THURSDAY, AUGUST, 5, 1880

MULTIPLE SPECTRA¹

II.

I CONCLUDED my last article under the above heading with a reference to the case of carbon, and gave the results successively arrived at by Attfield, Morren, Watts, and others; these went to show that besides the line-spectrum of carbon mapped by Ångström there exists a fluted spectrum of this substance.

Now comes my own personal connection with this matter.

In the year 1878² I communicated to the Royal Society a paper in which the conclusion was drawn that the vapour of carbon was present in the solar atmosphere.

This conclusion was founded upon the reversal in the solar spectrum of a set of flutings in the ultra-violet.³ The conclusion that these flutings were due to the vapour of carbon, and not to any compound of carbon, was founded upon experiments similar to those employed in the researches of Attfield and Watts, who showed that the other almost exactly similar sets of flutings in the visible part of the spectrum were seen when several different compounds of carbon were exposed to the action of heat and electricity. In my photographs the ultra violet flutings appeared under conditions in which carbon was the only constant, and it seemed therefore reasonable to assume that the flutings were due to carbon itself, and not to any compound of carbon; and this not alone from the previous work done in the special case of carbon, but from that which had shown that the fluted spectra of sulphur, nitrogen, and so forth were really due to these "elementary" substances.

Professors Liveing and Dewar have recently on several occasions called this result in question. Prof. Dewar, in a paper received by the Royal Society on January 8, 1880, writes as follows:—

"The almost impossible problem of eliminating hydrogen from masses of carbon, such as can be employed in experiments of this kind, prove conclusively that the inference drawn by Mr. Lockyer, as to the elementary character of the so-called carbon spectrum from an examination of the arc in dry chlorine, cannot be regarded as satisfactory, seeing that undoubtedly hydrogen was present in the carbon used as the poles."

Subsequently in a paper received by the Royal Society on February 2, Messrs. Liveing and Dewar wrote as follows:—

"Mr. Lockyer (*Proc. Roy. Soc.*, vol. xxvii. p. 308) has recently⁴ obtained a photograph of the arc in chlorine, which shows the series of fluted bands in the ultra-violet, on the strength of which he throws over the conclusion of Ångström and Thalén, and draws inferences as to the existence of carbon vapour above the chromosphere; in the coronal atmosphere of the sun, which, if true, would be contrary to all we know of the properties of carbon. We cannot help thinking that these bands were due to the presence of a small quantity of nitrogen."

It will be seen that on January 8 Mr. Dewar alone attributed the flutings to a hydrocarbon, while on February 2 Mr. Dewar, associated with Mr. Liveing, attributed them to a nitrocarbon.

¹ Continued from p. 7.

² *Proc. R. S.*, No. 187, 1878.

³ The approximate wave-length of the brightest member on the least refrangible edge is 38870.

⁴ That is, in 1878.—J. N. L.

In fact in the latter paper Messrs. Liveing and Dewar published experiments on the spectra of various carbon compounds, and from their observations they have drawn the conclusion that the set of flutings which I have shown to be reversed in the solar spectrum is really due to cyanogen, and that certain other sets of flutings shown by Attfield and Watts to be due to carbon are really due to hydrocarbon.

As Messrs. Liveing and Dewar do not controvert the very definite conclusions arrived at by Attfield, Morren, Watts, and others, I can only presume that they took for granted that all the experimental work performed by these men of science was tainted by the presence of impurities, and that it was impossible to avoid them. I therefore thought it desirable to go over the ground again, modifying the experimental method so as to demonstrate the absence of impurities. Indeed I have started upon a research which will require some time to complete. Still, in the meantime, I have submitted to the notice of the Royal Society some results which I have obtained, which I think settle the whole question, and it is the more important to settle it as Messrs. Liveing and Dewar have already based upon their conclusions theoretical views which appear to me likely to mislead, and which I consider to have long been shown to be erroneous. To these results I shall now refer in this place.

The tube with which I have experimented is shown in Fig. 1: A and B are platinum wires for passing the spark inside the tube; E is a small tube into which carbon tetrachloride was introduced; it was drawn out to a long narrow orifice to prevent the rapid evaporation of the liquid during the exhaustion of the tube. The tube was bent upwards and a bulb blown at C in order that the spark might be examined with the tube end-on, as it is found that after the spark has passed for some time a deposit is formed on the sides of the bulb immediately surrounding the platinum, thus obstructing the light. After a vacuum had been obtained the tube was allowed to remain on the Sprengel pump, to which it was attached by a mercury joint for the purpose of obtaining a vacuum for a long time, in order that the last traces of air and moisture might be expelled by the slow evaporation of the liquid.

The carbon tetrachloride was prepared by Dr. Hodgkinson, who very kindly supplied me with sufficient for my experiments.

On passing the spark without the jar in this tube, the spectrum observed consists of those sets of flutings which, according to Messrs. Liveing and Dewar, are due to hydrocarbon, and the set of flutings which is reversed in the sun, and ascribed by Messrs. Liveing and Dewar to cyanogen, also appears in a photograph of the violet end of the spectrum, Fig. 2. On connecting a Leyden jar with the coil and then passing the spark the flutings almost entirely vanish and the line spectra of chlorine and carbon take the place of the flutings without either a line of hydrogen or a line of nitrogen being visible.

As a long experience has taught me that these tubes often leak slightly at the platinum after they are detached from the pump, so that the evidence of such a *pièce justificatif* is only good for a short time, I took the occasion afforded by a visit of Dr. Schuster to my laboratory while

the experiments were being made to get my observations confirmed. He has been good enough to write me the following letter and to allow me to give it here:—

"March 21

"MY DEAR LOCKYER,—The following is an account of the experiment which I saw performed in your laboratory on Monday, March 15:—

"A tube containing carbon-tetrachloride was attached to the Sprengel pump. As exhaustion proceeded the air was gradually displaced by the vapour of the tetrachloride. The electrodes were a few millimetres apart. If the spark was taken without a condenser in the vapour the well-

known carbon bands first observed by Swan in the spectrum of a candle were seen with great brilliancy; I also saw the blue band which you said was identical in position with one of the blue bands seen in the flame of cyanogen or in the spectrum of the electric arc. When the condenser and air-break were introduced this spectrum gave way to a line spectrum in which I could recognise the lines of chlorine. *The lines of nitrogen were absent, not a trace of the principal double line in the green being seen.* The hydrogen line $H\alpha(C)$ was faintly visible when I first observed the spectrum, but it got gradually weaker and finally disappeared altogether. *When this line was no longer visible the condenser was taken out of circuit*

FIG. 1.

again, and the same carbon bands were seen as before. These bands, therefore, show themselves with great brilliancy when a strong and powerful spark does not reveal the presence either of hydrogen or nitrogen.

"March 21, 1880 (Signed) ARTHUR SCHUSTER"

This result, which entirely endorses the work of Atfield and Watts, has been controlled by many other experiments. I have also repeated Morren's experiment and confirm it, and I have also found that the undoubted spectrum of cyanogen is visible neither in the electric arc nor in the surrounding flame.

Hence then in the case of carbon, as in the prior cases

of hydrogen, nitrogen and the like, those who hold that the flutings are due to impurities must, it would seem, abandon their position; for the flutings are undoubtedly produced by carbon vapour. Nor is this all; the suggestion that the various difficulties which have always been acknowledged to attend observations of this substance may in all probability be due to the fact that the sets of carbon flutings represent different molecular groupings of carbon, in addition to that or those which give us the line spectrum, and that the tension of the current used now brings one set of flutings into prominence and now another, seems also justified by the facts. This suggests

FIG. 2.

the view that a body may have a fluted spectrum of compound origin as well as a line spectrum.

This conclusion is greatly strengthened by the preliminary discussion of a considerable number of photographs of the spectra of various carbon compounds.

A general comparison of the photographs first enables us to isolate the lines in the blue and ultra-violet portions of the spectrum (wave-lengths 4300–3800) of the substance associated with the carbon in each case.

In this manner the lines seen in the photographs of the spectra of CCl_4 , $C_{10}H_8$, CN , CHI_3 , CS_2 , CO_2 , CO , &c., have been mapped, and both the common and special lines and flutings thus determined.

The phenomena seen with more or less constancy are a blue line, with a wave-length of 4266; a set of blue flutings, extending from 4215 to 4151; and another set of ultra-violet flutings, which extend from 3885 to 3843 (all approximate numbers).

In a photograph of the spectrum of the electric *arc* (with a weak battery) between carbon poles in an atmosphere of chlorine, the blue flutings alone are visible, whilst, when the *spark* is similarly photographed, the ultra-violet

flutings and the blue line (4266) are also visible, whilst the blue flutings become fainter.

From this we may assume, in accordance with the working hypothesis of a series of different temperature

FIG. 3.—Action of three different temperatures on a hypothetical substance, assuming three stages of complete dissociation.

furnaces, as set forth in the paper of December, 1878 (see Fig. 3), that the different flutings and the line correspond to different temperature spectra, the blue flutings to the lowest and the blue line to the highest temperature, whilst the ultra-violet flutings occupy an intermediate position.

According to this working hypothesis there should be a

series of horizons forming a perfect gradation between the spectrum which contains the blue line alone and that which contains the blue fluting alone (Fig. 4). In comparing the spectra of carbon under different conditions, I find this to be true. *The blue line never appears in conjunction with the blue flutings, unless the ultra-violet flutings are also*

FIG. 4.—Spectra of the hypothetical substance in intermediate furnaces, assuming that the vapours are not completely dissociated.

present. In other words, the highest and the lowest hypothetical temperature spectra are never visible together without the spectrum of the intermediate hypothetical temperature.

But this is not all. By placing the spectra of the substances at different heat-levels, so to speak, I was enabled

to construct a map, which not only indicates the mere presence or absence of the lines and their relative intensities, but shows a perfect gradation between the spectrum which contains the line alone and that which contains the blue flutings alone (Fig. 5). I would point out that there is nothing theoretical in this map. All the

FIG. 5.—The photographed spectra of some carbon compounds.

horizons depicted are copied from photographs of carbon under the conditions indicated, and theory has merely enabled me to arrange them *in order*.

This map I submit, therefore, bears out the hypothesis of differences of temperature indicated above, for it is

seen that, while the blue line gradually thins out, the ultra-violet flutings appear first and grow in intensity. As these increase the blue flutings become visible, and further, as the latter augments and the line disappears, the ultra-violet flutings gradually die out altogether.

It is philosophical to infer from these observations that not only are the line and flutings in question produced by carbon, but that the blue line (4266), since it is visible at the highest temperature, corresponds to the most simple molecular grouping we have reached in the experiments, and the flutings to others more complex.

The result to which attention is most to be directed in this place is that touching the two sets of flutings, and should future research justify the double conclusion (1) that these flutings are truly due to carbon, a result I accept, though it is denied by Ångström and Thalén; and (2) that the different flutings really represent the vibrations of different molecular groupings; a great step, and one in the direction of simplification, will have been gained.

Indeed it is much to be hoped that this ground will be at once worked over again by men of science who are both honest and competent: that the truth is sure to gain by such work is a truism.

I have so often taken occasion to refer with admiration to the work of Ångström and Thalén that I shall not be misunderstood when I say that their conclusions, to which such prominence is given, and on which such great stress is laid by Messrs. Liveing and Dewar, rest more upon theory and analogy than upon experiment.

Their work, undertaken at a time when the existence of so-called "double spectra" was not established upon the firm basis that it has now, and when there was no idea that the spectrum recorded for us the results of successive dissociations, gave, as I have previously taken occasion to state, the benefit of the doubt in favour of flutings being due to compounds, and it was thought less improbable that cyanogen or acetylene should have two spectra than that carbon or hydrogen should possess them.

Indeed, later researches have thrown doubt upon the view that the fluted spectra of aluminium and magnesium are entirely due to the oxides of those metals instead of to the metals themselves—and this is the very basis of the analogy which Ångström and Thalén employed.

The importance of the observations to which I have referred is all the greater because of the general conclusions touching other spectra which may be drawn from them. Thus from what I have shown it will be clear that if my view is correct the conclusions drawn by Messrs. Liveing and Dewar from the assumed hydrogen-carbon bands touching both the spectrum of magnesium and the spectra of comets, are entirely invalid. These conclusions are best given in their own words:—

"The similarity in the character of the magnesium-hydrogen spectrum, which we have described, to the green bands of the hydrocarbons is very striking. We have similar bright maxima of light, succeeded by long drawn-out series of fine lines, decreasing in intensity towards the more refrangible side. This peculiarity, common to both, impels the belief that it is a consequence of a similarity of constitution in the two cases, and that magnesium forms with hydrogen a compound analogous to acetylene. In this connection the very simple relation (2 : 1) between the atomic weights of magnesium and carbon is worthy of note, as well as the power which magnesium has, in common with carbon as it now appears, of combining directly with nitrogen. We may

with some reason expect to find a magnesium-nitrogen spectrum. . . .

"The interest attaching to the question of the constitution of comets, especially since the discovery by Huggins that the spectra of various comets are all identical with the hydrocarbon spectrum, naturally leads to some speculation in connection with conclusions to which our experiments point. Provided we admit that materials of the comet contain ready-formed hydrocarbons, and that oxidation may take place, then the acetylene spectrum might be produced at comparatively low temperatures without any trace of the cyanogen spectrum or of metallic lines. If, on the other hand, we assume only the presence of uncombined carbon and hydrogen, we know that the acetylene spectrum can only be produced at a very high temperature, and if nitrogen were also present that we should have the cyanogen spectrum as well. Either, then, the first supposition is the true one, not disproving the presence of nitrogen, or else the atmosphere which the comet meets is hydrogen only, and contains no nitrogen."

The importance of the question here treated of comes out very well from these two extracts. We find the same spectral phenomenon at once called into court, and very properly called in, both to suggest the existence of chemical substances of which the chemist has never dreamt, and to explain the chemical nature of a large group of celestial bodies.¹

There is little doubt that when a complete consensus of opinion is arrived at among the workers, other suggestions more far reaching still will be derived from the prosecution of these inquiries. For the present, however, the chief point to bear in mind is that both in line-spectra and in fluted spectra we have indications which I think favour the view that in each case the origin is compound rather than simple.

J. NORMAN LOCKYER

Oban, July 20

THE EDUCATION DEBATE

THE chorus of approval with which Mr. Mundella's report on the progress of elementary education was received on Monday cannot but be gratifying to all who have at heart the highest welfare of the country. With one or two unimportant exceptions—members whose vision is so bizarre as to discern communism in the education of the children of the working classes, and who connect the increase of weeds with the spread of education—what criticism there was referred to details of method. All the members whose opinions are of any weight agreed that vast good had resulted to the country by the working of the Code. As to the special subjects, among which science is included, the weight of opinion was decidedly in favour of their retention. The greatest friends of the Fourth Schedule will admit that there is still much room for improvement in the teaching of these subjects; it cannot be expected that so great a novelty in the system of elementary education in the country can all at once be taught to perfection. About the success of the compulsory system of education it may be said that the House was all but unanimous. The analogy between the treatment of

¹ With special reference to this last question, that of cometary spectra, one of acknowledged difficulty, I may perhaps be permitted to add here by way of note that the view I put forward some years ago touching the relation of this spectrum to that of the nebulae has been lately strengthened by the observation that at a low temperature one of the brightest lines in the spectrum of iron is that coincident with the chief line in the nebula-spectrum.

² Paper read February 12, 1880.