DISCUSSION ON "ORGANIC CONSTITUENTS OF THE SOIL".

The **Chairman**: The discussion on this question of the organic constituents of the soil is now open. I wonder if Dr. Salisbury, in the course of his investigations, has come into contact with a problem that has often impressed itself upon me, namely, that in many of the districts where we find peat in large accumulations we have evidence that the peat is of comparatively recent production, and that it certainly was preceded by forest growth. I think it can be noticed that many deposits of peat of the Welsh Hills, on Dartmoor, on the carrs of Nottinghamshire, and so forth, have a forest growth at the bottom, and that forest growth must have died out when the peat formation set in. Why did not the forest formation persist? We are still lacking in that fundamental knowledge on what turn of events starts the soil growing acid, after which peat formation begins. I have ventured the hypothesis that after the glacial ice retreated the soil was for a time comparatively neutral and maintained neutral forest growth and vegetation, but somehow or other as a result of the decaying vegetation acid conditions set in and with them the destruction of the forest growth, followed by the accumulation of peat. I wonder if Professor Odén has got anything to say of experience of that kind in Sweden.

Professor Sven Odén: I have no personal experience with regard to vegetation and acidity, but I think that Dr. Olof Arrhenius, in Sweden, has done some work of the kind we are now discussing. He has made extensive researches on the hydrogen-ion concentration of the soil of plant associations in the coast region of Stockholm,¹ in which he found definite P_H values characteristic of each type of plant association, and has thus been able to group various plant associations according to P_H . I am not able here to give details of the work, but I think he found a close relation in the same direction as was mentioned between the optimum for each plant and the P_H of the soil solution. He has also tried the colorimetric method for determining the P_H value.

With regard to the purely chemical nature of the humic acid, there are some recently published researches by a German scientific man, W. Eller,² which ought to be mentioned, as, for the first time, through a simple oxidation of a phenol:—

substances were obtained which, not only in composition (58.05 per cent. C. 3.25 per cent. H.), but also in their colloidal and other physical and chemical reactions, seem to be identical with the natural humic acids. We must wait a little and see whether the formula put forward can be maintained,

¹ Dissertation at Stockholms Högskola, 1920.

² W. Eller, *Ber. d. deutsch. Chem. Ges.*, 1920, **53**, 1469; *Brennstoffchemie*, 1921, **1**, No. 9.

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but I think that the theories advanced by Eller are worthy of notice, and his experimental work on the constitution of the humic bodies is very promising.

Dr. J. A. Voelcker: I was somewhat surprised to hear the reader of the last paper mention that he had had experience of deep-rooting plants suffering from extreme acidity while shallow rooted plants did not. He certainly mentioned that there were exceptions to this, but I would call to mind that in our Woburn work on acid soils it was the deep-rooted wheat which grew for a considerable time under the influence of acid, whereas the shallow-rooted barley suffered the more quickly. Of course, there may be this difference, that in our case the acidity was not what one might call natural acidity, such as might be derived from organic matter, but was one which had been introduced by the application of sulphate of ammonia over a very long time, but, at all events, both wheat and barley had been subjected to the same amount of acidity, and the result was the reverse of that which the reader of the paper had experienced.

Dr. Wm. B. Brierley (Rothamsted): An aspect of this discussion to which one would like to see greater prominence given is the relation between many of the physico-chemical processes occurring in the soil and the soil fauna and flora. Mr. Keen has described the "soil-soil moisture" complex, but to visualise the conditions so is to oversimplify the matter: what we are dealing with is a "soil-soil moisture-soil organisms" complex, and many of the physical and chemical processes in the soil are causally dependent upon the last factor. Many organisms are present in certain soil types and not in others, and where present not only have a characteristic lateral and vertical distribution but also show a definite seasonal periodicity. For example, algæ are present in enormous quantity in soils. Certain algal species possess mucilaginous sheaths, others do not, and the varying abundance of these two types alone at different periods of the year must very considerably affect the soil-moisture system. Many fungi produce acid in quantity, and it would seem probable that the vertical distribution of acidity in the soil, described by Dr. Salisbury, must bear some relation to the vertical distribution of the fungi in the soil. There are also the bacteria and protozoa, each playing their distinct part in the soil economy. The whole problem of the physico-chemical reactions in the soil is undoubtedly made more difficult by the inclusion within one's purview of the soil organisms, but they cannot be neglected. Their presence has long been recognised, but we still know little about their activities. The investigations being carried out at Rothamsted will probably throw much light upon the obscure relations of these organisms to the total complex. I would emphasise the fact that even in a physico-chemical discussion such as this, the biological factors must not be omitted from consideration.

Dr. W. R. G. Atkins: In discussing this matter of soil acidity, it is usually assumed that the acidity is of an organic nature, but I do not

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think that need necessarily be the case always. In one case I have come across lately there is evidence that the soil acidity is due to sulphuric acid from the oxidation of iron pyrites. Mr. W. A. Davis, working at Pusa, in India, has kindly sent me samples taken in Assam over a large area, and these work out uniformly at a P_H value of 5.4 or 5.6. In samples of these soils you find small particles of iron pyrites distributed, and some of the sub-soils were just coarse sand. An interesting point is that, whereas the indigo plants grew to an extraordinary height (12 to 15 feet) in the Assam soils, in Bihar they did not surpass 4 feet. Mr. Davis' view was that this effect was due to phosphate. Apparently this acidity in the Assam soils resulted in a higher amount of available phosphate. I believe that a large amount of work has been done, mainly in the United States, lately, as to the beneficial results of composting sulphur with rock phosphate. There are a great many other points of interest in the papers, but I will not deal with them, as the time is so short.

Dr. W. R. Ormandy: I was very pleased when your Secretary sent me an invitation to join in the discussion on these papers to-night, and I was particularly pleased to see the papers to be read by Professor Sven Odén. There have been several papers by Professor Odén, and with regard to all of them there is much to be said. In the first place, I should like to refer to the paper regarding the method for estimating the acidity of humus by means of conductivity tests. I do not wish to say that what I have to bring forward will prove in the end in any way to destroy the validity of this very important work, but it certainly has an important bearing upon it, and it has this distinct advantage, that it is work carried out upon a comparatively simple problem, for there are not more than half a dozen "unknowns," whereas it seems to me that in most of the problems we have been dealing with to-night there are hundreds of unknowns, and each speaker gets up and points out further ones. At the present moment we are very much unaware as to what happens when water vapour is adsorbed on to a complex phase, like the surface of a china clay particle. Much has been said to-night as to what happens with a mixture consisting of finely divided mineral matter, clay, humus, admixed with micro-organisms, algæ, and other things, but it is obviously difficult to arrive at a definite conclusion under such complex conditions. Therefore, for that reason, I have carried out my experiments on the simplest colloids which I could hit upon, namely, pure china clay, and on a very allied substance—ball clay. It is quite clear that the acidity test of Professor Odén depends on certain conductivity work, and in this connection I would like to direct your attention to the following: If 100 gm. of clay be shaken up with caustic soda solution of various strengths containing, say, 1 per cent., 2 per cent., etc., of the weight of the clay it will be found that the amount totally adsorbed will vary with the time of contact, thus a given clay will in twenty-four hours with shaking completely adsorb 0.5 per cent. of its weight of caustic soda, whereas with ten days' contact a similar clay will adsorb 1.5 per cent. If the alkalinity of the liquid in contact with the clay be allowed to rise, the ratio of adsorbed to free alkali is much greater after ten days than after one day. When 3 per cent. of caustic soda is adsorbed by 100 gm. of clay only about $\frac{1}{3}$ of 1 per cent. of the amount of adsorbed alkali will be found free in the solution.

If now we take a one-day clay containing 0.5 per cent. of alkali or a

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ten-day clay containing .15 per cent. of alkali and subject these to treatment with boiling water in a soxhlet no alkali will be washed out.

We have found considerable difficulty in estimating the small amounts of alkali which were free in the water when treating clays with an amount of alkali above the amount that they would totally adsorb, particularly when the amount of alkali added was considerable, and very fine dispersion was arrived at. We thought therefore that we might turn to an electrical method for determining the conductivity and consequently the amount of free alkali. Attempts were made to determine this conductivity with nickel anode and cathode in a watery suspension of clay containing .2 per cent. adsorbed alkali. It was found that the conductivity of the solution, employing any voltage below 1.68, gave the usual type of curve independent of the time of passage of the current, but the moment the voltage exceeded 1.68 the conductivity increased with the time; in other words the adsorbed alkali, was set free. As the alkali thus set free is immediately re-adsorbed, there is a direct connection between the voltage in excess of 1.68 and the variation in conductivity with the time. We have had samples of natural clay sent from America which on refluxing in a soxhlet gave no traces of free alkali, but which on electrical treatment gave as much as 2.5 per cent. NaOH. The question arises as to whether this caustic soda can be taken as being chemically combined with the surface layers of clay. Professor Odén states at the end of his paper—"as I have shown elsewhere all this theory of breaking up by adsorption is highly doubtful". We have found that clay which has adsorbed the maximum amount of caustic soda to leave a neutral solution behind it will not adsorb copper, nickel, and other salts, but that such clay not treated with caustic soda does adsorb metallic salts. Similarly clay which is saturated with caustic soda will adsorb quite a lot of phenol phthalein without, however, becoming in any way coloured. If distilled water have clay suspended in it, and the mixture be titrated with caustic soda, alkali will be adsorbed, and it will appear as though it were an acid, but if the alkali be estimated electrically such adsorption will not be found if a voltage over 1.68 be employed. I would like to point out that this fact may have a bearing on measurements of cataphoretic velocities such as were carried out by Professor Hardy with globulin which had combined with alkali. It is fairly certain that colloidal particles will not move in an electric field in a liquid free from electrolytes, but it is quite possible that the necessary electrolytes may be set free by the current employed in producing the field in which the velocity is to be measured. If Professor Odén's figures are correct, it comes out that the humic acid adsorbed 1.1 per cent. caustic soda, and a normal sample of ball clay will have to contain 15 per cent. of humic matter in order to give exactly the same adsorption. As, however, a china clay gives practically the same alkali adsorption as ball clay, it is obvious that the adsorption in that case is not due to the humic materials which are present. The work of Mr. Craven and myself points to the fact that it is desirable to treat colloidal substances electrically for the removal of adsorbed bodies before investigations are carried out upon such bodies as to their adsorptive powers. In conclusion, I hope that you will consider that these points have some bearing on the very important matter raised by Professor Odén.

Professor Sven Odén: Dr. Ormandy has related some very interesting experiments, using china clay, in order, I think, to prove that my hypothesis regarding "disintegration through adsorption" is wrong. It is very difficult to answer him now, as I have only heard of these experiments

on clays during the last five minutes. The only way to answer is to again take up the matter experimentally. If I had based my conclusions solely on the conductivity measurements, which have been criticised by Dr. Ormandy, my case would be a weak one. Going into details, I should first like to point out that Dr. Ormandy uses a very large amount of material, namely, 100 gms. of clay, in a small volume of solution. With humic acids I have concentrations of the order of 0.002. Moreover, I am not quite clear about the origin of the clay which Dr. Ormandy has referred to. Has it been subjected to acid during weathering or not? But I will not go into details in this matter now, as it is very difficult to understand the whole matter without knowing the full experimental details. The main point of my paper on humic bodies is, that, in dealing with them I get a curve like *this* (Fig. 1).¹ As abscissa is the added soda. If I now add NaOH to a very small portion of humic bodies, and measure the hydroxyl concentration, it rises like *this* at a definite concentration. It is not quite sharp, because we have a little hydrolysis here. The main point is, that, even at this point, we have a great number of physical and chemical properties that are simultaneously changing, such as viscosity and colour, etc., and *this* point is nearly the same as I have determined by the conductivity method. The adsorption theory does not indicate any critical change at any concentration. I do not think a clay would behave in the same manner, but even for them I think that the theory of breaking up by adsorption is highly doubtful. It may be that Dr. Ormandy may be able to prove its correctness for clays, but what we here have to deal with is the humic portion of the soil, and I do not think we can get away from the fact that here we have an acid to deal with. Personally, I do not think that the theory of disintegration through adsorption is correct at all. At all events it is not *proved* to be correct in any case yet published.

Dr. W. R. Ormandy : I do not wish to say for one moment that the experiments I have done on clay will in any way prove what Professor Odén has done to be wrong. I merely point out that there is a very great similarity, but there is no time to go into all these points. One can show that the physical properties of the clay run exactly parallel with the statement which Professor Odén has made as to what he has found occurs in the case of humus material, but I do suggest that even from the point of view of the soil chemist it is worth while doing a great deal of this work on comparatively cheap bodies, and comparatively simple bodies, prior to undertaking a study of the properties of soils themselves. It would be better to experiment first on materials obtained in a state of very great purity, and china clay, which is got from a depth of 150 ft. below a decomposed granite formation, is not likely to have been subjected very much to acid treatment. The ball clay from near the surface may have been, but the ball clay with which I worked was taken from about 30 ft. down under a solid bed of impenetrable clay.

Dr. E. J. Salisbury, replying to the discussion, said : With reference to what you said yourself, Mr. Chairman, I should like to read a paragraph from my original manuscript :—

“Under conditions of undisturbed natural vegetation, the covering of plant débris tends to accumulate, and so added to the continued leaching action, we have a continually decreasing amount of non-available salts. Such areas tend to become more and more acid, and this increasing acidity

¹ See p. 291.

is manifest in the tendency for old woodlands to pass gradually into a more heath-like condition, and is probably one of the most important factors militating against their natural regeneration."

I think undoubtedly the work of Hesselman has shown that this has happened in Scandinavia, and there is little doubt it has occurred also in our own country. With regard to Mr. Brierley's comment, I should like to say that such estimations as I have made seem to indicate that except at the surface the humus gradient in the soil in the vertical direction corresponds very closely with the gradient in the amount of the live roots which one obtains from natural plant associations. This seems to indicate that, at all events, the humus derived from the decayed plant roots is the main factor in determining the vertical distribution of organic content.