

must have been introduced by former experimenters using a moist blotting-paper surface instead of the surface of the liquid itself.

A large number of discordant results were obtained in March, 1878, and their explanation led to the interesting result that the apparent contact difference of potentials between a metal and mercury, as measured inductively, varied much with small additions of temperature. The accidental difference of temperature in the different experiments arose from the mercury having been redistilled in the laboratory between every two experiments to remove all possible traces of impurities, and probably in some cases it had not become perfectly cold before a new experiment was made. The investigation of this apparent change of contact difference of potentials with temperature led to a consideration of the contact difference of temperature of mercury with air, since, of course, in all these inductive experiments two air contacts are included in the result. The results thus obtained will form part of the substance of the next paper.

Next follow a number of checks of the accuracy of the results based on the well known law that in any compound metallic circuit at uniform temperature there is no electromotive force. This is followed by some considerations regarding the measurement of the difference of potentials between substances and the air in contact with them, and of measurements of the Peltier effect.

It has usually been thought that the differences of potential of liquids in contact with one another were so small as to be almost inappreciable in comparison with the differences of potential of metals in contact; but the authors have ascertained, among other results, that strong sulphuric acid in contact with distilled water, solutions of alum, copper sulphate, and zinc sulphate has a measured difference of potentials of 1·3 to 1·7 volts, an electromotive force more than twice as high as that of zinc and copper in contact. And hence the importance of an apparatus that can directly measure the difference of potentials of two liquids.

March 20, 1879.

THE PRESIDENT in the Chair.

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

The following Papers were read:—

- I. "Note on some Spectral Phenomena observed in the Arc produced by a Siemens' Machine." By J. NORMAN LOCKYER, F.R.S. Received March 3, 1879.

In continuation of my work on the spectra of metallic vapours photographed when incandescent in the electric arc, I have recently employed a Siemens' dynamo-electric machine driven by a gas engine of ten horse-power, using an effective force of five or six.

The greatly increased length of arc obtained by these means has enabled me to observe and photograph a new set of phenomena of great beauty, and I think of the highest theoretical importance.

In my former work with a battery of thirty cells, in order to obtain the lengths of the lines, it was necessary, in consequence of the shortness of the arc, to throw an image of a horizontal arc on the vertical slit of the spectroscope. In this manner perfectly symmetrical photographs were obtained, the shortest lines due to the core, and the middle portions of the longest ones proceeding both from the core and the exterior portion, lying in the axis of the photograph.

With the Siemens' machine the arc is not only much longer, but when some substances are introduced into it, it is accompanied by a flame sometimes three or four inches long, of great complexity both with regard to colour and concentric envelopes.

The spectrum of this flame was first photographed side by side with that of the arc itself, and when the poles are clean the flame has been shown by eye observation to be chiefly due to the oxidation of the carbon and calcium vapours which exist in the free state in the air, thus giving us absolute demonstration of a combination brought about among vapours by reduction of temperature.

These flame phenomena also give us an opportunity of observing the inverse appearance of spectral lines, to which my attention has lately been much drawn. The following is a case in point:—In one photograph of the flame given by manganese the line at wave-length 4234·5 occurs without the triplet near wave-length 4030, while in another photograph the triplet is present without the line at 4234·5.

The various phenomena presented in these photographs, especially the greater breadth of the reversals in the case of some of the metallic lines in the flame, and the gradual introduction of new spectra, led me to imagine that in different regions of *the arc itself* the spectroscopic effects might vary greatly; and to test this I very carefully projected the image of a vertical arc on the slit, focussing that particular light which I was about to photograph.

In the plates thus obtained the spectra of those portions of the arc adjacent to the positive and negative poles are widely dissimilar.

We may say, roughly, that the carbons employed give a spectrum containing the flutings of carbon and the lines of calcium, some of them reversed, as I have shown many years ago, both in the case of this and other substances.

In the photographs of the arc taken under the conditions I have stated, the calcium lines cling to one pole and the carbon flutings to the other; the lines which reverse themselves in the case of calcium being those which have their intensity most pronounced close to the pole. That this is a phenomenon not dependent upon the chemical constitution of the two poles, but rather on some electrical separation, is rendered evident by the fact that on changing the direction of the current the calcium and carbon spectra change positions.

Although these phenomena are very marked in the photographic region, as is evidenced by the photographs which I submit to the Society, they yet appear more strongly developed in the less refrangible regions. The exquisite carbon flutings in the yellow-green, for instance, cling more closely to the pole than those in the violet.

So much for the spectrum of the poles themselves.

If now we introduce a metal and observe its vapour, we find a perfectly new set of phenomena. We get long and short lines, but the law which they obey is no longer the one in operation when the parts of the arc examined are symmetrical with reference to the positive and negative poles as when a horizontal arc is employed.

Some lines stretch across the spectrum with their intensities greatest close to one pole, while other lines invisible at this pole are most intense at the other. *In one photograph, for instance, the blue line of calcium is visible alone at one pole, the H and K lines without the blue lines at the other.*

More than this, there is a progression of lines, so to speak, from pole to pole. They lie *en échelon* along the spectrum.

In the case of other lines, only the central region is occupied, the line being enormously distended either like a spindle or a half-spindle, with the bulging portion in some cases on the more, in others on the less, refrangible side.

It is very difficult to understand what process is here at work if we are not in presence of separations brought about by temperature and electricity.

However this may be, a most convenient method is afforded of separating basic from non-basic lines. I have already, in previous communications, referred to the repetition of doublets in some spectra, and of triplets in others; and it often happens that one member of a doublet or triple group is basic. The wide iron triplet near G, to which I referred in my communication read on the 12th December, has its central member basic with calcium; and this is most beautifully shown by the extension of the iron triplet right across the arc, while

the central member alone is thickened along with the other calcium lines on one of the poles.

LIST OF PHOTOGRAPHS EXHIBITED.

Photograph of Mn lengths taken in the old way, showing that with a battery of 30 Grove cells and a horizontal arc a perfectly symmetrical photograph was obtained with the lines extending equally on either side of a horizontal ink line drawn through the axis of the photograph.

Photographs of Ba, Sr, and Mn, giving in each case the spectrum of the core compared with that of the flame of the arc.

I. Ba, showing that of two lines (wave-length 4130.5 and 4282.5) of equal intensity in the core, the less refrangible was visible almost alone in the flame.

II. Sr, showing two lines at 4078.5 and 4215.3. In the core the more refrangible has a much broader reversal than the other, while in the flame the less refrangible exists alone and reversed.

III and IV. Mn, in the flame-spectrum of one of these photographs the triplet at about 4030.0 exists with no other Mn lines; while it is absent from the flame-spectrum of the other photograph, although the Mn line at 4234.8 is present.

Photograph of flame-spectrum of Ca taken with an oblique slit, as the flame nearly always branches off at an angle.

Spectrum of Rb, showing that the carbon bands cling to the hotter pole, while the Ca and Rb lines cling to the opposite pole; one set of carbon bands, however, stretches right across the spectrum.

Two photographs showing reversal of phenomena by reversing the current.

I. Two spectra of Pb, obtained by normal current and reversed current, showing that the lines which, in the upper spectrum were thickened at their lower extremities, were in the lower spectrum thickened at their upper extremities, and that the general appearance of the two sets of lines was reversed.

II. Two spectra of Cu showing the same phenomena.

Spectrum of Mn obtained with the large arc of a Siemens' machine, in which the want of symmetry is so conspicuous that if a straight line be drawn through the centre of the photograph it will cut one set of lines at their centres, another near their upper extremities, while a third set of lines will be cut near their lower extremities.

Photographs showing separation of lines.

I. Spectrum of Li containing impurity lines of Ca, Sr, Fe, and Mn, the Ca and Mn lines clinging to one pole, and the Fe and Sr lines to the other.

II and III. Different parts of Fe spectrum, showing Ca lines starting from one pole, and Fe lines from the other.

IV. Spectrum of Cu, showing that this separation can exist not only between two metals, but even between lines of the same metal. In this the blue Ca line is seen thickened at the upper pole, while the H and K lines were only seen at the lower pole.

Spectra of Ti, Ni, and Mn, in which the lines were not all produced at the two poles, some occupying an intermediate position; the lines thus arranging themselves *en échelon* along the spectrum.

Spectra of Cu and Ni, showing the irregular thickening of different lines at different levels of the arc.

Photographs of the spectra of Sr, Cu, and Mg, showing central thickening.

- I. Sr, containing two lines, one Ba showing very little thickening, while the other true Sr line exists only at the centre as a broad, fluffily reversed line.
- II. Cu, all the Cu lines in this photograph have their central portions expanded, and most of them to a greater extent on the less than on the more refrangible side. Some of the Fe lines have also their centres expanded, which is not the case with the Ca lines, the Ca lines in the blue being developed at their extremities.
- III. Mg, showing line in the blue-green, with a central expansion on the less refrangible side, giving the line the appearance of a half spindle, *b* being quite normal.

Spectrum of Sn; showing lines of Ca and Fe; the former are expanded at their lower extremities, the Fe lines are not so expanded, but exist at a higher level than the Ca lines. The photograph shows that the line which is basic to Fe and Ca is carried up with the other Fe lines, and is also expanded at its lower extremity with the other Ca lines.

II. "Note on some Phenomena attending the Reversal of Lines." By J. NORMAN LOCKYER, F.R.S. Received March 5, 1879.

In the "Phil. Trans." for 1873, page 253, I gave an account of an experiment devised by Dr. Frankland and myself, in which the absorption line of sodium was made to vary considerably in thickness, owing to the variation in the quantity of sodium vapour which was produced in a tube when a mass of metallic sodium was heated in an atmosphere of hydrogen.

In the "Phil. Trans." for 1874, vol. clxiv, Part II, p. 805, speaking of the photographs of arc spectra which I had then commenced to take, I stated, "it not unfrequently happens that a very thick line will reverse itself, a circumstance which greatly facilitates its comparison with confronted lines, since a thin dark line then runs down the centre of the thicker bright one," and I pointed out in a note that the absorption line does not always occupy the exact centre of the bright band. I gave examples of this from the spectra of calcium and aluminium, the examples being reproductions of photographs of the arc. These were published with the paper.

In other subsequent communications, I have referred to these reversals, and I have elsewhere made general statements with regard to them, and drawn attention to the distinction between those substances which give us winged lines in arc spectra and those which do not.

If the method of throwing an image of the arc upon the slit be employed, a method which I suggested and utilised in 1870,* for

* "Phil. Trans.," 1873, p. 254.