

heat of considerable intensity was permitted to send its rays through the tube to the pile at its opposite extremity ; the deflection of the needle was very energetic. The second pile was now caused to approach the source of heat until its current exactly neutralized that of the other pile, and the needle descended to zero.

Here then we had two powerful forces in perfect equilibrium ; and inasmuch as the quantity of heat in action was very considerable, the absorption of a small fraction of it might be expected to produce a sensible effect upon the galvanometer-needle in its present position. When the tube was exhausted, the balance between the equal forces was destroyed, and the current from the pile placed at the end of the tube predominated. Hence the removal of the air had permitted a greater amount of heat to pass. On readmitting the air, the needle again descended to zero, indicating that a portion of the radiant heat was intercepted. Very large effects were thus obtained.

I have applied the same mode of experiment to several gases and vapours, and have, in all cases, obtained abundant proof of calorific absorption. Gases vary considerably in their absorptive power—probably as much as liquids and solids. Some of them allow the heat to pass through them with comparative facility, while other gases bear the same relation to the latter that alum does to other diathermanous bodies.

Different gases are thus shown to intercept radiant heat in different degrees. I have made other experiments, which prove that the self-same gas exercises a different action upon different qualities of radiant heat. The investigation of the subject referred to in this Note is now in progress, and I hope at some future day to lay a full description of it before the Royal Society.

VIII. "Photochemical Researches."—Part IV. By ROBERT W. BUNSEN, For. Memb. R.S., and HENRY ENFIELD ROSCOE, Ph.D., Professor of Chemistry in Owens College, Manchester. Received May 26, 1859.

(Abstract.)

In the three communications\* which they have already made to the Royal Society upon the subject of photochemistry, the authors showed

\* Phil. Trans. 1857, pp. 355, 381 and 601.

that they have constructed a most delicate and trustworthy instrument by which to measure the chemical action of light, and by help of which they have been able to investigate the laws regulating this action. In the present memoir, the authors proceed, in the first place, to establish a general and absolute standard of comparison for the chemical action of light; and in the second place, to consider the quantitative relations of the chemical action effected by direct and diffuse sunlight. They would endeavour, in this part of their research, to lay the foundation of a new and important branch of meteorological science, by investigating the laws which regulate the distribution, on the earth's surface, of the chemical activity emanating from the sun.

The subject-matter of the present communication is divided under five heads:—

1. The comparative and absolute measurement of the chemical rays.
2. Chemical action of diffuse daylight.
3. Chemical action of direct sunlight.
4. Photochemical action of the sun, compared with that of a terrestrial source of light.
5. Chemical action of the constituent parts of solar light.

The first essential for the measurement of photochemical actions, is the possession of a source of constant light. This the authors secured with a greater amount of accuracy than by the method described in their former communications, by employing a flame of pure carbonic oxide gas, burning from a platinum jet of 7 millims. in diameter, and issuing at a given rate, and under a pressure very slightly different from that of the atmosphere. The action which such a standard flame produces in a given time on the sensitive mixture of chlorine and hydrogen, placed at a given distance, is taken as the arbitrary unit of photochemical illumination. This action is, however, not that which is directly observed on the scale of the instrument. The true action is only obtained by taking account of the absorption and extinction which the light undergoes in passing through the various glass-, water-, and mica-screens placed between the flame and the sensitive gas. These reductions can be made by help of the determinations given in Part III. of these Researches, as well as by experiments detailed in the present Part. When these sources

of error are eliminated, it is possible, by means of this standard flame, to reduce the indications of different instruments to the same unit of luminous intensity, and thus to render them comparable. For this purpose, the authors define the photometric unit for the chemically active rays, as the amount of action produced in one minute, by a standard flame placed at a distance of one metre from the normal mixture of chlorine and hydrogen; and they determine experimentally for each instrument the number of such units which correspond to one division on the scale of the instrument. By multiplying the observed number of divisions by the number of photometric units equal to one division, the observations are reduced to a comparable standard. It is proposed to call this unit a *chemical unit of light*, and ten thousand of them *one chemical degree of light*.

According to this standard of measurement, the chemical illumination of a surface, that is, the amount of chemically active light which falls perpendicularly on the plane surface, can be obtained. It has thus been found that the distance to which two flames of coal-gas and carbonic oxide, each fed with gas at the rate of 4.105 cubic cent. per second, must be removed from a plane surface, in order to effect upon it an amount of chemical action represented by one degree of light, was, in the case of the coal-gas flame, 0.929 metre, in that of carbonic oxide 0.561 metre. The chemical illuminating power, or chemical intensity, of various sources of light, measured by the chemical action effected by these sources at equal distances and in equal times, can also be expressed in terms of this unit of light; and these chemical intensities may be compared with the visible light-giving intensities. In like manner, the authors define chemical brightness as the amount of light, measured photochemically, which falls perpendicularly from a luminous surface upon a physical point, divided by the apparent magnitude of the surface; and this chemical brightness of circles of zenith-sky of different sizes has been determined. Experiment shows that the chemical brightness of various sized portions of zenith-sky, not exceeding 0.00009 of the total heavens, is the same; or, that the chemical action effected is directly proportional to the apparent magnitude of the illuminating surface of zenith-sky.

It is, however, important to express the photochemical actions

not only according to an arbitrary standard, but in absolute measure, in units of time and space. This has been done by determining the absolute volume of hydrochloric acid formed by the action of a given source of light during a given space of time. For this purpose, we require to know—

$v$  = the volume of hydrochloric acid formed by the unit of light.

$h$  = the thickness of sensitive gas through which the light passed.

$q$  = the surface-area of the insulated gas.

$a$  = 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 these values 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 the light had been completely extinguished by passing through an infinitely extended atmosphere of dry chlorine and hydrogen, is found from the expression

$$V = \frac{v}{q} \cdot \frac{l}{1 - 10^{-ah}}.$$

In this way the chemical illumination of any surface may be expressed by the height of the column of hydrochloric acid which the light falling upon that surface would produce, if it passed through an unlimited atmosphere of chlorine and hydrogen. This height, measured in metres, the authors propose to call a *Light-metre*. The chemical action of the solar rays can be expressed in light-metres; and the mean daily, or annual height thus obtained, dependent on latitude and longitude, regulates the chemical climate of a place, and points the way to relations for the chemical actions of the solar rays, which in the thermic actions are already represented by isothermals, isotherals, &c.

In order to determine the chemical action exerted by the whole diffuse daylight upon a given point on the earth's surface, the authors were obliged to have recourse to an indirect method of experimenting, owing to the impossibility of measuring the whole action directly, by means of the sensitive mixture of chlorine and hydrogen. For the purpose of obtaining the wished-for result, the chemical action proceeding from a portion of sky at the zenith, of known magnitude, was determined in absolute measure, and then,

by means of a photometer, whose peculiar construction can only be understood by a long description, the relation between the *visible* illuminating power of the same portion of zenith sky and that of the total heavens was determined. As, in the case of lights from the same source but of different degrees of intensity, the *chemical* actions are proportional to the *visible* illuminating effects, it was only necessary, in order to obtain the chemical action produced by the total diffuse light, to multiply the chemical action of the zenith portion of sky by the number representing the relation between the visible illumination of the total sky and that of the same zenith portion.

The laws according to which the chemical rays are dispersed by the atmosphere can only be ascertained from experiments made when the sky is perfectly cloudless. In the determinations made with this specially-arranged photometer, care was therefore taken that the slightest trace of cloud or mist was absent, and the relation between the visible illuminating effect of a portion of sky at the zenith and that of the whole visible heavens, was determined for every half-hour from sunrise to sunset; the observations being made at the summit of a hill near Heidelberg, from which the horizon was perfectly free.

The amount of chemical illumination which a point on the earth's surface receives from the whole heavens, depends on the height of the sun above the horizon and on the transparency of the atmosphere. If the atmospheric transparency undergoes much change when the sky is cloudless, a long series of experiments must be made before the true relations of atmospheric extinction of the chemical rays can be arrived at. The authors believe, however, founding their opinion on the statement of Seidel in his classical research on the luminosity of the fixed stars, that the alterations in the air's transparency with a cloudless sky are very slight; and they therefore think themselves justified in considering the chemical illumination of the earth's surface, on cloudless days, to be represented simply as a function of the sun's zenith distance. Although, from the comparatively small number of experiments which have been made, owing to the difficulty of securing perfectly cloudless weather, the constants contained in the formulæ cannot lay claim to any very great degree of accuracy, the authors believe that the numbers ob-

tained are sufficient to enable them to determine the relation according to which the chemical energy proceeding from the sun is diffused over the earth when the sky is unclouded.

From a series of observations made on June 6, 1858, the relation between the amount of light *optically* measured falling from the whole sky, and the amount (taken as unity) which, at the same time, falls from a portion of zenith sky equal to  $\frac{1}{1000}$ th of the whole visible heavens, has been calculated for every degree of sun's zenith distance from  $20^\circ$  to  $90^\circ$ ; the results being tabulated, and also represented graphically. These numbers, multiplied by the *chemical* light proceeding from the same portion of zenith sky for the same zenith distances, must give the chemical action effected by the whole diffuse daylight. The amount of chemical light which falls from the zenith portion of sky is, however, the chemical brightness of that portion of sky. This chemical brightness has been determined, by the chlorine and hydrogen photometer, on various days, and at different hours, when the sky was perfectly cloudless. A table contains the chemical action, expressed in degrees of light, which is effected on the earth's surface by a portion of zenith sky equal in area to  $\frac{1}{1000}$ th of the whole visible heavens, under the corresponding sun's zenith distances from  $20^\circ$  to  $90^\circ$ . A curve representing the relation between the action and the height of the sun, shows that although the single observations were made on different years and at different times of the year and day, they all agree closely amongst themselves, and hence another proof is gained of the slight effect which variation in the air's transparency produces; and it is seen that the total chemical action effected by the diffuse light of day may be represented as a function of the sun's zenith distance.

The numbers thus obtained have only to be multiplied by the corresponding numbers of the former table, in order to give the chemical action effected by the total diffuse light of day for zenith distances from  $20^\circ$  to  $90^\circ$ . A table and graphic representation of these numbers is given. Knowing the relation between the sun's altitude and the chemical action, the chemical illumination effected each minute at any given locality at a given time may be calculated; this calculation has been made for a number of places for each hour on the vernal equinox, tables and curves representing the alteration

of luminous intensity with the height of the sun at these places being given.

From these data it is possible also to calculate the action produced by the whole diffuse light, not only for each minute, but during any given space of time. For the following places the amount of chemical illumination expressed in degrees of light which falls from sunrise to sunset on the vernal equinox, is—

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

Experiment has shown that clouds exert the most powerful influence in reflecting the chemical rays; when the sky is partially covered by light white clouds, the chemical illumination is more than four times as intense as when the sky is clear. Dark clouds and mists, on the other hand, absorb almost all the chemically active rays.

The chemical action of the direct sunlight was determined by allowing a known fractional portion of the solar rays to fall perpendicularly on the insolation vessel of the chemical photometer. The solar rays reflected from the mirror of a Silbermann's heliostat were passed through a fine opening of known area into the dark room, and a large number of reductions and corrections had to be made in order to obtain, from the direct observations, the action, expressed in degrees of light, which the sun shining directly upon the apparatus would have produced if no disturbing influences had interfered. This action of direct sunshine was determined on three different cloudless days for various altitudes of the sun. As the sun approached the zenith the observed action rapidly increased; thus at 7<sup>h</sup> 9' A.M., on September 15, 1858, when the sun's zenith distance was 76° 30', the reduced action amounted to 5·5 degrees of light, whilst at 9<sup>h</sup> 14' A.M. on the same day, the zenith distance being 58° 11', the action reached 67·6. This increase in the sun's illuminating power is owing to the diminution in length of the

column of air through which the rays pass. If we suppose the atmosphere to be throughout of the density corresponding to a pressure 0.76 and a temperature  $0^{\circ}$ , and consider it as a horizontal layer, and if  $A$  represent the action effected before entrance into the atmosphere, the action, when the ray has passed through a thickness of atmosphere  $=l$ , is represented by

$$W_0 = A 10^{-\alpha l},$$

where  $\frac{1}{\alpha}$  signifies the depth of atmosphere through which the ray has to pass to be reduced to  $\frac{1}{10}$ th of its original intensity, and where  $l$  is dependent on the atmosphere's perpendicular height  $=h$ , and the sun's zenith distance  $\phi$ . The numerical values of  $A\alpha$  and  $l$  may be calculated from the direct observations, and hence the action  $W_1$  effected at any other zenith distance  $\phi_1$ , and under a pressure  $P_1$ , is found from the equation

$$W_1 = A 10^{\frac{-\alpha h P_1}{\cos \phi_1 P_0}},$$

where  $P_0$  represents the atmospheric pressure under which  $A$  and  $\alpha$  are calculated. A comparison between the actions  $W_1$  thus obtained, and those,  $W_0$ , found by experiment, shows as close an agreement as could be expected where the observational errors are necessarily so large.

From these experiments it is seen, that if the sun's rays were not weakened by passage through the atmosphere, they would produce an illumination represented by 318 degrees of light; or they would effect a combination in one minute on a surface on which they fell perpendicularly, of a column of hydrochloric acid 35.3 metres in height, assuming that the rays are extinguished by passing through an infinitely extended atmosphere of chlorine and hydrogen. By help of the above formula, it is also found 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 have been lost by extinction and dispersion in the atmosphere. The total chemical action emanating from the sun during each minute is therefore represented by a column of hydrochloric acid 35 metres in height, and having an area equal to the surface of a sphere whose diameter is the mean



distance of the earth to the sun. Or the light which the sun radiates into space during each minute of time represents a chemical energy, by means of which more than 25 billions of cubic miles of chlorine and hydrogen may be combined to form hydrochloric acid. In like manner the amounts of chemical action have been calculated, which the sun's rays, undiminished by atmospheric extinction, produce at the surface of the chief planets. The first column of numbers gives the mean distances of the planets from the sun, the second contains the chemical action expressed in light-metres.

Mercury . . . . .	0·387	235·4 light-metres.
Venus . . . . .	0·723	67·5 „
Earth . . . . .	1·000	35·3 „
Mars . . . . .	1·524	15·2 „
Jupiter . . . . .	5·203	1·3 „
Saturn . . . . .	9·539	0·4 „
Uranus . . . . .	19·183	0·1 „
Neptune . . . . .	30·040	0·04 „

By aid of the formula already given, the authors have been enabled to calculate the chemical action effected each minute by the direct sunlight, not only at different points on the earth's surface, but at various heights above the sea's level. Both these series of relations are tabulated, and graphically represented. On comparing the numbers and curves giving the action of the total diffuse light with those of the direct solar light, the singular fact becomes apparent, that from the North Pole to latitudes below that of Petersburg, the chemical action proceeding from the diffuse light is, throughout the day on the vernal equinox, greater than that effected by the direct sunlight; and that in lower latitudes, down to the Equator, the same phenomenon is observed, if not for the whole, still for a portion of the day. It is further seen, that for all places, and on every day when the sun rises to a certain height above the horizon, there is a moment at which the chemical action of the diffused light is exactly equal to that of the direct sunlight. The times at which these phases of equal chemical illumination occur can be calculated; they can also be actually determined, by allowing the direct sunlight alone, and the whole diffuse daylight alone, to fall at the same time upon two pieces of the same sensitized photographic paper; the

period at which both papers become equally blackened, gives the time of the phase of equal chemical intensity. Experiment proved not only that these points of equality which the theory requires actually occur, but also that the agreement between the calculated and observed times of occurrence of the phases is very close, giving proof that the data upon which the theory is founded are substantially correct.

The formula, by help of which the chemical action of the direct sunlight effected at any place during any given time can be calculated, is next developed, and the direct solar action at the following places calculated for the vernal equinox from sunrise to sunset. Column I. gives the action of the direct sunlight during the whole day, expressed in degrees of light; Column II. the action for the same time effected by both direct and diffuse solar light; and Column III. the same action expressed in light-metres:—

	I.	II.	III.
Melville Island . . . . .	1196	11790	1306 metres.
Reykjavik . . . . .	5964	20980	2324 „
St. Petersburg . . . . .	8927	25340	2806 „
Manchester. . . . .	14520	32740	3625 „
Heidelberg. . . . .	18240	37340	4136 „
Naples . . . . .	26640	47190	5226 „
Cairo . . . . .	36440	58110	6437 „

The authors next proceed to examine the chemical brightness of the sun compared with a terrestrial source of light. For this purpose the intensely bright light produced by a wire of magnesium burning in the air was employed. Experiment showed that the chemical intensity of the sunlight, undiminished by atmospheric extinction, is 128 times greater than that from a surface of incandescent magnesium of like apparent magnitude; or that burning magnesium effects the same chemical illumination as the sun when  $9^{\circ} 53'$  above the horizon, supposing of course that both luminous sources present to the illuminated surface the same apparent magnitude. A totally different relation was found to exist between the visible illuminating power, *i. e.* the effect produced on the eye, of the two sources in question. Thus, when the sun's zenith distance was  $67^{\circ} 22'$ , the chemical brightness of that source was 36.6 times,

but the visible brightness 525 times as large as that of the terrestrial source of light.

In the last section of this communication the chemical action of the constituent parts of the solar spectrum is investigated. The sun's rays were reflected from a Silbermann's heliostat, and after passing through a narrow slit, they were decomposed by two quartz prisms. The spectrum thus produced was allowed to fall upon a white screen covered with a solution of quinine, and any desired portion of the rays could be measured by a finely-divided scale, and the position noted by observation of the distances from the fixed lines. For the purpose of identifying the fixed lines in the lavender rays, the authors were, by the kindness of Mr. Stokes, allowed the use of an unpublished map of the most refrangible portion of the spectrum, prepared by that gentleman. As the various components of white light are unequally absorbed by the atmosphere, it was obviously necessary to conduct all the measurements so quickly after one another, that no appreciable difference in the thickness of the column of air passed through should occur.

This has been accomplished, and a series of exact measurements of the chemical actions of the spectrum for one particular zenith-distance of the sun obtained. The action on the sensitive gas shows the existence of several maxima of chemical intensity in the spectrum. Between the lines G in the indigo and H in the violet the greatest action was observed, whilst another maximum was found to lie near the line I in the ultra-violet rays. Towards the red or least refrangible end of the spectrum, the action became imperceptible about the line D in the orange, but at the other end of the spectrum the action was found to extend as far as Stokes's line U, or to a distance from the line H greater than the total length of the ordinary visible spectrum. Tables and curves representing the action are given.