

II. *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.*

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## [PLATE 1.]

1. *Introductory.*

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 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. To make the investigation complete we have to vary as much as possible the pressure, the bore of the vacuum tube, and the strength of 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 paper contains much that is new, and will put some of the older facts on a firmer basis. When I first began to work, it was my intention to take the gases in groups, and to study their mixture; but as the following investigation has taken me a year's nearly continuous work, and is complete in itself, I trust it will not be found unworthy of publication. I must, of course, at present confine myself to the purely spectroscopic point of view. As several of the observations which I shall have to record bear directly on the general theory of double spectra, I must briefly refer to our knowledge on that point.

2. *Multiple Spectra.*

We may roughly divide all known spectra into three kinds or orders: continuous spectra, line spectra, and, standing between them, spectra of fluted bands or channelled spaces, as they are commonly called.

*Continuous spectra.*—During the first years of spectrum analysis it was generally supposed that a continuous spectrum was characteristic either of a solid or of a liquid body; but as our experimental knowledge gradually increased, it was found that the fact of a body being in its solid, liquid, or gaseous state only indirectly influenced the order of the spectrum. It was believed at first that a chemical compound always showed the spectrum of its individual molecules; in other words, that the vibrations of the molecules were made up of the vibration of the component atoms. If we accept this theory, then, of course, we have only one explanation of the different orders of spectra, viz., the influence of one molecule on another. According to this view, the state of aggregation of the body must be the direct cause of the change in the spectrum. Since the work of MITCHERLICH, however, it has gradually been recognised that a combination of atoms changes entirely the spectrum. This change is not slight, but fundamental. The whole vibrating system seems to have been altered; and there is at present, in the vast majority of cases, no hope that we may consider the vibrations of a molecule to be only the slightly disturbed vibrations of the atoms. We have now a second cause for a change in the different orders of spectra. We need no more look on a continuous spectrum as a line spectrum, disturbed by the shocks of other molecules; but we may explain it by the changes which have taken place in the individual molecule.

According to this view, liquid and solid bodies give generally continuous spectra, not because they are liquid or solid, but because in these states the molecules have a more complicated structure than in the gaseous state. Experiment has to decide between the two theories: the theory of molecular disturbance, and the theory of molecular structure. I think that the facts are decidedly in favour of the latter theory. Mr. LOCKYER's investigations have shown that most bodies give us a continuous spectrum, as a gas, before they condense, and many at a considerable temperature above the boiling point. Mr. LOCKYER has rightly drawn the conclusion from these facts, that the atomic aggregation of the molecules is the cause of the different orders of spectra. If we observe the changes in a spectrum which gradually take place on heating or cooling a vapour, we find that the continuous spectrum is produced, not by a widening of the bands, but by a direct replacement, which is sometimes sudden and sometimes gradual, and which leaves no doubt in the observer's mind that he has to deal with two vibrating systems, and not simply with a disturbed one. I do not, of course, mean to say that the impacts of other molecules have no observable influence. If the hydrogen lines widen through increased pressure, it is very likely that the alteration is produced by impacts; but the change from a line spectrum to a continuous spectrum, as a rule, is quite different from the change which takes place with hydrogen. According to the theory of molecular aggregation, it seems quite possible that a liquid should give the same spectrum as its vapour, and this, indeed, seems to be true in some cases.

I shall show that we can obtain a continuous spectrum of oxygen, not by an

increase, but by a decrease, in the strength of the spark. I shall prove that, at the lowest temperature at which oxygen is luminous, it gives a continuous spectrum, which disappears as the temperature is increased. It is not easy to see how this can be due to any other cause than the one which I have advocated.\*

*Channelled space spectra.*—Standing between line spectra and continuous spectra, we have, as I already mentioned, spectra of fluted bands or channelled spaces. Such spectra, when seen in spectroscopes of small dispersive powers, appear, as a rule, made up of bands, which have a sharp boundary on one side, and gradually fade away on the other. When seen with a more perfect instrument, each band seems to be made up of a number of lines of nearly equal intensity, which gradually come nearer and nearer together as we approach the sharp edge, and finally fuse together. The sharp edge is the limit toward which the lines gradually approach. This edge is sometimes towards the red and sometimes towards the blue end of the spectrum.

There is another class of channelled space spectra, which, though never accurately described or measured, is, as I have reason to believe, by no means uncommon. These spectra appear, in instruments of low dispersive power, as made up of bands covering

\* Since the above was written, Professor STOKES has suggested to me a way by which the continuous spectrum might be produced, and which differs from the one described above as that of molecular impacts.

We have reason to believe that the mere motion of matter through the ether is insufficient to produce vibrations. There must be two portions of matter exerting forces on each other in order that the ether should be thrown into agitation. In ordinary line spectra we consider that the two portions of matter form part of the same molecule. Now, it seems possible that also two portions of different molecules should in their rapid approach towards each other, or recession from each other, cause forces in the ether which produce vibration. These latter vibrations we might expect not to take place in fixed periods, but to produce what we call a continuous spectrum. We may suppose that at the lowest temperature at which, for instance, oxygen is luminous, the vibrations in the ether are chiefly produced by this rapid relative motion of different molecules, while at higher temperatures the relative motions of different portions of one molecule might have the upper hand; the continuous spectrum in one case, and the line spectrum in the other, might thus be explained.

I admit that there is much to be said in favour of this view, and must leave to further experimentation to decide whether it is the one most accordant with facts or not. That the discontinuous spectra of different orders (line and band spectra) are due to different molecular combination, I consider to be pretty well established, and analogy has led me (and Mr. LOCKYER before me) to explain the continuous spectra by the same cause; for the change of the continuous spectrum to the line or band spectrum takes place in exactly the same way as the change of spectra of different orders into each other. Analogy is not a strong guide, yet some weight may be given to it in a case like the one under discussion, where experiment hitherto has failed to give a decided answer. Professor STOKES has also suggested that the continuous spectrum which comes out under high pressures may really be only the continuous spectrum of low temperatures. At such pressures the discharge of an induction coil consists of a bright and sensibly instantaneous spark, followed by an apparently continuous discharge, for which the spark appears to open a path; and it is possible that the line spectrum may really belong to the spark, and the continuous background to the continuous discharge. Professor STOKES has suggested an experiment with a rotating mirror to decide the point: an experiment which I hope to be able to make before long.—Note added December 1, 1878.

a greater or smaller space, and do not gradually fade away on either side, but seem to have the same intensity throughout, with a sudden fall at both edges. Such are the bands which appear at the negative pole of oxygen tubes. With high dispersion I was able to resolve these bands into a series of lines. Their appearance, under these circumstances, is represented in Plate 1, figs. 1 and 2.

It seems remarkable that most bodies should, under certain conditions, give spectra which in character resemble each other so nearly as these channelled space spectra; and the idea seems natural, and almost necessary, that such a similarity of spectra should be produced by a similarity in molecular structure. We know that certain bodies giving line spectra show, when they combine with others, spectra of fluted bands; and this seems to me to lead to a necessary explanation of double spectra—the one which indeed has been adopted by most experimentalists. They hold that when a spectrum suddenly changes from a line spectrum to a band spectrum, we have to deal with a molecular combination either of the molecules of the same body or of different bodies.

*Line spectra.*—The appearance of these spectra is too well known to need any description. Until lately, line spectra have kept out of the way of the many difficulties which beset their brethren of different orders, but at last they could no more resist the invasion. It gradually appeared that lines which are prominent at one temperature may be comparatively weak at another. This fact is sometimes exaggerated to such a degree that all the lines which form the spectrum of lower temperature disappear without a remnant at higher temperatures, while the lines of higher temperature are not to be seen at lower temperatures. Oxygen, which is a typical gas for every difficulty in spectroscopy, is a case in point. Oxygen seems to have two perfectly distinct line spectra, each of which generally appears by itself and unmixed with a trace of the other spectrum.

Let us for a moment consider how we may explain these facts without having recourse to molecular combinations. We have to assume that, when the vibrations of a molecule are small, they take place in a series of periods, and consequently show lines in the spectroscopie at places corresponding to these periods. Now imagine the temperature to be raised. We must assume that, as the intensity of vibration increases, other periods come into play which rapidly increase in intensity, while those which were prominent at first gradually disappear, so that, after a while, a different set of vibrations is formed. I do not know that there is any fact which could be adduced against such an explanation, nor do I think that the explanation is theoretically impossible. Yet the passage of one line spectrum into the other resembles so very closely the passage of a band spectrum into that of a line spectrum, that one feels inclined to refer both phenomena to the same cause. In the case of oxygen, for instance, one line spectrum appears under precisely the same circumstances as the band spectrum of nitrogen, and it changes into the other line spectrum almost identically in the same way as the band spectrum of nitrogen changes into the line spectrum.

The homogeneousness of the phenomena seen in vacuum tubes is greatly increased, if we consider the one line spectrum of oxygen as the representative of the band spectrum of nitrogen, and I shall therefore consider it as such. I have called the spectrum the compound line spectrum of oxygen, because, according to the theory of molecular combination, it would be due to a more complicated molecular structure than the other (the elementary) line spectrum. I must, however, add that I do not at all feel certain that the two line spectra are necessarily to be explained the same way as the line and band spectra. I have found it necessary, for the sake of clearness, to explain the results of the investigation in the language of a definite theory. It will be easy for any one to separate the two. The fact that nearly all lines which make their appearance at low temperatures only are lines which widen easily seems to be suggestive.

*Spectra of the negative pole.*—It has long been known that in many gases the glow surrounding the negative electrode has a different colour from the remainder of the discharge. This colour appears generally more blue to the eye than that of the positive discharge, and this fact was the cause that a certain blueness was often associated with the idea of negative electricity. When examined with the spectroscope, it is found that the negative glow has a spectrum of its own, different, of course, in different gases. Here, also, I think, it will be found simpler to assume that a definite molecular combination is formed at the negative pole than to suppose that exterior forces peculiar to the pole modify the period of vibration. The following experiments seem to me to support strongly, if not to prove, this view. When the pressure is very small, the spectrum of the negative pole is seen throughout the tube.\* In vacuum tubes of the form usually employed for purposes of spectrum analysis, it is easy to obtain a state of exhaustion in which they show the spectrum of the negative pole throughout that half of the tube which contains the negative electrode (which I shall call the negative half), and also in the capillary part, but not in that half of the tube which contains the positive electrode (which I shall call the positive half). The experiments are supposed to be made at that stage.

*Experiment 1.*—Allow the spark to pass some time in one direction; the spectrum of the negative pole is seen in the negative half and in the capillary part only. Now reverse the current suddenly, and the spectrum will now be seen at first throughout the tube, but will gradually disappear in the positive half, so that finally the same permanent state as before is established, and the spectrum is only seen in the negative half and capillary part.

*Experiment 2.*—In order to show that it is the reversal, and not the interruption of the current which produces the appearance of the spectrum in the positive half, break the current and make contact the same way: no change can be observed.

*Experiment 3.*—But if, after the spark has passed some time, you break the contact and wait a little time, say one minute, so as to allow any compounds which might

\* GOLDSTEIN, 'Berliner Monatsberichte,' May, 1876.

have been formed in the negative half to diffuse into the other half, and then make contact either the same way as before, or the opposite way, the spectrum of the negative pole will be seen throughout the tube at first, and only gradually disappear in the positive half.

*Experiment 4.*—Make and break contact very rapidly, always changing the direction of the current; after a little time, when the effect of the first make has passed away, the permanent state will at once be established for each current in either direction, so that in this case the spectrum characteristic of the negative glow is always only seen surrounding the negative electrode; but I believe that the glow itself in this case is not so much developed.

*Experiment 5.*—After alternating the current quickly, as in Experiment 4, you wait a little while, and then make contact either way; the spectrum of the negative pole will be at first seen throughout the tube, and gradually die away in the positive half.

These experiments succeed as well in nitrogen as in oxygen. Experiments 4 and 5 weaken somewhat the argument. I have obtained, however, other results on suddenly reversing the current, which require further investigation. Without pretending to be able to give a complete explanation of the experiments, it seems to be proved by them that the spectrum of the negative pole may appear away from the pole, and must, therefore, be due to secondary causes. I have proved in another place that a mere difference in temperature cannot account for the production of the spectrum at the negative pole.\* I cannot help quoting, in this place, a passage taken out of FARADAY'S 'Experimental Researches.' After having referred to an explanation which makes the so-called unipolarity in the conduction of soap and similar bodies depend on secondary chemical phenomena, which take place at the poles, he says:—

“Probably the effects which have been called effects of unipolarity, and the peculiar differences of the positive and negative surface when discharging into air, gases or other dielectrics, which have been already referred to, may have considerable relation to each other.”†

### 3. *Description of Apparatus.*

In an investigation of the spectra of pure gases it is essentially necessary to avoid all traces of carbon impurities. Indiarubber tubings, as well as any joint involving the introduction of grease, paraffin, &c., cannot be used. I do not say that such joints are always detrimental to the correct experiment, but if the question has to be decided whether a certain spectrum is due to an impurity or not, all excuse for the presence of the impurity must be avoided. These precautions are absolutely necessary if a pure spectrum of oxygen is desired. I have examined a great number of tubes supposed to be filled with pure oxygen by various makers, but I have only seen one tube which did not show the spectrum of carbonic oxide. This spectrum has been described by various

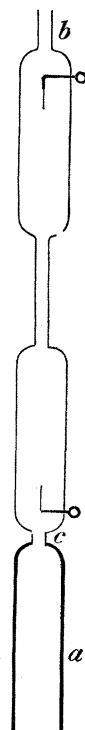
\* Proceedings of the Cambridge Phil. Soc., vol. iii., p. 57.

† 'Experimental Researches,' Series XIII., 1636.

observers as a spectrum of oxygen ; but ÅNGSTRÖM, WÜLLNER, and SALET have recognised it as identical with the spectrum of carbonic oxide. By taking the necessary precautions I have succeeded in filling a great number of tubes, which show no trace of the presence of any carbon compound. I have used a SPRENGEL pump, with air trap, such as is sold by Mr. J. J. HICKS. The connexion between the pump and the vacuum tube is made by means of a ball and socket-joint. The fall tube of the pump ends at its upper extremity in a hemispherical socket. A hollow sphere is ground together with this socket, so as to fit perfectly into it. The inner part of the sphere communicates with the pump by means of a small hole, and ends at the other side in a glass tube. I have always fused my vacuum tubes directly to this tube. For ordinary purposes the sphere is slightly covered with grease and fitted into the socket. A small quantity of mercury poured on the top will then make the joint perfectly tight. I have nearly throughout the investigation avoided even this trace of grease. Mercury alone will run through the joint as the air is exhausted, but I find that strong sulphuric acid, although running through the joint, will do so only very slowly ; so that if care be taken to fill up the sulphuric acid from time to time, the joint will keep perfectly tight. Such a joint allows great freedom of motion, which is of great convenience, as the spectroscopic examination is always best carried on while the tube is attached to the pump.

The vacuum tubes used were, as a rule, of the form given in the accompanying woodcut (fig. 1); that is, they had the shape of an ordinary PLÜCKER tube, to one end of which a tube of hard glass (*a*) was fused. On the other side it ended in a tube (*b*), which was fused to the air pump. The hard-glass tube was filled with some substance which gave off oxygen on heating. Permanganate of potash, chlorate of potash, and oxide of mercury were used, so as to eliminate any lines which might be due to the substance from which the oxygen was prepared. It is necessary to subject all these substances to a preliminary heating, in order to free them beforehand, as much as possible, from moisture, which always is attached to them. I find permanganate of potash to be the most convenient substance, and I have only used the others in test experiments. I have used capillary tubes of different bores, and I think that some of the contradictory statements made by different observers are simply due to the fact that the term "capillary tube" is rather vague, and comprises tubes of diameters sufficiently different to affect the spectrum. The dimensions of two kinds of tubes chiefly used are as follows :—

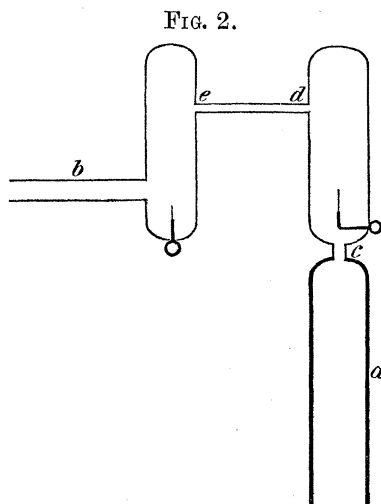
FIG. 1.



	A	B
Distance between the poles . . . . .	14	8
Length of capillary tube . . . . .	4	3·5
Diameter of capillary tube . . . . .	0·07	0·14

The measures are given in centimetres. Tubes with the dimensions given under the heading A were generally employed. I have sometimes suppressed the capillary tube

altogether, and I think I may say I have observed the spectrum of oxygen under as many different conditions as it is in our power to produce, at least for all pressures less than one atmosphere. When the light is weak, fig. 2 is a convenient form of tube; *ed* is the capillary part, and the collimator of the spectroscope is placed parallel to it, so as to receive the light from the whole length of the tube. These tubes were first used by M. VAN MONCKHOVEN.



The following was the usual way of preparing tubes for experiment :—A plug of clean asbestos was introduced into the tube *c*, separating the hard-glass tube *a* from the PLÜCKER'S tube. This plug prevents any solid substance from being bodily carried into the PLÜCKER'S tube. As the asbestos had been subjected beforehand to a considerable temperature, no gas could be given out by it; but to prevent any possibility of error, some tubes were filled without the asbestos, and showed not the least difference which could be traced to the asbestos. Permanganate of potash, which had been heated in a test tube until the crystals were disintegrated and fell into powder, was next introduced into the tube *a*, which was then drawn out at the blow-pipe. The tube *b* was then fused to the sphere of the ball and socket-joint. The joint was rendered air-tight by means of sulphuric acid, and the tube was ready for exhaustion. There was now no danger of any carbon compounds, except such as were unavoidably attached to the glass tube; and I found, indeed, that the tube had sometimes to be filled and exhausted ten times before the spectrum of pure oxygen appeared. It is not quite easy to get rid of all traces of moisture, but by continued exhaustion it is not impossible.

One of the difficulties in the investigation of the spectrum of oxygen consists in the oxidation of the electrodes. It is necessary to work while the tube is attached to the pump, so that it can always be refilled. If this is not done, the oxygen combines with the electrodes, and a vacuum is soon established which does not conduct electricity.



I have eliminated the effects of the electrodes by using different metals, such as aluminium, platinum, silver, brass, and iridium. Only in case of aluminium did I observe lines which could be traced to the electrodes. When the vacuum is very good a spectrum is sometimes faintly seen, which can be easily obtained from aluminium, and which I believe to be due to the oxide of aluminium. The spectrum, however, is capricious in its appearance, and as aluminium electrodes were used in the great majority of experiments, it is quite possible that an effect of the electrodes of other metals exists, but escaped my notice.

Any possible effect of the glass was eliminated by using tubes of different width. I have finally seen all the lines or bands which I ascribe to oxygen in a glass receiver six inches in diameter. The electrodes were about one inch apart, and no part of the spark was within two and a half inches from the glass.

#### 4. *Measurements.*

It is important to vary both the dispersive and magnifying power of the instrument. Some of the phenomena are best seen under small dispersion, others under large dispersion. I have examined the various spectra of oxygen with flint-glass prisms of  $55^\circ$  refracting angle, using almost any number from one up to seven. Whenever measurements are to be made it is best to use as large a dispersion as possible. Some of the measurements which I shall give are made with a dispersion of seven prisms. During the investigation, however, I procured from Mr. HILGER, in London, two very heavy flint-glass prisms (spec. grav. 5), of  $62^\circ$  each. These prisms contain much lead: they are yellow, and therefore can only be conveniently used to about the solar line G. The dispersive power of each is fully equal to that of two ordinary flint-glass prisms of the same refracting angle. Each prism under minimum deviation separated the D lines through an angular distance of 52 seconds. The focal length of the observing telescope was 17.4 inches. The micrometer screw of the eye-piece with which the measurements were made had 100 turns to the inch. The distance between the two D lines when both prisms were used was 0.88, taking as unit one turn of the screw. Most of the measurements were made with these prisms.

During the spring of 1872 I published an investigation on the spectrum of nitrogen (Proc. Roy. Soc., xx., 484), in which I showed that when nitrogen is heated up with sodium in a vacuum tube the nitrogen bands disappear, and a line spectrum appeared in my tubes, which, when measured with the instrumental means at my disposal, was found to agree fairly well with the line spectrum of nitrogen. SALET has since shown that the cause why the bands disappeared in my experiments must be looked for in the absorption of nitrogen by sodium, under the influence of the electric spark. The lines which I saw were really due to the metallic sodium. In order to avoid any similar error, I have carried my measurements to a degree of accuracy which renders any confusion between lines of different bodies quite impossible.

No measurements are of any value unless they are given in wave-lengths. It has been suggested to use the air lines as reference lines, between which we might interpolate any known line. It seems to me that a much better choice might be made. The air lines are not spread evenly through the spectrum; they are by no means sharp under high dispersion, and their wave-lengths have only been obtained by interpolation. I do not think that these possess the requisite degree of accuracy to be used again as reference lines. It should be our endeavour to make our measurements as homogeneous as possible, and as long as ÅNGSTRÖM'S solar maps is the standard work for wave-length measurements we should refer all our measurements to that map. THALÉN has adopted this plan in his excellent series of measurements, but the method which he used presents serious difficulties when the light to be examined is weak.

I have used as reference lines the bright lines of such metals as are present in the sun, the wave-lengths of which can therefore be directly found on ÅNGSTRÖM'S map. The lines of iron are very useful in this respect.

The interpolation formula which is usually employed is based on the fact that the difference in refractive indices of two lines varies nearly as the difference between the inverse squares of the wave-lengths. If reference lines can be found sufficiently close, the formula does pretty well; but I find that for the dispersion which I have used, the formula is no longer applicable when the distance between the reference lines is about ten times the distance between the two sodium lines. As it is not always possible to find good reference lines within that distance, I have generally used three reference lines, and taken the inverse fourth powers of the wave-lengths into account. I am not quite certain that even then the errors of interpolation did not exceed, in some cases, slightly the errors of observation. The reason why the ordinary interpolation formula cannot be used, does not lie so much in the fact that the law of the inverse square does not hold accurately for refractive indices (although this, of course, is also true), but that, except in automatic spectroscopes, our measurements are not proportional to refractive indices.

It is difficult to say to what degree of accuracy measurements are made, yet I trust that, except for the weakest lines, the error of my measurements will be seldom found to exceed  $0.5 \times 10^{-8}$  metre.

After these remarks I pass to the description of the various spectra of oxygen. I distinguish four such spectra. At the lowest temperature at which oxygen becomes luminous it gives a continuous spectrum. As the temperature is raised, the continuous spectrum changes successively into two line spectra, which, as I have already mentioned, I call 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 confounded with each other, have a separate existence; and that the generation of one involves the destruction of the other. The fourth spectrum is that which is seen at the negative pole.

### 5. *The Continuous Spectrum of Oxygen.*

WÜLLNER (POGG. Ann., 137, p. 350) has shown that when the pressure in his vacuum tube is gradually increased, the background begins to be illuminated at a pressure of 280 m.m. This illumination, according to him, first extends from the solar line E to a point about half way between F and G. As the pressure was increased, the continuous spectrum extended more towards both sides, but chiefly towards the blue. I do not know whether this continuous illumination of the background is due to the same cause as the continuous spectrum, which is seen under the circumstances presently to be described. There is nothing antagonistic to known facts in the assumption that the vibration of the gas, though chiefly taking place in certain definite periods, can be disturbed by mutual impacts in such a way that a slight admixture of vibrations of all periods is produced which increases as the pressure is increased. At any rate, if this is the cause of the continuous spectrum which is seen under great pressure, it has nothing to do with the continuous spectrum which appears by a reduction of temperature, and which is not the background to bright lines, but forms the whole visible spectrum. The following facts seem to me to prove that oxygen at the lowest temperature at which it is luminous gives a continuous spectrum :—

1. The wide part of a GEISSLER tube filled with pure oxygen generally shines with a faint yellow light; when analysed by the prism, this yellow light gives a continuous spectrum.

2. *Experiment 6.*—A spark was passed through oxygen gas at the atmospheric pressure. The maximum striking distance of the coil was about one inch. No jar was included in the circuit. The poles were about 4 m.m. apart. A lens concentrated the image of the spark on the slit on the spectroscope. Under these circumstances the elementary line spectrum of oxygen, which is the spectrum commonly observed at atmospheric pressure, is seen. But when the break of the induction coil was put out of adjustment, so that the spark decreased considerably in strength, it took a yellow colour, and the spectrum was perfectly continuous. The phenomena were very striking when I kept the wheel of the break in my hand, while looking through the spectroscope. A slight turn would change the line spectrum into a continuous spectrum, and *vice versa*. When the line spectrum was seen, the spark was considerably stronger and the poles became red hot. When the continuous spectrum was seen, the poles were not sufficiently heated to become luminous. The maximum intensity of the light was in the yellowish green, and decreased on either side.

I attach some importance to this experiment, as the sudden conversion of the line spectrum into a continuous spectrum cannot I think, be explained on any other hypothesis than of molecular combination.

3. An interesting observation of BECQUEREL, which he describes in a foot-note ('La Lumière,' vol. i., page 196), bears on this point. He says that an excess of oxygen in the oxyhydrogen flame makes itself visible by a yellow streak of light

at the point of the flame. He compares the colour to that of the phosphorescence seen in tubes containing a mixture of oxygen with a small quantity of nitrogen (pure oxygen does not show the phosphorescence). Now the colour of this phosphorescence is exactly the same as that of the spark in oxygen which gives the continuous spectrum.

It is reasonable to suppose that M. BECQUEREL heated up the oxygen to a sufficiently high temperature in the oxyhydrogen flame to render it luminous. That this is possible appears from an experiment made by PLÜCKER, who, working with an excess of hydrogen in the oxyhydrogen flame, saw the lines of hydrogen in his spectroscope.

I have already stated that I do not know whether the continuous background which is seen at higher pressure when the line spectrum appears has its origin in a separate cause, or whether it has to be brought into connexion with the continuous spectrum of low temperature. The following experiment may assist those who like to form an opinion on the matter :—

Mr. LOCKYER has made use of the fact that when a spark is taken between metallic poles, and a lens is employed to form an image of the spark on the slit of the spectroscope, the lines of the metals do not stretch across the field, but are confined to the neighbourhood of the poles. As the pressure is decreased, some of the lines decrease rapidly in length, and finally disappear, while the effect on others is little perceptible. I find that when oxygen is the gas through which the spark strikes, the lines of the gas as well as the metallic lines seem to stretch away from the poles and fade away towards the middle. The centre of the field is taken up by the second line spectrum, which I have called the compound line spectrum. Here is what happens :—

*Experiment 7.*—At atmospheric pressure the lines of the elementary line spectrum were seen to stretch across the field; the continuous spectrum illuminating the background was strongest in the green. As the pressure was decreased the compound lines appeared much broadened, and at the same time a dark streak was seen to pass through the continuous spectrum in the centre of the spark. This means that at that pressure the continuous spectrum is chiefly confined to the electrodes. As the pressure was decreased to about half an atmosphere, the continuous spectrum only occupied a narrow band adjoining the electrodes. The compound lines came out strong in the centre of the field and were better defined. At still lower pressures the lines of oxygen separated in the middle of the field, as the continuous spectrum had done before; and the continuous spectrum now seemed to be gradually absorbed into the electrodes, and finally disappeared altogether. Gradually the oxygen lines became shorter and shorter until they could be no more distinguished from the metallic lines. The centre of the field was now entirely occupied by the compound line spectrum. It is necessary to add that it appears conclusively from the experiments of WÜLLNER, as well as my own, that the continuous spectrum is really due to oxygen and not to the metallic poles. The reason why there should be a difference

in the spectrum of the gas in different cross sections of the spark seems to me to be that the lines of flow spread out more midway between the poles than they do at the poles, so that the temperature is not so high some distance away from the poles.

#### 6. *The Elementary Line Spectrum.*

This is the spectrum which is seen when a strong spark passes through oxygen at atmospheric pressure. It can be seen at all pressures in vacuum tubes, when a Leyden jar and air break are introduced into the circuit. PLÜCKER gives a drawing of the lines in his paper on "Double Spectra" (Phil. Trans., 1865); he does not give, however, his measurements. HUGGINS gives a measurement of the oxygen lines as seen at atmospheric pressure; but these are referred to an arbitrary scale, and some of the weaker lines are invisible at atmospheric pressure owing to the continuous background. THALÉN gives the wave-lengths of the air lines.

When the spark is taken in air, however, the oxygen lines are weak compared to the nitrogen lines, so that even some strong oxygen lines do not appear in THALÉN'S list. In their last paper on the spectra of metalloids, Messrs. ÅNGSTRÖM and THALÉN gave a drawing of the lines of oxygen.

This drawing is pretty complete, but the numbers which have been obtained by measurement are not given separately, so that we are dependent on the accuracy of the engraver, which cannot be relied on to any great extent. As far as can be judged from the map, THALÉN'S measurements agree fairly well with mine. SALET also has given some measurements, but the small dispersion which he used did not enable him to obtain great accuracy. There are two weak lines on ÅNGSTRÖM and THALÉN'S map ( $\lambda=5163$  and  $\lambda=4964$ ) which I have never been able to see, although I have been constantly on the look-out for them. On the other hand I see a number of weak lines not included in that map. Most of them are given by SALET. Some of these lines have a different appearance from the oxygen lines; they are not so well defined, and are sometimes bands. This may lead some observers to think that they are due to impurities. Greatly struck with the difference in appearance of these lines, and the ordinary oxygen lines, I have paid some attention to them, but I find they appear with electrodes of very different metals, and cannot be due to the glass, as I have seen them in the receiver, six inches in diameter, which I have mentioned. I have finally come to the conclusion that we have no evidence for rejecting them. I have tried to represent in the spectrum in Plate 1, marked A, the relative intensities of the oxygen lines. The intensities were carefully estimated, but cannot, of course, be greatly relied on except as far as the relative intensity of a group is concerned. It seems hardly possible to compare the intensity of a yellow and a blue line. The following table contains my measurements. I have not carried them beyond the group of lines which is near the solar line G. Photography will do the work much better in the extreme violet than I could have done.

## Elementary Line Spectrum of Oxygen.

Wave-length.	Intensity.	Remarks.
5205.4	6	This is the strongest line of Oxygen in the green group and well visible in the atmospheric lines. It is, however, omitted in THALÉN'S map of the atmospheric lines.
5189.6	3	
5175.4	3	
5159.3	5	
4954.4	3	
4942.2	8	
4940.2	3	
4923.7	6	
4906.1	5	
4890.1	3	
4871.0	4	
4864.0	3	
4860.2	3	
4856.2	4	
4850.0 4841.6	1	This is a very weak band, but it is always present.
4750.1	1	
4740.9	1	
4709.0	6	
4704.6	10	
4698.5	8	
4695.5	1	
4675.4	8	
4673.1	1	
4660.7	8	
4649.3	4	
4648.0	12	
4640.6	7	
4637.4	6	
4608.0	2	A weak band.
4605.7	1	
4595.1	6	
4589.9	6	
4469.2 4465.3	4 3	The space between these two lines is filled up with weak light.
4452.7	2	
4448.3	2	
4443.0	1	
4416.8	7	
4414.5	8	
4395.6	1	
4366.2	4	This line must not be mistaken for the line $O\delta$ of the compound spectrum, of which faint traces are sometimes seen at its less refrangible edge.
4353.5	5	
4349.0	6	
4346.9	5	
4345.0	1	
4341.4	1	
4336.6	1	
4319.2	3	
4316.5	3	

### 7. *The Compound Line—Spectrum of Oxygen.*

In one of his early papers (POGG. Ann., 107), PLÜCKER gives the spectrum of oxygen as consisting of four lines, with the following wave-lengths.

6150

5328

5185

4367

In his later drawing of the spectrum of oxygen (Phil. Trans., 1865) he gives a great many lines of which these four form part. WÜLLNER says that these four lines are always the first to appear in oxygen tubes. ÅNGSTRÖM and THALÈN 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 come out, and they seem to assume that they form part of the ordinary line spectrum of oxygen; yet when the ordinary line spectrum is brightest, these lines are quite invisible, and when these lines are brightest, no trace of the ordinary line spectrum can be detected. I must repeat that these lines come out equally well, whatever way the oxygen is prepared. WÜLLNER prepared his gas by electrolysis and saw the lines; I prepared my gas, as already mentioned, in three different ways. When I began work I was under the impression that these lines must be due to impurities; but after having spent a great deal of time in trying to trace their origin, I feel certain that they are due to pure oxygen. I have seen the lines almost daily for many months, and in at least 30 different tubes.

The appearance of an oxygen tube when a spark passes while it undergoes gradual exhaustion is as follows:—

*Experiment 8.*—At first the spark has a yellow colour, and the spectrum is perfectly continuous. Almost immediately, however, four lines are seen in the capillary part above the continuous spectrum. One of these lines is in the red, two are in the green, and one is in the blue. The discharge still passes as a narrow spark throughout the length of the tube. In the wide part the spectrum remains continuous, and it extends more towards the red and blue than in the capillary part. It seems as if the four lines had taken away part of the energy of the continuous spectrum. As the pressure diminishes, these lines increase considerably in strength; the spark spreads out in the wide part of the tube, and the intensity of the continuous spectrum is therefore considerably diminished, while it still forms a prominent part in the spectrum of the capillary part. When the pressure is small the continuous spectrum decreases in intensity. At the same time the negative glow with its own characteristic spectrum, gradually extends through the negative half of the tube into the capillary part. The continuous spectrum has now entirely disappeared; the bands of the negative pole and the four lines stand out on a perfectly black background. It is under these conditions that the change from the compound line spectrum to the

elementary line spectrum is best studied. The mere insertion of a Leyden jar, I find makes hardly a difference; the jar does not seem to be charged at all. If in addition to the jar we insert a movable air break, which can be opened or closed at will, while we look through the spectroscope, we shall be able to see alternately two perfectly distinct spectra. If the air break is closed the four lines of the compound spectrum only are seen; if the air break is opened these four lines will disappear entirely, and the elementary line spectrum will come out. We have here as complete a transformation as we have from the band to the line spectrum of nitrogen taking place under exactly the same circumstances. We have, therefore, the same right to consider the two line spectra of oxygen as two distinct spectra, as we have in the case of the two spectra of nitrogen.

There are two reasons why the existence of a separate line spectrum of oxygen might have escaped the notice of previous observers. The blue line of the compound line spectrum is very near a bright line of the elementary line spectrum, and cannot be distinguished from it unless a high dispersive power is used, and even then only when special attention is paid to the line.

To an observer who looks at this line with small power, it would seem as if on the introduction of the air break other lines spring up to its right and left, which are brighter than the blue line he is looking at; but he would not notice that the blue line itself has disappeared, and has been replaced by another line a little more refrangible and of about the same brightness.

Again, in tubes of rather wide capillary bore, as that of which the dimensions have been given on page 43, under the heading B, it is impossible to get rid altogether of the lines of the compound line spectrum. The effect of the jar and air break is only to widen the lines considerably; not to extinguish them. If the pressure in a tube is large, these lines widen to a considerable extent, and finally fuse together so as to form a continuous spectrum. This has been well described by WÜLLNER, who likened the lines in this respect to the hydrogen lines. The observations which refer to the disappearance of these lines must therefore be made under low pressure when the continuous spectrum has disappeared, and the phenomenon then is very striking. If a spark is taken through oxygen at atmospheric pressure, a strong red but flushy line is seen very nearly coincident with the red line of the compound spectrum. I confess I have not been able to find out with certainty whether the two lines are identical or not. The compound line spectrum widens considerably with increased pressure, and chiefly towards the less refrangible side. At first sight the atmospheric line is decidedly less refrangible than the line of the compound line spectrum, and the measurements by THALÈN and HUGGINS of the line in the atmosphere give a wavelength sensibly larger than that which I have obtained for the line of the compound spectrum. Yet if account be taken of a one-sided widening, so that the line has to be compared with the edge of the atmospheric band, not with its middle, I am inclined to think that the two may prove identical. It appeared to me sometimes, it is true,



that the line of the compound spectrum is more refrangible even than the edge of the atmospheric band, but I am not quite certain of this. I have left out therefore for the present the line from the list of the elementary line spectrum of oxygen.

In a letter to 'Nature' (Dec. 20, 1877) I have drawn attention to the fact that the lower temperature spectrum of oxygen seems to be reversed in the sun, and I have tried to bring this fact into connexion with the statement made by Professor DRAPER, that the higher temperature lines of oxygen appear bright on the solar disc. I have now nothing to add to what I have stated in my letter to 'Nature,' and only give the list of the exact wave-lengths of the compound line spectrum, together with the wave-lengths of the nearest solar lines.

Oxygen.	Width.	Solar Lines.	
		(A.)	(S.)
$\alpha$ 6156·86	$\pm 0\cdot3$	6156·70	6156·69
$\beta$ 5435·55	$\pm 0\cdot3$	5435·44	5435·56
$\gamma$ 5329·41	$\pm 0\cdot6$	5329·30	5329·10
$\delta$ 4367·62		4367·58	

The first column contains the wave-lengths of the compound line spectrum of oxygen ; the second column contains the number which has to be added to or subtracted from the wave-length, in order to get the edge of the lines, as it is their centres which are given in the first column ; the third and fourth columns give the wave-lengths of the corresponding solar lines as observed by ÅNGSTRÖM (A.) or myself (S.). In Plate 1, I have given a drawing of this spectrum, marked B.

### 8. *The Spectrum of the Negative Pole.*

This spectrum was first accurately described by WÜLLNER.\* When looked at, as he did, with low dispersive power, it seems to consist of four distinct, not shaded bands ; but, as I have already said, I was able to resolve the bands into separate lines. I have also in this case spared no trouble to show that the spectrum is really due to pure oxygen, and not either to impurities in the gas, to the nature of the electrode, or influence of the glass. It seems interesting to notice that in Experiment 6 (page 47), when the spectrum of the spark at atmospheric pressure was continuous, a purple point was seen on the negative electrode which gave the spectrum of the negative pole. The peculiar circumstances which favour the production of this spectrum always exist therefore at the negative pole, and are independent of the mode of discharge.

When examined with low power, the bands of the negative pole seem to occupy the following wave-lengths.

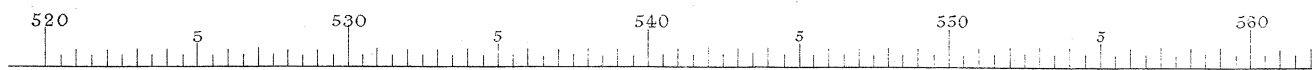
\* Pogg. Ann., 147, page 357.

6010 }  
 5960 }  
 5900 }  
 5840 }  
 5630 }  
 5553 }  
 5292 }  
 5205 }

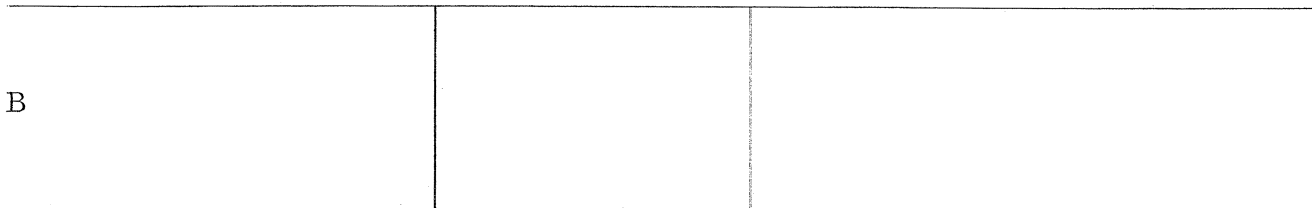
There is another band still more towards the red end than the least refrangible of these bands, but it was too weak to be measured. Unless care be taken, the two first bands might easily be regarded as one; but even with weak instruments a dark space is seen to separate them. The following are the more detailed measures of the centres of each line making up the two most refrangible bands. The second column gives half the width of each line. The maximum of light in most of the lines is, however, not in the middle but towards the least refrangible edge of each line. Plate 1 gives a drawing of the bands when seen with large magnifying powers. The excessive weakness of the bands is an insurmountable obstacle to any very great accuracy. Thus it is possible that the five most refrangible lines of the most refrangible band (Plate 1, fig. 1), which seem somewhat irregularly placed, are really at equal intervals, but I do not consider this likely. If the light is strong, the eye can readily detect an unsymmetrical arrangement without measurement; but, with the narrow slit necessary for measurement, the light was so weak that nothing but the line, which was specially fixed by the eye, could be seen, and no general view of the band could therefore be obtained.

Least refrangible of the two green bands.			Most refrangible of the two green bands.		
5552·8	±0·5	Limits of the maximum of light.	5205·0	±0·6	Brightest part.
5558·4	±0·5		5213·3	±0·6	
5564·5	±0·5		5216·9	±0·6	
5570·1	±0·5		5225·3	±0·6	
5575·8	0·5		5231·2	±1·7	
5576·5	}		5239·0	±0·6	
5586·0			5247·7	±1·9	
5591·4	0·7		5255·0	±1·9	
5601·2	0·5		5262·7	±1·7	
5611·2	0·5		5269·5	±1·6	
5618·8	0·5	5276·9	±1·0		
5629·6	0·5	5284·4	±1·2		
		5292·5	±0·6		

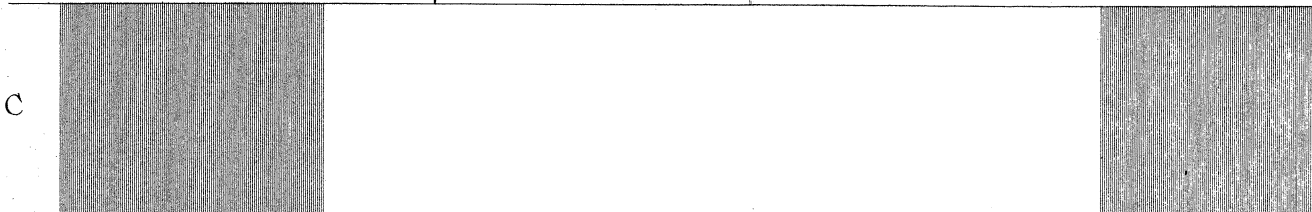
The experiments were all made in the Cavendish Laboratory, Cambridge, and I am much obliged to Professor CLERK MAXWELL for the kindness with which he has placed the resources of the laboratory at my disposal.



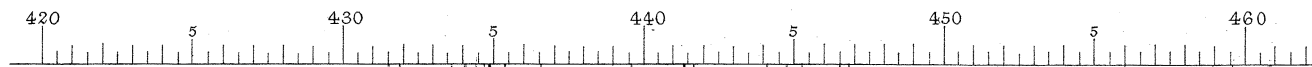
A



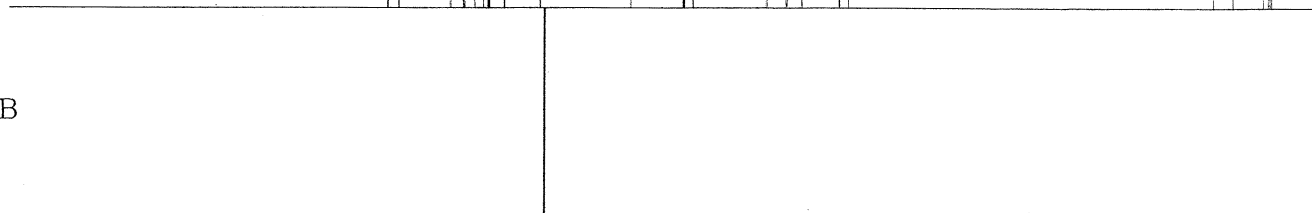
B



C



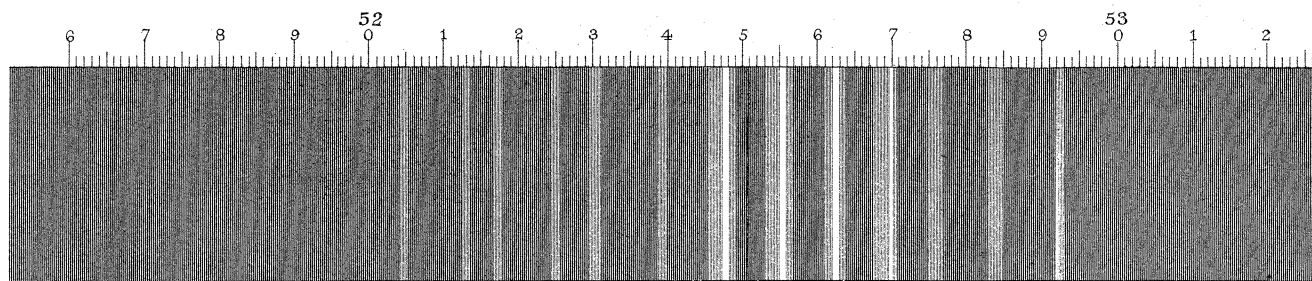
A



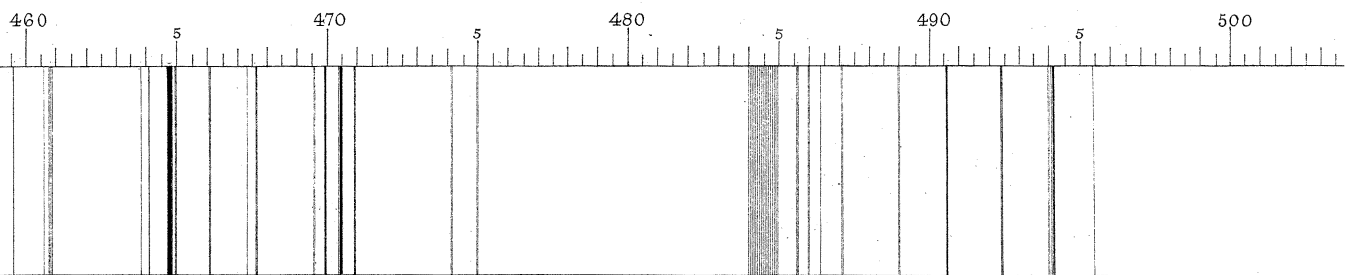
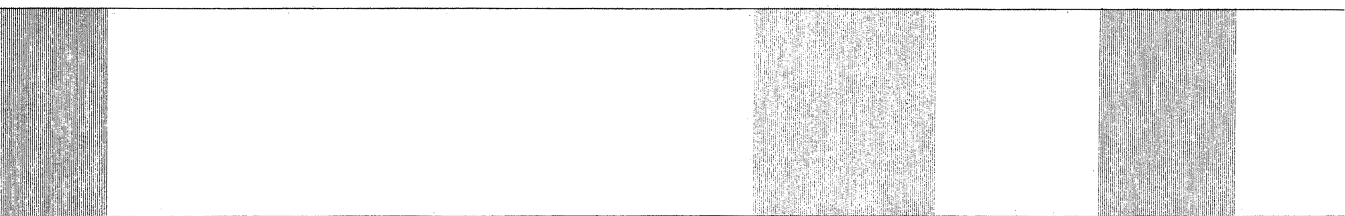
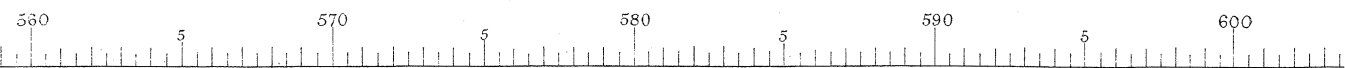
B

A. = Elementary Line Spectrum.

Spectrum



Spectra of Oxygen.



B = Compound Line Spectrum.

C = Spec

rum of Oxygen at Negative Pole.

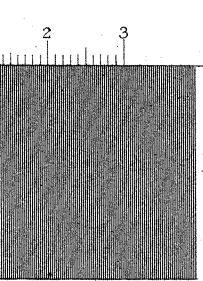


Fig. 1.

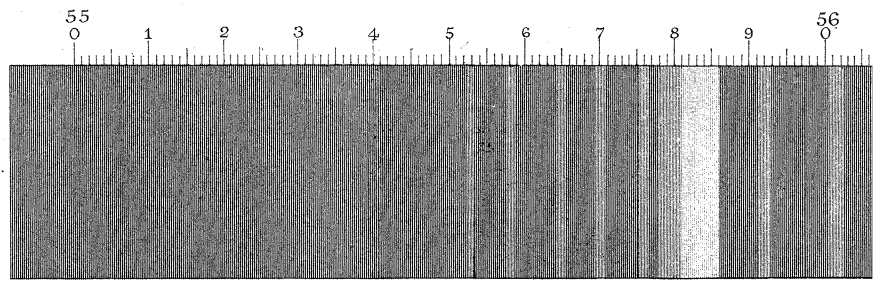
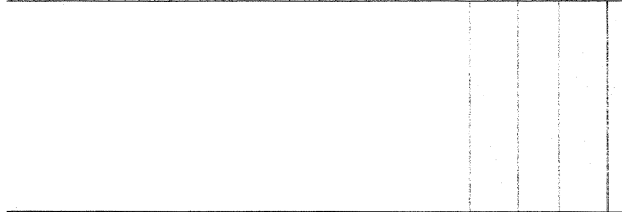
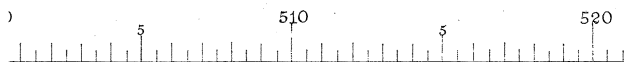
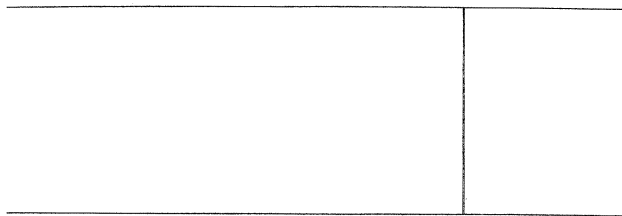
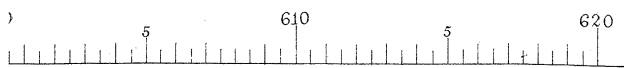
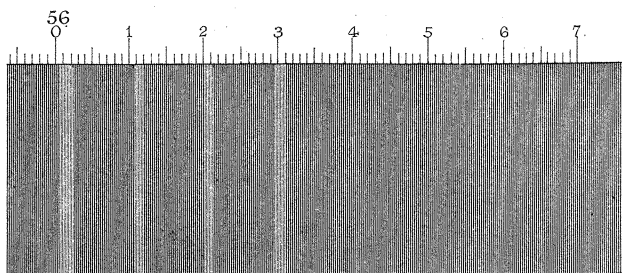
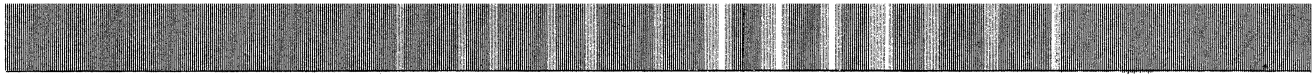


Fig. 2.

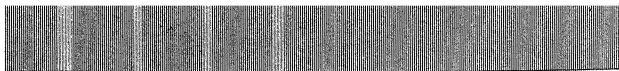


= *Spectrum of the Negative Pole.*



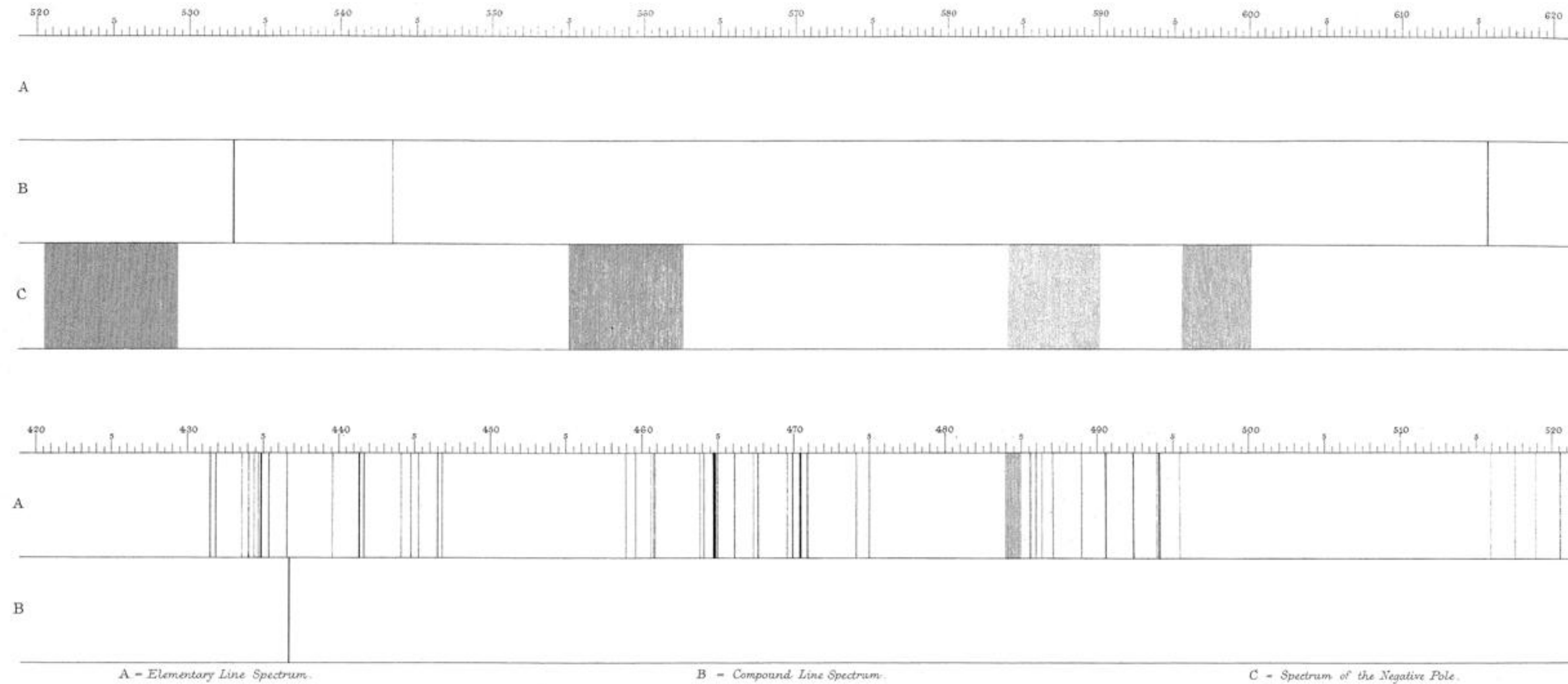






*West Newman & Co. so.*





## Spectrum of Oxygen at Negative Pole.

