XII.—*The Behaviour of the Nitrogen of Coal during Destructive Distillation; with some Observations on the Estimation of Nitrogen in Coal and Coke.*

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WHEN coal is submitted to destructive distillation in close vessels, as in coal-gas manufacture, ammonia-gas with numerous other substances is evolved. It is usual for writers on the subject to consider that the greater portion of the nitrogen of coal takes the form of ammonia-gas or its compounds. Professor Roscoe in his small manual has the following sentence:—"Coal contains about 2 per cent.

of nitrogen which, when the coal is heated in close vessels, mostly comes off in combination with the hydrogen of the coal as ammonia."

The experiments which I now bring before the Society have been made with the view of determining to what extent the nitrogen of coal is converted into ammonia during destructive distillation. Only a small fraction of the whole quantity of nitrogen is obtained as ammonia. Some nitrogen appears as cyanogen; some is presumably present in the coal-gas in the elementary condition, while a considerable portion remains behind in the coke.

One particular sample of Durham coal has been employed in these experiments. It is a kind in favour with certain metropolitan gas engineers, who are fairly well acquainted with its ammonia-producing capabilities. The results of the ultimate analysis of this sample are expressed by the following numbers:—

Carbon	84.34
Hydrogen	5.30
Nitrogen	1.73
Sulphur	0.78
Oxygen (by difference)	4.29
Moisture lost at 212° F.	1.14
Ash	2.42
	<hr/>
	100.00

On heating it in a close platinum crucible until gas ceased to come off, the following numbers were obtained:—

Volatile matter	25.54
Coke	74.46
	<hr/>
	100.00

The coke obtained in this way was reserved and its nitrogen estimated.

The observations made may be classed as follows:—

Estimation of the total nitrogen in the coal.

Estimation of the amount of nitrogen which is evolved as ammonia during destructive distillation.

Estimation of the amount of nitrogen evolved as cyanogen during destructive distillation.

Estimation of the amount of nitrogen which remains behind in the coke.

Estimation of the Total Nitrogen of the Coal.

Three methods in use for this purpose have been employed—that is (1) by heating with excess of soda-lime; (2) by heating with excess

of copper oxide in an atmosphere of carbonic anhydride; and (3) by heating with an excess of copper oxide *in vacuo*.

Soda-lime Method.—In these cases the ammonia evolved was received in hydrochloric acid, converted into the platinum-ammonium chloride, dried, and weighed. The last two experiments were as follows:—

Coal taken in grams.	Platinum-ammonium chloride obtained in grams.	Nitrogen obtained in grams.	Nitrogen percentage of coal.
2.339	0.629	0.03940	1.684
1.349	0.368	0.02305	1.708
Mean			1.696

Copper Oxide Method (in an Atmosphere of CO₂).—Three successful experiments by this method gave 2.01, 2.03, and 1.90 respectively as the nitrogen percentages; but as the carbonic anhydride was obtained from marble and hydrochloric acid in the usual way, the uncertainty arising from the presence of small quantities of air in the carbonic anhydride from this source renders it undesirable to employ the results obtained by this method in the present inquiry.

Copper Oxide Method (in vacuo).—These experiments were of the ordinary character, rough copper oxide being employed. The last three gave the following results:—

Coal taken in grams.	Nitrogen obtained in c.c. (uncorrected).	Nitrogen obtained in grams.	Percentage of nitrogen in coal.
0.534	8.4	0.00976	1.83
0.532	8.0	0.00936	1.76
0.559	8.0	0.00952	1.70
Mean			1.763

The Estimation of the Amount of Nitrogen which is Evolved as Ammonia during Destructive Distillation.

The process of coal-gas manufacture has been carried out on a small scale. A weighed quantity of the coal was placed in a combustion-tube sealed at one end, the outlet being connected with an arrangement containing hydrochloric acid for washing the coal-gas. In this way the whole of the ammonia was absorbed from the coal-gas. At the close of the operation the acid liquor was removed, the tar was washed with warm acidulated water, and the ammonia recovered from the mixed acid liquors by distillation with caustic soda. The ammonia was eventually converted into the double platinum-ammonium chloride, dried, and weighed.

Coal taken in grams.	Platinum salt obtained in grams.	Nitrogen obtained in grams.	Percentage of nitrogen of coal evolved as ammonia.
39·97	1·534	0·0961	0·251

The quantity of ammonia obtained in this experiment is a little higher than that obtained in the commercial way from this description of coal.

Estimation of the Amount of Nitrogen evolved as Cyanogen during Destructive Distillation.

After the coal-gas produced in the preceding experiment had been freed from ammonia, it was made to pass through a combustion-tube containing slaked lime kept at a high temperature by means of an external source of heat. In this way the cyanogen was decomposed, with production of a certain quantity of ammonia, which was absorbed by means of hydrochloric acid placed in suitable apparatus at the outlet. The ammonium chloride was converted into the platinum salt, dried, and weighed.

Coal taken in grams.	Platinum salt obtained in grams.	Nitrogen obtained in grams.	Percentage of coal evolved as cyanogen.
37·97	0·166	0·0104	0·027

Estimation of the Amount of Nitrogen which remains behind in the Coke.

Some observations on this subject by myself were made at the last Annual Meeting of the Gas Institute, and are published in its Transactions for 1882. Since that meeting attention has been directed to the matter by several gentlemen well known in the gas world. Dr. Siemens alludes to it in his recent address at Southampton.

The specimen of coke used was a mixture of two portions obtained in two distinct operations. One was that produced by heating the coal in a close platinum crucible until gas ceased to come off; the other was the coke taken from the combustion-tube in the experiment on destructive distillation. The two were well mixed and ground to a very fine powder in an agate mortar. The nitrogen present was estimated firstly by ignition with soda-lime, and secondly by ignition with copper oxide *in vacuo*.

Soda-lime Process.—The following are the last two experiments made:—

Coke taken in grams.	Platinum salt obtained in grams.	Nitrogen obtained in grams.	Percentage of nitrogen in coke.
1·805	0·337	0·0211	1·16
1·826	0·342	0·0214	1·17
Mean.....			1·165

Copper Oxide Process (in vacuo).—The last three experiments made were as follows:—

Coke taken in grams.	Nitrogen obtained in c.c. (uncorrected).	Nitrogen obtained in grams.	Percentage of nitrogen in coke.
0·510	4·0	0·0047320	0·928
0·547	5·8	0·0068266	1·240
0·636	6·2	0·0071858	1·130
Mean			1·099

A general consideration of these two methods of estimating nitrogen leads one to infer that higher numbers would be obtained by combustion with copper oxide *in vacuo* than by similar treatment with soda-lime; and such results are shown in the experiments on the coal. The results obtained with the coke are somewhat irregular, the mean not being in accordance with what was anticipated. However, the conditions best for an experiment were not realised at the time. From six to eight hours' steady and continuous heating of the charge is necessary for complete decomposition; and in the case of experiments in which the mercury pump has been used, it has been found advisable to maintain the pressure inside the combustion-tube as near that of the atmosphere as possible, until the decomposition of the charge has been complete. The gaseous products in the tube have then been quickly and completely removed. With copper oxide *in vacuo* much advantage has been derived by placing the combustion-tube in an outer tube of wrought iron, just sufficiently wide and long enough to encircle it the whole length of the highly heated part. For every cubic centimetre of nitrogen obtained there have been from 100 to 150 c.c. of carbonic anhydride to be dealt with. With the quantities of coal and coke operated on, large quantities of copper oxide in wide tubes have been used, and when the latter have been enclosed in an iron tube, the charges have been worked off with ease. Bursting of the combustion-tube has not only not occurred, but a ready and efficient control over the temperature of the charge has been maintained.

Having regard to the coal, the mean of the results of the soda-lime process is 1·696, and with copper oxide *in vacuo* the mean is 1·763. I have taken 1·730 as the percentage of nitrogen in the coal. The experiments on the coke with soda-lime furnish a mean of 1·165, and

110 FOSTER: THE BEHAVIOUR OF NITROGEN OF COAL, ETC.

with copper oxide *in vacuo* a mean of 1·099. I have taken 1·132 as the nitrogen percentage of the coke.

A summary of the results thus far obtained may be classed as follows:—

Percentage of nitrogen in the coal	1·730
Percentage of nitrogen of coal evolved as ammonia during destructive distillation	0·251
Percentage of nitrogen of coal evolved as cyanogen during destructive distillation	0·027
Amount of nitrogen remaining in coke furnished by 100 parts of coal	0·842
	<hr/> 1·120
Nitrogen from 100 parts of coal unaccounted for, the larger portion of which is presumably present as free nitrogen in the coal-gas. Some is no doubt in the tar	0·610

If we further reduce these figures to percentages on 100 parts of nitrogen, their relation to each other becomes more intelligible:—

Nitrogen of coal evolved as ammonia	14·50
Nitrogen of coal evolved as cyanogen	1·56
Nitrogen of coal present in the coal-gas in the elementary condition	35·26
Nitrogen remaining behind in the coke	48·68
	<hr/> 100·00

I have not made any experiments on the amount of nitrogen in the tar, nor am I in possession of any information on the subject. I have assumed that the quantity is relatively small.

Some lengthy observations have been made on the production of ammonia at stated intervals during the period of destructive distillation. They are being published in the *Journal of Gas Lighting*. It appears from the results obtained, that the coal-gas is richest in ammonia during the middle of the period and poorest at the close; in fact, the poverty of the coal-gas (so far as ammonia is concerned) at the close of the process of distillation is very marked.