

limits. These lines are mapped on the same scale as Ångström's and Cornu's maps of the solar spectrum. The paper describes the method of taking the measures, and gives in detail the quantities observed and the data on which the calculations are founded.

Part II. Received June 15, 1882.

(Abstract.)

In the second part of this paper the authors have given a map of the ultra-violet lines of potassium, sodium, lithium, barium, strontium, calcium, zinc, mercury, gold, thallium, aluminium, lead, tin, antimony, bismuth, and carbon, as developed in the arc. They point out that in several cases the lines are in all probability harmonically related, as shown by the repetition of similar groups of lines at regularly diminishing distances, the groups being alternately sharply defined and diffuse, and becoming more diffuse as they die away at the end of the series. They had previously called attention to this kind of relationship between the visible lines in the spectra of the alkalies and of magnesium. The like relationship holds good in the ultra-violet spectra of those metals, and is strongly marked in the cases of calcium and zinc, less strongly in some other metals.

XII. "General Observations on the Spectra of Carbon and its Compounds." By Professor G. D. LIVEING, M.A., F.R.S., and Professor JAMES DEWAR, M.A., F.R.S. Received June 12, 1882.

In our two former papers on the spectra of the compounds of carbon with hydrogen and nitrogen ("Proc. Roy. Soc.," vol. 30) we described the results of a long series of synthetical and analytical experiments which had enabled us to trace satisfactorily a fluted band spectrum which occurs in the arc and spark discharge in many compounds of carbon, and generally when carbon poles are used to transmit the current of the arc or spark in air, to the compound substance cyanogen. This led to a further investigation of the carbon ultra-violet line spectrum in order to complete the series of simple vibrations which originate from this substance. After all this work a great deal remains to be ascertained regarding the conditions which cause a variation of intensity in the different series of carbon flutings which originate from cyanogen, and also their persistency and development.

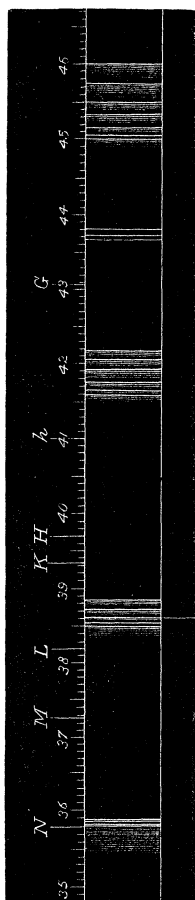
The present paper is a short record of the particular variations in the carbon groups which are revealed in the different photographs of the spectrum of the arc discharge that we have had occasion to take

for other purposes, together with some new observations on the genesis of the cyanogen spectrum during combustion.

The remarkable discovery of Dr. Huggins, regarding the occurrence of two of the most marked series of cyanogen bands in last year's comet, adds considerable interest to this question, and has induced us to make a further study of the chemical reactions in flames which cause this particular spectrum to appear at a relatively low temperature.

Electric Discharge between Carbon Poles in different Gases.

In order to facilitate reference the general appearance of the portion of the cyanogen spectrum to which we shall refer is given in the following diagram :—



The apparatus used in the experiments has been already described in our paper on the spectrum of the compounds of carbon with hydrogen and nitrogen ("Proc. Roy. Soc.," vol. 30). No attempt was made to use perfectly pure gases or to remove all traces of nitrogen from the vessels employed; the object being to study the variation of the groups of lines, perfect purity in the gases was not required.

The arc discharge between graphite poles in carbonic acid shows the triple set, beginning about 4380, with traces of the other sets of cyanogen bands at 4218 and 3883. If the carbonic acid gas is displaced by air, the triple set are very much weakened and are sometimes invisible, while the other fluted series at 4218 and 3883 are greatly strengthened.

The spark discharge does not show the cyanogen sets in carbonic acid, but a series of five groups appear between the limits of the lines S and N of the solar spectrum, which may possibly be due to carbonic acid or carbonic oxide. The carbonic oxide flame, however, does not show this set. If the spark discharge is taken between graphite poles in nitrogen all the cyanogen series appear; but in hydrogen they sometimes disappear. As a rule, however, they remain faint even when a current of the gas is kept continuously passing through the bulb in which the discharge is taken. With the arc discharge in hydrogen the triple set are well marked, while the series at 4218 disappear, and the ultra-violet group are just visible; the hydrocarbon set, however, at 4310 come out strong.

In order to ascertain how the pressure of the surrounding atmosphere affected the emissive power of the cyanogen produced synthetically in the arc discharge, a series of observations on the spectra obtained under diminished pressure of the gaseous atmosphere was undertaken. The pressure in different gases was reduced to a mean value of about 1 inch of mercury, and under such conditions the intermittent discharge of the De Meritens machine was examined. The arc in air, under these circumstances, showed the blue hydrocarbon set; all the cyanogen series of bands together with a nitrogen series near H. Carbonic acid at the same pressure had the triple set of lines strongly marked, while the others were decidedly weaker, as in the experiments with the gas at atmospheric pressure.

In hydrogen, at equal pressure, the triple set disappear, and the hydrocarbon set at 4310 occur, which series is not generally seen in the photographs of the arc spectrum. But what is very remarkable is the appearance of two lines of carbon, viz., 2836.3 and 2837.2 (also 2506 and 2508) in the spectrum of the discharge, whereas these spark lines are not generally found in the arc spectrum.

The following lines of carbon have been observed in the arc discharge of the Siemens continuous current machine, as well as in that

of the De Meritens intermittent current, taken in air. We have observed in previous experiments that the De Meritens arc in hydrogen produces a sufficient temperature to render the C line of hydrogen permanently visible. The continuous Siemens current, under the same circumstances, only shows this line when the arc is produced by breaking the contact of the poles, not with the steady arc.

Approximate Wave-lengths of Carbon Arc-lines.

2434·8 absent from spark.

2478·3 strongest line.

2506·6.

2514·1.

2515·8.

2518·8.

2523·9.

2528·1.

2881·1 not in spark.

We have here another instance of the lines of high refrangibility appearing, under certain circumstances, when no trace of strong lines belonging to the less refrangible portion of the spectrum can be detected. Thus the strong carbon line in the blue at 4266 does not appear in the photographs of the arc spectra. Of course it is possible that a very long exposure of the photographic plate might reveal some of the missing lines, as we have shown in other cases. The presence of these carbon lines is a proof that carbon vapour of a definite, but probably low, tension exists in the arc discharge, and this is doubtless the reason why under such conditions carbon combines with hydrogen and nitrogen with such facility. By a careful series of experiments carried out at different pressures with varying electric power we hope to ascertain with greater precision the variations in the carbon line spectrum.

Eye Observation of Spectra.

When the spectrum of different parts of a magnified image of the electric arc is examined, all the more refrangible cyanogen groups may be seen near the positive pole, together with a series of channellings in the red. When the arc is steady the cyanogen spectrum is permanently visible at the negative pole, when no trace of the hydrocarbon series can be seen. In the same way the arc in the middle of a magnesia crucible often shows no trace of the hydrocarbon set, although the cyanogen are strong. If, however, puffs of air or carbonic acid are passed into the arc, the hydrocarbon lines are produced. There is always, under these circumstances, far greater

variation in the brightness of the hydrocarbon series than of the cyanogen, in fact, the presence of magnesia rather favours the steady formation of cyanogen. When the hydrocarbon spectrum is strong the brilliancy and number of the cyanogen groups that are visible are undoubtedly increased, so that the one variety of vibrations seems to affect the other. This is easily accounted for by the chemical interaction which takes place between acetylene, nitrogen, and hydrocyanic acid. The hydrocarbon spectrum is brought out at once in the magnesia crucibles by moistening one of the poles. All such actions seem to show that hydrogen is essentially connected with the production of this fluted spectrum just as nitrogen is with the cyanogen series.

Arc Discharge in Fluids.

The De Meritens arc, taken in water, shows the hydrocarbon spectrum alone; no cyanogen bands can be seen by eye observation, even when ammonia or nitrate of potash is added to the water. In this case the observations are rendered uncertain from the great intensity of the continuous spectrum. If glycerine is used instead of water no cyanogen groups of lines can be recognised, but on adding a little nitrobenzol the set of three lines (about 4380) peculiar to the cyanogen spectrum appear, this being the only group which can be detected by the eye on the continuous background. This result supports the observations on the varying intensity of this group in different gaseous media, and seems to show that conditions can be found where it is the most characteristic group of cyanogen. These three lines are easily seen in the spectrum of the arc taken in carbonic acid, although they disappear from the spectrum of the arc taken in air.

Vacuum Tube Spectra.

In our former experiments with vacuum tubes we did not use a capillary glass tube, but preferred to examine the photographic spectrum obtained from a short spark taken between platinum wires. Objection has been taken to this plan of working on the ground that, as the capillary form of vacuum tube increases the brilliancy of the spectrum, particular lines or groups of the spectrum which otherwise would be missed, might be revealed in them, and such tubes ought, therefore, to have been employed. In order to answer this objection we have prepared and examined vacuum tubes of this kind containing benzol and benzol with naphthalene in solution, using all the precautions to avoid the presence of nitrogen formerly described, and have always found such tubes free from any trace of the cyanogen spectrum. When such tubes are, however, examined daily, the cyanogen bands often appear after a time, and this can be traced in all such cases to a leak or crack at the point where the platinum is sealed into the glass. No per-

fectly pure hydrocarbon gives the series of bands we attribute to cyanogen.*

Observations on Flames.

The temperature produced by the combustion of hydrocarbons and other non-nitrogenous organic bodies well supplied with oxygen, is not sufficient to induce the combination of nitrogen with carbon, so that the cyanogen spectrum is absent from such flames. We know, however, that hydrocyanic acid is often produced in the oxidation of organic bodies containing nitrogen, and that ammonia reacts with carbon at a white heat, producing hydrocyanic acid and hydrogen. Such actions led us to expect that the cyanogen spectrum ought to appear in the flames of organic compounds containing nitrogen, provided the temperature were sufficient to render the radiation of this substance sufficiently intense. Our first experiments did not succeed. The most careful examination by the eye of the spectrum of a hydrogen flame which had passed through a solution of hydrocyanic acid or of a flame of alcohol containing nitrobenzol or nitrite of ethyl, did not result in any recognition of the strong cyanogen groups. This failure led to a chemical examination of the composition of the gases withdrawn from the interior of such flames, in order to ascertain the combustible mixtures which react during combustion to produce hydrocyanic acid. The gases were extracted from the flame with an apparatus similar in principle to that employed by Deville in his "Chemical Researches on Flame." When coal gas is passed through a solution of ammonia and burnt, the flame gases contain hydrocyanic acid and acetylene, but if oxygen is well supplied to the flame no cyanogen reaction is given by the extracted gas. Carbonic oxide mixed with ammonia in the same way gave no trace of hydrocyanic acid during combustion: even when a large quantity of the mixture was burnt and the flame gases continuously withdrawn no appreciable cyanogen reaction could be detected. Similarly hydrogen mixed with a little carbonic acid and ammonia gave no cyanogen reaction. When hydrogen is passed through ammonia solution mixed with chloroform, tetrachloride of carbon, bisulphide of carbon,

* It is worthy of note that the strong carbon line wave-length 2478.3 present in both the arc discharge and in the spark discharge in carbon compounds at atmospheric pressure, is not found in the spectrum of the spark in cyanogen at low pressure. We have tried to obtain a photograph of it from a "Plücker" tube fitted with a quartz end, and placed end-on in front of the spectroscope, but found no trace of it. As this line appears in the spectrum of the flame of cyanogen, its absence from the spark discharge in cyanogen of low tension seems intelligible only on the supposition that the discharge is selective in its course, and lights up only certain of the substances present, or else that the quantity of carbon vapour present at any instant is so minute, as to produce no sensible effect on the photographic plate.—July 10, 1882.

or picoline, cyanogen can always be recognised in the flame gases. Chloroform under such circumstances yields the largest amount. When a mixture of carbonic oxide and ammonia is passed through a porcelain tube heated in a furnace, large quantities of hydrocyanic acid are produced, especially when the moist gases are employed. Ammonia passed over perfectly pure graphite at a white heat produces hydrocyanic acid, and the vapour of chloride of ammonium is equally efficient in bringing about this reaction. It appears to result from the experiments that hydrocyanic acid can always be separated from the interior of flames such as we have employed, provided that portion of the flame which, in carbon compounds, is characterised as reducing, be selected. That stage of combustion during which free carbon or dense hydrocarbon vapours containing very little hydrogen are formed, is favourable to the formation of hydrocyanic acid, as ammonia can at this stage react on the carbon. It is quite possible, however, that hydrocyanic acid may exist in small quantity in some of the flames which tested according to this method appear to contain none, and that notion is favoured by the consideration of the dissociation phenomena which are known to occur in flames. This led us again to spectroscopic examination as the most delicate test for the presence of cyanogen, but instead of trusting to the eye as in former experiments, photographs were taken of the spectra of flames by means of a quartz and calcspar train, and the exposure of the plate purposely prolonged. Thus examined, it was found that coal gas well supplied with oxygen gave only the hydrocarbon groups, together with the two interesting additional lines first discovered by Dr. Huggins, having the wave-lengths 3872 and 3890; but when the coal gas passed through ammonia the photographs revealed the characteristic cyanogen groups at 3883 and 4218, the most refrangible group being the strongest. The cyanogen spectrum can then be produced synthetically from nitrogen compounds in flames along with the hydrocarbon spectrum, so that the appearance of the groups of cyanogen is not always associated with a very high temperature such as we have in the electric arc. Cyanogen once formed gives its peculiar spectrum at the relatively low flame temperature produced by burning cyanogen mixed with carbonic acid. Of course the mean temperature of a flame is very different from the temperature of individual molecules, and this complicates the problem we are discussing. The thermal equivalents of cyanogen and acetylene being highly negative, it is certain that these substances yield on combustion the highest temperature of any two compounds burning in oxygen; and we have shown in a former paper that burning cyanogen in nitric oxide gas, which probably induces a still higher temperature, does not bring about any marked change in the character of the spectrum. Spectroscopic analysis can thus detect very small quantities of cyanogen under

widely different physical conditions. As the temperature of the flame of cyanogen probably approaches the temperature of the carbon poles of the electric arc, and as we have shown that carbon undoubtedly exists in the form of vapour in the arc discharge, from the fact of the ultra-violet line spectrum being present, the question naturally arises, is carbon present in the form of vapour in the cyanogen flame? In order to answer this question we have taken photographs of the ultra-violet spectrum of the cyanogen flame fed with oxygen, and with long exposures have had no difficulty in detecting one of the strongest carbon lines, viz., that at 2478·3, along with a trace of what may be the pair of lines at 2837, but more probably is a mercury line. No other carbon line was found in the photographs. It seems, therefore, proved that carbon vapour does exist in the flame of cyanogen, although to a much smaller extent than in the arc discharge. Observations must be made on the spectra of flames under high pressures, in order to solve many problems connected with spectroscopic enquiry, and this subject we hope to discuss in a future communication.

XIII. "Further Observations upon Liquid Jets, in continuation of those recorded in the Royal Society's 'Proceedings' for March and May, 1879." By Lord RAYLEIGH, F.R.S., Professor of Experimental Physics in the University of Cambridge. Received June 8, 1882.

The experiments herein described were made in the spring and summer of 1880, with the assistance of Mrs. Sidgwick. Section 2 was indeed written out as it now stands in August of that year. There were some other points which I had hoped to submit to examination, but hitherto opportunity has not been found.

On some of the Circumstances which influence the Scattering of a nearly Vertical Jet of Liquid.

§ 1. It has been already shown that the normal scattering of a nearly vertical jet is due to the rebound of the drops when they come into collision. If, by any means, the drops can be caused to amalgamate at collision, the appearance of the jet is completely transformed. This result occurs if a feebly electrified body be held near the place of resolution into drops, and it was also observed to follow the addition of a small quantity of soap to the water of which the jet was composed. In trying to repeat the latter experiment in May, 1880, at Cambridge, I was astonished to find that even large additions of soap failed to prevent the scattering. Thinking that the difference might

