III.—*On the Action of Permanganate of Potash on Urea, Ammonia, and Acetamide in strongly Alkaline Solutions.*

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It has been pointed out by Chapman and Smith,* that permanganate of potash *in presence of excess of alkali* is an oxidizing agent of a most singular kind. It attacks alcohol much in the same way that nitric acid does, producing the diatomic acids glycollic and oxalic, but not aldehyde nor acetic acid. It is, at the same time, strangely inactive towards certain substances. Boiled with oxalic acid it does not suffer any decomposition; and, as is seen in the working of the new method for the determination of albuminoid matter in waters, it may be boiled with ammonia without the occurrence of any chemical change.

The following experiments on the action of this re-agent on urea, ammonia, and acetamide:—

will serve as a contribution to its chemical history.

Urea.

The urea taken for this research was prepared by the well known process from ferrocyanide of potassium. One of the

* Journ. of the Chemical Society [2], v, p. 302, June, 1867.

† Ibid., v, p. 449, Sept. 1867.

samples was proved to be pure by getting it to combine with the theoretical quantity of nitrate of mercury. Another sample was analysed by Dr. Affleck, who got from it the theoretical percentage of nitrogen by Dumas' method.

I.	0.100	grm. of urea,
	1.000	„ permanganate of potash,
	10.0	„ solid caustic potash,
	10.0	„ water,

was sealed up in a tube and heated to 130° C. for twelve hours. After the experiment the contents of the tube were free from unacted upon manganate or permanganate of potash—showing that much oxidation had taken place. On opening the tube under water there was an escape of 15.7 cub. cent. of gas.

In order to ascertain whether this evolution of gas was due to the permanganate giving up oxygen, or whether it was an evolution of nitrogen from the urea, a gas-analysis was made. (Frankland's apparatus was employed for this and the other gas-analyses given in this paper).

Volume taken.....	86
After adding hydrogen.....	139
After explosion	99

The gas therefore consisted of

Oxygen.....	15.50
Nitrogen	84.50
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	100.00

Obviously therefore, inasmuch as there was less oxygen than atmospheric air contains, the evolution of gas in our experiment was not evolution of oxygen but of nitrogen.

The space in the digestion tube unoccupied by liquid was measured and equalled 38.1 c.c. We are thus provided with data for determining whether the permanganate had evolved oxygen, and also how much nitrogen came from the urea.

	cub. c.
Volume of gas left in tube	38.1
Volume of gas escaped from tube	15.7
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Total volume of gas after experiment	53.8

consisting of 8·34 c.c. of oxygen and 45·46 c.c. of nitrogen.

Now the 38·1 c.c. of air originally present in the tube when it was sealed up contained 8·00 c.c. of oxygen and 30·1 c.c. of nitrogen.

We have therefore—

Oxygen present originally	8·00
Oxygen found after experiment	8·34

No oxygen, or only a trace of oxygen, was set free from the permanganate. Also the urea had evolved about 15 c.c. of nitrogen gas.

This amount of nitrogen is not half that which the urea contained (0·100 grm. urea contains 37·2 c.c. of nitrogen gas at 0°C. and 760 mm. pressure). A little of the nitrogen is accounted for as ammonia, for ·0032 grm. of nitrogen was found in the tube after the experiment in the form of ammonia, which was distilled off and estimated by titration. There thus remains about half of the total nitrogen to be accounted for, and which must have been converted into nitric acid. The circumstance that the 1 grm. of permanganate of potash had been completely reduced to the state of bi- or sesqui-oxide of manganese, and that there was no evolution of oxygen gas, is in itself sufficient proof that a considerable quantity of the nitrogen of the urea had been oxidized to nitric acid.

In this experiment, therefore, a little less than half of the nitrogen of the urea appeared as nitrogen gas, about half was oxidized to nitric acid, and a small portion was found as ammonia.

II. In a second experiment the proportion of permanganate was increased, the object proposed being to ascertain whether greater oxidizing effect would be the result of increasing the quantity of oxidizing agent.

0·050	grm. urea
1·00	„ permanganate of potash
10·00	„ potash
10·	„ water

were sealed up and heated to 200° C. for four hours. After this treatment there remained much manganate still unreduced. On opening the tube there was a considerable escape of gas, which

was lost. Not so much as '0001 grm. of ammonia was to be found in the tube.

The experiment was repeated in order to have an opportunity of examining the gas.

0·100 grm.	urea
2·00	„ permanganate of potash
10·00	„ caustic potash
12·	„ water

sealed up and heated to 160° C. for one hour. Abundance of manganate of potash remained after the experiment. On opening under water, there was an escape of gas. The total volume of gas was carefully measured and found to be 47 c.c. at 11° C. and 744 mm. pressure equal to 44·20 c.c. at 0° C. and 760 mm.

On analysis :—

Volume taken..	160
After adding hydrogen.....	231·5
After explosion	207·5

From which is deduced—

Oxygen.....	5·00
Nitrogen	95·00
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	100·00

Allowing for the nitrogen originally present in the tube when it was sealed up, which may be done by taking the 5 per cent. of oxygen to be the measure of atmospheric air, we shall arrive at the result that 33·68 c.c. at 0° C. and 760 mm. is the quantity of nitrogen furnished by the urea.

Thus we have :—

0·100 grm. urea give 33·68 c.c. of nitrogen.

Theory requires that 0·100 grm. urea contains 37·2 c.c. of nitrogen.

We arrive at the startling result that by increasing the proportion of permanganate, we put a stop to the oxidation.

This fact, so singular at first sight, would appear to indicate that the oxidation of urea by permanganate is quick but superficial, whilst the oxidation at the expense of manganate is slower but deeper. Obviously (as will be apparent on referring to the actual quantities of permanganate and urea employed)

there would still remain unattacked urea in the first experiment after the permanganate had exhausted itself and passed into manganate. In the second experiment, on the contrary, there was enough permanganate to transform all the urea into carbonic acid, water, and nitrogen, without suffering deoxidation lower than to the stage of manganate, and nitrogen once in the free state is beyond the reach of oxidizing agents. For some interesting considerations concerning the difference of action between permanganates and manganates we would refer to Chapman and Smith's paper, which we cited at the beginning of this notice.

Thus far we have been dealing with very concentrated solutions at temperatures considerably above the boiling-point of water. Taking weaker solutions and operating at about 100°C ., we meet with a similar decomposition, only slower. The following experiment illustrates this: we dissolved 4.75 milligrammes of urea in about 400 c.c. of pure water, added a little carbonate of soda, about 5 grm. of caustic potash, and about 0.5 grm. of permanganate of potash, and distilled for a very long time. A slow evolution of ammonia took place. Ultimately this evolution became very slow and then stopped. The quantity of ammonia obtained was estimated by the Nessler test, and amounted to 0.575 milligramme. Theory requires 2.692 milligrammes. About 22 per cent. of the nitrogen in the urea was obtained in the form of ammonia, the rest, of course, being either evolved as nitrogen gas, or converted into nitrate. An experiment on a still smaller quantity of urea gave a very similar result. Here the remark may be made that this result is hardly compatible with Mr. Dugald Campbell's statement, published in the "Laboratory," which is in effect that a weak solution of urea gives up all its nitrogen in the form of ammonia when it is partially decomposed with carbonate of soda, and then attacked with potash and permanganate of potash. If Mr. Campbell did not get off the full quantity of nitrogen in the form of ammonia by the treatment with carbonate of soda, he would not get the full quantity on employing permanganate.

Ammonia.

Urea being resolved into carbonic acid and ammonia by the simple assimilation of water,

it might be supposed that an oxidizing agent applied to urea in presence of water would, in effect, operate on the ammonia; and on this ground it was necessary to study the oxidation of ammonia.

Experiment I.—

0·050	gram. of NH_4Cl
2·00	gram. of permanganate of potash
10·00	gram. of caustic potash
10·	gram. of water

was heated to 150°C . for an hour and a half. Opened the tube; only minute traces of gas escaped. The gaseous contents of the tube were analysed:—

Oxygen	= 23·00
Nitrogen	= 77·00
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	100·00

showing that the minute evolution of gas was evolution of oxygen, and not of nitrogen. The residue in the tube contained only ·0033 gram. of nitrogen in the form of ammonia; therefore, there had been oxidation of most of the ammonia to the state of nitric acid.

In a second experiment sulphate of ammonia was substituted for the chloride of ammonium, the other things being the same, and the proportion the same. The temperature was a little higher than in the first experiment. Result: no ammonia and no gas.

Acetamide.

I. 0·050	gram. acetamide
1·00	gram. permanganate of potash
10·	gram. caustic potash
10·	gram. water

sealed up and heated to 160°C . for one hour.

After the experiment there remained abundance of manganate, but some peroxide of manganese had been deposited. No gas was given off, and only 0·0005 gram. of ammonia was found in the tube. The appearance of peroxide of manganese

proves that reaction had taken place Nitrates or nitrites must, therefore, have been formed.

The results arrived at in this paper are the following :—

Urea and great excess of permanganate, in presence of much caustic potash, gives all the nitrogen in the form of nitrogen gas.

Urea, with less permanganate, gives part of the nitrogen as gas, and part as nitric acid.

Ammonia, whether as chloride or sulphate, is totally oxidized to nitrates when heated with great excess of permanganate and alkali. Acetamide behaves like ammonia. These reactions occur at temperatures above the boiling-point of water.

The foregoing result has an important bearing on the rational formula for urea, and goes a long way to show that it is not the amide of carbonic acid. Ammonia and the amides yield nitrates on oxidation with alkaline permanganate. Urea, if it were really carbamide, should do the same, but it gives nitrogen gas instead. Moreover, urea, as is well known, is not resolved into ammonia and carbonic acid with anything like sufficient ease to admit of its being carbamide. We are,

therefore, led to write $C \begin{Bmatrix} NH \\ NH_2 \\ OH \end{Bmatrix}$ for urea. It is marsh-gas

wherein imidogen, amidogen, and peroxide of hydrogen replace hydrogen. This formula is not new. Very simple and natural changes in this formula express the passage from urea to cyanate of ammonia and to carbamide.

The following formulæ express the relation between guanidine and urea :—