

$$\begin{aligned} & \frac{2}{2s+1} \frac{2m+1}{m+1} \frac{n+1}{2n+1} \frac{A(s-m) A(s-n-1) A(s-p)}{A(s)} \\ & + \frac{2}{2s-1} \frac{2m+1}{m+1} \frac{n}{2n+1} \frac{A(s-1-m) A(s-n) A(s-1-p)}{A(s-1)} \\ & - \frac{2}{2s-1} \frac{m}{m+1} \frac{A(s-m) A(s-n-1) A(s-1-p)}{A(s-1)}. \end{aligned}$$

It is now a matter of easy algebraical work to put these three terms together by the aid of the essential property of the function  $A(r)$ . If we put the second and third terms together we shall get

$$\frac{2}{(m+1)(2n+1)} \frac{(m-n)(s-p)}{(s-m)(2s-2n-1)} \frac{A(s-m-1) A(s-n) A(s-p)}{A(s)},$$

and the first term is equal to

$$\frac{2}{2s+1} \frac{(2m+1)(n+1)(2s-2m-1)(s-n)}{(m+1)(2n+1)(s-m)(2s-2n-1)} \frac{A(s-m-1)A(s-n)A(s-p)}{A(s)};$$

the aggregate of the last two expressions is

$$\frac{2}{2s+1} \frac{A(s-m-1) A(s-n) A(s-p)}{A(s)};$$

as it should be.

I may observe that the definite integral was discussed by Dr. N. C. Schmit in a dissertation published at Brussels in 1858; but no simple result is there obtained.

III. "On the Spectra of Metalloids. Spectrum of Oxygen." By ARTHUR SCHUSTER, Ph.D., F.R.A.S. Communicated by J. CLERK MAXWELL, F.R.S., Professor of Experimental Physics in the University of Cambridge. Received April 25, 1878.

(Abstract.)

The many unexplained phenomena attending the passage of electricity through gases will probably for some time to come occupy the attention of experimental physicists. It is desirable that the subject should be approached from as many different sides as possible. One of our most powerful instruments of research is the spectroscope, but before it can be applied to the study in question we have to settle the chemical origin of the different spectra, which we observe in vacuum tubes, and to discuss in what way such spectra are liable to change under different circumstances. A special investigation has to be made

for each gas; we have to study the effect of various impurities, the influence of the electrodes, and that of the glass which in the tubes generally used is considerably heated up by the spark. I have chosen oxygen as a first subject of investigation. Though Plücker and Wüllner have, as far as their experiments went, accurately described the phenomena seen in oxygen tubes, the following contains much that is new, and will put some of the older facts on a firmer basis.

As some of the facts brought to light by the investigation bear directly on the question of double spectra, our knowledge on that point must be briefly referred to. We divide all known spectra into three orders. Continuous spectra, channelled space spectra, and line spectra. With regard to continuous spectra, it is shown that the older statement which limited them to liquid and solid bodies is no longer tenable. Most gases give continuous spectra long before they condense. Two theories of continuous spectra are noticed. The one considers that the vibrations of a molecule always tend to take place in a fixed period, but that the impacts of other molecules may, when the pressure is great or in liquid and solid bodies, prevent complete oscillations taking place, and thus produce a continuous spectrum. The other theory considers that, when a gas condenses, molecular combinations take place, which make the molecular structure more complicated, and may produce channelled space spectra or continuous spectra. According to the latter theory such molecular combinations are possible before the gas condenses, and thus the state of aggregation of the gas only indirectly affects the spectrum. The latter theory seems to be more consistent with experiment than the former one. For instance, it is shown that oxygen gives a continuous spectrum at the lowest temperature at which it is luminous. If the temperature be raised, the continuous spectrum is replaced by a line spectrum. This seems to be inexplicable by theory of molecular impacts.

With regard to channelled space spectra attention is drawn to a new kind, which finds a representative in the spectrum of the negative pole in oxygen. The ordinary channelled space spectra show bands, which when seen under small dispersion appear to have a sharp boundary on one side, and fade gradually away towards the other. When seen under large dispersion these bands appear to be made up of a number of lines which get nearer and nearer to each other as they approach the sharp boundary. The spectrum of the negative pole in oxygen, when looked at with small powers, seems to be made up of a number of bands which are uniformly illuminated throughout, but with high powers each band is found to be made up of a number of lines at about equal intervals.

With regard to line spectra it is shown that a body may at a low temperature show a different set of lines altogether from what it shows at a high temperature. It is difficult to decide whether the

change from one line spectrum to another is due to the same cause as that of a band spectrum to a line spectrum.

The chief difficulty in the way of a complete investigation of the spectrum of oxygen consists in the great disturbing influence of the presence of even a small quantity of any carbon compound. Amongst a great many oxygen tubes which were filled by various makers, I only found one which showed the spectrum of pure oxygen; all the others gave a spectrum of carbonic oxide. It is therefore necessary in filling oxygen tubes, to avoid all greased joints and all india-rubber tubings. I have used a Sprengel air-pump, which communicated with the vacuum tube by means of a ball and socket joint. The joint was kept air-tight solely by means of strong sulphuric acid. The vacuum tube was fused directly to the ball of the joint. To one end of the vacuum tube a piece of hard glass tubing had been fused. This was filled with different substances which, on heating, gave off pure oxygen. The oxygen therefore came only into contact with glass, mercury, and sulphuric acid, and the metal of the electrode. By repeatedly filling and exhausting the tube all extraneous matter, which always is attached to the inner surface of the glass, could be swept away. Permanganate of potash, oxide of mercury, and chlorate of potash, were used in turn to prepare the oxygen, but no effect was observed which could be traced to the substance used. The effect of the electrodes was eliminated by varying the metals. Aluminium, platinum, silver, brass, and iridium were used as electrodes. Any possible effect of the glass was eliminated by finally repeating all experiments in a glass receiver six inches in diameter, so that no part of the spark came nearer than  $2\frac{1}{2}$  inches to the glass. In this way it is believed all possibility of error due to the presence of any possible impurities was avoided.

All measurements were reduced to wave-lengths by interpolation. The lines of iron or any metal whose lines are reversed in the solar spectrum were taken as reference lines. The wave-length of the reference lines could therefore always be found on Ångström's solar map. As a rule the dispersion was equal to that of four heavy flint-glass prisms of a refracting angle of  $62^\circ$ , and it is believed that the accuracy of the measurements equals that of any other spectroscopic measurements.

Four different spectra of oxygen must be distinguished. At the lowest temperature at which oxygen becomes luminous it gives a continuous spectrum. As the temperature is gradually raised the continuous spectrum is successively transformed into two distinct line spectra, which I call respectively the compound line spectrum and the elementary line spectrum. It is one of the principal objects of this paper to show that these two line spectra which have been much mixed up together have a separate existence. The generation of one

always involves the destruction of the other. The fourth spectrum is that which is always seen at the negative pole in vacuum tubes filled with oxygen.

*The Continuous Spectrum.*—The following facts prove the statement that at the lowest temperature at which oxygen is luminous it shows a continuous spectrum.

1. The wide part of a Plücker tube generally shines with a faint yellow light. When looked at by means of a prism the spectrum is perfectly continuous.

2. If a spark of an ordinary Ruhmkorff coil is taken in oxygen at atmospheric pressure, one of the line spectra generally appears, but when the break is put out of adjustment so as to weaken the spark, the lines disappear and are replaced by a continuous spectrum which has its maximum of intensity in the greenish-yellow, and gradually fades away towards both ends of the spectrum.

3. Becquerel mentions an observation according to which the point of the oxyhydrogen flame takes a yellow colour when an excess of oxygen is present. The description of the somewhat characteristic colour which Becquerel gives coincides exactly with the colour of the spark in oxygen, when it shows the continuous spectrum. According to Plücker an excess of hydrogen shows the hydrogen lines, and it is therefore reasonable to suppose that in Becquerel's experiment the oxygen was sufficiently heated up to become luminous.

The continuous spectrum must not be confounded with the continuous spectrum which under high pressure forms the background to the line spectrum.

*The Elementary Line Spectrum.*—This is the spectrum which is seen when a strong spark passes through oxygen at the atmospheric pressure. It can be seen at all pressures when a jar and air break are introduced into the circuit. Several measurements exist of these lines, but only those of Thalèn are given in absolute measure. Thalèn's measurements, however, refer to the lines seen when a spark passes through air. Under these circumstances the oxygen lines are weak compared to the nitrogen lines, and some strong oxygen lines do not appear at all in Thalèn's list. I have made a careful measurement of all the lines. Some of the weaker bands have a different appearance and suggest, therefore, a doubt whether they are really due to oxygen; but they always appear with the same relative intensity, and I could not obtain any evidence which would justify their exclusion from the list of oxygen lines.

*The Compound Line Spectrum.*—Plücker in his first investigation of oxygen says it consists of four lines, one in the red, two in the green, and one in the blue. In his later drawing of the spectrum of oxygen, he gives a great number of lines of which these four form a part. Wüllner says that the four lines in question are always the

first to appear in oxygen tubes. Thalèn and Ångström do not give these lines; Huggins does not give them; Salet does not give them. Plücker and Wüllner are the only observers who experimented under the circumstances under which the lines appear. They come out equally well whatever way the oxygen is prepared, whatever the nature of the electrode, and I have seen them under the large glass receiver already mentioned. The following is the appearance of an oxygen tube as it undergoes gradual exhaustion.

When the pressure is sufficiently diminished to allow the spark to pass, it shows a yellow colour and the spectrum is perfectly continuous. Almost immediately, however, the four lines are seen in the capillary part of the tube above the continuous spectrum. The continuous spectrum in the wide part is then stronger than in the narrow part. The four lines seem to have taken away part of the energy of the continuous spectrum. As the exhaustion proceeds the spark spreads out in the wide part, and the continuous spectrum is therefore diminished and becomes less intense than in the capillary part; but it gradually loses in intensity also in the narrow part, until the four lines stand out on a perfectly black background. If under these circumstances the jar and air break is inserted in the circuit, everything will disappear and the elementary line spectrum will come out. We have here as complete a transformation as from the band spectrum of nitrogen to the line spectrum of nitrogen taking place under precisely the same circumstances; and it is therefore not unlikely that the two phenomena are due to the same cause. There are two reasons why the existence of the compound line spectrum of oxygen as a separate spectrum may have escaped previous observers. There is a blue line in the elementary line spectrum which is nearly coincident with the blue line of the compound line spectrum. It requires considerable dispersion to notice the difference; the complete disappearance of the compound line spectrum has therefore escaped notice. The two green lines and the red line widen easily at higher pressures, and as has been remarked by Wüllner, even fuse together to a continuous spectrum. If the experiment is therefore made at a pressure at which oxygen has a continuous background, the disappearance of these lines might be taken for their widening and fusing together. No such mistake is possible when the vacuum is good. I have not been able to determine with certainty whether the red line seen at atmospheric pressure is a remnant of the compound line spectrum, or whether it is a line of the elementary line spectrum closely coincident. I am inclined to the former view, although it often seemed as if the line seen at atmospheric pressure was less refrangible than the red line of the compound line spectrum. I have drawn attention in a letter to "Nature" (December 20), to the fact that the compound line spectrum of oxygen seems to be reversed in the sun. I have no further

information to add on that point, and the wave-length of the lines will be found in my letter.

*The Spectrum of the Negative Pole.*—This spectrum has first been correctly described by Wüllner. It consists of five bands, one of which is too weak to be measured. The appearance of each band has already been described (page 384). Careful measurements of the bands have been taken. With regard to the explanation of the separate spectra found at the negative pole in nearly all gases, I incline to the view that they are due to separate molecular compounds which are formed at the pole. The following experiments seem to support that view. When the pressure is very small the spectrum of the negative pole extends throughout that half of the tube which encloses the negative pole, and which I shall call the negative half. If the current be suddenly reversed the spectrum of the negative pole will still be seen at first, in that part which was the negative half and now is the positive half of the tube; but it will gradually disappear and a permanent state will be established, in which the spectrum of the negative pole is, as before, only seen in the negative half. That it is the reversal and not the interruption of the current which produces the result is easily proved by interrupting the current and at once closing it again the same way, when no difference will be seen. If, however, the current be left interrupted for some time, say one minute, so that any compounds which may have been formed in the negative half may diffuse into the other half, and if then the current is closed either the same or the opposite way, the negative spectrum will be seen at first throughout the tube, but gradually disappear in the positive half.

If the current be rapidly reversed in succession, after a little while, when the effect of the first reversal has disappeared, the permanent state will always be established at once, and the spectrum of the negative pole will appear only in the negative half.

If after the last experiment the current be interrupted for some time and then closed, the spectrum of the negative pole will at first be seen throughout the tube, and gradually disappear in the positive half.

It is not quite easy to see the explanation of the last two experiments.

The experiments were all made in the Cavendish Laboratory, Cambridge, and I am much obliged to Professor Clerk Maxwell, for the kindness with which he has placed the resources of the Laboratory at my disposal.