

evacuation the sac very quickly filled again, notwithstanding pressure exercised upon it.

The examination after death showed that the fluid was collected in the expanded tissue of the pia mater, or subarachnoid spaces, about the cauda equina. The pia mater presented appearances of inflammation long past, as well as of that which had probably been the cause of death. The canal in the axis of the spinal cord was distinct in its whole length. Commencing, below a large fourth ventricle, with a diameter of about one-fourth of a line, it gradually widened, till, at the lumbar part of the cord, it had a diameter of a line and a half. Its termination at the end of the cord could not be traced in the confusion of parts caused by the distension and inflammation of the membranes.

III. "On the Oxidation of Ammonia in the Human Body."

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In the last edition of Professor Lehmann's *Animal Chemistry*, vol. ii. p. 363, a very decided opinion is expressed against the conclusion to which I arrived in consequence of some experiments published in the *Philosophical Transactions* for 1851.

I considered it proved that ammonia was partly at least converted into nitrous acid in its passage through the body. In opposition to this Professor Lehmann states,—

1st. That the method which I employed must of necessity give a reaction resembling that given by nitrous acid; his words are, "Es wäre nun leicht einzusehen dass schweflige Säure, durch welche bekanntlich Iodwasserstoff zersetzt wird, in die Vorlage übergeht und so jene vermeintliche salpetersaure Reaction bedingt."

2ndly. That when nitric acid was added to urine and it was distilled with phosphoric acid instead of sulphuric acid, no trace of blue colour with starch and iodide of potassium could be obtained. "Das nach Anwendung von Phosphorsäure erhaltene Destillat giebt aber auch jene vermeintliche salpetersaure Reaction nicht, ja selbst dann nicht, wenn dem Harn vorher absichtlich einige Tropfen Salpetersäure zugesetzt worden waren."

It appeared to me undesirable merely to reply to Professor Lehmann, that I had expressly stated that the indigo and protosulphate of iron tests were used, and gave as decided proof of the presence of nitrous acid in the urine as Price's test gave; and that sulphurous acid could not have produced the same effect as nitrous acid in these tests. It seemed more desirable to repeat the experiments which had been made in Professor Lehmann's laboratory on the action of sulphurous acid, and on the effect of using phosphoric instead of sulphuric acid in the distillation of the urine.

I was fortunate enough to obtain the assistance of Mr. Malone to carry on the experiments continuously from day to day, and through the kindness of Dr. Hofmann this was done in the College of Chemistry.

1st. On the action of sulphurous acid on starch and iodide of potassium and very dilute hydrochloric acid.

In England it is by no means well known that sulphurous acid decomposes hydriodic acid. On the contrary, theoretically it should not liberate iodine, and experimentally not only does it not liberate iodine, but it hinders the liberation of iodine and stops the formation of the blue colour when Price's test is used and nitrous acid is present; and if sulphurous acid be added after the blue colour is formed it makes it disappear.

Pure sulphurous acid was prepared, some nitre was fused, and a dilute solution was made, and it was tested by Price's test (starch, iodide of potassium and very dilute hydrochloric acid), then the dilute nitre solution immediately gave the deep blue iodide of starch; but when much or little sulphurous acid was added previously to the nitre solution, no blue colour at all was produced; and when, instead of the nitre solution, much or little sulphurous acid alone was added, contrary to the statement of Lehmann, no decomposition of the hydriodic acid could be obtained.

If instead of pure iodide of potassium it was mixed with iodate of potassa, an immediate blue colour was of course observed. I can only suppose that in this way Professor Lehmann obtained the reaction which he has attributed wrongly to the action of sulphurous acid on hydriodic acid, unless indeed no sulphurous acid at all was present and the acidity of the distillate was unneutralized. Dr. Lehmann is however right as well as wrong, in saying that Price's test

for nitric acid fails when sulphurous acid is present. The test fails, not, as he says, because sulphurous acid has the same action as nitrous acid in liberating iodine, but because it has exactly the opposite property of hindering the iodide from being set free even when nitrous acid in small quantity is present.

It is possible that in distilling the urine with sulphuric acid, the distillation, if carried too far, may give rise to sulphurous acid, and that thus Price's test may fail to detect nitrous acid in the urine. Moreover, portions of the distillate may be projected against the sides of the hot retort, by which the sulphuric acid acting on the organic matter may be decomposed, and minute quantities of sulphurous acid may be liberated. This sulphurous acid, instead of decomposing hydriodic acid, causes the reformation of hydriodic acid when nitrous acid liberates iodine in Price's test.

2ndly. Lehmann states that experiments were made by distilling urine to which a few drops of nitric acid were added with phosphoric acid, and that then the distillate gave no reaction with Price's test.

The following experiments were made with every precaution.

Anhydrous phosphoric acid was prepared, and it was found to be free from nitrous acid. Some healthy urine was taken and some pure nitrate of potassa, in the proportion of two grains of salt to an ounce of fluid, and distilled with phosphoric acid (ten ounces of urine, twenty grains of nitre, and one ounce of anhydrous phosphoric acid). On concentrating, the neutralized dilute nitrous acid was detected by all the tests, namely, the indigo test, the protosulphate of iron and Price's test.

In a second experiment, five ounces of urine with five grains of nitre and half an ounce of anhydrous phosphoric acid, gave nitrous acid by all the tests. The distillation was continued until the contents of the retort were viscid.

In a third experiment, three ounces of urine with a grain and a half of nitre were distilled with three drachms of glacial phosphoric acid; the distillate neutralized and evaporated gave no trace of nitrous acid; the same urine with the same quantity of nitre and three drachms of sulphuric acid, when distilled, gave a distillate, which when neutralized and evaporated gave decided evidence of nitrous acid.

In my former paper I showed that by distilling with sulphuric

acid when only one-tenth of a grain of nitre was added to each ounce of urine, nitrous acid could be detected.

From these experiments it appears that distillation with sulphuric acid is to be preferred to distillation with phosphoric acid; but even with this last acid, when a grain of nitre is added to an ounce of urine, the nitrous acid can be detected.

I then endeavoured, by using phosphoric instead of sulphuric acid in distilling urine passed after a salt of ammonia had been taken into the stomach, to detect nitrous acid in the urine.

Two drachms of muriate of ammonia were taken in seven ounces of distilled water. The urine was collected for six hours afterwards. Twelve ounces of this urine were distilled with one ounce of phosphoric acid (anhydrous). The distillate, when concentrated, did not give any evidence of nitrous acid by Price's test.

The same experiment was repeated with no better result.

In another experiment, sulphuric acid, six drachms to twelve ounces of urine, was used instead of phosphoric acid. The distillate as soon as it was obtained gave the slightest precipitate with chloride of barium insoluble in nitric acid, showing that a trace of sulphuric acid was carried over into the receiver. The distillate was made alkaline with pure carbonate of soda, evaporated, and nitrous acid was immediately detected by the indigo and iron test, as well as by Price's test. A portion of the distillate left exposed to the air, on the following day had lost the power of liberating iodine. This arose from the nitrous acid passing into nitric acid.

Pure nitre gives no colour with starch, iodide of potassium and dilute hydrochloric acid, but when fused it produces the liberation of iodine immediately. If the solution of fused nitre is exposed to the air it loses this property, but regains it when the solution is evaporated to dryness and refused and again dissolved.

In another experiment six ounces of urine passed before the muriate of ammonia was taken were distilled with half an ounce of sulphuric acid, the distillate was highly acid, and gave a slight precipitate with chloride of barium; it was made slightly alkaline, evaporated to a small residue, and then gave no evidence of nitrous acid. Then two drachms of muriate of ammonia were taken in seven ounces of distilled water, eight ounces of urine passed four hours afterwards were distilled with half an ounce of sulphuric acid. The

distillate was fractional ; the first portion gave no colour with starch test ; it contained a minute trace of sulphurous acid. The second portion was highly acid ; it was made slightly alkaline, evaporated nearly to dryness, and then gave most positive evidence of nitrous acid by Price's test, and also by decolorizing a deep solution of indigo.

Thus before the salt of ammonia was taken no nitrous acid could be detected in the urine, whilst after the ammonia nitrous acid was proved to be present, not only by Price's test, but by the indigo test also.

In conclusion, it results from these experiments,—1st, That in Price's test sulphurous acid produces exactly the opposite effect to nitrous acid, and even hinders nitrous acid from liberating iodine from hydriodic acid.

2ndly. That phosphoric acid, when mixed with urine containing nitre and distilled very low, does liberate nitrous acid ; though when used instead of sulphuric acid, it does not enable the nitrous acid to be detected so readily as when the latter acid is employed.

Hence the experiments performed in Professor Lehmann's laboratory by Herr Jaffé*, do not invalidate Price's test for nitrous acid in the way Professor Lehmann supposes ; and by again repeating some of my former experiments, I still arrive at the conclusion that when ammonia is taken into the body nitric acid may be detected in the urine, but that the quantity which can be made to appear is so small that the most delicate method is required for its detection. This however is no proof that a much larger quantity may not be lost in the process for obtaining it from the urine.

* Erdmann's Journal, vol. lix. p. 238, 1853.