

XLI.—*On the Oxidation of Organic Matter in Water by Filtration through various Media ; and On the Reduction of Nitrates by Sewage, Spongy Iron, and other Agents.*

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In a paper read by Dr. Frankland to the Chemical Society (*Chemical Society's Journal*, July, 1880), the question of oxidation of organic matter in water was treated of at length. Dr. Frankland showed

that the alleged self-purification of rivers by flow, was to be accounted for by other reasons than those advanced in a paper by Dr. Tidy (*Chem. Soc. Journal*, May, 1880). In one instance in which the Thames was referred to as an example of oxidation by flow, Dr. Frankland says:—"For several miles above Hampton, the Thames runs through a vast deposit of flint-gravel and sand, which sops up its water like an immense sponge, restoring it again to the river, either near the place of absorption, after floods, or below the next lock in dry weather. Thus vast volumes of Thames water are purified by this exhaustive filtration through gravel and sand, that is to say, by oxidation in a porous medium, which I have again and again shown to be the most potent agency in nature for the removal of organic matter in water."

Bearing in mind the previous experiments on the oxidation of organic matter in water by filtration through various media (published in the Sixth Report of the Rivers Pollution Commissioners), I have investigated the influence of intermittent filtration through sand on animal and vegetable matters dissolved in water. The reduction of nitrates by sewage and other agents, and the influence of filtration through spongy iron on animal and vegetable matters in water, were also subjects of my investigation.

The inquiry divides itself therefore into three heads, which may be stated thus :

1. On the influence of intermittent filtration, through sand, on animal and vegetable matters dissolved in water.
2. On the reduction of nitrates by sewage and other agents.
3. On the influence of filtration through spongy iron on animal and vegetable matters dissolved in water.

Throughout the whole of these experiments, wherever practicable, estimations of the amount of dissolved atmospheric air contained in the water or mixture experimented upon, have been made. The method employed for these observations was that recommended by Miller in his "Organic Chemistry."

#### 1. *The Influence of Intermittent Filtration through Sand on Animal and Vegetable Matters dissolved in Water.*

For the purpose of studying this branch of my subject, a glass tube, 14 feet long and  $3\frac{1}{2}$  inches in diameter, was fixed in a vertical position and 12 feet of the whole length was filled with sand. At the foot of the tube a smaller glass tube was let in for the purpose of allowing the water to filter through, drop by drop. To filter four litres of water took a whole day, the sand and apparatus being repeatedly washed with distilled water, until the filtered water contained no

estimable amount of organic impurity, and no nitrogen as nitrates or nitrites.

For estimation of dissolved atmospheric air after filtration, the sample, with the exception of the first experiment, was always collected directly from the tube into a bottle filled with mercury and standing inverted in a mercury trough.

For the first experiment a sample of natural peaty water was diluted with its own volume of distilled water and filtered through 96 feet of sand. This experiment occupied eight days, the water being passed through once daily.

The following were the results obtained :—

Dissolved atmospheric air *before filtration*.

From 345 c.c. of water (345 c.c. being the capacity of the bulb employed for boiling out) 6·9367 c.c. of air were obtained, which corresponds to 20·106 c.c. air per 1000 c.c. of water.

The percentage composition of the gases from analysis was :

		Parts per 100,000.
CO <sub>2</sub> . . . .	1·98	Organic carbon . . . . . 2·912
O . . . . .	31·96	Organic nitrogen . . . . . 0·167
N . . . . .	66·05	N as nitrates and nitrites.. 0·000
	99·99	

*After filtration* through 96 feet of sand an analysis of dissolved atmospheric air gave the following figures :—

Volume of air from 345 c.c. of the water 7·7920, or 22·58 c.c. per 1000 c.c. water.

The percentage composition was :—

		Parts per 100,000.
CO <sub>2</sub> . . . .	6·55	Organic carbon . . . . . 1·385
O . . . . .	31·53	Organic nitrogen . . . . . 0·144
N . . . . .	61·92	N as nitrates and nitrites.. 0·007
	100·00	

It will be observed from these results that the decrease of organic carbon by filtration through 96 feet of sand is 1·527, or 0·00015 per cent.

The organic nitrogen decreased 0·023, or 0·0023 per cent.

The increase in nitrogen as nitrates and nitrites was only 0·007.

The CO<sub>2</sub> in the dissolved air increased 4·56 per cent., and the water became aerated, 3·04 c.c. per 1000 c.c. of the water used.

These results show that the organic nitrogen of peat is very little affected by filtration through sand, and that a peaty water would have

to filter through immense depths of porous material, before all the nitrogenous matters would be converted into their inorganic representatives.

The next experiment was made with a view to ascertain whether the presence of a nitrifying agent in the water would determine the nitrification of the peat. It was made with the same peaty water, but with the addition of some stale urine. The mixture contained  $1\frac{1}{4}$  litres peaty water,  $1\frac{1}{4}$  litres distilled water, and 2.5 c.c. of stale urine. This mixture gave the following results:—

An analysis of dissolved atmospheric air showed that the mixture contained 7.3917 c.c. of air per 345 c.c. water, or 21.42 c.c. air per litre of the mixture.

Percentage composition of the gases:—

		Parts per 100,000.	
CO <sub>2</sub>	.... 10.07	Organic carbon	..... 5.444
O	..... 30.09	Organic nitrogen	..... 1.353
N	..... 59.84	N as nitrates and nitrites..	0.007
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100.00			

This mixture was then passed through the sand eight times, and so filtered through 96 feet of porous material.

*After filtration* an estimation of dissolved atmospheric air gave 7.3317 c.c. of air from 345 c.c. of the filtered mixture; or 21.25 c.c. air per 1000 c.c. of the water.

Percentage composition of the gases:—

		Parts per 100,000.	
CO <sub>2</sub>	.... 7.56	Organic carbon	..... 2.013
O	..... 30.90	Organic nitrogen	..... 1.199
N	..... 61.54	N as nitrates and nitrites..	0.044
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100.00			

The temperature during the filtration of this last mixture was rather low (average from 16.5—18.5° C.). Suspecting that the organic nitrogen was converted into ammonia, another experiment was made with a stronger mixture of urine and peaty water.

This second mixture consisted of peaty water 2 litres, distilled water 2 litres, and stale urine 5.0 c.c.

An analysis of dissolved gases gave the following percentage composition:—

CO <sub>2</sub>	..... 10.09
O	..... 29.19
N	..... 60.72
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100.00	

The volume of air from 345 c.c. was 7·4390,  
 Or per 1000 c.c. of the water, 20·73 c.c. of air.  
 The mixture also contained—

	Parts per 100,000.
Organic carbon .....	8·003
Organic nitrogen .....	1·457
Nitrogen as nitrates and nitrites..	0·027
Ammonia .....	0·088

The experiment was performed under conditions similar to those of the previous one, but at a higher average temperature, the range being 20·0—26·0° C.

The nitrogen as nitrates and nitrites was estimated daily after each filtration of 12 feet, so as to observe the increase in nitric nitrogen. These daily observations were made with a standard solution of indigo according to directions given by Warington.

The following table shows the results.

*Daily increase of nitrogen as nitrates and nitrites, by filtration through sand of a mixture of peaty water and urine. Taken by the indigo method.*

	Nitrogen as nitrates and nitrites per 100,000.
Before filtration.....	0·027
1st day after filtration through 12 feet of sand..	0·027
2nd   "       "       "       24   "   ..	0·030
3rd   "       "       "       36   "   ..	0·044
4th   "       "       "       48   "   ..	0·072
5th   "       "       "       60   "   ..	0·090
6th   "       "       "       72   "   ..	0·150
7th   "       "       "       84   "   ..	0·300
8th   "       "       "       96   "   ..	0·750
9th   "       "       "      108   "   ..	1·152
10th  "       "       "      120   "   ..	1·204
11th  "       "       "      132   "   ..	1·204

*After filtration* of the mixture of peaty water and urine through 132 feet of sand, analysis of dissolved atmospheric air gave the following results :—

CO <sub>2</sub> .....	11·46
O .....	21·62
N .....	66·92
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	100·00

The volume of dissolved atmospheric air from 345 c.c. of the mixture, after filtration through 132 feet of sand, was 7·4547,

Or per 1000 c.c. of the mixture, 20·73 c.c. of air.

The mixture after filtration through 132 feet of sand also yielded on analysis the following results :—

Organic carbon .....	0·807
Organic nitrogen .....	0·164
Nitrogen as nitrates and nitrites..	1·204
Ammonia .....	0·218

From the previous analysis of the mixture of peat and distilled water given in the first of my experiments, I am enabled to arrive at the following data connected with the experiment now being considered :—

The organic carbon due to urine in this mixture was 5·091.

The organic carbon due to peat was 2·912.

The organic nitrogen due to urine, or animal organic nitrogen, 1·290.

The organic nitrogen due to peat or vegetable organic nitrogen, 0·167.

It will be seen that the total decrease in organic carbon was 7·196 pts. per 100,000.

The total decrease of organic nitrogen 1·293 pts. per 100,000.

The organic nitrogen left unoxidised during the filtration was 0·164, or *almost exactly* the amount of organic nitrogen due to peat.

From an inspection of the results of the analysis of the first peaty water experiment, it will be seen that the results just stated are very easily arrived at. For instance, the organic nitrogen from a previous analysis of the same peaty mixture was 0·167. After the addition of the 5 c.c. of urine the organic nitrogen is increased to 1·437. Therefore by subtracting, this gives 0·167 pt. vegetable organic nitrogen, and 1·290 pts. animal organic nitrogen per 100,000 pts. of the mixture. The total decrease in organic nitrogen was 1·293 pts. per 100,000 ; and subtracting this from the amount originally present, gives 0·164 pt. per 100,000 of unoxidised organic nitrogen, the amount of vegetable organic nitrogen present before the filtration of the mixture being 0·167.

It may therefore be concluded that animal organic matter is quickly oxidised by filtration through sand ; but that vegetable organic matter is not so quickly oxidised, and that peaty organic nitrogen, in the presence of animal organic matter, which is itself undergoing conversion into ultimate inorganic substances, does not, to any considerable extent, become converted into either ammonia or nitrates.

The results obtained from the dissolved atmospheric air experiments are significant. The oxygen has decreased to the extent of 8.56 per cent., and the CO<sub>2</sub> has increased 1.37 per cent., while the general volume of dissolved air curiously enough has become but slightly altered.

In order to ascertain whether the results just stated applied also to other kinds of vegetable organic matter in water, a solution of rape cake, prepared by infusing rape cake in warm water. After it had digested a short time, the whole was filtered through linen. The extract was of a deep brown colour and very frothy, giving off an unpleasant odour. This was diluted considerably, and the following experiments made with it:—

The volume of dissolved atmospheric air, &c., from 350 c.c. was 8.0189 or 22.20 c.c. of air per 1000 c.c. of the solution.

This percentage composition of the air was—

		Parts per 100,000.	
CO <sub>2</sub>	..... 22.78	Organic carbon	..... 6.532
O	..... 23.63	Organic nitrogen	..... 1.404
N	..... 53.59	N as nitrates and nitrites..	0.035
	———	Ammonia	..... 0.066
	100.00		

The solution was then filtered nine times through the tube, making 108 feet of sand in all. The temperature average 18.0—20.5° limits. A specimen was taken after each filtration, and the amount of nitrogen as nitrates and nitrites estimated daily by the indigo method.

*Table of the Increase of Nitrogen as Nitrates and Nitrites by Filtration of a Solution of Rape Cake through 108 feet of Sand,*

		Indigo method.	Gas method.
Before filtration	.....	0.040	0.030
1st day after filtration through 12 feet	..	0.040	—
2nd	„ „ 24 „ ..	0.040	—
3rd	„ „ 36 „ ..	0.075	—
4th	„ „ 48 „ ..	0.075	—
5th	„ „ 66 „ ..	0.112	—
6th	„ „ 72 „ ..	0.112	—
7th	„ „ 84 „ ..	0.112	—
8th	„ „ 96 „ ..	0.112	—
9th	„ „ 108 „ ..	0.150	0.198

After the filtration through 108 feet of sand, the volume of dissolved atmospheric air from 350 c.c. of the solution was 7.9938, or per 1000 c.c. 22.83 c.c. of air, having the following percentage composition:—

		Parts per 100,000.	
CO <sub>2</sub> . . . .	17·29	Organic carbon . . . . .	1·088
O . . . . .	23·02	Organic nitrogen . . . . .	0·298
N . . . . .	59·69	Ammonia . . . . .	1·300
	100·00	N as nitrates and nitrites..	0·150

It will be seen that the oxygen and the CO<sub>2</sub> have decreased, and the nitrogen increased, while the general volume remains the same. All these samples for the estimation of dissolved atmospheric air after filtration were collected over mercury.

The decrease in organic carbon was 5·444. The decrease in organic nitrogen, 1·106 pts. per 100,000. The increase in ammonia, 1·234, corresponding to 1·026 pts. increase in N per 100,000 pts. The increase in N as nitrates and nitrites, 0·115.

From this experiment it will be seen that the oxidation of certain kinds of vegetable matters is rapid. The organic carbon is quickly oxidised. The organic nitrogen is for the most part converted into ammonia.

In order to confirm this last experiment a second one was made with a fresh solution of rape cake, and the following data were obtained:—

Before filtration the volume of dissolved atmospheric air from 340 c.c. was 8·1030, or 23·83 c.c. per litre of the solution, having the following percentage composition:—

		Parts per 100,000.	
CO <sub>2</sub> . . . .	22·10	Organic carbon . . . . .	8·458
O . . . . .	24·14	Organic nitrogen . . . . .	1·970
N . . . . .	53·76	Ammonia . . . . .	0·680
	100·00	N as nitrates and nitrites..	0·000

Under circumstances almost exactly similar to those of the last experiment, at an average temperature of 17—21·5°, this mixture was filtered nine times through 12 feet of sand, making 108 feet altogether.

On the completion of the filtration a specimen collected for dissolved air determination gave 7·2450 c.c. of air from 340 c.c., or 21·30 c.c. of air per litre.

The percentage composition was—

		Parts per 100,000.	
CO <sub>2</sub> . . . .	11·76	Organic carbon . . . . .	2·071
O . . . . .	22·04	Organic nitrogen . . . . .	0·293
N .. . . .	67·30	Ammonia . . . . .	2·000
	100·00	N as nitrates and nitrites..	0·016



From this it will be seen that the increase in ammonia was 1·920, corresponding to 1·581 pts. of N per 100,000 pts. solution.

The increase in N as nitrates and nitrites, 0·016.

The decrease in carbon, 6·387.

The decrease in organic nitrogen was 1·677.

In the first experiment with rape cake solution, the total loss in organic nitrogen was 1·106 pts. per 100,000, of which 1·026 pts. became ammonia, and 0·115 pt. was oxidised to nitric and nitrous acids (the excess, 0·035 pt., may fairly be stated as experimental error).

In the second experiment the total loss in organic nitrogen is 1·677 pts. per 100,000, of which 1·581 pts. became ammonia, 0·016 pt. becoming oxidised (the error or loss here is 0·090). In the second experiment the dissolved air results show a marked diminution in oxygen.

The increase of the formation of nitrates and nitrites is shown by the following table :—

*Nitrogen determined by the Indigo Process.*

1st day after filtration through	12 feet	...	0·000
2nd	„	24 „	0·000
3rd	„	36 „	0·000
4th	„	48 „	0·010
5th	„	60 „	0·013
6th	„	72 „	0·016
7th	„	84 „	0·016
8th	„	96 „	0·016
9th	„	108 „	0·016

2. *On the Reduction of Nitrates by Sewage and other Agents.*

The reduction in the quantity of nitric nitrogen which takes place when fresh sewage is added to a solution of nitre is an observation which has been recorded by the Rivers Pollution Commissioners, but no authenticated experiments have to my knowledge been made on the subject. In the following pages will be found the results of my investigations on the subject.

A solution was made of 0·0853 gram of  $\text{NO}_2\text{KO}$  in distilled water; 5 per cent. of moderately clear fresh sewage was then added. The sewage was full of bacteria.

Before adding the sewage the solution contained :—0·514 pt. of nitrogen as nitrates and nitrites per 100,000, according to the gas method, and 0·526 pt. according to a standard indigo solution.

The mixture was then put into a large stoppered bottle, and agitated

from time to time. Estimations of nitrogen as nitric nitrogen were made daily, at first, and then after at intervals, with the following results:—

Decrease of nitrogen as nitric nitrogen.	Indigo method.	Temp. Centigrade.
1st day after admixture with the sewage..	0.451	18.1°
2nd " " " "	0.376	21.5
5th " " " "	0.338	23.0
7th " " " "	0.338	21.0
8th " " " "	0.301	23.5
9th " " " "	0.301	24.0
10th " " " "	0.370	23.7
11th " " " "	0.370	22.0
12th " " " "	0.413	22.5
16th " " " "	0.450	19.0
30th " " " "	0.500	21.0

Another experiment was made with a solution containing 0.0835 gram of  $\text{NO}_2\text{KO}$  and 5 per cent. of similar sewage, and the whole mixture kept at 0° C. in an ice safe.

Before adding the sewage the solution contained 0.512 pt. of nitric nitrogen per 100,000 by a gas method experiment, and 0.526 pt. by the indigo process.

The reduction is shown in the following table:—

	Indigo method.	Temp.
1st day after admixture.....	0.451	0°
5th " " .....	0.413	0
7th " " .....	0.376	0
9th " " .....	0.376	3
11th " " .....	0.313	4
16th " " .....	0.313	5
30th " " .....	0.313	0

From these experiments it will be seen that the reduction is very gradual, but is more rapid with a higher temperature. Nitrification of the sewage itself seems to set in in the case of the specimen kept at the temperature of the laboratory after the reduction, and this nitrification was suspended, if not stopped, by the lower temperature.

I next made a solution of nitre containing 0.0745 gram per 2250 c.c. water, and added to this 25 per cent. of fresh clear sewage, containing no nitrates. This was kept in a bottle, which stood neck downwards over mercury. The air standing over the nitre solution and sewage was analysed, and also the dissolved atmospheric air. These experiments were made at the commencement and close of the

observation. A specimen of the liquid for the estimation of nitric nitrogen was removed daily, without letting in air, by an arrangement which has already been described.

The nitrogen as nitrates and nitrites before the addition of the sewage was—

Gas method.		Indigo.		
0.406		0.375 pt. per 100,000.		
Table of reduction.			Temp.	Indigo process.
2 days after admixture with sewage	..	18.0	0.228	
3       "       "	..	21.0	0.150	
4       "       "	..	20.0	0.150	
5       "       "	..	23.0	0.150	
8       "       "	..	24.5	0.150	
16      "      "	..	21.7	0.075	

At the commencement an analysis of dissolved atmospheric air gave 9.1800 c.c. from 346 c.c. of water, or 26.55 c.c. of air per litre, having the following percentage composition:—

		Air standing above.
CO <sub>2</sub> .....	31.52	0.08
O.....	15.88	20.73
N.....	52.60	79.19
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	100.00	100.00

The high percentage of CO<sub>2</sub> is accounted for by the sewage, and also by the fact that the distilled water contained a large volume of CO<sub>2</sub>.

After the mixture had stood, with agitation from time to time, for eight days, an estimation of dissolved atmospheric air gave the following data:—

Volume of gas from 345 c.c. = 9.9270, or per litre, 28.77 c.c. of air, having the percentage composition—

		Air standing above.
CO <sub>2</sub> .....	32.52	0.02
O.....	20.37	15.77
N .....	47.11	84.11
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	100.00	100.00

The CO<sub>2</sub> in the dissolved atmospheric air has increased 1.00 per cent., and 0.06 per cent. of this has been absorbed from the air standing over the liquid.

The oxygen in the dissolved atmospheric air has increased 4.49 per cent., while the oxygen in the air standing in the bottle has decreased

4.96 per cent. From this it will appear that during the reduction of nitrates by sewage  $\text{CO}_2$  is generated in the liquid, and perhaps free nitrogen given off while oxygen is absorbed. The level of the liquid in the bottle marked from day to day did not alter.

In order to confirm these results, and also to observe the effect of the reduction on a much stronger solution of nitre, I tried another experiment of a similar nature, only with a much stronger solution of nitre.

15 per cent. of thick sewage was added to this solution.

Before the admixture with the sewage the solution gave the following results:—

	Indigo method.	Gas method.
Nitrogen as nitrates and nitrites. .	2.483	2.509

The experiment was performed under the same conditions, and in fact at the same time as the one just described.

An analysis of dissolved atmospheric air, after immediate admixture with the sewage, gave—

Volume of gas from 346 c.c. = 7.8730, or per 1000 c.c. 22.75 c.c. of air.

The percentage composition of which was—

$\text{CO}_2$ . . . . .	30.25
O . . . . .	17.29
N . . . . .	52.46
	100.00

The former analysis of the air of the laboratory previously mentioned was taken.

The following table represents the rate of reduction of the nitric nitrogen estimated by the indigo process:—

	Temp.	Parts N per 100,000.
2 days after admixture . .	19.5°	2.483
3   "           "   ..	18.5	1.956
4   "           "   ..	20.0	1.655
5   "           "   ..	22.3	1.505
8   "           "   ..	24.0	1.505
16  "           "   ..	25.0	1.279

The total reduction during 16 days effected by 25 per cent. of thick sewage being 1.204 pts. of nitric nitrogen per 100,000.

In no experiment on the reduction of nitrates by sewage except the first, which was continued for 30 days, was I enabled to observe the subsequent nitrification of the sewage itself after the reduction of the nitric nitrogen.

After this mixture had stood eight days an analysis of dissolved atmospheric air gave from 345 c.c. of the water, 8·9683 c.c. of gas, or 25·99 c.c. per litre.

The percentage composition being—

		Air standing above.
CO <sub>2</sub> . . . . .	28·21	0·60
O . . . . .	21·71	16·51
N . . . . .	50·08	82·89
	100·00	100·00

In this second experiment with the thick sewage sediment oxygen was absorbed, as before, to the extent of 4·42 per cent. in the liquid, and a loss of 4·22 per cent. in the air. But in this experiment CO<sub>2</sub> was given off, or there was at least a loss of 2·04 per cent. of CO<sub>2</sub> in the liquid, and again of 0·52 per cent. of CO<sub>2</sub> in the air standing above. This experiment only shows the difference in the action of clear and thick sewage on nitrates, the reduction in the second case being greater than the former. The fact of free nitrogen being given off cannot of course be established, but it seems a probable and certainly a possible action. The temperatures in both cases were about the same.

The effect of SH<sub>2</sub> on nitrates was next studied. A solution containing 0·0385 gram KNO<sub>3</sub> per 7 litres was made.

The amount of nitric nitrogen per 100,000 pts. was determined, and gave 0·188 by the gas method. 50 c.c. of saturated SH<sub>2</sub> solution was added, and the whole allowed to stand. After immediate admixture, the mixture gave 0·155 pt. of nitrogen per 100,000 pts., which, when the dilution caused by the 50 c.c. of water being added is taken into account, is no reduction at all. When nearly saturated with gas, the solution gave 0·075 pt. of nitric nitrogen; and after standing two days, no nitrates could be detected at all.

A similar experiment gave—

KNO<sub>3</sub>, 0·0385 gram.

Before adding SH<sub>2</sub>, 0·188.

After adding 20 c.c. SH<sub>2</sub> solution, 0·158.

Saturated and allowed to stand two days 0·000.

From these experiments it seems reasonable to conclude that small quantities of SH<sub>2</sub> do not reduce nitrates; but that when the water is saturated with gas the nitric nitrogen is wholly reduced.

I next tried the effect of shaking up, in a bottle, a solution of nitre with spongy iron. Before adding the spongy iron, an analysis of dissolved atmospheric air gave—

6·8703 c.c. of air from 340 c.c. of solution; or 20·20 c.c. of air per litre of the solution.

The percentage composition being—

CO <sub>2</sub> .....	11·99
O .....	30·36
N .....	57·64
	99·99

The large quantity of CO<sub>2</sub> present is accounted for by the fact that distilled water was used, which I always found to contain a large quantity of CO<sub>2</sub>.

Estimations of nitrogen as nitrates and nitrites, and of ammonia before the spongy iron was added gave—

Ammonia .... 0·016 part per 100,000.

	Gas method.	Indigo method.
Nitrogen as nitrates and nitrites..	6·059	6·059

The spongy iron was then added, there being 100·0 grams of it in 2 litres of the solution. The bottle filled with the solution stood neck downwards in a mercury cup. The whole was shaken up from time to time. There was no great oxidation of the iron.

After standing 10 days, the results on analysis of dissolved air were :—

6·2873 c.c. of air from 340 c.c., or per litre 18·49 c.c. of air.

Percentages of gases—

CO <sub>2</sub> .....	0·00
O .....	5·49
N .....	94·47
	99·96

During the 10 days the experiment lasted, there was a constant evolution of gas, but in quantities too small for analysis. In the dissolved atmospheric air 11·99 per cent. of CO<sub>2</sub>, being all that was present, has been absorbed by the iron, the iron becoming carbonate. The oxygen, too, has been greatly reduced, and the gas remaining dissolved is now almost pure nitrogen.

The nitric nitrogen was estimated and found to be—

Indigo process.	Gas process.
3·361	3·360

The ammonia was 1·200 pts. per 100,000. Thus the total decrease in nitrogen as nitrates and nitrites was 2·698; while the total increase in ammonia was 1·184 pts. per 100,000, which corresponds to 0·975 pt.

of N. There is thus a loss of 1.723 pt. of N during the conversion of the nitric nitrogen into ammonia. It is also safe to conclude that oxygen and carbonate of iron can exist together in solution. The spongy iron converts the nitrogen present as nitric nitrogen into ammonia, the bases probably becoming carbonates.

3. *On the Effect of Filtration through Spongy Iron on Animal and Vegetable Matters in Solution in Water.*

I began this subject by first studying the effect of filtration through spongy iron on solutions of nitre.

A solution containing 1.0113 gram of nitre was made. This, before filtration, gave results as follows:—

	Gas method.	Indigo method.
Nitrogen as nitrates and nitrites. .	2.648	2.653
Ammonia . . . .	0.011.	

The decrease of nitrogen as nitrates and nitrites after each filtration is given in the following table:—

Once through the filter . . . . .	2.257
Twice through the filter . . . . .	2.030
Three times through the filter (allowed to stand overnight)	0.376
Four times through the filter . . . . .	0.075
Five times through the filter . . . . .	0.000

The decrease in nitric nitrogen is therefore 2.633.

An estimation of ammonia, after five filtrations, gave 1.840 pts. per 100,000, corresponding to 1.515 pts. per 100,000 of N. There is here again a loss of N during the transformation of nitric nitrogen into ammonia, and in this case the loss is 1.118 pts. per 100,000.

Dissolved atmospheric air estimations were made at the commencement and at the close of the experiment. To collect the sample for the experiment after filtration five times, a tube was attached to the filter and led into the boiling-out flask, itself filled with mercury. By this means all exposure was prevented.

*Dissolved Atmospheric Air Results.*

<i>Before filtration.</i>	<i>After 5 filtrations.</i>
Vol. of air from 340 c.c. OH <sub>2</sub> = 6.9177, or per litre of water = 20.34.	Vol. of air from 340 c.c. OH <sub>2</sub> = 6.4372, or per litre of water = 18.93.
Percentage composition—	Percentage composition—
CO <sub>2</sub> . . . . 22.60	CO <sub>2</sub> . . . . 0.00
O . . . . . 24.42	O . . . . . 23.30
N . . . . . 52.98	N . . . . . 76.70
100.00	100.00

Although there was a marked diminution in O, and the CO<sub>2</sub> had all disappeared, I am confident there would have been a far greater diminution in the volume of gas, had it not been for the unavoidable exposure caused by pouring into the filter for a second filtration and running out. In the second and all subsequent experiments with the spongy iron filter, this exposure was avoided as much as possible by collecting the water, in a bottle closed with a bored cork (with two holes in it), and pouring it into the filter quickly but gently. The following results will show that these precautions were to some extent successful.

*Before filtration* :—

	Indigo method.	Gas method.
Nitrogen as nitrates and nitrites. .	1·986	2·006
Ammonia . .	0·018 per 100,000 parts.	

*A second experiment* was tried with a fresh solution of nitre in distilled water.

I generally found distilled water to contain about 0·016 of NH<sub>3</sub> and a large quantity of CO<sub>2</sub> in solution.

The solution was then passed through the spongy iron filter eight times.

The decrease of nitric nitrogen per 100,000 is shown by the following table :—

*Decrease of Nitrogen after each Filtration.*

	Indigo method.
Before filtration. . . . .	0·006 parts per 100,000.
After one filtration . . . . .	1·580           ,,
After two filtrations . . . . .	1·200           ,,
After three filtrations . . . . .	0·903           ,,
After four filtrations. . . . .	0·602           ,,
After five filtrations . . . . .	0·489           ,,
After six filtrations . . . . .	0·225           ,,
After seven filtrations . . . . .	0·075           ,,
After eight filtrations . . . . .	0·000           ,,

Although the reduction has not taken place so quickly in this experiment the result is the same, the total reduction is 2·006 ammonia, after eight filtrations 1·400, corresponding to 1·152 pts. of N. There is here a loss of 0·854 pt. of N during the reduction.



*Results of Dissolved Atmospheric Air.*

<i>Before filtration.</i>	<i>After four filtrations.</i>	<i>After six filtrations.</i>
Volume of gas from 340 c.c. 7·6300, or per litre 22·44 c.c. air.	Volume of gases from 340 c.c. 5·455, or per litre 16·04 c.c. air.	Volume of gases from 340 c.c. 5·2079, or per litre 15·31 c.c. air.
Percentage composition—	Percentage composition—	Percentage composition—
CO <sub>2</sub> . . . 19·89	CO <sub>2</sub> . . . 0·00	CO <sub>2</sub> . . . 0·00
O . . . . . 27·87	O . . . . . 14·05	O . . . . . 14·02
N . . . . . 52·24	N . . . . . 85·95	N . . . . . 85·98
—————	—————	—————
100·00	100·00	100·00

Although the precautions before referred to were put in force during this experiment, I was unable to reduce the percentage of oxygen below 14·02 per cent. This seems to point again to the fact before stated, that oxygen and carbonate of iron can exist together in solution. On standing, after filtration, most of these solutions deposited oxide of iron.

The effect of filtration through spongy iron on a solution of peat was next tried.

An infusion of peat in hot distilled water was made. The whole was filtered hot through paper, and then estimations of dissolved atmospheric air, and of organic carbon, &c., made.

The following results were obtained :—

Volume of air from 340 c.c. . . . . 7·267  
or per litre of the solution . . . 21·37

Percentage composition of gases—

CO <sub>2</sub> . . . . . 43·040	Organic carbon . . . . . 2·296	Parts per 100,000.
O . . . . . 0·006	Organic nitrogen . . . . . 0·650	
N . . . . . 56·953	N as nitrates and nitrites . . . 0·000	
CH <sub>4</sub> . . . . . 0·000	Ammonia . . . . . 0·144	
—————		
99·999		

The solution was then filtered through a spongy iron and gravel filter. It required about 25 minutes for the whole to pass through. The filter was covered and precautions taken for the prevention of the entrance of "blacks" and other organic matter. During the filtration, some slight evolution of gas was observed. This fact was ascertained by thrusting a steel needle into the filter when small bubbles of gas were seen to rise. An attempt to collect any quantity failed.

A sample was collected after each filtration, and an estimation of organic carbon made.

*Decrease of Organic Carbon and Nitrogen after each Filtration.*

	1.	2.	3.	4.	5.	6.
C ..	1·513	0·484	0·276	0·192	0·075	0·060
N ..	0·414	0·187	0·080	0·028	0·000	0·000

Thus the total decrease in organic carbon by six filtrations is 2·236; the total loss in organic nitrogen is 0·650.

The increase in ammonia was studied after each filtration and is shown in the following table:—

*Increase in Ammonia after each Filtration.*

Before filtration.....	0·144 part per 100,000.
Once through.....	0·200 „
Twice through.....	0·437 „
Thrice through.....	0·589 „
Four times through.....	0·750 „
Five times through.....	0·900 „
Six times through.....	0·900 „

Thus the total increase in ammonia is 0·756, corresponding to 0·622 pt. of N per 100,000; and the total loss of organic N of peat is 0·650. Allowing for experimental error, it is seen that the whole of the organic nitrogen of peat becomes in time ammonia during filtration through spongy iron. There was no nitrogen as nitrates or nitrites after six filtrations.

A dissolved atmospheric air estimation gave—

5·5028 c.c. of air from 340 c.c. of water, or 16·18 c.c. of air per litre.

An analysis of the gas was made, and suspecting that  $\text{CH}_4$  might be formed, the O was determined with pyrogallic acid and potash.

$\text{CO}_2$ .....	0·00
O .....	16·50
N .....	76·69
$\text{CH}_4$ .....	6·79
	<hr/>
	99·98

The results drawn from this experiment are that the organic nitrogen of peat is wholly converted into ammonia; and the organic compounds and substance partly reduced to marsh-gas. No nitric nitrogen is found.

I next tried the effect of filtration on a solution of egg albumin. A portion of the white of an egg was poured into 8 litres of distilled

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water. This was then filtered through linen, and estimation of dissolved air and organic carbon, &c., made.

The following results were obtained :—

Volume of dissolved air from 340 c.c., 7·3148, or per 1000 c.c.

Having the following percentage composition :—

		Parts per 100,000.
CO <sub>2</sub>	. . . . . 12·40	Ammonia . . . . . 0·125
O	. . . . . 28·10	N as nitrates and nitrites. . . . . 0·00
N	. . . . . 59·49	Organic carbon. . . . . 25·200
	99·99	Organic nitrogen . . . . . 7·162

This solution was then filtered through the spongy iron filter eight times, and allowed to remain after each filtration all night. It thus took eight days to filter.

The results obtained after filtration are given below :—

Ammonia . . . . .	0·500
N as nitrates and nitrites . . . . .	0·000
Organic carbon . . . . .	0·492
Organic nitrogen . . . . .	0·220

The decrease in organic carbon was 24·708, and of organic nitrogen 6·942, of which only 0·375 pt. is transformed in ammonia; no nitric nitrogen is formed.

An estimation of dissolved atmospheric air gave—

4·958 c.c. of air from 34 c.c. of water.

An analysis gave the following figures :—

CO <sub>2</sub> . . . . .	0·00
O . . . . .	13·72
N . . . . .	85·65
CH <sub>4</sub> . . . . .	0·61
	99·98

The conclusion drawn from the experiments as to the influence of spongy iron on organic matter in water are: 1. That it acts as a very powerful reducing agent on the carbon compounds composing the organic matter dissolved in water. In some cases marsh-gas itself was produced; probably the organic matter was first oxidised to CO<sub>2</sub>, and then the action of metallic iron on this gas giving rise to CH<sub>4</sub> by the ordinary decomposition of water. 2. The organic nitrogen is in nearly all cases reduced to ammonia.