XLIX.—*The Structure and Chemistry of the Cyanogen Flame.*

By ARTHUR SMITHELLS, B.Sc., and FRANKLAND DENT, B.Sc., 1851 Exhibition Science Scholar (1894), the Yorkshire College, Leeds.

The general character of the flame of burning cyanogen and the separation of the two cones, of which it consists, were briefly described by Smithells and Ingle, in their paper "On the Structure and Chemistry of Flames" (*Trans.*, 1892, **61**, 204).

Professor H. B. Dixon, in connection with his important investigations on the rate of explosion in gases, has also been led to examine the cyanogen flame (*Phil. Trans.*, 1893, **184**, 122), but has kindly left to us the investigation of the subject.

The following pages contain an account of a more detailed examination of the cyanogen flame.

Preparation of the Gas.—The cyanogen was prepared by heating dried mercuric cyanide in a hard glass tube, which was enclosed in a brass tube laid along a combustion furnace. A considerable amount of paracyanogen was formed in each experiment, and this was mixed with the mercuric cyanide employed in subsequent preparations of the gas. The cyanogen was led direct into an iron gas-holder, trapped with mercury and kept under slight pressure. The mercury, which was formed by the decomposition of the mercuric cyanide, and which condensed and accumulated in the tubes, was allowed to escape from time to time, through a T-piece, provided with a tap on one limb.

The gas thus prepared usually contained 96 to 98 per cent. of cyanogen and 4 to 2 per cent. of air.

The Flame of Cyanogen in the Cone Separating apparatus.—The flame of cyanogen, burning at a small circular orifice, consists of two distinct parts, as shown at *a* in the figure. The inner cone-shaped region is of a bright peach-blossom tint, whilst the enveloping cone shades off from a bright blue to a greenish-grey. If, now, we burn the cyanogen in a cone-separating apparatus and gradually add air, the inner cone becomes smaller, and eventually enters and descends the outer tube. But whilst this process of detachment is in progress, the inner cone is surrounded by a rosy halo, which still adheres to it after the descent. If more air be added, the rosy halo disappears and is almost immediately replaced by a blue one. The outer cone of the flame, which remains all the while at the top of the outer tube, preserves its original appearance, namely, blue shading off to greenish-grey. More air extinguishes the outer cone, and causes the inner one itself to take a bluer and its halo a greener tint.

The diagrams exhibit the chief phases of the flame.

Phases of cyanogen flame in the separator:—*a*. Ordinary flame. *b*. Flame with cones separated. *c*. Ditto, with less cyanogen. *d*. Ditto, with minimum of cyanogen. The dark shading represents rose colour, the lighter shading blue.

Mode of Experimenting and Analysis of the Interconal Gases.—A preliminary examination of the interconal gases showed they might contain some or all of the following:—carbon dioxide, carbon monoxide, cyanogen, nitrogen, nitric oxide and nitrogen peroxide, and it was, therefore, necessary to devise a suitable method for the determination of all these gases. The air used for the flame was dried by passing it through three U-tubes containing calcium chloride, sulphuric acid and pumice, and stick potash, lastly it was passed through a tube containing phosphorus pentoxide. The cyanogen was passed through a U-tube, containing fused caustic potash (to remove hydrocyanic acid) and then through a phosphorus pentoxide tube.

A sample of the interconal gases was withdrawn in two samplers; one was used for the eudiometric analysis, and the other for a special determination of carbon dioxide and cyanogen.

The eudiometric analysis was conducted as follows in a Dittmar-Lennox apparatus:—

The gas-measuring tube and mercury being thoroughly dry, a quantity of the gas from the sampler was measured off: it was then

transferred to the caustic potash pipette, for the absorption of carbon dioxide, cyanogen, and nitrogen peroxide. (The measuring tube was kept moist during the operations, subsequent to this absorption of nitrogen peroxide.) The gas containing carbon monoxide, nitrogen, and nitric oxide was transferred to the explosion vessel, and sufficient oxygen (with the addition of electrolytic gas) introduced for the explosion. Before explosion and after standing for half an hour in contact with the wet explosion vessel, to admit of the absorption of nitrogen peroxide formed from the nitric oxide, the gas was again measured, the diminution of volume being due to the absorption of nitrogen peroxide formed by the union of nitric oxide with oxygen. The gas was then exploded and measured, the carbon dioxide absorbed in the potash pipette, the residual oxygen absorbed by alkaline pyrogallate, and the remaining gas measured off as nitrogen.

The total oxides of nitrogen were determined in a fresh sample by adding air to a measured quantity of the gas and treating with water, the solution was reduced with some copper-zinc couple, and the ammonia distilled off and Nesslerised. The special analysis for cyanogen and carbon dioxide, consisted in passing a quantity of the interconal gases through baryta water contained in a funnel. The funnel was provided with a filter paper and had a stopcock on its stem; it was also enclosed in an air-tight glass cylinder, in order to prevent the absorption of atmospheric carbon dioxide by the baryta water. This cylinder was connected with an ordinary Mariotte's bottle by means of a glass tube, having a set of glass bulbs, containing baryta water, joined at its centre. The carbon dioxide and cyanogen formed with the baryta water insoluble barium carbonate and soluble barium cyanide and cyanate. The barium carbonate was washed, dissolved in hydrochloric acid on the filter and the barium precipitated by sulphuric acid; from the weight of barium sulphate obtained the amount of carbon dioxide was easily calculated. The filtrate, containing the barium cyanide and cyanate, was acidified with dilute nitric acid, and silver nitrate added; the precipitated silver cyanide was washed, dried, ignited, and weighed as silver. From this weight the amount of cyanogen was calculated. A direct determination of the cyanate was unnecessary, as each molecule of barium cyanide would be accompanied by one molecule of barium cyanate.

Regulation and Measurement of the Flow of Gases.—The dry cyanogen and air, after having passed through the drying tubes, were each led through a Wright's small dry gas governor and a micrometer tap, before being allowed to mix at the base of the cone-separator. The governors insured the delivery of the gas at a constant pressure, whilst the quantity could be regulated by the micrometer taps; by manipulation of the latter, the flame was brought

into the condition desired for the experiment. After the experiment was concluded and the sample taken, the rate of flow of the gases and the proportion between the two was measured as follows:— Without altering the taps, the air supply was again turned on from the calibrated gas-holder, and the time taken to pass about 60 litres was noted, from this the number of cubic centimetres per second was calculated. While air was passing through the one gas-governor, coal gas was passed through the other, so as to reproduce the same conditions of gas pressure as existed in the actual experiment. To determine the rate of flow of the cyanogen, air from the calibrated gas-holder was allowed to pass through both gas-governors simultaneously. The difference between the flow in this case and in the previous case gave the rate of flow of the cyanogen.

The details of a single experiment are subjoined.

Vol. of dry gas taken.....	18·21	c.c. of dry gas at 0° and 760 mm.	
After absorption with KOH	16·85	"	"
Added oxygen	7·00	"	"
„ electrolytic gas	3·70	"	"
Volume after standing	27·44	"	"
„ „ explosion	21·30	"	"
„ „ absorption w.			
KOH.....	16·67	"	"
„ „ absorption with			
alk. pyrogallate	12·18	"	"

(a.)

(CN) ₂ , CO ₂ , N ₂ O ₄	18·21 - 16·85	1·35	7·41
NO	4/7 (16·86 + 7·00 + 3·70) - 27·44	0·06	0·33
CO	21·30 - 16·67	4·63	25·42
N ₂	12·18	66·88	
Sum of constituents	18·22	100·04	
Gas actually taken	18·21	—	

(b.) *Determination of Total Oxides of Nitrogen.*—17·48 c.c. of the gas at 760·01 mm. and 9·5° gave ammonia equal to 5·43 c.c. standard ammonium chloride solution = 1·19 per cent. NO.

(c.) *Calculation of Amount of N₂O₄.*—The quantity of NO found in a, subtracted from the total oxides of nitrogen expressed as NO in b, gives the amount of N₂O₄, expressed as NO.

$$\text{Amount of N}_2\text{O}_4 = \frac{1·19 - 0·33}{2} = 0·43 \text{ per cent.}$$

(d.) *Determination of Cyanogen and Carbon Dioxide.*—

From the special experiment we have CO ₂ ..	0·83 per cent.
„ „ „ (CN) ₂ ..	6·10 „

We may now sum up the analysis as follows.

CO	25.4
CO ₂	0.8
(CN) ₂	6.1
N ₂	66.9
NO	0.3
NO ₂	0.4
	<hr/>
	99.9

Diameter of inner tube of cone-separator 1.6 cm.

„ outer „ „ 2.8 „

Rate of flow of air 33.56 c.c. per sec.

„ gas 9.96 „

$$\therefore \frac{\text{air}}{\text{gas}} = 3.37 \text{ and } \therefore \frac{\text{air}}{(\text{CN})_2} = 3.52 \text{ (calculated} = 3.56).$$

Velocity of gases through inner tube 21.64 cm. per sec.

„ „ „ outer „ 7.07 „

Experimental Results.—Subjoined is a tabulated statement of the results obtained in experiments made under a variety of conditions.

$\frac{\text{air}}{(\text{CN})_2}$	Rose-coloured halo.				(5) 5.57	Blue halo.	
	(1) 3.31	(2) 3.56	(3) 4.02	(4) 4.06		(6) 6.02	(7) 6.74
(CN) ₂	7.4	6.1	4.3	3.8	0.1	none	none
CO ₂	0.5	0.8	1.4	1.5	4.7	5.8	8.6
CO	25.5	25.4	25.2	24.4	22.0	19.9	15.3
N ₂	65.8	66.9	68.5	69.2	73.3	74.3	75.2
N ₂ oxides ...	0.8	0.7	0.6	1.1	0.0	0.4	0.9
	100.0	99.9	100.0	100.0	100.1	100.4	100.0
Velocities through inner tube }	21.1 $\frac{\text{cm.}}{\text{sec.}}$	21.6	19.2	15.7	23.1	19.1	22.2

The apparatus used in experiments 1, 2, 3, 5, 6, and 7, had the following dimensions, diam. inner tube, 1.6 cm.; outer tube, 2.8 cm.; in Experiment (4), diam. inner tube, 0.95 cm.; outer tube, 1.7 cm.

A glance at the above table will show that the following conclusions may be drawn from the analytical results.

1. The separation of the cones of a cyanogen flame is possible, in the apparatus used, when the ratio of air to cyanogen is 3.3 : 1 (that is, about one-third of the amount required for complete oxidation),

and the cones remain intact, until the air supply is increased to twice this amount. After this, the interconal gases become so diluted with nitrogen and carbon dioxide, that they can no longer burn in a second cone.

2. When cyanogen is burning in the apparatus, with the addition of the minimum quantity of air necessary for the separation of the cones, carbonic oxide is practically the only oxidation product.

3. A small quantity of carbon dioxide is, however, found in the interconal gases. As the air supply increases, the quantity of carbon dioxide increases, until it amounts to about one-half the volume of the accompanying carbon monoxide.

4. The interconal gases contain unburnt cyanogen, amounting in the case of the minimum air supply to $7\frac{1}{2}$ per cent., and diminishing in quantity to nil, as the air supply increases.

5. Small and variable quantities of oxides of nitrogen occur in the interconal gases.

6. A variation in the dimensions of the apparatus makes no important difference in the results.

Looking at the analyses as a whole, we see that they are generally in accord with the view that, in the combustion of cyanogen, the carbon is first burnt to carbon monoxide. That cyanogen burns in this way has been proved by Dixon, who shows that the rate of explosion of cyanogen and oxygen is greatest when the quantities are in accordance with the equation

When added in further quantity, oxygen acts as a dilutant, and, like a neutral gas, diminishes the rate of explosion.

In our analyses, however, we find in certain cases the coexistence of sensible quantities of carbon dioxide with unburnt cyanogen. Thus in analysis (4) we have 1.5 per cent. $(\text{CO})_2$, 3.8 per cent. $(\text{CN})_2$, and 24.4 per cent. CO. The occurrence of this carbon dioxide is not easy to account for. Three possible explanations seem to suggest themselves. (1.) When a certain percentage of cyanogen has burnt to carbon monoxide, the remaining oxygen is distributed between the carbon monoxide and the rest of the cyanogen. (2.) When cyanogen burns, the carbon burns to carbon dioxide, and this subsequently reacts with the remaining cyanogen to form carbon monoxide. (3.) When cyanogen burns, the carbon is oxidised to carbon monoxide, and the nitrogen is also partly oxidised. The oxide of nitrogen subsequently oxidises the carbon monoxide.

We cannot regard any of these explanations as satisfactory. The first is hardly consistent with the fact, that the inner cone of the flame is virtually a wave-front, in which an almost instantaneous reaction is in progress. The second is in opposition to the results of

Dixon's experiments. The third explanation is partly hypothetical, as we have no evidence that oxides of nitrogen are formed directly in the combustion of cyanogen.

The formation of oxides of nitrogen during the combustion of cyanogen has been noticed by Berthelot (*Matières Explosives*), and Dixon (*Trans.*, 1886, **49**, 390). Small and irregularly varying quantities appear recorded in most of our analyses. In one case (Analysis No. 5) no oxides of nitrogen appear. In this case, precautions were taken to remove all air from the space between the two tubes of the separator, by drawing the interconal gases down, by means of a small glass tube passing through the india-rubber junction; a sample of the gases was then collected in the usual way. Whenever this precaution was taken, no oxides of nitrogen were found in the interconal gases. On the other hand, when a gentle supply of air was led into the interconal space, the gases simultaneously withdrawn contained large quantities of oxides of nitrogen, and the base of the inner cone assumed a peculiar greenish-yellow tint. From these experiments it appears that the oxides of nitrogen are not formed in the inner cone, but immediately outside it, provided that oxygen be present. The oxygen may unite directly with the heated nitrogen coming from the inner cone, or with the nitrogen of the infiltrated air. A similar formation of oxides of nitrogen in the outer cone seems probable, from the fact that it always has a greenish-yellow border and tip, which is characteristic of flames to which oxides of nitrogen have been added (see Dixon, *loc. cit.*).

It will be noticed that in the description of the behaviour of cyanogen in a separator, we have described the inner cone as being surrounded by a halo, which varies in tint as the quantity of air is increased, from a rose colour, through blue to yellowish-green. At one point, however, there is no visible halo, and our analytical results indicate that this happens when cyanogen has just ceased to be present in the interconal gases, and when the amount of carbon dioxide is yet small. We are unable to give a satisfactory explanation of this halo. It is possible that the rose-coloured halo may be due to cyanogen, which, though not actually in combustion, is intensely heated from below by the sheet of flame which forms the inner cone. The blue halo may, in like manner, be due to intensely-heated carbon dioxide, and the green to oxides of nitrogen. But we have found it impossible to render cyanogen incandescent at the highest temperature obtainable in a tube furnace, nor does paracyanogen, when held in the oxy-hydrogen flame or alone in the inner cone of an air-coal gas flame, give any glow. We hope, by comparison of the behaviour of the cyanogen flame with that of other flames, to be able to get more certain ideas as to the cause of the halos.

610 STRUCTURE AND CHEMISTRY OF THE CYANOGEN FLAME.

Returning now to the ordinary cyanogen flame, as formed when the gas issues, unmixed with air, from a circular orifice, we consider that our experiments show that the sharp differentiation of the flame into a rose-coloured cone and a blue investing mantle corresponds approximately to the two stages of combustion—the first occurring where the external air has penetrated the stream of cyanogen sufficiently to oxidise the carbon to carbon monoxide; the second marking the region in which the carbon monoxide produced in the first stage is oxidised to carbon dioxide.

If this be the explanation, it would seem possible to subject it to a crucial test, by introducing the flame of dry cyanogen into dry air. According to Dixon's well-known observation, the flame of dry carbon monoxide is extinguished in dry air. We might, therefore, expect the outer blue portion of a cyanogen flame to disappear, when the combustion was conducted in absence of moisture. To test this question we dried cyanogen by contact with phosphorus pentoxide, and then ignited the gas in a bottle of air sufficiently dry to inhibit the combustion of carbon monoxide. The cyanogen flame, however, presented the usual appearance. Thinking that possibly the extremely high temperature of the carbon monoxide (if that gas were really burning in the blue part of the flame) might be the cause of its inflaming, even in dry air, we modified the procedure to test this point. The dry cyanogen was burnt in a cone-separator, and admixed with enough dry air to produce a separation of the cones. When these cones were widely separated, the upper one, in which the combustion was almost wholly that of carbon monoxide to carbon dioxide, was immediately extinguished, when a bottle of dry air was brought over it; but on approximating the cones a point was soon reached, where it was impossible any longer to extinguish the outer cone, by immersing it in a bottle of dry air. It appears, then, that when the carbon monoxide is hot its flame persists in air which is dry enough to extinguish the flame of the unheated gas; and, consequently, the fact that a cyanogen flame is unaltered in well-dried air does not contradict the conclusion drawn from our experiments—that the blue region is essentially due to the combustion of carbon monoxide.

We conclude, therefore, that the differentiation of the ordinary cyanogen flame into an inner cone of a peach blossom tint, and an outer one of a blue tint corresponds to two stages in the oxidation of the carbon, carbon monoxide being formed in the first cone and carbon dioxide in the second one. The greenish fringe to the outer cone we attribute to the presence of small quantities of oxides of nitrogen.