

XXIX.—*On the Prismatic Spectra of the Flames of Compounds of Carbon and Hydrogen.* By WILLIAM SWAN, F.R.S.E.

(Read 21st April 1856.)

The phenomena presented by the prismatic spectra of flames have occupied the attention of many and excellent investigators. In most instances, however, no attempt has been made to procure accurate measurements of the positions of the bright lines which many of the spectra exhibit; and much in this field of observation, therefore, remains to be accomplished. I purpose, from time to time as I shall have leisure, to make a series of observations, whose object shall be the actual numerical determination of the positions of the bright lines in the spectra of flames; and I have commenced the series with an examination of the spectra of the flames of compounds of carbon and hydrogen. In an investigation into the phenomena of flames, the compounds of carbon and hydrogen claim our first attention, as constituting the most important means of artificial illumination; for it is scarcely necessary to remark, that, with the grand exception of sun-light, the combustion of these substances is the source of nearly all the light and heat from which we derive such extensive benefits in the arts and in domestic economy. It will be found, moreover, that the spectra of carbohydrogen flames possess, in common, remarkable features, which seem as yet to have received little attention, but which promise to be of service in explaining the general phenomena of artificial light.

If we examine the spectrum of the brightest part of the flame of an oil-lamp or a tallow-candle, it will be found that it exhibits no dark intervals, and that its colour and brightness vary gradually from point to point with scarcely any breach of continuity. If, however, we observe only the light proceeding from the blue part of the flame, which surrounds the upper part of the wick, a totally different result is obtained. The extreme red and violet rays become nearly or altogether invisible, and the intermediate portion of the spectrum exhibits a series of bright lines separated by dark intervals.* Similar lines occur in the flames of alcohol, sulphuric ether, and wood spirit. They are seen, however, with great difficulty in the flame of impure wood spirit, and are scarcely, if at all visible, in the more luminous flames of oil of turpentine and coal naphtha. Before offering an explanation of these differences, it will be necessary to premise some particulars regarding the nature of flame.

* For descriptions of lines in the spectrum of an oil lamp flame, see FRAUNHOFER, *Astronomische Abhandlungen*, 1823, p. 16; HERSCHEL, *Edin. Trans.*, vol. ix., p. 455, and article *Light*, *Encyc. Metrop.*, art. 522. The spectrum of the blowpipe cone is described by FRAUNHOFER, BREWSTER'S *Journal of Science*, vol. vii., p. 7; and by DRAPER, *Phil. Mag.*, vol. xxxii., p. 111.

On the Nature of Flame.

We owe to HOOKE, probably the first careful inquiry into the constitution of flame. More recently, the subject has been studied by Sir HUMPHRY DAVY and Professor DRAPER.*

The flame of coal gas or of a common candle, as is well known, consists of several portions, readily distinguishable by the eye, and in which the matter composing the flame exists in very different conditions. There is, first, the interior non-luminous portion, composed of gases not yet ignited; secondly, a blue conoidal shell, near the wick or burner, which, as it extends upwards, seems gradually to change its colour to a brilliant yellowish white; and, thirdly, an outer mantle or envelope of faintly luminous matter. On a careful examination, it will be found that the blue cone envelopes the white one; the blue, gradually thinning out towards the top, and the white, towards the bottom of the flame.

It has been supposed that, in the blue portion of the flame, the supply of oxygen is sufficient to insure the complete combustion of the gases, so that, in a carbohydrogen flame, there is the immediate production of water and carbonic acid.† The bright white light of the upper portions of the flame was proved by Sir HUMPHRY DAVY to proceed from the separation of solid carbon, which becomes brilliantly incandescent at the high temperature to which it is exposed, and which, when not converted into carbonic acid, escapes in the form of smoke.

The external mantle of the flame, according to Professor DRAPER, derives its light chiefly from incandescent carbonic acid and aqueous vapour.

While in the ordinary flames of coal gas and oil, solid carbon is separated, it is well known that by burning a mixture of gas and air, the separation of carbon may be entirely prevented, and a smokeless flame obtained. My attention was at first accidentally directed to the subject of this paper while using a species of gas lamp in which this object is effected in a very simple manner. As this lamp—the invention of Professor BUNSEN of Heidelberg—has only lately been introduced‡ into this country, and as I have made extensive use of it in my experiments, it may be proper to explain its construction.

It consists of a common “union” or “bat-wing” gas burner, which, when used in the ordinary manner, would produce a flat, fan shaped flame. The burner is surrounded by a brass tube, 0·4 inch in diameter, and about 3 inches in height, having apertures immediately below the burner, which can be opened or closed, so as to admit a regulated supply of air. The gas issuing from the burner in a fan shape strikes obliquely the walls of the tube, and being reflected from

* Works of Sir H. DAVY, vol. vi., Lond. 1840. DRAPER on the Production of Light by Chemical Action, Lond. Phil. Mag., 1848, vol. xxxii., p. 100.

† KANE'S Chemistry, p. 239.

‡ By Dr ROBERT FERGUSON, whose interesting account of the lamp will, I believe, appear in the Transactions of the Royal Scottish Society of Arts.

them, becomes effectually mixed with the air which enters at the bottom; and the mixture of gas and air, when lighted, burns at the top of the tube with a voluminous flame, without smoke. A thorough mingling of the gas and air is essential to the success of the arrangement, which will be found to fail when a plain burner is substituted for the "*union jet*."

The flame of the Bunsen lamp consists of at least two distinct portions,—a luminous hollow cone of a strong bluish green colour, about two inches in height, and a very diffuse outer mantle, about 6 inches in height, reddish towards the interior, but externally of a pale lavender tint. In this, also, as in the ordinary flame of coal gas, but in much greater profusion, there is a perpetual scintillation of yellow sparks, arising apparently from foreign matter suspended mechanically, partly in the gas, and probably more abundantly in the air which enters the tube and mingles with the gas before combustion. This matter is projected continually through the walls of the flame, where it becomes for a moment incandescent.*

The light of the exterior envelopes of flames, is, I conceive, chiefly due to the presence of minute particles of solid matter, derived partly from the substance undergoing combustion, and often, as in the case of the Bunsen lamp, from the air which enters the flame. The outer envelope of the flame of the Bunsen lamp possesses so little inherent luminosity, that it is peculiarly susceptible of having its colour influenced by the accidental presence of foreign matter. As the salts of sodium are well known to be remarkably energetic in producing homogeneous yellow light, I made the following experiment, in order to ascertain how small a portion of matter could in this way render its presence sensible.

One-tenth of a grain of common salt, carefully weighed in a balance indicating $\frac{1}{100}$ of a grain, was dissolved in 5000 grains of distilled water. Two perfectly similar slips of platinum foil were then carefully ignited by the Bunsen lamp, until they nearly ceased to tinge the flame with yellow light; for to obtain the total absence of yellow light is apparently impossible. One of the slips was dipped into the solution of salt, and the other into distilled water, the quantity of the solution of salt adhering to the slip, being considerably less than $\frac{1}{20}$ grain, and both slips were held over the lamp until the water had evaporated. They were then simultaneously introduced into opposite sides of the flame; when the slip which had been dipped into the solution of salt, invariably communicated to a considerable portion of the flame a bright yellow light, easily distinguishable from that caused by the slip which had been dipped into pure water. It is thus proved, that a portion of chloride of sodium, weighing less than $\frac{1}{1,000,000}$ of a grain is able

* If the air be *dusty* from any cause, these scintillations become very abundant. Thus, if the floor be swept, or a piece of charcoal be scraped with a knife at a little distance from the lamp, minute particles are carried by the current of air into the tube, and cause a profusion of sparks, which exhibit a very beautiful appearance, while they confirm the opinion that the ordinary sparks are occasioned chiefly by particles of dust carried by the air.

to tinge a flame with bright yellow light; and as the equivalent weights of sodium and chlorine are 23 and 35·5, it follows, that a quantity of sodium not exceeding $\frac{1}{2,500,000}$ of a troy grain renders its presence in a flame sensible. If it were possible to obtain a flame free of yellow light, independently of that caused by the salt introduced in the experiment, it is obvious that a greatly more minute portion of sodium could be shown to alter appreciably the colour of the flame. It therefore follows, that much caution is necessary in referring the phenomena of the spectrum of a flame to the chemical constitution of the body undergoing combustion. For the brightest line in the spectrum of the flame of a candle,—the yellow line R* of FRAUNHOFER,—can be produced in great brilliancy, by placing an excessively small portion of salt in a flame, in whose spectrum that line is faint or altogether absent. The question then arises, whether this line in the candle flame is due to the combustion of the carbon and hydrogen of which tallow is chiefly composed, or is caused by the minute traces of chloride of sodium contained in most animal matter. When indeed we consider the almost universal diffusion of the salts of sodium, and the remarkable energy with which they produce yellow light, it seems highly probable that the yellow line R, which appears in the spectra of almost all flames, is in every case due to the presence of minute quantities of sodium.

The view, which would attribute a great portion of the light of the envelopes of flames to the adventitious presence of minute traces of foreign matter, may possibly serve to explain certain anomalous diversities of colour which are observed in the envelopes of flames arising from the combustion of the same elements. Thus tallow, coal gas, anhydrous alcohol, and weak spirit of wine, all contain the same combustible substances, carbon and hydrogen: yet the envelope of the flame of a candle is bright yellow, that of a coal gas flame is purple, and those of strong alcohol and weak spirit differ greatly in luminosity.

It is important also to remark, that while the luminosity communicated to the exterior envelope of a flame by such substances as the salts of sodium or of copper, may be so great as to disguise that of the inner bright cone of the flame, or in some cases to render it altogether invisible; yet I have ascertained that the light of the blue portion of the flame, or of the inner cone, remains absolutely unchanged in colour and intensity. The proof of this curious property of flame will be given in the sequel.†

Prismatic Analysis of Flame.

Reserving, meantime, a more complete description of the apparatus I have employed, it may be sufficient to premise, that, in what I shall have to say regarding the spectra of flames, the object observed is supposed to be a narrow illuminated slit, viewed through a glass prism mounted before a telescope, which has been adjusted to focus on the slit.

* SCHUMACHER'S *Astronomische Abhandlungen*, 1823, p. 18.

† See p. 419.

It has already been stated, that certain carbohydrogen flames afford spectra exhibiting bright lines separated by dark spaces. In no spectrum are these lines more easily observed than in that of the Bunsen gas lamp. In order to distinguish the phenomena of the spectrum which are due to different portions of the flame, it is sufficient to place the lamp before a narrow vertical slit not exceeding 0.2 inch in *height*, through which its light passes to the prism.* If the lamp be gradually raised before the slit, the spectrum first seen will be derived exclusively from the envelope of the flame, which reaches high above the top of the interior cone. This spectrum is tolerably bright, extending without the least interruption, from the line C, nearly to the line H of FRAUNHOFER, and exhibiting no bright line whatever except the yellow line R. That line, however, is extremely flickering, so as often to disappear completely; and it seems due entirely to the yellow scintillations which abound in the exterior envelope. When the flame is raised still higher, so as to bring the top of the green cone into view, four other bright lines begin to appear; and as we continue to raise the flame so as to derive light from lower and lower portions of the flame, the bright lines become more and more clearly defined, owing to the intervening spaces becoming darker; and some fainter lines become visible. At length, when light passes through the slit only from the lowest portions of the flame where the exterior envelope nearly disappears, the bright lines become so sharply defined as to admit of their places being ascertained by actual measurement, with almost the same accuracy which is attainable in observations of the dark lines of the solar spectrum.

From the facility with which the lines of the carbohydrogen spectrum are obtained, I conceived they might be of use in optical researches; and I soon found them of great service in the prosecution of my experiments. I was, therefore, anxious to ascertain whether they belonged really to the gas flame, or were caused by the accidental presence of foreign matter; for it is well known that some metals, such as copper, when present in a flame, produce bright lines in its spectrum. For this purpose I burned a mixture of coal gas and air, successively, from an iron tube, a glass tube, a tube formed of a coil of platinum foil, and the brass tube of the Bunsen lamp; but in every case the lines remained unchanged in number and position, proving that they arose entirely from the combustion of the gas, and not from any matter derived from the lamp.

On the Apparent Diversity of the Spectra of Compounds of Carbon and Hydrogen.

Having thus studied the general phenomena of the spectra of carbohydrogen flames, some of which exhibit continuous, and others interrupted spectra, we may now resume the question, Whence do these differences arise?

It has been found by Professor DRAPER that an incandescent solid body emits

* Or we may adopt Professor DRAPER's ingenious mode of observing flames through a *horizontal* slit, Phil. Mag., vol. xxxii. p. 106.

light of every degree of refrangibility between limits varying with its temperature. Thus, when carbon burns in oxygen, or when a strip of platinum is heated, to a temperature of 2130° Fahr., by the passage of a current of electricity, a perfectly continuous spectrum is produced, without any bright lines or dark spaces, and extending at least from the line B to the line H of the solar spectrum.* This enables us to explain why we may see, in the spectrum formed by the blue portion of a flame, bright lines and dark spaces, which are totally invisible in the spectrum of the bright inner cone. For the light of the inner cone arises from incandescent solid carbon deposited in the flame, which, as we have just now seen, must produce a brilliant continuous spectrum. The light of this spectrum overpowers the comparatively faint illumination of the bright lines of the spectrum formed by the blue part of the flame, while it fills up the dark intervals between them; and both causes conspiring render the lines invisible. Again, lines may easily be seen in the spectrum of the blue part of a spirit lamp or candle flame, which fail to show themselves when we examine the flames of oil of turpentine or coal naphtha; for the latter bodies contain so much carbon that it begins to be deposited almost at the very bottom of the flame. The blue conoid is thus reduced to an extremely narrow ring; and it is practically impossible, however small the aperture through which light passes to the prism, to obtain the spectrum of the blue light separated from that of the incandescent carbon.

We can also similarly explain why lines may be visible in the spectrum of alcohol, which may not be easily seen in that of weak spirit of wine, or of impure wood spirit. The exterior envelope, like the interior bright cone, derives most of its light from incandescent solid matter, and produces a continuous spectrum, as was shown in the case of the Bunsen lamp. Now the exterior envelope of the flame of weak spirit of wine, or of wood spirit, is very voluminous and fully developed, and hence of unusual thickness near the bottom of the flame. The light derived from the incandescent matter it contains, will therefore operate precisely like that of the interior luminous cone, in rendering the bright lines of the spectrum invisible.

On Methods of Observing the Spectra of Carbohydrogen Flames.

Since the continuous spectra due to the light of incandescent matter offer no distinguishing features, it follows, that in searching for phenomena characteristic of the chemical constitution of bodies undergoing combustion, we must examine that part of the flame in which any solid molecules, which are being deposited, have not been able to collect into masses. This state of things exists in the blue portion of the carbohydrogen flames, where the supply of air is sufficient completely to consume the gases. In flames, such as that of oil of turpentine, $C_{10}H_8$, where there is much carbon, it becomes necessary to burn the carbon by an

* Phil. Mag., vol. xxx., p. 349.

artificial supply of air. Two methods occurred to me of effecting this object, so as to convert the carbon into carbonic acid, without its intermediate separation in a solid form. One was to burn the vapours of the substances under examination in the Bunsen lamp; but this I rejected as inconvenient, and perhaps even in some cases dangerous, from the risk of explosion, where it would have been necessary to boil highly volatile liquids in close vessels. The other was simply to pass a stream of air through the flame by means of a table blowpipe. By means of the latter expedient I succeeded so completely in preventing the separation of solid carbon, as to obtain spectra with bright lines and dark spaces, in the case of every compound of carbon and hydrogen which I have as yet submitted to examination.

Comparison of the Spectra of the Flames of various Substances containing Carbon and Hydrogen.

The hydrocarbon compounds which I have examined, and which are enumerated in the following table, may be divided into two classes; one consisting of substances containing only carbon and hydrogen, of which the general formula is $C_r H_s$, and the other of substances containing carbon, hydrogen, and oxygen, represented by the formula $C_r H_s O_t$.

$C_r H_s$		
Light carburetted hydrogen,	$C H_2$
Olefiant gas,	$C_2 H_2$
Paraffin,	$C_{20} H_{20}$
Oil of turpentine,	$C_{10} H_8$
$C_r H_s O_t$		
Methylic alcohol,	$C_2 H_4 O_2$
Alcohol,	$C_4 H_4 O_2$
Ether,	$C_4 H_5 O$
Methylic ether,	$C_2 H_3 O$
Glycerine,	$C_6 H_8 O_6$
Spermaceti,	$C_{64} H_{66} O_4$
Camphor,	$C_{10} H_8 O$
Wax,	} Of indefinite composition.
Tallow,	
Coal gas,	
Coal naphtha,	

Of these substances, the light carburetted hydrogen was made by heating acetate of soda, hydrate of potassa, and quicklime; and the methylic ether from wood spirit and sulphuric acid. The gases were generally burned from a platinum jet, immediately after passing through a tube filled with pieces of quicklime. The glycerine, a substance which burns with difficulty, was heated in a platinum capsule; and the paraffin, camphor, and spermaceti, which were colourless, crystalline, and apparently pure specimens, were also similarly treated, in order to corroborate the conclusion stated at p. 415, that the lines observed in the spectra were

all due to the combustion of the carbohydrogen compounds, and not to the presence of foreign matter. The alcohol, ether, and other liquids, were burned in lamps made of small phials,—a glass tube furnished with a cotton wick serving as a burner.

Taking the spectrum of the Bunsen lamp as a standard, the spectra of the other flames were compared with it, by viewing both simultaneously,—the light from the two flames passing through the same narrow slit.

The result of this comparison has been, that, in all the spectra produced by substances, either of the form $C_r H_s$, or of the form $C_r H_s O_t$, the bright lines have been identical. In some cases, indeed, certain of the very faint lines, which occur in the spectrum of the Bunsen lamp, were not seen. The brightness of the lines varies with the proportion of carbon to hydrogen in the substance which is burned, being greatest where there is most carbon. Thus, in the spectra of light carburetted hydrogen, pyroxylic spirit, and glycerine—substances which contain comparatively little carbon—certain of the fainter lines of the Bunsen lamp spectrum were not seen; but all those that *were* seen were identical with the lines of the coal-gas flame. I have no doubt that the fainter lines were really present, but were invisible, merely owing to their feeble luminosity; and this is rendered more probable by the fact that the number of lines visible in any spectrum varies with the brightness of the light. Thus in the solar spectrum, or in that of the Bunsen lamp, the fainter lines disappear when the intensity of the light is diminished.

The absolute identity which is thus shown to exist between the spectra of dissimilar carbohydrogen compounds is not a little remarkable. It proves, *1st*, that the position of the lines in the spectrum does not vary with the proportion of carbon and hydrogen in the burning body; as when we compare the spectra of light carburetted hydrogen, $C H_2$, olefiant gas, $C_2 H_2$, and oil of turpentine, $C_{10} H_8$; and, *2dly*, that the presence of oxygen does not alter the character of the spectrum; thus, ether, $C_4 H_5 O$, and wood spirit, $C_2 H_4 O_2$, give spectra which are identical with those of paraffin, $C_{20} H_{20}$, and oil of turpentine, $C_{10} H_8$.

In certain cases, at least, the mechanical admixture of other substances with the carbohydrogen compound does not affect the lines of the spectrum. Thus I have found that a mixture of alcohol and chloroform burns with a flame having a very luminous green envelope—an appearance characteristic of the presence of chlorine—and no lines are visible in the spectrum. When, however, the flame is urged by the blowpipe, the light of the envelope is diminished, and the ordinary lines of the hydrocarbon spectrum become visible.

Comparison of the Carbohydrogen and Solar Spectra.

Having ascertained, that probably all substances of the forms $C_r H_s$ and $C_r H_s O_t$ produce, when burning, spectra which are absolutely identical, I was desirous to compare their spectra with that of sun light.

For this purpose I at first attempted to view the solar spectrum and that of the Bunsen lamp simultaneously, but the great comparative faintness of the latter rendered that mode of comparison exceedingly difficult. I therefore determined to measure separately the minimum deviations for the principal lines of the solar and gas spectra; the intervals between the adjacent smaller lines of the latter spectrum being ascertained by means of a micrometer.

The instruments I employed were an excellent theodolite by ADIE, and a very fine flint-glass prism by SECRETAN of Paris, whose faces have an area of four square inches, and which shows, with great distinctness, the finest lines in FRAUNHOFER'S map of the solar spectrum. I am indebted for the use of these instruments to the kindness of Mr JOHN ADIE and Professor FORBES.

The prism being placed in its position of minimum deviation, the indices of refraction given in the sequel were calculated by the formula

$$\mu = \frac{\sin \frac{1}{2}(I + D)}{\sin \frac{1}{2} I};$$

where I is the angle of the prism, and D the deviation of the transmitted light.

I have denoted the five brightest lines of the carbohydrogen spectrum by the letters, $\alpha, \beta, \gamma, \delta, \zeta$; and the fainter lines by which they are accompanied by $\beta_1, \beta_2, \gamma_1$, &c. In the tables, $D_A, D_\gamma, \mu_A, \mu_\gamma$, &c., denote respectively the minimum deviation of the rays, and the index of refraction for the lines A and γ of the solar and flame spectra.

A comparative diagram of the spectra of sunlight and the hydrocarbon flames is given in Plate VIII., fig. 1, where α is the double yellow line R of FRAUNHOFER. I have thought it advisable to introduce this line in the diagram, as it is almost constantly visible in ordinary artificial light, although, for reasons already fully stated, I conceive it is not peculiar to the spectra of carbohydrogen compounds. This conclusion is strongly corroborated by the remarkable phenomena pointed out at p. 414, namely, that the salts of sodium tinge the exterior envelope of the Bunsen lamp flame with so brilliant a yellow light, as completely to overpower the comparatively feeble blue light of the inner cone, and to render it altogether invisible; while yet the light of that portion of the flame remains absolutely unchanged. This remarkable property of flame is easily demonstrated by holding a slip of platinum, with some salt placed on it, in the flame, while the spectrum is observed through a telescope. The instant the salt reaches the flame, the yellow line R or α , which before may have been extremely faint, or altogether

imperceptible, shines out in great brilliancy; while the lines β , γ , δ , and ζ remain totally unchanged in position, colour, and intensity.

While the line α is thus exceedingly variable in its brightness, the lines β , γ , δ , and ζ , on the other hand, are perfectly steady; and being never absent in carbohydrogen spectra, there is every reason to believe that they are really characteristic of the body undergoing combustion. Beyond α on the less refracted side there is a faint trace of red light, which, as it becomes so feeble as almost to disappear when the light is derived from the lowest point of the flame of the Bunsen lamp, is probably due to the exterior envelope of the flame, and not to the interior cone. The line α is separated from β by an extremely dark space, almost destitute of light. The line β is of a faint yellowish green colour, but well defined, and is accompanied by four almost equidistant lines β , β_2 , &c., which diminish in brightness as their distance from β increases. After another very dark interval, the extremely beautiful line γ follows, which is exceedingly brilliant, and of such absolutely definite refrangibility as, like α , to form a perfectly sharp image of the slit through which the light passes. Its colour is a fine slightly bluish or pea green, and it is accompanied by a fainter line γ_1 . The next line δ is the less refracted edge of a broad band of light containing four fine lines. This group, which is of a pale ashy colour, is separated by dark intervals from γ and ζ . The line ζ belongs to a brilliant but not very well defined band of a fine purple tint, which is accompanied by a fainter line ϵ .

I have completed observations of the minimum deviations for the lines α , β , γ , δ , and ζ ; and also for the principal lines of the solar spectrum, which are given in Series I, Tables II. and III., pp. 427, 428. From an examination of these tables it appears, that while several lines in the carbohydrogen spectrum coincide nearly in position with remarkable lines in the solar spectrum; yet in no case, if we except the line α , has the observed coincidence been exact. The observations, therefore, rather tend to prove that the *bright lines* of the carbohydrogen spectrum coincide, not with the *dark lines*, but with the *bright spaces* of the spectrum of sun light.

*Postscript added since the preceding Paper was read.**

From the well known coincidence discovered by FRAUNHOFER, to exist between the line R, in the spectrum of a lamp, and D of the solar spectrum, taken in connection with similar phenomena, which have since been observed, it might be inferred, as a general law of the spectra of flames, that their bright lines always coincide with dark lines of the solar spectrum.

The result of the investigations which have now been detailed, is obviously unfavourable to such a conclusion. In publishing observations bearing on a question of so much interest and importance, I was anxious, if possible, to leave no

* Printed by permission of the Council.

doubt as to their accuracy; and since the preceding paper was read, I have made a much more extensive series of experiments, than the limited time I can devote to such researches, had then enabled me to overtake, involving the determination, with more or less accuracy, of the positions of all the bright lines in the carbon-hydrogen spectrum, whose presence I have been able to detect. These experiments, with some account of my methods of observation, I have deemed it desirable to append to the preceding paper.

Methods of Observation.

The theodolite A, fig. 2, which was used in measuring the deviations of the refracted rays, has a limb 7·5 inches in diameter, with two verniers reading 10", and a telescope B, of 1·6 inch aperture, furnished with a parallel wire micrometer. The stage carrying the prism P, furnished with screws to render its faces perpendicular to the divided circle, was mounted over the centre of the theodolite; and, in order to avoid parallax, the object viewed was an extremely narrow slit placed in the principal focus of the object glass of a 30 inch telescope CL, which thus acted as a collimator.* The telescope rested in Ys, in a solid cast-iron stand, DD, which also carried the theodolite: so that the collimator preserved an invariable position in relation to the theodolite, notwithstanding any instability of the floor of the room in which the observations were made; and the zero of the circle was found to remain exceedingly constant. A diaphragm with a vertical slit was placed before the collimator lens, so as to limit the aperture in the plane of refraction to 0·4 inch, and thus to allow only a nearly central pencil of rays to fall on the prism. Any errors, which might have arisen, either from imperfect adjustment of the collimator to sidereal focus, or from defective aplanatism in its lens, were thus avoided as much as possible.

The deviations of the refracted rays were observed first to the right, and then to the left,—the prism being always adjusted to its position of minimum deviation,—so that the difference of the readings of the verniers in the two positions of the prism, gave double the minimum deviation of the refracted rays.

The angle of the prism was ascertained, by first turning it with its edge towards the object glass of the telescope, as represented in fig. 3, where ABC is the prism, and T the telescope. The stage carrying the prism was rigidly connected with the telescope, so that when the telescope was moved, the prism moved along with it; and being left undisturbed, the inclinations of its faces AB, AC, to the line of collimation of the telescope remained invariable. The telescope was then turned, until the image of the illuminated slit of the collimator, seen by reflection, successively in the two faces of the prism, was made to coincide with the telescope wires; and, at each intersection, the verniers were read off. The difference

* I have described this mode of observation in my paper on the Ordinary Refraction of Iceland Spar, Edin. Trans., vol. xvi.

of the readings then gave double the angle of the prism. For, if DGI, FHK represent the course of the reflected rays, since the telescope has been adjusted to sidereal focus, GI and HK, must be parallel; and the angle DEF, will obviously be double the angle BAC. Now, since DE and EF, are at the times of observation successively in the *same* direction, namely, that of the parallel rays emerging from the collimator, it follows that the telescope must have been turned through the angle DEF. Hence the difference of the readings is DEF, or twice BAC.

In order to test the adjustment of the collimator to sidereal focus, I made two series of observations of the angle of the prism given in Table I.; Series I. having been made by means of the collimator, and Series II. on a definite point of the tower of St Stephen's Church, distant about 2240 feet, where the parallax due to any difference in the directions of the rays incident on the two faces of the prism could not have caused an error exceeding 4" in the measured angle.

These results agree so closely as to show that any want of parallelism in the rays emerging from the collimator, arising from want of perfect adjustment to sidereal focus, could not have appreciably affected the observations of the absolute deviations of the refracted rays. I may also observe, that since, during the observations of the carbohydrogen and solar spectra, the whole apparatus remained unaltered, any want of parallelism in the rays incident on the prism, whether arising accidentally from imperfect adjustment of the collimator, or necessarily from the unavoidable want of perfect achromatism in its lens,—for either cause might modify the apparent direction of the observed object, if the pencil of rays incident on the prism were not accurately *central*,—would affect the observed deviations in the two spectra alike. The accuracy of the observations, viewed merely as affording a comparative view of the relative positions in the scale of refrangibility occupied by the lines in the two spectra, would thus remain entirely unimpaired.

I have ascertained, however, by actual experiment, that the observations of *absolute* deviation cannot have been sensibly affected by any want of achromatism in the lens of the collimator. Having caused the telescope wires to coincide accurately with the image of the collimator slit, I illuminated the slit alternately with the extreme red and the extreme violet rays of the solar spectrum formed by a flint-glass prism. I then found that the image of the slit did not in the slightest perceptible degree alter its apparent position; so that, while the illumination was changed from red to violet light, the wires continued to bisect the slit with perfect accuracy.

As the spectrum of the Bunsen lamp is so faint that the telescope wires, when projected on all but its brightest lines, are invisible, it became necessary to illuminate the wires; but I speedily found that, from the feeble luminosity of the spectrum, observations with an illuminated field were nearly impracticable, and I was therefore obliged to observe with illuminated wires on a dark field. The arrangement for illuminating the wires which I devised is so simple, and

proved so successful, that I venture to describe it, in the hope that it may prove useful in similar researches. A hole, a (see fig. 4), 0.1 inch in diameter, was drilled in the side of the tube in which the eye piece slides, at a point between the field lens of the eye piece and the wires w ; a small lamp, L , furnished with a condensing lens c , and a conical tube with a small aperture e , through which alone light was allowed to pass, was attached to the telescope, so that the light, indicated by $r r$, emerging from the conical tube, and entering the hole in the eye piece tube, crossed the axis of the telescope at an angle of about 70° , so as to illuminate the intersection of the wires at w , on the side *next* the eye, while all the rest of the field remained perfectly dark. By slightly varying the position of the lamp, the illumination of the wires could be adjusted with the utmost nicety to suit the brightness of that portion of the spectrum which was under examination.

Notwithstanding the most careful adjustment of the illumination of the wires, I still found the observation of the fainter lines of the carbohydrogen spectrum extremely difficult. The brightness of the lines in the spectrum of the Bunsen lamp is, however, considerably augmented by urging the flame by the blowpipe; and I found it useful to employ three jets placed one behind another, so that the combined illumination of three blowpipe cones might fall upon the prism. This apparatus, which is useful in exhibiting the fainter lines of the carbohydrogen spectrum, is easily constructed by forming three blowpipe jets of glass tube, about 0.2 inch in diameter, in the ordinary manner, and placing them, side by side, in a perforated cork. The cork is then inserted in a short piece of wide tube, having at its other end a second cork, connected with a flexible tube conveying a current of air from a table blowpipe.

I have also carefully compared, by simultaneous observations, the spectrum of the Bunsen lamp flame urged by a jet of oxygen gas, with the spectrum obtained by means of the triple air blowpipe. The lines in the two spectra were almost equally bright, and differed neither in number nor in position.

In the observations, Series I., Tables II. and III., I used an eye piece giving a magnifying power of 11, which was afterwards superseded by another magnifying 21 times, with which Series II. was made.

Comparison of the Carbohydrogen and Solar Spectra.

The second series of observations having been made with a higher magnifying power, and in some other respects also in more favourable circumstances than the first, is to be regarded as more trustworthy; yet the results of both agree so closely, that any additional accuracy which might have been obtained by ascertaining, separately, the probable errors of the two series, and their most probable result, when combined, could scarcely have repaid the labour of the necessary computation. I have, therefore, deemed it sufficient to give all the observa-

tions equal weight, and to take simply the arithmetical mean of the whole. The mean results of the two series, and the number of observations in each, being tabulated separately, the reader will be able to form some judgment regarding the probable accuracy of the final determinations obtained from the two series combined. In Fig. 1, which is a graphic construction of the observations in Tables II. and III., the lines were drawn by the engraver through points laid down by me on the copper to a scale,—adopted to suit the size of the plate,—of one inch to 2200". I have ascertained the errors in the positions of these lines to amount, in one case only to .01 inch (corresponding to 22"), and to be generally much less; so that the spectra are represented in the figure with tolerable fidelity.

In addition to the observations of the carbohydrogen and solar spectra contained in Table II., where the deviation for each line of either spectrum was separately determined by the theodolite or micrometer, I have also made simultaneous observations of the spectra of sun light and of olefiant gas. The gas, which was prepared by heating alcohol with sulphuric acid, was conducted through wash bottles containing caustic potash and sulphuric acid, to a gas holder; from which it afterwards passed, through a tube filled with pieces of quicklime, to a platinum jet where it was burned.

The lines in the spectrum of olefiant gas are very distinct, being well seen without using the blowpipe; but like the lines in the other carbohydrogen spectra, they are not sufficiently luminous to be seen when projected on the solar spectrum, unless the latter is made so faint, that its lines have disappeared. I succeeded, however, in observing the spectra simultaneously, by intercepting the sun light which fell upon one half of a narrow slit, and illuminating the whole slit with the flame of olefiant gas. The gas spectrum then appeared immediately over that of the sun, and the *brighter* lines in it were well seen, especially when the flame was urged by the blowpipe. The intervals between the lines of the gas spectrum and the nearest lines of the solar spectrum, given in Table V., were measured by the micrometer, with a magnifying power of 21; and the observations for the brighter line β , γ , and δ , agree well with those of Table III.

The line a was rarely visible in the spectrum of olefiant gas, and its appearance was only momentary, which confirms the opinion already stated, that it does not properly belong to the carbohydrogen spectra. To the proof already adduced in support of this opinion, I may here also add, that I have found it permanently absent in the flames of carbonic oxide, and of light carburetted hydrogen.* The continued invisibility of so brilliant a line of the spectrum, coupled with its

* I have found that the column of heated air rising from the flame of a spirit lamp with a salted wick, is most energetic in communicating yellow light to the exterior envelope of the flame of the Bunsen lamp. This effect is apparently confined to the outer, or oxidizing portion of the flame, where there is no excess of hydrogen, to decompose the chloride of sodium; and the experiment is interesting, as tending to prove that the yellow light may be caused by simple *incandescence*, without the actual *combustion* of sodium.

almost instantaneous appearance at very long intervals,—for it did occasionally appear for a moment,—satisfactorily proved it to be due merely to foreign matter which had accidentally entered the flame.

From an examination, either of Table IV., or of Plate VIII., fig. 1, it will be seen that certain of the lines in the carbohydrogen spectrum occupy nearly the same places in the scale of refrangibility with dark lines in the solar spectrum. These are the lines α , γ , δ_3 , and ζ , which coincide more or less exactly with the lines D, b_2 , F_1 , and G. The first of these coincidences has been long known, having been discovered by FRAUNHOFER;* and similar remarkable relations have been observed by Sir DAVID BREWSTER to exist between certain lines in the spectrum produced by “deflagrating nitre,” and the corresponding lines of the solar spectrum.†

From these singular coincidences occurring in so many different cases, the inference might be drawn, that *all* bright lines in the spectra of flames coincide with dark lines in the solar spectrum; and the extremely close proximity of the lines γ and b_2 , δ_3 and F_1 , ζ and G indicated in Table IV., might at first sight seem to confirm such an opinion. For it might be argued, that so close agreements in the ascertained deviations indicate absolute identity; the minute differences observed being attributed simply to errors in the observations. It will be seen, however, that the observed deviations of the lines b_2 and γ , differ by no less a quantity than $40''$, which is quite beyond the sum of the probable limits of error in the observations for these lines, which I have ascertained to be only about $5''$; and thus their coincidence is shown to be highly improbable.

But any remaining doubt on the subject is completely removed, by the simultaneous observations of the spectra of sun light and olefiant gas, given in Table V., where the micrometrical measurement of the interval between the lines b and γ differs only by $11''$ from that obtained by the theodolite observations. In fact, the bright line γ was *seen* when the spectra were viewed simultaneously, to coincide, not with the dark line b_2 , but with the clear space immediately beyond it. If we omit the line α , which, for reasons already fully stated, I do not regard as properly belonging to the carbohydrogen spectrum, not one of the other twelve lines which I have observed in that spectrum occurs near any conspicuous dark line of the solar spectrum, with the exception of the lines γ , δ_3 and ζ , which fall near b_2 , F_1 and G. Now, of these, γ has been proved beyond doubt, not to coincide with b_2 , but with a bright space in its vicinity; and from the simultaneous observation of the spectra of sun light and of olefiant gas, as well as from the results of the theodolite observations, I believe that the other *bright lines* of the carbohydrogen spectrum also coincide not with *dark lines*, but with *bright spaces* in the solar spectrum.

* SCHUMACHER'S *Astronomische Abhandlungen*, 1823, p. 29. See also BREWSTER'S *Edinburgh Journal of Science*, vol. viii., p. 7. M. FOUCAULT has lately verified this result with the double yellow line seen in the spectrum of the voltaic arc, between charcoal electrodes. See DE LA RIVE'S *Electricity*, vol. ii., p. 322.

† Report of British Association, 1842, p. 15.

From the fact just stated, that most of the lines in the carbohydrogen spectrum occupy positions where, in the solar spectrum, no conspicuous dark lines occur, direct comparison of the spectra, by simultaneous observation, seems almost impossible; for, before the fainter lines of the carbohydrogen spectrum become visible, the solar spectrum must be rendered so faint, that its finer lines have disappeared. On the other hand, to make a complete comparison of the spectra by actually measuring with the theodolite, the positions of the finest lines of the solar spectrum, would be a most formidable task. For when we consider that FRAUNHOFER has represented on his map of the solar spectrum, 350 lines, while Sir DAVID BREWSTER, by the aid of very excellent optical means, has observed the spectrum to be “divided into more than 2000 visible and easily recognized portions, separated from each other by lines more or less marked,”* it follows, allowing 5° for the angular dispersion of the extreme rays of the spectrum,—that the average interval between the lines observed by him is only $9''$. Extremely delicate theodolite measurements would therefore be required, in order to determine, whether or not any bright line of a flame spectrum was or was not coincident with one or other of the numerous small lines of the solar spectrum; and even where a coincidence was ascertained, it might be fairly attributed to chance, just as a binary star may be only optically, and not necessarily physically double.

In cases, however, where there is a remarkable analogous configuration of two groups of lines, accompanied by exact coincidence, as between the double lines α and D; and more especially where we actually view the striking phenomenon of the lines in the spectra optically superimposed, the impression of some physical connection between the two groups becomes irresistible.

The coincidence of γ , the most brilliant line of the carbohydrogen spectrum, with the clear space immediately beyond b_2 ,—the most refracted line of a group, which, whether we regard the singular configuration or the strength of the lines which compose it, is perhaps the most notable in the solar spectrum,—is a phenomenon which seems deserving of attention as probably indicating also some physical relation.

In conclusion, I may observe, that from the facility with which, by means of the Bunsen lamp, the carbohydrogen spectrum may be obtained, and from the definite and readily identifiable character of the lines which compose it, these lines may be useful in optical researches, where, from any cause, sun light cannot be employed. It will be seen, from Table IV., that, for most practical purposes, the lines α , γ , δ_3 , and ζ , may be assumed as identical with D, b_2 , F₁, and G of the solar spectrum; any error in the index of refraction calculated on that assumption, affecting only the fourth or fifth place of decimals.—*7th June.*

* Edinburgh Trans., vol. xii., p. 528.

TABLE I. *Observations of the Angle of the Prism.*

SERIES I.		SERIES II.		Total Number of Observations.	Mean of all the Observations.
Number of Observations.	Mean of the Observations.	Number of Observations.	Mean of the Observations.		
5	60° 0' 15"	3	60° 0' 18"	8	60° 0' 16"

TABLE II. *Observations of the Solar Spectrum.*

Line of Spectrum.	SERIES I.		SERIES II.		Difference of Means I. and II.	COLLECTED OBSERVATIONS OF MINIMUM DEVIATIONS.	
	Number of Observations.	Mean I.	Number of Observations.	Mean II.		Total Number of Observations.	Mean of all the Observations.
A	3	47° 20' 27"	3	47° 20' 21"	0' 6"	6	47° 20' 24"
<i>a</i>	2	47 29 54	4	47 30 2	0 8	6	47 29 59
B	2	47 39 52	3	47 39 51	0 1	5	47 39 51
C	2	47 50 22	3	47 50 10	0 12	5	47 50 12
C ₁ *	1	48 0 50	...	1	48 0 50
D	2	48 18 15	4	48 18 12	0 3	6	48 18 13
E	2	48 55 24	4	48 55 26	0 2	6	48 55 25
<i>b</i> †	4	49 1 45	5	49 1 44	0 1	9	49 1 45
<i>b</i> ₁	2	49 2 37	1	49 2 35	0 2	3	49 2 36
<i>b</i> ₂	2	49 2 55	3	49 2 56	0 1	5	49 2 55
F	2	49 29 9	3	49 29 19	0 10	5	49 29 15
F ₁ *	4	49 49 2	...	4	49 49 2
G	2	50 35 2	3	50 35 5	0 3	5	50 35 4
H	1	51 34 50	6	51 34 43	0 7	7	51 34 44
Mean Temp. of Prism, 53·3 F. Mean Barom. . . . 30·21		Mean Temp. of Prism, 64·2 F. Mean Temp. of Air, . . 62·5 Mean Barom. 29·98					

* C₁ and F₁ are used here to denote very strong lines adjacent to FRAUNHOFER'S lines, C and F.

† FRAUNHOFER denotes by *b* the two most refracted lines of a remarkable group, represented by three strong lines in his map of the solar spectrum. I have here denoted these lines by *b*, *b*₁, *b*₂, in the order of their refrangibility. On 20th May, about 7^h 10^m P.M., when the sun was rather low in the horizon, but free from clouds, I observed with a power of 21, the line *b*₂ to be very finely but distinctly double, so that the group consists of four lines.

TABLE III. *Observations of the Carbohydrogen Spectrum.*

Line of the Spectrum.	SERIES I.		SERIES II.		Difference of Means I. and II.	COLLECTED OBSERVATIONS OF MINIMUM DEVIATIONS.	
	Number of Observations.	Mean I.	Number of Observations.	Mean II.		Total Number of Observations.	Mean of all the Observations.
α	5	48° 18' 14"	2	48° 18' 13"	0' 1"	7	48° 18' 14"
β	3	48 32 9	6	48 32 7	0 2	9	48 32 7
β_1	9	48 35 12		9	48 35 12
β_2	9	48 37 50		9	48 37 50
β_3	9	48 40 10		9	48 40 10
γ	9	49 3 35	4	49 3 31	0 4	13	49 3 34
γ_1	9	49 6 23			
δ	2	49 41 58	6	49 41 58	0 0	8	49 41 58
δ_1	9	49 44 48		9	49 44 8
δ_2	9	49 46 37		9	49 46 37
δ_3	9	49 48 41		9	49 48 41
ϵ	4	50 27 54		4	50 27 54
ζ	3	50 35 37	6	50 35 28	0 9	9	50 35 33
Mean Temp. of Prism, 53° F.		Mean Temp. of Prism, 62.6 F.					
Mean Barom., . . . 30.02		Mean Temp. of Air, 60.4					
		Mean Barom. . . 29.56					

In Table III., the deviations of the lines α , β , γ , δ , and ζ , were alone determined by the theodolite; the other lines were then referred to α , β , &c., by micrometer observations.

TABLE IV. *Comparison of Contiguous Lines in the Solar and Carbohydrogen Spectra.*

SOLAR SPECTRUM.			CARBOHYDROGEN SPECTRUM.						
Line.	Deviation (D.)	Index of Refraction (μ .)	Line.	Deviation (D.)	Index of Refraction (μ .)				
D	48° 18' 13"	1.621079	α	48° 18' 14"	1.621083	$D_\alpha - D_D$	0' 1"	$\mu_\alpha - \mu$	0.000004
b_2	49 2 55	1.628659	γ	49 3 34	1.628769	$D_\gamma - D_{b_2}$	0 39	$\mu_\gamma - \mu_{b_2}$	0.000110
F_1	49 49 2	1.636407	δ_3	49 48 41	1.636349	$D_{F_1} - D_{\delta_3}$	0 21	$\mu_{F_1} - \mu_{\delta_3}$	0.000058
G	50 35 4	1.644068	ζ	50 35 28	1.644147	$D_\zeta - D_G$	0 24	$\mu_\zeta - \mu_G$	0.000079

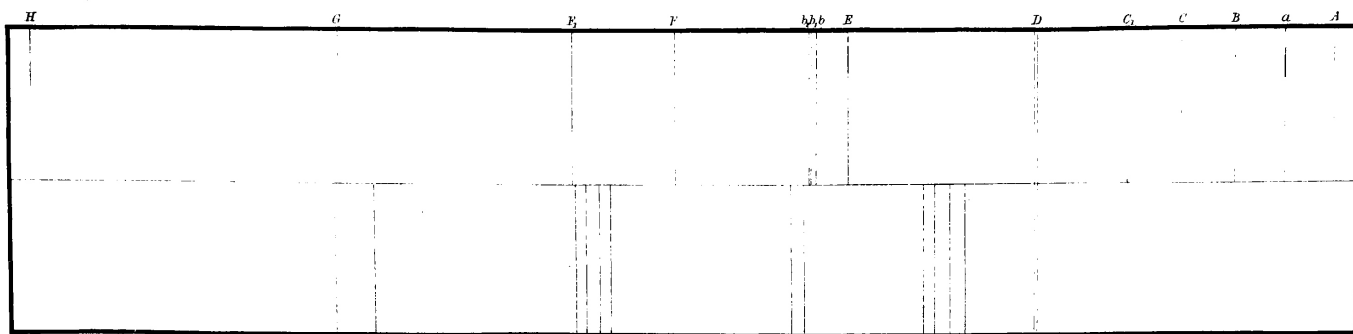
TABLE V. *Observations on the Spectrum of Olefiant Gas.*

Minimum Deviations for Lines in Solar Spectrum, from Table II.		Intervals between Lines in the Solar and Gas Spectra, measured by the Micrometer.			Minimum Deviations.	
			No. of Observations.			
D_D	48° 18' 13"	$D_\beta - D_D$	4	14' 10"	D_β	48° 32' 23"
		$D_{\beta_1} - D_D$	4	17 10	D_{β_1}	48 35 23
		$D_{\beta_2} - D_D$	3	19 58	D_{β_2}	48 38 24
		$D_{\beta_3} - D_D$	3	22 37	D_{β_3}	48 40 50
D_b	49 1 45	$D_\gamma - D_b$	3	1 38	D_γ	49 3 23
		$D_{\gamma_1} - D_b$	3	4 33	D_{γ_1}	49 6 18
D_F	49 29 15	$D_\delta - D_F$	3	12 44	D_δ	49 41 59
		$D_{\delta_3} - D_F$	1	20 29	D_{δ_3}	49 49 44

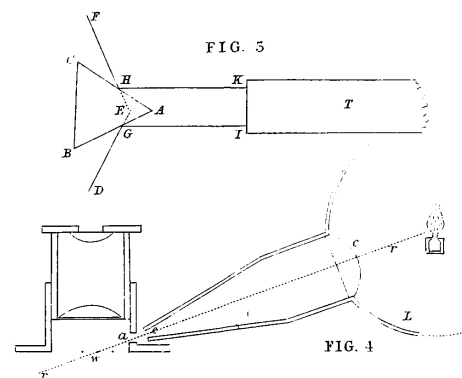
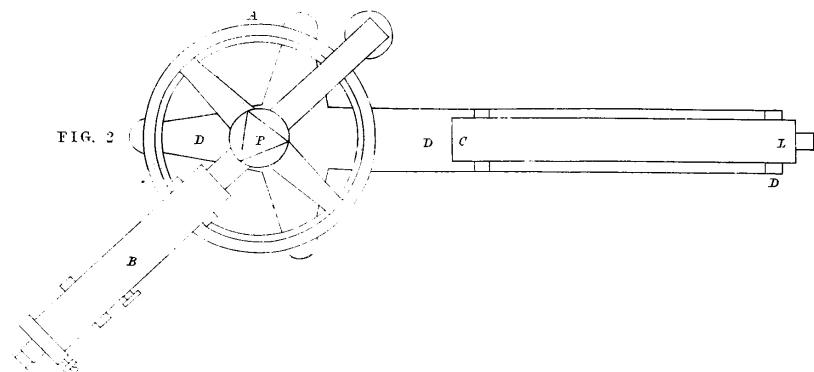
Solar Spectrum

M^r Swan's observations of the Carbohydrogen Spectrum.

FIG. 1



Carbohydrogen Spectrum



M^r PONTON'S PHOTOMETER.

FIG. 1 1/2 size

FIG. 2 1/2 size

FIG. 3

FIG. 3

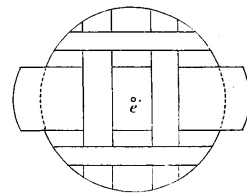
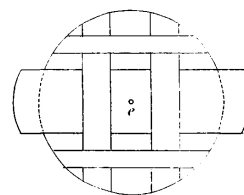
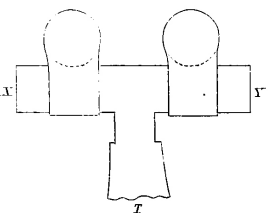
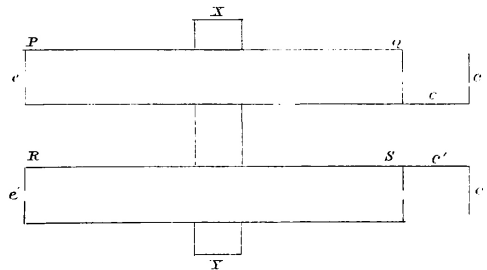


FIG. 6

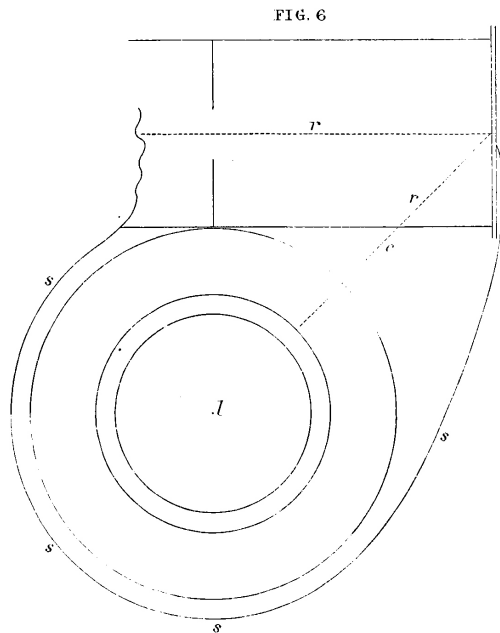
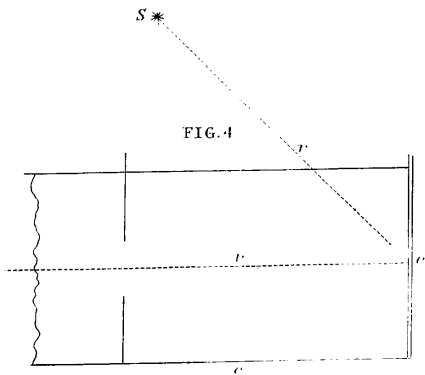


FIG. 5

