LIII.—*Action of Humic Acid on Atmospheric Nitrogen.*

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OF the various problems which present themselves to the agricultural chemist, perhaps not one is of greater interest than that of the supply of nitrogen to the soil. Many theories have been propounded to account for the supply, but not one of them will account for the whole supply. Amongst these, the humic acid theory is not the least remarkable. This states that the humic acid in the soil is capable of absorbing nitrogen directly from the air, and of transforming the nitrogen so absorbed into ammonia. Bretschneider (*Chem. Ackersm.*,

1871) found that the presence of humic acid greatly promotes the absorption of nitrogen from the air, and that the quantity absorbed depends on the amount of acid present. Déhéraïn (*Compt. rend.*, **73**) observed that humic acid mixed with a solution of potash also absorbed nitrogen to the amount of 7.2 per cent. Again, in the report of the *Landw. Versuchs.-Stat.*, **18**, 457, E. Simon gives the result of experiments made by him on the same subject. The experiments were as follow:—(1.) Humic acid and water sealed up in a flask for 14 days absorbed a part of the nitrogen also enclosed in the flask, and ammonia was produced in such quantities as could be easily detected. (2.) Nitrogen was passed for 12 hours through a Liebig's potash-bulb containing water and humic acid; the solution afterwards gave a precipitate with platinum tetrachloride. (3.) Humic acid and water in a glass flask, whose mouth was closed by a caoutchouc stopper which was occasionally opened, contained ammonia after 14 days.

The results obtained by Simon appeared so remarkable, that as I had not been able to gather any further information on this subject, I decided on repeating the experiments, so as to determine if possible the rate at which the absorption took place.

Two samples of humic acid were employed, the one (1) prepared by Messrs. Hopkins and Williams yielding 0.225 per cent. of ammonia when distilled with magnesia and a little potash, the other (2) prepared by myself from peat according to the method recommended by Detmer (*Landw. Versuchs.-Stat.*, **14**), and yielding 0.77 per cent. of ammonia. Both samples possessed the properties of humic acid as described by Detmer, with the exception that that prepared by myself from peat was of a slightly brownish tint instead of black.

Experiment (a).—Three grams of humic acid (2) were hermetically sealed up in a glass tube with 20 c.c. of water and 76.6 c.c. of air, and left exposed to the light for 18 months.

Experiment (b).—An excess of acid (1) was boiled with a solution of potassium carbonate, and the dark solution so obtained was found to contain 0.0000476 gram NH_3 per 1 c.c. 100 c.c. of this solution were placed in a large flask, and air purified from ammonia by passing through wash-bottles containing glass moistened with sulphuric acid and Nessler's solution was caused to bubble through the solution twice a day for three months, so that roughly speaking the solution was brought in contact with 300 litres of air = 237 litres N.

Experiment (c).—Humic acid (1) and water were, by means of the apparatus briefly described above, also brought in contact with 300 litres of air in a large glass flask.

Experiment (d).—Humic acid (2) and water were placed in a flask, into the neck of which was fitted by means of a cork a doubly bent

glass tube, which when partially filled with water could act as a pressure-gauge, indicating by change of level any diminution of pressure occurring inside the flask, due to absorption of the nitrogen of the enclosed air; the water also would shut off communication from the external air.

It was expected that these experiments would show, firstly, if there were any absorption (*d*); if there were absorption of the nitrogen, whether all the nitrogen of the air would be removed (*a*); whether the absorption occurred when the acid was in the free state (*c*); also when there was free acid in the presence of potassium humate (*b*). Experiments (*b*) and (*c*) would also determine the rate at which the absorption took place, if the solutions were periodically examined for ammonia.

The results of the experiments were as follows:—

Experiment (a).—When the tube was opened, it was found that a slight reduction of the volume of the air had taken place, as after making the proper allowances for barometric pressure, solution of the air in water, &c., there still remained 1.97 c.c. of air to be accounted for. The water, which was colourless, was proved to contain ammonia in quantity equivalent to 0.19 c.c. N; the remainder of the air had probably been employed in converting a portion of the ammonia into nitric acid, as nitric acid was present, and the amount was determined by the zinc-copper couple; but as the quantity (of a substance reducible by the couple) had not been estimated in the original substance at the commencement of the experiment, no calculations can be made from the analytical figures obtained.

The residue when dried yielded 0.172 per cent. of ammonia, and when treated with the zinc-copper couple it yielded ammonia equivalent to 0.251 per cent. of N_2O_5 . The following figures show that certainly no appreciable quantity of ammonia was produced during the 18 months that the experiment lasted.

In 3 grams of original acid there were 0.527 c.c. of N as NH_3 .

After contact of 3 grams with air and water, there was found in the water 0.19 c.c. N as NH_3 , and in the residue 0.339 c.c. N as NH_3 ; total = 0.529 c.c. As some air was absorbed, it is possible that ammonia may have been formed and oxidised to nitric acid, but owing to the omission of the estimation of this acid at the commencement of the experiment, it is impossible to say how much of the above 0.251 per cent. of N_2O_5 was or was not originally present.

Experiment (b).—After exposure to 300 litres of air, the solution of potassium humate showed no increase whatever of ammonia. The analytical results show a slight diminution in the amount of ammonia present after the lapse of three months, as compared with the quantity present at the commencement of the experiment, but the

difference can only be due to experimental error, or else to the formation of a nitrate.

The figures are as follows :—

Ammonia in the original alkaline solution = 0.0000476 gram per 1 c.c.

Ditto, after three months, under circumstances mentioned above = 0.0000428 gram per 1 c.c.

Experiment (c).—No results were forthcoming, as owing to the severe frost in January the flask was broken and the liquid lost, but I might mention that there was apparently no change, as the water had remained up to January perfectly colourless.

Experiment (d) showed but little change of pressure taking place inside the flask, no more than would be expected when the fluctuations of the barometric pressure and temperature of the laboratory are taken into account; the water remained colourless, and no ammonia was obtained from the mixture except what was present in the original material.

Finding my results to be as described above, I exposed for several weeks in a room adjoining the laboratory, a solution of potassium humate containing humic acid, in excess, so that every opportunity was afforded for the absorption of nitrogen with production of ammonia, and for the absorption of free ammonia, but the solution when boiled with potash yielded only the faintest traces of ammonia.

The conclusions which I am bound to draw from these experiments are opposed to those of Simon and others. The cause of the difference is at present to me unaccountable, unless it be that the materials employed by us are not identical; still, as before said, the properties and the analysis agree with those described by Detmer, and also by Simon, with this exception, that whereas Simon's acid colours distilled water slowly, mine does not appear to dissolve at all in distilled water.

Experiment (a) may show an absorption of nitrogen and possible conversion into nitric acid, as Déhérein says; but as this absorption, if it takes place, does not appear to be very rapid, but in fact very slow, it cannot be considered as a very fruitful source of nitrogenous plant food. Perhaps if a very large column of nitrogen were left in contact with humic acid for a considerable time, some more satisfactory results might be obtained. This I had purposed doing, but circumstances have occurred which oblige me to postpone the experiment until some future date.