V. "Note on the History of the Carbon Spectrum." By G. D. Liveing, M.A., F.R.S., Professor of Chemistry, and J. Dewar, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received May 26, 1880.

In a "Note on the Spectrum of Carbon," read before the Society on April 29, 1880, Mr. Lockyer has in the first place alleged that we have advanced within a very short period inconsistent opinions as to spectra of compounds of carbon; he has next implied that we have given an unfair representation of the history of the carbon spectrum, and, lastly, has directly challenged the correctness of some of the conclusions we have drawn from our experiments. We propose in this paper to reply to him on the historical questions, and in another paper to deal with the experimental evidence which he has produced in contravention of our conclusions.

That the inconsistency alleged has not really existed in our opinions, will be seen by any one who reads the first passage referred to as it appeared in the published "Proceedings of the Society" (vol. xxx, p. 87), which stands as follows:—

"The well-nigh impossible problem of eliminating hydrogen from masses of carbon, such as can be employed in experiments of this kind, proves 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* and in all probability nitrogen in the chlorine*."

Mr. Lockyer has quoted the *confidential, uncorrected, proof* instead of the published paper which had been issued before Mr. Lockyer's paper was read. In the published paper a clause, accidentally omitted before, and no way altering the general drift of the passage, had been inserted to make the sense clearer. The paper from which he quotes deals with the chemical interactions taking place in the arc between the matter of the poles and the constituents of the surrounding atmosphere. It is there demonstrated that specially purified carbon poles continue to produce in dry air cyanogen compounds, and that hydrogen always forms an essential ingredient of such poles. No reference was made in this paper to the specific origin of any flutings in the spectrum of the arc, the sole question under consideration being the possible existence of carbon compounds in the electric arc taken in dry chlorine, on the non-existence of which Mr. Lockyer bases his proof of the elementary character of the carbon spectrum. That part of the paper from which the quotation is taken related particularly to the combination of nitrogen with the carbon of

* Mr. Lockyer having italicized the former half of the last clause, we italicize what he chose to omit.

the poles, and the final clause added in the published paper accords with it.

There is no inconsistency between the opinion there expressed and that subsequently given in the paper "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen;" and that such a charge could have been made is due only to Mr. Lockyer's having quoted the *uncorrected proof.*

To come to the omissions we have made in reference to the work of others. The complaints appear in such remarks as the following, which we extract from Mr. Lockyer's paper :—

"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 have taken for granted that the experimental work performed by these men was tainted by the presence of impurities, and that it was impossible to avoid them."

"The only reference to this admirable work, in which vacuum tubes and the electric discharge were largely employed, which I can find in Messrs. Dewar and Liveing's paper is the following :—"The spectrum of hydrocarbon *burning in air* has been . . . described . . . . by Attfield."

It was not our intention to give a complete historical account of what had been done previous to the date of the paper by Ångström and Thalèn ("Nov. Acta Reg. Soc. Upsal.," 1875), as in that paper they had discussed the observations of experimenters who had been engaged on this subject before that time. Nor had we any desire to avoid or controvert, or take anything for granted, in the work of early investigators. We merely passed over for the sake of brevity such work as had not stood the test of subsequent investigation. We could hardly accept Dr. Attfield's work, however good for its time, as authoritative, seeing that his experiments were made, as he allows ("Phil. Mag.," 1875), with very imperfect appliances, and evidently without his being so well aware as we now are of the nicety required in regard to the purity of his materials. In fact, he found no distinction between the spectrum of carbonic oxide and that of hydrocarbons, and found the lines of nitrogen in the spectrum of the flame of cyanogen.

We can hardly be charged with ignoring Morren's work, for we have referred to it again and again. The particular passage quoted by Mr. Lockyer embodies observations and conclusions which are at variance with those of Plücker and Hittorf, as well as of Watts; and are substantively discussed by us in our paper.

Dr. Watts' position with reference to this subject deserves very special consideration, as he has perhaps directed his attention to it more continuously and laboriously than any other investigator. And as his publications have extended over a long period of years, it is clear that a grave injustice is done him if his early work be selected

for quotation instead of the maturer product of his latest study. This kind of selective quotation does not represent the true scientific spirit.

The quotation from Dr. Watts' paper ("Phil. Mag.," 1869) which Mr. Lockyer prefaces by this remark—"His work was thus summarised by himself,"—has in reality no reference to a complete summation of his experiments, but has solely to do with "the typical form of the first carbon spectrum, that obtained when olefiant gas and oxygen are burnt together in an oxyhydrogen blowpipe jet." That this is the correct view of Dr. Watts' position, the following extracts will show:—"The spectrum obtained from cyanogen varies with the mode of production. The flame of cyanogen in oxygen exhibits γ, δ, and ϵ; the red group is replaced by a series of bands which show an opposite character to the rest of the spectrum, inasmuch as each band is brightest at the most refracted edge. If cyanogen be burnt in air instead of in oxygen these bands are more numerous, extending nearly to δ and replacing γ, which is then not to be seen. Instead of the group *f* we have two very brilliant groups of lines, ξ, which includes seven lines, and θ, which is composed of six lines."

The two very brilliant groups of lines which are referred to as ξ and θ by Watts, and which distinguish the flame of cyanogen, are two of the sets of channelled groupings which we, in our paper on "The Spectra of the Compounds of Carbon with Hydrogen and Nitrogen," referred to a compound of carbon with nitrogen. Further on, in the same paper of Dr. Watts, the following occurs:—"In comparing the spectra of fig. 1, we notice that the changes take place at the ends of the spectra, the central groups, γ, δ, ϵ, remain substantially the same. If we pass from the spectrum of the olefiant gas-flame to that of the cyanogen-flame, we find the change at the blue end of the spectrum consisting in the disappearance of the group *f* and its replacement by the groups ξ and θ. The group *f* is not absolutely proved to belong to carbon (that is, it may be caused by carbonic oxide or carbonic anhydride); but the groups ξ and θ, since they are common to carbonic oxide, cyanogen, and naphthaline, must be due to carbon, and their presence may, with much probability, be attributed to the higher temperature of the cyanogen-flame." *

* When Mr. Lockyer makes the following statement:—"I have also repeated Morren's experiment and confirmed it, and I have also found that the undoubted spectrum of cyanogen is visible neither in the electric arc nor in the surrounding flame,"—he is referring to a different part of the spectrum altogether from the one we have been discussing, and the application of the term "undoubted" to the specific part of the spectrum to which he here refers is simply an expression of his own view. Ångström and Thalèn in their "Recherches sur les Metalloïdes," 1875, have the following passage:—"Les groupes nuancês de cyanogène, situês dans les parties bleues et violettes du spectre, se montrent aussi, soit quand l'étincelle traverse la partie luisante d'une flamme à gaz, soit dans l'arc voltaïque entre des électrodes du charbon d'une pile puissante. Cependant, ce dernier spectre du

On the ground of observing these two characteristic groups of lines ξ and θ (our seven blue and six violet nitrocarbon bands) in the spark spectra of carbonic oxide, cyanogen, and naphthaline, Dr. Watts was entitled at the time to infer that they must be due to the common element carbon. Dr. Watts has, however, made many experiments on the carbon spectrum since the date of that paper, and to neglect to take into consideration papers published by him since 1869 is to misrepresent his position. In the "Phil. Mag." for 1874, he wrote in a "Note on the Carbon Spectrum" as follows:—"In the 'Phil. Mag.' for October, 1869, I described four different spectra as spectra of *carbon*. One of them was the ordinary spectrum from hydrocarbon flames, first described by Swann; the second was the spectrum obtained from vacuum tubes inclosing carbonic oxide, carbonic anhydride, or olefiant gas; the third was the spectrum of the Bessemer flame; and the fourth, the high tension spark in carbonic anhydride or carbonic oxide.

"I have since shown ('Phil. Mag.,' 1873) that the Bessemer flame spectrum, instead of being a spectrum of carbon, is the spectrum of manganese oxide; and I have had now to add the result of recent observations, which show that the second spectrum also is due, not to carbon itself, but to some *oxide* of carbon. This spectrum was held to be a spectrum of carbon because it was common to compounds of carbon with hydrogen and with oxygen.

"I have now found that it is not given by spectral tubes inclosing olefiant gas if special care be taken to exclude all traces of oxygen. . . . . We have therefore only one spectrum which can be proved to be due to *carbon*—that, namely, which is common to the flame of olefiant gas or cyanogen, the electric discharge in cyanogen or carbonic oxide at the ordinary pressure, and to the electric discharge in vacuum tubes inclosing cyanogen, olefiant gas, or hydrocarbons, such as benzol."

We infer from this, that the groups ξ and θ (our seven blue and six violet nitrocarbon bands), which are certainly not common to all the spectra here enumerated, are not included in the one spectrum which Dr. Watts at that time assigned to carbon. However that may be, it is unnecessary to say more about it here, for we have quoted enough to show that Dr. Watts' conclusions, in 1869, were not so certain that they could now be quoted as authoritative against the inferences drawn from later observations, and that we did our subject no injustice in making no more particular allusions to them than we did.

But, further, after describing an experiment with carbon tetrachloride, Mr. Lockyer says:—"This result, which entirely endorses the work of Attfield and Watts, has been controlled by many other experiments." If we may assume that the work of Attfield and Watts

cyanogène, qui est remarquable par l'éclat vif des raies, n'est pas pur, mais mêlé des raies des carbures d'hydrogène, dont le splendeur est encore plus magnifique."

alluded to is that described in the previous quotations, it is not a little remarkable that Mr. Lockyer's experiments should so "entirely endorse" what Watts himself has shown to have been in part erroneous.

Lastly, we cannot allow Mr. Lockyer's assertion that Ångström and Thalèn's conclusions "rest more upon a theory which has been shown to be false since the labours commenced, and analogy, than upon experiment," to remain uncorrected. Their conclusions are eminently inductions from experiments carried on, as they say, during several years, of which the most important are particularly described. Many of the experiments which led up to their conclusions had been previously published by Thalèn in 1866 ("Årsskrift, Upsala"), in a paper in which he correctly described and distinguished the spectra of hydrocarbons, of oxide of carbon, and of carbon respectively, and besides described the spectrum of the spark between carbon poles in nitrogen. This paper is an admirable sample of good experimental work, and its perusal, together with the later paper of 1875, leaves no doubt that, whatever theories they may have held, Ångström and Thalèn relied mainly on experiment and observation to prove the soundness of their conclusions.

In conclusion, Mr. Lockyer introduces a reference to a former work of ours on the magnesium-hydrogen spectrum, and to a theoretical deduction regarding the interactions which might produce the cometic spectrum, making the following remark :—

"From what I have shown it will be clear that the consequences drawn in the following paragraphs by Messrs. Liveing and Dewar from the assumed hydrogen-carbon bands are entirely invalid."

As this opens out a question entirely beside that in hand, depending on the validity of the premises from which Mr. Lockyer draws his conclusion, we prefer to deal with it when we discuss, in our next paper, the spectra of carbon compounds and the experimental evidence Mr. Lockyer has adduced in support of such assertions.

VI. "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen. No. II." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received May 27, 1880.

In our last communication on this subject (*ante*, p. 152), we thus summarised the results of our observations as to the "nitrocarbon spectrum."*

* In using this term we merely mean that we are dealing with a spectrum invariably associated with the presence of nitrogen and carbon in such conditions that chemical union takes place, without any reference to the particular compound produced.