

June 15, 1882.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Mr. Gabriel Auguste Daubrée (Foreign Member), Dr. George Stewardson Brady, Dr. George Buchanan, Mr. Francis Darwin, Professor William Dittmar, Dr. Walter Holbrook Gaskell, Mr. William Davidson Niven, and Mr. Robert Henry Inglis Palgrave were admitted into the Society.

The President read a despatch from H.M. Consul-General at Florence, transmitted through the Foreign Office, giving an account of a commemoration in honour of the late Charles Darwin, held in the great hall of the Istituto di Studi Superiori.

A preliminary (oral) Statement of Results of observation of the total Eclipse of the Sun on May 17, as seen in Egypt, was made by Mr. J. N. Lockyer, F.R.S.

The following Papers were read :—

- I. "Researches on Spectrum Photography in relation to New Methods of Quantitative Chemical Analysis." By W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin. Communicated by Professor G. G. STOKES, Sec. R.S. Received May 19, 1882.

Preliminary Note.

(1.) Since I perfected the instrument employed by me in investigating the molecular structure of organic compounds, I have been engaged in studying the spark spectra of elementary bodies with the object of applying my method of working to the purposes of technical chemical analysis. Progress in the course of this research has proved it to be necessary to investigate all kinds of spectra *de novo* in the hitherto little explored *ultra-violet* region.

Some fourteen years' practice in photography has convinced me that when a plate is properly exposed the development of the image is the simplest of all operations; in order, therefore, to simplify spectroscopic work, I have carefully ascertained the time of exposure required to produce the most characteristic spectra under various

VOL. XXXIV.

G

conditions, such as intensity of spark and conductivity, &c., of the electrodes. This, in the instrument I prefer to use, is generally a period of half a minute. ("Journal of the Chem. Soc.," vol. xli, p. 84, 1882.)

(2.) A long series of experiments has been made with the object of comparing the spectra of various compounds in solution with those of the elements they contain. In the process of photographing the spectra of solutions it is desirable to eliminate all foreign lines as far as possible, hence the selection of suitable electrodes was a matter of the first consideration, the method of working being almost entirely dependent on this for its accuracy and value. No method like that of Bunsen is convenient, in which charcoal points are employed in conjunction with a spark from a coil without a condenser, by reason of the prolonged exposure rendered necessary, the intensity of the emitted rays being small. Electrodes of gold, platinum, iridium, and other metals were used, and those of gold proved decidedly the best, as containing the fewest lines and the metal being a most excellent conductor of electricity.

All these metals are, however, useless compared with electrodes of graphite. The spectrum of graphite consists of eleven or twelve insignificant lines due to the carbon, and about sixty-six lines and bands due to air.

The air-lines are easily recognised from their "physiognomie," as M. Lecoq de Boisbaudran calls it, or as I have elsewhere described this peculiarity in relation to spectrum photographs, their "*graphic character*." In no case with the intensity of spark which I employ and the normal exposure have I ever been troubled with the presence of such impurities as may be contained in points of good Siberian or Ceylon graphite. Such points have been submitted to the continuous action of a condensed spark for something like ten hours at a time, the same solution being used and the electrodes unaltered. It is usual to take fresh electrodes for each solution.

(3.) In comparing the spectra of solutions of salts with those of metallic electrodes, it was found that in almost all cases the lines of metals were exactly reproduced from the solution, the *graphic character* being retained except in regard to their continuity. Discontinuous but long lines, or in certain cases even short lines, appear as long lines in the spectra taken from solutions. The peculiarities of the spectra of magnesium, of cadmium, and iron, were exactly reproduced, line for line, from the chlorides. An alteration was noticed in the spectrum of graphite, the short lines became long, that is to say, discontinuous became continuous lines, when the electrodes were wetted with water or acids.

An exceptional instance of variation in a spectrum was seen in that of zinc. The pure metal exhibits a series of highly characteristic ex-

cessively short lines or dots, which are totally absent from the photographs of solutions of zinc made from the same metal. Certain discontinuous lines in the spectrum of iridium become continuous when moistened with calcic chloride solution. It has been remarked by me elsewhere (*loc. cit.*) that the more volatile, and I may now add, the more unoxidisable a metal, the more continuous are its lines. The compounds in solution are more volatile than the metals, and hence the greater continuity in the lines. In the case of graphite it is doubtless a volatile carbon compound, either carbon dioxide or a hydrocarbon, which is formed by the heat of the spark when the points are moistened with water. In the case of iridium it is difficult to suppose that the calcic chloride solution forms a chloride by the simple action of heat on such a refractory metal; but this is the only explanation that will account for the greater continuity of the lines. Insoluble compounds give no spectra when mixed with water or glycerine and exposed to the spark. The non-metallic constituents of salts do not yield any marked series of lines, and therefore do not obscure the metallic spectra.

The spectrum of aluminium as obtained from perfectly pure solutions is free from a group of short or discontinuous lines seen in my published photographs of spectra. By prolonged exposure, as I have elsewhere shown, these lines have been proved to be due to iron. The spectrum of aluminium is thus proved to be a very simple one. In all these spectra the rays lying between 4500 and 2000 on the scale of wave-lengths are completely focussed on one plate, and the relative intensities of the lines exhibit the relative intensities of the rays. Any modification in the relative intensity of a line or in its length is accurately registered on the sensitive plate. As many as fifteen different spectra have been photographed on one plate, and developed by one immersion in the developing solution. It has been proved experimentally that *accidental alterations* in the period of normal exposure, which are not very noticeable, do not affect the spectra. Any irregularities such as may be unavoidable in the passage of the spark do not alter the normal densities of the images of the various rays. The development of the photographs is completed in about thirty seconds. These points are of vital importance in placing this method of working on such a basis that it may be employed in quantitative methods of chemical analysis, for if the intensity of the rays be so great that the period of exposure is rendered much shorter, difficulties would arise in obtaining photographs with neither more nor less than the requisite density. And, again, were the exposure much prolonged the method would become somewhat tedious, or, at least, it would be impaired in value.

(4.) Of all methods likely to yield results of practical importance in estimating the relative proportions of the constituents of either an

alloy or a mineral, only those have recommended themselves to me which depend upon the use of solutions; and for the reason that most alloys are not homogeneous, and the portion of a metallic electrode exposed to the action of the spark is volatilised from one point, and is too minute in quantity to represent the composition of the mass. Now, the composition of a solution represents in every part the composition of the entire mass dissolved; it is, therefore, quite unimportant how small a fraction of it is used for the purpose of obtaining the spectrum of its constituents.

It is a remarkable fact that at the present time we know little or nothing of the sensitiveness of the spectrum reaction *under various conditions*, notwithstanding that such knowledge is absolutely necessary for the purpose of giving stability to numerous theories and arguments which are based on spectrum observations. I have made some experiments in this direction by determining the extent of dilution which serves to modify in various ways the spectra of solutions of metallic salts, and that which finally causes the extinction of the most persistent line or lines. The sensitiveness of the reaction varies with different elements and with the period of exposure, the intensity of the spark, and other conditions; I have no difficulty whatever, when working in the manner here indicated, in recognising spectra yielded by solutions which contain no more than $\frac{1}{10000}$ th of a *per cent.* of calcium, silver, copper, and $\frac{1}{100000}$ th of a *per cent.* of manganese. It is necessary, however, for me to withhold a full account of my experiments until I have determined the wave-lengths of the lines in the various spectra under observation, for it is quite impossible to describe the changes in the spectra without reference to accurate measurements of the metallic lines. For some time past Mr. W. E. Adeney has been working in conjunction with me at these determinations, and I hope with as little delay as possible to have the honour of submitting to the Royal Society all details here omitted, both with regard to these new methods of analysis, and the wave-length determinations.

II. "On the Reversal of the Metallic Lines as seen in Over-exposed Photographs of Spectra." By W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin. Communicated by Prof. G. G. STOKES, Sec. R.S. Received May 19, 1882.

In preparing series of photographs of metallic elements when their spectra are obtained by the action of a condensed spark passed between metallic electrodes, I have been very careful to ascertain the exact period of exposure of the sensitive plate to the rays, which will bring