SECTION II.—PAPERS AND DISCUSSION ON "SOIL MOISTURE".

THE SYSTEM SOIL—SOIL MOISTURE.

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The system soil-soil moisture is exceedingly complex. On the one hand there is the soil—a mass of particles of all shapes and sizes, of varying chemical composition, and intimately associated with both organic and inorganic colloidal materials; on the other hand there is the soil moisture, holding in solution certain substances, some of which are essential, others detrimental, to plants and organisms. The system as a whole is subject to ever-changing meteorological conditions, as well as the effects of growing vegetation and organisms, and, at frequent intervals, abrupt changes in many factors occur owing to manurial and cultivation operations. Practically all of the factors are interdependent—if one of them changes, the remainder will also change in the necessary amount to suit the new conditions.

Another way of stating this is that soil phenomena are dynamic in character, not static.

When the relations between the soil and its moisture content were first examined the obvious hypothesis to take as a starting point was that the moisture was distributed in a thin continuous film over and around the soil particles. This view was eventually set out by Briggs (1) over twenty years ago, who treated the water films from the standpoint of the surface tension over their curved surfaces. This treatment is closely modelled on the well-known experiments of Reinold and Rücker (2) on soap bubbles which hardly need further mention here. It is instructive, however, to consider one case. Imagine a long row of wet spheres each of the same radius and touching one another, and let the row be raised from a horizontal to a vertical position. The liquid will drain downwards and drip from the bottom sphere. When equilibrium is established, the curvature of the annular ring of water between adjacent spheres will diminish, and the actual volume of this ring will increase from top to bottom of the row, the difference of pressure between adjacent rings being that necessary to support the weight of the film connecting them. Hence in a cylinder of moist soil, made up of coarse particles, there is a progressive increase in moisture content from top to bottom; in a finer soil this gravitational effect is much less marked owing to the smaller interstices between the grains. For each case, however, and for a given depth of soil, a distinction can be drawn between gravitational water, which drains away under the action of gravity, and capillary water, which is capable of movement over the soil particles under the forces of surface tension, whenever the equilibrium is disturbed. Briggs further distinguishes hygroscopic water, which, as the name implies, is the
thin film of condensed vapour deposited on soils when in the presence of water vapour. This hygroscopic moisture is held with considerable force, and is presumed to be incapable of movement under capillary and gravitational forces.

The classification of soil moisture into hygroscopic, capillary and gravitational water is too broad to afford a clear picture of the moisture relationships in most soils, and it suffers from the defect that a soil is regarded essentially as a mass of sand grains which functions mainly as an inert framework over which the moisture film is distributed. A perusal in chronological order of the literature on soil moisture clearly shows—although explicit reasons were seldom given—that investigators considered the classification incomplete, and attempts were made to remedy this. Two courses were possible: to examine the above three divisions of soil water in greater detail, or to introduce a number of "equilibrium points" which would give a certain precision to the relations between the soil and its moisture content, when the latter varied over a wide range.

Taking the "equilibrium points" first, we may mention the "moisture equivalent" introduced by Briggs and McLane (3), and the "wilting coefficient" due to Briggs and Shantz (4). The former is defined as the amount of water retained in soil previously saturated, when subjected 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 remaining—the moisture equivalent—gives a single figure which expresses the power of a given soil to retain water under these conditions. Comparison of different soils on this basis is relatively simple. The moisture equivalent shows up the effect of both organic material and the clay fraction in increasing the water-holding power of the soil, and therefore gives more precision to the relations between soil and water:

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Moisture Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vernon sand</td>
<td>3.6</td>
</tr>
<tr>
<td>Vernon fine sand</td>
<td>4.3</td>
</tr>
<tr>
<td>Vernon sandy loam</td>
<td>10.3</td>
</tr>
<tr>
<td>Vernon fine sandy loam</td>
<td>12.3</td>
</tr>
<tr>
<td>Vernon silt loam</td>
<td>19.8</td>
</tr>
<tr>
<td>Vernon clay (loam)</td>
<td>23.1</td>
</tr>
</tbody>
</table>

The method apparently does not suffer to any appreciable extent from the defect of many methods of soil examination—the disturbance of the packing of the soil grains as it exists in the field. This disturbance mainly affects the larger pore spaces, but not necessarily the smaller ones associated with the soil aggregates or compound particles, and as we have seen it is these latter which are of importance in the determination of the moisture equivalent.

The "wilting coefficient" is an attempt to correlate the requirement of the plant for water and the power of the system soil plus water to supply it. The assumption is that the roots of any given variety of plant can exert a definite maximum pull on the soil moisture, which will be given up by the soil to the roots less and less readily as the moisture content of the soil decreases. Eventually a point will be reached at which the soil will not part

1 This value was chosen as the most convenient after a series of experiments with different speeds of centrifuging. Over a fairly wide range a linear relation existed between the moisture equivalent and the reciprocal of the centrifugal force.
with further water and the plant wilts. The percentage of water in the soil when permanent wilting of the plant occurs, is defined as the "wilting coefficient". Like the moisture equivalent the wilting coefficient increases with increasing fineness of the soil particles, and under the experimental conditions which Briggs used, it is largely independent of the kind of plant used, and has a value a little over half the figure for the moisture equivalent:

<table>
<thead>
<tr>
<th>Fine sand</th>
<th>Fine sandy loam</th>
<th>Clay loam</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.59</td>
<td>9.66</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Wilting Coefficient for Kubanka Wheat (Briggs and Shantz) in

It will readily be seen that if these two "equilibrium coefficients" be true ones, they will help considerably in forming a mental picture of the relations between the soil and its moisture content. The wilting coefficient has been investigated both by Alway (5) and Shull (6) among others, who give reasons to doubt the validity of its conception—at least in its original form. Alway showed that plants could live in soil containing less water than the wilting coefficient if the atmospheric conditions were modified; they could in fact utilise the water down to the hygroscopic coefficient, which as we shall see later is, according to Briggs, only \( \frac{7}{2} \) times the wilting coefficient.

Shull's work was undertaken to find some means of measuring the force with which particles of soil of varying fineness retain moisture at different degrees of dryness, and to obtain information on what may be called the "back-pull" of soil when its moisture content is so low as to be unavailable to growing plants. Special interest, therefore, centres in the conditions occurring in the region around the wilting coefficient. Advantage was taken of the discovery of Brown (7) and others, that certain seeds have semi-permeable coats, and Xanthium seeds were taken because of their rapid establishment of moisture equilibrium after a disturbance. The experiments fell into two sections. First of all, the amount of water taken up by air-dry seeds under various osmotic pressures was determined. This was done either by immersing the seeds in salt solutions of known osmotic pressure, or by suspending the seeds over the vapour of sulphuric acid of known strengths and then calculating the corresponding osmotic pressure of the acid by means of Walkers' equation connecting osmotic and vapour pressures. These experiments gave values for the osmotic pressure at different moisture contents of the seeds.

The second group of experiments consisted in allowing the dry seeds to come to moisture equilibrium with soil, moistened to different degrees. Having determined the percentage of moisture in the seeds and soil when equilibrium was attained, the corresponding osmotic pressure of varying percentages of soil moisture is obtained at once from the first set of data. Comparison of the results in the region of the wilting coefficient leads to some interesting conclusions: firstly, seeds take up nearly as much water from soil whose moisture content is equal to the wilting coefficient as they do when placed direct into water, and, secondly, in soil at this moisture content, the osmotic pressure is not more than 3.4 atmospheres. Now the average root-cell sap pressure is 7-8 atmospheres. The plant wilts, therefore, although both the amount of soil moisture and pressure gradient are in its favour. The explanation of this apparent anomaly is that evaporation continues from the leaves of a plant somewhat regardless of the conditions below the soil surface. At the wilting coefficient the rate of movement of soil water falls below that
needed to maintain the turgidity of the aerial parts of the plant, which consequently wilts.

The conclusion to be drawn from the work of Alway and Shull discussed above is that the wilting coefficient is not a definite constant for a given soil but is made up of complex factors in which the soil, the plant, and the atmospheric conditions all enter.

Leaving for the moment questions dealing with the wilting point and moisture equivalent, we will briefly consider the other direction in which attempts were made to remedy the incomplete nature of the classification of soil moisture into hygroscopic, capillary, and gravitational divisions. This was an examination of the divisions in greater detail. The hygroscopic water has been studied by many workers (8) most of whom have considered the soil as a whole, and taken the value of the hygroscopic coefficient as a measure of the power of that soil to absorb water vapour. Little work has been done on the relative absorbing powers of different portions of the soil complex. Yet it is obvious that different portions may take up water in very different ways. There may be surface condensation on the non-colloidal portion, adsorption and imbibition by the colloids, and chemical effects, such as hydrolysis, especially with the organic matter. Hygroscopicity is therefore a complex phenomenon, but, in view of the importance now attached to the colloidal properties of soil, the subject could profitably be re-opened. There is ample scope for work in at least two directions: firstly the development of similar statistical studies to those of Luxmoore (9) on Dorset Soils, in which the hygroscopicity of a large number of soils is correlated with other physical properties; and secondly, an extension of Mitscherlich's (10) investigations on the amount of vapour absorbed by soil placed over a number of different liquids. Mitscherlich uses 10 per cent. sulphuric acid, and one of various organic liquids of high molecular weight. The vapour of the latter is supposed to condense only on the outer surface of the compound particles, or soil crumbs, whereas the water vapour from the sulphuric acid condenses both on the outer and internal surfaces of the crumbs. Comparison of the two values for different soils enables an estimate to be made of the extent to which the soil is aggregated into compound particles, and the method, therefore, is likely to be of use in extending our present scanty knowledge of the relation between good tilth and the formation of compound particles. At the same time a parallel series of experiments could be done on the "heat of wetting," following the work of Müntz and Gaudechon (11). These workers found that the greater part of the heat evolution when water was added to dry soil was due to the colloidal portion of the clay.

Heat Evolved on Wetting a Soil and its Component Fractions.
(Müntz and Gaudechon.)

<table>
<thead>
<tr>
<th>Soil Fractions (after Kopecky)</th>
<th>Percentage of Fractions Present in Soil</th>
<th>Heat Evolved by 1 Kilo. of each Fraction</th>
<th>Calculated Heat Evolution for Percentage of Fraction Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse sand &gt; 1 mm.</td>
<td>11.30</td>
<td>0.00 kilo-calories</td>
<td>0.00 kilo-calories</td>
</tr>
<tr>
<td>Fine sand &gt; 0.05 ins.</td>
<td>16.52</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>Sandy silt &gt; 0.05-0.01 mm</td>
<td>44.89</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>Clay silt &lt; 0.01 mm.</td>
<td>27.09</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Total . .</td>
<td>100</td>
<td></td>
<td>1.16</td>
</tr>
</tbody>
</table>

Experimental value for the soil 1.14.
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The organic matter, weight for weight, was even more effective, but the major portion of the heat evolution is due to the clay, owing to the small amount of organic material present in most soils. Mitscherlich (12) did some work on the relation between heat of wetting and the hygroscopic coefficient of soils, but could find no apparent connection. The whole subject could profitably be reopened in the light of present knowledge.

The hygroscopic water, although of great importance in physical studies of soil, is not directly of use to growing plants, and probably for this reason the next division of soil water—the capillary film—has received more attention. Both the wilting coefficient and the moisture equivalent already mentioned lie in this region. Special interest attaches to the lower, and to a lesser degree the upper limits of capillary water. The former limit has been examined by Widtsoe and McLaughlin (13) in connection with irrigation studies in Utah. As already mentioned, a soil containing water only slightly in excess of the hygroscopic coefficient supports plant life with difficulty, and, on the water film hypothesis of soil moisture, this is because the movement of water in the soil is very slow at this moisture content. Widtsoe and McLaughlin consider that the point at which moisture movements become very sluggish can be ascertained from determinations of moisture content after irrigation. They call this point the "lento-capillary point" and define it as "the point at which capillary movements largely cease, and at which plant roots must secure water through greater effort, by actual contact with the water holding particle, or possibly by thermal transference of water".

In addition to the hygroscopic coefficient and the lento-capillary point, Widtsoe and McLaughlin also define the "maximum capillary water capacity" and the "optimum capillary water capacity" or field water capacity. Water present in excess of the former—which has a value of 24 per cent. for the soil used—is assumed to be free water, while the latter represents the amount of water found in the irrigated soil when full distribution has occurred. Its value is about 18 per cent. for the soil used, and it indicates the most favourable percentage of moisture for plant growth. Practical men recognise a comparatively narrow range of moisture content for any given soil, within which plants attain their maximum development; below this range there is insufficient water, and above it the additional water necessarily restricts the air supply.1 The optimum capillary water capacity is an attempt to give a physical significance to this value. Numerous studies have been made on it, among which the work of Cameron and Gallagher (14) may be mentioned. They had the help of several experienced greenhouse men, to decide by inspection when each soil was at its "optimum moisture content" for plant growth. Various physical properties, such as apparent specific gravity, cohesion, penetrability, rate of evaporation of water, and so on, were measured for each soil at different moisture contents, and the results indicated that these properties passed through either a maximum or a minimum at the optimum moisture content.

In addition to the various constants already mentioned, there is a further one, known as the "maximum water capacity". This is simply a measure of the pore space in the soil, under the experimental conditions. The best known method is that devised by Hilgard (8) which consists essentially of saturating a thin layer of soil, from below, to expel as much air as possible, and measuring the increased weight due to the water. The

1 The influence of soil aeration on plant growth has been studied by A. Howard and G. L. C. Howard. See Bulls. 52 (1915); 61 (1926), Agric. Res. Inst., Pusa.
value is always in excess of the maximum found in the soil under field conditions, for obvious reasons.

The original divisions of soil moisture and the further sub-divisions and equilibrium points may be diagramatically represented as follows:

![Diagram of soil moisture and equilibrium points]

Obviously, there has been considerable elaboration of the original divisions, but a general criticism of the scheme can yet be made: the additional divisions and equilibrium points have no very obvious relations with each other—they resemble a series of water-tight compartments—nor is there any clear indication of the relations between the soil and the moisture content. Attempts were made to remedy this. The work of Cameron and Gallagher, already mentioned (14), brought out the interesting point that the moisture equivalent was very approximately equal to the optimum moisture content. Briggs and his collaborators (3; 4) introduced a series of cross relations between some of the equilibrium points, and studied the effect of the soil type upon them. They arrived at the series of relations shown:

\[
\text{Wilting coefficient} = \frac{\text{moisture equivalent}}{1\cdot84(1 \pm 0\cdot007)} - \frac{\text{hygroscopic coefficient}}{0\cdot68(1 \pm 0\cdot018)} - \frac{\text{moisture holding capacity } (a) - 21}{2\cdot90(1 \pm 0\cdot021)} - \frac{0\cdot01 \text{ sand } + 0\cdot12 \text{ silt } + 0\cdot57 \text{ clay } (b)}{(1 \pm 0\cdot025)}.
\]

(b) Sand \(0.2\) to \(0.5\) mm. in diameter.
Silt \(0.05\) to \(0.005\) " " "
Clay \(<0.0025\) " " "

The primary purpose of these ratios was to enable the wilting coefficient—a troublesome thing to determine experimentally—to be calculated from more easily obtained soil constants, the tacit assumption being made that a linear relationship exists between the variables. A similar assumption
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led to the following expression connecting the moisture equivalent with the type of the soil as defined by its mechanical analysis:

\[ 0.4 C + 0.59 D + 0.53 E = M \pm 1.1 \]

where

- \( M \) = moisture equivalent
- \( C \) = percentage of particles \( 0.05-0.005 \) mm. in diameter
- \( D \) = " " " " " " below \( 0.005 \) " " " " " " organic matter.

The soils to which this equation refers are a typical and well-defined series derived mainly from one geological source. For another series the coefficients, in general, have a fresh set of values, although these referring to the clay fraction \( D \) and the organic matter \( E \) do not differ greatly from one another. This indicates that clay and organic matter weight for weight have equal influence on the moisture equivalent. The influence of particles of larger size than group \( C \) is very small—a change of 50 per cent. in the amount of coarse sand resulting in a change of 1 per cent. in the moisture equivalent.

These attempts of Briggs to link into a coherent whole the various divisions and equilibrium points have been subjected to criticism. It could hardly be expected that a series of cross relationships based on the assumption of a linear relation between the variables would suffice to specify the complex system soil–soil moisture, but a certain degree of approximation might be expected in some cases. Alway and his collaborators (15) have already made a long series of valuable studies on the subject, and typical papers are given in the attached bibliography. It is impossible to give an adequate summary of them here; they are mainly concerned with the relations of the soil constants mentioned above, to the amounts of water found, and its rate of movement in the soil under certain conditions. Those who wish to pursue the matter further will find a discussion of Alway's results in a recent paper by the present writer (16). Generally speaking, the results show, as in the case of the wilting coefficient mentioned earlier, that the equilibrium points and sub-divisions need to be interpreted with caution, because they are not necessarily by themselves a reliable specification over the wide range of moisture content met with in soil.

However, if the constants are to have any significance at all, beyond a somewhat indirect and qualitative physiological one, some fundamental hypothesis must be found which shall account for them all and, at the same time, show their relationships to the behaviour of moisture under field conditions.

Taking a broad view of the problem it is suggestive to treat the movement of moisture in soil on analogous lines to the flow of heat and electricity. This implies the existence of a capillary transmission constant, or potential factor, which will enable us to calculate the flow of soil moisture between two places of different moisture content, in the same way that the thermal conductivity, and a knowledge of the temperature at two points in a solid, enable us to calculate the heat flow. A pioneering investigation along these lines was published by Buckingham (17) in 1907, and recently Gardner (18) has reopened the problem. The mathematical treatment is somewhat difficult, because in practice the capillary transmission "constant" is itself a variable function, but Gardner has been able to obtain encouraging agreement between theory and experiment in a number of cases. The underlying idea in the work, as expressed by Gardner, is that "a knowledge of the functional relation between the potential, the moisture content, and the effective radius of the soil particle,
whether obtained empirically or by theoretical speculation, would not only be equivalent to a knowledge of the various moisture constants, but also relations that may exist between them, such as the Briggs system of equations, to which reference has already been made (3; 4).

These investigations of Gardner are still in their early stages. It is apparent that one of the greatest difficulties in the work will be the derivation of a proper function to represent the capillary potential in the differential equations for water movement. It is quite certain that the original hypothesis regarding the soil as a framework of inert sand grains will be insufficient for this purpose; the effects of the colloidal material in the soil must be included. The modern hypothesis—which seems to have been first put forward in definite form by J. Dumont (19)—is that this colloidal complex, derived both from inorganic and organic material, may be regarded as a coating around the soil particles, especially those of smaller size. This coating can hardly have a definite outer surface. It may be considered as surrounding the soil particle in a series of shells of gradually increasing hydration as Hall (20) has suggested, so that there is a continuous transition from a solid nucleus to soil solution. With regard to the relation of the coating to the root hairs of plants, Comber (1) has put forward an interesting suggestion to explain the well-known difficulty of washing the roots entirely free from small soil particles. It is suggested that the root hair makes an indissoluble attachment with the colloidal coating of the particle, the outer wall of the cell being converted into a mucilaginous substance. The possibility therefore arises that the plant may be able to absorb directly colloidal substances from the soil.

The constitution of this soil colloidal complex is as yet largely unknown, and even the percentage of it present is uncertain. The classical experiments of Schloesing (21) and the recent repetition of the work by Ehrenberg and Given (22) gave figures of 1-2 per cent., while experiments of Tempany (23) based on the shrinkage of moist soils when dried, led to much higher values. In some soils nearly the whole of the clay fraction seemed to be in the colloidal condition. In the majority of soils there is reason to believe that the colloidal constituents derived by weathering and other agencies from the soil particles—the inorganic colloids—are mainly responsible for the effects observed. Possibly the organic matter, weight for weight, produces effects of the same order as the clay, but the latter is usually present in excess, and in any case the inorganic and organic colloids are so intimately mingled in the soil, that it is very difficult to ascribe separate functions to them. Information can be obtained, however, by using an extreme type of soil. This has been done by Crump (24) who worked with moorland and peat soils, and examined the ratio which he calls the "coefficient of humidity".

The values for this ratio were obtained as follows:—

\[
\begin{align*}
\text{Water content} &= \text{weight when sampled} - \text{weight at } 15^\circ \text{C.} \\
\text{Humus content} &= \text{weight at } 100^\circ \text{C.} - \text{weight after ignition.}
\end{align*}
\]

Naturally, the variation in total moisture content due to meteorological conditions, will affect the value for the ratio, but a sufficient number of experiments will give a frequency curve from which the modal value may be taken as typical for the soil in question. Crump found that if samples were taken during the growing period of plants and not immediately after heavy

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1 Private communication.
rain, that the values for the coefficient of humidity of a given soil did not vary appreciably, so that the labour of taking a large number of samples was not necessary. An important fact brought out by the work was that the value of the coefficient of humidity is sensibly constant for different layers of a soil whose constitution alters greatly with depth:—

Values of the coefficient of humidity (Crump):—

<table>
<thead>
<tr>
<th>Material</th>
<th>Water at 15° C.</th>
<th>Humus.</th>
<th>Water Homus</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Humus at 1-29 ins.</td>
<td>170'0 per cent.</td>
<td>55'5 per cent.</td>
<td>3'06</td>
</tr>
<tr>
<td>(ii) Sandy soil below (t)</td>
<td>30'4 ''</td>
<td>10'4 ''</td>
<td>2'92</td>
</tr>
<tr>
<td>(i) Black soil at 4-18 ins.</td>
<td>67'4 ''</td>
<td>33'4 ''</td>
<td>2'01</td>
</tr>
<tr>
<td>(ii) Same at 14-22 ins.</td>
<td>40'3 ''</td>
<td>18'0 ''</td>
<td>2'76</td>
</tr>
</tbody>
</table>

The table shows that in spite of the wide difference in water content of two such layers, the coefficient of humidity is not sensibly different; from the point of view of the plant roots, both layers are equally moist. When the work was extended to a number of peat soils having the same habitat it was found that the values of the coefficient of humidity for these peats, although the samples were taken at widely different times, did not differ greatly from the mean value, and further, in the case of the sub-peats from the same localities a different, but still approximately constant value of the coefficient was obtained. It is apparent that Crump’s work opens up a very promising field of research in ecological studies. It is important that similar investigations should be made on arable soils and permanent pastures, where the clay fraction has to be considered as well as the organic matter, in the valuation of the coefficient of humidity.

For our present purpose the main interest in the work is the demonstration of close relations between the moisture content and certain soil constituents possessing colloidal properties.

These relations have been demonstrated in another way by the present writer (25). A study was made of the evaporation of water from moist soil over sulphuric acid, using an apparatus devised to overcome experimental errors as far as possible. The results showed, in contradiction to some earlier work of Patten and Gallagher (26), that the evaporation curves for thin layers of moist sand and soil were different, and that, further, this difference was largely due to the colloidal property of the clay fraction. The evidence for this last statement was obtained from the evaporation curves (Fig. 1) given by a rich garden soil, which was divided into three portions, and treated as follows:—

Portion C: untreated, for control.
Portion B: soluble humus removed by extraction with 2 per cent. NaOH in the usual way.
Portion A: ignited to remove all organic matter and to destroy the colloidal properties of the clay.

The evaporation curve for portion B shows a slightly increased rate of evaporation, but the curve is not much different from that for portion C, whereas the curve for portion A is identical with that given by moist sand. Recently further experimental evidence has been obtained on the relative effects of organic matter and clay on evaporation by using soils which differ only in their manurial treatment. The results will shortly be published in
full elsewhere, but it may be stated here that the differences due to manurial treatment are not so important as those due to the amount of clay in the soil.

The general conclusion is that the evaporation from soil under the experimental conditions is mainly controlled by the colloidal portion of the clay fraction; further, the evaporation curve is continuous, and shows no breaks or abrupt changes of direction. There is, for instance, nothing to indicate a rapid diminution of vapour pressure immediately below the optimum moisture content as deduced by Cameron and Gallagher (14). In fact, the rate curves for a soil containing about 20 per cent. of clay can be fitted over practically their whole range by an equation of the form:

\[ B \frac{dW}{dt} = \frac{w}{s} \left( \frac{w}{100} + 1 \right) \left[ 2.303 \log (w + k) - \log_e k \right] \]

where \( \frac{dW}{dt} \) = time rate of evaporation
\( w \) = moisture content (percentage on dry weight of soil)
\( s \) = true specific gravity of the soil
\( B \) and \( k \) = constants for each type of soil used.

The right hand side of equation contains two factors: that in square
brackets is empirical, and in all probability is connected with the vapour pressure at different moisture contents. By itself it does not completely fit the rate curves, but when the second factor \( \frac{3 \sqrt{\frac{100}{110} + r}}{100} \) is introduced, the agreement is very good. This factor expresses the effect of diminishing surface from which evaporation can take place as the soil dries out; the thickness of the moist film diminishes and hence its surface area diminishes also.

From the foregoing discussion it will be seen that, as agricultural science has progressed, the complexity of the relations between the soil and its moisture content has become more and more evident, and at the same time it has been realised that there is a continuity in these relations over a wide range of moisture content. It is perhaps appropriate to emphasise at this point that the ultimate value of any relations shown to exist between the soil and its moisture content will largely depend on the help they give to another great branch of agricultural research—the relations between the plant and the nutrient soil solution. The soil moisture containing various substances in solution, and possibly also in colloidal suspension, occupies, as it were, the central position; on the one side there is the soil, and on the other the plants and organisms.

In the above discussion we have consistently used the terms moisture or water, in accordance with the usual convention. The term soil solution could with more correctness have been used, although it is by custom employed only when special attention is being directed to the substances, soluble and suspended, in the soil moisture.

It is obvious that if we could remove the soil solution from the soil, we should at once be able to test a large number of important points connected with its relations with both the soil and plants. It is quite easy to remove liquid from soil of course, but it is another matter to say whether the liquid so removed is a true sample of the soil solution as it exists in situ. A large number of different methods have been described and their relative values discussed, and it is not proposed to consider them here. The reader is referred for this information to papers by Stiles and Jørgensen (27), Bouyoucos (28), Morgan (29), and C. B. Lipman (30). Neither is it proposed to consider the controversy on the composition of the soil solution, which centred around the deductions of Whitney and Cameron (31) that the soil solution is saturated with compounds of phosphoric acid and potash to the same low degree of concentration in all soils, and the well-known refutation of this idea set out by Hall, Brenchley and Underwood (32). It is sufficient to remark that the former hypothesis has been shown untenable in its original form, and that the composition of the soil solution does vary significantly from soil to soil, in general accordance with the soil type and its manurial treatment.

Investigations on the soil solution have recently been stimulated by the employment of two methods that enable the soil solution to be studied in situ. These are the dilatometer and freezing point methods, and their adaptation to soils is due to Bouyoucos, who has developed them in a number of interesting papers (33).

The dilatometer experiments show that a certain proportion of the water in soil fails to freeze at a temperature of \(-1.5^\circ C\). A certain amount of this "unfree" water can be frozen if the temperature is reduced to \(-4^\circ C\), while some will not freeze at \(-78^\circ C\). On the basis of these results Bouyoucos arrives at a new division of soil water, indicated in the scheme...
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below. The relative proportions of the different groups vary from soil to soil. The physiological significance which Bouyoucos attaches to the different groups is also shown:

Gravitational . . . . “superavailable”.
Free . . . . very available.
  capillary-adsorbed . . slightly available.

Unfree
  combined
  water of solid solution
  water of hydration
  unavailable.

The freezing point experiments are done direct on the moist soils in the usual Beckmann apparatus, and the depression of the freezing point is measured for different moisture contents. In moist quartz sand, and some extreme types of sandy soil, where the soil solution would be very dilute, the depression of the freezing point was found to be inversely proportional to the water content. This points to the moisture in the sand obeying the same law as dilute solutions—the freezing point depression varying approximately as the concentration. With the majority of ordinary soils, this relation did not hold. It was found that the freezing point depression rapidly increased as the moisture content decreased (Fig. 2). Bouyoucos

![Freezing point depression graph]

**Fig. 2.** Increase in freezing point depression, with decrease in moisture content (Bouyoucos).
interpreted this to mean that in soils a certain part of the moisture was rendered "unfree," in the sense that it did not take part in the freezing point depression.

Both the dilatometer and freezing point experiments, therefore, supported the idea of "unfree" water bound in some way to the soil. Since the freezing point determinations were done at a variety of moisture contents the experimental results offered material which seemed suitable for quantitative investigation. This was carried out by the present writer (34) and led to a series of interesting results. The fundamental assumption was that the freezing point depression at any moisture content was proportional to the effective concentration. This effective concentration was necessarily taken as inversely proportional to the free water present, i.e. inversely proportional to the total moisture content minus the "unfree water".

With this assumption the experimental results lead to a relation between the "free" and total moisture, shown for two soils in the curves of Fig. 3. Both these curves are fitted by an equation of the type

\[ Y_n = cM_n^{x} \]

where \( Y_n \) = free water at total moisture content of \( M_n \)
\( c \), and \( x \) = constants for any one soil.

Knowing that \( M_n = Y_n + Z_n \), where \( Z_n \) is the unfree moisture, we arrive at the following equation for the relations between free and unfree water:

\[ Z_n = \frac{1}{c} \left( \frac{1}{Y_n} \right)^{\frac{1}{x}} - Y_n. \]
However, this equation contains an unknown quantity in the constant \( c \), and cannot be used directly. But we can obtain a series of values for \( Z \) from Fig. 3. At the highest moisture content \( (M_0 = 21) \) for the sandy loam soil, the free water \( Y \) obviously lies between 0 and 21. Let it be given any arbitrary value, say 15, or 9; we then get a set of values for \( Y \), at various known total moisture contents and therefore obtain, by subtraction, the corresponding values for \( Z \), the unfree water. Fig. 4 shows the relation between free and unfree water for various assumed values of \( Y \). It is not easy to say which of the four curves is most likely to be nearest the truth. One would hardly imagine that the lower two curves would apply, as they indicate a maximum in the unfree water when the total water is about 12-15 per cent. It is difficult to conceive any physical reason why the unfree water should show such a maximum, although it is suggestive to associate this point with the optimum moisture content of Cameron and Gallagher (14), already mentioned. Probably the higher curves of Fig. 4 are nearer the truth. These curves, since they are also satisfied by the same general equation as the other two, have also a maximum, but it is comparatively flat, and eventually corresponds to a total moisture content of a higher amount than the soil could take up, and therefore is not compatible with actual conditions.

It will be seen, however, that interesting and important relations hold
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between free, unfree, and total moisture content, if the assumptions underly-
ing the application of the freezing point method to soil solution in situ are legitimate. Further, the results emphasise the continuous nature of the
relations between soil and soil solution brought out in the writers’ experi-
ments on evaporation (25).

One very interesting point brought out by the curves is that the sugges-
tion of Bouyoucos that the unfree water is constant in amount, is not in
accordance with the experimental data of the freezing-point determinations.
This has led Bouyoucos to an experimental examination of unfree water at
different moisture contents, using the dilatometer method (35). He finds
that the unfree water does not vary in amount, but is a constant quantity
for any given soil, whatever the total moisture content. Thus the deduc-
tions from the freezing point method do not agree with the experimental
evidence of the dilatometer method, if it is assumed that the unfree water
as measured by one method is identical with that measured by the other.

Bouyoucos’ paper has only recently appeared, hence nothing can be
done at the present moment except to record the differences between ex-
periment and deduction. It is obvious that the whole matter is in an ex-
traordinarily interesting position, and in view of the extended use now being
made of these methods—especially the freezing point determinations—in
Michigan, California, and elsewhere, it is important that the causes of the
discrepancy mentioned should be examined; work in this direction has
therefore been put in hand at Rothamsted.

In this discussion of the relations between the soil and its moisture
content a comparison has been made between the original hypothesis and
the modern one. It has been shown that the colloidal material in the soil
exercises a profound effect on the moisture relations, and that these relations
are continuous over a wide range of moisture content. The majority of the
various subdivisions and equilibrium points which were developed on the
older hypothesis are not to be regarded as having any deep physical signifi-
cance, and in one or two cases their interest is physiological rather than
physical.

Further progress in our knowledge of the moisture relations in soil is
most likely to follow if its colloidal properties are taken into account.

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