause of this change of view is probably connected with his investigation on this law² which shows that its verification necessitates more exact data than are obtained by ordinary fertiliser experiments. The Hellriegel sand culture method is advised.

Mitscherlich's method is promising, and his attempts to distinguish "outer" and "inner" surfaces in soil aggregates is worthy of attention. The condensation of moisture on the grain surface is, however, a complex phenomenon, because this surface may vary in any one experiment, from that presented by quartz sand to a typical gel, the latter of course imbibing water vapour and swelling during the experiment. It follows that any preliminary treatment of the soil affecting the soil colloids may have a corresponding influence on the value of the hygroscopic coefficient. For this reason Ehrenberg³ considered that the preliminary air-drying of the soil in Mitscherlich's method reduced the surface, especially where the percentage of humus was high; he therefore suggested the use of undried soil. Mitscherlich and Floess⁴ contend that these colloidal changes are eliminated, or at any rate rendered negligible by the establishment of the vapour pressure equilibrium when the dry soil is exposed to 10 per cent. H_2SO_4 . In a later paper⁵ they examine the Ehrenberg-Pick modification of their method and find it unreliable owing to the time required by an experiment; and, as would be expected, the hygroscopicity varies with the original water content. Changes in the surface area of the soil could not be measured.

A large amount of work on the hygroscopic coefficient has been done in America, the method used being the well-known one devised by Hilgard⁶, many years ago, in which water is employed, instead of 10 per cent. sulphuric acid. American investigators use the hygroscopic coefficient thus found not only as a measure of relative fineness of texture,

¹ *Fühling's Landw. Zig.*, 54 (1905), p. 673.

² *Landw. Vers. Stat.*, 75 (1911), p. 231.

³ *Ztsch. Angew. Chem.*, 23 (1910), p. 1841.

⁴ *Landw. Jahrb.*, 40 (1911), p. 645.

⁵ *Inter. Mittl. Bodenk.*, 2 (1912), p. 463.

⁶ *Amer. Journ. Sci.*, 7 (1874), p. 9.

and also for calculating the approximate amount of water available for ordinary crop plants, which, according to Alway¹, is the difference between total moisture content and hygroscopic coefficient. Hilgard at various times investigated the limits of accuracy of his method, which has also been studied by other workers. Contradictory conclusions have resulted from incomplete or super-saturation of the atmosphere, and the absence of any accurate control of temperature. For purposes of field observations of moisture, etc., of different soils this lack of accuracy is unimportant providing reasonable care is maintained.

Although a large amount of work has been done on the hygroscopic coefficient of soils, only a small proportion of it has aimed at ascertaining which portion of soil constituents is mainly responsible for absorbing moisture, and a still smaller proportion on the mechanism of this absorption. The idea underlying most of the investigations has been to consider the value of the hygroscopic coefficient of the soil as a whole, as a measure of the average power of that soil to absorb moisture. But it is obvious that the different portions of the soil complex may take up moisture in very different ways, as mentioned above (p. 57). There will be a certain amount of surface condensation, analogous to the deposition of surface films studied by Rayleigh², Trouton³ and others, on the non-colloidal portion of the soil; the colloidal material will give rise to a large range of adsorption and imbibition effects; and there is the probability of chemical combination, or hydration, especially in the organic matter. Luxmoore⁴ has made a good pioneering investigation on the varying factors making up the total hygroscopicity, employing for the purpose a large number of Dorset soils, and using the correlation method. The experimental methods employed were not very refined but the general conclusions to which they lead are probably correct.

He finds that the joint effect on the hygroscopic capacity of organic material and mineral particles is more than additive, and is probably due to the organic material being more effective than the coarser particles in keeping the smaller particles apart and free to exercise surface attraction. Table VII shows the amount of water found in five soils placed over atmospheres of increasing humidity, compared with the amount calculated from the contents of their respective soil fractions. It will be seen that the former is in excess in nearly every case.

¹ *Nebraska Agric. Expt. Sta. Res. Bull.*, 3 (1913).

² *Phil. Mag.*, 30 (1890), p. 285, p. 456.

³ *Proc. Roy. Soc.*, 77 A (1906), p. 292; 79 A (1907), p. 383

⁴ *Journ. Agric. Science*, 1 (1905-6), p. 304.

Table VII.

Comparison of experimental and calculated water contents for five soils over atmospheres of increasing humidity (Luxmoore).

Soil number	...	17		28		29		27		30	
		Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found
Normal Atmosphere		1.44	2.23	1.55	2.24	1.02	1.50	.51	.81	.32	.42
Moist	„ ...	2.99	3.75	2.85	3.84	2.30	2.84	1.17	1.48	.69	.82
„	„ ...	4.37	5.22	4.55	5.63	3.62	4.12	1.76	2.11	1.17	1.11
„	„ ...	4.80	6.13	5.23	6.44	4.01	4.36	1.88	2.33	1.31	1.01
Very moist	„ ...	6.21	8.00	7.23	7.72	5.86	5.65	2.62	2.39	2.15	1.14

The organic substance in different soil fractions has apparently not identical hygroscopic power, and a similar remark applies to mineral particles of the same size in different soils. While increasing fineness of particles results in an increase in hygroscopic capacity, the experimental data do not show that this increase is proportional to the additional surface presented. Luxmoore explains this by supposing that the smaller particles during their formation from the larger ones by fracture and attrition, tend to become more nearly spherical, and will therefore offer less surface than if they were reduced images of the larger ones.

The relations between the hygroscopic coefficient and the “heat of wetting” of soils have been investigated to a certain extent. This latter phenomenon has been ably studied by Müntz and Gaudechon¹. They

Table VIII.

Heat evolved on wetting a soil and its component fractions (Müntz and Gaudechon).

Soil fractions (after Kopecky)	Percentage of fractions present in soil	Heat evolved by one kilo. of each fraction	Calculated heat evolution for per- centage of fraction present
Coarse sand, > .1 mm.	11.30	0.0 kilo-calories	0.0 kilo-calories
Fine sand, .1–.05 mm.	16.52	0.26 „	0.04 „
Sandy silt, .05–.01 mm.	44.89	0.64 „	0.28 „
Clay silt, < .01 mm.	27.29	3.1 „	0.84 „
Total	100		1.16

Experimental value for the soil 1.14.

find that the greater part of the observed heat evolution when water is added to soil, is due to the clay fraction as shown in Table VIII. The organic matter weight for weight is even more effective although its effect

¹ *Ann. Sci. Agron.* (3 sér.), 4, II. (1909), p. 393.

is masked somewhat by the small percentage present in soil. The ultra-microscopic or colloidal portion of the clay is shown to be responsible for the greater amount of the heat evolved. But the phenomenon is not entirely a physical one; something else is evolved besides adsorption effects, for if the soil is moistened with alcohol, benzene, etc. instead of water, the heat evolved is small in comparison (see Table IX). If mixtures of

Table IX.

Heat evolution of soil fractions of increasing fineness in various liquids
(Müntz and Gaudechon).

No. of fraction	Heat evolved per kilo. in		
	water	benzene	toluene
1 (coarsest)	0.36	0.22	0.17
2	0.44	0.27	0.16
3	0.95	0.46	0.42
4	3.28	0.76	0.85
5 (finest)	4.84	1.28	—

alcohol and water are added, the amount of heat evolved is again considerable, and in all cases the density of the solution decreases, i.e. water is abstracted from the solution by the substance, especially when the latter is organic. Müntz and Gaudechon conclude that the heat effect is probably mainly due to chemical combination. Bouyoucos¹ studied the heat of wetting from a slightly different standpoint and arrived at conclusions in substantial agreement with Müntz and Gaudechon. Mitscherlich² did some preliminary work on the relation between heat of wetting and the hygroscopic coefficient of the soil, but could find no apparent connection. The whole subject could profitably be re-opened in the light of present knowledge of colloidal phenomena.

(C) ATTEMPTS TO OBTAIN A MORE COMPLETE THEORY OF SOIL MOISTURE RELATIONS.

A salient point brought out by a study of the above sub-sections is that each one is more or less detached from its neighbours. It has been recognised for some time that this division of soil moisture fails to give a complete picture of the *continuous* processes operative between the soil and its moisture content when the latter changes over wide limits. This has led to a number of investigations—mainly by American workers—in which an attempt is made to give more precision to the relation of varying moisture content to soil texture and plant growth.

¹ *Mich. Agric. Coll. Tech. Bull.*, 42 (1918).

² *Journ. Landw.*, 46 (1898), p. 255; 48 (1900), p. 71.

These investigations have followed, in the main, two lines. The divisions of soil water discussed in the preceding paragraphs, have been amplified by additional "equilibrium values" of soil water under defined conditions, and attempts have been made to discover inter-relationships between these values.

Among these investigations may be mentioned those on the "wilting coefficient"—defined as the amount of water remaining in the soil when permanent wilting of the plant occurs—by Briggs¹ and others, in which an attempt is made to correlate the requirement of the plant for water and the power of the system soil plus water to supply it; the "moisture equivalent," also due to Briggs² and fellow workers, defined as the amount of water retained in soil after subjection to a centrifugal force, 3000 times the gravitational force. This force is supposed to remove the water held in the larger capillary spaces of the soil; the amount of water then remaining—the moisture equivalent—gives a better quantitative comparison of soils than the water retaining capacity mentioned above. This amount of water is correlated with the soil texture as determined by the usual mechanical analysis. It is found that for a typical and well defined series of soils in which the material is mainly derived from the same geological source, the relation existing is given by the equation:

$$0.4 C + 0.59 D + 0.53 E = M \pm 1.1,$$

where M = moisture equivalent,

C = percentage of particles .05–.005 mm. in diameter,

D = ,, ,, below .005 ,, ,,

E = ,, ,, organic matter.

For other series of soils, the values of the numerical coefficients are, of course, different.

The influence of particles of larger size than group C is apparently very small and may be neglected. A change of 50 per cent. in the amount of coarse sand amounts generally to a change of only 1 per cent. in the moisture equivalent. Further work on the relation between the moisture equivalent and the mechanical analysis seems to show that no general formula is universally suitable, a modification having to be made for each soil type. This has been pointed out by Alway³ in a paper embodying an examination of Briggs and Shantz⁴ indirect methods for determining

¹ Briggs, L. J. and Shantz, H. L. *U.S. Bureau Plant Ind., Bull.* 230 (1912).

² Briggs, L. J. and McLane, J. W. *U.S. Bureau of Soils, Bull.* 45 (1907).

³ *Journ. Agric. Res.*, 6 (1916), p. 833.

⁴ *Loc. cit.*

the wilting coefficient. The latter investigation resulted in a series of ratios for the indirect calculation of the wilting coefficient from either the mechanical analysis, moisture holding capacity, moisture equivalent or hygroscopic coefficient (Table X). Alway, in the paper cited, examined the various indirect values for the hygroscopic coefficient,

Table X.

(Briggs and Shantz.)

(The second term in the brackets shows the probable error of the relationship.)

$$\begin{aligned}\text{Wilting coefficient} &= \frac{\text{moisture equivalent}}{1.84 (1 \pm 0.007)} \\ &= \frac{\text{hygroscopic coefficient}}{.68 (1 \pm 0.018)} \\ &= \frac{\text{moisture holding capacity}^1 - 21}{2.90 (1 \pm 0.021)} \\ &= \frac{0.01 \text{ sand} + 0.12 \text{ silt} + 0.57 \text{ clay}^2}{(1 \pm 0.025)}\end{aligned}$$

¹ Hilgard's method. *Soils* (1906), p. 209. New York.

² { Sand .2-.05 mm. in diameter.
 { Silt .05-.005 " "
 { Clay <.005 " "

obtained by proportionally altering the above ratios in the necessary manner, and showed that caution was necessary in their use, owing to the influence of soil type on the ratios. Other results of Alway¹ cast doubts on the validity of the conception of a wilting coefficient, in its original form at least, because it is shown that plants can utilise approximately all the water in soil down to the hygroscopic coefficient, which, according to the above mentioned ratios of Briggs, is only about .7 times the wilting coefficient. Some results obtained by Shull, and Bouyoucos, and referred to in more detail later point in the same direction².

Alway and McDole³ have established a series of relations between the moisture equivalent, the hygroscopic coefficient, and the water retaining capacity. They find with certain loams of known hygroscopic coefficients, that the amount of water retained bears a relation to the hygroscopic coefficient, being from 2.1 to 3.1 this value according to the particular

¹ Ref. 1, p. 58.² For a detailed summary of work on the wilting coefficient, which lies rather outside the scope of the present paper, see V. H. Blackman (*Journ. Ecology*, 2 (1914), p. 43). The papers of Alway and Shull should also be read in this connection.³ *Journ. Agric. Res.*, 9 (1917), p. 27.

soil (Table XI), while its relation to the moisture equivalent is somewhat closer—0.8 to 1.01 (Table XII). An important result, shown by Table XI,

Table XI.

Ratio of water content to hygroscopic coefficient for five soils, arranged in 2" layers and in different orders in a draining cylinder (Alway and McDole).

Order of soils	Ratio	Order of soils	Ratio
L	2.1	A	2.4
J	2.4	D	3.1
H	2.9	H	3.0
D	3.1	J	2.5
A	2.3	L	2.1

Table XII.

Ratio of final water content in the surface 3" section of loams to the moisture equivalent (Alway and McDole).

Soil	Final water content 1-3 ins.	Moisture equivalent	Ratio	Soil	Final water content 1-3 ins.	Moisture equivalent	Ratio
A	26.2	29.5	0.88	H	17.1	19.7	0.87
B	24.2	25.8	.94	I	15.1	16.8	.90
C	22.2	24.1	.92	J	11.7	13.5	.87
D	22.9	27.8	.82	K	7.4	7.5	1.00
E	19.6	22.5	.87	L	5.8	7.2	.86
G	16.8	21.2	.80	M	8.0	7.9	1.01

is that if a draining soil column is made up of successive layers of soils differing in texture, the order of their arrangement exerts no influence on the final water content of each layer. An apparent anomaly is shown when a layer of coarse sand or gravel is interposed in the soil column. The layers of soil above the sand then show a higher moisture content than when they are in direct contact with the subsoil into which drainage takes place. It is well known that a gravel or sand subsoil in the field tends towards a better drainage of the surface soil. Any considerable mass of water in the surface soil is able to escape more quickly, other things being equal, owing to the larger size of the pores in the gravel subsoil. But when the moisture content is sufficiently reduced to bring the capillary pull into prominence in distinction to the mere gravitational drainage, then the layer of coarse sand effectively breaks the capillary tubes and the downward movement of the water is slowed up very considerably. If these results are correct the logical conclusion would be that the effect of a sand layer is to cause a more rapid initial drainage

from a wet soil, but to leave a higher final moisture content in the surface soil. On the other hand, a finer textured subsoil, although giving a slower rate of initial drainage, will give a lower final value for the surface soil moisture owing to the persistence of the capillary pull in the subsoil.

It will be seen that while most of the above investigations attempt to define, either completely or partially, the relations between the soil and the moisture content, they are mainly applicable over some small range of moisture content, or to some approximate equilibrium value. These values are of course interesting and important, but they do not lead to any clear conception of the laws holding between the soil and its water content, when the latter varies between and through these equilibrium values. Investigations of a different type are necessary for this purpose, and the most promising lines are summarised in the succeeding section.

(D) SURFACE FORCES IN SOILS AND THE COLLOIDAL HYPOTHESIS.

It will be realised from the facts presented in the preceding sections that any consistent explanation of the varying facts observed must take into account the intimate relations existing between soil moisture and the soil grains over a wide range of water content. It cannot be said as yet that we have a complete knowledge of these relations, and the various papers mentioned in this section should be regarded as indicating lines along which the problem may be attacked.

By far the most important soil constituents in any examination of surface forces are the clay and the humus. Recent work of Tempary¹, in which the shrinkage was measured of various soils, previously moistened and worked into a condition of maximum plasticity, gives a valuable insight into the connection between colloidal portions of the soil and the water content. A linear relation is found to exist between the linear shrinkage and the pore space in the contracted (oven-dried) soils, for soils of widely differing mechanical analyses (Fig. 2). The pore space in the contracted soil decreases with increasing content of colloidal clay. Tempary's method enables an estimate to be made of the amount of total clay which exists in the colloidal state, provided certain probable assumptions are made, for which the original paper should be consulted. The percentage works out to a much greater value than that given by the earlier methods of Schloesing² or the later determinations on the same lines by Ehrenberg and Given³, where the amounts are about 1 per cent.

¹ *Journ. Agric. Sci.*, **8** (1916-17), p. 312.

² *Encyclopédie Chimique*. Frémy (Paris, 1885), **10**, p. 67.

³ *Koll. Zeit.*, **17** (1915), p. 33.

only (see Table XIII). In this latter method the clay is acidified and washed to remove calcium and magnesium salts, and then allowed to settle over a long period in water to which a little ammonia has been added. The colloidal material remains in the supernatant liquid. These sedimentation methods, however, do not give a quantitative value for the amount of colloidal material present in clay. On the provisional hypothesis mentioned earlier, that the soil grains are coated more or less

Fig. 2. Relation between pore space and linear shrinkage (Tempany).

with colloidal material, one would not expect more than a fraction of it to remain in suspension. A considerable amount undoubtedly remains on the grain surface. Apparently no examinations have been made by any investigators of the clay after this 1 per cent. colloidal material has been removed, to see if any great alteration has taken place

in its properties. A determination on these lines would show at once whether the 1 per cent. in suspension represents the bulk or only a fraction of the colloidal clay.

Table XIII.

Proportion of total fine silt and clay, and colloidal clay in various soils (Tempany).

Soil	Linear shrinkage per cent.	Content of fine silt and sand as determined by Osborne's beaker method ¹ per cent.	Content of colloidal clay calculated from linear shrinkage per cent.
A	13.0	59.3	55
B	12.1	60.6	51
C	8.8	45.0	37
D	6.0	42.1	25
E	2.9	33.5	12
1	2.0	32.3	9
2	2.7	25.0	11
3	3.1	28.6	13
15	14.0	63.0	60
16	15.0	70.5	64

¹ { Fine silt .01-.005 mm. in diameter.
 { Clay <.005 " "

A knowledge of the amount of colloidal clay present in soils is certain to be of great use in studying soil relationships. For instance the effect of the small amount of pore space in a soil containing a high percentage of colloidal clay, will be operative over a wide range of moisture content, down to oven dryness, in modifying the movement of water and water vapour in the soil interstices. And again, a large amount of water will be present in the clay-gel, thus existing under very different conditions from the so-called "free water" in soil.

A study of the evaporation of water from this aspect has been made by the present writer¹. It is shown that evaporation from soil and sand is very different in character. From the latter evaporation proceeds in accordance with the known laws of diffusion, and the results confirm the deductions of Briggs² and Leather³ in which the soil is regarded as a framework of mineral particles. But when proper experimental methods are employed the evaporation from soil follows a very different course. A mathematical examination of the evaporation curves shows that two factors are operating over the whole range of water content. Judging by the hygroscopic coefficients of those American soils comparable with

¹ *Journ. Agric. Sci.*, 6 (1914), p. 456.

² *U.S. Bureau of Soils, Bull.* 10 (1897).

³ *Loc. cit.*

the soils used in the writer's experiments, the initial percentage of water present was considerably above the hygroscopic coefficient, which therefore must be regarded as an equilibrium value of moisture content, and not solely as an expression of water present in one definite physical state. The controlling factor in the evaporation of the soil moisture is apparently not the organic matter *per se*, as the removal of the "soluble humus" by 2 per cent. NaOH makes very little difference. But when the colloidal property of the clay is destroyed by igniting the soil to a dull red heat the evaporation curve becomes identical with that given by sand, in spite of the fact that the ignited soil still contains a large number of very small particles¹. It is in all probability the clay fraction, which, owing to its colloidal nature, profoundly modifies the process of evaporation. The effect is expressed in the equation deduced for the rate of evaporation by an expression of an exponential type, which, until further data are obtained on the relations existing between water content and other physical factors such as vapour pressure, must be regarded as empirical. The curve given by this empirical expression does not exactly fit the experimental one until allowance is made for the effect of the diminishing surface from which evaporation proceeds as the thickness of the moisture film diminishes. When this is done very good agreement is obtained over the whole range of moisture content used in the experiments. The actual general equation developed to express the two factors discussed above is:

$$B \frac{dw}{dt} = \sqrt[3]{\left(\frac{ws}{100} + 1\right)} [2.303 \log (w + K) - \log_e K]$$

where $\frac{dw}{dt}$ = time rate of evaporation.

w = moisture content (percentage on dry weight of soil).

s = specific gravity (true) of the soil.

B and K = constants for each type of soil used.

These results show that there is an intimate connection between the soil complex and its moisture content over a wide range. Some very interesting work of Shull² on the surface forces in soils emphasises this aspect of the question. Using Xanthium seeds, which have almost a perfect semi-permeable coating, and rapid moisture equilibrium adjustment, he obtained two sets of data: (1) by suspending the dry seeds over the vapour of sulphuric acid and water mixtures of varying strengths, employing Walker's equation³ for the relation between vapour and

¹ The soils used in these experiments when ignited gave, on shaking the bottle, a cloud of fine particles, which floated away like smoke when the stopper was removed.

² *Bol. Gaz.*, 62 (1916), p. 1. ³ *Introduction to Phys.-Chem.* 7th ed. 1913. Macmillan.

osmotic pressures, he obtained the corresponding osmotic pressures for varying water content of the seeds when in equilibrium with the vapour; (2) the dry seeds were allowed to come to moisture equilibrium with soil moistened to different degrees, arrangements being made to ensure that the seeds came into contact in turn with every part of the moist soil. Having determined the percentages of moisture in the soil and seeds when equilibrium is attained, the corresponding osmotic pressure of the soil moisture at varying water contents is obtainable at once from the first set of data. Shull finds great differences in the surface forces for soil and sand. The surface forces for the soil used are of the order of a few atmospheres only, down to about 20 per cent. of water. At this point there is a rapid increase, until at a moisture content of 10 per cent. it is about 1000 atmospheres. Sand shows this rapid increase only at very low percentages when the surface film effect comes into play.

An indication of the value of an investigation such as the above may be gained by applying the results to the percentage of moisture in the soil at the wilting-coefficient. Shull shows, firstly, that the seeds take up nearly as much water at the wilting coefficient, as when placed directly into water, and that secondly, the force with which the soil particles withhold moisture from seeds (and plants) is not more than 3-4 atmospheres, whereas the average root-cell sap pressure at this point is about 7-8 atmospheres. The plant wilts although both the amount and pressure gradient of the soil moisture are in its favour. Shull concludes that the wilting coefficient therefore must be regarded as a measure of the water in the *plant* and not in the soil at the time of wilt. The cause of wilting is due to the slow movement of the soil moisture, the rate falling below that necessary to maintain turgidity of the cells of the aerial parts even under conditions of low transpiration.

These experiments of Shull, while showing that the surface forces existing between soil and water are considerable over a wide range of moisture content, are not in themselves conclusive proof that the colloidal nature of soil is mainly responsible for the observed effects. However, by attacking the problem from a different point of view, Bouyoucos¹ and fellow workers have obtained a large number of interesting data, the interpretation of which requires a recognition of the intimate relations between the soil complex and its moisture content. These papers fall naturally into two sections, the first dealing with the expansion of a

¹ The various papers discussed in this connection appear in *Michigan Agric. Coll. Expt. Station Technical Bulletins*, Nos. 24 (1915); 31 (1916); 36 (1917); 42 (1918); and in the *Journ. Agric. Res.*, 8 (1917), p. 195; 15 (1918), p. 331.

moist soil when freezing occurs, and the second, on the lowering of its freezing point under different conditions. In the first series a dilatometer was used, the moist soil being introduced into the bulb which was then closed and the free space filled up with ligroin. The dilatometer was then cooled down to definite temperatures, and from the observed rise in level of the ligroin, the amount of water freezing at any given temperature could be calculated at once. The method has been employed by Foote and Saxton¹ with inorganic hydrogels and they find that by no means all of the water present can be frozen at temperatures slightly below 0° C. In fact some of the water present could not be frozen even at as low temperature as - 78° C. The experiments led to the conclusion that the water could be broadly divided into three divisions: free water, capillary-adsorbed water and combined water. There was no definite line of demarcation between these three groups and more or less arbitrary temperature depressions were taken in classifying the total water content into the divisions, but the experiments clearly indicate that the forces existing between the water and the substances used are of a very close and intimate character.

Bouyoucos finds that similar conditions hold for soil, although the relative amounts of the three groups vary considerably. In sandy soils, for instance, the free water appears to predominate largely, the remainder being almost entirely combined water. In loams and silt loams the same conditions hold except that more water is present in the combined form, while in soils containing much clay and humus, the division is more equal among the three postulated groups of water content. Bouyoucos could obtain no quantitative agreement between the amount of water that failed to freeze, and certain of the experimental characteristics of soils, such as the mechanical analysis, moisture equivalent, hygroscopic coefficient and wilting coefficient, although in some cases, notably the last two, a qualitative agreement was found. This discordance is by no means surprising in view of Tempany's experiments, mentioned above, on the varying proportion of colloidal clay present in the clay fraction of soil, and when it is realised that such measurements, as the hygroscopic coefficient for instance, attempt to give a single-valued expression to what is in reality a complex set of variables.

Bouyoucos' second line of research—the depression of the freezing point of the soil-solution measured *in situ*—also indicates that very different relations exist between soil and its moisture content from those between sand and water. These experiments were done in the usual

¹ *Journ. Amer. Chem. Soc.*, 38 (1916), p. 588, and 39 (1917), p. 1103.

Beckmann apparatus, both on soil extracts and on the actual moist sands and soils themselves, i.e. on the soil solution *in situ*. The results show that for moist sands the product of the freezing point and the percentage of moisture is approximately a constant, in other words, the depression is inversely proportional to the concentration. Soils show a different behaviour, the freezing point depression increasing very rapidly with decrease in moisture content. The approximate relation is that the depression increases in geometrical progression as the moisture content decreases in arithmetical progression. The authors advance possible qualitative explanations of this difference, by assuming that in soils, part of the water is rendered unfree, in the sense that it takes no part in the freezing point depression of the soil solution, as measured by the Beckmann apparatus. The present writer¹ has been able to give this hypothesis a quantitative basis, and has shown by an examination of their experimental data that the total moisture, free, and unfree water are related by the equations:

$$Y_n = aM_n^x,$$

$$Z_n = \frac{1}{a^{\frac{1}{x}}} \cdot Y_n - Y_n,$$

where M_n = total moisture,

Z_n = unfree „

Y_n = free „

x and a = constants.

The terms “free” and “unfree” in these expressions are used with the meaning Bouyoucos assigns to them: the free water contains in solution the various soluble salts, and follows the law for dilute solutions, viz., that the freezing point depression varies inversely as the concentration: the unfree water takes no part in the depression of the freezing point. It is pointed out by the present writer in the paper on the above quantitative relations that these definitions are provisional only, until further information is obtained on the possible physical—or chemical—differences in the two cases.

All the experiments discussed above have a direct bearing on the soil solution considered as the nutrient medium for plant growth. They show that the soil and soil solution are bound together by intimate relationships. A change in the moisture content is reflected in the resulting alteration of all the complex variables involved. Consequently,

¹ Keen, B. A. *Journ. Agric. Science.* 9 (1918–19), p. 400.

conclusions based on an examination of soil solution *after it has been removed from the soil*¹ cannot be regarded as necessarily quantitative, and it is open to doubt whether they are always qualitative. As a result some considerable controversy has been aroused, which has mainly centred around the deductions of Whitney and Cameron², that the soil solution is very dilute and practically constant in composition. It is hardly necessary in the present paper to give an account of the various views expressed, as this has been done elsewhere³. The point which really needs emphasis in all studies of the soil solution is the recognition that the system soil + soil solution must be treated as a whole. This point is brought out in all the experiments discussed in this concluding section of the present paper. The relations between the soil and its moisture content are exceedingly complex, and considerations of surface films distributed over an inert mineral framework, such as sand-grains, are insufficient to explain the observed facts, for they give rise, as already noted in Sections (B) and (C) above, to a classification of soil moisture into more or less arbitrary and water-tight compartments.

On the other hand the papers discussed in this concluding section are characterised by the development of continuous relations between the soil and its moisture content. Study of the soil from the colloidal point of view appears to be the most promising way of obtaining further knowledge of these vital, but intricate, relationships.

¹ Summaries of the various methods of extracting soil solution are given by Stiles and Jørgensen (*Journ. Ecology*, **2** (1914), p. 245, and Bouyoucos (*Mich. Tech. Bull.*, **24** (1915)).

² *U.S. Bureau of Soils, Bull.* **22** (1903).

³ A full account of work on the soil solution is given by E. J. Russell, in *Soil Conditions and Plant Growth*, 3rd ed. (1917), p. 104. Longmans. See also, by the same author, *Chem. Soc. Ann. Reports*, **15** (1918), p. 172 ("Agricultural Chemistry and Vegetable Physiology"), in which are discussed experiments at the University of California, giving results in opposition to the views of Whitney and Cameron.

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