

XVIII. *Researches in Spectrum-Analysis in connexion with the Spectrum of the Sun.*—No. II. *By* J. NORMAN LOCKYER, *F.R.S.*

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IN my former communication under the above title I pointed out that the new method of spectroscopic research adopted by Dr. FRANKLAND and myself had enabled me to establish:—

(1) That when a metallic vapour is subjected to admixture with another gas or vapour, or to reduced pressure, its spectrum becomes simplified by the abstraction of the shortest lines and by the thinning of many lines.

(2) That when metals are chemically combined with another element (I used chlorine) only the longest lines of the metal remain in the spectrum of the chloride—the number being large in the case of elements of low atomic weight, and small in the case of elements of high atomic weight and of twice the atom-fixing power of hydrogen.

(3) That I had reason to believe that by means of mechanical admixtures the spectrum of a metal could be made simple in the same manner, thereby giving a foreshadowing of a quantitative spectrum-analysis.

I then showed the bearing of these determinations on several questions connected with Solar Physics.

I have now the honour of communicating to the Royal Society the results of the continuation of my inquiries.

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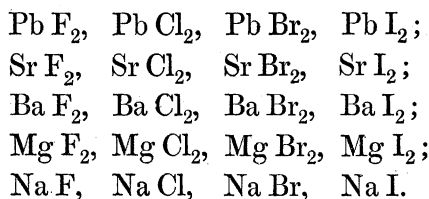
I. CHEMICAL COMPOUNDS.

In extension of the former experiments to which I have alluded, it became of importance to try several series of salts in which the atomic weights varied :

1st. In each series.

2nd. In the associated elements in each series.

With this view the spectra of the following series were mapped:—

*Conditions of the Experiments.*

The conditions of the experiments were as follows:—The salts were rammed into the small aluminium cups described in the former paper, and the cups fastened to copper rods which passed through a cork into the interior of a wide glass tube. An aluminium point* formed, as in the former experiments, the opposite pole, which was also fastened to a copper rod passing through a cork fitted into the opposite end of the tube. Both corks were pierced and furnished with narrow glass tubes; one of these served to admit hydrogen, while the opposite one served as an exit-tube for the gas. The hydrogen was prepared from zinc and sulphuric acid, and passed first through a scrubber filled with broken pumice-stone saturated with solution of plumbic acetate to free it from sulphuretted hydrogen, then through a wash-bottle containing concentrated sulphuric acid, and lastly through a tube containing fragments of sodium, the latter serving both as a drying tube and freeing the gas from any acid mechanically carried over by it.

The hydrogen thus purified was admitted in a gentle stream into the tube containing

* “ An examination of the spectrum of the spark by the new method shows that the light given out by the discharge depends upon the amount of vapour lying between the poles, and that if both poles are composed of equally volatile metals, or the same metal, the bridge is formed by an equal, or nearly equal, amount of vapour lying round each pole; hence, supposing that the vapours do not intermingle, it follows that the longest line can only be half the length of the actual distance between the poles.

“ When, however, the poles are unequally volatile, the bridge appears to be formed entirely of vapour from the most volatile pole; hence the longest line can extend almost or quite across the space from pole to pole.

“ It was on account of these observations that aluminium was used for the poles in the experiments described, it having been found that that metal was extremely refractory in the spark, *i. e.* that all its lines in the most visible portions of the spectrum were very short—the vapour which extended above the short line region being practically capable of giving but the two lines of aluminium which fall between H_1 and H_2 .

“ There are, however, many phenomena in connexion with this which are well worth study; for instance, in a case where the spectrum of copper was examined with a plumbago point opposite to the copper pole, the effect of the former was shown by the remarkable way in which the copper lines were shortened. Even when the poles were almost touching, the copper lines were confined to the copper pole, and did not extend across the spectrum.”—*Extracts from Laboratory Notebook, 23rd September and 30th October, 1872.*

the poles, and the spark was then passed, the induction-coil already mentioned being used. When it was desired simply to observe the spark in air, the hydrogen apparatus was disconnected, or the poles were placed in an ordinary spark-stand.

Results of Experiments.

The following are the results of some experiments made with the spark in air, the jar being thrown out of the circuit.

LEAD.

Plumbic Fluoride, $Pb F_2$.—It will be seen on referring to the map of this spectrum (Plate LI.) that the eleven longest lines of the following wave-lengths*, 4167·5, 4246·0, 4386·5, 5163·0, 5372·0, 5523·5, 5546·0, 5607·0, 6040·0, 6059·0, and 6452·0, were seen.

Of these it is to be remarked that 4246·0 and 4386·5 are only seen for a short time when the spark first begins to pass, 6452·0 is very faint, and 5523·5 very short; so that practically the spectrum contains but seven distinctly visible lines.

Plumbic Chloride, $Pb Cl_2$.—On observing the spectrum of this salt, it is found to have been simplified in the following manner:—

The lines left are 4167·5, 5163·0, 5372·0, 5523·5, 5546·0, 5607·0, 6040·0, 6059·0, and 6452·0, nine in number; 5523·5 has become excessively short, and 6452·0 rather brighter than it was in the fluoride.

Plumbic Bromide, $Pb Br_2$.—4167·5 still maintains its brilliancy undimmed, 5163·0, 5372·0, 5546·0, and 5607·0 remain; 5523·5 is just distinguishable as a dot on the pole, but 6040·0, 6059·0, and 6452·0 are completely lost, the spectrum thus being reduced to five lines.

Plumbic Iodide, $Pb I_2$.—4167·5 is little or not at all altered in appearance, 5163·0, 5372·0, 5607·0 yet remain; 5546·0 has become a dot, and faint indications of 5523·5, in the same state but much fainter, are visible.

The composition by weight of these compounds is as follows:—

$Pb F_2$,	Pb to F	1·0 to 0·18
$Pb Cl_2$,	Pb „ Cl	1·0 „ 0·34
$Pb Br_2$,	Pb „ Br	1·0 „ 0·77
$Pb I_2$,	Pb „ I	1·0 „ 1·22

If these results are expressed in another way, by making the non-metallic element unity, we have:—

$Pb F_2$,	F to Pb	1·0 to 5·4
$Pb Cl_2$,	Cl „ Pb	1·0 „ 2·9
$Pb Br_2$,	Br „ Pb	1·0 „ 1·2
$Pb I_2$,	I „ Pb	1·0 „ 0·8

Now the lines in the spectrum of lead increase in length and number as we ascend the above series, *i. e.* as the percentage weight of lead increases, as is shown in the second

* From THALÉN'S observations.

Table. The fact may then be simply stated, that in the case of lead the complexity of the spectrum increases as the atomic weight of the non-metallic element with which it is combined decreases.

BARIUM.

The next metal experimented on was barium, an element of much lower atomic weight than lead, and in this respect occupying a position not very much above the mean atomic weight of the elements. It was soon found that the facts observed with lead did not completely hold with regard to barium, although they include the phenomena presented by the chloride, bromide, and iodide. Even with these salts, however, the phenomena, though the same in kind, differ somewhat in degree. For instance, the same number of metallic lines was observed in all these salts, and between the appearance of the chloride and the bromide spectrum there was no appreciable difference. In the case of the iodide, however, there was a sensible change in the direction expected from the behaviour of lead—*i. e.* the spectrum became dimmer, that is, exhibited a tendency to die out.

When, however, baric fluoride was examined, a different state of things was observed. Instead of the spectrum becoming more complex it became simpler, exhibiting in fact only the four longest lines of barium with any degree of distinctness, and these showing but little brilliancy.

STRONTIUM and MAGNESIUM.

Strontium behaved in this particular in the same way as barium did, the falling off of the lines in the fluoride being very marked. In the case of magnesium (which, as regards its chloride, bromide, and iodide, followed the behaviour of the alkali metals, to which I shall immediately refer, rather than that of barium and strontium), the fluoride exhibited the same stubborn resistance to the action of the spark. It is to be remarked that these three fluorides are non-volatile, and so infusible that even after long exposure to the current there was little or no indication of coherence; in fact, in the case of magnesian fluoride, the salt was distinctly seen to be blown out of the cup as a cloud of dust, and when one of these particles was converted into vapour in the spark, the spectrum exhibited fragments of lines *sharp at both ends*.

On blowing a cloud of magnesian fluoride in fine powder through the spark, *b* in particular was seen as a series of three pointed lines.

It will be seen from the above experiments, and from the annexed map of the strontium salts observed in air (Plate LI.) taken as a type of this group, that the general statement made for lead does not apply to barium or strontium, the chlorides, bromides, and iodides of which metals are pretty equally volatile, while their fluorides are apparently not readily volatile at any temperature which I could employ.

SODIUM.

Sodium and lithium, elements of low atomic weight, were the next metals experimented upon.

Some *sodic fluoride* was inserted into one of the aluminium cups, and opposite was placed a clean blunt aluminium point* ; the small coil and a jar were employed.

On passing the spark, D only was seen. The break was then readjusted and the spark made heavier, but the result was the same. Some new and moist sodic fluoride was then placed in the cup, but the result still remained as before.

Sodic Chloride was then treated in the same way, a fresh aluminium pole being reserved for it and placed opposite to its cup. D was present and was bright; the double line in the red once flashed in, but it was not again seen though the cup was charged and recharged with the salt repeatedly.

Sodic Bromide treated in the same way gave D, the red line being seen but once; D, however, was brighter than before.

Sodic Iodide treated as above gave D and the red double line, which remain constantly visible, the double green line near D being also occasionally seen. D was intensely brilliant, and the salt fumed away from the pole in a dense white smoke.

The following day a fresh attack with more powerful apparatus was made. One of APP'S 6-inch quantity coils and a jar with about 224 square inches of coated surface were employed with a powerful battery of five one-pint GROVE'S cells. The results, however, went exactly in the same way. Na I and Na Br gave all the metallic lines of sodium, which were very brilliant; whilst Na Cl gave D and the double red very bright, and stretching all across the spectrum. Na F gave also D and the double red line; but the latter only extended three quarters across the spectrum, and neither D nor the red line was so bright as they were in the chloride. Further observations showed that under certain circumstances all the lines appeared even in these latter salts; but they were so dim as to be scarcely visible, and the fact of these compounds behaving in direct contra-vention to the observations with lead was established.

LITHIUM.

The following experiments were made with lithic iodide and chloride in coal-gas.

Lithic Iodide gave the red line of this metal, 6705, extending all across the spectrum, but it was very faint. 6102, the orange line, was very brilliant and about two thirds across. 4603, the blue line, was very short and nebulous when seen, which was only on one occasion. This differs but little from the spectrum given by the metal itself, except that the lines are in the latter case much brighter, and that the red and orange extend right across the spectrum, and the blue three quarters across.

A line at 4972 was seen also in the spectrum when the metal was used; but this has never been seen by KIRCHHOFF, THALÉN, or any other observer except HUGGINS, in lithium.

THALÉN, however, saw this line alone in cæsium, of which metal it constitutes the entire spectrum.

HUGGINS has nevertheless included this line in his map of the lithium spectrum. But

* Special precautions being taken to keep the poles the same distance apart in all the experiments.

there can be no doubt that it is the cæsium line, and that it is due to the presence of a trace of cæsium existing as an impurity in the lithium, as it does not appear in the spectrum of the pure salts; and no one but Dr. HUGGINS has seen it in lithium, at any rate with sufficient distinctness to consider himself justified in including it in a map or list.

Lithic Chloride gave 6705·2, the red line, thin and faint, but all across the spectrum; the orange very bright and across the spectrum; the blue line was also visible, but it did not extend across the spectrum.

It will be seen from the above that lithium, the least electro-positive of the alkali metals, approaches in its spectroscopic behaviour the metals of the alkaline earths, strontium and barium, as it approaches them in some points of its chemical behaviour. Thus the spectrum of its iodide differs from that of the chloride as the spectrum of baric iodide differs from that of baric chloride, and not as the spectrum of sodic iodide does from sodic chloride, as might have first been supposed from the usual position, among the alkalies, assigned to the metal.

On the difference between Flame-spectra and those produced by a weak electric discharge.

The following experiments were made with beads of the various substances mentioned, heated in the Bunsen flame on loops of platinum wire.

BARIUM.

Baric Iodide.—This salt gave the spectrum since proved to be due to the oxide and the line 5534·5 very distinctly; it coloured the flame a greenish yellow, and fused to a globule.

Baric Bromide gave the oxide spectrum and 5534·5 with difficulty; the spectrum was not very bright, and the flame but little coloured.

Baric Chloride gave the same spectrum as the two salts mentioned above; but the spectrum was much brighter, and the flame was coloured a bright pale green.

Baric Fluoride gave scarcely a trace of the oxide spectrum, and 5534·5 was very faint indeed; but no signs of fusion were visible, no bead being formed, and the flame was only coloured slightly and in parts.

STRONTIUM.

Strontic Iodide, heated on platinum wire in the Bunsen flame, gives the spectrum in the red, so well represented in BUNSEN'S and KIRCHHOFF'S drawing, and the great blue line 4607·5 of the metal.

Strontic Bromide behaves much as the iodide does, but shows more of the structure in the red. 4607·5 is also always present, and is very bright, a considerable change from its appearance in the iodide, in the spectrum of which it is for a time faint and then becomes brighter.

Strontic Chloride gives the bands very brightly at first, but not so brightly after a time; 4607·5 is fainter, but is very distinct.

Strontic Fluoride refused to give any trace either of the strontium or compound spectrum; it is, in fact, only capable of being heated to a white heat and giving a continuous spectrum.

CONCLUSIONS.

It is to be observed, then, that when the spectra before referred to produced by flames are compared with those produced by the low-tension spark, the spectra of the metals in the combination are in the former case invariably more simple than in the latter, and that they are *simplified to such an extent that only the very longest line is left*; thus:—

Baric Iodide with the low-tension spark gives five and twenty lines. In the flame it gives but one, and that the longest, namely 5534·5.

Baric Bromide gives five and twenty lines with the spark; only one in the flame, the same longest line 5534·5.

Baric Chloride five and twenty lines in spark and one, 5534·5, in flame.

Baric Fluoride four lines in spark, 5534·5 alone in flame.

Again, taking the case of strontium, we find that in the case of strontic iodide thirty-two lines are observed in the spark, one alone in the flame, and that is the longest, namely 4607·5, a line by far the longest in the spectrum of strontium.

Strontic Bromide gives also thirty-two lines in the spark and but one in the flame, the same longest line 4607·5.

Strontic Chloride gives thirty-two lines in the spark, but only this one, 4607·5, in the flame.

Strontic Fluoride gives fourteen lines in the spark, but in the flame does not even give the longest line. There is, in fact, no spectrum at all due either to the metal or the compound.

It is especially to be remarked that strontic oxide furnishes us with an intermediate condition of things between the chloride and fluoride.

In this compound the band near D is the only representative of the spectrum of the compound. The longest metallic line, 4607·5, is also invisible. We are justified, therefore, in assuming that only a small quantity of the undissociated compound is present in the reaction.

Experiments to determine the cause of the similarity of the spectra of the various salts observed in air.

It was noticed in the earliest observations of the spectra of salts in the spark that after a time the spectrum was nearly the same, whatever salt had been placed in the cup. I therefore determined upon a careful study of the phenomena when the salt was submitted to the heat of the ordinary Bunsen flame; and after some preliminary observations, I requested Mr. FRISWELL to make a detailed examination of the various stages of the reactions in question. I now append his observations, which, taken in connexion with the other branches of the inquiry, clearly establish that the band spectrum is that of the oxide.

CONDITIONS OF THE EXPERIMENTS.

The observations about to be detailed were made as follows:—

The large Steinheil spectroscope was used with four prisms, such as were used for the ordinary observations of the metallic spectra with the spark.

The slit was, however, wider. The salt was placed in a tangled loop on a piece of platinum wire held in a clip. The source of heat was a small Bunsen burner.

SPECTRA OF STRONTIUM SALTS.

Strontic Iodide.—When the wire was first inserted into the flame the salt fused, and the flame showed an intense yellow coloration.

The spectrum during this stage exhibited the D line very strongly, and the orange band of the strontic salt spectrum lying just on the least refrangible side of D; *but the metallic line 4607·5 was invisible*, or at the best but very faint.

If the fused bead be now quickly withdrawn from the flame and held in front of a sheet of white paper, it is seen to be evolving dense violet fumes of iodine. If the bead be again thrust into the flame and the heat continued, it gradually becomes less and less fusible, and ultimately solidifies; the yellow tinge now vanishes from the flame, and D drops out of the spectrum, the flame becoming red; the band spectrum and 4607·5 are now very brilliant, and the solidified mass becomes white-hot and emits a continuous spectrum. If it be placed in a test-tube and treated with an acid it effervesces; and if submitted to the action of nitric acid and starch no blue colour is produced.

Evidently, then, the iodine has been driven off, and the mass consists in all probability mainly of strontic oxide with some strontic carbonate.

It seems then that the breaking up of the compound and the volatilization of the iodine consume so much heat that the Sr I_2 never gets sufficiently heated to enable it to be volatilized; and hence we should not see its spectrum even were the flame sufficiently hot to render its vapour luminous, and the body sufficiently stable to bear such a heat without decomposition. The fact, however, is, that what spectrum is seen is produced by the decomposing action of the flame acting either on small quantities of the Sr I_2 , which do get volatilized, or, what is more probable, are mechanically carried off by the ascending currents of iodine vapour. It is to be remarked that when the bead has become infusible the spectrum begins to die out; the orange band then only appears very faintly, and 4607·5 has utterly gone. We then have the non-volatile oxide only left in the flame, and it of course cannot give any thing but the continuous spectrum due to its own incandescence.

Strontic Bromide behaves very much in the same manner as the iodide, the difference that exists depending on the greater stability of the latter compound in the flame. On removing the bead but slight fuming is observable, and there is very little odour of bromine. After the bead has been roasted for a long time it still evolves bromine, when treated with sulphuric acid and manganic oxide.

Strontic Chloride never shows any tendency to undergo decomposition; it remains

clearly transparent and fusible to the end, and evolves chlorine when treated for that purpose.

Strontic Fluoride was the most stable of all; it would not fuse, gave no coloration to the flame, and obstinately retained its fluorine to the last, as was shown by the mass giving the usual reaction of fluorine when treated on a glass plate with sulphuric acid.

CONCLUSION.

These facts justify us in coming to the conclusion that the similarity of the spectra observed under the conditions in question is due to the fact that the spectrum observed is that of the oxide; for whereas in the first instance there is a differentiation between the various spectra, after the action of the flame has been continued for some little time the spectra observed are the same.

Considerations which follow from the above observations in connexion with the spectra of chemical compounds.

GENERAL DISCUSSION OF SPECTRA.

In what has been said before, both in this communication and in my former paper on the spectra of chemical compounds, I have only referred to the lines of the metals.

I now propose to discuss the spectra generally.

Some of the earliest observations of this nature (1860) have been described by KIRCHHOFF and BUNSEN*. They remark, "We have compared the spectra represented on the Plate†, which we have obtained from the pure chlorides, with those produced when the bromides, iodides, hydrated oxides, sulphates, and carbonates of the several metals are brought into the following flames:—

“ Into the flame of sulphur.
 „ „ bisulphide of carbon.
 „ „ aqueous alcohol.
 Into the non-luminous flame of coal-gas.
 Into the flame of carbonic oxide.
 „ „ hydrogen.
 Into the oxyhydrogen flame.

“ As the result of these somewhat lengthy experiments, the details of which we here omit, it appears that the alteration of the bodies with which the metals employed were combined, the variety in the nature of the chemical processes occurring in the several flames, and the wide differences of temperature which these flames exhibit, *produce no effect upon the position of the bright lines in the spectrum which are characteristic of each metal.*

“ It was found that the same metallic compound, placed in one of these flames, gives

* Translated in Philosophical Magazine, 1860, vol. xx. pp. 91–93.

† The spectra shown on the Plate are those known as flame-spectra.

a more intense spectrum the higher the temperature of the flame. In the same flame, those of the compounds of a metal give the brightest spectra which are most volatile.

“In order to prove still more conclusively that each of the above-mentioned metals always produces the same bright lines in the spectrum, we have compared the spectra represented in the Plate with those produced when the electric spark passes between electrodes made of these metals.

“Small pieces of sodium, potassium, lithium, strontium, and calcium were fastened to fine platinum wires and melted two by two into glass tubes, so that the pieces of metal were separated by about 1 to 2 millims., and the platinum wires were melted through the sides of the glass tubes. Each of these tubes was placed in front of the spectrum-instrument, and by means of a Ruhmkorff's induction-apparatus*, sparks were allowed to pass between the pieces of metal inside the tube; the spectrum thus produced was then compared with that given by a gas-flame in which the chloride of the metal was brought. The flame was placed behind the glass tube. By alternately bringing the induction-apparatus into and out of action, it was easy, without measuring, to convince ourselves that in the brilliant spectrum of the electric spark, the bright lines of the flame-spectrum were present in their right position. Besides these lines, other bright ones appeared in the electric-spark spectrum; some of these were produced by foreign metals present in the electrodes, others arose from nitrogen, which filled the tubes after the oxygen had combined with a portion of the electrodes”†.

As already mentioned in a note, the Plate given with this communication shows that the spectra thus referred to by the illustrious German chemists were the flame-spectra of the elements in question.

This question was advanced in 1862 by MITSCHERLICH‡ and by Professors ROSCOE and CLIFTON§, from whose memoirs I proceed to give extracts, and in 1865 by DIACON||. MITSCHERLICH, in his memoir, after detailing some experiments, goes on to remark:—

“It follows from these experiments that metallic compounds do not always give a spectrum, and that in the case of those that do, the spectra are not always the same; and, further, that the spectra are different when they are due to a metal or its combinations. We have also the right to conclude that each binary compound which gives a spectrum gives one peculiar to itself, excepting always of course when the combination is destroyed by the flame. Up to the present time we are acquainted with little beyond the spectra of the metals themselves, by reason of the facility with which the flame reduces their combinations.

“Up to the present time also it has been admitted that metals always give the same spectra with whatever they are combined¶. As in the above experiments this was not

* No mention is made of a jar, which doubtless was not employed.

† I shall produce evidence in the sequel to show that this explanation is probably not the correct one.

‡ Ann. de Chim. et de Phys. 1862, p. 175.

§ Trans. Lit. and Phil. Society, Manchester, 1862.

|| Annales de Chimie et de Physique, 4 ser. vol. vi. p. 5.

¶ This is a reference to KIRCHHOFF's and BUNSEN's paper just quoted.

found to be the case, it became necessary to determine whether the ordinary spectra are due to the metals or their oxides, since according to my experiments all compounds which contain the metal in the form of oxide give the same spectra."

As a result of his experiments on sodium, he states that in the flames which give the line of sodium the spectrum is due to the metals and not to the oxide. Hence he concludes that in the case of oxides the spectrum is the spectrum of the metals*.

He then states that the new lines which had then lately been discovered without corresponding elemental lines were probably due to binary compounds.

The main view in MITSCHERLICH'S paper, that each binary compound has a spectrum of its own, is borne out by the conclusion arrived at by CLIFTON and ROSCOE, who remark in their paper above referred to:—

"KIRCHHOFF, in his interesting memoir on the Solar Spectrum and the Spectra of the Chemical Elements, noticed in the case of the calcium-spectrum that bright lines which were invisible at the temperature of the coal-gas flame became visible when the temperature of the incandescent vapour reached that of the intense electric spark. We have confirmed this observation of KIRCHHOFF'S, and have extended it, inasmuch as we, in the first place, have noticed that a similar change occurs in the spectra of strontium and barium; and, in the second place, that not only new lines appear at the high temperature of the intense spark, but that the broad bands characteristic of the metal or metallic compound at the low temperature of the flame or weak spark totally disappear at the higher temperature. The new bright lines which supply the part of the broad bands are generally not coincident with any part of the band, sometimes being less and sometimes more refrangible. Thus the broad band in the flame-spectrum of calcium named $\text{Ca } \beta$ is replaced in the spectrum of the intense calcium-spark by five fine green lines, all of which are less refrangible than any part of the band $\text{Ca } \beta$; whilst in the place of the red or orange $\text{Ca } \alpha$, three more refrangible red or orange lines are seen. The total disappearance in the spark of a well-defined yellow band seen in the calcium-spectrum at the lower temperature was strikingly evident. We have assured ourselves, by repeated observations, that in like manner the broad bands produced in the flame-spectra of strontium and barium compounds, and especially $\text{Sr } \alpha$, $\text{Sr } \beta$, $\text{Sr } \gamma$, $\text{Ba } \alpha$, $\text{Ba } \beta$, $\text{Ba } \gamma$, $\text{Ba } \delta$, $\text{Ba } \epsilon$, $\text{Ba } \eta$, disappear entirely in the spectra of the intense spark, and that new bright non-coincident lines appear. The blue $\text{Sr } \delta$ line does not alter either in intensity or in position with alterations of temperature thus effected; but, as has already been stated, four new violet lines appear in the spectrum of strontium at the higher temperature.

"If, in the present incomplete condition of this most interesting branch of inquiry, we may be allowed to express an opinion as to the possible cause of the phenomenon of the disappearance of the broad bands and the production of the bright lines, we would suggest that, at the lower temperature of the flame or weak spark, the spectrum observed is produced by the glowing vapour of some compound, probably the oxide, of the difficultly reducible metals; whereas at the enormously high temperature of the intense

* This opinion he corrects in his next communication, to which reference will be made hereafter.

electric spark these compounds are split up, and thus the true spectrum of the metals is obtained."

Two years later (in 1864) MITSCHERLICH, in a second communication*, expanded his views and brings an overwhelming mass of evidence in favour of them. The methods he employed were as follows:—

The substances were heated :

1. In the flame of a Bunsen burner.
2. In the flame of coal-gas burning in oxygen.
3. In the flame of hydrogen burning in chlorine.
4. In the flame of mixtures of hydrogen and bromine or iodine-vapour burning in air or oxygen.

5. *In the case of combustible gases* they were allowed to emerge out of the middle aperture of an oxyhydrogen burner, and were burnt in air or oxygen.

In the case of non-combustible gases they were mixed with a combustible gas, such as carbonic oxide or hydrogen.

6. *In the case of solid substances* they were introduced into a tube one end of which was connected with a Rose's hydrogen-apparatus; the substance was then volatilized, and the gas kindled at the other end of the tube.

7. Or the spark was taken between *poles* containing the metal or compound *in any gas*; or between,

8. *Liquid electrodes*, in which the temperature is much lower than in 7.

From the beautiful series of researches carried on by these several methods, he concludes "that every compound of the first order which is not decomposed, and is heated to a temperature adequate for the production of light, exhibits a spectrum peculiar to this compound, and independent of other circumstances."

BEARING OF THE NEW OBSERVATIONS.

The experiments I have lately made, taken in conjunction with my determination of the long and short lines of metallic vapours, and the consequent simplification of the spectra by the reduction of pressure or molecular distance, set this question at rest, and in the direction indicated by MITSCHERLICH, CLIFTON, ROSCOE, and DIACON; while much light has been thrown upon all the prior observations, as a consequence of which they are brought much more into harmony than at first appeared.

First. I have observed † that whether the spectra of iodides, bromides, &c. be observed in the flame or weak spark, *in air*, the spectrum is in the main the same, as maintained by KIRCHHOFF and BUNSEN; but that this is not the spectrum of the metal is established by the facts, *that with a low temperature only the longest lines of the metals are present*, showing that only a small quantity of the simple metal is present as a result of partial dissociation, and that by increasing the temperature, and consequently the amount of dissociation, *the other lines of the metals appear in the order of their length with each rise of temperature.*

* Translated in Philosophical Magazine, 1864, vol. xxviii. p. 169.

† See *antè*, p. 645.

Secondly. I have convinced myself that this is the spectrum of the oxide, because *in air*, after the first application of heat, the spectra *and metallic lines are in the main the same*, while *in hydrogen* the spectra are different for each compound, *and true metallic lines are represented according to the volatility of the compound, only the very longest lines being visible in the spectrum of the least volatile compound.*

In proof of this statement I append a drawing (Plate LII.), on the scale of the maps of the last paper, representing the spectra of the chloride, bromide, and iodide of strontium. In order to avoid the introduction of the oxide spectrum, and so to secure the differentiation of the three spectra if possible, they were observed in hydrogen, which gas had been carefully treated in such a manner as to secure as far as possible the exclusion of any trace of oxygen. It will be seen at a glance that the spectra differ not only from the spectrum given by the metal, or by its salts in air at a high temperature, but considerably amongst themselves. In the experiments care was taken to keep the spark temperature as low as possible; and of course no jar was used, its presence in the circuit being instantly felt by the introduction of large numbers of metallic lines and the disappearance of the banded spectrum.

The drawings were made from readings of the scale of the Steinheil spectroscope, and then approximately laid down on a scale of wave-lengths.

GENERAL STATEMENT.

These and other facts which I have observed can be included in a general statement such as the following.

1. A compound body, such as we have been considering, has as definite a spectrum as a simple one; but while the spectrum of a simple metal consists of lines, the number and thickness of some of which increase with molecular approach, the spectrum of the compound consists in the main of channelled spaces and bands, which increase in like manner. In short, the molecules of a simple body and a compound one are affected in the same manner by their approach or recess, in so far as their spectra are concerned; *in other words, both spectra have their long and short lines*, the lines in the spectrum of the element being represented by bands or channelled lines in the spectrum of the compound; and in each case the greatest simplicity of the spectrum depends upon the greatest separation of molecules, and the greatest complexity (a continuous spectrum) upon their nearest approach.

2. The heat required to act upon a compound, so as to render its spectrum visible, dissociates the compound according to its volatility: the number of true metallic lines which thus appear is a measure of the dissociation; and as the metal lines *increase in number*, the compound bands *thin out**.

* The above statement is confirmed by the following experiments. A bead of strontic chloride was interposed between two aluminium electrodes; the induced current, without a jar, was then passed. The red-band spectrum of the oxide was very intense, and the only metallic *line* of any strength was 4607.5. The wire and bead soon became red-hot, and the latter evaporated, the spectrum disappearing. A jar of 186 square centims.

It will be seen from the above that my researches have convinced me that the opinion held by the illustrious ÅNGSTRÖM, that metallic elements (in which I include hydrogen) have only one spectrum, is the only tenable one; and it is to be hoped that science will soon be enriched by the results of more experiments similar to those recently made with such success by Mr. SCHUSTER.

SPECTRA OF THE METALLOIDS.

MITSCHERLICH, in the paper to which I have so often referred, calls attention to the fact that the metalloids show the same spectra with regular shading as compound bodies; but I think there is the difference to be remarked that, as a rule, the structure of the spectrum of the metalloids extends further along the spectrum from the least refrangible end than in the case of the spectra of compound bodies. As I do not think it is too much to say that, as a rule, the lines of the metallic elements are more prominent in the green and more refrangible parts of the spectrum than in the red (which may even be gathered from an inspection of the solar spectrum), the question arises whether it be a possibility that the molecules of a metalloid, in structure, lie between those of elements on the one hand and compounds on the other.

Applications of these considerations to Solar and Stellar Spectra.

MITSCHERLICH, in his first memoir, thus refers to the bearing of his observations with regard to the solar spectrum:—

“Ces essais montrent comment l'analyse spectrale peut conduire à la connaissance des affinités mutuelles des corps simples à la température de l'atmosphère solaire. Si l'on observait, par exemple, le spectre d'un chlorure alcalin terreux dans la lumière du soleil, on en pourrait conclure que son métal possède, à la température du soleil, une affinité pour le chlore plus grande que le potassium ou le sodium, ces derniers métaux existant à l'état de liberté. Réciproquement, la connaissance des combinaisons existant dans l'atmosphère solaire pourra conduire à connaître la température de cet astre, si toutefois nous ne parvenons jamais nous-mêmes à approcher de cette température.

“La présence du sodium libre dans l'atmosphère conduit à admettre qu'il n'y existe pas de corps électro-négatifs libres, tels que l'oxygène ou le soufre, et qu'ils n'y existent même pas autrement en quantité assez abondante pour se combiner avec tout le sodium.

coated surface was then introduced into the secondary current. The metallic lines appeared all along the spectrum, the “structure” (oxide spectrum) became fainter, and its intervals wider; the bead soon became red-hot. A jar of 467 centims. gave lines only and no structure, and one of 2214 centims. the same result, the bead remaining cold.

On using the bead as the electrode, the results were nearly the same; but the heating-effect continued when somewhat larger jars were used than the one with 362 centims., which did not show this effect with the former arrangement. When the slit was very narrow it was observed that several of the bands of the oxide spectrum broke up into masses of fine lines, exactly like those of the iodine vapour absorption-spectrum; and this remarkable resemblance was rendered still more striking by the appearance of a beat like that shown by iodine.

En outre, tous les métaux que le sodium chasse de leurs combinaisons doivent aussi y exister à l'état de liberté.

“Les nouveaux spectres que j'ai fait connaître pourront conduire à constater dans l'atmosphère solaire la présence du chlore, du brome, de l'iode, du phosphore, etc.

“D'un autre côté, de l'absence des raies d'un métal dans le spectre solaire on ne saurait conclure celle du métal lui-même dans l'atmosphère du soleil ; il peut, en effet, s'y trouver des métaux, le lithium, par exemple, qui y sont engagés dans des combinaisons qui ne donnent pas de spectre.”

In the former communication I have given, I trust, the true explanation of the absence of certain lines from the solar spectrum ; and I think in what has gone before there is ample evidence that the explanation advanced by MITSCHERLICH is absolutely untenable ; for at the temperature of the sun, which is high enough to allow hydrogen and even sodium to exist uncombined and in a state of incandescence above the photosphere, there would be heat enough to dissociate compounds, and therefore to cause the longest lines, at all events, of the metalloids to be visible even if they existed in combination as a rule, but former observers have recorded* no trace of any metalloids in the solar spectrum.

As further evidence that there is no chemical combination whatever in the photosphere, the structure of the spectrum may be also instanced ; it certainly would be very different from what it is, did compounds exist in the solar atmosphere ; the least refrangible end of the spectrum would, I hold, be the more, instead of the less complex ; and although Professor YOUNG has recently recorded in the spectrum of a sun-spot certain appearances which might be imagined to favour the idea of the existence of compounds in the comparatively cold downrush into a spot, the general facts, to say the least, seem to point the other way, and in all my observations of sun-spots I have never seen any thing approaching to the appearance put on by a compound spectrum.

On this I would also remark that with our present knowledge it is not difficult to gather from Father SECCHI'S observations on stellar spectra, that if the atmosphere of a star contains compound molecules, they at once make themselves very obviously visible. Several stars, the spectra of which have been mapped by him, have undoubtedly, in my opinion, atmospheres containing compound molecules ; and it may be that the phenomena of variable stars may be connected with a delicate state of equilibrium in the temperature, so that at one time we get the feeble line-absorption of the *dissociated*, and at another the strong band-absorption of the *associated* elements in their atmospheres†. Father SECCHI'S idea that we have in such stars a prevalence of spot-spectrum‡, will, I think, not hold ; but this point, which is one of extreme interest, I propose to dwell on at greater length in a future communication. In the mean time I may remark that I am inclined to attribute spots more to an accumulation of absorbing material *at a greater pressure* than to a similar accumulation *at a lower temperature*.

* ÅNGSTRÖM, 'Recherches sur le Spectre Solaire,' p. 37.

† I find that in this conclusion, drawn from my long and short line observations, I have been anticipated by ÅNGSTRÖM, who reasoned from less precise data, *op. cit.* p. 39.—Note added, January 21, 1874, J. N. L.

‡ SECCHI, 'Le Soleil,' p. 288 *et seq.*

II. MECHANICAL MIXTURES.

The mechanical mixtures experimented on in continuation of the researches referred to in my previous communication were prepared in the following manner.

Method employed in preparing mixtures.

A quantity of the larger constituent, generally from five to ten grammes, was weighed out, the weighing being accurate to the fraction of a milligramme; and the requisite quantity of the smaller constituent was calculated to give, when combined, a mixture of a definite percentage composition by weight (this being more easily obtainable than a percentage composition by volume).

The quantities generally chosen were 10, 5, 1, and 0·1 per cent.

In a few cases with metals known to have very delicate spectral reactions a mixture of 0·01 per cent. was prepared.

The larger constituent was then introduced into a small crucible (the bowl of a common clay tobacco-pipe). A tube conveying a stream of pure dry hydrogen was introduced into the mouth of the crucible, and the metal heated by a Bunsen burner.

As soon as it was melted, the metal, the spectrum of which was to be examined, was introduced in fragments, the hydrogen stream being kept up, and the heat raised if necessary until the last added metal had melted. When this had taken place, the fused mixture was agitated by rapidly shaking the crucible, or by causing the hydrogen to bubble through the melted mass.

When the mixing was judged to be complete, the mass was poured out. On cooling, a point was cut from it and placed in the spark-stand, the opposite pole being made of the metal which constituted the bulk of the mixture. Thus an alloy of 90 parts tin and 10 parts cadmium would have a tin pole opposite, and one of 90 parts lead and 10 zinc a lead pole, and so on.

It is important that each electrode of a mixture should have its corresponding electrode of the pure metal which exists in the greatest quantity in the mixture, as when the spectrum is observed the long and short lines of this constituent are seen stretching from top to bottom of the spectrum, the longest lines being continuous across, while the lines of the smaller constituent are seen *only* at the top or bottom of the spectrum, according to the place occupied by the mixture in the spark-stand.

Observations.

The observations thus made have been recorded in the accompanying maps* in the following manner:—First the pure spectrum of the smallest constituent has been observed, and the lines laid down from THALÉN'S map generally.

The mixture containing the greatest percentage of the substance whose spectrum is to be studied is then inserted in the spark-stand with its opposite electrode of the substance with which it is mixed, and the spectrum observed. This process is repeated until the lowest percentage is reached.

* These maps were exhibited to the Society, but they have not been engraved.

In the maps the spectrum of the pure vapour is shown below, the spectra of the mixtures above, the highest spectrum being that of the mechanical mixture containing the smallest percentage.

The series mapped are as follows:—

Sn + Cd	percentages of Cd	10, 5, 1,	0·15
Pb + Zn	,,	Zn 10, 5, 1,	0·1
Pb + Mg	,,	Mg 10, 1,	0·1, 0·01

I may remark that these substances were used in consequence of their low fluid temperatures and of the consequent ease with which the mixtures could be made with the arrangements at my disposal.

An inspection of the maps will render any long verbal statement of the results obtained superfluous. I may, however, remark that although we have here the germs of a quantitative spectrum-analysis, the germs only are present, because from the existence of several "critical points"* and great variations due to causes which have not yet been investigated, the results thus obtained are not sufficiently close or constant for practical application.

Further researches, however, have shown me that, by discarding altogether this method of eliminating lines from the spectrum and adopting a different procedure, it is possible by means of spectrum-analysis to make quantitative determinations of certain mixtures with almost if not quite as great accuracy as that generally obtained by the methods in use.

As these researches are still incomplete, I shall defer an account of them and the process adopted till a future occasion.

Application of these observations to the Solar Spectrum.

Let it be assumed for a moment that subsequent investigations may justify us in applying these considerations to the composition of the reversing layer in the sun's atmosphere, and suppose it to be composed of a mixture of zinc and lead vapours.

The percentage of zinc indicated by the number of lines actually known to be reversed in the solar spectrum would certainly be between one and five per cent.

Similarly, the percentage of sodium would be 100 per cent., of magnesium 100 per cent. at the maximum sun-spot period, a little less at other times; the percentage of iron always something less than 100 per cent., and so on. Adding these percentages together, we get an apparently impossible percentage composition of the reversing layer. But here another set of considerations comes in. In each case the percentage composition has been assumed to be determined by the lines omitted from the spectrum observed at atmospheric pressure—a pressure accidental to this planet.

* For instance, in the cadmium experiments but little difference occurs between 10 per cent. and 5 per cent. In the case of zinc between 10 per cent. and 5 per cent. only a very small change occurs. In the case of magnesium only two lines are lost between 100 and 10 per cent.

It follows, however, from what has gone before, that the number of lines in a spectrum increases as the molecular distance is diminished within the range of atmospheric pressure; and there is no doubt whatever that this will go on with greater pressures until a continuous spectrum is reached, as in FRANKLAND'S classical experiment with hydrogen, in which the lines *broadened*—a peculiarity confined, so far as I know, to that spectrum.

If this be so, with *increased* pressure we shall get *reduced* percentages; and some day we possibly shall be able to largely increase our present knowledge by observing the pressure at which, with the increased number of spectral lines in the pure vapours known to be in the sun, the percentages of the known solar elements, determined by their reversed lines, will together make up 100 or thereabouts. It is clear, however, already that a pressure of several earth atmospheres would be required.

Such an inquiry might not so much make us familiar with the existence of new elements in the reversing layer as it would enable us to allocate the unnamed lines of the spectrum to those already known to exist there; and it may also be remarked that now the absence of any element from the sun is much more easily determined than before, as its longest line only need be considered. If *that* is not reversed the inquiry need be carried no further, for all other lines will certainly be absent. I do not wish to imply that a *trace* of an element can be detected in this way, my experiments rather tend in the other direction; besides which it must not be forgotten that we have bright lines in the solar spectrum itself, and that in the chromosphere I have recorded bright lines; and Professor YOUNG has recently recorded more in some observations, to which I shall take a future opportunity of referring.

It is a pleasing duty to me to again take an opportunity of expressing my obligations to Mr. FRISWELL for the valuable assistance he has afforded me in these inquiries. All the maps have been constructed by him.

I have also to express my thanks to G. GORE, Esq., of Birmingham, who supplied me with the fluorides used in the experiments, and to J. MELLOR, Esq., of the Magnesium Metal Works, Salford, for a present of a large quantity of magnesium, potassium, and other metals, which have also been used in these inquiries; they were sent anonymously, but I have learnt the donor's name from Professor ROSCOE.

EXPLANATION OF THE PLATES.

PLATE LI.

UPPER HALF.

Spectra of strontium salts in air with low-tension spark.

A,	spectrum of	Sr I ₂ .
B,	„ „	Sr Br ₂ .
C,	„ „	Sr Cl ₂ .
D,	„ „	Sr F ₂ .
E,	„ „	metallic strontium.

Notes.—Some of the lines in the red in the spectrum of strontic fluoride are seen, but the “ structure ” of the compound spectrum renders it difficult to decide which.

The structure (for the first three salts) is at first exceedingly brilliant and varies with each salt, but after a time it gets dimmer and is the same for all salts.

The brilliant compound spectrum renders the presence of the lines at W. L. 5970·5 and 5850·0 in the salts very doubtful.

The line 4226·3 has since been proved to belong to calcium.

The line 4161·0 is always very faint.

LOWER HALF.

Spectra of lead salts in air with low-tension spark.

A,	spectrum of	Pb I ₂ .
B,	„ „	Pb Br ₂ .
C,	„ „	Pb Cl ₂ .
D,	„ „	Pb F ₂ .
E,	„ „	metallic lead.

Notes.—The line 6452·0 was very faint and difficult of observation in Pb F₂.

The line 5163·0 is coincident with an air line, and its length is uncertain in the metallic spectrum, though it is brilliant. It is, however, long in the salts.

The lines 4386·5 and 4246·0 only appear for a short time in the spectrum of Pb F₂, though the time is longer than in the other salts. In Pb I₂ they flash in and instantly vanish; in Pb Cl₂ they vanish nearly as quickly.

The line 4062·5 is faint; it is probably not a lead line.

4058·0 is the longest line.

PLATE LII.

UPPER HALF.

Spectra of strontium salts in hydrogen with low-tension spark.

- A, spectrum of Sr I₂.
 B, „ „ Sr Br₂.
 C, „ „ Sr Cl₂.
 D, „ „ metallic strontium.

Notes.—The lines in the red have been omitted, as they are difficult of observation, and the point is proved by the more refrangible lines. The bands are *approximately* laid down on the wave-length scale from readings of the scale of the Steinheil spectro-scope.

LOWER HALF.

Spectrum of the oxide of aluminium compared with the spectrum of the pure metal.

- A, spectrum of aluminium oxide.
 B, „ „ aluminium.

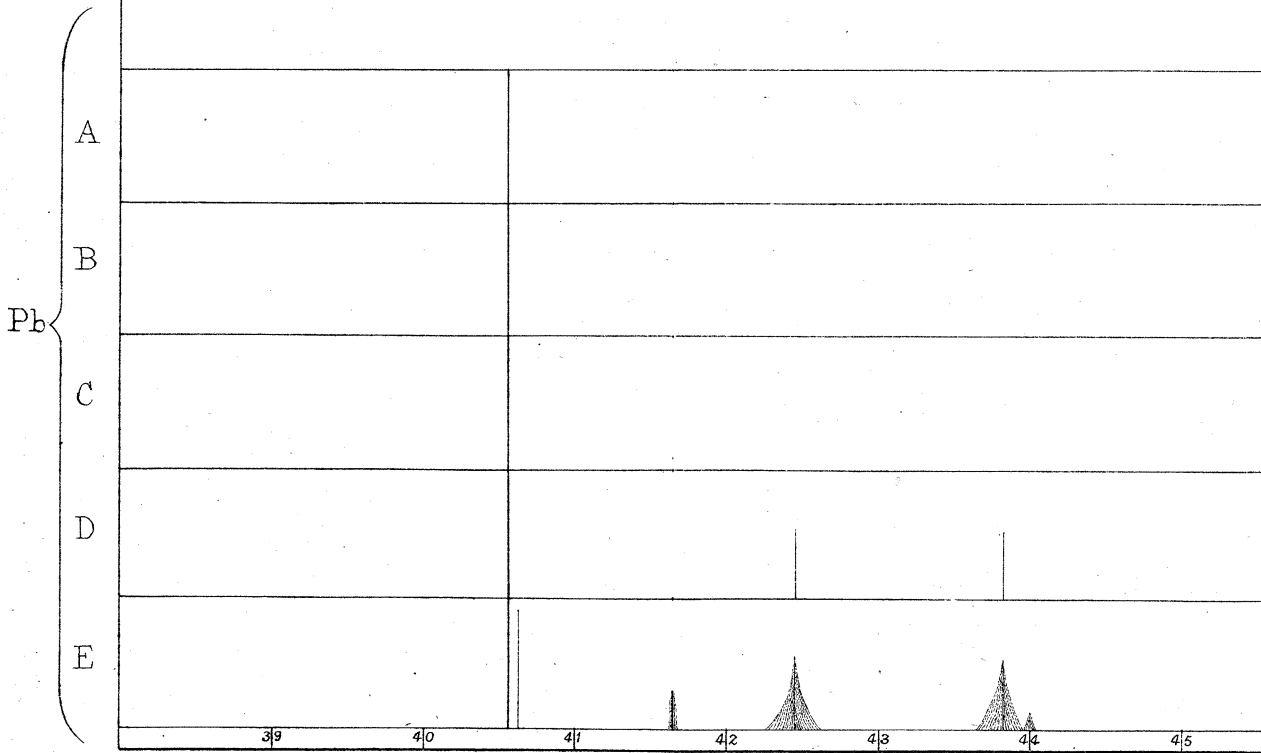
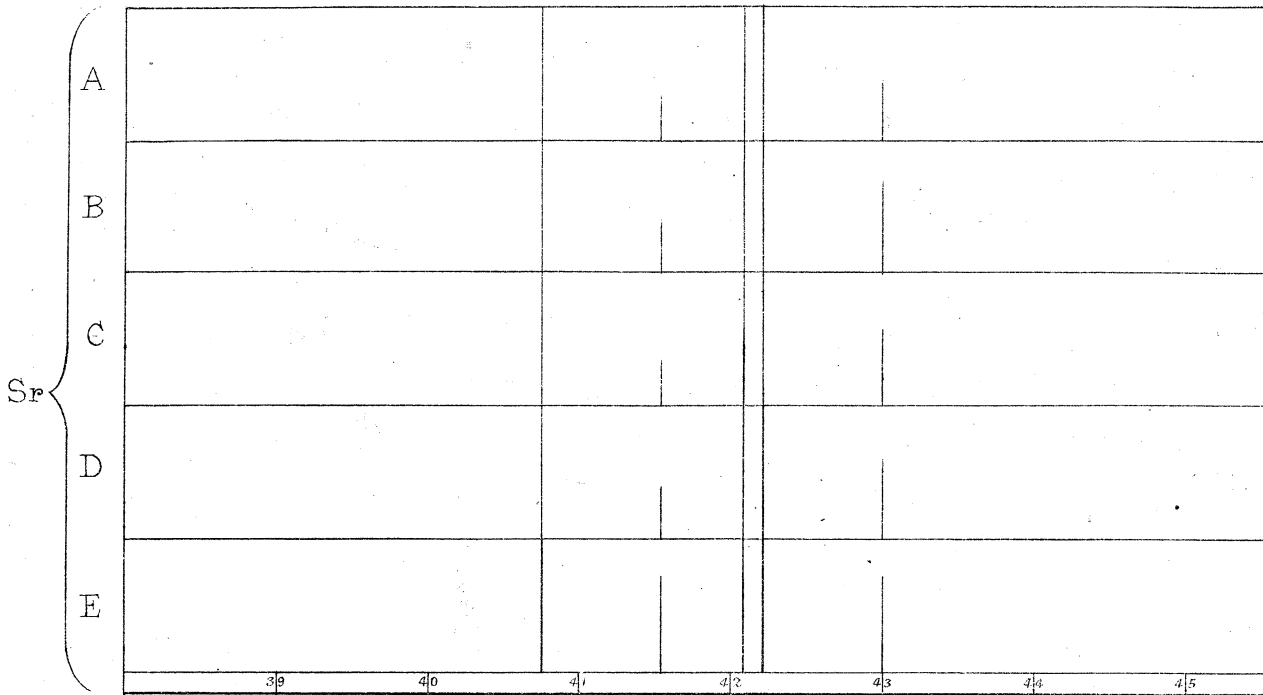
Notes.—The lines at W. L. 6371·0 and 6344·5 are not shown; they have not been identified though seen by THALÉN.

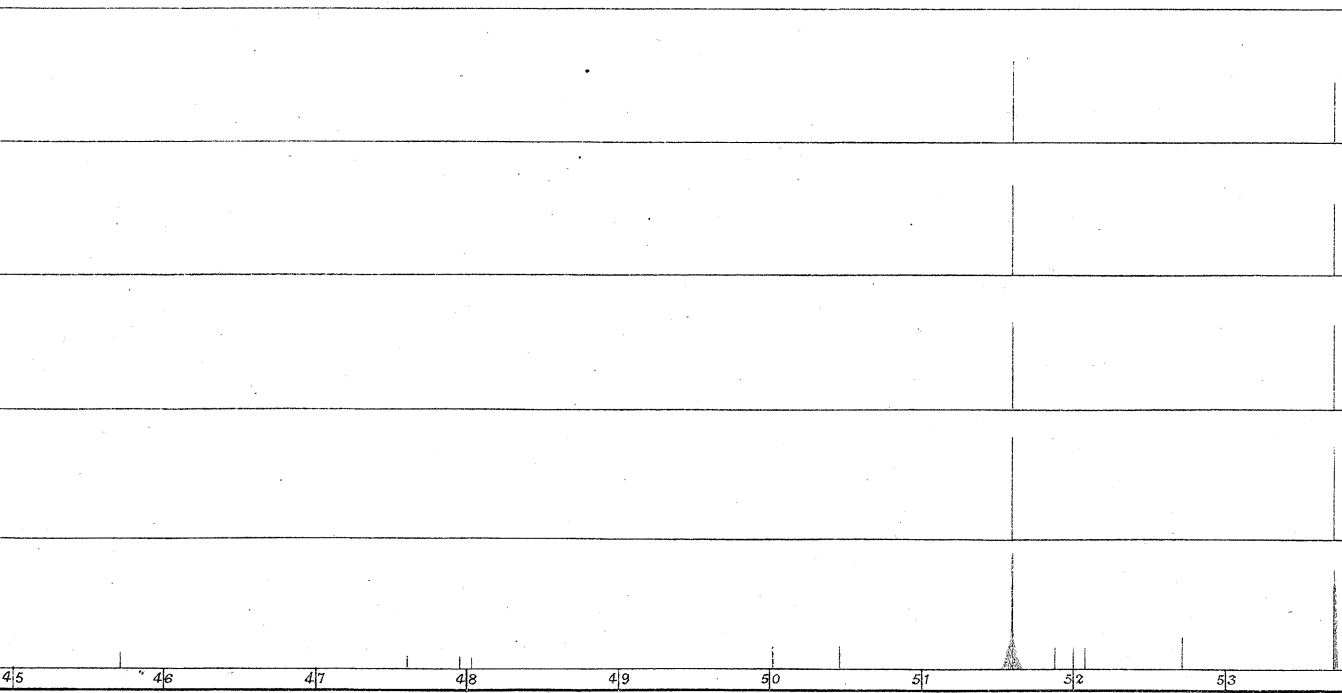
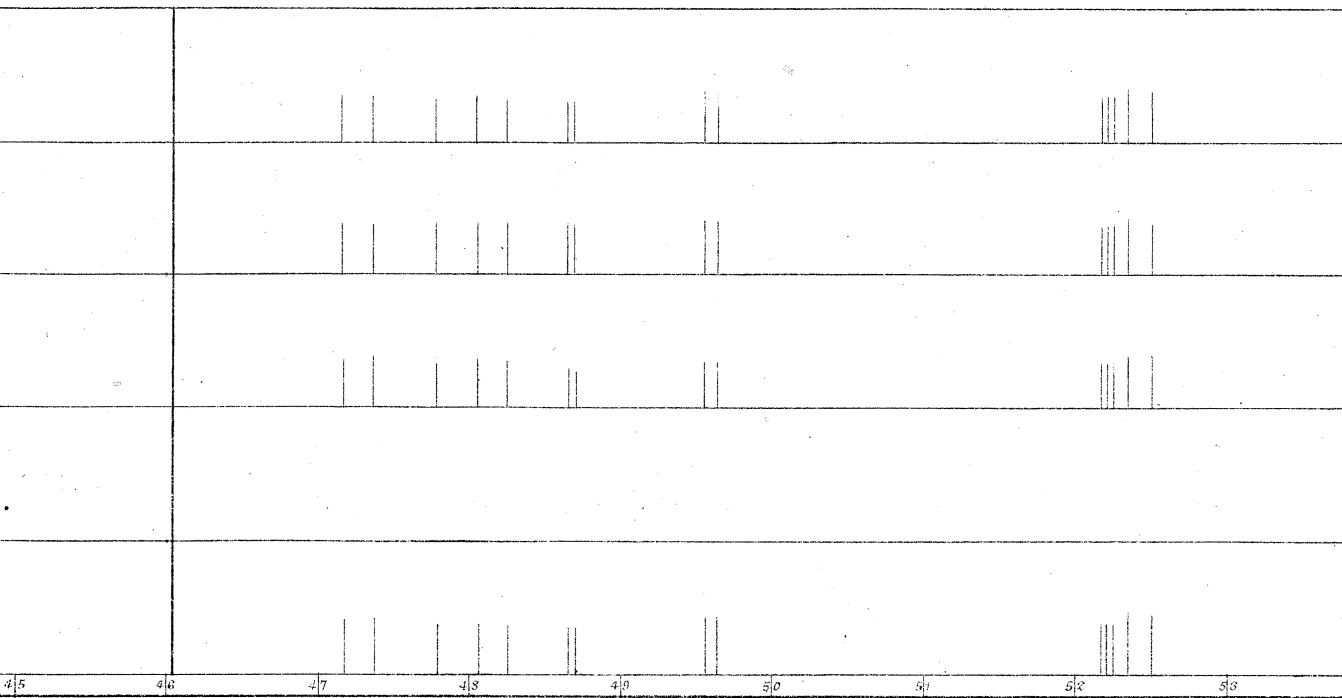
The spectrum A disappears in hydrogen.

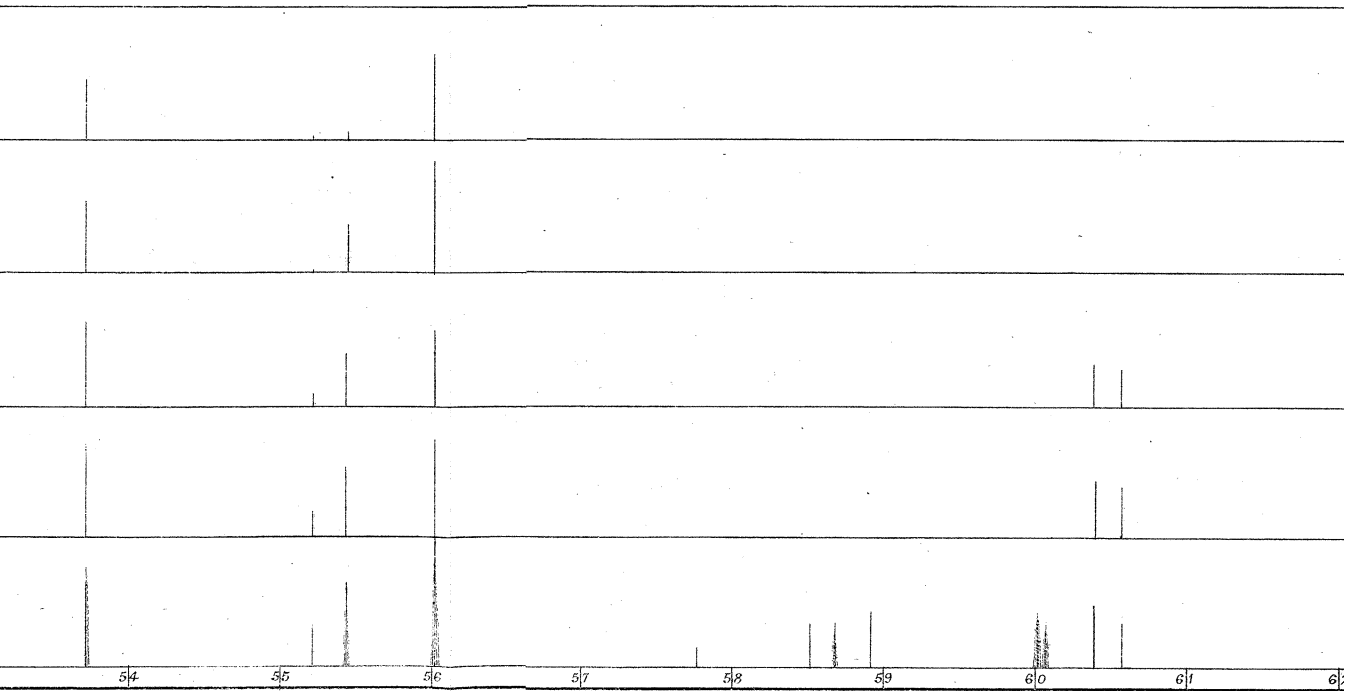
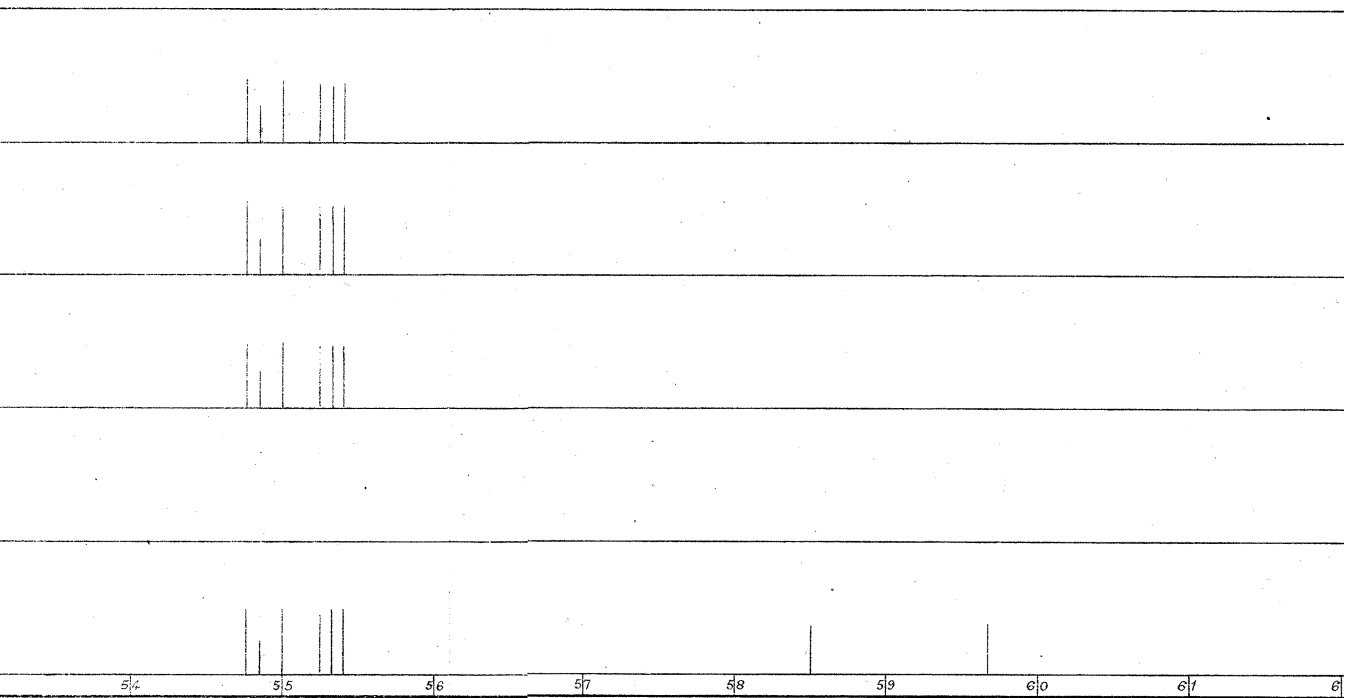
In air, with a low-tension spark, none of the metallic lines are seen, indicating that the oxide (Al₂O₃?) is not at all dissociated.

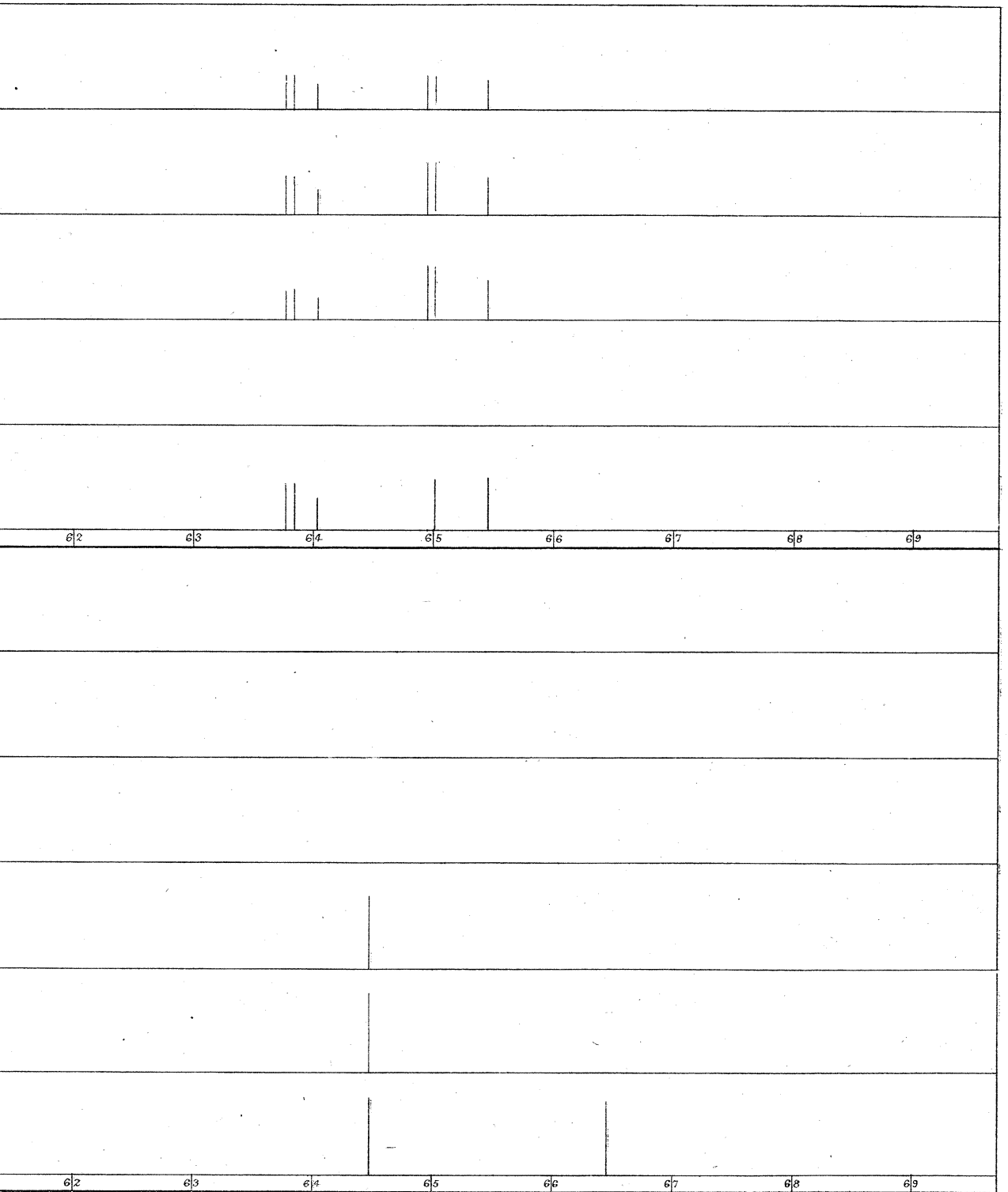
The oxide spectrum is laid down on a wave-length scale from careful approximations to the lines of air, copper, and zinc.

Lockyer.









Lockyer

