

Dielectric.	\sqrt{K} .	Nearest value of μ .	Ray for which μ is nearest.
Double extra dense flint glass.....	1·7783	1·7460	Band in extreme violet in magnesium spark spectrum.
Extra dense flint	1·7474	1·6757	
Light flint.....	1·7343	1·5113	
Hard crown	1·7629	1·5920	
Plate glass	1·8009	1·543	Rays of infinite wave length.
Paraffin	1·4119	1·422	
Sulphur.....	1·6060	2·115	
Bisulphide of carbon...	1·3456	1·6114	

VI. "Researches in Spectrum Analysis in connexion with the Spectrum of the Sun. No. VII." By J. N. LOCKYER, F.R.S. Received December 11, 1878. Read December 12.

Discussion of the Working Hypothesis that the so-called Elements are Compound Bodies.

PART I.

It is known to many Fellows of the Society that I have for the last four years been engaged upon the preparation of a map of the solar spectrum on a large scale, the work including a comparison of the Fraunhofer lines with those visible in the spectrum of the vapour of each of the metallic elements in the electric arc.

To give an idea of the thoroughness of the work, at all events in intention, I may state that the complete spectrum of the sun, on the scale of the working map, will be half a furlong long; that to map the metallic lines and purify the spectra in the manner which has already been described to the Society, more than 100,000 observations have been made and about 2,000 photographs taken.

In some of these photographs we have vapours compared with the sun; in others vapours compared with each other; and others again have been taken to show which lines are long and which are short in the spectra.

I may state by way of reminder that the process of purification consisted in this: When, for instance, an impurity of Mn was searched for in Fe, if the longest line of Mn was absent, the short lines must also be absent on the hypothesis that the elements are elementary; if the longest line were present, then the impurity was traced down to the shortest line present.

Table II. Final reduction—Titanium.

Intensity in Sun.	Wave-length and length of line.	Coincidences with Short Lines.									
	39										
1	0000	Zr									
	3	4									
4	0048	Th									
	3	4									
5	1040		Mn	Ce	Di						
	5		4	5	3						
2	1360					Va					
	3					4					
5	1915			Ce							
	8			4							
4	2050						U		La		
	3						3		3		
3	2368					Va					
	2					3					
3	3718	Th		Ce							
	5	4		4							
2	4775							Fe			
	1							2			
2	5722	Zr								Rh	
	1	1								3	
4	6175						U				
	2						3				
3	6335					Di				Ta	
	2					3				5	
2	8083							Fe			
	1							2			
3	8152									Mo	
	2									3	
1	8922		Mn								Cr
	1		4								4
2	9798					Va					
	longest					longest					

*The Hypothesis that the Elements are Simple Bodies does not include all
the Phenomena.*

The final reduction of the photographs of all the metallic elements in the region 39-40—a reduction I began in the early part of the present year, and which has taken six months, summarised all the observations of metallic spectra compared with the Fraunhofer lines accumulated during the whole period of observation. Now this reduction has shown me that the hypothesis that identical lines in different spectra are due to impurities is not sufficient. I shall show in detail in a subsequent paper the hopeless confusion in which I have been landed. I limit myself on the present occasion to giving tables showing how the hypothesis deals with the spectra of iron and titanium.

We find short-line coincidences between many metals the impurities of which have been eliminated, or in which the freedom from mutual impurity has been demonstrated by the absence of the longest lines.

Evidences of Celestial Dissociation.

It is five years since I first pointed out that there are many facts

Following out these views, I some time since communicated a paper to the Society on the spectrum of calcium, to which I shall refer more expressly in the sequel.

Differentiation of the Phenomena to be observed on the Two Hypotheses.

When the reductions of the observations made on metallic spectra, on the hypothesis that the elements were really elementary, had landed me in the state of utter confusion to which I have already referred, I at once made up my mind to try the other hypothesis, and therefore at once sought for a critical differentiation of the phenomena on the two hypotheses.

Obviously the first thing to be done was to inquire whether one hypothesis would explain these short-line coincidences which remained after the reduction of all the observations on the other. Calling for simplicity's sake the short lines common to many spectra *basic lines*, the new hypothesis, to be of any value, should present us with a state of things in which basic molecules representing bases of the so-called elements should give us their lines, varying in intensity from one condition to another, the *conditions* representing various compoundings.

Suppose A to contain B as an impurity and as an element, what will be the difference in the spectroscopic result?

A in both cases will have a spectrum of its own;

B as an impurity will add its lines according to the amount of impurity, as I have shown in previous papers.

B as an element will add its lines according to the amount of dissociation, as I have also shown.

The difference in the phenomena, therefore, will be that, with gradually-increasing temperature, the spectrum of A *will fade*, if it be a compound body, as it will be increasingly dissociated, and it *will not* fade if it be a simple one.

Again, on the hypothesis that A is a compound body, that is, one compounded of at least two similar or dissimilar molecular groupings, then the longest lines at one temperature will not be the longest at another; the whole fabric of "impurity elimination," based upon the assumed single molecular grouping, falls to pieces, and the origin of the basic lines is at once evident.

This may be rendered clearer by some general considerations of another order.

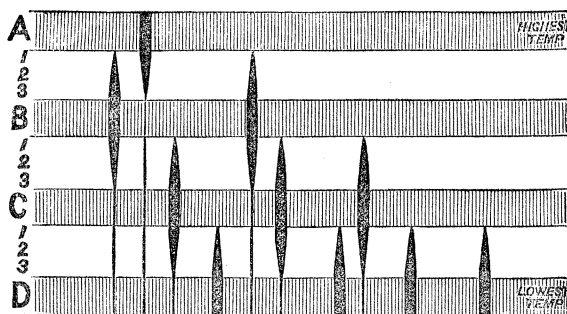
General Considerations.

Let us assume a series of furnaces A . . . D, of which A is the hottest.

Let us further assume that in A there exists a substance *a* by itself competent to form a compound body β by union with itself or with something else when the temperature is lowered.

Then we may imagine a furnace B in which this compound body exists alone. The spectrum of the compound β would be the only one visible in B, as the spectrum of the assumed elementary body a would be the only one visible in A.

FIG. 1.*



A lower temperature furnace C will provide us with a more compounded substance γ , and the same considerations will hold good.

Now if into the furnace A we throw some of this doubly-compounded body γ , we shall get at first an integration of the three spectra to which I have drawn attention; the lines of γ will first be thickest, then those of β ; finally a will exist alone, and the spectrum will be reduced to one of the utmost simplicity.

This is not the only conclusion to be drawn from these considerations. Although we have by hypothesis β , γ , and δ all higher, that is, more compound forms of a , and although the strong lines in the diagram may represent the true spectra of these substances in the furnaces B, C, and D, respectively, yet, in consequence of incomplete dissociation, the strong lines of β will be seen in furnace C, and the strong lines of γ will be seen in furnace D, *all as thin lines*. Thus, although in C we have no line which is not represented in D, the intensities of the lines in C and D are entirely changed.

In short, the line of a strong in A is *basic* in B, C, and D, the lines of β strong in B are *basic* in C and D, and so on.

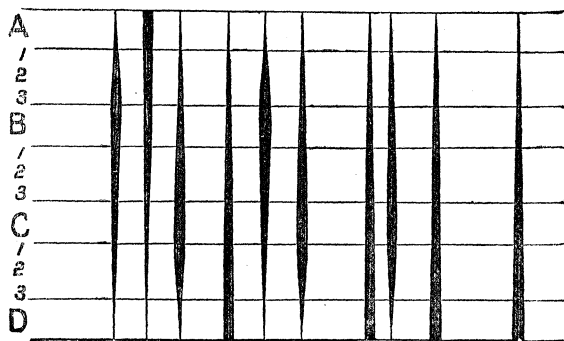
I have prepared another diagram which represents the facts on the supposition that the furnace A, instead of having a temperature sufficient to dissociate β , γ , and δ into a is far below that stage, although higher than B.

It will be seen from this diagram that then the only difference in the spectra of the bodies existing in the four furnaces would consist in the relative thicknesses of the lines. The spectrum of the sub-

* The figures between the hypothetical spectra point to the gradual change as the spectrum is observed near the temperature of each of the furnaces.

stances as they exist in A would contain as many lines as would the spectrum of the substances as they exist in D; each line would in

Fig. 2.



turn, be *basic* in the whole series of furnaces instead of in one or two only.

Application of these General Considerations to Impurity Elimination.

Now let us suppose that in the last diagram (Fig. 2) the four furnaces represent the spectra of say, iron, broken up into different finenesses by successive stages of heat. It is first of all abundantly clear that the relative thicknesses of the iron lines observed will vary according as the temperature resembles that of A, B, C, or D. The positions in the spectra will be the same, but the intensities will vary; this is the point. *The longest lines, represented in the diagram by the thickest ones, will vary as we pass from one temperature to another.* It is on this ground that I have before stated that the whole fabric of impurity elimination must fall to pieces on such an hypothesis. Let us suppose, for instance, that manganese is a compound of the form of iron represented in furnace B, with something else; and suppose again that the photograph of iron which I compare with manganese represents the spectrum of the vapour at the temperature of the furnace D. To eliminate the impurity of iron in manganese, as I have eliminated it, we begin the search by looking for the longest and strongest lines shown in the photograph of iron, in the photograph of manganese taken under the same conditions. I do not find these lines. I say, therefore, that there is no impurity of iron in manganese, but although the longest iron lines are not there, some of the fainter basic ones are. This I hold to be the explanation of the apparent confusion in which we are landed on the supposition that the elements are elementary.

Application of these Considerations to Known Compounds.

Now to apply this reasoning to the dissociation of a known compound body into its elements—

A compound body, such as a salt of calcium, has as definite a spectrum as a simple one; but while the spectrum of the metal itself consists of lines, the number and thickness of some of which increase with increased quantity, 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 quantity 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 fluted lines in the spectrum of the compound; and in each case the greatest simplicity of the spectrum depends upon the smallest quantity, and the greatest complexity (a continuous spectrum) upon the greatest.

The heat required to act upon such a compound as a salt of calcium 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 quantity of the metal resulting from the dissociation, and as the metal lines increase in number, the compound bands thin out.

I have shown in previous papers how we have been led to the conclusion that binary compounds have spectra of their own, and how this idea has been established by considerations having for a basis the observations of the long and short lines.

It is absolutely similar observations and similar reasoning which I have to bring forward in discussing the compound nature of the chemical elements themselves.

In a paper communicated to the Royal Society in 1874, referring, among other matters, to the reversal of some lines in the solar spectrum, I remarked :*—

“It is obvious that greater attention will have to be given to the precise *character* as well as to the position of each of the Fraunhofer lines, in the thickness of which I have already observed several anomalies. I may refer more particularly at present to the two H lines 3933 and 3968 belonging to calcium, which are much thicker in all photographs of the solar spectrum [I might have added that they were by far the thickest lines in the solar spectrum] than the largest calcium line of this region (4226·3), this latter being invariably thicker than the H lines in all photographs of the calcium spectrum, and remaining, moreover, visible in the spectrum of substances con-

* “Phil. Trans.,” vol. clxiv, part 2, p. 807.

taining calcium in such small quantities as not to show any traces of the H lines.

“ How far this and similar variations between photographic records and the solar spectrum are due to causes incident to the photographic record itself, or to variations in the intensities of the various molecular vibrations under solar and terrestrial conditions, are questions which up to the present time I have been unable to discuss.

An Objection Discussed.

I was careful at the very commencement of this paper to point out that the conclusions I have advanced are based upon the analogies furnished by those bodies which, by common consent and beyond cavil and discussion, are compound bodies. Indeed, had I not been careful to urge this point the remark might have been made that the various changes in the spectra to which I shall draw attention are not the results of successive dissociations, but are effects due to putting the same mass into different kinds of vibration or of producing the vibration in different ways. Thus the many high notes, both true and false, which can be produced out of a bell with or without its fundamental one, might have been put forward as analogous with those spectral lines which are produced at different degrees of temperature with or without the line, due to each substance when vibrating visibly with the lowest temperature. To this argument, however, if it were brought forward, the reply would be that it proves too much. If it demonstrates that the h hydrogen line in the sun is produced by the same molecular grouping of hydrogen as that which gives us two green lines only when the weakest possible spark is taken in hydrogen inclosed in a large glass globe, it also proves that calcium is identical with its salts. For we can get the spectrum of any of the salts alone without its common base, calcium, as we can get the green lines of hydrogen without the red one.

I submit, therefore, that the argument founded on the overnotes of a sounding body, such as a bell, cannot be urged by any one who believes in the existence of any compound bodies at all, because there is no spectroscopic break between acknowledged compounds and the supposed elementary bodies. The spectroscopic differences between calcium itself at different temperatures is, as I shall show, as great as when we pass from known compounds of calcium to calcium itself. There is a perfect continuity of phenomena from one end of the scale of temperature to the other.

Inquiry into the Probable Arrangement of the Basic Molecules.

As the results obtained from the above considerations seemed to be so far satisfactory, inasmuch as they at once furnished an explanation

of the *basic lines* actually observed, the inquiry seemed worthy of being carried to a further stage.

The next point I considered was to obtain a clear mental view of the manner in which, on the principle of evolution, various bases might now be formed, and then become basic themselves.

It did not seem unnatural that the bases should increase their complexity by a process of continual multiplication, the factor being 1, 2, or even 3, if conditions were available under which the temperature of their environment should decrease, as we imagined it to do from the furnace A down to furnace D. This would bring about a condition of molecular complexity in which the proportion of the molecular weight of a substance so produced in a combination with another substance would go on continually increasing.

Another method of increasing molecular complexity would be represented by the addition of molecules of different origins. Representing the first method by $A + A$, we could represent the second by $A + B$. A variation of the last process would consist in a still further complexity being brought about by the addition of another molecule of B, so that instead of $(A + B)_2$ merely, we should have $A + B_2$.

Of these three processes the first one seemed that which it was possible to attack under the best conditions, because the consideration of impurities was eliminated; the prior work has left no doubt upon the mind about such and such lines being due to calcium, others to iron, and so forth. That is to say, they are visible in the spectra of these substances as a rule. The inquiry took this form: Granting that these lines are special to such and such a substance, does each become basic in turn as the temperature is changed?

I therefore began the search by reviewing the evidence concerning calcium, and seeing if hydrogen, iron, and lithium behaved in the same way.

Application of the above Calcium Views to Calcium, Iron, Lithium, and Hydrogen.
Calcium.

It was in a communication to the Royal Society made in 1874 ("Proc. Roy. Soc.," vol. xxii, p. 380), that I first referred to the possibility that the well-known line spectra of the elementary bodies might not result from the vibration of similar molecules. I was led to make the remark in consequence of the differences to which I have already drawn attention in the spectra of certain elements as observed in the spectrum of the sun and in those obtained with the ordinary instrumental appliances.

Later ("Proc. Roy. Soc.," No. 168, 1876) I produced evidence that the molecular grouping of calcium which, with a small induction coil and small jar, gives a spectrum with its chief line in the blue, is nearly

broken up in the sun, and quite broken up in the discharge from a large coil and jar, into another or others with lines in the violet.

I said "another" or "others," because I was not then able to determine whether the last-named lines proceeded from the same or different molecules; and I added that it was possible we might have to wait for photographs of the spectra of the brighter stars before this point could be determined.

I also remarked that this result enabled us to fix with very considerable accuracy the electric dissociating conditions which are equivalent to that degree of dissociation at present at work in the sun.

In fig. 3 I have collected several spectra copied from photographs, in order that the line of argument may be grasped.

First we see what happens to the non-dissociated and the dissociated chloride. Next we have the lines with a weak voltaic arc, the single line to the right (W. L. 4226·3) is much thicker than the two lines (W. L. 3933 and 3968) to the left, and reverses itself.

We have next calcium exposed to a current of higher tension. It will be seen that here the three lines are almost equally thick, and all reverse themselves.

Now it will be recollected that in the case of known compounds the band structure of the true compounds is reduced as dissociation works its way, and the spectrum of each constituent element makes its appearance. If in 3 we take the wide line as representing the banded spectrum of the compound, and the thinner ones as representing the longest elemental lines making their appearance as the result of partial dissociation, we have, by hypothesis, an element behaving like a compound.

If the hypothesis be true, we ought to be able not only to obtain with lower temperatures a still greater preponderance of the single line, *as we do*; but with higher temperatures a still greater preponderance of the double ones, *as we do*.

I tested this in the following manner: employing photography, because the visibility of the more refrangible lines is small, and because a permanent record of an experiment, free as it must be from all bias, is a very precious thing.

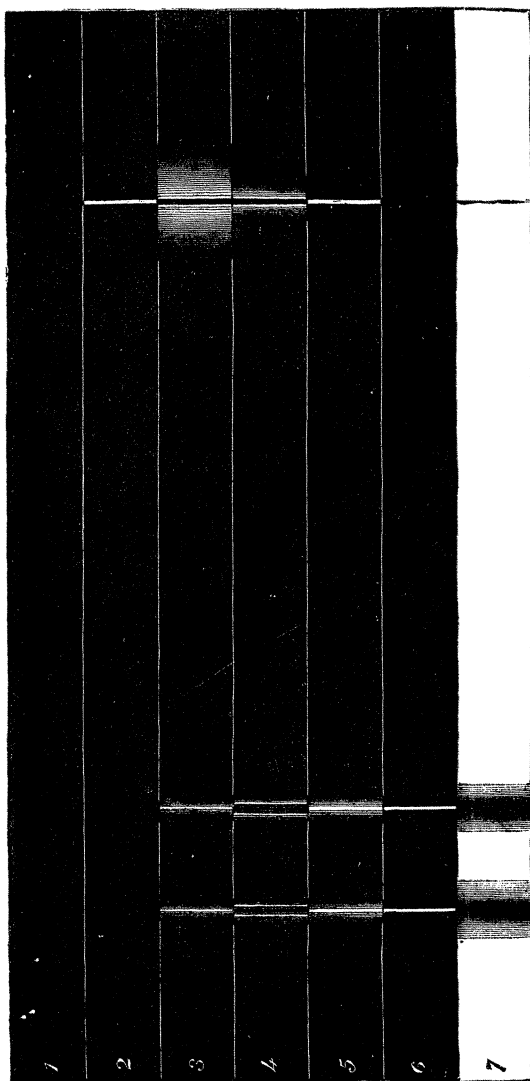
Induced currents of electricity were employed in order that all the photographic results might be comparable.

To represent the lowest temperature, I used a small induction coil and a Leyden jar only just large enough to secure the requisite amount of photographic effect. To represent the highest, I used the largest coil and jar at my disposal. The spark was then taken between two aluminium electrodes, the lower one cup-shaped, and charged with a salt of calcium.

In the figure I give exact copies of the results obtained. It will be seen that with the lowest temperature only the single line (2) and

with the highest temperature only the two more refrangible lines (6) are recorded on the plate.

FIG. 3.--The blue end of the Spectrum of calcium under different conditions.



1. Calcium is combined with chlorine (CaCl_2). When the temperature is low, the compound molecule vibrates as a whole, the spectrum is at the red end, and no lines of calcium are seen.
2. The line of the metal seen when the compound molecule is dissociated to a slight extent with an induced current.
3. The spectrum of metallic calcium in the electric arc with a small number of cells.
4. The same when the number of cells is increased.
5. The spectrum when a coil and small jar are employed.
6. The spectrum when a large coil and large jar are used.
7. The absorption of the calcium vapour in the sun.

This proved that the intensity of the vibrations was quite changed in the two experiments.

Perhaps it may not be superfluous here to state the reasons which induced me to search for further evidence in the stars.

It is abundantly clear that if the so-called elements, or more properly speaking their finest atoms—those that give us line spectra—are really compounds, the compounds must have been formed at a very high temperature. It is easy to imagine that there may be no superior limit to temperature, and therefore no superior limit beyond which such combinations are possible, because the atoms which have the power of combining together at these transcendental stages of heat do not exist as such, or rather they exist combined with other atoms, like or unlike, at all lower temperatures. Hence association will be a combination of more complex molecules as temperature is reduced, and of dissociation, therefore, with increased temperature there may be no end.

That is the first point.

The second is this :—

We are justified in supposing that our “calcium,” once formed, is a distinct entity, whether it be an element or not, and therefore, by working at it alone, we should never know whether the temperature produces a single simpler form or more atomic condition of the same thing, or whether we actually break it up into $x + y$, because neither x nor y will ever vary.

But if calcium be a product of a condition of relatively lower temperature, then in the stars hot enough to enable its constituents to exist uncompounded, we may expect these constituents to vary in quantity; there may be more of x in one star and more of y in another; and if this be so, then the H and K lines will vary in thickness, and the extremest limit of variation will be that we shall only have H representing, say, x in one star, and only have K representing, say, y in another. Intermediately between these extreme conditions we may have cases in which, though both H and K are visible, H is thicker in some and K is thicker in others.

Professor Stokes was good enough to add largely to the value of my paper as it appeared in the “Proceedings” by appending a note pointing out that “When a solid body such as a platinum wire, traversed by a voltaic current, is heated to incandescence, we know that as the temperature increases not only does the radiation of each particular refrangibility absolutely increase, but the proportion of the radiations of the different refrangibilities is changed, the proportion of the higher to the lower increasing with the temperature. It would be in accordance with analogy to suppose that as a rule the same would take place in an incandescent surface, though in this case the spectrum would be discontinuous instead of continuous. Thus, if A, B, C, D, E denote conspicuous bright lines of increasing refrangibility, in the spectrum of the vapour, it might very well be that at a comparatively low temperature A should be the brightest and the most persistent: at a higher temperature, while all were brighter than before, the relative

brightness might be changed, and C might be the brightest and the most persistent, and at a still higher temperature E."

On these grounds Professor Stokes, while he regarded the facts I mentioned as evidence of the high temperature of the sun, did not look upon them as *conclusive* evidence of the dissociation of the molecule of calcium.

Since that paper was sent in, however, the appeal to the stars to which I referred in it has been made, and made with the most admirable results, by Dr. Huggins.

The result of that appeal is, that the line which, according to Professor Stokes's view, should have prevailed over all others, as Sirius is acknowledged to be a hotter star than our sun, if it exists at all in the spectrum, is so faint that it was not recognised by Dr. Huggins in the first instance.

In Sirius, indeed, the H line due to one molecular grouping of calcium is as thick as are the hydrogen lines as mapped by Secchi, while the K line, due to another molecular grouping, which is equally thick in the spectrum of the sun, has not yet made its appearance.

In the sun, where it is as thick as H, the hydrogen lines have vastly thinned.

While this paper has been in preparation, Dr. Huggins has been good enough to communicate to me the results of his most important observations, and I have also had an opportunity of inspecting several of the photographs which he has recently taken. The result of the recent work has been to show that H and *h* are of about the same breadth in Sirius. In α Aquilæ, while the relation of H to *h* is not greatly changed, a distinct approach to the solar condition is observed, K being now unmistakably present, although its breadth is small as compared with that of H. I must express my obligations to Dr. Huggins for granting me permission to enrich my paper by reference to these unpublished observations. His letter, which I have permission to quote, is as follows:—

"It may be gratifying to you to learn that in a photograph I have recently taken of the spectrum of α Aquilæ there is a line corresponding to the more refrangible of the solar H lines [that is K], but about half the breadth of the line corresponding to the first H lines.

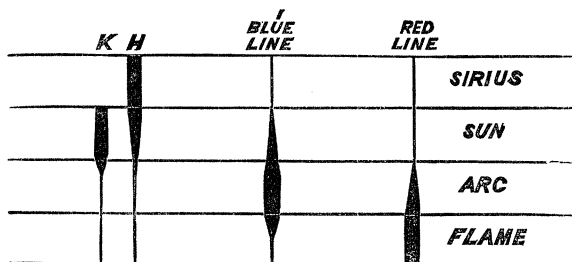
"In the spectra of α Lyræ and Sirius the second line is absent."

Professor Young's observations of the chromospheric lines, to which I shall afterwards refer, give important evidence regarding the presence of calcium in the chromosphere of the sun. He finds that the H and K lines of calcium are strongly reversed in every important spot, and that, in solar storms, H has been observed injected into the chromosphere seventy-five times, and K fifty times, while the blue line at W. L. 4226.3, the all-important line at the arc temperature, was only injected thrice.

Further, in the eclipse observed in Siam in 1875, the H and K lines left the strongest record in the spectrum of the chromosphere, while the line near G in a photographic region of much greater intensity was not recorded at all. In the American eclipse of the present year the H and K lines of calcium were distinctly visible at the base of the corona, in which, for the first time, the observers could scarcely trace the existence of any hydrogen.

To sum up, then, the facts regarding calcium, we have first of all the H line differentiated from the others by its almost solitary existence in Sirius. We have the K line differentiated from the rest by its birth, so to speak, in *a* Aquilæ, and the thickness of its line in the sun, as compared to that in the arc. We have the blue line differentiated from H and K by its thinness in the solar spectrum while they are thick, and by its thickness in the arc while they are thin. We have it again differentiated from them by its absence in solar storms in

FIG. 4.



which they are almost universally seen, and, finally, by its absence during eclipses, while the H and K lines have been the brightest seen or photographed. Last stage of all, we have calcium, distinguished from its salts by the fact that the blue line is only visible when a high temperature is employed, each salt having a definite spectrum of its own, in which none of the lines to which I have drawn attention appear, so long as the temperature is kept below a certain point.

Iron.

With regard to the iron spectrum, I shall limit my remarks to that portion of it visible on my photographic plates, between H and G. It may be described as a very complicated spectrum, so far as the number of lines is concerned, in comparison with such bodies as sodium and potassium, lead, thallium, and the like; but unlike them, again, it contains no one line which is clearly and unmistakably reversed on all occasions. Compared, however, with the spectrum of such bodies as cerium and uranium, the spectrum is simplicity itself.

Now, among these lines are two triplets, two sets of three lines each, giving us beautiful examples of those repetitions of structure in

the spectrum which we meet with in the spectra of almost all bodies, some of which have already been pointed out by Mascart, Cornu, and myself. Now the facts indicate that these two triplets are not due to the vibration of the same molecular grouping which gives rise to most of the other lines. They are as follows. In many photographs in which iron has been compared with other bodies, and in others again in which iron has been photographed as existing in different degrees of impurity in other bodies, these triplets have been seen almost alone, and the relative intensity of them, as compared with the few remaining lines, is greatly changed. In this these photographs resemble one I took three years ago, in which a large coil and jar were employed instead of the arc, which necessitated an exposure of an hour instead of two minutes. In this the triplet near G is very marked; the two adjacent lines more refrangible near it, which are seen nearly as strong as the triplet itself in some of the arc photographs I possess, are only very faintly visible, while dimmer still are seen the lines of the triplet between H and *h*.

There is another series of facts in another line of work. In solar storms, as is well known, the iron lines sometimes make their appearance in the chromosphere. Now, if we were dealing here with one molecular grouping, we should expect the lines to make their appearance in the order of their lengths, and we should expect the shortest lines to occur less frequently than the longest ones. Now, precisely the opposite is the fact. One of the most valuable contributions to solar physics that we possess is the memoir in which Professor C. A. Young records his observation of the chromospheric lines, made on behalf of the United States Government, at Sherman, in the Rocky Mountains. The glorious climate and pure air of this region, to which I can personally testify, enabled him to record phenomena which it is hopeless to expect to see under less favourable conditions. Among these were injections of iron vapour into the chromosphere, the record taking the form of the number of times any one line was seen during the whole period of observation.

Now, two very faint and short lines close to the triplet near G were observed to be injected thirty times, while one of the lines of the triplet was only injected twice.

The question next arises, are the triplets produced by one molecular grouping or by two? This question I also think the facts help us to answer. I will first state, by way of reminder, that in the spark photograph the more refrangible triplet is barely visible, while the one near G is very strong. Now, if one molecular grouping alone were in question, this relative intensity would always be preserved, however much the absolute intensity of the compound system might vary, but if it is a question of two molecules, we might expect that, in some of the regions open to our observation, we should get evidence of cases in

which the relative intensity is reversed or the two intensities are assimilated. What might happen does happen; the relative intensity of the two triplets in the spark photograph is grandly reversed in the spectrum of the sun. The lines barely visible in the spark photograph are among the most prominent in the solar spectrum, while the triplet which is strong in that photograph is represented by Fraunhofer lines not half so thick. Indeed, while the hypothesis that the iron lines in the region I have indicated are produced by the vibration of one molecule does not include all the facts, the hypothesis that the vibrations are produced by at least three distinct molecules includes all the phenomena in a most satisfactory manner.

Lithium.

Before the maps of the long and short lines of some of the chemical elements compared with the solar spectra, which were published in the "Philosophical Transactions" for 1873, Plate 9, were communicated to the Society, I very carefully tested the work of prior observers on the non-coincidence of the red and orange lines of that metal with the Fraunhofer lines, and found that neither of them were strongly, if at all, represented in the sun, and this remark also applies to a line in the blue at wave-length 4603.

The photographic lithium line, however, in the violet, has a strong representative among the Fraunhofer lines.

Applying, therefore, the previous method of stating the facts, the presence of this line in the sun differentiates it from all the others. For the differentiation of the red and yellow lines I need only refer to Bunsen's spectral analytical researches, which were translated in the "Philosophical Magazine," December, 1875.

In Plate 4 two spectra of the chloride of lithium are given, one of them showing the red line strong and the yellow one feeble, the other showing merely a trace of the red line, while the intensity of the yellow one is much increased, and a line in the blue is indicated. Another notice of the blue line of lithium occurs in a discourse by Professor Tyndall, reprinted in the "Chemical News," and in a letter of Dr. Frankland's to Professor Tyndall, dated November 7, 1861. This letter is so important for my argument that I reprint it entire from the "Philosophical Magazine," vol. xxii, p. 472:—

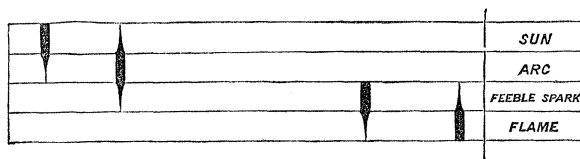
"On throwing the spectrum of lithium on the screen yesterday, I was surprised to see a magnificent blue band. At first I thought the lithic chloride must be adulterated with strontium, but on testing it with Steinheil's apparatus it yielded normal results without any trace of a blue band. I am just now reading the report of your discourse in the 'Chemical News,' and I find that you have noticed the same thing. Whence does this blue line arise? Does it really belong to the lithium, or are the carbon points or ignited air guilty of its pro-

duction? I find these blue bands with common salt, but they have neither the definiteness nor the brilliancy of the lithium band. When lithium wire burns in air it emits a somewhat crimson light; plunge it into oxygen, and the light changes to bluish-white. This seems to indicate that a high temperature is necessary to bring out the blue ray."

Postscript, November 22, 1861.—"I have just made some further experiments on the lithium spectrum, and they conclusively prove that the appearance of the blue line depends entirely on the temperature. The spectrum of lithic chloride, ignited in a Bunsen's burner flame, does not disclose the faintest trace of the blue line; replace the Bunsen's burner by a jet of hydrogen (the temperature of which is higher than that of the Bunsen's burner) and the blue line appears, faint, it is true, but sharp and quite unmistakable. If oxygen now be slowly turned into the jet, the brilliancy of the blue line increases until the temperature of the flame rises high enough to fuse the platinum, and thus put an end to the experiment."

These observations of Professors Tyndall and Frankland differentiate this blue line from those which are observed at low temperatures. The line in the violet to which I have already referred is again differentiated from all the rest by the fact that it is the only line in the spectrum of the sun which is strongly reversed, so far as our present knowledge extends. The various forms of lithium, therefore, may be shown in the following manner.

FIG. 5.



It is remarkable that in the case of this body which at relatively low temperature goes through its changes, its compounds are broken up at the temperature of the Bunsen burner. The spectrum, *e.g.* of the chloride, so far as I know, has never been seen.

Hydrogen.

All the phenomena of variability and inversion in the order of intensity presented to us in the case of calcium can be paralleled by reference to the knowledge already acquired regarding the spectrum of hydrogen.

Dr. Frankland and myself were working together on the subject in 1869. In that year ("Proc. Roy. Soc.," No. 112) we pointed out

that the behaviour of the *h* line was *hors ligne*, and that the whole spectrum could be reduced to one line, F.

"1. The Fraunhofer line on the solar spectrum, named *h* by Ångström, which is due to the absorption of hydrogen, is not visible in the tubes we employ with low battery and Leyden-jar power; it may be looked upon, therefore, as an indication of relatively high temperature. As the line in question has been reversed by one of us in the spectrum of the chromosphere, it follows that the chromosphere, when cool enough to absorb, is still of a relatively high temperature.

"2. Under certain conditions of temperature and pressure, the very complicated spectrum of hydrogen is reduced in our instrument to one line in the green, corresponding to F in the solar spectrum."

As in the case of calcium also, solar observation affords us most precious knowledge. The *h* line was missing from the protuberances in 1875, as will be shown from the accompanying extract from the Report of the Eclipse Expedition of that year:—

"During the first part of the eclipse two strong protuberances close together are noticed; on the limb towards the end these are partially covered, while a series of protuberances came out at the other edge. The strongest of these protuberances are repeated three times, an effect of course of the prism, and we shall have to decide if possible the wave-lengths corresponding to the images. We expect *à priori* to find the hydrogen lines represented. We know three photographic hydrogen lines: F, a line near G, and *h*. F is just at the limit of the photographic part of the spectrum, and we find indeed images of protuberances towards the less refrangible part at the limit of photographic effect. For, as we shall show, a continuous spectrum in the lower parts of the corona has been recorded, and the extent of this continuous spectrum gives us an idea of the part of the spectrum in which each protuberance line is placed. We are justified in assuming, therefore, as a preliminary hypothesis, that the least refrangible line in the protuberance shown on the photograph is due to F, and we shall find support of this view in the other lines. In order to determine the position of the next line the dispersive power of the prism was investigated. The prism was placed on a goniometer table in minimum deviation for F, and the angular distance between F and the hydrogen line near G, *i.e.*, H γ , was found, as a mean of several measurements, to be 3'. The goniometer was graduated to 15'', and owing to the small dispersive power, and therefore relatively great breadth of the slit, the measurement can only be regarded as a first approximation. Turning now again to our photographs, and calculating the angular distance between the first and second ring of protuberances, we find that distance to be 3' 15''. We conclude, therefore, that this second ring is due to hydrogen. We, therefore,

naturally looked for the third photographic hydrogen line, which is generally called h , but we found no protuberance on our photographs corresponding to that wave-length. Although this line is always weaker than $H\gamma$, its absence on the photograph is rather surprising, if it be not due to the fact that the line is one which only comes out at a high temperature. This is rendered likely by the researches of Frankland and Lockyer ("Proc. Roy. Soc.," vol. xvii, p. 453).

"We now turn to the last and strongest series of protuberances shown on our photographs. The distance between this series and the one we have found reason for identifying with $H\gamma$ is very little greater than that between $H\beta$ and $H\gamma$. Assuming the distances equal, we conclude that the squares of the inverse wave-lengths of the three series are in arithmetical progression. This is true as a first approximation. We then calculated the wave-length of this unknown line, and found it to be approximately somewhat smaller than 3,957 tenth-metres. No great reliance can be placed, of course, on the number, but it appears that the line must be close to the end of the visible spectrum.

"In order to decide, if possible, what this line is due to, we endeavoured to find out both by photography and fluorescence whether hydrogen possesses a line in that part of the spectrum. We have not at present come to any definite conclusion. In vacuum tubes prepared by Geissler containing hydrogen, a strong line more refrangible than H is seen, but these same tubes show between $H\gamma$ and $H\delta$, other lines known not to belong to hydrogen, and the origin of the ultra-violet line is therefore difficult to make out. We have taken the spark in hydrogen at atmospheric pressures, as impurities are easier to eliminate, but a continuous spectrum extends over the violet and part of the ultra-violet, and prevents any observation as to lines. We are going on with experiments to settle this point.

"Should it turn out that the line is not due to hydrogen, the question will arise what substance it is due to. It is a remarkable fact that the calculated wave-length comes very close to H . Young has found that these calcium lines are always reversed in the penumbra and immediate neighbourhood of every important sun-spot, and calcium must therefore go up high into the chromosphere. We draw attention to this coincidence, but our photographs do not allow us to draw any certain conclusions.

"At any rate, it seems made out by our photographs that the photographic light of the protuberances is in great part due to an ultra-violet line which does not certainly belong to hydrogen. The protuberances as photographed by this ultra-violet ray seem to go up higher than the hydrogen protuberances, but this may be due to the relative greater length of the line."

In my remarks upon calcium I have already referred to the fact that

the line which our observation led us to believe was due to calcium in 1875, was traced to that element in this year's eclipse. The observations also show the curious connexion that, at the time when the hydrogen lines were most brilliant in the corona, the calcium lines were not detected; next, when the hydrogen lines, being still brilliant, the *h* line was not present (a condition of things which, in all probability, indicated a reduction of temperature), calcium began to make itself unmistakably visible; and finally, when the hydrogen lines are absent, H and K become striking objects in the spectrum of the corona.

To come back to *h*, then, I have shown that Dr. Frankland and myself, in 1869, found that it only made its appearance when a high tension was employed. We have seen that it was absent from among the hydrogen lines during the eclipse of 1875.

I have now to strengthen this evidence by the remark that it is always the shortest line of hydrogen in the chromosphere.

I now pass to another line of evidence.

I submit to the Society a photograph of the spectrum of indium, in which, as already recorded by Thalèn, the strongest line is one of the lines of hydrogen (*h*), the other line of hydrogen (near G) being absent. I have observed the C line in the spark produced by the passage of an induced current between indium poles in dry air.

As I am aware how almost impossible it is to render air perfectly dry, I made the following differential experiment. A glass tube with two platinum poles about half an inch apart was employed. Through this tube a slow current of air was driven after passing through a U-tube one foot high, containing calcic chloride, and then through sulphuric acid in a Wolff's bottle. The spectrum of the spark passing between the platinum electrodes was then observed, a coil with five Grove cells and a medium-sized jar being employed. Careful notes were made of the brilliancy and thickness of the hydrogen lines as compared with those of air. This done, a piece of metallic indium, which was placed loose in the tube, was shaken so that one part of it rested against the base of one of the poles, and one of its ends at a distance of a little less than half an inch from the base of the other pole. The spark was then passed between the indium and the platinum. The red and blue lines of hydrogen were then observed, both by my friend Mr. G. W. Hemming, Q.C., and myself. Their brilliancy was most markedly increased. This unmistakable indication of the presence of hydrogen, or rather of that form of hydrogen which gives us the *h* line alone associated into that form which gives us the blue and red lines, showed us that in the photograph we were not dealing with a physical coincidence, but that in the arc this special form of hydrogen had really been present; that it had come from the indium, and that it had registered itself on the photographic plate, although ordinary hydrogen persistently refuses to do so. Although I was

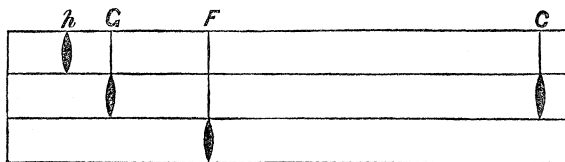
satisfied from former experiments that occluded hydrogen behaves in this respect like ordinary hydrogen, I begged my friend, Mr. W. C. Roberts, F.R.S., Chemist to the Mint, to charge a piece of palladium with hydrogen for me. This he at once did; and I take this present opportunity to express my obligation to him. I exhibit to the Society a photograph of this palladium and of indium side by side. It will be seen that one form of hydrogen in indium has distinctly recorded itself on the plate, while that in palladium has not left a trace. I should add that the palladium was kept in a sealed tube till the moment of making the experiment, and that special precautions were taken to prevent the two pieces between which the arc was taken from becoming unduly heated.

To sum up, then, the facts with regard to hydrogen; we have *h* differentiated from the other lines by its appearance alone in indium; by its absence during the eclipse of 1875, when the other lines were photographed; by its existence as a short line only in the chromosphere of the sun, and by the fact that in the experiments of 1869 a very high temperature was needed to cause it to make its appearance.

With regard to the isolation of the F line I have already referred to other experiments in 1869, in which Dr. Frankland and myself got it alone.* I exhibit to the Society a globe containing hydrogen, which gives us the F line without either the red or the blue one.

The accompanying drawing shows how these lines are integrated in the spectrum of the sun.

FIG. 6.



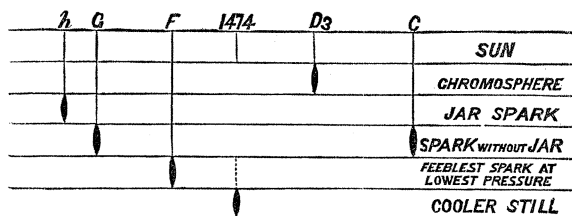
I have other evidence which, if confirmed, leads to the conclusion that the substance which gives us the non-reversed line in the chromosphere and the line at 1474 of Kirchhoff's scale, termed the coronal line, are really other forms of hydrogen. One of these is possibly more simple than that which gives us *h* alone, the other more complex than that which gives us F alone. The evidence on this point is of such extreme importance to solar physics, and throws so much light on star structure generally, that I am now engaged in discussing it, and shall therefore reserve it for a special communication.

In the meantime I content myself by giving a diagram, in which I have arranged the various groupings of hydrogen as they appear to

* See also Plücker, "Phil. Trans.," Part I, p. 21.

exist, from the regions of highest to those of lowest temperature in our central luminary.

FIG. 7.



Summation of the above Series of Facts.

I submit that the facts above recorded are easily grouped together, and a perfect continuity of phenomena established on the hypothesis of successive dissociations analogous to those observed in the cases of undoubted compounds.

The other Branches of the Inquiry.

When we pass to the other possible evolutionary processes to which I have before referred, and which I hope to discuss on a future occasion, the inquiry becomes much more complicated by the extreme difficulty of obtaining pure specimens to work with, although I should remark that in the working hypothesis now under discussion the cause of the constant occurrence of the same substance as an impurity in the same connexion is not far to seek. I take this opportunity of expressing my obligations to many friends who have put themselves to great trouble in obtaining specimens of pure chemicals for me during the whole continuance of my researches. Among these I must mention Dr. Russell, who has given me many specimens prepared by the lamented Matthiessen, as well as some of cobalt and nickel prepared by himself; Professor Roscoe, who has supplied me with vanadium and caesium alum; Mr. Crookes, who has always responded to my call for thallium; Mr. Roberts, chemist to the Mint, who has supplied me with portions of the gold and silver trial plates and some pieces of palladium; Dr. Hugo Müller, who has furnished me with a large supply of electrolytically-deposited copper; Mr. Holtzman, who has provided me with cerium, lanthanum, and didymium prepared by himself; Mr. George Matthey, of the well-known metallurgical firm of Johnson and Matthey, who has provided me with magnesium and aluminium of marvellous purity; while to Mr. Valentin, Mr. Mellor, of Salford, and other friends, my thanks are due for other substances.

I have already pointed out that a large portion of the work done in

the last four years has consisted in the elimination of the effects of impurities. I am therefore aware of the great necessity for caution in the spectroscopic examination of various substances. There is, however, a number of bodies which permit of the inquiry into their simple or complex nature being made in such a manner that the presence of impurities will be to a certain extent negligible. I have brought this subject before the Royal Society at its present stage in the hope that possibly others may be induced to aid inquiry in a region in which the work of one individual is as a drop in the ocean. If there is anything in what I have said, the spectra of all the elementary substances will require to be re-mapped—and re-mapped from a new standpoint; further, the arc must replace the spark, and photography must replace the eye. A glance at the red end of the spectrum of almost any substance incandescent in the voltaic arc in a spectroscope of large dispersion, and a glance at the maps prepared by such eminent observers as Huggins and Thalén, who have used the coil, will give an idea of the mass of facts which have yet to be recorded and reduced before much further progress can be made.

In conclusion, I would state that only a small part of the work to which I have drawn attention is my own. In some cases I have merely, as it were, codified the work done by other observers in other countries. With reference to that done in my own laboratory I may here repeat what I have said before on other occasions, that it is largely due to the skill, patience, and untiring zeal of those who have assisted me. The burthen of the final reduction, to which I have before referred, has fallen to Mr. Miller, my present assistant; while the mapping of the positions and intensities of the lines was done by Messrs. Friswell, Meldola, Ord and Starling, who have successively filled that post.

I have to thank Corporal Ewings, R.E., for preparing the various diagrams which I have submitted to the notice of this Society.

December 19, 1878.

W. SPOTTISWOODE, M.A., D.C.L., President, in the Chair.

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

The following Papers were read :—

FIG. 1.*

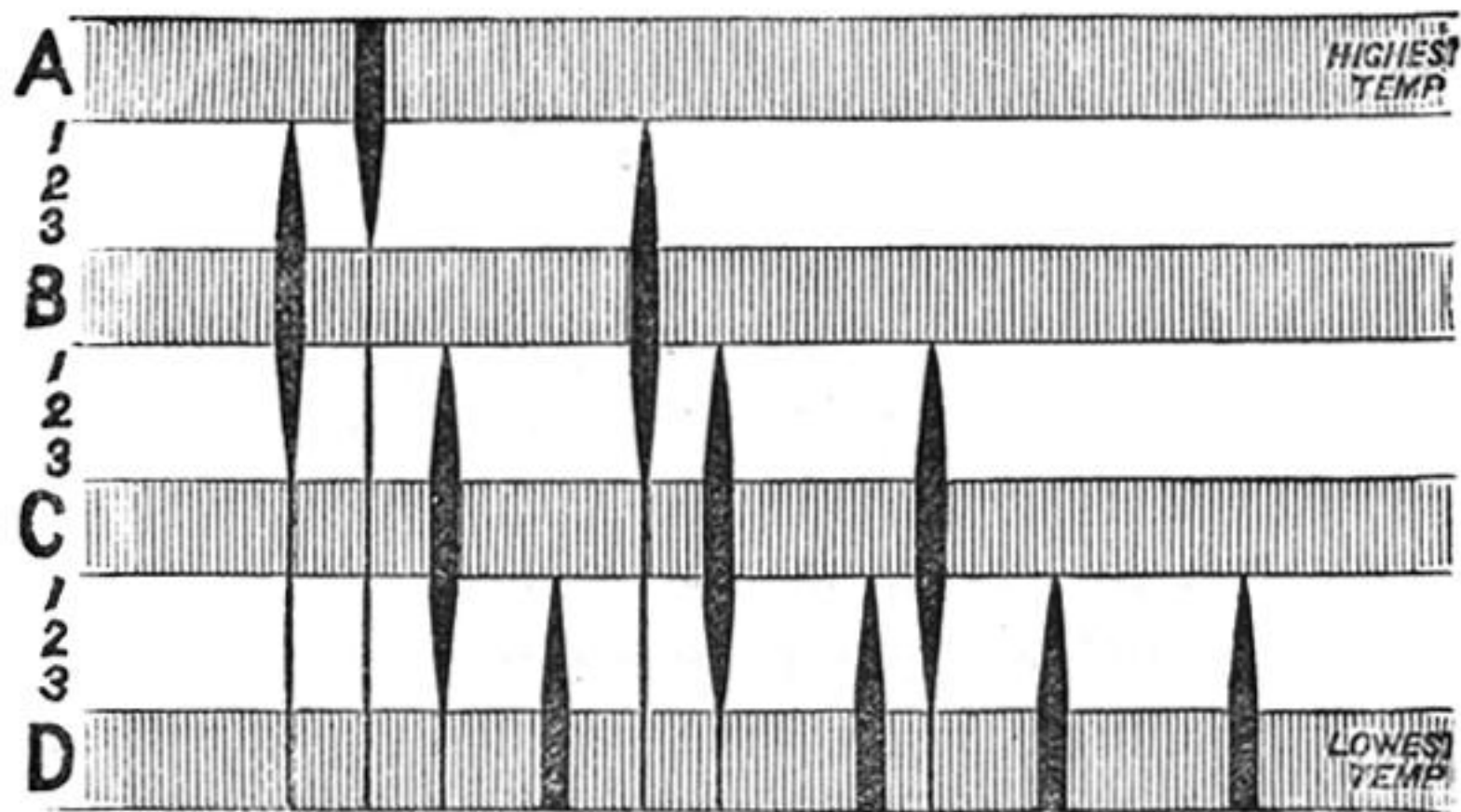


Fig. 2.

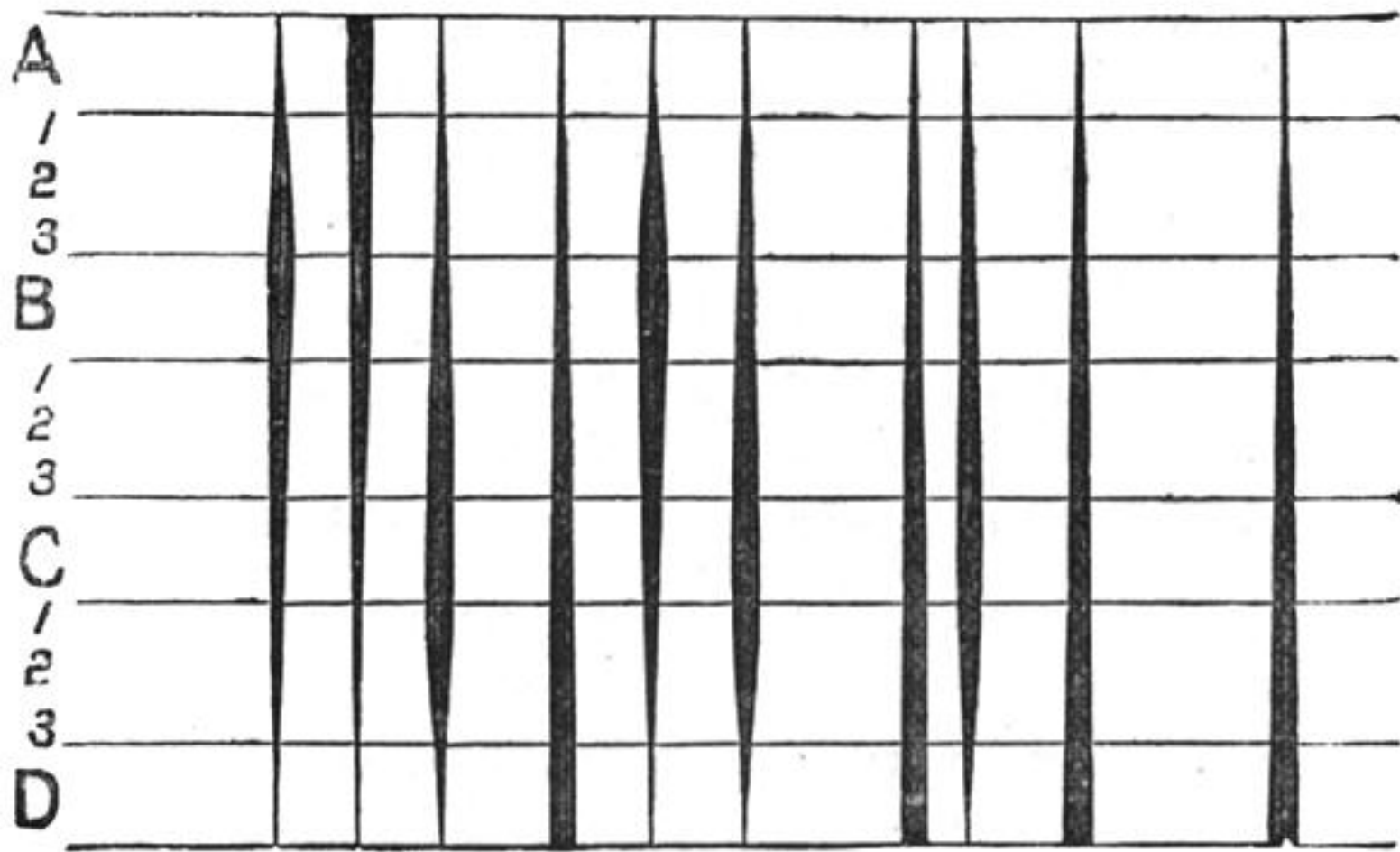
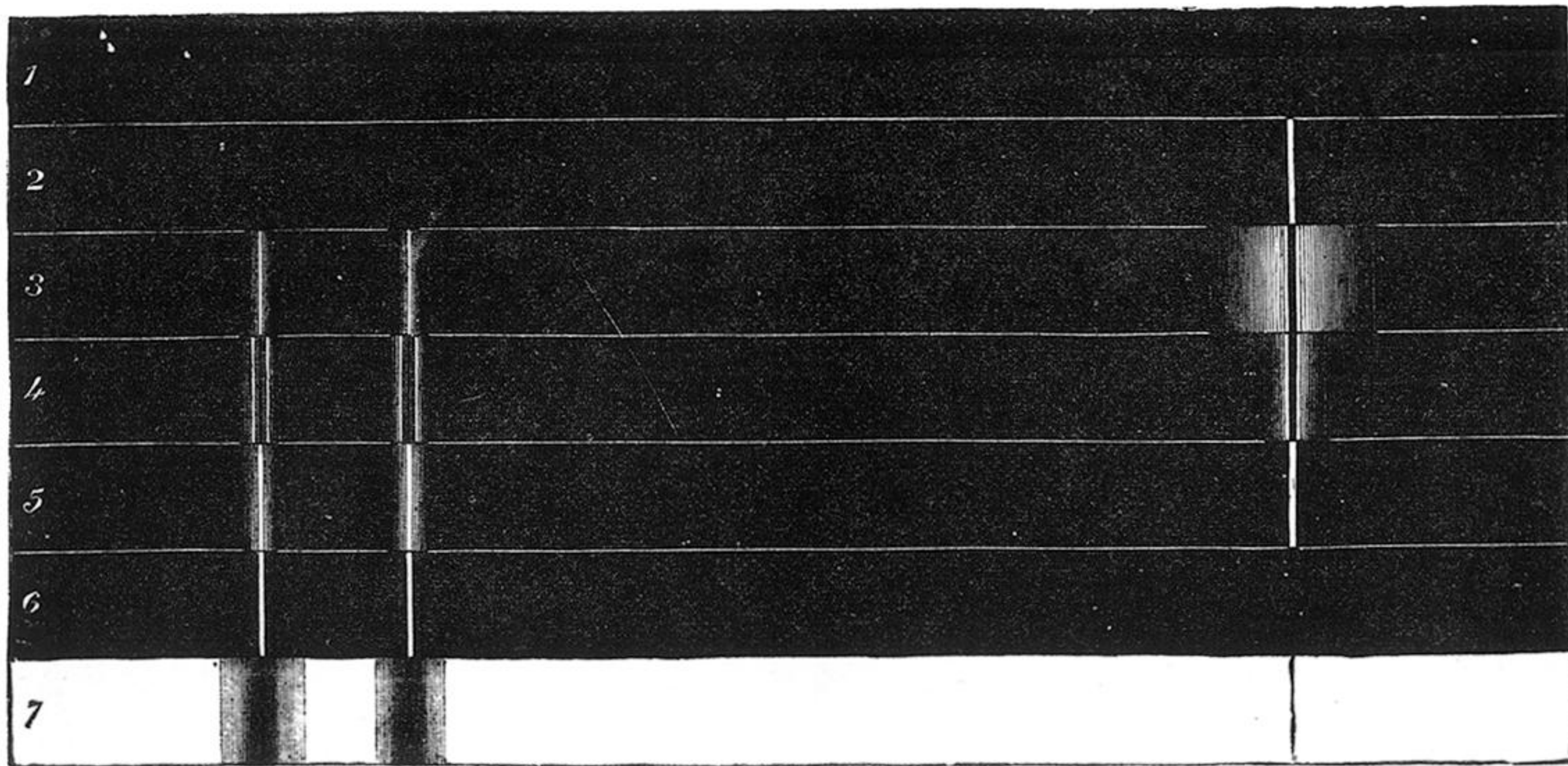


FIG. 3.--The blue end of the Spectrum of calcium under different conditions.



1. Calcium is combined with chlorine (CaCl_2). When the temperature is low, the compound molecule vibrates as a whole, the spectrum is at the red end, and no lines of calcium are seen.
2. The line of the metal seen when the compound molecule is dissociated to a slight extent with an induced current.
3. The spectrum of metallic calcium in the electric arc with a small number of cells.
4. The same when the number of cells is increased.
5. The spectrum when a coil and small jar are employed.
6. The spectrum when a large coil and large jar are used.
7. The absorption of the calcium vapour in the sun.

FIG. 4.

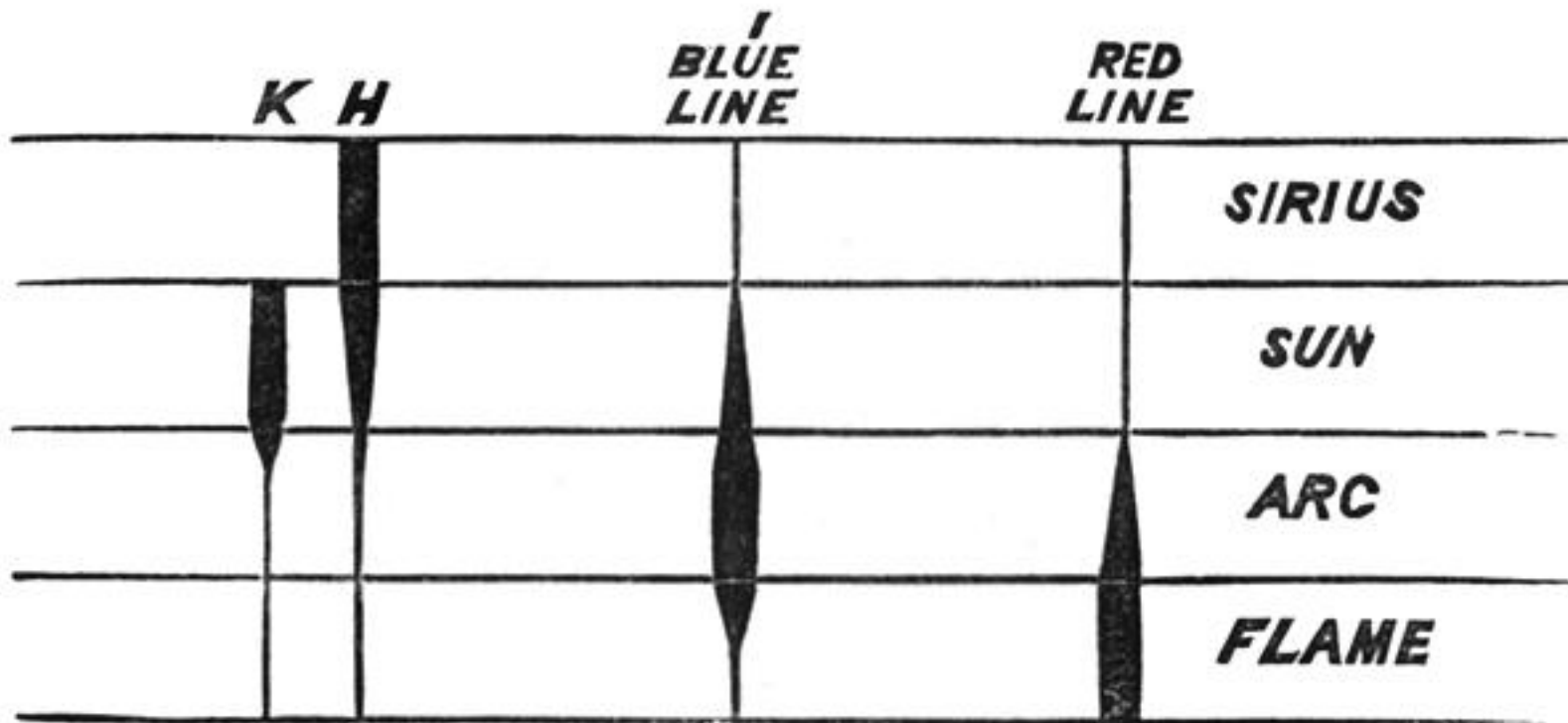


FIG. 5.

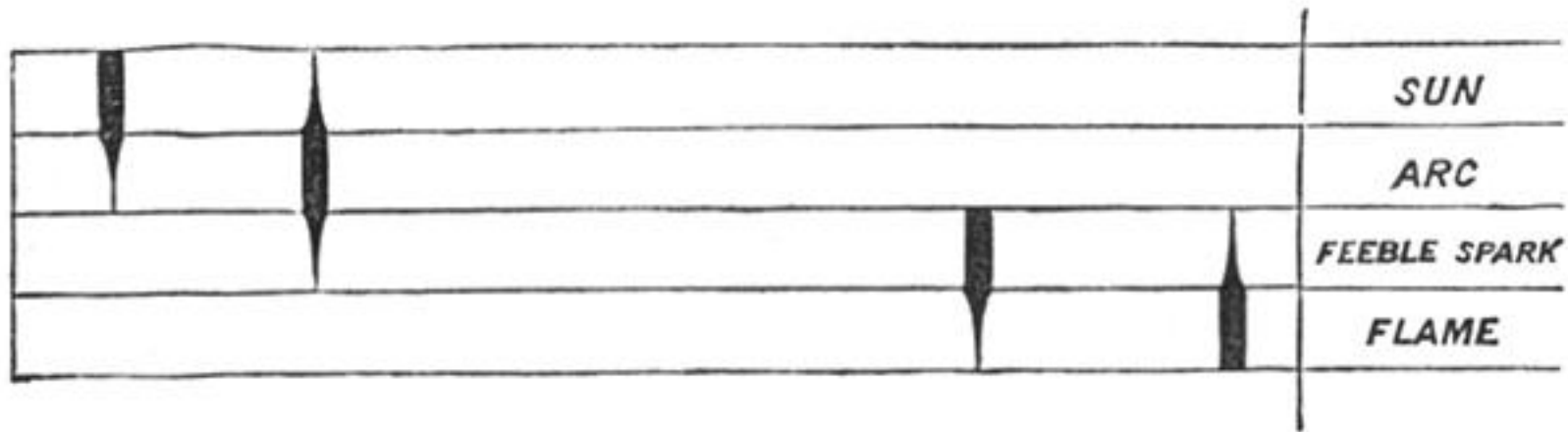


FIG. 6.

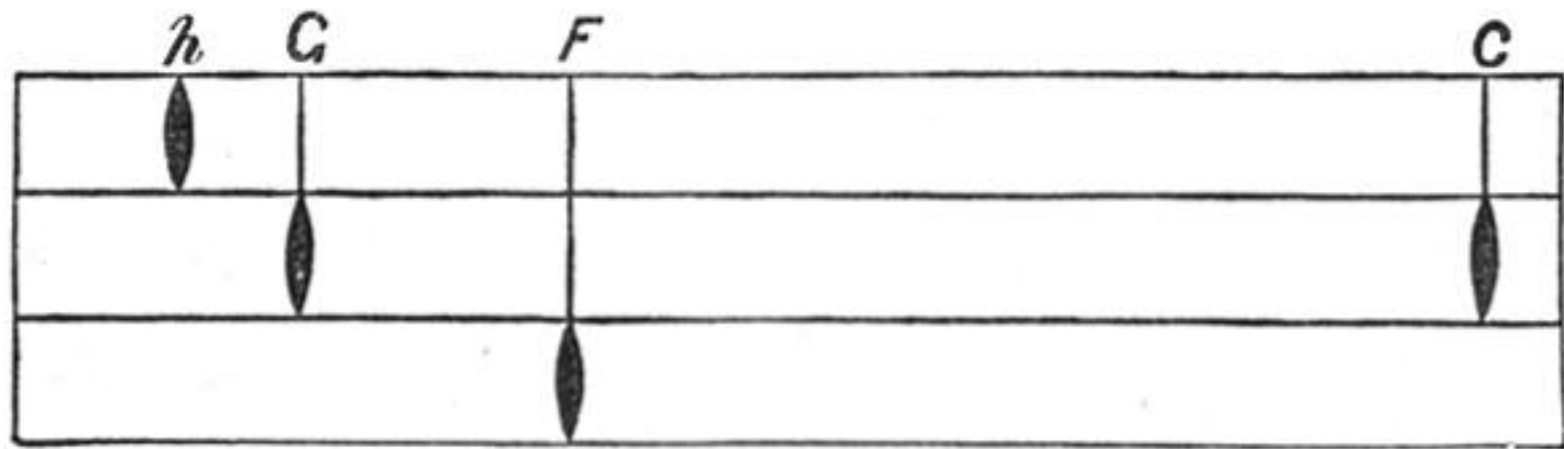


FIG. 7.

