XXXV. *Photo-chemical Researches.*—Part IV.

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The measureless store of energy which Nature has amassed in the sun's body flows in an unceasing current as solar rays throughout the universe.

The labour expended on the earth's surface in the maintenance of the animal and vegetable creation, and in the production of geological change, is derived, almost exclusively, from this source.

Those of the sun's rays which vibrate most slowly, and form the red portion of the solar spectrum, including the rays visible and invisible which surround them, give rise by their absorption, more especially to the thermic actions observed on the surface of the earth, and in both the fluid zones which as ocean and atmosphere encircle the solid crust of our planet. These rays constitute the sources of heat which, in those grand processes of distillation and atmospheric deposit, have effected those vast transformations of the earth's crust, by the study of which we obtain some idea of the immensity of the sun's action exerted during geological ages upon our globe.

Of a totally different kind, on a scale less magnificent, but not less important, are the effects mainly produced by the more highly refrangible and more rapidly vibrating portions of the solar rays. These rays exert the most marked influence upon the chemical changes on which the vegetable world depends; and are therefore of the greatest importance as regards the character and geographical distribution of organic nature.

Although the atmospheric phenomena regulating the amount and distribution of the chemical action of light on the earth's surface have not as yet been systematized to the same extent as the thermic, electrical, and magnetic phenomena of meteorology, the reason is not so much that their importance has been overlooked, as that the difficulties which surround an exact investigation of the subject have up to the present time proved insurmountable. If in the following research we have attempted to clear a path towards this new field of meteorological inquiry, we trust that these acknowledged difficulties may in some degree prove an excuse for the many failings which our investigation presents.

All experiments on the above subject can be of no value until some method has been discovered for expressing the chemical action of light in terms of some general and comparable measure. To this point, therefore, we were first obliged to direct our attention.

I. COMPARATIVE AND ABSOLUTE MEASUREMENT OF THE CHEMICAL RAYS.

In all photometric measurements, whether made with the eye, or by means of thermic, thermo-electric, or chemical agencies, the great difficulty has been to obtain a convenient constant source of light.

The flames of ordinary candles or lamps are subject to variation in their optical and chemical illuminating power, such as to prevent their being employed when any great degree of accuracy is required. The intensity of the light evolved by a wire heated to whiteness between the poles of a constant battery is also extremely variable, as an imperceptible alteration in the quantity of circulating electricity effects a considerable change in the luminosity of the incandescent wire. These difficulties are, however, overcome when a flame is employed which is fed by a current of gas issuing with uniform velocity. Olefiant gas cannot be advantageously used for the production of such normal flames, not only on account of the difficulty of preparing large quantities of this gas in a state of purity, but also because on combustion it suffers very complicated decompositions. Carbonic oxide, on the other hand, burns without elimination of carbon, does not undergo other secondary decompositions, and forms one product of combustion, namely, carbonic acid. In other respects too, especially on account of the considerable chemical action which it effects, as also from the ease with which it can be prepared in a state of purity from the salts of formic acid, the flame of carbonic oxide is particularly well adapted for absolute photo-chemical measurements.

The amount of light radiating from a flame does not merely depend on the mass and constitution of the illuminating material, but is often even more influenced by the particular circumstances under which the combustion is effected. We have therefore been obliged to determine, more accurately than we had previously done*, the conditions most favourable to the constant evolution of light from flames of various kinds. The flames formed by the combustion in free air of gases issuing from small openings under a pressure of even only a few millimetres of water, are subject to such changes in form and temperature, arising from the production of lateral currents of air, that they cannot be employed as constant sources of light. When, however, the pressure under which the gas issues differs but very slightly from that of the atmosphere, the flame assumes a perfectly constant form. In the following experiments the rate at which the gas issued from the burner during the combustion of the carbonic oxide, which formed our constant source of light, was only 129·9 millimetres in the second. By means of the formula for the rate of issue of gases, not regarding the friction, which in this case is very small, we have calculated the amount of the difference of pressure which forces the gas out, and found it to be equal to a column of water of 0·001 millimetre in height. When the gas issues under so slight a pressure, and burns from an opening of several millimetres in diameter, placed in the blackened tin box which we have formerly described†, the flame assumes the form of a very obtuse cone and burns perfectly steadily.

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* Philosophical Transactions, 1857, p. 374.

† Ibid. p. 375.

The flame of carbonic oxide, upon which all our measurements are founded, issued from a circular platinum burner 7 millimetres in diameter. The normal velocity with which the gas issued, was taken to be such that 5 cubic centimetres of gas, at 0° C. and 0·76 pressure, passed through the burner in 1 second of time. As, however, it was practically impossible so to regulate the supply of gas that it should issue exactly at the required rate, we were obliged to determine, first of all, the relation existing between the supply of gas and the luminosity of the flame. This determination we have made, by means of photo-chemical measurement, for velocities of issue lying near the standard rate of 5 cubic centimetres per second. The carbonic oxide used for these experiments was prepared by the action of sulphuric acid on pure formiate of soda, and after being washed with potash, was collected in a large gasometer, previously calibrated, in which the volume of gas could at any moment be read off, and the temperature and pressure observed by means of a thermometer and manometer. The insolation-vessel of our chemical photometer was placed at a distance of 176 millims. from the flame. The gas contained in the gasometer under a constant pressure of $0^{m}\cdot 8$ of mercury, passed through a very narrow stopcock into the wide tube on which the burner was placed, so that when the gas issued from the burner the excess of pressure over that of the atmosphere, measured by a small manometer, amounted to a column of water a very small fraction of a millimetre in height.

The actual observations which are thrown together in the annexed Table, were made in the following manner. One observer at fixed intervals read off the chemical action of the flame as seen on the index of the instrument, whilst another noted the volume of gas contained in the gasometer before and after the experiment, as also the temperature and pressure.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII. *g*.	VIII. *w*.
			m	°			
1	3	5342·7 4274·2	0·8230 0·8244	20·0 C. 20·0 C.	41·8	5·950	13·932
2	6	3907·3 2237·9	0·8254 0·8280	20·0 C. 20·0 C.	56·7	4·673	9·450
3	5	6596·7 5439·5	0·8179 0·8195	19·5 C. 19·5 C.	34·0	3·839	6·799
4	10	8600·8 6762·1	0·8199 0·8219	20·0 C. 20·0 C.	41·5	3·053	4·152

Column I. gives the number of the experiment; column II. the duration of the experiment in minutes; column III. the volume of gas, in cubic centimetres, contained in the gasometer before and after the experiment; columns IV. and V. the observed pressure and temperature; column VI. the chemical action effected during the experiment, read off on the scale of the instrument; column VII. the volume (*g*) of carbonic oxide, reduced to 0° and 0·76, which issued in one second; and, lastly, in column VIII. the chemical action (*w*) effected in one minute expressed in divisions of the photometer-scale.

The observed action (w) does not, however, express the total action of the carbonic oxide flame, for between the burner and the sensitive gas several screens were placed. The light had to pass, in the first place, through the water-screen, then through two plates of mica, and also through the glass sides of the insolation-vessel before it reached the mixture of chlorine and hydrogen. Hence in order to find what the action would have been if the light had not been diminished by passing through these screens, we must multiply these values of w by a constant dependent on the absorbent character of these media. This constant, which we will call K, is made up of three parts:—

1. The diminution which the light suffers in passing through the mica-plates $=$L.
2. The diminution the light suffers by passing through the water-screen $=$M.
3. The light lost by reflexion from the surfaces of the insolation-vessel $=$N.

The value of L is easily found from the coefficient of reflexion for mica, which we have already determined*. From the experimental number $\varrho=0{\cdot}1011$, the value of $L=1{\cdot}450$ is found from the equation $L=\frac{1+3\varrho}{1-\varrho}$. We determined the value of M by observing, twelve times successively, the action effected in 30 seconds by a constant gas flame, the water-screen being alternately placed before the flame and removed. The following Table contains the results of these observations:—

TABLE II.

No.	Action without screen.	Action with screen.
1	12·69	9·25
2	12·85	9·59
3	12·46	9·81
4	12·31	9·59
5	13·47	9·00
Mean ...	12·76	9·45

By dividing the numbers in the second column by the corresponding numbers in the third, the mean value of $M=1{\cdot}351$ is obtained.

The value of N is arrived at by help of the following considerations:—Let A A_2 (fig. 1, Plate XLIII.) represent the surface of the insolation-vessel nearest the flame, and B B_1 that furthest from the flame. The space between these two surfaces being supposed to be filled with sensitive gas, let 1 represent the intensity of the light falling perpendicularly on the insolation-vessel; and let $r=\frac{2\varrho}{1+\varrho}$ represent the amount of light reflected from both surfaces of the side A A_2 of the insolation-vessel, when ϱ is the coefficient of reflexion for glass and air; and let $\gamma=10^{-\alpha h}$ represent the amount of light remaining after passing from A to $B=h$, when α represents the coefficient of extinction of the chlorine and hydrogen gas; and lastly, let $d=1-\frac{2\varrho}{1+\varrho}$ represent the

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* Philosophical Transactions, 1857, p. 609.

intensity of the original unit amount of light after having passed through the side $A\,A_2$ of the insolation-vessel. For the sake of clearness, we have represented the rays of light, which are in reality reflected perpendicularly from the surface $B\,B_1$, by the lines AB, BA_1, A_1B_1, &c. At these several points the unit quantity of light falling on the insolation-vessel has the following intensities:—

At A in the line AB the intensity is d.
At B in the line BA the intensity is $d\gamma$.
At B in the line BA_1 the intensity is $d\gamma r$.
At A_1 in the line BA_1 the intensity is $d\gamma^2 r$.
At A_1 in the line A_1B_1 the intensity is $d\gamma^2 r^2$.
At B_1 in the line A_1B_1 the intensity is $d\gamma^3 r^2$.
At B_1 in the line B_1A_2 the intensity is $d\gamma^3 r^3$.
At A_2 in the line B_1A_2 the intensity is $d\gamma^4 r^3$.
&c.

Hence the chemical action proportional to these various intensities is found to be

$d\beta$ in the line AB.
$d\gamma r\beta$ in the line BA_1.
$d\gamma^2 r^2\beta$ in the line A_1B_1.
$d\gamma^3 r^3\beta$ in the line B_1A_2.

The sum of these actions is, however,

$$d\beta(1+\gamma r+\gamma^2 r^2+\gamma^3 r^3+\cdots\cdots)=\frac{d\beta}{1-\gamma r},$$

or, as $d=1-r$, we have $$\frac{1-r}{1-\gamma r}\cdot\beta.$$

We can therefore eliminate the error arising from the infinite number of reflexions which the light suffers in the interior of the insolation-vessel, by multiplying the action, as read off on the scale of the instrument, by the factor

$$\frac{1-\gamma r}{1-r}=\mathrm{N}. \quad \ldots\ldots\ldots\ldots \quad (1.)$$

The numbers thus obtained represent the amount of photo-chemical action which would have been observed if the sensitive gas had not been surrounded by a reflecting medium.

In the third part of our researches* we determined the value of $\varrho=0{\cdot}0509$ and $\alpha=0{\cdot}00427$ for the flame of coal-gas; $\alpha_1=0{\cdot}0136$ for the diffuse cloudless zenith light of morning; and $\alpha_2=0{\cdot}0174$ for the cloudless zenith light of evening. The depth of the insolation-vessel was $h=9{\cdot}4$ millims. When these values are substituted in formula (1.),

N is found to be equal to 1·010 for a coal-gas flame;
N is found to be equal to 1·028 for morning zenith light of an unclouded sky;
N is found to be equal to 1·034 for evening zenith light of an unclouded sky;

and if we take the mean of these closely agreeing numbers, $\mathrm{N}=1{\cdot}024$, as representing the loss by reflexion of the flame of carbonic oxide, we have, as the value of the product L, M, N, $$\mathrm{K}=2{\cdot}005.$$

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* Philosophical Transactions, 1857, p. 605, &c.

The numbers contained in column VIII. of Table I. must therefore be multiplied by this constant, 2·005, in order to obtain the action (w_1) which the flame would have produced if no loss of light from mica-plates, water-screen, or by reflexion from the insolation-vessel had occurred. The following numbers give the values of w_1, the normal action effected when the gas issued at the corresponding rates g:—

g.	w_1.
5·950	27·86
4·673	18·90
3·839	13·60
3·053	8·30

If the values of A, B, and C are calculated from the above values of g and w_1 in the following series of powers of $(5-g)$,

$$w_1 = A + B(5-g) + C(5-g)^2 + \cdots,$$

it is seen that the value of C is so small, that the third term $C(5-g)^2$ may be struck out. The values of A and B, calculated according to the method of least squares, give the following simple equation,

$$w_1 = 21{\cdot}34\{1 - 0{\cdot}3153(5-g)\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

From this it is seen that, although the rates at which the gas issues differ considerably, the increase in the action effected by the flame is, within the observed limits, directly proportional to the increase in the rate of issue of the gas. The straight line (fig. 2, Plate XLIV.) shows how closely the observations agree with this assumption. The abscissæ represent the volumes (in cub. cent.) of carbonic oxide, measured at 0° and $0^{m}{\cdot}76$, which escaped from the burner in one second; and the ordinates give the corresponding chemical actions observed in divisions of the instrument in one minute, when the distance from the burner to the insolation-vessel was 176 millims. The observations are denoted in the figure by black dots on or near the line.

By means of the foregoing equation (2.) it is easy to calculate, from the chemical action observed for any particular rate of issue of the gas lying between 3 and 6 cub. cent. per second, what the chemical action would have been if the gas had issued at the rate $g=5$ instead of at the observed rate, other circumstances remaining of course the same.

The standard flame which we employ to compare all the sources of light we have to measure may be thus defined:—"*The standard flame is that produced by the free combustion in atmospheric air of carbonic oxide gas issuing at the rate of* 5 *cub. cent. per second* (*reduced to* 0° *and* $0^{m}{\cdot}76$) *from a circular platinum burner* 7 *millims. in diameter, under a pressure differing but very slightly from that of the atmosphere.*"

By means of the standard flame we are enabled to reduce the indications of different instruments to the same unit of luminous intensity, and thus to render them comparable. For this purpose we define the photometric unit for the chemically active rays to be that amount of action which is produced in one minute by a standard flame placed at a distance of 1 metre; and we determine experimentally for each instrument the number of such units (n) which correspond to one division on the observation-tube. By multiplying the observed number of divisions (t) by the number of photometric units (n) equal to one division, the observations are reduced to a comparable standard, whose unit is taken to be the amount of action which a standard flame at the distance of one metre effects on the normal mixture of chlorine and hydrogen in one minute, when the depth of insolated gas is so small that the alteration of the value of the coefficient of absorption for different sources of light becomes inappreciable.

We call this unit a chemical unit of light, and ten thousand of these units, one chemical degree of light.

In the following experiments we have always employed the same insolation-vessel, but two observation-tubes. On one of the observation-tubes, or scales, which we shall henceforward call "the narrow," or "No. 1 scale," one division corresponded to $n=0{\cdot}6612$; on the wide, or "No. 2. scale," one division corresponded to $n=2{\cdot}249$. One division on the narrow scale had a capacity of 0·7642 cubic millimetres; one division on the wide scale contained 2·598 cubic millimetres.

A few examples will best explain the use of this measure of light.

1. By *Chemical Illumination* we signify that amount of chemically active light which falls perpendicularly on a plane surface. If the insolation-vessel of our instrument be supposed to form a part of this plane, the number of divisions on the scale which the index has passed in one minute, multiplied by n, expresses the number of units of light to which that plane is illuminated. As an example of this kind, we will determine, for two different sources of light, the distance at which they must be placed, in order that a given surface may be illuminated with one degree of light. We chose as the sources of light flames of carbonic oxide and coal-gas, which were each fed with gas at the rate of 4·105 cub. cent., at 0° and $0^{\mathrm{m}}{\cdot}76$ per second. The carbonic oxide issued from the large platinum burner, the coal-gas from an ordinary burner, and both gases were expelled from the burners under a pressure but very slightly exceeding that of the atmosphere. The rays from both flames had to pass through two plates of mica and a water-screen; the narrow scale, No. 1, was employed in these experiments. The carbonic oxide flame, placed at a distance of $0^{\mathrm{m}}{\cdot}176$ from the insolation-vessel, produced an action of 7·68 divisions in one minute. This corresponds to $\mathrm{K}n.7{\cdot}68=10{\cdot}15$ degrees of light. As the amount of illumination is inversely proportional to the square of the distance from the source of light to the illuminated surface, the distance (r) at which the source of light must be placed in order that the surface may be illuminated one degree, is found to be

$$r=\sqrt{0{\cdot}176^2.10{\cdot}15}=0{\cdot}5607 \text{ metre.}$$

The flame of coal-gas, burnt under the same conditions, gave at a distance of $0^{\mathrm{m}}{\cdot}216$ from the insolation-vessel an action of 13·98 divisions in the minute, corresponding to $\mathrm{K}.n.13{\cdot}98=18{\cdot}48$ degrees of light. This flame accordingly effects a chemical illumination of one degree at a distance equal to

$$r=\sqrt{0{\cdot}216^2\times 18{\cdot}48}=0{\cdot}9287 \text{ metre.}$$

In like manner it is found that when the carbonic oxide flame is removed to a distance of $0^{m}\cdot 3349$, and the coal-gas flame to a distance of $0^{m}\cdot 4309$, the surface is chemically illuminated by 5 units of light.

2. *The chemical illuminating power*, or the chemical intensity of various sources of light which may be considered as luminous points, is measured by the chemical action effected by the rays emanating from such sources in equal times and at equal distances. As, however, in the case of such sources of light, the chemical illuminating power is directly proportional to the square of the distances at which an equal amount of chemical illumination is obtained, and as the standard flame produces an illumination of one unit of light at a distance of 1 metre, we have, in order to compare the chemical illuminating power of any luminous source of the kind described, with the unit of chemical light of the standard flame, only to take the square of the distance at which the luminous source in question produces the illumination of one unit of light. If we carry out this calculation for the three flames already mentioned, we find that the chemical intensities of the standard flame, the carbonic oxide flame of the above dimensions, and the coal-gas flame, are respectively represented by the numbers

1, 0·718, and 1·972.

It is of some interest to compare the chemical with the visual[*] illuminating power of these different flames. For this purpose we have compared the visual illumination produced by the carbonic oxide flame burning under the prescribed conditions, and issuing at the rate of 6·032 cub. cent. per second, with that of the flame of coal-gas above described. Although these photometric measurements could not be made very exactly, owing to the different colour of the two flames, we were nevertheless able to assure ourselves that a coal-gas flame, burning at the rate of 4·105 per second, produced a visual illumination of *at least* 150 times as great an intensity as the carbonic oxide flame, burning at the rate of 6·032 cub. cent.

The chemical illuminating powers of flames of carbonic oxide issuing at the rate of 5 cub. cent., 6·032 cub. cent., and 4·105 cub. cent. in the second, are found from formula (2.) to be in the relation of 21·34, 28·28, and 15·32. As in one and the same source of light the chemical and visual intensities are proportional, the visual intensities of these three flames are to the visual intensity of the coal-gas flame, issuing at the rate of 4·105 cub. cent., as 21·34, 28·28, and 15·32, to 42·42. Hence we have

	Visual intensity.	Chemical intensity.
Flame of carbonic oxide issuing at rate of 5 cub. cent. per second	1·000	1·000
Flame of carbonic oxide issuing at rate of 4·105 cub. cent. per second	0·718	0·718
Flame of coal-gas issuing at rate of 4·105 cub. cent. per second	198·800	1·972

From this we see that the visual illuminating power of the above coal-gas flame is nearly 200 times as large as that of the normal carbonic oxide flame, whereas the chemical illuminating power of the same is not double that of the normal flame; and hence

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[*] By "visual" illuminating power we intend to signify the luminous intensity as measured by its effect on the eye.

we conclude that, in the case of different luminous sources, the amount of light received by the eye in no degree serves as a measure of the chemical action which the light can effect.

3. *Chemical Brightness.*—The amount of light measured photo-chemically which falls perpendicularly from a luminous surface upon a physical point, divided by the apparent magnitude of the surface, we designate as the *intrinsic chemical brightness.* As unit of apparent magnitude, we select the thousandth part of a hemisphere; and as unit of intrinsic brightness, we select the amount of light which must proceed from this thousandth part in order to communicate an illumination of 1 degree of light to a physical point placed in the centre of the hemisphere.

In order to measure the amount of the chemical brightness of a surface, all we need is to allow the light proceeding from this surface to fall through a circular opening upon the insolation-vessel, and to measure in degrees of light the chemical illumination thus effected. Let l signify the observed number of light-degrees, d the diameter of the circular opening, r its distance from the insolation-vessel: we then have $\frac{2\pi r^2}{1000}$ as the thousandth part of a hemisphere whose radius is r, and $2\pi r^2 . 2\sin^2\frac{\theta}{2}$ as the portion of this hemisphere occupied by the circular opening, when the value of θ is obtained from the equation $\sin\theta = \frac{d}{2r}$. The portion of the hemisphere cut out by the circular opening, is to the thousandth part of the hemisphere in the proportion of $2\sin^2\frac{\theta}{2}$ to $\frac{1}{1000}$. Hence we obtain the intrinsic brightness H expressed in the above units from the following equation,—

$$\mathrm{H} = \frac{l}{2000 \sin^2 \frac{\theta}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

in which l signifies the number of observed degrees of light.

As an example of such a measurement, we select a comparison of various sized circular portions of the zenith of a cloudless sky. The elements for this calculation are obtained from the following experiment:—Outside the window of our dark room (*aa*, fig. 3) was placed a mirror (*b*), inclined at an angle of 45° towards the horizon; by means of this mirror the light from the zenith could be reflected through a horizontal tube (*c*, fig. 3, Plate XLIII.) upon the insolation-vessel (*i*) in the dark room. On the end of the tube nearest the mirror, and outside the window, circular diaphragms were placed, the diameters (*d*) of which are given in column I. of Table III. The distance of the insolation-vessel from this opening was, as is seen in column II., for all the experiments $2^{\mathrm{m}}{\cdot}225$. Before the insolation-vessel, a screen (*g*, fig. 3, Plate XLIII.) containing two plates of mica was placed. The chemical action (*w*), effected in one minute, obtained from the mean of six observations made with the scale No. 2, is found in column III. The number of degrees of light (l) seen in column IV., which illuminate the insolation-vessel, is found from the equation $\mathrm{N.L.R.}n.w = l$, in which the following constant values occur:—

R[*] =1·777 for the loss of light by the reflexion from mirror.
L =1·450 for the loss of light from the mica-plates.
N =1·031 for the loss of light from the glass sides of insolation-vessel.
n =2·249 for the reduction of the observed divisions on scale No. 2 to degrees of light.

Column V. gives the required mean brightness calculated from formula (3.); column VI. contains the magnitude of the observed surface compared with that of the hemisphere taken as unity.

TABLE III.

No. of experiment.	I. *d.*	II. *r.*	III. *w.*	IV. *l.*	V. H.	VI.
	m.	m.				
1.	0·0590	2·225	10·89	65·1	0·741	0·0000878
2.	0·0359	2·225	4·04	24·1	0·744	0·0000325
3.	0·0590	2·225	10·59	63·3	0·720	0·0000878
4.	0·0530	2·225	8·71	52·0	0·733	0·0000708
5.	0·0590	2·225	10·60	63·3	0·721	0·0000878
6.	0·0359	2·225	3·89	23·2	0·715	0·0000325

From these numbers it is seen that, within the limits of experimental error, the portions of sky near the zenith are equally bright; hence that the chemical action effected by portions of zenith-sky not exceeding 0·00009 of the total heavens, may be taken to be directly proportional to their apparent magnitudes, when the sun does not materially alter its position.

The determinations hitherto considered all depend upon the comparison of the light which has to be measured with that of a constant luminous source. In many cases, however, it is of importance to express the chemical action of light, not only comparatively in *units of light* or in *degrees of light*, but also *absolutely*, that is, in *units of time and space*. Such an absolute measure can be obtained from the observations of our instrument when the following data are given:—

v = the volume of hydrochloric acid, measured at 0° C. and $0^{m}{\cdot}76$, formed by the unit of light;
h = the thickness of sensitive gas (reduced to 0° and 0·76) through which the light passed;
q = the surface-area of the insolated gas;
α = the coefficient of extinction of the chlorine and hydrogen for the light employed;
l = the number of observed units of light in the time t.

When the values of these quantities are known, the volume of hydrochloric acid which would be formed in the time t, by the rays falling perpendicularly on the unit of surface, if $h=\infty$, or if the light had been completely extinguished in passing through an indefinitely extended atmosphere of dry chlorine and hydrogen gas, is found from the equation

$$V=\frac{v}{q}\cdot\frac{l}{1-10^{-\alpha h}} \quad \ldots\ldots\ldots\ldots \quad (4.)$$

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[*] The value of R was determined by a special experiment with candle-light.

As an example of such a measurement, we cite the experiment made with the coal-gas flame, detailed in the Philosophical Transactions for 1857, page 379. This flame gave an action of 14·2 divisions of scale No. 2 in one minute at a distance of $0^{m}\cdot216$ at a temperature of 22°·7 C., and under $0^{m}\cdot753$ barometric pressure. From the capacity of the observation-tube, the volume of hydrochloric acid produced by one unit of light is found to be

$$v=0\cdot001155 \text{ cubic centimetre.}$$

The exposed area of the insolation-vessel was

$$q=3\cdot3 \text{ square centimetres.}$$

The thickness of gas (h) through which the light passed is obtained from the thickness of the insolation-vessel $d=0\cdot94$ centimetre, by help of the following equation:—

$$h=\frac{d(\mathrm{P}-p)}{(1+0\cdot00366t)0\cdot76},$$

in which P represents the barometric pressure, and p the tension of aqueous vapour at the temperature t of the experiment. By calculation h is found to be $h=0\cdot837$. According to our former experiments*, the reciprocal of the coefficient of extinction for gas-light in pure chlorine and hydrogen, at 0° C. and 0·76, is $\frac{1}{23\cdot4}$ centimetre. As between flame and insolation-vessel two plates of mica and a water-screen were placed, the number of units of light (l) corresponding to the observed alteration on the scale is obtained by multiplying this alteration by the factors $k=2\cdot005$ and $n=0\cdot6612$. When this is carried out a value $l=18\cdot56$ is obtained, which, when substituted in formula (4.), gives

$$\mathrm{V}=0\cdot08204 \text{ cubic centimetre.}$$

We thus see that the chemical rays which fall on a surface of one square centimetre from the flame of coal-gas of above dimensions, placed at a distance of 21·6 centimetres, produce in one minute the combination of a column of hydrochloric acid of 0·08204 centimetre in height over the whole area of this square centimetre, under the supposition that the chemical action of the rays had been completely expended in passing through a layer of sensitive gas of indefinite thickness. If we imagine the flame to be placed in the centre, and the insolation-vessel at the surface of a sphere whose radius is equal to the distance of the flame from the insolation-vessel, $r=21\cdot6$ c. m.; the amount of hydrochloric acid formed in one minute is V cubic centimetre on every square centimetre of surface, or on the whole surface of the sphere

$$4\pi r^2\mathrm{V}=481\cdot1 \text{ cubic centimetres.}$$

As the rate of issue of the coal-gas was 4·105 cub.cent. per second, the quantity of coal-gas which was burnt during the time in which 481·1 cub. cent. of hydrochloric acid was formed is 246·3 cub. cent.

The result of this calculation may be thus expressed: when one cubic centimetre of coal-gas burns in the above-mentioned manner, such an amount of chemical rays is

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* Philosophical Transactions, 1857, p. 616.

evolved, that 1·95 cubic centimetre of hydrogen and chlorine can be thereby combined as hydrochloric acid.

The mean composition by volume of the coal-gas burnt in the flame is, however,—

Hydrogen	41·42
Marsh-gas	39·49
Carbonic oxide	5·97
Elayl	4·57
Ditetryl	3·25
Nitrogen	5·10
Carbonic acid	0·20
	100·00

In the combustion of one cubic centimetre of this gas, an amount of heat is evolved sufficient to raise 1 grm. of water from 0° to 6°·8 C.; one cubic centimetre of hydrogen, on the other hand, on combining with chlorine, evolves heat enough to raise 1 grm. of water from 0° to 2°·08 C.; hence we may conclude that for every thermal unit evolved by the union of the components of the coal-gas flame in question with the oxygen of the air, there are only 0·30 thermal units evolved from the chemical combination effected by this flame upon an infinitely extended atmosphere of chlorine and hydrogen.

When it is required to represent in absolute measure the amount of light which falls during a time t on the unit of surface, it is most convenient to express the photo-chemical action of the rays falling on such a surface according to formula (4.), as a column of hydrochloric acid at 0° C. and 0·76, which would have been produced if the light had passed in a parallel direction through an unlimited atmosphere of chlorine and hydrogen. This light, measured in metres, we propose, for the sake of abbreviation, to call a *Light-metre.*

The chemical action of the solar rays is best expressed in these light-metres. The intensity of the chemical illuminating power which a unit of the earth's surface receives either directly from the sun, from the diffuse light of a cloudless sky, or from clouds, can in this way be represented by the height of a column of gas, which, as we shall see in the sequel, when the atmosphere is clear, rapidly increases as the sun rises above the horizon until it reaches the meridian, as rapidly diminishing when the sun has passed that point; and rising and falling under the influence of passing clouds, forms, as it were, a wave accompanying the clouds in their motions, now ascending to a great elevation when bright white clouds reflect much light, and now sinking to a lower and permanent level when the sky is covered with grey clouds or obscured by mist. The mean daily, monthly, or annual height of this column of gas, dependent upon the latitude and longitude, regulates the chemical climate of a place, and points the way to relations for the chemical action of the solar rays, which in the thermic actions are already represented by Isothermals, Isotherals, Isocheimals, and Isonomals.

II. CHEMICAL ACTION OF DIFFUSE DAYLIGHT.

It would be extremely difficult to measure directly, by means of our chemical photometer, the amount of light which a point of the earth's surface receives from the whole atmosphere by dispersion. Experiments of this kind can of course only be made in the open air, either at an elevated situation with an extended horizon, or in the middle of a large plain removed from all objects which could obstruct or reflect light. When, in addition to this, we remember that the instrument with which the observations are made is so sensitive that a violent explosion occurs when a feeble ray of sunlight falls upon the apparatus, it will not appear surprising that we endeavoured to obtain the wished-for result in another manner. For this purpose we determined *chemically* in absolute measure, the action of the rays falling from a measured portion of cloudless sky situated near the zenith, and then compared the *visual* luminosity of this same portion of zenith-sky with that of the total heavens.

In order to be able to make this comparison, we had to carry out a somewhat lengthy series of experiments, which, as they form the basis of our present measurements, we must consider in detail.

As the light from certain zones of sky varying with the sun's altitude is polarized, and may therefore disappear on reflexion, it is impossible, in these determinations of the visual luminosity of the atmosphere, to employ any arrangement of mirrors. It appeared at first sight, that instead of reflecting the light it would be most convenient to illuminate one side of a sheet of white paper, first with the light falling from a measured portion of the zenith, and afterwards with the light from the whole heavens, determining in each case, at the other side of the paper, by means of a photometric arrangement, the amount of visual illumination. As, however, this method of observation can only give satisfactory results when the illumination of one side of the paper is proportional to the intensity of the rays which fall on the other side with very various angles of incidence, it was necessary, first of all, to determine whether these conditions were sufficiently fulfilled under the circumstances of the experiment.

The following arrangement was made in order to determine this point. A, fig. 4, Plate XLIII. represents a blackened tube closed at one end (*a*) by the paper about to be examined. On a table in front of the tube (A), a large divided quadrant (B) is so placed that the centre of the circle rests on the table directly below the centre of the disk of paper at *a*. In connexion with the quadrant is a moveable scale (C) divided into millimetres, and upon this scale the standard burner is placed, so that the rays proceeding from the flame can be made to fall upon the paper (*a*) at any given angle of incidence. Inside the tube at *e* is fixed a diaphragm of drawing-paper, the centre of which had been rendered transparent by a small piece of stearic acid. When this diaphragm is illuminated from D by a small constant flame, the stearine spot, as seen through the eye-tube (*b*), appears in a certain position of the lamp (*g*), to be white on a black ground; if the lamp be now brought nearer, at a certain point the spot disappears; and when the flame is brought still nearer, the spot is again seen, but now appears black upon a white ground. In order to obtain the wished-for proof, the flame (*g*) is first so placed that the rays fall perpendicularly on the paper screen (*a*), and then moved over the graduated circle (B), so that the rays fall upon the screen with the angle of incidence φ, care being in each case taken that the lamp is moved along the scale (C) until the spot of stearine disappears, so that in both positions of the flame the illumination of the side of the screen (*e*) next the eyepiece should be the same. When the distances have been found at which the flame (*g*) must be placed in the two positions, in order that the *back* of the paper screen should be illuminated to the same extent, it is easy to calculate the amount of light which falls on the *front* of the screen, and which, in order to answer the required purpose, ought to be equal to that seen through the tube (*b*). If φ and φ_1 represent the complements of the two angles of incidence, measured on the divided quadrant, with which the light fell upon the paper screen, and $r\,r_1$ the distances between the screen and flame at which the stearine spot vanished, then the following equation is true, provided the assumptions made at the commencement are correct:—

$$\frac{\sin\varphi . r_1^2}{\sin\varphi_1 . r^2}=1.$$

Experiment gave the following numbers:—

TABLE IV.

	Writing-paper.			Drawing-paper.	Filter-paper.
φ…………	90°	90°	90°	90°	90°
r…………	250	262	203	146	300
φ_1 ………	56° 15′	33° 45′	22° 30′	33° 45′	33° 45′
r_1 ………	205	167	81	103	186
$\frac{\sin\varphi . r_1^2}{\sin\varphi_1 . r^2}$ ……	0·83	0·73	0·42	0·89	0·69

It is seen that the numbers in the lowest horizontal column differ widely from 1, and that no simple relation exists between the amount of light falling on the front and that issuing from the back of the screen. It now only remained to be seen whether a better result is obtained when the diaphragm with the stearine spot is itself directly illuminated. For this purpose the experiments were repeated, with the sole difference that the diaphragm *e* was placed at the end of the tube at *a* instead of the paper screen. With this arrangement the following numbers were obtained:—

TABLE V.

φ…………	90°	90°	90°	90°	90°
r…………	225	199	178	220	224
φ_1 ………	22° 30′	33° 45′	45° 0′	67° 30′	78° 45′
r_1 ………	140	150	150	214	221
$\frac{\sin\varphi . r_1^2}{\sin\varphi_1 . r^2}$ ……	1·01	1·02	1·00	1·02	0·993

The numbers in the lowest division are all so nearly equal to 1, that the slight differences may with certainty be ascribed to the unavoidable errors of observation.

From these experiments we see that a paper diaphragm, with a transparent spot of stearic acid, can be most advantageously employed for the photometric measurement of rays of light falling upon a point at very various angles of incidence.

In order to determine the intensity of the sky's brightness with ease and exactitude, we have employed the photometer depicted in fig. 5, Plate XLIII. *a*, fig. 5, represents the paper diaphragm with the spot of stearine, which closes the vertical tube (*b*), and is in the same plane as the horizontal plate (*c*) fastened on to the tube (*b*). This tube (*b*) is coloured in the inside white, and into it is soldered the narrow tube (*d*), blackened inside, and placed at such an angle below the diaphragm (*a*), that on looking through it the stearine spot on the paper is plainly seen. The observations are more conveniently made when a small blackened box (*e*), containing a mirror and carrying an eyepiece (*f*), is placed on the end of the tube (*b*), and thus the change of shade in the stearine diaphragm noted. The tube *b* is fixed into the top of the tin case *hi*, one side of which is open, and the lower end of the tube *b* is closed by a divided circle, half of which, as is seen in fig. 6, *a a*, Plate XLIII., has been removed. This semicircular opening can be partially or totally closed at pleasure by a moveable disk of metal, and the angle thus left open read off on a divided circle. Supposing that a constant source of light be placed in the case *hi*, the lower surface of the stearine diaphragm receives a quantity of light which is determined by the divided scale of the semicircular opening at the bottom of the tube. If we suppose that the semicircular arc is opened to its full extent (180°), and that the amount of light which is thrown on the lower surface of the diaphragm is larger than that which falls on the upper surface, the spot of stearine will appear dark on a bright ground. If the opening be now gradually closed, the spot will be observed to become lighter, until at a certain position of the divided circle the spot entirely disappears, and a homogeneous white surface is seen. If the size of the open sector be still diminished, the spot again appears, but this time it is bright on a dark ground. When the divided arc has been placed in such a position that for a given illumination (A) the spot of stearine disappears, any other source of light placed in *a*, which under like conditions does not cause the spot to appear, is equal in intensity to A.

For the purpose of measuring the diffuse light of day, the diaphragms are best made of white drawing-paper, of about double or treble the thickness of ordinary writing-paper. When the whole of the paper, with the exception of a small ring, is saturated with stearic acid, the observations are more exact than when a paper with merely a spot of stearic acid is made use of. In order to prepare such a diaphragm, the drawing-paper, with a piece of filter-paper under it, is laid upon a warm metallic plate, and a piece of fused stearic acid (a stearine candle answers the purpose when the pure acid is not at hand) gradually rubbed into the heated paper, so that a small circle in the centre of the paper is the only part not saturated with the stearine. When the plate is cool, a small piece of the acid is laid in the centre of the circle, and the plate gently warmed until the stearic acid has sunk into the pores of the paper, so that only a small ring not saturated with acid remains, the breadth of which should be about 1 to 2 millimetres, and the diameter from 5 to 6 millims.

We have already mentioned that we were only able to measure the chemical action produced by a small circle of sky at the zenith. In order to be able to determine the action effected by the light from the whole visible heavens, it was in the first place necessary to compare, by means of the photometer just described, the amount of light which a point on the earth's surface receives from the whole sky, with that which the same point receives from a measured circular portion of sky at the zenith. As the quantity of light which emanates from the measured portion of sky in the zenith is from 300 to 800 times less than that reflected from the whole sky, and as with this photometer we are unable to measure such large differences in the amount of light, it was necessary to employ some known fraction of the total diffuse light of day. For this purpose a hollow hemispherical metallic cap (fig. 7, Plate XLIII.) was made use of. This cap, which is painted black, can be placed concentric with the diaphragm (*a*, fig. 4), on the plate *cc*, and is perforated at regular distances with 184 equal-sized holes, the diameter of which was accurately determined. In order to measure the light from a circle of sky at the zenith of known magnitude, the blackened tube (fig. 6, Plate XLIII.) was employed; this tube is furnished at its upper end with a semicircular moveable disk, similar to the one already described as placed at the lower end of the photometer-tube (*b*, fig. 5), and can be fixed on the plate *cc*, so that the ring of the paper diaphragm (*a*) falls exactly below the centre of the divided semicircle.

The observations are commenced by placing the blackened cap on the plate over the diaphragm; the diffuse light falls through the holes upon the diaphragm, and the divided disk in the tube (*b*) is moved until the ring on the paper, seen through the eyepiece *b*, disappears. The amount of light which under these circumstances is reflected from the sky upon the diaphragm we will call 1. Let the total surface of the hemispherical cap be Q_1, and that portion which has been removed by the holes be Q; then the amount of light which would have fallen on the diaphragm from the whole sky if the cap had not been present is equal to $\frac{Q_1}{Q}$. If the cap be removed, and in its stead the tube (fig. 6) placed on the plate, without otherwise altering the arrangement, and then the divided circle on the *upper* end of the tube moved until the ring disappears, the diaphragm (*a*) is again illuminated with the intensity 1. Let q represent the fraction of the total hemisphere from which the light falls through the open sector of the tube upon the diaphragm, and let q_1 represent the area of a given circle of sky at the zenith expressed in the same units as q; the amount of light which would fall upon the diaphragm from the whole circle of sky q_1 is $\frac{q_1}{q}$; and hence the relation between the light from the whole heavens and that from the circle of sky q_1 is $\frac{Q_1}{Q}\cdot\frac{q}{q_1}$. If, therefore, we know the amount of chemical action (w) which the light reflected from a circle of sky q_1 at the zenith effects on a given point, the action (W) which the light from the whole sky would produce on the same point is obtained by the equation

$$W=\frac{Q_1}{Q}\cdot\frac{q}{q_1}\cdot w.$$

The relation $\frac{Q_1}{Q}$ is easily found by help of the following considerations. If r be the radius of the hemispherical cap, we have $Q_1=2\pi r^2$; and if d is the diameter of the hole, its area is $4\pi r^2\sin^2\frac{\theta}{2}$, when $\sin\theta=\frac{d}{2r}$; and if there are n holes,

$$Q=n.4\pi r^2\sin^2\frac{\theta}{2},\quad\text{or}\quad\frac{Q_1}{Q}=\frac{1}{2n.\sin^2\frac{\theta}{2}}.$$

In the apparatus above described the values of these constants were as follows:—$n=184$; $d=0{\cdot}775$ millim.; $r=77{\cdot}5$ millims.; hence we obtain $\frac{Q_1}{Q}=436$. The value of q is determined in the following manner:—Let d_1 be the diameter of the circle through the open sector of which the light falls on the diaphragm; let r_1 be the distance from any point in the circumference of this circle to the centre of the paper diaphragm; and lastly, let ψ be the number of degrees to which the sector was opened; we have then

$$q=\frac{\psi}{360}.4\pi.\sin^2\frac{\theta_1}{2},$$

when $\frac{d_1}{2r_1}=\sin\theta_1$, and the area of the whole visible sky $=2\pi$. If we suppose that q_1 has an arbitrary value of the $\frac{1}{1000}$th of the hemisphere, that is, if $q_1=\frac{2\pi}{1000}$, we have $\frac{q}{q_1}=\frac{50}{9}\psi.\sin^2\frac{\theta_1}{2}$. The values of these constants in our instrument are, $d_1=45{\cdot}5$ millims.; $r_1=190{\cdot}6$ millims.; hence $\frac{q}{q_1}=0{\cdot}0197\,\psi$. The amount of light (I) which a point on the earth's surface receives from the whole sky, expressed in units of the amount which is reflected from a portion of sky at the zenith equal in area to $\frac{1}{1000}$th part of the whole, is found from the equation

$$I=\frac{Q_1}{Q}\cdot\frac{q}{q_1}\psi=8{\cdot}58\,\psi.$$

In order to obtain the exact value of I certain precautions must be taken, which if neglected would give rise to very considerable errors. It is of primary importance to notice, when two observations have to be compared together, that the amount of light which the white surface of the inside of the photometer receives, and which is reflected on to the lower side of the diaphragm, remains perfectly constant. If the inside of the photometer is illuminated by the reflected light from houses, hills, or other neighbouring objects, a passing shadow may render the observations useless. Even when a portion of the light which should fall into the photometer is by chance obstructed by the hand whilst altering the opening of the divided circle, an error of considerable magnitude is introduced. In order to avoid irregularities of this kind, it was found most convenient to expose the white sides of the photometer to the diffuse light of the cloudless sky, avoiding altogether other reflected or direct sunlight. It is self-evident that no direct sunshine must be allowed to fall during the experiment, either upon the opening of the tube (fig. 6), or upon the hollow metallic cap (fig. 7). This is best prevented by holding a round sheet of pasteboard fixed on a pole between the sun and the photometer, at a distance of about 3 metres from the latter, so that the amount of diffuse light cut off is inappreciable.

As the relative amount of illumination of the sky is materially altered by the presence of the smallest cloud, it is only when the heavens are perfectly clear that any general conclusion can be drawn from these observations. Perfectly cloudless days are, however, so uncommon in our latitudes, that on an average not more than six or eight occur at Heidelberg in a year*. We must hence consider it fortunate that we were able to complete a series of hourly observations from sunrise to sunset upon a day during the whole of which the blue sky was not obstructed by the smallest particle of cloud.

A series of these observations was made on June 6th, 1858, at the summit of the Geisberg, a hill in the neighbourhood of Heidelberg, the height of which is 376 metres above the sea, and 105 metres above the river Neckar. On the highest point of the wooded hill, a platform, of about 40 feet in height, had been built, rising above the tops of the trees; and on this platform, which commanded a perfectly free horizon on every side, the visual illumination of the heavens was determined. During the course of the observations, which lasted from sunrise to near sunset, a strong breeze blew from the eastward, and the air was so clear, that the Haardt Mountains, situated at a distance of twenty miles, were seen not only in distinct contour, but in relief.

The amount of the illumination of the sky was determined in the following manner: the hollow cap was first fixed on the photometer, shaded from direct sunlight by the paper screen, and the divided circle so placed that the diaphragm-ring disappeared; the time was then noted and the hollow cap quickly removed. The tube (fig. 6, Plate XLIII.) was next fixed on the photometer, and the divided circle attached to the tube moved until the diaphragm-ring disappeared, when the time was again observed; the mean of these two observations was taken as the time of the experiment. The opening (ψ) of the divided circle, measured in degrees and tenths of degrees, when multiplied by 8·58, gives, as we have already shown, the amount of light (I) which the diaphragm-ring receives from the *whole sky*, when the unit amount of light is represented by the amount which falls upon the same diaphragm-ring during the same time from a portion of zenith-sky equal to $\frac{1}{1000}$th part of the total visible heavens.

The following Table gives the mean of four independent series of observations made on the 6th of June, 1858. The first vertical column contains the numbers of the observations; the second the times of the experiment reduced to true solar time; the third the values of ψ; and lastly, the fourth contains the required values of I calculated from the values of ψ.

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* According to observations of Padre SECCHI, extending over a period of eight years, not more than twenty-one cloudless days occur in Rome in the course of a year.

TABLE VI.

I.	II.	III. ψ.	IV. I.
	h m		
1	5 38 A.M.	88·8	762
2	6 8 A.M.	86·0	738
3	7 25 A.M.	74·2	637
4	8 52 A.M.	56·0	481
5	9 32 A.M.	50·4	432
6	10 9 A.M.	47·2	405
7	10 43 A.M.	42·0	360
8	11 26 A.M.	37·8	324
9	0 1 P.M.	35·8	307
10	0 32 P M.	38·4	330
11	0 57 P.M.	42·0	360
12	1 24 P.M.	47·4	407
13	2 4 P.M.	50·0	429
14	2 38 P.M.	53·0	455
15	3 21 P.M.	60·8	522
16	3 57 P.M.	68·8	590
17	4 42 P.M.	76·0	652
18	5 20 P.M.	79·6	683
19	6 2 P.M.	88·0	755

The amounts of light which fall upon the diaphragm-ring and are arranged in column IV. of the foregoing Table, in no way represent the mean brightness of the whole sky as compared with the respective brightnesses of the zenith, for it is only the zenith rays which fall perpendicularly upon the unit of surface; the rays from other points of the sky with a greater zenith-distance fall upon the diaphragm with a larger angle of incidence. This relation between the luminosity of the zenith and the mean luminosity of the whole sky, could be easily found if, instead of the perforated cap used, another were employed in which the number or area of the holes was in the inverse proportion of the cosines of their distance from the vertical.

The amount of chemical illumination which a horizontal unit on the earth's surface receives from the whole heavens, depends upon the height of the sun above the horizon, and upon the constitution of the atmosphere. If, when the sky is cloudless, the atmosphere undergoes considerable change in its transparency, a long series of determinations made at different times of the year would be necessary before we could hope to arrive at any general expression for the atmospheric extinction and dispersion of the chemical rays. Fortunately, however, we learn from Professor SEIDEL'S classical research on the Brightness of the Fixed Stars*, that the atmospheric extinction varies so slightly when the sky is cloudless that the differences may be altogether neglected. In a lecture given at Munich†, SEIDEL says, "It has fortunately been proved, although one could scarcely have expected it, that the variations in the amount of transparency of the air on

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* Abhandl. der Kön. Bayer. Acad. d. Wiss. 2te Classe, Bd. vi. Abth. 3.

† Wissenschaftliche Vorträge, gehalten zu München im Winter, 1858, p. 301. Braunschweig bei Vieweg und Sohn.

different nights may, by care in the selection of nights, be reduced to within very narrow limits."

Hence we think that we are justified in setting aside the alterations in the extinction of the cloudless sky, and in considering the chemical illumination of the earth's surface as being merely a function of the sun's zenith-distance. We are at the same time perfectly well aware that the constants contained in our formulæ, derived as they are from a comparatively small number of observations, cannot lay claim to any very great degree of accuracy. Still we believe, and we hope in the sequel to show, that the amount of reliability which our experiments present is sufficient to permit us to deduce therefrom the empirical laws according to which the chemical energy proceeding from the sun is diffused over the earth's surface when the sky is unclouded.

The following formula gives the value of the zenith distance (φ) for the observed times of experiment:

$$\cos\varphi = \cos\delta \,.\, \cos t \cos p + \sin\delta \,.\, \sin p \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (5.)$$

where δ signifies the sun's declination on the day of the experiment $(+22° \; 39' \; 30'')$; p gives the latitude of the place $(49° \; 24' \; 25'')$, and t represents the sun's hour-angle.

In the following Table the observations of June 6, 1858, are arranged with the corresponding zenith-distance of the sun. The first column contains the times of observation in true solar time; the second gives the sun's hour-angle corresponding to the time of observation; the third contains the corresponding zenith-distances of the sun; and the fourth shows the amount of light which the unit of area receives from the whole sky, compared with that which the same area receives at the same time from a portion of sky at the zenith equal in area to the $\frac{1}{1000}$th part of the whole heavens.

TABLE VII.

Number of experiment.	I. Time of observation.	II. t hour-angle of the sun.	III. φ zenith distance of the sun.	IV. I.
	h m	° ′	° ′	
1	5 38 A.M.	95 30	76 25	762
2	6 8 A.M.	88 0	71 44	738
3	7 25 A.M.	68 45	59 19	637
4	8 52 A.M.	47 0	45 24	481
5	9 32 A.M.	37 0	39 28	432
6	10 9 A.M.	27 45	34 31	405
7	10 43 A.M.	19 15	30 45	360
8	11 26 A.M.	8 30	27 34	324
9	0 1 P.M.	0 15	26 47	307
10	0 32 P.M.	8 0	27 29	330
11	0 57 P.M.	14 15	29 1	360
12	1 24 P.M.	21 0	31 27	407
13	2 4 P.M.	31 0	36 11	429
14	2 38 P.M.	39 30	40 54	455
15	3 21 P.M.	50 15	47 26	522
16	3 57 P.M.	59 15	53 10	590
17	4 42 P.M.	70 30	60 28	652
18	5 20 P.M.	80 0	66 38	683
19	6 2 P.M.	90 30	73 18	755

The several values of I in the 4th column can be expressed, as exactly as the observational errors allow, as functions of the zenith-distance φ by help of the simple equation

$$I = 77{\cdot}0 + 9{\cdot}275\,\varphi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.)$$

By means of this equation we have calculated and thrown together in the following Table, the luminosity of the whole sky for zenith distances varying from 20° to 90°.

Table VIII.

φ.	l.	φ.	l.	φ.	l.	φ.	l.	φ.	l.	φ.	l.	φ.	l.	φ.	l.	φ.	l.
20°	263	28°	337	36°	411	44°	485	52°	559	60°	634	68°	708	76°	782	84°	856
21	272	29	346	37	420	45	494	53	569	61	643	69	717	77	791	85	865
22	281	30	355	38	430	46	504	54	578	62	652	70	726	78	801	86	875
23	290	31	365	39	439	47	513	55	587	63	661	71	736	79	810	87	884
24	300	32	374	40	448	48	522	56	597	64	671	72	745	80	819	88	893
25	309	33	383	41	457	49	532	57	606	65	680	73	754	81	828	89	902
26	318	34	392	42	467	50	541	58	615	66	689	74	764	82	838	90	912
27	327	35	402	43	476	51	550	59	624	67	699	75	773	83	847		

The curve (fig. 8, Plate XLIV.) represents the relation between the values of φ as abscissæ and those of l as ordinates. The points about the curve marked with a cross represent the observations made in the morning; those marked by a dot show the brightness of the afternoon sky. From these it is seen that the illumination effected by the diffuse daylight for the same zenith-distance of the sun before and after noon remains nearly constant, although at these times of day the temperature and humidity of the air must differ widely.

From Table VIII. we can find, for any given zenith distance of the sun, the relation between the amount of light, optically (or visually) measured and taken as unity, which falls from a certain spherical surface of sky in the zenith and that (also optically measured) falling from the whole sky. The amount of light, chemically measured, which falls from this same surface of zenith-sky, multiplied by the amount of optically measured light which the whole sky gives, must therefore give the chemical action which the whole sky would produce on a horizontal unit of surface. According to our former definition, however, the amount of light falling from a circle of zenith-sky upon the unit of area is the chemical brightness of that piece of zenith-sky. We have carried out, according to the method already described, a series of determinations of this chemical brightness at various times and at different zenith-distances of the sun. Some of these observations were made on the 18th of October, 1856, others on July 23rd and August 5th, 1858. During all the experiments the sky was perfectly cloudless, and the gas had reached the maximum degree of sensibility. The observations are contained in the following Table (IX.).

TABLE IX.

Number of experiment.	True solar time.	Sun's zenith-distance.	Action in scale-divisions.	Chemical brightness in units of light of a piece of zenith-sky $\frac{1}{1000}$th of the whole sky.
	h m	° ′		
1	1856, 18 Oct. 6 46 A.M.	90 4	0·000	0·0
2	6 51 A.M.	89 17	0·63	23·2
3	6 55 A.M.	88 39	0·88	32·5
4	7 3 A.M.	87 25	1·92	71·1
5	7 7 A.M.	86 48	2·19	81·0
6	7 17 A.M.	85 16	3·15	116·3
7	7 23 A.M.	84 22	3·42	126·5
8	7 41 A.M.	81 41	4·81	177·6
9	8 5 A.M.	78 14	6·01	222·2
10	8 11 A.M.	77 25	6·40	236·8
11	8 33 A.M.	74 27	7·82	289·2
12	9 8 A.M.	70 7	8·56	316·6
13	3 53 P.M.	77 58	5·44	200·8
14	1858, 23 July. 7 30 A.M.	60 21	6·94	485·8
15	7 52 A.M.	56 47	7·93	555·1
16	8 52 A.M.	47 21	10·06	704·2
17	9 46 A.M.	39 36	11·82	827·4
18	10 15 A.M.	36 0	13·04	912·8
19	10 48 A.M.	32 37	13·72	960·4
20	11 20 A.M.	30 22	15·26	1068·2
21	12 0 A.M.	29 18	16·04	1122·8
22	1858, 5 Aug. 7 46 A.M.	60 1	7·59	531·3
23	8 11 A.M.	56 1	8·65	605·4
24	8 51 A.M.	49 52	9·79	685·3
25	9 17 A.M.	46 5	10·32	722·4

In experiments 1 to 13 the following data were employed for the calculation of the brightness, expressed in units of light, found in the 5th column: R=1·777, L=1·45, N=1·031, $n=2\cdot249$, $d=0^{m}\cdot0530$, $r=1^{m}\cdot474$. In the other experiments these values remained constant, except $d=0^{m}\cdot059$, and $r=2^{m}\cdot260$.

The chemical brightness (w) of the circle of zenith-sky equal in area to $\frac{1}{1000}$th part of the whole heavens, as seen in the last column of the preceding Table, can be represented as a function of the corresponding zenith-distance of the sun (φ), with sufficient accuracy by help of the following equation,

$$w=1182\cdot7-13\cdot857+\frac{8884\cdot9}{\varphi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.)$$

in which the numbers are calculated from all the observations according to the method of least squares. From this equation Table X. is calculated. It gives for every zenith-distance of the sun from 20° to 90° the amount of light, expressed in light-units, which falls perpendicularly upon a unit of area on the earth's surface, from a portion of zenith-sky equal to $\frac{1}{1000}$th part of the whole heavens.

TABLE X.

Zenith-distance. φ.	Chemical brightness in light-units. w.	Zenith-distance. φ.	Chemical brightness in light-units. w.	Zenith-distance. φ.	Chemical brightness in light-units. w.	Zenith-distance. φ.	Chemical brightness in light-units. w.	Zenith-distance. φ.	Chemical brightness in light-units. w.	Zenith-distance. φ.	Chemical brightness in light-units. w.
20°	1350·0	32°	1017·2	44°	775·1	56°	565·7	68°	371·5	80°	184·8
21	1315·0	33	994·9	45	756·8	57	549·0	69	355·8	81	170·4
22	1281·9	34	973·0	46	738·7	58	532·5	70	340·1	82	155·0
23	1250·6	35	951·7	47	720·8	59	515·9	71	324·3	83	139·7
24	1220·5	36	930·9	48	703·0	60	499·6	72	308·9	84	125·5
25	1192·0	37	910·4	49	685·3	61	483·5	73	293·4	85	110·3
26	1164·4	38	890·1	50	667·8	62	467·2	74	277·7	86	95·0
27	1137·7	39	870·2	51	650·4	63	451·1	75	262·2	87	79·8
28	1112·2	40	850·6	52	633·4	64	435·1	76	246·6	88	64·6
29	1087·4	41	831·5	53	616·3	65	419·2	77	231·1	89	49·5
30	1063·4	42	812·5	54	599·2	66	403·3	78	216·7	90	34·4
31	1039·9	43	793·6	55	582·3	67	387·2	79	201·2		

The curve (fig. 9, Plate XLV.) shows how closely the actual observations approach the calculated values. The simple points about the curve represent the observations made on July 23, 1858; the small circles denote the experiments of August 5, 1858; and the crosses those of October 18, 1856. As these observations were made in different years and at different times of the day and year, we may conclude from the near approach of the single points to the calculated curve, that in this case, as in that of the determination of visible illumination, alterations in the humidity and temperature of the air have but a very slight influence upon the dispersion of light in the atmosphere when free from clouds or mist; and that, therefore, the chemical actions effected at equal hour-angles on each side of the sun's culminating point, may, without risk of appreciable error, be taken as equal.

After this investigation we may now pass to the determination of the chemical action which the whole visible heaven effects upon a horizontal unit area of earth's surface at various zenith-distances of the sun. The numbers marked l in Table VIII. give the relation of the light falling on a unit of area from the whole sky, visually measured, to that falling from a given portion of zenith-sky, also measured visually. In Table X. we find the chemical actions produced by the same portion of zenith-sky. Now, as we have formerly shown that in light from the same source the chemical is proportional to the visual action, we have only to multiply together the numbers in each Table corresponding to the same zenith-distance, in order to have the required chemical action of the whole heavens. The action (w_1) thus obtained can be expressed in a form adapted for calculation, as a function of the sun's zenith-distance, according to the following formula,

$$w_1 = a + b\cos\varphi + c\cos^2\varphi + \dots, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8.)$$

in which the fourth term can be neglected. The values of the coefficients a, b, and c have been calculated, according to the method of the least squares, from the following eight values of φ and w_1:—

TABLE XI.

ϕ.	w_1.
90	31370
80	151400
70	246800
60	316700
50	361300
40	381100
35	382500
30	377500

Hence we obtain

$$w_1=27760+808490\cos\phi-459960\cos^2\phi, \quad . \quad . \quad . \quad . \quad . \quad (9.)$$

by help of which the following Table (XII.) is calculated. The chemical action (w_1) effected by the diffuse light from the whole sky is here expressed, not in units of light, but in degrees of light, each of which is equal to 10,000 units of light.

TABLE XII.

ϕ.	w_1.	ϕ.	w_1.	ϕ.	w_1.	ϕ.	w_1.	ϕ.	w_1.	ϕ.	w_1.
31	38·29	41	37·60	51	35·45	61	31·17	71	24·22	81	14·30
32	38·26	42	37·47	52	35·11	62	30·60	72	23·37	82	13·15
33	38·24	43	37·31	53	34·78	63	30·00	73	22·48	83	11·95
34	38·21	44	37·14	54	34·40	64	29·38	74	21·56	84	10·72
35	38·14	45	36·96	55	34·02	65	28·73	75	20·62	85	9·47
36	38·08	46	36·74	56	33·61	66	28·06	76	19·64	86	8·19
37	38·01	47	36·53	57	33·17	67	27·34	77	18·64	87	6·88
38	37·93	48	36·30	58	32·72	68	26·61	78	17·60	88	5·54
39	37·85	49	36·02	59	32·22	69	25·84	79	16·53	89	4·17
40	37·72	50	35·75	60	31·70	70	25·05	80	15·43	90	2·77

These degrees of light (w_1) express the chemical action which the diffuse light from the whole sky effects during one minute upon the horizontal unit of area on the earth's surface when the corresponding zenith-distance of the sun is ϕ. The curve (fig. 10, Plate LV.) represents the relation of this chemical action to the sun's zenith-distance, marked as abscissæ. The points on the figure denote the values of Table XI., from which the curve is derived; their approximation to the line shows how closely the results obtained by calculation agree with the observed numbers.

By means of formula (5.), $\cos\phi=\cos\delta\cos p\cos t+\sin\delta\sin p$, already given, and either formula (9.) or Table XII., the illuminating effect of the cloudless sky at a given locality and at a given time, can be calculated. As an example of this method, we give the results of the calculation of the chemical illuminating effect produced by the cloudless sky during the various hours of the day on the vernal equinox at Cairo, Naples, Heidelberg, Manchester, Petersburg, Reykiavik, and Melville Island.

Table XIII.

	Melville Island.	Reykiavik.	Petersburg.	Manchester.	Heidelberg.	Naples.	Cairo.
h m							
6 A.M. or 6 P.M.	2·77	2·77	2·77	2·77	2·77	2·77	2·77
7 A.M. or 5 P.M.	8·06	11·32	12·49	14·19	15·09	16·84	18·59
8 A.M. or 4 P.M.	12·61	18·22	20·13	22·81	24·21	26·77	29·15
9 A.M. or 3 P.M.	16·20	23·34	25·64	28·72	30·24	32·87	35·03
10 A.M. or 2 P.M.	18·78	26·76	29·20	32·30	33·74	35·80	37·58
11 A.M. or 1 P.M.	20·32	28·67	31·14	34·10	35·43	37·20	38·23
12 A.M.	20·83	29·30	31·74	34·67	35·91	37·49	38·30

The curves (fig. 11, Plate XLVI.) drawn from these numbers show graphically the hourly variation in the chemical diffused light on the equinox at the several localities.

We may now proceed to the consideration of the chemical actions produced by diffuse light upon the horizontal unit area of earth's surface during a longer period of time.

Let w_1 signify, as before, the action effected by the light in one minute, when the sun's hour-angle is t; and let W be the action during a period in which the hour-angle increases from $t_{/}$ to $t_{//}$, then we have

$$W=\frac{12\times 60}{\pi}\int_{t_{/}}^{t_{//}} w_1 dt,$$

where the unit in which the hour-angle is expressed is the angle whose arc is equal to the radius. We have, however,

$$w_1=a+b\cos\varphi+c\cos^2\varphi,$$

and
$$\cos\varphi=\sin\delta\sin p+\cos\delta\cos p\cos t;$$

hence when $\sin\delta\sin p=\alpha$, and $\cos\delta\cos p=\beta$,

$$W=\frac{12\times 60}{\pi}\left\{\begin{array}{l}\left(a+b\alpha+c\left(\alpha^2+\frac{\beta^2}{2}\right)\right)(t_{//}-t_{/})+(b\beta+2c\alpha\beta)(\sin t_{//}-\sin t_{/}) \\ +\frac{1}{4}c\beta^2(\sin 2t_{//}-\sin 2t_{/})\end{array}\right\} \quad . \quad . \quad . \quad (10.)$$

This expression is somewhat simplified, if the action for the whole day, from sunrise to sunset, be calculated; for then $t_{/}=-t_{//}$, and

$$\cos t_{//}=-\tan\delta\tan p, \text{ or } =-\frac{\alpha}{\beta};$$

and hence

$$W=\frac{24\times 60}{\pi}\left\{\left(a+b\alpha+c\left(\alpha^2+\frac{\beta^2}{2}\right)\right)t_{//}+\left(b\beta+\frac{3}{2}c\alpha\beta\right)\sin t_{//}\right\}.$$

If the calculation be made for the time of the equinoxes, the equation becomes much more simple; for in this case

$$\delta=0, \quad \alpha=0, \quad \beta=\cos p, \quad t_{//}=\frac{\pi}{2},$$

or

$$W=12\times60\left(a+\frac{2}{\pi}b\cos p+\tfrac{1}{2}c\cos^2 p\right);$$

or substituting the values of a, b, and c,

$$W=1998{\cdot}7+37058\cos p-16559\cos^2 p.$$

By applying this formula for the places given in Table XIII., we obtain the following numbers as representing the chemical action, expressed in degrees of light, which, at the time of the equinoxes, the whole heaven effects on the unit of area in each of these places, from sunrise to sunset:—

TABLE XIII*b*.

Melville Island	10590
Reykiavik	15020
St. Petersburg	16410
Manchester	18220
Heidelberg	19100
Naples	20550
Cairo	21670

We need scarcely remark that these numbers, as well as the data from which they are obtained, only hold good for skies free from cloud and mist, and for situations not too far distant from the sea's level. In places which lie nearer to the higher portions of the atmosphere, it is evident that the conditions will be totally different. The law according to which the atmospheric diffused light varies with the height above the sea, might in like manner be determined empirically, but such a series of experiments entail an expenditure of time and money which we have unfortunately been unable to afford.

The chemical action of diffused sunlight becomes extremely irregular when either clouds or mists intercept the clear blue sky. The chemically active light, which under these circumstances reaches the earth's surface, varies as irregularly as do the other meteorological phenomena dependent on the thermic and hygrometric state of the atmosphere. Without at present entering into an explanation of a method by which, taking cognizance of these circumstances, photo-chemical determinations may be made, we will here give one example to show the variable nature of the diffuse light from a clouded sky. The following Table contains the results of a series of observations made at Heidelberg on October 5, 1856. The columns marked I. give the time of observation; those marked II. the amount of light expressed in units of light radiated from a portion of sky at the zenith equal to the $\frac{1}{1000}$th part of the whole sky.

TABLE XIV.

I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
h m		h m		h m		h m		h m	
7 24 A.M.	617	9 12 A.M.	1537	10 47 A.M.	1881	11 38 A.M.	1650	2 28 P.M.	765
7 54 A.M.	670	9 15 A.M.	1469	10 53 A.M.	1731	0 4 P.M.	1660	3 20 P.M.	370
8 2 A.M.	963	9 30 A.M.	1686	11 0 A.M.	1881	1 1 P.M.	1494	3 27 P.M.	450
8 36 A.M.	1165	9 50 A.M.	1797	11 6 A.M.	1921	1 7 P.M.	1475	3 33 P.M.	445
8 42 A.M.	1314	9 56 A.M.	1631	11 31 A.M.	2274	2 11 P.M.	675	4 16 P.M.	304
9 0 A.M.	1687	10 2 A.M.	1934	11 37 A.M.	2231	2 22 P.M.	836	4 41 P.M.	188

In order to give a clear idea of the daily changes of chemical luminosity in such a piece of sky over which clouds passed, we have represented the observations by a curve (A, fig. 12, Plate XLVI.), in which the times are marked as abscissæ, and the chemical actions expressed in units of light as ordinates. For the sake of comparison we have calculated the action which would have taken place on that day if the sky had been perfectly cloudless, and we have represented this action by the second curve, B. From 7^h A.M. to nearly noon the sky was covered with a layer of cloud of varying thickness, through which the sun but slightly shone. In the afternoon the clouds gradually disappeared, so that after 2 o'clock only light detached clouds passed over the zenith, and after about half-past 3 the sky became cloudless. These alterations are clearly seen on the curve, which shows that a thin film of cloud increased the quantity of light reflected from the portion of sky under observation to beyond four times the amount reflected from the same portion of sky when cloudless; and that the chemical action before noon rose much more rapidly, and was more irregular than the action in the afternoon when the clouds were gradually disappearing. It is seen too that, at 2^h 22^m and at 3^h 30^m, the action attained two maxima limits, owing to the passage at those times of a bright white cloud through the zenith.

These observations prove that the presence of a thin film of cloud increases the amount of chemical illuminating effect in the most striking manner; we have, however, also convinced ourselves, by a large number of experiments, that a thicker layer of clouds, such as those which precede rain or thunder-storms, or dense mists or fogs, may so diminish the chemical light reflected from the portion of heavens under examination, that our instrument is unable to measure its amount. The clouds act, therefore, not merely as collectors of atmospheric moisture, they also serve as mighty reflectors of light, regulating the supply of chemical rays, which are as necessary to the growth and well-being of plants as the warmth or moisture of the earth and air.

After these considerations on the diffuse daylight, we may pass on to the measurement of the chemical action effected by the direct solar rays.

III. CHEMICAL ACTION OF THE DIRECT SUNLIGHT.

In order to obtain data for the determination of the theory of this action, the volume of hydrochloric acid was measured, which was produced each minute in our instrument upon a cloudless day and at various zenith-distances of the sun, when the direct sunlight, diminished to a known extent, was allowed to fall perpendicularly over the whole surface of our insolation-vessel. For this purpose we directed the solar rays, by means of a SILBERMANN'S heliostat, through a fine opening in a thin plate, and allowed the sun's image thus formed so to fall upon the insolation-vessel that every portion of the sensitive mixture of chlorine and hydrogen was equally exposed. The position in which this takes place is easily found by holding a piece of paper behind the apparatus, and then moving the instrument until the shadow of the insolation-vessel appears exactly in the middle of the sun's image. The fine hole in the plate must be very carefully bored, as its area has to be accurately determined. We found that the best way of obtaining a perfectly circular opening was to lay a thin piece of copper foil upon a thick sheet of tin or lead, and to bore a small hole through the copper with a fine needle, afterwards rubbing the foil upon a moistened hone to separate all irregularities, and boring carefully with the needle, until, under the microscope, the edge of the hole was seen to be sharp and circular.

The diameter of the fine opening was determined by measurement with a micrometer, and the distance from the insolation-vessel to the point on the shutter of our dark room, where the opening was placed, was also determined. If we suppose that this distance be called b, and the diameter of the opening d, the apparent diameter (λ) of the opening, as seen from the insolation-vessel, is found from the formula

$$\tan \tfrac{1}{2}\lambda=\frac{d}{2b}.$$

The square of this apparent diameter (λ) is to the square of the apparent diameter of the sun (λ_{I}), as the observed action is to the action which the sun would have produced if it had shone direct upon the insolation-vessel. In order to obtain the total action proceeding from the sun, it is necessary to multiply the observed action by the factor

$$\Lambda=\frac{\lambda_{\mathrm{I}}^2}{\lambda^2}.$$

The factor for the transformation of the direct observations into units of light is, as in the former calculations,

$$n=2\cdot249.$$

The factor N, by help of which the experimental results are made independent of reflexion in the insolation-vessel, is found from the formula (1.),

$$\mathrm{N}=\frac{1-\gamma r}{1-r},$$

when $\frac{2\varrho}{1+\varrho}=r$ and $10^{-\alpha h}=\gamma$, and when ϱ signifies the coefficient of reflexion from glass into air, h the thickness of exposed sensitive gas in the insolation-vessel, and α the coefficient of extinction of direct sunlight for the chlorine and hydrogen mixture. As ϱ and h were known from our former experiments, we had only to determine the value of α; this was accomplished in the following way. Between the small opening in the shutter and the insolation-vessel, we placed one of our transparent cylinders* filled with air, and then measured the amount of action (w_1) effected by the direct sunlight falling on the instrument. The empty cylinder was next replaced by a similar one filled, the usual precautions being adopted, with the mixture of chlorine and hydrogen, and the action (w) again determined. After removal of this cylinder, the former one containing air was replaced and the action once more measured, and the mean of the three times of observation noted. From the first and third observations, with the cylinder containing air, the

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* Philosophical Transactions, 1856, p. 357.

action (w_1) was calculated which the sun's image would have effected at the mean time of observation if no chlorine and hydrogen mixture had been present. If we call h_1 the thickness of chlorine and hydrogen, reduced to 0° and $0^{m}\cdot76$, contained in the transparent cylinder, and if we neglect, as we can do without appreciable error, the reflexion from the interior of the transparent cylinder, the coefficient of extinction (α) is obtained from the equation*

$$\alpha=\frac{1}{h_1}\log\left(\frac{w_1}{w}\right).$$

The following Table gives the values of w and w_1 as found by experiment for the corresponding zenith-distances (ϕ) of the sun, and the values of α calculated therefrom. The thickness of the layer of chlorine and hydrogen collected at 22° C. and $0^{m}\cdot757$ was 32·3 millims., giving at 0° and $0^{m}\cdot76$ a thickness of 29·8 millims.

Table XV.

ϕ.	w.	w_1.	α.
61° 28′	3·41	14·03	0·0190
58 26	3·72	15·45	0·0191
50 20	4·35	18·40	0·0194

The mean of these numbers gives as the value of the coefficient of extinction for direct sunlight in the chlorine and hydrogen mixture $\alpha=0\cdot01923=\frac{1}{52}$ millim. The value of N is then found to be, according to formula (1.), by help of this number,

$$N=1\cdot036.$$

The experiments still require very considerable correction. The sunlight was reflected into our dark room by means of a Silbermann's heliostat. This was so placed that its mirror of speculum metal lay in one horizontal plane with the opening in the window-shutter. In one series of experiments, the rays, after having passed through the opening, were again reflected by means of a steel mirror; in the other experiments the rays fell without a second reflexion, in the same horizontal plane upon the insolation-vessel. In the case of two reflexions, a portion of the light is lost by absorption and polarization in quantities varying with the angles of incidence, and the angles at which the planes of polarization cut one another. This variable loss of light must be brought into calculation, and it is obtained by help of the following considerations.

A ray of light is reflected from a steel mirror in the angle i (fig. 13, Plate XLIII.); suppose that this ray when falling on the mirror has the intensity 1, and suppose that the reflected ray has the intensity p^2 when the ray is polarized parallel to the plane of incidence, and the intensity s^2 when the ray is polarized at right angles to this plane. In Poggendorff's 'Annalen'† are found two tables of Jamin's, in one of which are found the values of p, and the other those of s expressed as functions of i.

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* Philosophical Transactions, 1857, p. 603.

† Ergänzungs, Band ii. 1848, p. 445.

When $i=i_1$, then $p=p_1$, and $s=s_1$.

When $i=i_2$, then $p=p_2$, and $s=s_2$.

Suppose that a ray of light be reflected from both the mirrors 1 and 2 (fig. 14, Plate XLIII.), of which the first is of speculum metal and the second of steel, with the angles of reflexion i_1 and i_2; and suppose that the angle which the two planes of reflexion make with each other be β. The incident ray has the intensity 1, and consists of white light; the intensity of the twice reflected ray is then

$$S=\frac{1}{2}\{p_1^2(p_2^2\cos^2\beta+s_2^2\sin^2\beta)+s_1^2(p_2^2\sin^2\beta+s_2^2\cos^2\beta).$$

The observed chemical action, therefore, divided by S, gives the action which would have been observed if the sunlight had fallen directly without previous reflexion on the insolation-vessel. In order to calculate S, the values of i_1, i_2, and β must be determined for each observation. The second angle of incidence (i_2) was measured once for all.

In order to calculate the angle of incidence (i_1) varying with the position of the sun, we conceive the point of reflexion of the ray on the mirror of the heliostat to be the centre of a sphere, from which centre lines are drawn to the sun, to the earth's pole, to the south point of the horizon, and in the direction of the reflected ray. Let the four points produced by these lines cutting the sphere be represented by $SPMR_1$, fig. 15, Plate XLIII. The angle SR_1 is twice the angle of incidence of the ray; it is found from the spherical triangle PSR_1. In this triangle we know the side $PS=90-\delta$, when δ is the sun's declination. The sides R_1P and the angle R_1PS are thus found. In the spherical triangle PMR_1 the side MR_1, the azimuth of the opening in the shutter, directly measured, is known; the angle PMR_1 is a right angle, and $MP=180-p$ when p is the latitude of the place.

Hence

$$\cos PR_1=-\cos MR_1\cos p$$

and

$$\sin MPR_1=\frac{\sin MR_1}{\sin PR_1}.$$

The angle SPR_1 is, however, $=MPR_1+t$, when t signifies the hour-angle of the sun, positive before noon. Hence we have for R_1S, or for the angle $2i_1$ which the incident rays make with the ray reflected from the heliostat mirror,

$$\cos R_1S=\cos 2i_1=\cos PR_1\cos(90-\delta)+\sin PR_1\sin(90-\delta)\cos(R_1PM+t).$$

The angle β is thus obtained: SR_1, fig. 15, is the first plane of reflexion, R_1R_2 is the second plane of reflexion; hence

$$\beta=PR_1M-PR_1S,\quad\text{and}\quad\sin PR_1S=\frac{\sin PS\sin SPR_1}{\sin SR_1}.$$

When there is only one reflexion, we have for the value of S simply

$$S=\frac{1}{2}(p_1^2+s_1^2).$$

If we consider all these corrections together, we find that the action (W_0) expressed in degrees of light, which the sun shining freely upon the insolation-vessel would have produced if no disturbing influences were acting, is obtained from the direct observations of our instrument (w_0) by means of the following formula:—

$$W_0 = \frac{n_1 N \Lambda}{10000\, S} w_0. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11.)$$

The subjoined Table (XVI.) gives a series of observations made, as just described, on the 3rd of August, 1857, and on the 14th and 15th of September, 1858, the sky being perfectly cloudless and the gas having reached the maximum degree of sensibility. In the series of observations made on August 3, 1857, in which two mirrors were employed, namely, the heliostat mirror of speculum metal and another mirror of steel, the data for the calculation of Λ and S were as follows:—

$\lambda = 17''{\cdot}34$; $\lambda_1 = 1894''{\cdot}6$; $i_2 = 72^\circ\ 50'$; $MR_1 = 45^\circ\ 7'$; $\delta = +17^\circ\ 29'$; $p = 49^\circ\ 24'$.

In the experiments made on September 14 and 15, 1858, in which only one mirror was used, the data were

$\lambda = 21''{\cdot}22$; $\lambda_1 = 1912''$; $MR_1 = 73^\circ\ 44'$; $\delta = +3^\circ\ 26'$ for the 14th, and
$\delta = +3^\circ\ 4'$ for the 15th; $p = 49^\circ\ 24'$.

TABLE XVI.

I. True time.	II. Sun's zenith-distance.	III. Observed action, w_0.	IV. W_0.	V. S.
August 3, 1857. Barometer=$0^{m}{\cdot}7560$.				
h m	° ′			
7 59	57 35	8·70	63·13	0·384
8 42	50 51	12·11	89·21	0·378
9 14	46 8	12·56	92·96	0·376
September 14, 1858. Barometer=$0^{m}{\cdot}7550$.				
8 1	68 34	8·84	26·23	0·631
September 15, 1858. Barometer=$0^{m}{\cdot}7562$.				
7 9	76 30	1·52	5·54	0·637
7 26	73 49	4·22	15·50	0·633
7 40	71 37	6·09	22·43	0·631
8 0	68 34	7·56	27·85	0·631
8 7	67 30	8·38	38·87	0·631
8 26	64 42	12·48	45·85	0·633
8 54	60 48	17·09	62·59	0·634
9 14	58 11	18·51	67·61	0·636

The increase in the chemical action on diminution of the sun's zenith distance, as seen in the numbers of the second and fourth columns, arises from the extinction of the chemical rays effected by passage through the atmosphere. In order to obtain from these observations the law of this extinction, we may, without sensible error, disregard the curvature of the earth's surface, and consider the atmosphere as a horizontal layer. As the extinction in one and the same mass of substance of different densities remains the same, the question becomes still simpler if we consider the atmosphere to be of equal density throughout and measured at $0^{\mathrm{m}}\cdot76$ and 0° C.; in the following we shall therefore suppose the existence of such an ideal atmosphere. If we represent the chemical action of a solar ray before entering such an atmosphere by A, and its action when it has passed through a layer of atmosphere of the thickness l, by W_0, we find from the preceding considerations,

$$W_0 = A10^{-\alpha l},$$

when $\frac{1}{\alpha}$ represents the depth of atmosphere through which the ray has to travel until the chemical action produced is reduced from its original amount A to $\frac{1}{10}$th of that amount. The value of l is determined by the height of this ideal atmosphere and the zenith-distance of the sun.

Let us suppose that $c_{\prime}$, fig. 16, Plate XLIII., represents the place where the chemical action is measured, situated under the ideal atmosphere (L) measured at 0° and $0^{\mathrm{m}}\cdot76$; and let $c_{\prime}b$ represent the direction of the zenith, $c_{\prime}a$ that of the sun; then $bca=\varphi$, *i. e.* the sun's zenith-distance, $c_{\prime}b=h$ the perpendicular height of the atmosphere, and $ac_{\prime}=l$ the depth of atmosphere traversed by the ray. We have then $l=\frac{h}{\cos\varphi}$, and

$$W_0 = A10^{-\frac{\alpha h}{\cos\varphi}}. \quad \ldots \ldots \quad (12.)$$

If the values of A and αh are calculated from the observations of August 3, 1857, and September 14 and 15, 1858, by the method of least squares, we obtain $A=318\cdot3$, $\alpha h=0\cdot3596$. The mean barometric pressure in the three experiments was $0^{\mathrm{m}}\cdot7557=P_0$. The perpendicular height (h) to which the atmosphere at the time of observation would have extended, if its density had throughout been that corresponding to $0^{\mathrm{m}}\cdot7557$ and 0° C., is easily found from the specific gravities of air and mercury. Taking REGNAULT'S number 0·000095084 as representing the relation of the density of air and mercury, we have for our experiment—

$$h=\frac{0\cdot7557}{0\cdot000095084}=7947 \text{ metres.}$$

This number, substituted in $\alpha h=0\cdot3596$, gives for α the value 0·00004525. The sun's rays must therefore pass through a column of air at 0° and $0^{\mathrm{m}}\cdot76$ of $\frac{1}{0\cdot0004525}$ $=22100$ metres in length in order to reduce the chemical action to $\frac{1}{10}$th of its original amount. If we call P_0 the barometric pressure observed in the experiments from which α and A were found, the action which would have been observed under another pressure P, and under the zenith distance φ, is found from the equation

$$W_0 = A10^{-\frac{\alpha h P}{\cos\varphi P_0}}; \quad \ldots \ldots \quad (13.)$$

or substituting the experimental values of A, α, and P,

$$W_0 = 318\cdot3\times10^{-\frac{0\cdot4758 P}{\cos\varphi}}. \quad \ldots \ldots \quad (14.)$$

In the following Table (XVII.) the numbers calculated by means of this formula are compared with the action actually observed:—

TABLE XVII.

No. of the experiment.	Sun's zenith-distance.	Calculated chemical illumination in degrees of light.	Observed chemical illumination in degrees of light.
1	57° 35′	67·9	63·1
2	50 51	85·8	89·2
3	46 8	96·4	93·0
4	68 34	33·1	26·2
5	76 30	9·2	5·5
6	73 49	16·3	15·5
7	71 37	24·5	22·4
8	68 34	33·1	27·9
9	67 30	36·6	38·9
10	64 42	47·9	45·9
11	60 48	58·3	62·6
12	58 11	66·2	67·6

The probable error of the observations is

$$0{\cdot}6745\sqrt{\frac{\Sigma v^2}{12-1}}=\pm 2{\cdot}7 \text{ degrees of light.}$$

This mean error must be regarded as extremely small when we consider,—1st, the great difficulty experienced in keeping the mixture of chlorine and hydrogen at the maximum degree of sensibility during the whole range of experiments; 2ndly, the numerous reductions by means of which all the disturbing influences must be eliminated; and 3rdly, the slight alterations in the extinction of the light which local changes in the air's transparency may effect.

Formula (14.) shows that the sun's rays before their entrance into the earth's atmosphere would effect an illumination of 318·3=L degrees of light. If the rays producing this degree of illumination passed through an infinitely extended atmosphere of chlorine and hydrogen until they were completely extinguished, the absolute height (H) of the column of hydrochloric acid, measured at 0° and $0^{\mathrm{m}}{\cdot}76$, thus produced in one minute, is found from formula (4.), already given on page 888,

$$H=\frac{V}{q}\cdot\frac{1}{1-10^{-\alpha h}}\cdot L.$$

In the experiment from which the number 318·3 is obtained, one degree of light effected a combination per minute of $V=0{\cdot}00001155$ cubic metre of hydrochloric acid measured at 0° and $0^{\mathrm{m}}{\cdot}76$. According to our former experiments, the coefficient of extinction of sunlight for chlorine and hydrogen is $\alpha=\frac{1}{0{\cdot}052}$ metre. The internal area of the insolation-vessel was $q=0{\cdot}00033$ square metre. The internal diameter of the same, $d=0{\cdot}0094$ metre. The gas in the insolation-vessel was contained, during the observation, under a pressure of $P=0{\cdot}7551$ metre, and at a temperature of 18° C., for which the tension of aqueous vapour is $p=0^{\mathrm{m}}\cdot0154$. Hence the value of h is found to be

$$h=0\cdot00858 \text{ metre.}$$

By substitution of this number in the last formula, we have

$$\mathrm{H}=35\cdot3 \text{ metres.}$$

From this we see that the sun's rays, if they fell on the earth's surface without being weakened by passing through the atmosphere, would exert an action represented by 35·3 light-metres; that is, they would effect in one minute a combination, on a surface upon which they fall perpendicularly, of a column of hydrochloric acid 35·3 metres in height, assuming that the rays are extinguished by passing through an infinitely extended column of the sensitive gas.

By help of formula (14.) we find, moreover,—

That the sun's rays, after they have passed in a perpendicular direction through the atmosphere to the sea's level under a mean pressure of 0·76 metre, only effect an action of 14·4 light-metres, or that under these conditions, nearly two-thirds of their chemical activity has been lost by extinction and dispersion in the atmosphere.

If we assume that the mean distance of the sun to the earth is $r=20682329$ geographical miles, and if we imagine the sun in the centre of a sphere whose radius $=r$, the surface of this sphere is $4\pi r^2$. The light radiated from the sun upon this sphere would, if all the light were extinguished in the chlorine and hydrogen gas, produce in each minute a layer of hydrochloric acid of 35·3 metres, or 0·004756 geographical mile in height. Hence it follows,—

That the light which the sun radiates into space during each minute of time, represents a chemical energy, by means of which more than twenty-five and a half billions of cubic miles of chlorine and hydrogen may be combined to form hydrochloric acid.

In a similar way the chemical action has been calculated which the sun's rays, undiminished by atmospheric extinction, produce at the surface of each of the eight chief members of our planetary system. The second column of the following Table (XVIII.) contains the mean distances of these planets from the sun; the third column shows the chemical action represented in degrees of light effected by the sun's rays on the planet whose name is found in column I.; and in column IV. this same action is given in light-metres.

TABLE XVIII.

I.	II.	III.	IV.
			light-metres.
Mercury	0·387	2125·0	235·4
Venus	0·723	608·9	67·5
The Earth	1·000	318·3	35·3
Mars	1·524	137·1	15·2
Jupiter	5·203	11·8	1·2
Saturn	9·539	3·5	0·4
Uranus	19·183	1·0	0·1
Neptune.........	30·040	0·4	0·04

From these numbers it is seen how lavish Nature has been in her distribution of chemical energy throughout the universe. The Earth receives but an infinitely small portion of this radiation, whilst Saturn and the more remote planets obtain so much less, that on these bodies the existence of any organic life at all similar to that enjoyed on our globe must be impossible.

After these considerations touching the magnitude of the total chemical energy radiated from the sun, we may proceed to consider the conditions under which the small portion reaching the surface of our earth is distributed.

Compared with the thermic actions of the sun's rays, we immediately see an important difference. The heat, produced in the first instance by the absorption of the sun's rays, is so irregularly distributed by radiation and by oceanic and atmospheric currents over the earth's surface, that it rarely, if ever, is completely transformed at the time and at the place of its formation into real labour; so that the simple law, according to which the thermic climate of a place is dependent upon its elevation above the sea's level and the mean height of the sun, becomes completely obscured. The photo-chemical climate, on the other hand, is not subject to any such sweeping irregularities; for the chemical action which the sun effects upon a place, varying with its elevation above the sea and its geographical position, cannot be made to act at any point on the earth's surface other than the one on which the rays directly fall. Hence the diffusion and arrangement of the photo-chemical energy follows a much more simple law than that exhibited in the distribution of heat on the earth's surface.

By means of formula (14.) the amount of chemical energy effected by the sun's rays at a given time when the atmosphere is cloudless, can be calculated for any place whose geographical position is known, and for any height above the level of the sea.

In the following Table (XIX.) is found the chemical action expressed in degrees of light which the direct sun's rays effect at heights represented by barometric pressures of $0^{m}\cdot8$ to $0^{m}\cdot05$, with varying sun's zenith-distances from 90° to 0°. The highest horizontal division gives the zenith-distances, the first vertical column the atmospheric pressures, and the remaining columns the corresponding chemical actions. The curves (fig. 17, Plate XLVII.) show graphically the dependence of the chemical illumination upon the barometric pressure. The abscissæ denote sun's zenith-distances, the ordinates the chemical action in light-degrees effected at these zenith-distances. With each curve the corresponding barometric pressure is given. From this we see how unequal, under otherwise similar circumstances, the chemical illumination of low-land and high-land must be, and how this illumination increases as the distance above the sea becomes higher in a greater ratio than corresponds to the diminution of atmospheric pressure.

TABLE XIX.

	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.	90°.
m 0·80	132·5	130·7	125·2	115·7	102·3	81·4	55·2	24·5	2·1	0·0
0·75	139·8	138·2	132·7	123·2	108·9	88·1	61·5	28·8	2·8	0·0
0·70	147·8	146·1	140·7	131·3	116·9	96·5	68·7	33·8	3·8	0·0
0·65	156·2	154·5	146·6	139·6	125·7	105·2	76·6	29·2	5·3	0·0
0·60	165·0	163·3	158·1	149·0	135·0	114·5	85·5	46·6	7·2	0·0
0·55	174·2	172·6	167·6	158·7	145·0	124·7	95·4	54·7	9·9	0·0
0·50	184·1	182·5	177·7	169·0	155·7	135·7	106·4	64·2	13·6	0·0
0·45	194·4	193·0	188·4	180·1	167·2	147·8	118·8	75·3	18·6	0·0
0·40	205·3	204·0	199·6	191·9	179·7	161·0	132·5	88·4	25·5	0·0
0·35	216·9	215·7	211·6	204·4	193·0	175·3	147·8	103·8	35·0	0·0
0·30	229·1	228·0	224·4	217·8	207·2	190·9	165·0	121·7	48·0	0·0
0·25	241·9	241·0	237·8	231·9	222·6	207·9	184·1	142·9	65·8	0·0
0·20	255·7	254·8	252·1	247·2	239·1	226·3	205·3	167·7	90·1	0·0
0·15	269·5	269·4	267·3	263·2	256·8	246·5	229·1	196·9	123·5	0·0
0·10	285·2	284·7	283·2	280·5	275·8	268·4	255·7	231·1	169·3	0·0
0·05	301·3	301·0	300·2	298·7	296·3	292·2	285·2	271·1	232·1	0·0
0·00	318·3	318·3	318·3	318·3	318·3	318·3	318·3	318·3	318·3	0·0

From the curves we also see that the variations in the illumination appear most strikingly the lower the sun is above the horizon. When, for instance, at Reykiavik, under a barometric pressure of $0^{m}{\cdot}770$, the sun is 10° above the horizon, the ground is illuminated by direct sunlight to 2·5 degrees of light; if the barometer sinks 10 millims., the illumination rises to 2·9 degrees of light. On the highest point of the neighbouring crater of Hecla, upon which one of us observed a barometric pressure of $0^{m}{\cdot}6290$ on the 26th of July, 1846, the illumination from direct sunlight must rise to 6·1, and on the summit of Dwalaghiri to at least 90 degrees of light. At the time when the sun has nearly reached the zenith in the latitude of the Himalayas, the amount of the direct sunlight which falls on the valleys of the Thibetian high-lands where grain is cultivated, is nearly one and a half time as large as that falling on the neighbouring low-lands of Hindostan. This difference increases in so rapid a ratio with increasing zenith-distance, that when the sun is 45° removed from the zenith, the direct solar rays on the high table-land of Thibet give more than twice the chemical action of those falling on the plains of India.

From these few examples it is seen how rapidly the chemical intensity of the sunshine increases with considerable elevation above the sea's level. Yet the variations effected by reason of these changes are small when compared with the differences brought about by alterations in the latitude of the place of observation. In order to give an idea of these variations, we have calculated the chemical action which the sun's rays effect under a barometric pressure of $0^{m}{\cdot}76$ at the spring equinox during every hour of the day, on a horizontal unit of area situated at the points on the earth's surface for which the chemical illumination of the whole diffuse light has already been determined. The results of this calculation are contained in Table XX. The formula

$$W_0=318{\cdot}3\times10^{-\frac{0{\cdot}4758\,P}{\cos\phi}}$$

gives the chemical illumination for the unit of area upon which the sun's rays fall perpendicularly. In order that the supposed surface may be considered to be in the plane of the horizon and not at right angles to the incident ray, the values of W_0 have been multiplied by cos φ.

TABLE XX.

	Melville Island.	Reykiavik.	Petersburg.	Manchester.	Heidelberg.	Naples.	Cairo.
h h							
6 A.M. or 6 P.M. ...	0·00	0·00	0·00	0·00	0·00	0·00	0·00
7 A.M. or 5 P.M. ...	0·00	0·02	0·07	0·22	0·38	0·89	1·74
8 A.M. or 4 P.M. ...	0·07	1·53	2·88	5·85	8·02	13·31	20·12
9 A.M. or 3 P.M. ...	0·67	6·62	10·74	18·71	23·99	35·88	50·01
10 A.M. or 2 P.M. ...	1·86	13·27	20·26	32·91	40·94	58·46	78·61
11 A.M. or 1 P.M. ...	3·02	18·60	27·55	43·34	53·19	74·37	98·33
12 A.M.	3·51	20·60	30·26	47·15	57·62	80·07	105·3

The curves (fig. 18, Plate XLVIII.) represent the illuminations at the various places and times given in the foregoing Table (XX.). The ordinates represent the chemical actions, expressed in degrees of light, effected at the hours measured on the abscissæ for the places named on the curves. If we compare these curves with those of fig. 11, Plate XLVI. representing the diffuse light, the singular fact becomes apparent, that at the time of the vernal equinox the chemical actions which the direct sunlight effects from the north pole to below the latitude of Petersburg is, during the whole day, *less* than that effected by the total diffuse daylight; and that even in lower latitudes, down to the equator, the same phenomenon is observed, if not for the whole, yet for a portion of the day.

A further comparison of formulæ (9.) and (14.), shows that not only at the vernal equinox, but at all times and in all places where the sun rises more than 20° 56′ above the horizon, from sunrise till it attains a given height above the horizon, the chemical action effected by the diffuse daylight exceeds that of the direct sunlight; and that as the sun gradually rises, a point is reached at which both sunlight and diffuse daylight produce exactly the same amount of chemical action, whilst beyond this point the effect of the sunshine is most powerful. This "*phase of equal chemical illumination*" between daylight and sunshine, occurs twice daily, and represents a certain zenith-distance of the sun (φ), which may be found by a method of approximation from the formula

$$2\cdot776+80\cdot849\cos\varphi-45\cdot996\cos^2\varphi=\frac{318\cdot3}{\text{num log}=\dfrac{0\cdot4758P}{\cos\varphi}},$$

where the expression to the right denotes the chemical action effected by the sunlight at the pressure P (formula 14.), and that on the left hand gives the action proceeding from the whole heavens (formula 9.).

If we assume that the barometric pressure was $0^{m}\cdot76$, that the plane of the surface illuminated by the sunlight was placed perpendicular to the incident rays, and that the area illuminated by the daylight lay in the plane of the horizon, we find, on calculation, that the illumination of the sunshine is equal to that from the daylight when the distance of the sun from the zenith is 71° 12′.

These daily phases of equal chemical intensity can be determined by allowing the diffuse daylight and the direct sunlight to fall separately on two pieces of the same photographic paper, and by observing the time at which the same degree of colour is brought about on both pieces. From the correspondence of these observed times with those calculated according to the foregoing method, a good idea can be formed of the degree of reliability which our experiments, and the theory based thereon, warrant.

On February 21st and 22nd, and March 7th and 11th, 1859, the sky was perfectly cloudless from sunrise to sunset, and hence these days were well-adapted for the purpose of the experiments. The observations were made in a darkened space under the roof of the Heidelberg laboratory by two persons, one of whom, outside the roof, allowed the whole diffuse light of day, excluding the direct sunshine, to act upon the prepared paper, whilst the other observer allowed the direct sun's rays to fall inside the darkened space for an equal length of time perpendicularly upon another portion of the same paper. The sunlight passed through a hole in the roof, on to a blackened box with a circular opening of 1 inch in diameter. In order to preserve the paper always at right angles to the incident rays, it was fixed on a piece of board held in the hand, upon which an upright pin was fastened, and the board was so placed that the shadow of the pin on the paper was never thrown to one side or the other.

Allowing for the actual height of the barometer observed, $0^{m}\cdot764$, the zenith-distance of the sun, at which the chemical illumination from the direct sunlight is equal to that from diffuse light, is found to be 71° 4′. The sun reached this point on February 21, 1859, at 9^{h} 7^{m} A.M., and at 2^{h} 53^{m} P.M. The experiments on this day began at 11^{h} 30^{m} A.M., when the blackening effected by the sunlight was much more considerable than that produced by daylight; at a later hour this difference between the actions diminished; at 3^{h} 1^{m} scarcely any difference could be observed, and at 3^{h} 16^{m} the point of equal colour was passed, as the paper exposed to the sunlight was at this time considerably less coloured than that exposed to diffuse daylight. The phase required lies therefore between 3^{h} 1^{m} and 3^{h} 16^{m}; according to calculation, it should have occurred at 2^{h} 53^{m}. Another determination, made on the following day, showed that the phenomenon occurred in the afternoon between 3^{h} 23^{m} and 3^{h} 39^{m}, instead of at 2^{h} 56^{m}; and in the morning between 8^{h} 30^{m} and 8^{h} 43^{m}, instead of at 9^{h} 4^{m}. On March 7, 1859, under a barometric pressure of $0^{m}\cdot752$, the phase occurred in the afternoon between 4^{h} 17^{m} and 4^{h} 27^{m}, when, according to calculation, it should have occurred at 3^{h} 33^{m}. On March 11, 1859, the sky was intensely blue; the phase of equal colour appeared, under a pressure of $0^{m}\cdot764$, in the morning at 7^{h} 42^{m} instead of 8^{h} 22^{m}. From these experiments, it is not only seen that these phases which the theory requires actually occur, but also that the agreement between the observed and calculated time of appearance of these phases is very close. The point at which the phenomenon is observed in the morning is indeed about forty-five minutes earlier than the calculated point, whilst in the afternoon the calculated is about thirty minutes earlier than the observed point. These differences are, however, satisfactorily explained by the fact, that, in the situation at which the observations were made, the horizon towards north, west, and east is not free, owing to the hills of the Neckar Valley which rise 12° above the horizon, in consequence of which a deviation in the direction observed must occur.

We pass now to the consideration of the total chemical effect which the direct sunlight, varying with the time of day, produces on a unit of area lying in the plane of the horizon during a given time.

As has been already shown, the formula

$$W_1=\cos\varphi\times 318{\cdot}3\times 10^{-\frac{0{\cdot}4758\,P}{\cos\varphi}} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (15.)$$

gives the chemical effect (W_1) which the sun's rays exert on a horizontal unit of surface in the space of one minute. For the further calculation, it is, however, simpler to express W_1 by a series of powers of the sun's zenith-distance,

$$W_1=a\cos^2\varphi+b\cos^3\varphi+c.\cos^4\varphi+\ldots$$

By help of formula (15.) we have calculated the value of W_1 for every 10° of zenith-distance between 0° and 90°, and then by the method of least squares found the values of the coefficients a, b, and c. The calculation gives

$$W_1=-31{\cdot}99\cos^2\varphi+417{\cdot}6\cos^3\varphi-248{\cdot}7\cos^4\varphi. \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (16.)$$

The accompanying numbers show that the differences between the values of W_1, calculated according to the two formulæ (15.) and (16.), are so inconsiderable, as to fall within the unavoidable errors of observation.

According to formula 15.		According to formula 16.
138·4	0°	136·9
134·6	10	133·8
123·3	20	124·3
105·4	30	107·3
82·2	40	83·3
56·0	50	55·2
30·1	60	29·6
9·5	70	9·6
0·5	80	1·0
0·0	90	0·0

We will now calculate the amount of the chemical rays which fall during a given time and at a given situation upon a unit of surface in the plane of the horizon.

The sun's zenith-distance is connected with the true solar time of a place by the equation

$$\cos\varphi=\cos\delta\cos p\cos t+\sin\delta\sin p,$$

when δ represents the sun's declination, p the latitude of the place, and t the sun's hour-angle. If, for the sake of shortness, we call $\sin\delta\sin p=\alpha$, and $\cos\delta\cos p=\beta$, and develope formula (16.) in a series of powers of cos *t*, we have

$$\begin{aligned}W_1=&a(\alpha^2+2\alpha\beta\cos t+\beta^2\cos^2 t)\\&+b(\alpha^3+3\alpha^2\beta\cos t+3\alpha\beta^2\cos^2 t+\beta^3\cos^3 t)\\&+c(\alpha^4+4\alpha^3\beta\cos t+6\alpha^2\beta^2\cos^2 t+4\alpha\beta^3\cos^3 t+\beta^4\cos^4 t).\end{aligned}$$

The integral $\int W_1 dt$ has now to be determined. For this purpose we consider

$$\int dt=t$$

$$\int\cos t dt=\sin t$$

$$\int\cos^2 t dt=\frac{\cos t\sin t}{2}+\tfrac{1}{2}t$$

$$\int\cos^3 t dt=\frac{\cos^2 t\sin t}{3}+\tfrac{2}{3}\sin t$$

$$\int\cos^4 t dt=\frac{\cos^3 t\sin t}{4}+\tfrac{3}{8}\cos t\sin t+\tfrac{3}{8}t.$$

For the equinox $\alpha=0$ and $\beta=\cos p$; if the action for the whole day is required, the integration must be taken from

$$t=-\frac{\pi}{2}\text{ to }t=+\frac{\pi}{2};$$

for these limits we have—

$$\int dt\quad=\pi$$

$$\int\cos t dt\quad=2$$

$$\int\cos^2 t dt\quad=\frac{\pi}{2}$$

$$\int\cos^3 t dt\quad=\tfrac{4}{3}$$

$$\int\cos^4 t dt=\tfrac{3}{8}\pi;$$

also

$$\int w dt=\frac{\pi}{2}a\cos^2 p+\tfrac{4}{3}b\cos^3 p+\tfrac{3}{8}\pi\cos^4 p,$$

and

$$W=12\times 60\left(\frac{a}{2}\cos^2 p+\frac{4}{3\pi}b\cos^3 p+\tfrac{3}{8}c\cos^4 p\right);$$

on substitution of the values of *a*, *b*, and *c*,

$$W=-11520\cos^2 p+127600\cos^3 p-67140\cos^4 p.$$

Calculated according to this formula, the following Table (XXI.) contains the total amount of sunlight, expressed in degrees of light, falling during the day at the vernal equinox upon the horizontal unit of area at the previously mentioned places. Division I. contains the names of the places for which the calculation has been made; division II. the latitudes of these places; division III. the chemical degrees of light to which the horizontal area is illuminated by sunshine alone; division IV. the degrees of light, already given in Table XIII. *b*, to which the same area is illuminated by the total diffuse daylight; division V. the chemical illumination effected by both the sun and diffuse light together; and lastly, division VI. the height of the column of hydrochloric acid (at 0° and $0^{\text{m}}\cdot76$), calculated according to formula (4.), which the total illumination of sun and daylight is able to combine during this one day.

Table XXI.

I.	II.	III.	IV.	V.	VI. metres.
Melville Island	74° 47′ N.L.	1196	10590	11790	1306
Reykiavik	64 8 N.L.	5964	15020	20980	2324
Petersburg	59 56 N.L.	8927	16410	25340	2806
Manchester...............	53 20 N.L.	14520	18220	32740	3625
Heidelberg	49 24 N.L.	18240	19100	37340	4136
Naples......................	40 52 N.L.	26640	20550	47190	5226
Cairo	30 2 N.L.	36440	21670	58110	6437
Bombay	19 0 N.L.	43820			
Ceylon	10 0 N.L.	47530			
Borneo	0 0 N.L.	48940			

From the numbers in division V. it is seen that the total chemical energy which the earth receives simultaneously from the whole heavens and from the sun, varies comparatively slightly with the latitude of the place. At Cairo the total chemical action is about five times, and at Heidelberg about twice as large as it is on Melville Island, which is only about 15° distant from the north pole. Notwithstanding this small difference, the highest position of the sun above the horizon on the day in question at these three places is very different; viz. at Melville Island, 15° 13′; at Heidelberg, 40° 36′; and at Cairo, 59° 58′. The explanation of this remarkable relation is to be found in the large dispersive power of the atmosphere, which acts as a regulator of the photochemical processes occurring on the earth's surface, modifying and lessening the great differences in the chemical illumination produced by the direct sunlight. This is plainly seen on reference to the numbers in divisions III. and IV. The numbers representing the chemical activity developed by sunlight alone in Melville Island, Heidelberg, and Cairo, are nearly in the relation of 1:15·3:30·5, whereas the chemical actions brought about by diffuse daylight at these places, when the amount of direct sunlight on Melville Island is taken as unity, are as 8·9:16:18·1.

A comparison of columns III. and IV. show moreover that, singularly enough, the amount of chemical energy effected by the diffuse daylight is, down to the latitude of Heidelberg, larger than that produced by the direct sunlight. At Heidelberg the action from both sources is nearly equal; at Petersburg that of the diffuse daylight is almost double of that of the sunlight; and at Melville Island the effect produced by the former source is nearly ten times as large as that effected by the latter.

IV. THE PHOTO-CHEMICAL ACTION OF THE SUN COMPARED WITH THAT OF A TERRESTRIAL SOURCE OF LIGHT.

We have made a few experiments for the purpose of comparing the light evolved from the sun's body with that liberated from a terrestrial source. The most suitable light for this object, appeared to be the intense illumination produced by the combustion of magnesium wire in the air. In the following experiments we have employed a piece of magnesium wire, the radius of which, measured under a microscope, was $r=0·1485$ mm.; this wire was pressed out of a steel press by the method employed by one of us for the preparation of potassium and sodium wire, and applied by Dr. MATTHIESSEN to the metals of the alkaline earths. When the end of such a wire is raised in temperature, it takes fire and burns on regularly throughout its entire length, leaving a coherent thread of magnesia.

In order to compare the light thus evolved with that of the sun, it was necessary to know the length of wire which remained incandescent during the combustion. This cannot be measured directly, because a surface of a few square millimetres appears during the ignition like a ball of fire as large as a nut. If the enormous intensity of the light be weakened by transmission through dark coloured glasses, the edges of the wire can be more distinctly seen; but, owing to the rapidity with which the combustion proceeds, even in this way no exact measurement is possible. The length of the incandescent piece of wire may, however, be obtained, with sufficient accuracy, in the following way:—Between 30 and 40 millimetres of wire of the above thickness were held in front of a photometric stearinized diaphragm illuminated by a gas-flame burning in the tin box described in our former papers, and then burnt at such a distance from the diaphragm that the ring just disappeared. If, now, all the arrangements remaining the same, shorter pieces of wire of exactly known length are burnt, the ring always disappears until the length of the wire taken is less than the part which during the combustion is kept incandescent. From this time forward the ring appears plainly, and is seen to be black on a white ground. Two experiments made in this way showed that pieces of wire above 10 millims. in length rendered the ring invisible, whilst with pieces shorter than 10 millims. the ring was seen to be dark on light ground. The length of wire kept continually incandescent during the combustion is therefore $h=10$ millims. in length. The wire burning at a distance of 2440 millims. from the insolation-vessel of our photometer, effected an action of 181·7 units of light, or of 0·01817 degree of light per minute. The light producing this action emanated from a cylinder of magnesium, having a radius 0·1485 millim. and a height of 10 millims. The surface of this half cylinder gives out as much light as an equally intensely illuminated rectangle whose base is equal to the diameter, and whose height is the same as the height of the cylinder. This rectangle had, in our experiment, the area $2rh=2·97$ square millimetres, or a circular area having a radius of 0·9725 millim. radius. If this surface had been placed at a distance of 208·7 millims. from the insolation-vessel, instead of 2440 millims., the action, instead of being 0·01817 degree of light, would have been

$$\frac{0{\cdot}01817 \times 2440^2}{208{\cdot}7^2} = 2{\cdot}482 \text{ degrees of light.}$$

This distance (208·7) is, however, that at which the luminous circular area of burning magnesium seen from the insolation-vessel has the apparent magnitude of the sun's disk. As the sun, before its rays suffered diminution by passing through the atmosphere, would effect upon the insolation-vessel an illumination of 318·3 degrees of light (seen from formula 14.), the chemical brightness, or the chemical activity of the rays proceeding from the sun's surface is $\frac{318{\cdot}3}{2{\cdot}482}$, or 128·2 times larger than that of the rays evolved from magnesium wire burnt in the way described. By help of the same formula (14.) it is seen that the chemical brightness of our incandescent magnesium wire is equal to that of the sun when it stands about 9° 53′ above the horizon. A burning surface of magnesium wire, which, seen from a point at the sea's level, has an apparent magnitude equal to that of the sun, effects on that point the same chemical action as the sun would do when shining from a cloudless sky at a height of 9° 53′ above the horizon. If, for instance, such a surface had a diameter of 1 metre, the chemical action which it would produce at a distance of 107 metres is the same as the sun would effect when shining perpendicularly on any object from an elevation of 9° 53′ above the horizon.

As a matter of interest we have, in contradistinction to the *chemical*, compared the *visual* brightness of these two sources of light, *i. e.* the brightness as measured by the eye.

For this purpose the direct rays of the sun at 12 o'clock at noon on the 13th of November, 1858, when the sky was cloudless, were reflected by means of a mirror of black glass through a circular opening of 0·399 millim. diameter on to the stearinized diaphragm of the photometer, and then the gas-flame of the photometer was so arranged that the diaphragm ring disappeared. In order to counterbalance the different colour of gas- and sun-light, a piece of pale blue glass was placed between the flame and the diaphragm.

Let us suppose that the intensity of the light when the ring disappears is I. Let S be the intensity which the unit amount of sunlight possesses after the one reflexion, g the apparent area which the hole through which the sun passes appears to have when seen from the diaphragm, and g_1 the apparent area of the sun's disk; then the following fraction gives the intensity of the sun's direct rays falling perpendicularly upon the diaphragm,

$$\frac{\mathrm{I}g_1}{\mathrm{S}g}.$$

In order to compare with this, the intensity of the burning magnesium, the wire was burnt before the diaphragm of the photometer, at such a distance that the ring, as in the case of illumination with the sun, disappeared. If we call g_2 the apparent area of the incandescent surface of the wire as seen from the photometer ring, the burning portion of the wire will illuminate the diaphragm, when its apparent area is equal to that of the sun, with the intensity

$$\frac{Ig_1}{g_2}.$$

The visual brightness (G) of the sun, compared with that of a burning magnesium wire, is therefore

$$G=\frac{g_2}{Sg}.$$

If the radius of the opening through which the sun shines be r; the distance of the opening from the photometer diaphragm d; the radius of the incandescent surface of magnesium considered as circular r_1; and the distance of this surface from the diaphragm d_1, the brightness of the sun compared with that of the magnesium is

$$G=\frac{d^2 r_1^2}{S d_1^2 r^2}.$$

S is found from the formula

$$S=\frac{\sin^2(\phi-\phi')}{\sin^2(\phi+\phi')}+\frac{\tan^2(\phi-\phi')}{\tan^2(\phi+\phi')},$$

when ϕ signifies the angle of incidence and ϕ' the angle of refraction of the ray. ϕ_1 is calculated from the refractive index of the mirror $=1{\cdot}55=\frac{\sin\phi}{\sin\phi_1}$, when the angle of incidence (ϕ) is known. The value of ϕ is obtained from the azimuth (A) of the opening through which the rays pass; from the sun's declination (δ) on the day of experiment; from the time of observation (t), and from the latitude of Heidelberg (p), by means of the formula (8.) already employed. By substituting the following numerical values, $A=73°\ 44'$; $\delta=-17°\ 58'$; $t=0°\ 0'$; $p=49°\ 24'$ in the formula, we have

$$S=0{\cdot}05101.$$

Direct measurement gave

$r=0{\cdot}1995$ millim.; $r_1=0{\cdot}9725$ millim.; $d=2590$ millims.; $d_1=2440$ millims.

Hence

$$G=524{\cdot}7.$$

The observations were made on November 13th, 1858, at $12^h\ 0^m$, when the sun's zenith-distance was 67° 22′. The brightness of the sun's disk, as measured by the eye, is therefore, at this zenith-distance, 524·7 times as great as that of the burning magnesium wire, whilst at the same zenith-distance the chemical brightness of the sun is only 36·6 times as great.

The steady and equable light evolved by magnesium wire burning in the air, and the immense chemical action thus produced, render this source of light valuable as a simple means of obtaining a given amount of illumination expressed in terms of our measurement of light. According to the above experiment, a piece of magnesium wire 0·987 metre long and 0·297 millim. in diameter, effects at a distance of 2·44 metres an action of 181·7 units of light, of which 10,000 are equal to 1 degree of light. For every millimetre of magnesium wire burnt, there is therefore produced 1·1 unit of light at a distance of 1 metre. These numbers cannot be supposed to be very accurate, as the quantity of magnesium upon which we could operate was but small, and we were therefore unable to eliminate the errors arising from the phenomenon of induction as completely as could be wished.

The combustion of magnesium constitutes so definite and simple a source of light for the purposes of photo-chemical measurement, that the wide distribution of this metal becomes desirable. The application of this metal as a source of light may even become of technical importance. A burning magnesium wire of the above thickness evolves, according to a measurement we have made, as much light as 74 stearine candles*, of which five go to the pound. If this light lasted one minute, 0·987 metre of wire, weighing 0·1204 grm., would be burnt. In order to produce a light equal to 74 candles burning for 10 hours, whereby about 20 lbs. of stearine is consumed, 72·2 grms. of magnesium would be required. The magnesium wire can be easily prepared by forcing out the metal by great pressure from a heated steel press having a fine opening at bottom: this wire might be rolled up in coils on a spindle which could be made to revolve by clock-work, and thus the end of the wire, guided by passing through a groove or between rollers, could be continually pushed forward into a gas- or spirit-lamp flame in which it would burn.

V. CHEMICAL ACTION OF THE CONSTITUENT PARTS OF SOLAR LIGHT.

The chemical action effected by the several portions of the solar spectrum depends not only upon the nature of the refracting body, but also upon the thickness of the column of air through which the light has to pass before decomposition. In the following experiments we have employed prisms and lenses of quartz, cut by Mr. DARKER of Lambeth, instead of glass prisms, which, as is well known, absorb a large portion of the chemically active rays. In order to render our experiments as free as possible from the irregularities arising from variation in the atmospheric absorption, the observations were made quickly one after the other, so that the zenith-distance of the sun altered but very slightly.

A perfectly cloudless day was chosen for these observations, and the direct sunlight reflected from the speculum-mirror of a SILBERMANN'S heliostat through a narrow slit into our dark room. The spectrum produced by the rays passing through two quartz prisms and a quartz lens, fell upon a white screen which was covered with a solution of sulphate of quinine, to render the ultra-violet rays and the accompanying dark lines visible. In this screen a narrow slit was made through which the rays from any wished-for portion of the spectrum could be allowed to pass, so as to fall directly upon the insolation-vessel situated at a distance of from 4 to 5 feet. A finely divided millimetre-scale was also placed on the screen, by means of which the distance between the FRAUNHOFER'S lines could be accurately measured, and the portion of light employed thus exactly determined.

In order to recognize with accuracy the various portions of the spectrum, we employed a map of the dark lines prepared by Mr. STOKES, which he most kindly placed at our

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* This number must only be regarded as an approximation to the truth, as the diaphragm of the photometer had to be illuminated with light passing a light-blue glass.

disposal. The figure (fig. 19, Plate XLVII.) contains a copy of Mr. STOKES'S map, with the distances measured by him, and letters given according to his notation. We have divided the space between the letter A in the red to the last ray STOKES observed, W in the lavender rays, into 160 equal parts, and we represent the position and breadth of the bundle of rays which effected a given action upon the insolation-vessel as follows:—If a bundle of rays lying between the abscissæ 20·5 and 34 in fig. 15 had to be represented, we should call the edge of the bundle towards A, $\frac{1}{2}$ DE, and that towards W, $\frac{1}{4}$ FG, whilst the middle of the bundle, or the portion of the spectrum which produces the action, we call "$\frac{1}{2}$ DE to $\frac{1}{4}$ FG." The breadth of this bundle of rays, in which the insolation-vessel was completely bathed, was $\frac{8}{100}$ of the total length of the spectrum.

The following Table gives the direct results of a series of observations made by perfectly cloudless sky at Heidelberg, on the 14th of August, 1857, under a barometric pressure of $0^{m}\cdot7494$. The first column gives the numbers of the observations in the order in which they were made; column II. the times of observation in true solar time; column III. the portion of spectrum under examination; and column IV. the action corresponding to this portion.

I.	II.	III.	IV.
	h m		
1	10 54 A.M.	From $\frac{3}{5}$ GH to I	48·80
2	10 58 A.M.	From $\frac{1}{5}$ DE to E	1·27
3	11 4 A.M.	From C to $\frac{1}{2}$ DE	0·47
4	11 8 A.M.	From N_1 to $\frac{3}{4}$ QR.........	18·28
5	11 13 A.M.	From $\frac{1}{2}$ RS to $\frac{2}{3}$ ST......	2·03
6	11 41 A.M.	From $\frac{3}{4}$ ST to $\frac{2}{3}$ UV......	1·27
7	11 47 A.M.	From $\frac{1}{2}$ N_4Q to $\frac{1}{3}$ RS ...	11·73
8	11 50 A.M.	From $\frac{3}{4}$ ST to $\frac{2}{3}$ UV......	1·02
9	11 54 A.M.	From $\frac{4}{5}$ IM_1 to N_4	37·87
10	11 57 A.M.	From H_1 to $\frac{3}{4}$ IM_1	57·42
11	0 1 P.M.	From H_1 to $\frac{3}{4}$ IM_1	52·30
12	0 4 P.M.	From $\frac{1}{5}$ GH to H.........	61·38
13	0 7 P.M.	From $\frac{1}{5}$ FG to G	27·64
14	0 16 P.M.	From $\frac{1}{5}$ FG to G	28·74
15	0 20 P.M.	From $\frac{3}{4}$ DE to F	1·39
16	0 25 P.M.	From $\frac{1}{2}$ N_4Q to $\frac{1}{3}$ RS ...	13·19
17	0 32 P.M.	From $\frac{1}{2}$ N_4Q to $\frac{1}{3}$ RS ...	12·41
18	0 40 P.M.	From G to $\frac{4}{5}$ GH.........	53·78
19	0 42 P.M.	From $\frac{1}{5}$ GH to H.........	58·74
20	0 45 P.M.	From $\frac{3}{5}$ GH to I	53·9

If the fraction of the unit amount of incident light which is reflected from the mirror of the heliostat at the commencement and at the end of the series of experiments be calculated, we get the numbers 0·644 and 0·642, which differ so slightly, that the variations brought about by the reflexion may be neglected without overstepping the observational errors. At the times of observation on the 14th of August, 1857, the sun's zenith-distance was as follows:—

h m	°
At 10 54 A.M.	37 35
At 0 0 A.M.	35 13
At 0 45 P.M.	36 16

The chemical intensity of the sun's rays at these various periods may be calculated by formula (14.). They are in the proportion of the numbers 1·002, 1·000 and 1·016. Although the differences between these numbers are but small, we have reduced all the observations to that chemical action which would have been observed if they had all been made at $12^h\ 0^m$ A.M. upon the day in question. The following Table contains the numbers thus reduced, the mean value having been taken of those observations which occur more than once:—

No.	True solar time.	Position in the spectrum.	Relative chemical action.
	h m		
1	10 54 A.M.	From $\frac{3}{5}$ GH to I …………	52·7
2	10 58 A.M.	From $\frac{1}{5}$ DE to E …………	1·3
3	11 4 A.M.	From C to $\frac{1}{2}$ DE …………	0·5
4	11 8 A.M.	From N_1 to $\frac{3}{4}$ QR…………	18·9
5	11 13 A.M.	From $\frac{1}{2}$ RS to $\frac{2}{3}$ ST ………	2·1
6	11 41 A.M.	From $\frac{3}{4}$ ST to $\frac{2}{3}$ UV………	1·2
7	11 47 A.M.	From $\frac{1}{2}$ N_4Q to $\frac{1}{3}$ RS ……	12·5
8	11 54 A.M.	From $\frac{4}{5}$ IM_1 to N_4…………	38·6
9	0 1 P.M.	From H_1 to $\frac{3}{4}$ IM_1 ………	55·1
10	0 4 P.M.	From $\frac{1}{5}$ GH to H…………	60·5
11	0 16 P.M.	From $\frac{1}{5}$ FG to G …………	28·4
12	0 20 P.M.	From $\frac{3}{4}$ DE to F …………	1·4
13	0 40 P.M.	From G to $\frac{4}{5}$ GH …………	54·5

The lines *a a a a* (fig. 19, Plate XLVII.) give a representation of the relative chemical action which the various parts of the spectrum, the rays of which have only passed through air and quartz, effect on the sensitive mixture of chlorine and hydrogen. It is seen that this action attains many maxima, of which the largest lies by $\frac{1}{5}$ GH to H, and the next at I, and also that the action diminishes much more regularly and rapidly towards the red than towards the violet end of the spectrum.

The sun, when it was employed for these experiments, was 35° 13′ removed from the zenith. If the atmosphere were throughout of the density corresponding to $0^m{\cdot}76$ and 0° C., the perpendicular height which, during our experiment, it would have possessed, is

$$\frac{0{\cdot}7494}{0{\cdot}000095084}=7881 \text{ metres.}$$

The depth of atmosphere through which the rays had to pass in this experiment was, however,

$$\frac{7881}{\cos 35^\circ\ 13'}=9647 \text{ metres.}$$

We have stated in one of our previous communications*, that the solar rays which at different hours of the day pass through the same column of chlorine, are altered in a very different manner. This shows that rays of different chemical activity are absorbed in very different ways by the air. The above results are therefore only applicable for sunlight which has passed through a column of air, measured at $0^m{\cdot}76$ and 0° C., of 9647 metres in thickness. For rays which have to pass through a column of air of a different length from this, the chemical action of the various constituents of the spectrum must

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* Philosophical Transactions, 1857, p. 617, &c.

be different. The order and degree in which the chemical rays are absorbed, may be obtained by repeating the observations according to the above method from hour to hour during a whole day. Such a series of experiments we have unfortunately as yet been unable to execute, owing to the variability of the weather in our latitudes. One very imperfect series of observations we can, however, quote, and they suffice to show that the relation between the chemical action of the spectral colours is perceptibly altered when the thickness of air through which the rays pass changes from 9647 to 10,735 metres.

These experiments were likewise made on August the 14th, 1857, in the short space of time from $9^h\ 44^m$ to $10^h\ 19^m$ A.M., and gave the following numbers reduced to the zenith-distance (42° 46′), corresponding to $10^h\ 0^m$ A.M. They were, however, made with a bundle of rays of a different thickness from the former experiments, and therefore cannot be compared with those.

No.	Time.	Portion of spectrum.	Relative chemical action.
	h m		
1	9 44 A.M.	From $\frac{3}{5}$ GH to I	14·5
2	9 48 A.M.	From N_3 to R_2	10·1
3	9 54 A.M.	From $\frac{1}{10}$ R_2S to $\frac{1}{5}$ ST......	2·4
4	9 59 A.M.	From $\frac{1}{2}$ ST to U	0·0
5	10 4 A.M.	From G to $\frac{4}{5}$ GH	13·0
6	10 8 A.M.	From F to $\frac{3}{4}$ FG...........	7·1
7	10 11 A.M.	From *b* to $\frac{1}{2}$ FG	3·2
8	10 15 A.M.	From $\frac{1}{2}$ DE to $\frac{3}{4}$ EF	0·4

These observations are represented by the lines *b b b* (fig. 19, Plate XLVII.) in which, it must be remembered, a unit different from that of the other experiments is employed. From this it is seen that the relation of the chemical action of the spectrum from the line E to the line H undergoes a considerable alteration when the rays have to pass through a column of air 10,735 metres in height instead of 9647 metres.

An extended series of measurements of the chemical action of the several portions of the solar spectrum under various conditions of atmospheric extinction, may prove of great interest, if, as we can now scarcely doubt, the solar spots appear at regular intervals, and our sun belongs to the class of fixed stars of variable illuminating power. It is possible that such observations, made during the presence and during the absence of the solar spots, may give rise to some unlooked-for relations concerning the singular phenomena occurring on the sun's surface. Whether, however, the atmospheric extinction can ever be determined with sufficient accuracy to render visible the alteration in the light which probably occurs with the spots, is a question which can only be decided by a series of experimental investigations which must extend far beyond the scope of any single observer.

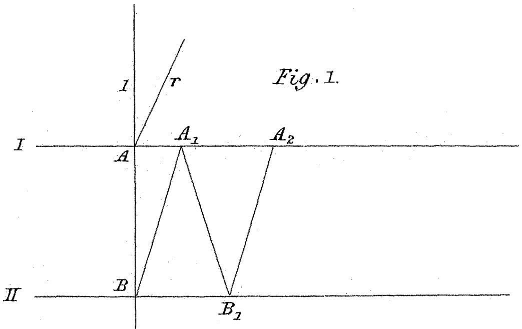
Fig. 1.

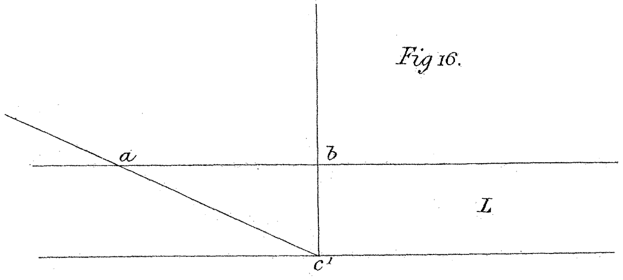
Fig. 16.

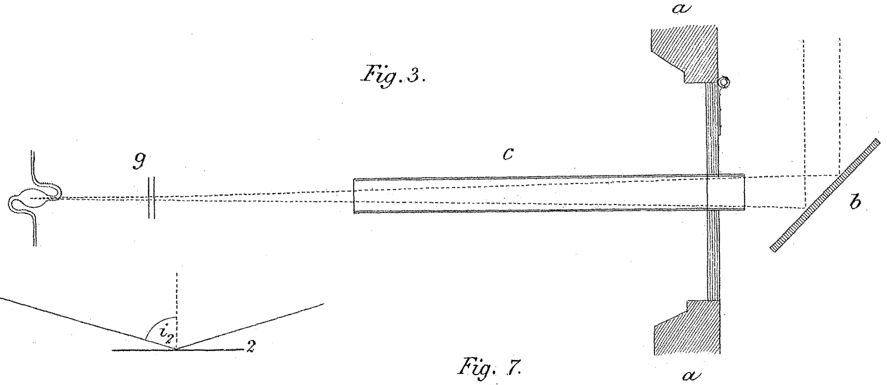
Fig. 3.

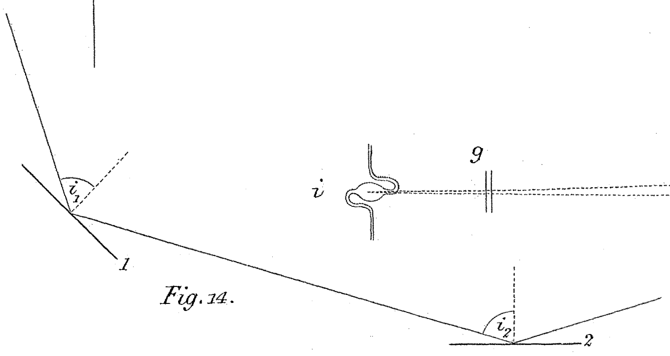
Fig. 14.

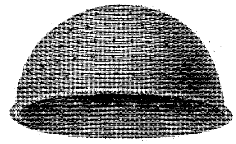
Fig. 7.

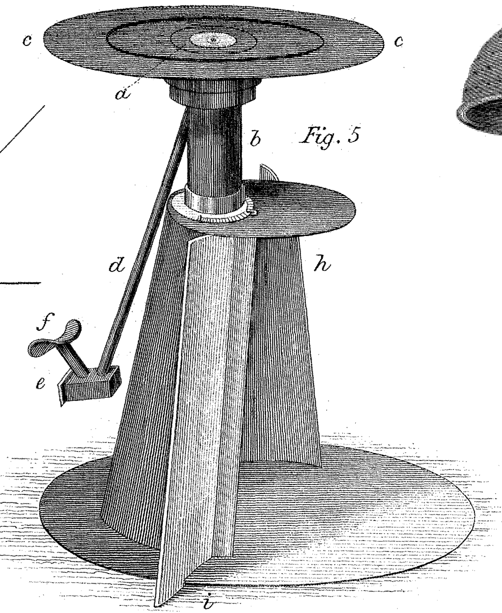
Fig. 5

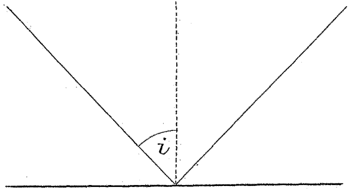
Fig. 13.

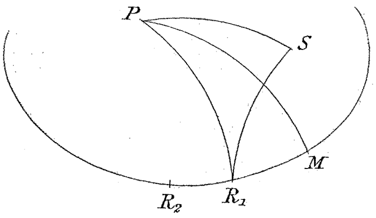
Fig. 15.

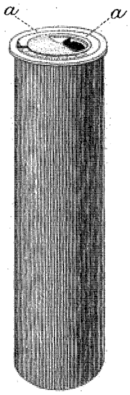
Fig. 6.

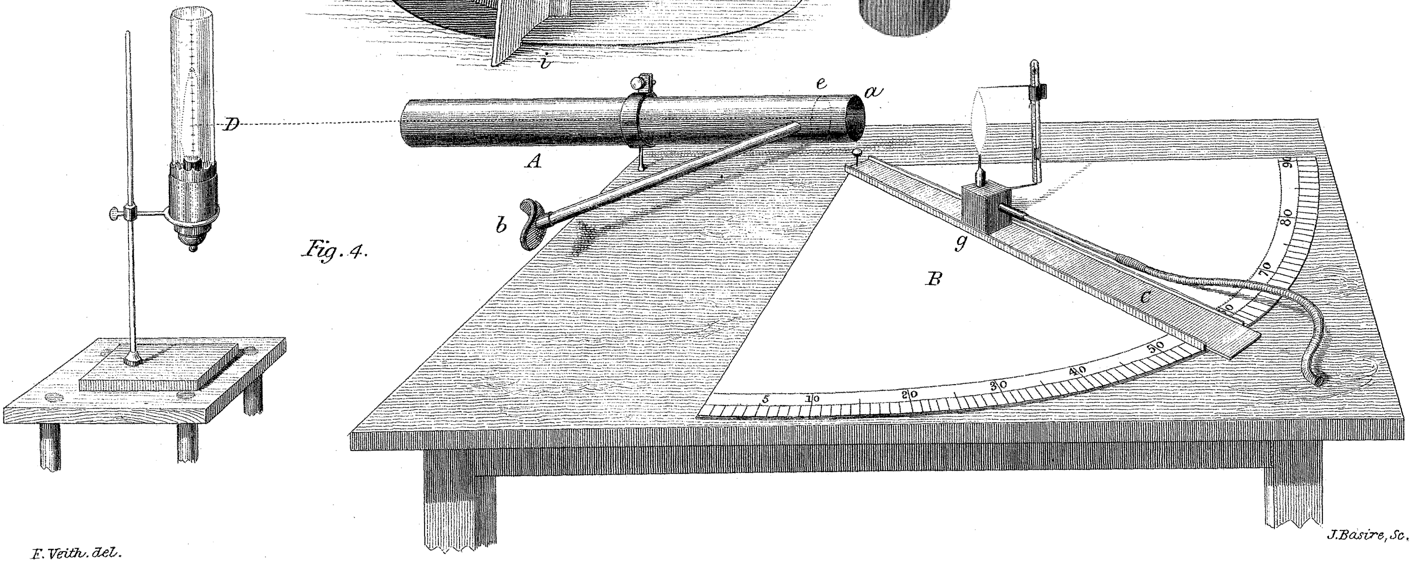
Fig. 4.

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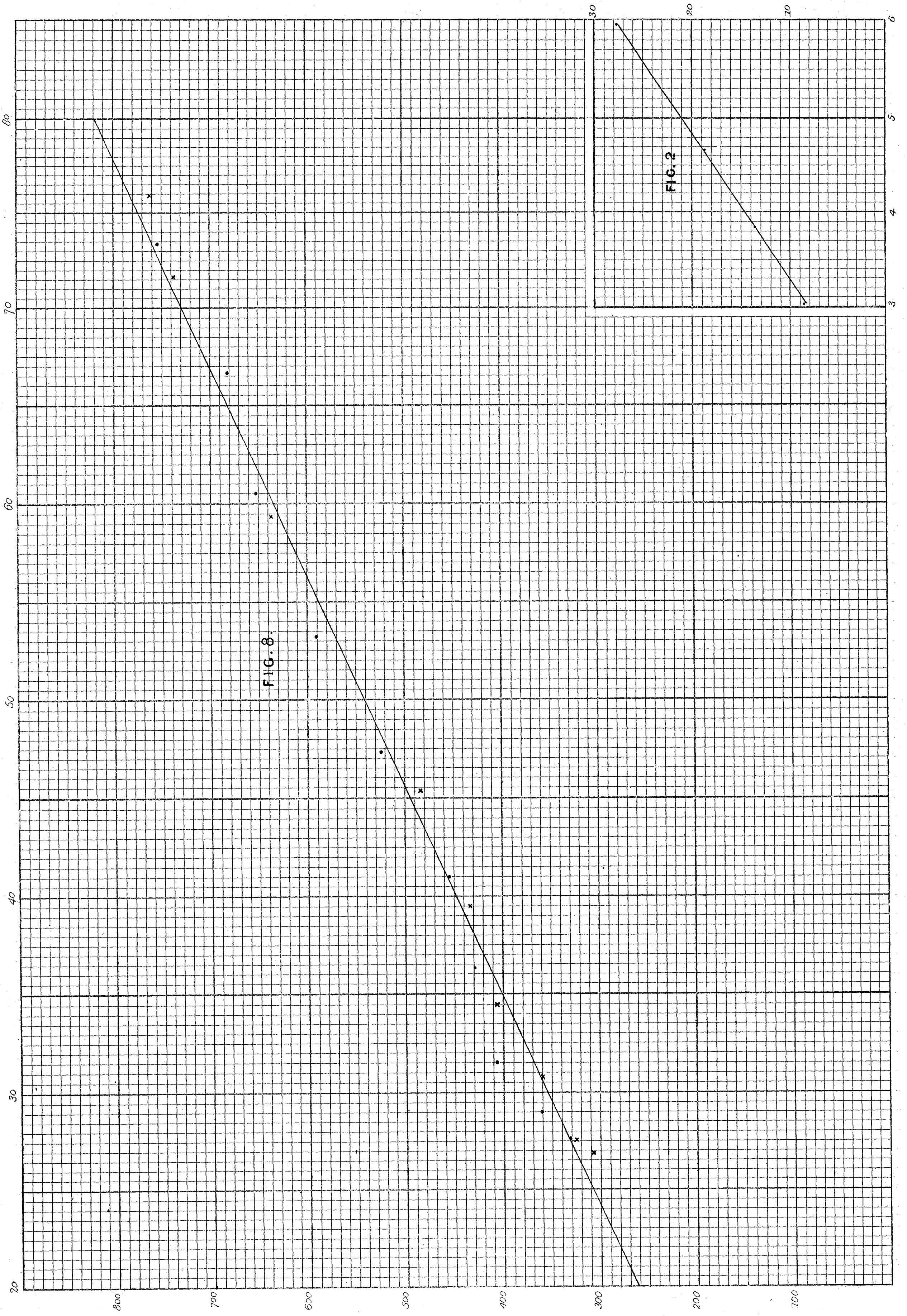
FIG. 8
FIG. 2
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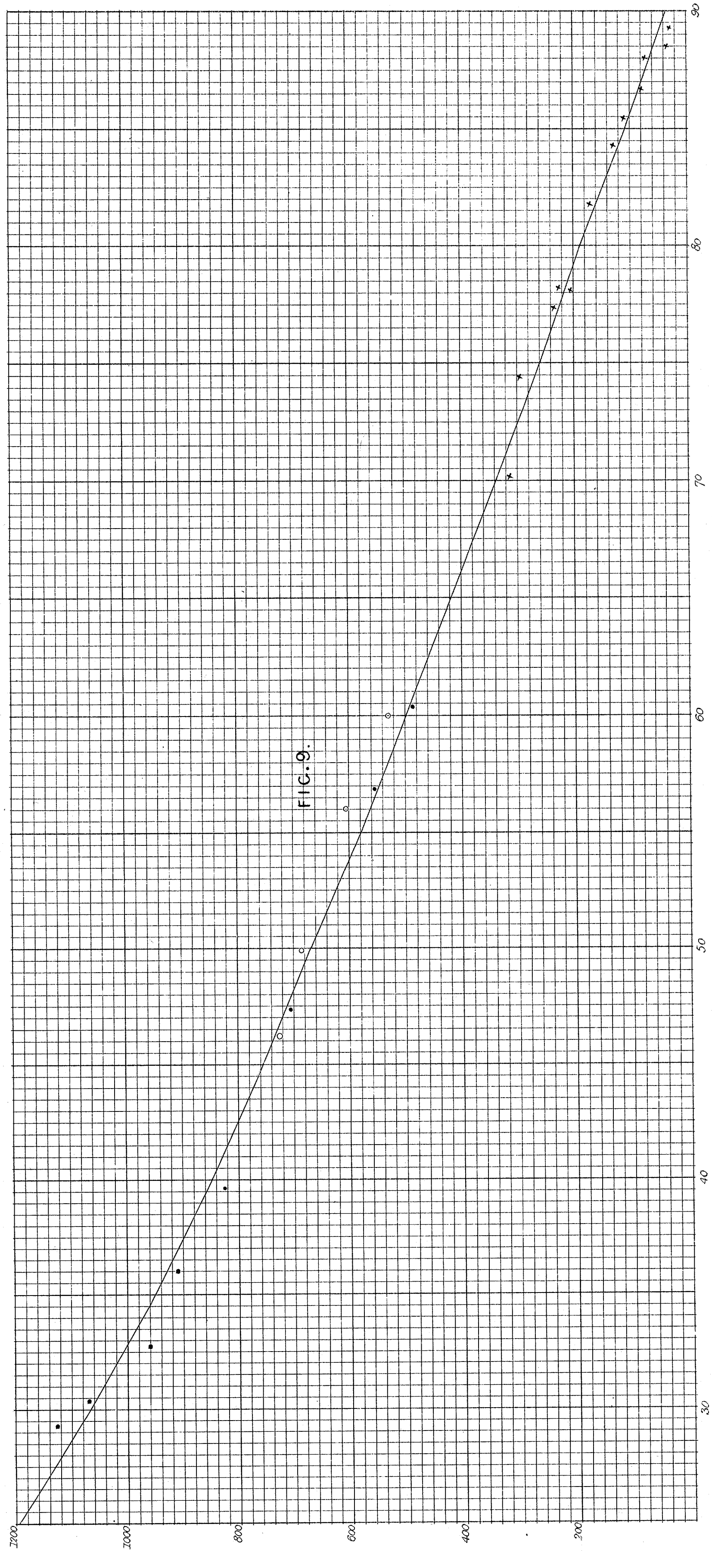
FIG. 9.

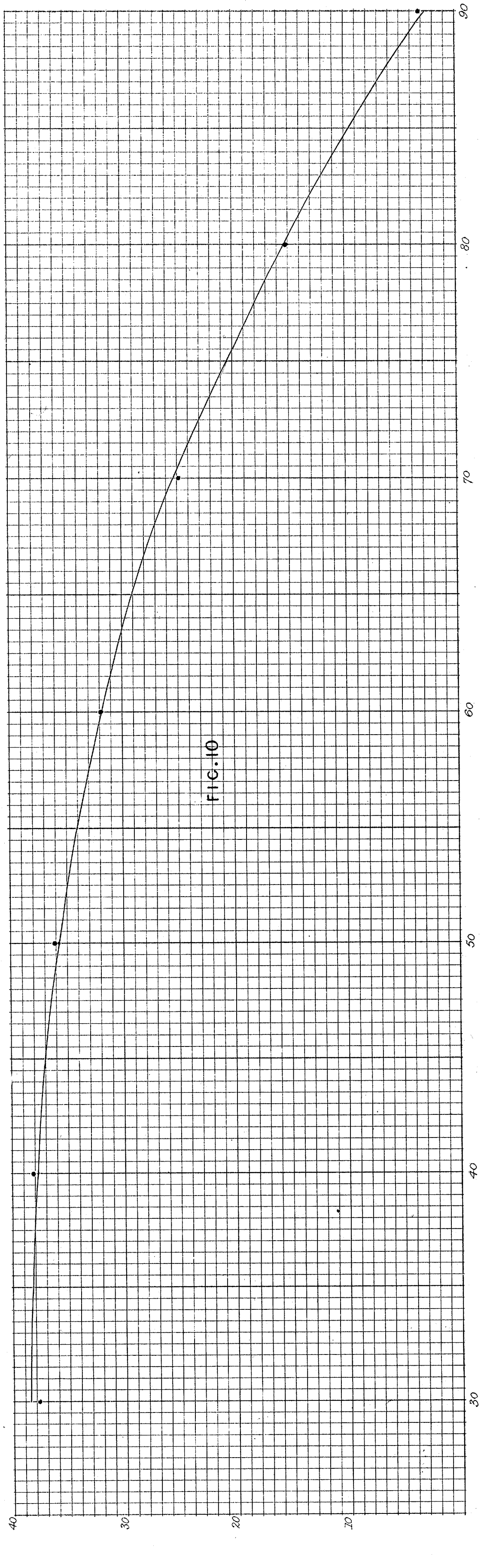
FIG. 10

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FIG. 11

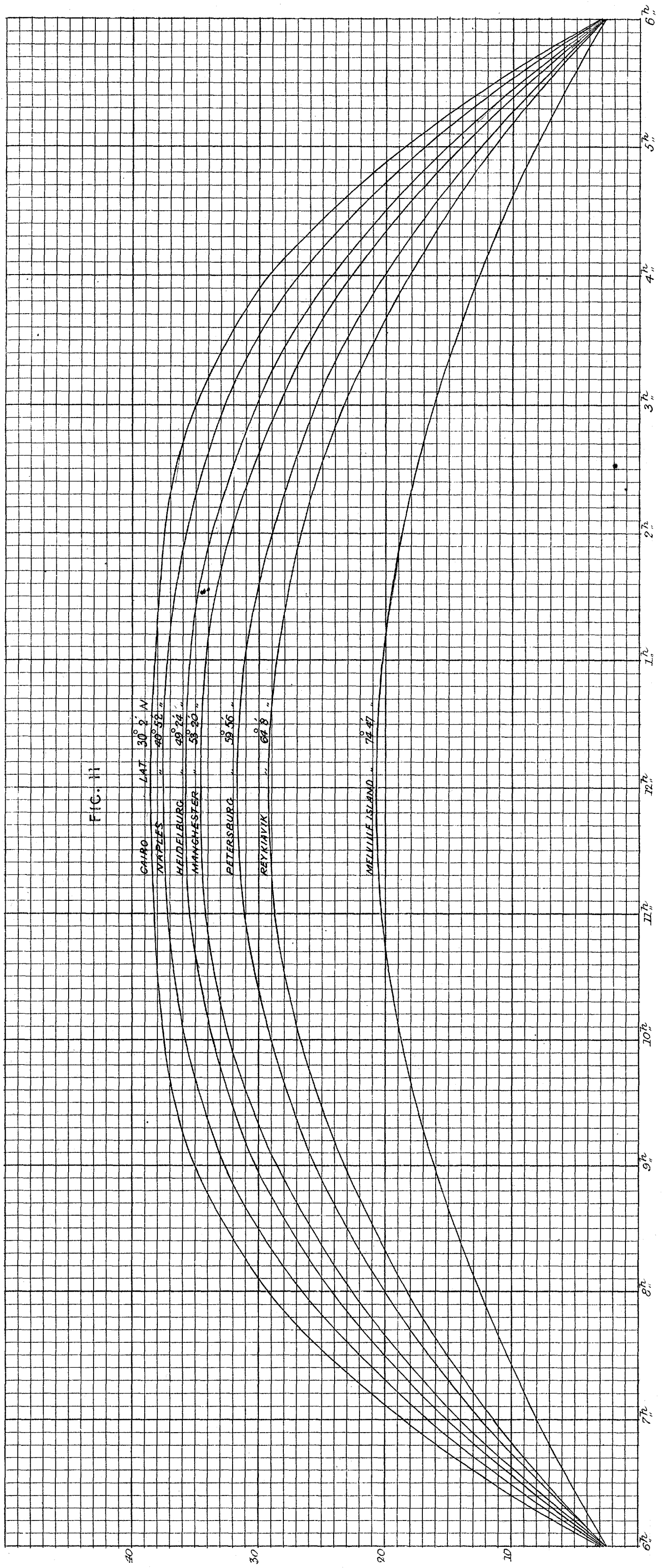

FIG. 12

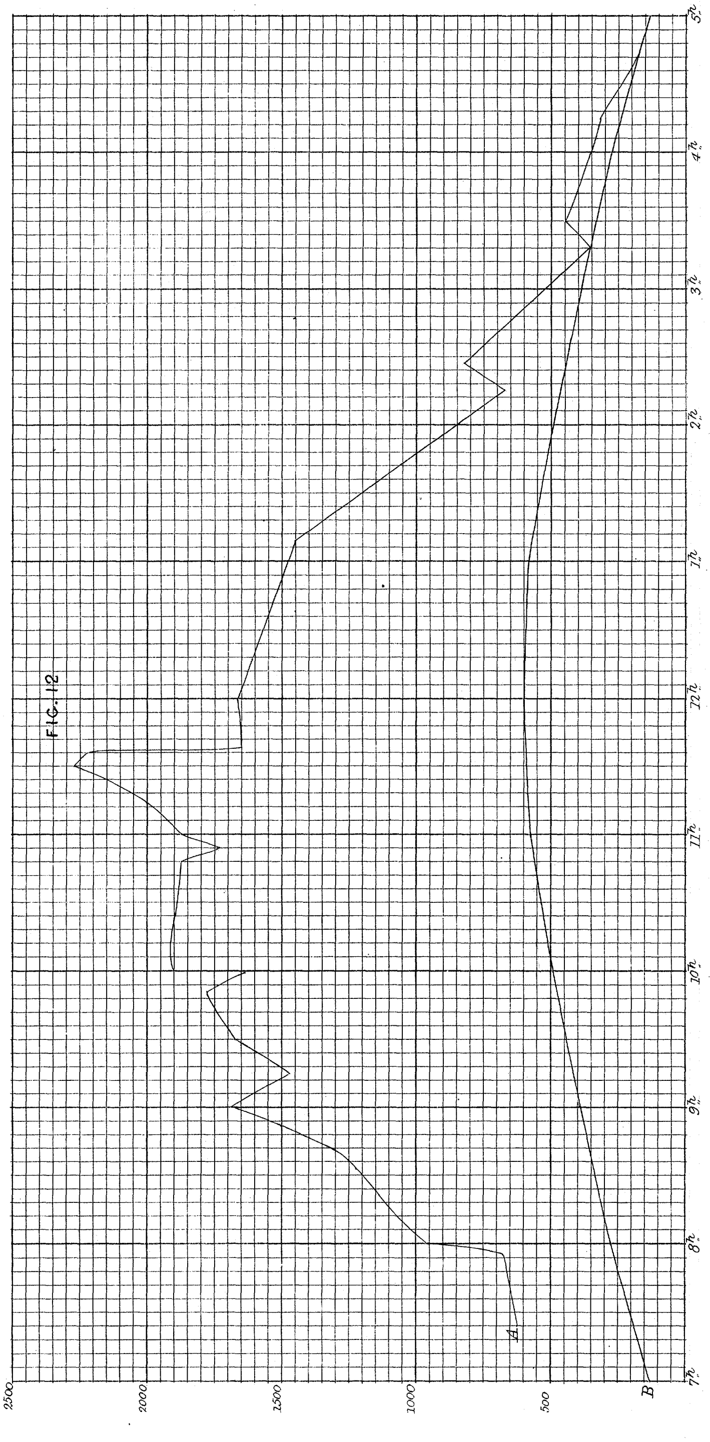

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FIG. 17.

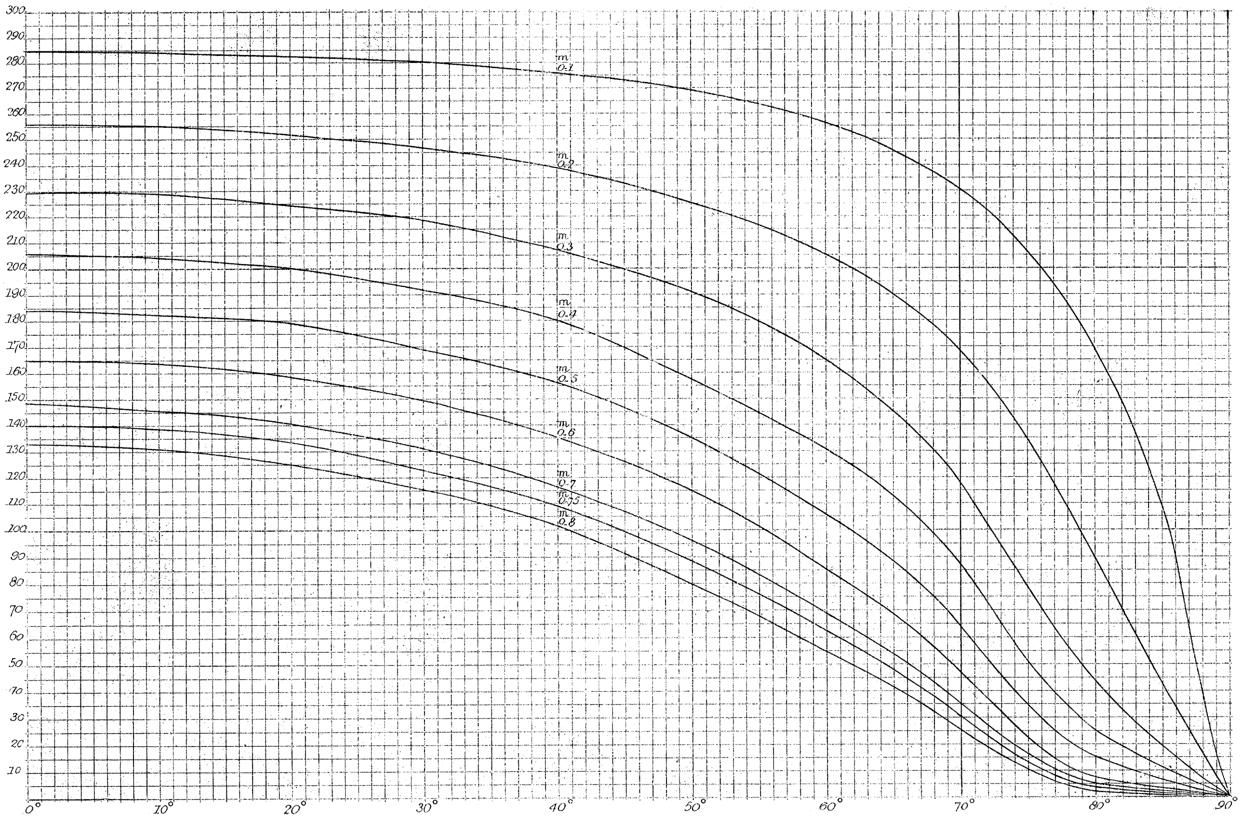

FIG. 19.

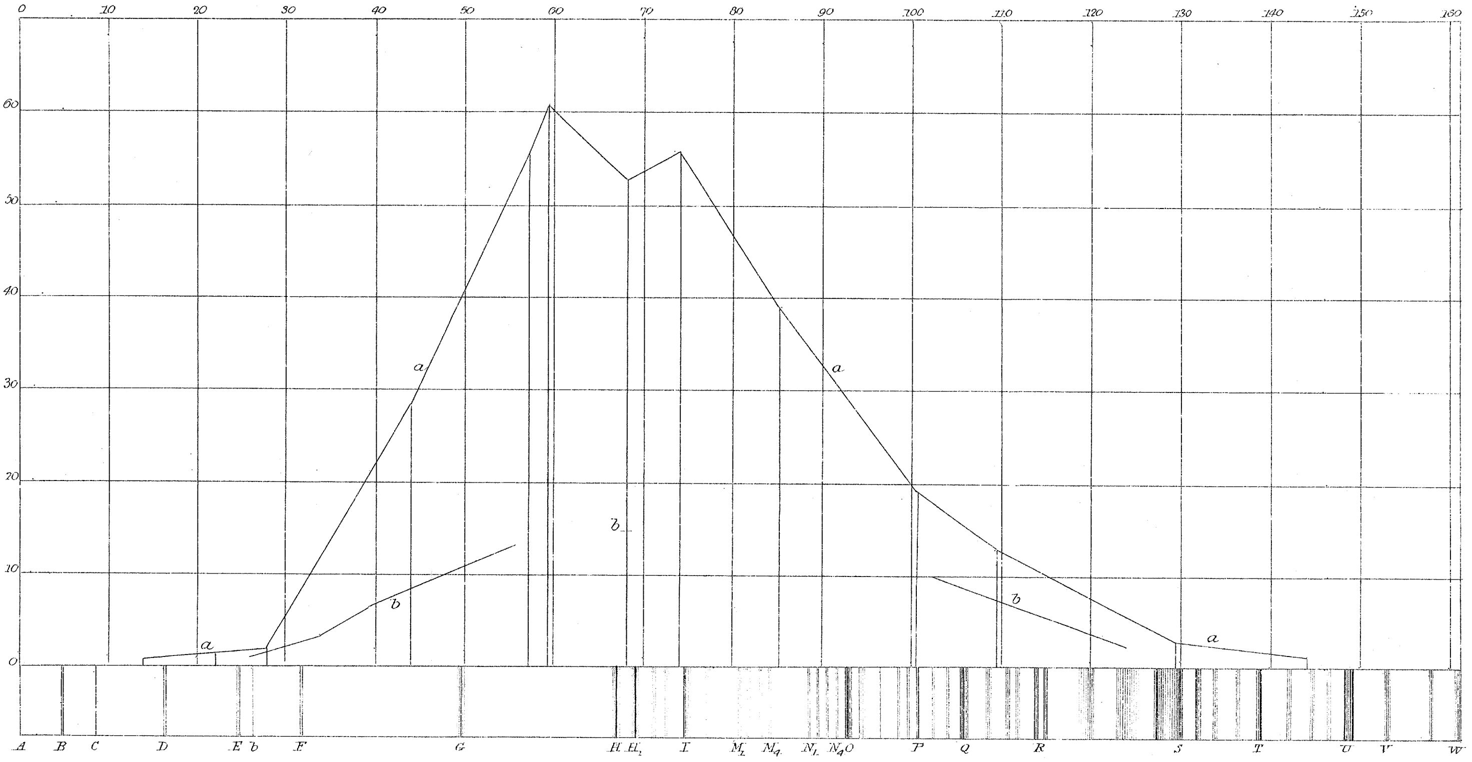

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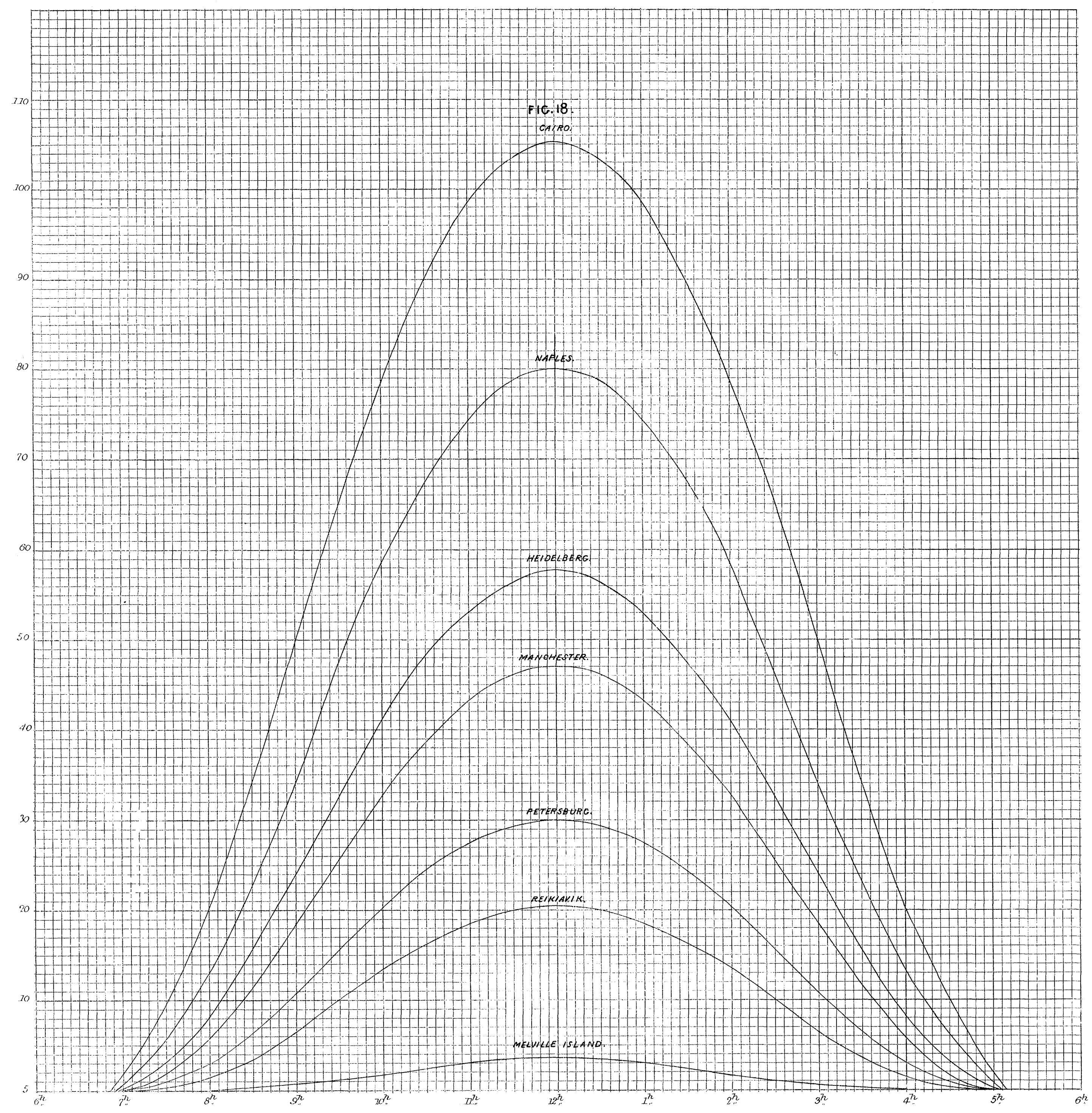
FIG. 18.



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J. Basire Sc.