

*Measurements of the Amount of Ozone in the Earth's Atmosphere  
and its Relation to other Geophysical Conditions.*

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[PLATE 4.]

TABLE OF SYMBOLS.

The following symbols are used throughout this paper:—

$\lambda$  = wave length.

$\text{\AA}$  = Angstrom unit =  $10^{-8}$  cm.

\* $k$  = absorption coefficient of atmosphere.

$\delta$  = absorption coefficient due to particles large compared with  $\lambda$ .

\* $\beta$  = absorption coefficient due to particles small compared with  $\lambda$ .

\* $\gamma$  = absorption coefficient of 1 cm. of pure ozone at N.T.P.

$x$  = thickness of equivalent layer of ozone.

\* $I_0$  = intensity of radiation outside the earth's atmosphere.

\* $I$  = intensity of radiation at surface of earth.

\* $K$  = wedge constant.

$y$  = ordinate (in measurement of photographs taken through a wedge).

$z$  = sun's zenith distance.

§ 1. INTRODUCTION.

Several attempts have been made to determine the amount of ozone in the earth's atmosphere during recent years. Until 1920 only chemical methods were employed, and these yielded very discordant results, the difficulty being to separate the chemical action of ozone from that of other oxidizing constituents of the atmosphere.<sup>†</sup> Rayleigh<sup>†</sup> in England, and Götz<sup>§</sup> in the Alps, have shown that there cannot be more than a very small amount of ozone in the air near the earth's surface. The first accurate measurements of the total amount of ozone in the atmosphere over any given region were made by Fabry and Buisson,<sup>||</sup> who measured spectroscopically the intensity of the ultra-violet absorption band in the solar spectrum, which is due to ozone in the earth's atmosphere. From measurements made on 14 days in May and June, 1920,

\* Function of  $\lambda$ .

† Pring, 'Roy. Soc. Proc.', vol. 90 (1914).

‡ Strutt, 'Roy. Soc. Proc.', vol. 94 (1917-18).

§ Götz, 'Die Sterne'—Potsdam, August-September, 1925.

|| Fabry and Buisson, 'Astrophys. Journ.', December, 1921.

they found the amount of ozone to be equivalent to a layer of pure ozone about 3 mm. thick at normal temperature and pressure. Small variations were observed from day to day.

Ozone has a very strong absorption band, extending from about 3300 Å towards the shorter wave-lengths and reaching a maximum at about 2550 Å, and a weak band in the visible, which, however, absorbs some 4 per cent. of the solar energy at 6000 Å, and only rather narrow bands in the infra-red at about  $9\cdot5\mu$  and  $4\cdot5\mu$  (whose width and intensity are not accurately known); therefore its equilibrium temperature under solar and terrestrial radiation is high. It is thus of considerable interest to determine what variations in the amount of ozone take place over a long period, since these may have important relations to other geophysical phenomena.

Details of a scheme of measuring the amount of ozone daily, by a method similar in principle to that used by Fabry and Buisson, were worked out in 1924, and during 1925 observations were made on every day possible. The results have shown that there is a marked relation between the amount of ozone and the conditions in the upper atmosphere, and while the full details of this cannot be obtained from one year's observations, it seems worth while at this stage to place on record the values so far obtained, and the details of the method employed.\*

## § 2. THEORY OF MEASUREMENT OF THE ABSORPTION COEFFICIENTS OF THE ATMOSPHERE FOR ULTRA-VIOLET RADIATION, AND DEDUCTION OF THE AMOUNT OF OZONE.

Ozone has absorption bands between about 3300 Å and 2000 Å. The absorption of solar radiation is almost complete at 2900 Å, and forms the limit of the solar spectrum at the earth's surface.

The amount of ozone in the atmosphere is obtained by taking spectrograms of sunlight, and measuring the intensity of the ultra-violet absorption band due to ozone. Since the absorption of sunlight is practically complete near the centre of the band, measurements can only be made near its long wave-length limit.

Two separate methods are possible : (a) (Long Method or Series.) We may obtain the actual atmospheric absorption coefficients for a number of wave-lengths by making observations at various altitudes of the sun, and so deduce

\* For brief summary of early results, see 'Quart. Journ. Roy. Meteor. Soc.', October, 1925.

the amount of ozone. (b) (Short Method.) Having once obtained the necessary constants, we may assume the ratio of the intensities of light of two adjacent wave-lengths, as emitted by the sun, to remain constant. If these wave-lengths are chosen near the edge of the band, so that ozone absorption coefficients are very different, measurement of the relative intensities reaching the earth's surface may be used to give the amount of ozone.

While the second method involves assumptions about the sun, it only requires one photograph instead of a series, and in such a cloudy climate as that of England is the only one that can be used to give daily routine values.

§ 2 (a) *Long Method.*—Let  $I_0$  be the intensity of radiation of wave-length  $\lambda$  outside the earth's atmosphere, and  $I$  the intensity measured at the surface of the earth.

If the radiation were to pass normally through a layer of air of unit thickness, the intensity would be reduced to  $I_0 \times 10^{-a}$ , where  $a$  is called the coefficient of absorption of the air, and is a function only of the composition and density of the air.

After passing through a thickness  $x$ , the intensity would be

$$I_0 \times 10^{-ax}.$$

The air, however, is not constant in composition or density, but the former changes considerably, and the latter decreases, with height. Let  $a$  be the coefficient of absorption at a height  $h$  above the earth's surface. We assume here that the earth is flat, and that the air is uniform over any plane parallel to the surface, so that  $a$  is a function only of  $h$ . The error introduced by the curvature of the earth, and that due to refraction by the air, are quite negligible for values of  $\sec z$  less than 4 ( $z$  being the sun's zenith distance).

After passing through a thickness  $dh$  at an angle  $z$  to the normal,  $I_0$  is reduced to

$$I_0 \times 10^{-a \sec z dh},$$

since the thickness of the layer is effectively  $x = dh \cdot \sec z$ .

Thus

$$\begin{aligned} \log I &= \log I_0 - \int_0^\infty a \sec z dh \\ &= \log I_0 - k \sec z; \end{aligned} \tag{1}$$

where  $k = \int_0^\infty a dh$ .  $k$  is, therefore, independent of  $z$ , and is called the

coefficient of absorption of the atmosphere (for vertical transmission).

The intensity of the solar radiation which reaches the earth's surface is measured in arbitrary units for about 10 wave-lengths between 3300 and 2900 Å, at different times during the same morning or afternoon. (This is described in § 2 (b).) The logarithms of these values to the base 10 are plotted against  $\sec z$  (fig. 1).

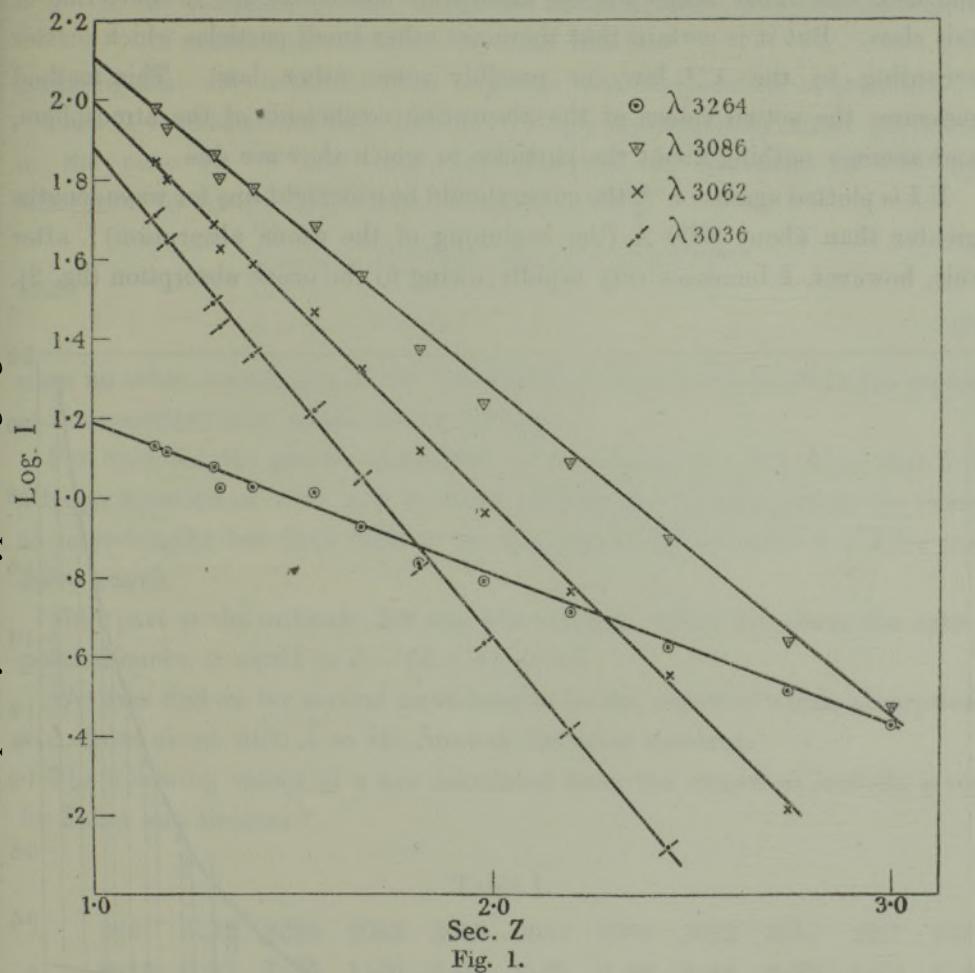


Fig. 1.

Equation (1) shows that  $\log I$  is a linear function of  $\sec z$ , provided that  $I_0$  and  $k$  remain constant during a series of observations. It is not likely that  $I_0$  varies appreciably during one day, and any irregular changes of  $k$  will appear when the points are plotted.\* These points (fig. 1) should lie on a straight line, the tangent of whose inclination to the  $\sec z$  axis is equal to  $k$ . Hence  $k$  is found for any desired number of wave-lengths.

\* See § 5 (a) (i).

The loss of light due to scattering in the atmosphere can be roughly divided into two classes—that which is due to particles small compared with  $\lambda$ , and is proportional to  $\lambda^{-4}$ , and that which is due to large particles (so-called dust, including water drops), and is independent of  $\lambda$ .\*

Fabry and Buisson assumed that the only small particles were air molecules, and used calculated values for the absorption coefficient due to scattering of this class. But it is certain that there are other small particles which scatter according to the  $\lambda^{-4}$  law, or possibly some other law. This method measures the actual values of the absorption coefficients of the atmosphere, and assumes nothing about the particles to which they are due.

If  $k$  is plotted against  $\lambda^{-4}$ , the curve should be a straight line for wave-lengths greater than about 3300 Å (the beginning of the ozone absorption); after this, however,  $k$  increases very rapidly, owing to the ozone absorption (fig. 2).

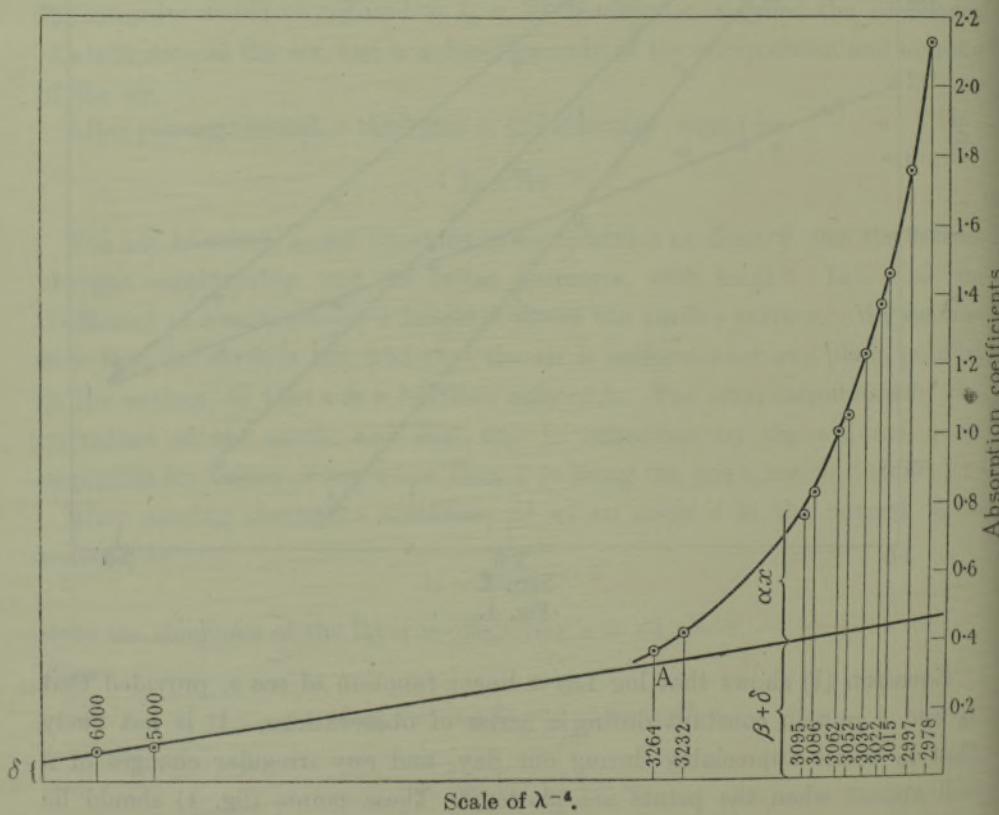


Fig. 2.

\* In justification of this see 'Smithsonian Misc. Collections,' vol. 69, No. 3.

Let  $\beta$  be the absorption coefficient due to scattering by small particles for  $\sec z = 1$ .

$\delta$ , the same for large particles.

$\alpha$ , the absorption coefficient for 1 cm. thickness of pure ozone at N.T.P., and

$x$ , the thickness in cms. which the ozone actually present would have if reduced to a uniform layer at N.T.P.,

assuming that the absorption does not vary with temperature or pressure.

Then  $I_0$  is reduced in the ratio  $10^{-\beta \sec z}$  by scattering by small particles, in the ratio  $10^{-\delta \sec z}$  by large particles, and in the ratio  $10^{-\alpha x \sec z}$  by absorption by ozone. Therefore, we suppose that

$$I = I_0 \times 10^{-\beta \sec z} \times 10^{-\delta \sec z} \times 10^{-\alpha x \sec z}$$

and

$$k = \beta + \delta + \alpha x, \quad (2)$$

since no other constituent of the atmosphere is known to absorb in the region of the spectrum with which we are dealing.

For wave-lengths greater than 3300 Å,  $\alpha = 0$  and  $k = \beta + \delta$ , so that  $k$  is a linear function of  $\lambda^{-4}$ ; and by extrapolating the straight part of the curve to wave-lengths less than 3300 Å, we can obtain the value of  $\beta + \delta$  for any wave-length.

That part of the ordinate, for any wave-length, which lies above the extrapolated curve, is equal to  $k - (\beta + \delta)$ , or  $\alpha x$ .

We thus find  $\alpha x$  for several wave-lengths in the region of ozone absorption, viz., from about 3100 Å to the limit of the solar spectrum.

The following values of  $\alpha$  are calculated from the empirical formula given by Fabry and Buisson.\*

Table I.

$\lambda$ ...	3264	3232	3095	3086	3062	3052	2036	3022	3015	2997	2978
$\alpha$ ...	0.15	0.22	1.35	1.50	2.05	2.33	2.88	3.44	3.75	4.75	6.03

Dividing  $\alpha x$  by  $\alpha$  gives the value of  $x$ , the thickness of the equivalent layer of ozone at N.T.P. The values of  $x$  obtained ought, of course, to be the same for all wave-lengths.

In the next section will be described the method of making the measurements of intensity which give the points in fig. 1, and details in the construction of fig. 2.

\* Fabry and Buisson, 'Journ. de Phys.', (5) 3, 196 (1913).

§ 2 (b). Photographs of the sun's spectrum in the region 3350 to 2900 Å are taken with a quartz spectrograph. The radiation, before falling on the plate, passes through an optical wedge placed against the plate, with its lines of equal density parallel to the dispersion.

If  $i$  is the intensity (uniform over the whole height of the image) of any wave-length  $\lambda$  *incident on the wedge*, the intensity, at any point, of the radiation which falls on the *plate* is

$$i \times 10^{-Ky}, \quad (3)$$

where  $y$  is the distance of the point from the line of zero density of the wedge, and  $K$  is called the wedge constant for wave-length  $\lambda$ . A line  $\lambda$ , therefore, as it appears on the plate, decreases in density from one end to the other.

Six spectra, at six different values of sec  $z$ , are taken on the same plate, with equal times of exposure (30 secs.). About 12 photographs altogether are taken on one morning or afternoon. (These will be referred to as a "series.") In order to make all plates comparable, by eliminating variations in development and sensitivity, a strip of the plate is exposed to a uniform, constant light for 30 secs. This exposure is the same for all plates.\* The source of light is a 12-volt gas-filled lamp, run at 9 volts.† The light from the lamp passes through a piece of Chance's ultra-violet glass, which transmits a trace of the extreme red and a band in the ultra-violet with a maximum at about 3600 Å.

The plate is measured with a photometer at certain fixed wave-lengths, and the distances, from the thin end of the wedge (or rather from a reference line near this end) to the points where the density is equal to the density of the standard strip, are recorded. The wave-lengths chosen are well-marked Fraunhofer transmission spaces. The distances so measured we call  $y$ .

Then, since the density of the standard strip corresponds to a constant and invariable intensity (though of a different wave-length from any of these in the spectra), we have, from equation (3)

$$i \times 10^{-Ky} = \text{constant}.$$

Thus  $y$  is a measure of  $i$ , the intensity of wave-length  $\lambda$ , and we have the equation

$$\log I = Ky. \quad (4)$$

\* For description of the optical wedge and of the method of standardizing the plates, see 'Photographic Photometry,' by G. M. B. Dobson, I. O. Griffith and D. N. Harrison (Clarendon Press).

† For a discussion of constant sources of light, see "Photoelectric Photometry," G. E. C. Research Staff—'Journ. Sci. Inst.,' October, 1925.

The ordinates plotted in the  $\log I - \sec z$  curves (fig. 1) are therefore the values of  $K_y$ .

In this way the values of  $k$  are obtained for several wave-lengths shorter than  $3300 \text{ \AA}$ . For practical reasons which will be dealt with in § 3 (b), it was found inconvenient to photograph wave-lengths longer than  $3300 \text{ \AA}$ , and so to obtain points on the straight part of the  $k - \lambda^{-4}$  curve. We therefore measure the absorption coefficients of the atmosphere for green light and for red light by means of a visual photometer. The sun's light passes through a rectangular opening, an image of which is thrown by a lens on to a white screen. Alongside of this image is that of a similar aperture in a diaphragm, illuminated by an electric lamp. A variable resistance controls the voltage on the lamp, which is measured by a voltmeter. A movable filter, transmitting either the red or the green, is placed between the eye and the screen, and the voltage on the lamp is adjusted till the patches of light from lamp and sun are of equal brightness. Thus the voltage  $V$  is a measure of the intensity  $I$  of the sun's light. The photometer is calibrated, so that the value of  $I$  can be expressed in terms of  $V$ ,\* and a series of values of  $\log I$  for wave-lengths about  $6000$  and  $5000 \text{ \AA}$  are obtained, and plotted against  $\sec z$  in the same way as for the ultra-violet.

The absorption coefficients are thus obtained for these two wave-lengths; they are equal to  $\delta + \beta_{5000}$  and  $\delta + \beta_{6000}$ . The straight line in the  $k - \lambda^{-4}$  curve is drawn through the points for  $\lambda 6000$  and  $\lambda 5000$ , and the point A at  $\lambda 3264$ , obtained by assuming  $x = 0.3 \text{ cm.}$  (its mean value).  $\lambda 3264$  is the longest wave-length which is convenient for measurement, and, as will be seen from Table I, the value of  $\alpha$  for this wave-length is so small that no appreciable error is introduced by this assumption, since the maximum variation of  $x$  is about 30 per cent. on either side of its mean value of  $0.3 \text{ cm.}$ † We therefore say that

$$\delta + \beta_{3264} = k_{3264} - 0.15 \times 0.3 = k_{3264} - 0.045.$$

If it was found that for any series the amount of ozone was unusually low or high, a more nearly correct value of  $x$  could afterwards be substituted.

$\sec z$  cannot, of course, be less than 1, but, as the distance which the light travels through the atmosphere before reaching the surface of the earth is proportional to  $\sec z$ , we may extrapolate the  $\log I - \sec z$  curves to  $\sec z = 0$ , and find what is the value of  $\log I$  before the light enters the atmosphere. This value is denoted by  $\log I_0$ .

\*  $\log I = 5.50 \log V$  for red.

$\log I = 6.06 \log V$  for green. See § 3 (c).

† *i.e.* 6.

In a similar way, by extrapolating the  $k - \lambda^{-4}$  curve to meet the  $k$  axis, we find  $\delta$ , the coefficient of the haze, or large particles, which scatter all wave-lengths alike.

§ 2 (c). *Calculation of Ozone from One Photograph (Short Method).*—For any wave-length we have

$$\log I_0 - \log I = (\beta + \delta + \alpha x) \sec z,$$

and for any second wave-length

$$\log I_0' - \log I' = (\beta' + \delta + \alpha' x) \sec z.$$

Therefore

$$x = \frac{(\log I_0 - \log I_0') - (\log I - \log I') - (\beta - \beta') \sec z}{(\alpha - \alpha') \sec z}.$$

Thus  $\delta$  is eliminated, and we can calculate the value of  $x$  from one photograph, if we assume a value for  $(\beta - \beta')$ , and that  $\log I_0 - \log I_0'$  is constant.

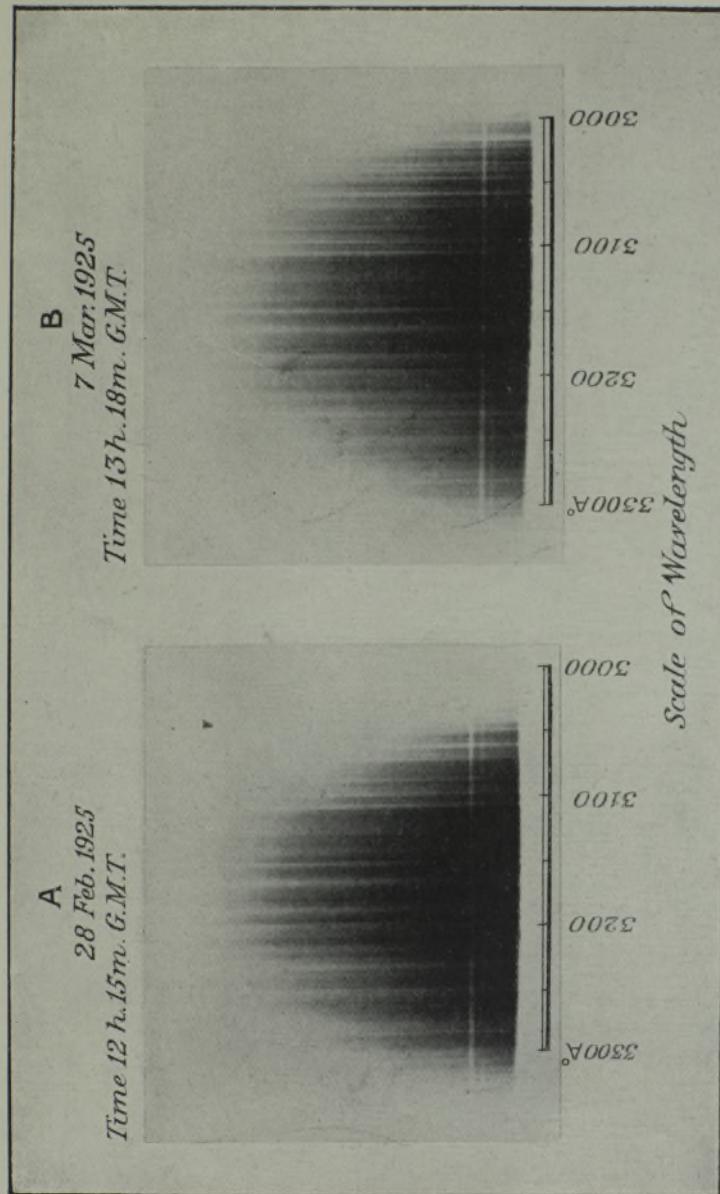
The basis of this method is, of course, the measurement of the difference between the absorptions undergone by the two wave-lengths.  $\alpha$  increases very rapidly for wave-lengths less than 3050 Å, so that it is an advantage to use two wave-lengths as far apart as possible, in order that  $\log \frac{I_0}{I} - \log \frac{I_0'}{I'}$  may be large compared with  $\beta - \beta'$  and with the errors of measurement; but, on the other hand, the shorter wave-lengths are completely cut off earlier than the longer, and we want to be able to obtain measurements at large values of  $\sec z$ .

If one wave-length is at the edge of the absorption band, where  $\alpha$  is small, the longest wave-length which gives sufficient accuracy as the second of the pair, and is convenient for measurement, is 3062; this is obtained as far as  $\sec z =$  about 2·5, *i.e.* from February till November.

The values of  $\alpha$  used are given in Table VI.

For the values of  $\beta$  we have taken those calculated from Rayleigh's formula on the assumption that the scattering is due to the air, the surface pressure being 1012 mb.

Plate 4 shows enlargements of two spectra, both taken with the sun at approximately the same altitude. On February 28 the amount of ozone was 0·370 cm., and on March 7 it was 0·245 cm. It will be seen that although the longer wave-lengths which are not absorbed by ozone are stronger on February 28, the shorter wave-lengths are much weaker owing to the greater amount of ozone.



Photographs on days with much and little ozone present.

## § 3. APPARATUS.

§ 3 (a). *The Spectrograph.*

It was thought desirable to avoid the use of a heliostat, and therefore it is necessary to work out of doors. It was therefore impossible to use two spectrographs at right angles, as Fabry and Buisson did, to eliminate scattered light, as these would not form a portable apparatus. A spectrograph was required which would give a dispersion of not less than  $15 \text{ \AA}$  per mm., would be convenient for use out of doors, and could be adapted so that all undesired light was removed. This latter point is always a difficulty in ultra-violet solar spectroscopy (see § 3 (b)).

A spectrograph to suit our requirements was not available, and one was therefore made.

The Féry type was considered most suitable because it gives an apparatus of more convenient shape than the one- or two-prism type, in which the light is turned through approximately  $45^\circ$  or  $90^\circ$ ; also because it has the minimum number of surfaces at which scattering can take place, and the lines are straight and not curved. It has, however, the disadvantage of small aperture.\* The lens, prism, and wedge (see § 3 (c)) are of quartz. The spectrograph is designed to give uniform illumination along the whole length of the lines on the plate.

The plate ( $12 \times 9$  cms.) is held in a metal plate-holder which slides between guides. The exposures are given by an electric shutter, worked by a current carried from the laboratory on overhead wires to the spectrograph out of doors. A pendulum in the laboratory makes contact every second, and an exposure of any whole number of seconds can be given by means of a bell-push attached to the spectrograph.

The spectrograph is carried on an alt-azimuth mounting, and is quite free to move, being held in position by hand during exposure.

A view-finder on the top of the spectrograph enables it to be pointed at the sun with sufficient accuracy, and it has been verified that no error of pointing likely to be made will result in any appreciable change of illumination.

Sec  $z$  is measured by means of an arm carrying a spirit-level, pivoted at the side of the spectrograph. During exposure the arm is turned so that it is horizontal, and the value of sec  $z$  is read off a scale fixed to the spectrograph.

\* We are indebted to Prof. T. R. Merton, F.R.S., for his advice in selecting the most desirable form of spectrograph.

§ 3 (b). *Elimination of Scattered Light.*

One of the greatest difficulties in photographing the extreme ultra-violet part of the sun's spectrum is the fogging of the plate by scattered light from the longer wave-lengths. The intensity of the shortest wave-length is extremely small compared with that of the visible and near ultra-violet, so that, unless great precautions are taken, light scattered from the surfaces of lenses and prisms swamps that which it is desired to use. Ultra-violet light is scattered much more than visible light, so that the fogging is greater than might be expected if the prism is viewed by the eye. It is impossible to make the optical system perfect enough, and some means have to be employed to remove radiation of all wave-lengths except those which are to be used.

Fabry and Buisson used two dispersions at right angles. This requires a rigid apparatus in the laboratory, together with a heliostat, the use of which we desired to avoid. It was found, however, that a suitable filter could be made of a mixture of bromine vapour and chlorine contained in a tube with quartz ends. Bromine vapour absorbs strongly from the green to about 3600 Å, and chlorine absorbs wave-lengths shorter than 3600, with a maximum at about 3400, becoming more transparent again for shorter wave-lengths.

Peskov\* has described a method for making a light-filter of bromine and chlorine for any desired part of the ultra-violet by calculation, but we found it more convenient to obtain the best amounts of the two gases by trial. Bromine was found by trial to have relatively small absorption beyond about 3600 Å, so that it does not affect the intensity of the radiation with which we are dealing. The amount of bromine required is, therefore, the maximum which it is possible to have ; and this is limited by the lowest temperature at which the apparatus is to be used. The filter must remain constant, so that no bromine can be allowed to condense, and the amount required is such as will not produce saturation at the lowest working temperature (about 0° C.).

The amount of chlorine required is that which will make  $\lambda$  3350 and  $\lambda$  2950 about equally dense on the plate for the smallest values of sec  $z$ . The intensity of the radiation which reaches the earth decreases very rapidly with  $\lambda$  in this region, owing chiefly to absorption by ozone, and if there is not enough chlorine, the ratio of the photographic intensity of the longest wave-lengths to that of the shortest which we use is too great. The chlorine equalizes matters in this respect by absorbing the longer wave-lengths of our region more than the shorter. If there is too much chlorine, the long wave-length end of this part

\* N. P. Peskov, 'Journ. Phys. Chem.', vol. 21, p. 386 (1917).

of the spectrum is completely cut off. The correct amount of chlorine was obtained by trial.\*

As sec  $z$  increases, the absorption by ozone cuts off the short wave-lengths, and the wave-length of maximum intensity increases.

It is, of course, necessary that the vessel in which the gases are contained should have ends of quartz, not glass, and that these ends should be as perfect optically as possible. It was found most suitable to have the whole tube made of transparent silica with optically worked ends.

### § 3 (c). Wedge, Standard Lamp, Photometer, etc.

The wedge, which consists of carbon in a gelatine film between quartz plates, was made by Messrs. Ilford. It was designed to give a ratio of  $10^{3.5}$  for the intensities transmitted at the top and bottom of the 2.5 cm. image at  $3000 \text{ \AA}$ . The wedge constants are determined by measuring the change in the ordinate,  $y$ , produced by a known change in the intensity of the radiation. Thus, if we know that a change of intensity in the ratio  $1 : a$  produces a change of  $b$  cms. in  $y$ , then

$$Kb = \log a, \quad \text{or} \quad K = \frac{\log a}{b}.$$

The sun's light is cut down in a known ratio by a metal disc, perforated with small holes, which is rotated in front of the spectrograph lens.† Photographs of the sun are taken alternately with and without the disc, the difference of the mean ordinates for the two sets of images giving the change  $b$ , due to the known change in the intensity of the light.

Great difficulty was found, owing to the variability of the atmosphere, but no laboratory source of ultra-violet light was available which would remain constant. Finally, the following values were adopted:—

$\lambda \dots$	3264	3232	3095 to $2978 \text{ \AA}$
$K \dots$	1.17	1.21	1.29 per cm.

$K = 0.65$  per cm. for visible wave-lengths.

The visual photometer was calibrated in a similar way by measuring the change of voltage corresponding to a known change in intensity, for the relation between brightness and voltage is of the form  $I = V^n$ .

Therefore,  $\log (I_1/I_2) = n \log (V_1/V_2)$ ,

whence  $n$  can be found.  $n = 5.50$  for the red, and  $6.06$  for the green filter used.

\* It was found that special precautions were necessary when filling the bromine and chlorine tubes, to ensure purity and dryness.

† A sector wheel must be avoided, on account of the intermittency effect and the fact that it varies the time of exposure and not the intensity.

We hoped at first to have for the standardizing image the spectrum of a half-watt lamp with a quartz window, so that each wave-length measured could be compared with the same wave-length on the standard, and a lamp was made for this purpose. It was found, however, impossible to get enough light of the required wave-lengths, and the plates are now exposed to a uniform light of wave-lengths about 3600 Å. The light from the lamp, after passing through a piece of ultra-violet glass, falls on a strip of opal glass by which it is reflected to the plate, only a narrow strip of which is exposed. The lamp is run on a lower voltage than it normally takes ; the voltage is regulated by a rheostat and voltmeter. Exposures are made by an electrically worked Thornton-Pickard shutter.

The plates are measured by means of an electric photometer. The photometer\* consists of a potassium cell, illuminated alternately by each of two beams of light from a lamp, one of which passes through the plate and the other through a movable wedge. The current passed by the cell is measured by an electrometer and a high-resistance leak. The plate rests on a travelling stage, and the distance from the zero line to the point at which the density is equal to the proper density on the wedge (as previously determined from the standard patch) is measured by the movement of the plate. The image of the photometer lamp, which has a short straight filament, is focussed on the plate by a microscope objective mounted in a tube. The width of the image is about 1/20 mm., which is slightly less than the width of the lines on the plate.

#### § 4. RESULTS OF SERIES.

Nine good series were obtained during the summer of 1925. It is only during the time when the value of  $\sec z$  is less than 1.5 at noon (*i.e.* from the beginning of April to the beginning of September) that it is worth while to take series. The largest value of  $\sec z$  at which enough light is obtained for measurements to be made is 3, and even at this value the shortest wave-length obtainable with 30 seconds exposure on clear days is 3086 Å. A  $\sec z$  range of 1.5 is the least which it is thought worth while to have.

In fig. 1 are shown some of the  $\log I - \sec z$  curves for the series of June 4. The tangents of the angles which these straight lines make with the  $\sec z$  axis are tabulated under the heading  $k$  in the first column of Table II. These figures are plotted on a  $\lambda^{-4}$  scale in fig. 2. The values of  $\delta$ ,  $\beta$  and  $\alpha x$  are indicated in the figure, and appear in Table II, together with the values of  $\alpha$

\* See 'Photographic Photometry,' referred to previously.

calculated from Fabry and Buisson's formula. The straight line giving  $(\beta + \delta)$  is, as explained above (§ 3 (b)), drawn through the points at  $\lambda$  6000 and 5000 Å, and the point A at  $\lambda$  3264 obtained by assuming  $x = 0.3$  cm.

Table II.—Results of Series of June 4 (Morning).

$\lambda$ .	$k$ .	$\beta$ .	$\alpha x$ .	$\alpha$ .	$x$ .	$\log I_0$ .
3264	0.38	0.29	—	—	—	1.57
3232	0.43	0.30	—	—	—	1.86
3095	0.77	0.35	0.36	1.35	0.269	2.78
3086	0.83	0.36	0.42	1.50	0.283	2.94
3062	1.01	0.37	0.59	2.05	0.287	3.00
3052	1.055	0.37	0.63	2.33	0.270	3.10
3036	1.23	0.38	0.80	2.88	0.278	3.11
3022	1.38	0.39	0.94	3.44	0.274	3.03
3015	1.46	0.39	1.02	3.75	0.271	3.03
2997	1.76	0.40	1.31	4.75	0.277	3.17
2978	2.13	0.41	1.67	6.03	0.276	3.26

$$\delta = 0.05.$$

It will be seen that in fig. 2 the points at  $\lambda$  3095 and  $\lambda$  3052 lie distinctly below the smooth curve. This is probably due to the presence of irregularities in the absorption band of ozone, as the same effect is observed in all series.\*

The last column in Table II gives the values of  $\log I_0$ , obtained by extrapolating the curves of fig. 1 to sec  $z = 0$ . It should be particularly noted that these values are not comparable with each other, as they depend on the amount of absorption undergone by each wave-length in the apparatus, and the plate sensitivity; they are merely the values of  $K_y$  which would have been obtained if photographs had been taken with ourspectrograph and bromine-chlorine filter at a point outside the atmosphere. When it is found, as it often is, that the series is very irregular, owing to changes in the atmosphere, we subtract from the value of  $\log I$  for each wave-length, the corresponding value for  $\lambda$  3264, which is the longest wave-length convenient for measurement. Changes in haziness, which reduce all wave-lengths in the same proportion, are thus eliminated. This is the procedure adopted by Fabry and Buisson in their original measurements, and results in a great improvement in the curves. The values of  $k - k'$  (where  $k'$  is the absorption coefficient for  $\lambda$  3264) are thus obtained, and subtracting the value of  $\beta - \beta'$  calculated from Rayleigh's formula we get  $x(\alpha - \alpha')$ , and hence  $x$  for each wave-length. We also get  $\log I_0/I_0'$ .

\* In a recent paper—'Publ. Inst. of Technology,' Mass., vol. 60, No. 56—Fabry gives detailed absorption coefficients for ozone for wave-lengths larger than 3060 Å, but unfortunately these are all longer wave-lengths than those we require.

The results of the nine series may be summarised as follows :—

(1) The values of ozone from different wave-lengths in any one series agree well, and their slight discrepancies indicate that the absorption coefficients used are not correct. When the amount of ozone given by each wave-length is expressed as a percentage of the mean for the series, each wave-length shows a remarkable consistency through all the series (see Table III).\*

Table III.—Values of  $x$  expressed as Percentages of Means for  $\lambda\lambda 3095-15$ .  
June, 1925.

$\lambda$ .	2nd.	3rd.	4th.		5th.	10th.	11th.	15th.		Mean.
			a.m.	p.m.				a.m.	p.m.	
3095 .....	95	98	97	97	98	100	107	99	99	98.9
3086 .....	102	106	103	106	107	101	109	100	109	104.8
3062 .....	105	104	104	106	103	103	101	103	105	103.7
3052 .....	98	97	98	95	94	93	96	95	96	95.8
3036 .....	103	101	101	98	99	101	97	99	96	99.4
3022 .....	96	100	99	98	104	99	94	99	96	98.3
3015 .....	103	95	98	100	97	100	96	98	97	98.2
2997 .....	—	99	100	—	—	—	92	99	94	96.8
2978 .....	—	111	—	99	—	—	94	101	115	104.0

The figures below the line in each series were obtained from points extending over a range of sec  $z$  of less than 1.

This is strong proof that the absorption is due only to ozone. The final column in Table III indicates approximately how much the values of  $\alpha$  are in error, assuming the mean for all wave-lengths to be correct; for instance, that for  $\lambda 3052$  should be multiplied by about  $\frac{95.8}{100}$ . The corrected values of  $\alpha$  are given in Table IV.

Table IV.—Corrected Values of  $\alpha$ .

$\lambda$	...	3095	3086	3062	3052	3036	3022	3015
$\alpha$	...	1.33	1.57	2.13	2.23	2.86	3.38	3.68

The fact that the different wave-lengths do not agree in the values of  $x$  which they give, might be due to errors in the wedge constant K, but there is no indication in the measurements of K that the absorption of "neutral"

\* In calculating the mean, only  $\lambda\lambda 3095-3015$  are taken into account, in order that the series may be comparable. Some earlier series do not agree well with the ones shown, because the sun's altitude was too small to give sufficient points for accuracy.

gelatine film varies in an irregular manner with wave-length, whereas we know that ozone has well-marked bands.\*

(2) In the two cases in which two series have been obtained on the same day, the amounts of ozone given by the morning and afternoon series agree well, although  $\beta$  and  $\delta$  are not the same.

(3) The values of  $\log I_0$  are fairly consistent, especially when differences are taken instead of absolute values. The values of  $\log I_0 - \log I_{0_{3264}}$  are given in Table V.†

Table V.—Values of  $\log I_{\lambda} - \log I_{0_{3264}}$ . June, 1925.

$\lambda$ .	2nd.	3rd.	4th.		5th.	10th.	11th.	15th.		Mean.
			a.m.	p.m.				a.m.	p.m.	
3232 .....	0.23	0.27	0.29	0.28	0.26	0.27	0.29	0.30	0.28	0.28
3095 .....	1.18	1.24	1.21	1.24	1.25	1.24	1.29	1.25	1.24	1.24
3086 .....	1.32	1.39	1.37	1.43	1.41	1.37	1.41	1.41	1.42	1.39
3062 .....	1.38	1.43	1.43	1.49	1.44	1.41	1.40	1.43	1.44	1.43
3052 .....	1.46	1.50	1.53	1.55	1.51	1.46	1.54	1.50	1.50	1.51
3036 .....	1.49	1.55	1.54	1.56	1.56	1.51	1.50	1.53	1.48	1.53
3022 .....	1.34	1.48	1.46	1.51	1.56	1.40	1.38	1.45	1.41	1.44
3015 .....	1.34	1.41	1.46	1.56	1.49	1.44	1.43	1.46	1.43	1.45

The figures below the line in each series were obtained from points extending over a sec  $z$  range of less than 1.

## § 5. ACCURACY AND SOURCES OF ERROR.

### § 5 (a). Errors in $k$ , $x$ and $\log I_0$ found from Series.

§ 5 (a) (i) *Changing Atmosphere*.—Changes in the atmosphere are the greatest source of error. If the absorption coefficient changes during a series, it is not at first obvious what meaning should be given to the observed values. It can, however, be shown that if the change is uniform with time, the points obtained will lie on approximately straight lines, whose slopes give values of  $k$  which were the true ones when  $\sec z = \infty$ , i.e. at sunrise and sunset.

If the change were due to haze alone,  $\beta$  and  $x$  remaining constant, all wavelengths would be affected equally, and even if the points did not lie on straight lines, the slopes of all the mean lines would be altered by equal amounts; all the points on the  $k - \lambda^{-4}$  curve would then be raised or lowered equally, and the result would be an error in  $\delta$ , but not in  $\beta$  or  $x$ . Similarly, a change

\* Fowler and Strutt, 'Roy. Soc. Proc.,' A, vol. 93, p. 577 (1917).

† See § 5 (a) (i).

in  $\beta$  during the series will alter the slope of the straight part of the  $k - \lambda^{-4}$  curve, and therefore the value deduced for  $\beta$ , but not  $\delta$  or  $x$ . A change in the amount of ozone will likewise affect the value of  $x$  alone.

The two series of June 4 give an interesting illustration of a varying atmosphere. The amounts of ozone are practically the same for morning and afternoon, but  $\beta$  and  $\delta$  are greater for the afternoon. The afternoon values of  $\log I_0$  are greater than the morning ones, which indicates that the change was a gradual one, and did not take place during the interval at noon; and the smoothness of the  $\log I - \sec z$  curves shows that the change was fairly regular.

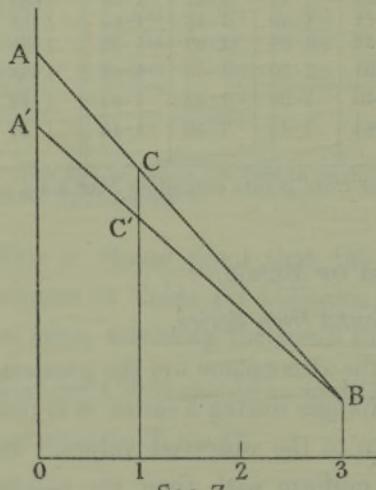
It is difficult to estimate the probable error in  $\log I_0$  due to changes in the atmosphere, but we can get some idea of it in the following way:—

Suppose that the true value of  $\log I_0$  is given by  $A$  (fig. 3), and that when  $\sec z = 3.0$  the value of  $k$  is given by  $AB$ . Then if  $k$  remained constant, the points would lie on  $AB$ . Suppose that  $\delta = 0.10$  and that it increases ( $\beta$  and  $x$  being constant) in such a way that the points lie on the line  $BC'$ , and that by noon, when  $\sec z$  is nearly  $1.0$ , it has changed by  $0.02$ , or  $20$  per cent. of its former value. Then  $CC' = 0.02$ , and the value of  $\log I_0$  obtained by extrapolation will be  $A'$ ,  $AA'$  being equal to  $0.03$ .

We may thus expect considerable inaccuracy in our values of  $\log I_0$ , but as explained above, the differences should show much less error. It is evident from fig. 3 that  $AA'$  is the same whatever the value of  $k$ . If  $\delta$  increases uniformly during the whole day, the mean of  $\log I_0$  for morning and afternoon series will be the correct value. Similar considerations apply to changes in  $\beta$  and  $x$ . The importance of

correct values of  $\log I_0$  will be discussed in § 5 (b) (iii).

§ 5 (a) (ii) *Other Absorbing Gases in the Atmosphere.*—If there were another gas in the atmosphere, which absorbed at any of the wave-lengths which we measure, the absorption coefficients for these wave-lengths would be abnormally large, and the values of  $x$  deduced from them would not be in agreement with the rest. It is therefore unlikely that there is such a gas, although there are certain inconsistencies in Table III (e.g. on June 11).



§ 5 (a) (iii) *Wedge Constant*.—Since all the observed values of  $\log I$  are proportional to  $K$  (equation (4)), an error in  $K$  would produce a proportional error in  $k$ . Consequently different wave-lengths would be affected differently (see § 4), and part of the discrepancy between the values of  $x$  given by different wave-lengths may be due to this cause. It is probable, however, that the absorption coefficient of the material of which the wedge is made increases regularly towards the shorter wave-lengths, so that, as our values of  $K$  lie on a smooth curve, no irregular effect is to be expected.

The observed values of  $\log I_0$  are, of course, directly proportional to  $K$ .

§ 5 (a) (iv) *Plate Errors*.\*—When the values of  $\log I_{3264}$  are subtracted before plotting, the irregularities of  $\delta$  are eliminated, and almost those of  $\beta$ , which should appear progressively greater for shorter wave-lengths. Any remaining irregularities may be put down to errors in the plate, and a study of the  $\log I - \sec z$  curves from this point of view gives an indication of the size of such errors. As an example, in the series illustrated in fig. 1, at  $\sec z = 3.00$ ,  $\lambda 3086$  is too high by 0.03.

It is found that the probable error in  $\log I$  is 0.005, which is equivalent to about 1 per cent. in  $I$ .

If we assume that the atmosphere remains constant during a series, the probable error in the observed values of  $k$  due to errors of the plate will be about 0.005, with a  $\sec z$  range of 2. The resulting error in  $x$  depends on  $\alpha$ , and for  $\lambda 3052$  is about 0.002 cm., or less than 1 per cent., since  $x = 0.3$  cm. We do not attach much weight to those values which are obtained from a  $\sec z$  range of less than 1.

#### § 5 (b). Errors in amount of Ozone calculated from Single Photographs.

§ 5 (b) (i) *Errors in  $\beta$* .—For the values of  $\beta$  we have taken those calculated from Rayleigh's formula on the assumption that the scattering particles are the air molecules at 760 mm. pressure.  $\beta$  is, of course, proportional to the pressure, so that a change of 3 per cent. in either direction may be expected from this cause. The error introduced by wrong values of  $\beta$  is proportional to  $\frac{\beta - \beta'}{\alpha - \alpha'}$  on this account, as mentioned above, it is advisable to use wave-lengths as widely separated as possible. The value of  $\frac{\beta - \beta'}{\alpha - \alpha'}$  for  $\lambda\lambda 3232$  and 3052, one

\* For a study of the inaccuracy due to irregularity of the plate, and also a description of the best methods of development, etc., see 'Photographic Photometry,' to which we have already referred.

of the pairs which we have used, is 0·04, so that a 25 per cent. change in  $\beta$  from its calculated value would introduce an error of 0·01 cm. in  $x$ . We do not think that such a change ever takes place;  $\beta$  cannot, of course, have much less than its calculated value, but it may be greater owing to the presence of other particles small enough to scatter according to the  $\lambda^{-4}$  law. The results of the series show  $\beta$  changes.

§ 5 (b) (ii) *Photographic Errors*.— $\alpha - \alpha'$  for  $\lambda\lambda 3232$  and  $3052$  is 2·03, so that an error of 0·03 in  $\log I - \log I'$  produces an error of 0·01 cm. in  $x$ , at  $\sec z = 1\cdot 5$ . Considerations of the accuracy of the plate show that the probable error in  $x$  due to this cause is about 0·002 cm.

§ 5 (b) (iii) *Errors in Log  $I_0$* .—If the adopted values for  $\log I_0 - \log I'_0$  are wrong, systematic errors will be introduced. For if the value used for any pair of wave-lengths be too great by an amount  $i$ , then the calculated value of  $x$  will be too great by  $i/(\alpha - \alpha')$  sec  $z$ ; thus, a regular change with  $\sec z$  will be introduced, the error being inversely proportional to  $\sec z$ . The fact that no such effect is observed shows that our values of  $\log I_0/I'_0$  cannot be far wrong.

§ 5 (b) (iv) *Changes in Sun*.—It is, of course, possible that the relative intensities of two wave-lengths emitted by the sun may vary, and some of the observed irregularities may be due to this cause. It can be shown from Planck's formula for radiation that if the sun radiates as a black body at  $6000^\circ a$ , a change of  $500^\circ$  will result in a change of 0·04 in  $\log I_0 - \log I'_0$  for  $\lambda\lambda 3232$  and  $3052$ , which would give rise to an error in ozone of 0·01 cm. at  $\sec z = 2$ , and changes in the gases of the photosphere may give greater variations than this.

§ 5 (b) (v) *Errors in  $\alpha$* .—If the values of  $\alpha - \alpha'$  are still wrong, all the values of  $x$  will be wrong in the same proportion. This is not a serious matter, and can easily be further adjusted if experience shows it to be necessary.

§ 5 (b) (vi) *Wedge Constant*.—The amount of absorption undergone by any wave-length is given by

$$\log I_0 - \log I = k \sec z = K (y_0 - y), \quad (5)$$

where

$$Ky_0 = \log I_0 \text{ (cf. § 5 (a) (iii)).}$$

Thus the true value of  $x$  is (equation (5))

$$\frac{K(y_0 - y) - K'(y'_0 - y') - (\beta - \beta') \sec z}{(\alpha - \alpha') \sec z}.$$

The observed value is

$$\frac{pK(y_0 - y) - qK'(y'_0 - y') - (\beta - \beta') \sec z}{(\alpha - \alpha') \sec z},$$

where  $pK$  and  $qK'$  are the adopted values of  $K$ .

Therefore error

$$\begin{aligned} &= \frac{(p-1)K(y_0 - y) - (q-1)K'(y_0' - y')}{(\alpha - \alpha') \sec z} \\ &= \frac{(p-1)k - (q-1)k'}{\alpha - \alpha'}. \end{aligned}$$

Thus an approximately constant error is introduced, since  $k$  and  $k'$  do not vary greatly. Of course, the corrections applied to  $\alpha$  depend on the adopted values of  $K$  (§ 4), but these are, as a matter of fact, small.

The small differences between the mean value of the ozone for different wave-length pairs may perhaps be partly accounted for in this way.

§ 5 (b) (vii) *Scattered Light*.—A certain amount of light is unavoidably scattered inside the spectrograph; most of this being naturally of those wave-lengths which are strongest in our spectrograms. Therefore the ratio of the total scattered light to the useful light of any one wave-length varies with  $\sec z$ , as the wave-length of maximum intensity varies. Nevertheless, it has been found that the total scattered light is negligible compared with the intensity of any of the wave-lengths which we use.

§ 5 (b) (viii) *Other Absorbing Gases in Atmosphere* (*cf.* § 5 (a) (ii)).—It is also possible that other gases than ozone absorb in the region of the spectrum with which we are dealing. None of the other constituents of the atmosphere are known to have such an absorption, but if this were the case the values of the ozone calculated from different pairs of wave-lengths would not agree.

The amount of ozone was calculated from equation (5), using the constants obtained from the series (Tables IV and V), for five pairs of wave-lengths, or as many as could be measured in the photographs, for a large number of days. The results for the month of May are shown in fig. 4. The different curves agree well, and this is additional proof that the absorption is, a matter of fact, as due to ozone, and that the errors are not large. Nevertheless, it is possible that certain anomalies in the behaviour of the curve in fig. 5 may be explained in this way.

§ 5 (b) (ix) *Photometer Measurements*.—The measurements of the plates are very accurate, and can usually be repeated to within 0.05 mm. Moreover, as the discrepancy between two independent sets of readings is mainly due to errors in setting on the zero line, or in estimating the mean density of the background near the image or of the standard strip, all wave-lengths are affected by the same amount, and the resulting error in  $x$  is negligible.

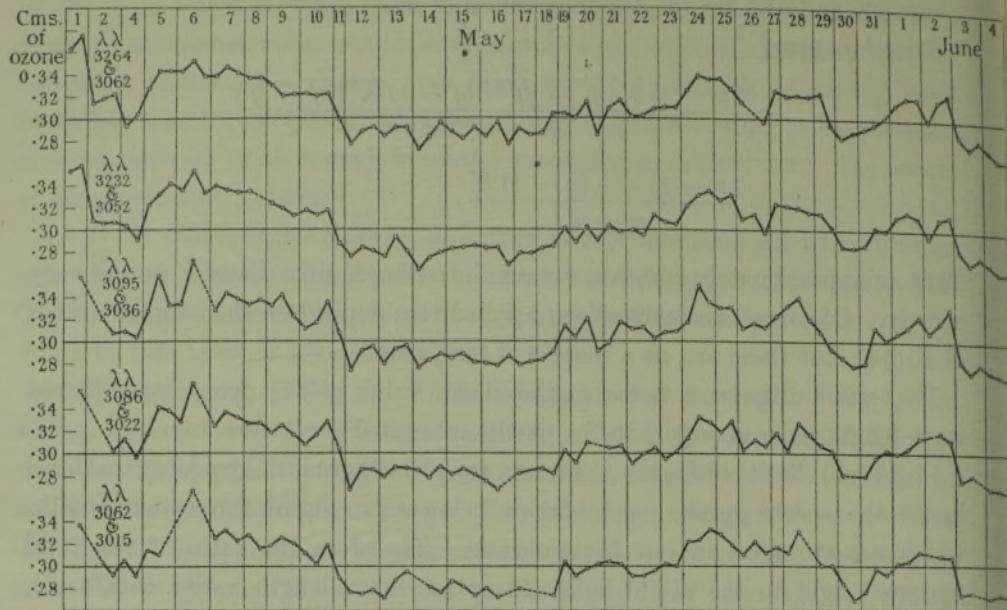


Fig. 4.

Finally, we estimate that the probable error of any one determination of the amount of ozone is not greater than 0.005 cm., excluding systematic errors, such as those in  $\alpha$ .

Two independent measurements of twelve images gave the following values for the ozone :—

First measurement, 0.251, 0.249, 0.239, 0.233, 0.244, 0.240,  
Second measurement, 0.251, 0.249, 0.238, 0.233, 0.244, 0.240,

First measurement, 0.234, 0.228, 0.214, 0.212, 0.209, 0.206.  
Second measurement, 0.235, 0.229, 0.216, 0.212, 0.212, 0.205.

#### § 6. VARIATION OF OZONE DURING 1925.

The mean values of the ozone expressed as the thickness in cms. of an equivalent layer of pure ozone at N.T.P., for every day during 1925 on which photographs could be taken, are tabulated in Table VI, together with the barometric pressure at Oxford, and the sunspot numbers.\*

\* See § 7 (*f*).

The ozone and pressure daily values are plotted in fig. 5; the pressure is plotted so that it decreases upwards, in order to bring out the connection between it and the ozone. The series of horizontal lines marked A and C above the curves refers to the weather conditions ; the upper ones (C) mark the occurrence of cyclones, the lower (A) of anticyclones ; dots mean that the conditions were not well defined.

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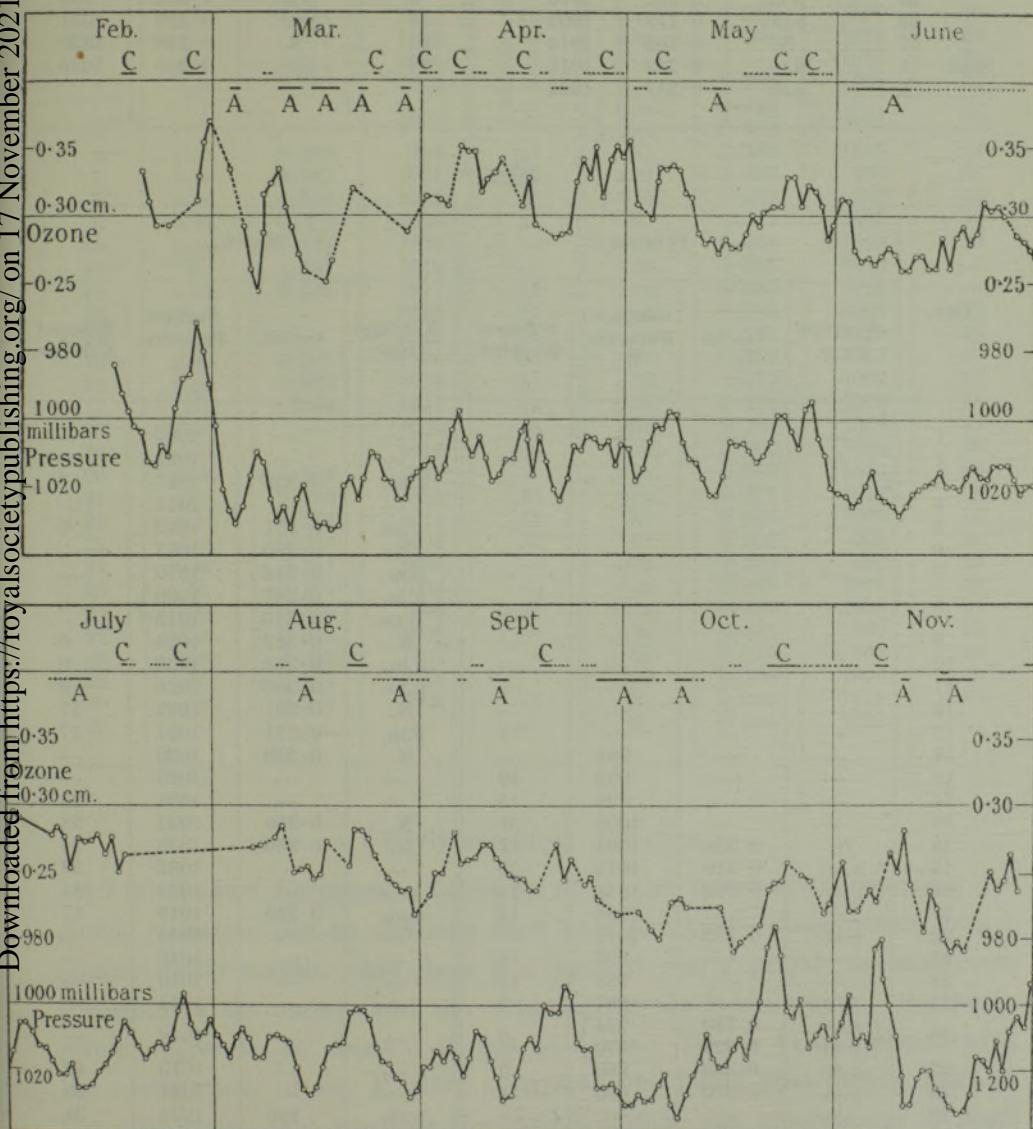


Fig. 5.—Daily Values of Ozone and Pressure.

Table VI.—1924.

Date.	Average time,	Ozone. Cms.	Surface pressure. Mb.	Date.	Average time.	Ozone. Cms.	Surface pressure. Mb.
Aug. 18 .....	p.m.	0.301	994	Sept. 10 .....	{ a.m.	0.253	1012
" 19 .....	N.	0.302	999		{ p.m.	0.231	1014
" 20 .....	N.	0.289	998	Oct. 6 .....	p.m.	0.244	1006
" 22 .....	p.m.	0.262	1002	" 8 .....	p.m.	0.251	998
" 23 .....	a.m.	0.279	1003	" 14 .....	p.m.	0.226	1031
" 27 .....	N.	0.262	1014	" 23 .....	N.	0.236	1030
Sept. 1 .....	p.m.	0.229	1016	" 24 .....	a.m.	0.236	1026
" 3 .....	p.m.	0.247	1023				

1925.\*

Day.	February.				March.			
	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	—	—	—	—	—	—	1002	—
2	—	—	—	—	—	—	1021	8
3	—	—	—	—	a.m.	0.333	1027	7
4	—	—	—	—		—	1031	—
5	—	—	—	—	p.m.	0.291	1026	0
6	—	—	—	—	N.	0.260	1017	—
7	—	—	—	—	p.m.	0.244	1010	—
8	—	—	—	—	{ a.m.	0.287	1006 }	0
					{ p.m.	0.315	1013 }	
9	—	—	—	—	N.	0.323	1024	0
10	—	—	—	—	a.m.	0.333	1030	0
11	—	—	—	—	p.m.	0.305	1026	9
12	—	—	—	—	N.	0.291	1032	17
13	—	—	—	71	p.m.	0.271	1024	17
14	—	—	984	—	N.	0.259	1020	—
15	—	—	993	49	—	—	1029	—
16	—	—	998	15	—	—	1032	20
17	—	—	1002	31	N.	0.250	1031	28
18	N.	0.338	1004	12	N.	0.266	1033	34
19	a.m.	0.310	1013	36	—	—	1032	32
20	p.m.	0.292	1014	13	—	—	1020	24
21	—	—	1008	11	a.m.	0.320	1018	17
22	p.m.	0.293	1011	—	—	—	1024	—
23	—	—	997	14	—	—	1018	—
24	—	—	988	13	—	—	1010	—
25	—	—	987	0	—	—	1011	—
26	{ a.m.	0.310	974 }	7	—	—	1018	—
	{ p.m.	0.329	970 }					
27	a.m.	0.353	980	0	—	—	1019	43
28	p.m.	0.370	990	14	—	—	1024	38
29	—	—	—	—	p.m.	289	1024	34
30	—	—	—	—	—	—	1018	24
31	—	—	—	—	—	—	1016	22

\* See also pp. 683-8.

Table VI.—1925—*continued.*

Day.	April.				May.			
	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	N.	0.314	1014	10	a.m.	0.355	1009	19
2	—	—	1012	8	a.m.	0.308	1019	23
3	a.m.	0.312	1018	7	—	—	1015	35
4	a.m.	0.307	1014	14	p.m.	0.298	1007	35
5	—	—	1003	19	{ p.m.	0.325	1004	31
6	p.m.	0.352	998	17		0.335		
7	a.m.	0.347	1006	24	a.m.	0.334	1003	43
8	a.m.	0.347	1011	21	p.m.	0.336	998	37
9	a.m.	0.317	1006	31	N.	0.334	999	34
10	a.m.	0.327	1012	—	a.m.	0.317	1007	43
11	N.	0.331	1019	—	a.m.	0.314	1012	39
12	a.m.	0.342	1017	52	a.m.	0.287	1013	—
13	—	—	1012	57	a.m.	0.280	1018	—
14	—	—	1012	42	a.m.	0.283	1023	27
15	p.m.	0.307	1004	35	a.m.	0.272	1023	38
16	p.m.	0.327	1003	31	N.	0.283	1017	47
17	N.	0.294	1017	42	p.m.	0.277	1007	47
18	—	—	1006	35	p.m.	0.277	1008	78
19	—	—	1012	60	a.m.	0.286	1008	83
20	p.m.	0.284	1021	—	p.m.	0.300	1010	70
21	N.	0.286	1024	40	p.m.	0.293	1013	69
22	a.m.	0.288	1018	44	a.m.	0.301	1011	74
23	p.m.	0.325	1008	36	N.	0.307	1007	71
24	a.m.	0.341	1009	—	N.	0.306	999	54
25	N.	0.327	1005	—	p.m.	0.329	1004	32
26	a.m.	0.350	1006	—	a.m.	0.307	1009	28
27	a.m.	0.314	1008	—	p.m.	0.323	997	41
28	p.m.	0.342	1007	7	N.	0.319	995	40
29	N.	0.351	1014	7	a.m.	0.308	1006	28
30	a.m.	0.344	1008	16	N.	0.284	1011	17
31	—	—	—	—	N.	0.295	1021	—

## § 7. GEOPHYSICAL RESULTS.

§ 7 (a) *Annual Variation.*—Naturally no precise information regarding the annual variation can be obtained from only one year's observations, but it appears fairly certain that there is a marked yearly period, the maximum occurring in the spring, and the minimum in the late autumn; the range would appear to be about 0.15 cm. of ozone. This is in accordance with the observations of Dr. P. Götz at Arosa, who found that during 1922–23 the ultra-violet light reaching the earth's surface was a minimum in April and a maximum in December. The dates of maximum and minimum are peculiar, and not what might at first sight be expected if the variations are

Table VI.—1925—*continued*.

Day.	June.				July.			
	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure. Mb.	Sunspot Number.
1	N	0.314	1022	40	N.	0.295	1015	22
2	a.m.	0.312	1023	83	a.m.	0.290	1006	28
3	N.	0.275	1026	92	—	—	1006	39
4	N.	0.266	1024	80	—	—	1009	47
5	a.m.	0.269	1020	94	—	—	1012	66
6	N.	0.264	1016	73	—	—	1014	50
7	a.m.	0.273	1023	89	p.m.	0.277	1018	48
8	p.m.	0.277	1024	118	a.m.	0.288	1022	61
9	p.m.	0.272	1026	114	N.	0.276	1022	—
10	p.m.	0.260	1029	109	p.m.	0.252	1019	43
11	a.m.	0.260	1026	102	a.m.	0.275	1026	38
12	p.m.	0.270	1022	89	N.	0.272	1026	37
13	a.m.	0.271	1021	88	N.	0.274	1025	39
14	p.m.	0.261	1020	56	a.m.	0.278	1021	20
15	N.	0.262	1019	35	a.m.	0.263	1019	21
16	N.	0.285	1016	17	a.m.	0.276	1015	41
17	a.m.	0.263	1020	8	p.m.	0.250	1011	40
18	a.m.	0.285	1020	13	a.m.	0.263	1006	31
19	p.m.	0.293	1021	7	—	—	1009	28
20	N.	0.280	1017	0	—	—	1013	35
21	p.m.	0.288	1014	0	—	—	1017	38
22	a.m.	0.311	1017	18				
23	N.	0.305	1018	14				
24	p.m.	0.308	1014	7				
25	N.	0.300	1014	12				
26	—	—	1014	11			No observations.	
27	p.m.	0.287	1018	16				
28	p.m.	0.284	1022	14				
29	N.	0.276	1020	11				
30	a.m.	0.271	1020	17				

due to the varying altitudes of the sun. The annual variation is very much complicated by the superimposed variations associated with pressure changes (*see (d) and (e)* below).

§ 7 (b) *27-Day Period*.—During a period of some months (May to August) there were indications of a 27-day period such as might be associated with the period of revolution of the sun. However, if changes apparently associated with barometric pressure variations are eliminated, this periodicity largely disappears, and up to the present there seems no certain evidence of such a period, though the apparent connection with sunspots and magnetic data would indicate that such a period was not improbable.

§ 7 (c) *Diurnal Variation*.—No evidence of such a variation has been obtained. It can be shown that if there were a regular diurnal variation

Table VI.—1925—*continued*.

Day.	August.				September.			
	Average Time.	Ozone,	Surface Pressure, Mb.	Sunspot Number.	Average Time.	Ozone.	Surface Pressure, Mb.	Sunspot Number.
1	—	—	—	—	—	—	1019	76
2	—	—	—	—	p.m.	0.235	1019	59
3	—	—	—	—	a.m.	0.250	1014	80
4	—	—	—	—	N.	0.250	1017	73
5	—	—	1007	8	—	—	1013	60
6	—	—	1010	23	N.	0.281	1016	71
7	p.m.	0.269	1016	28	p.m.	0.257	1021	43
8	p.m.	0.270	1016	40	N.	0.260	1016	38
9	—	—	1010	56	p.m.	0.262	1008	65
10	p.m.	0.276	1009	70	a.m.	0.272	1010	47
11	a.m.	0.285	1010	57	a.m.	0.271	1017	36
12	—	—	1011	47	N.	0.260	1022	30
13	p.m.	0.250	1019	46	p.m.	0.257	1029	21
14	N.	0.252	1026	31	N.	0.249	1028	30
15	a.m.	0.254	1027	7	a.m.	0.246	1021	42
16	a.m.	0.246	1025	7	p.m.	0.246	1013	60
17	a.m.	0.249	1019	7	a.m.	0.236	1010	—
18	p.m.	0.274	1013	10	a.m.	0.236	1013	51
19	—	—	1012	28	—	—	1000	60
20	—	—	1001	24	—	—	1002	67
21	a.m.	0.255	1002	30	N.	0.271	1002	76
22	a.m.	0.283	1001	19	p.m.	0.245	994	83
23	a.m.	0.282	1001	31	p.m.	0.260	997	77
24	N.	0.277	1004	30	—	—	1011	—
25	a.m.	0.263	1013	—	a.m.	0.241	1013	76
26	—	—	1017	64	N.	0.247	1013	82
27	N.	0.246	1018	64	N.	0.230	1025	86
28	N.	0.242	1022	71	—	—	1025	77
29	N.	0.237	1023	77	—	—	1024	77
30	a.m.	0.239	1028	—	N.	0.218	1026	—
31	a.m.	0.219	1026	92				

with maximum or minimum at local noon, no evidence of it would be shown, and the values found would apply to the amount of ozone present at about sunrise or sunset. This is due to the fact that in calculating the amount of ozone by the long method (*see § 2 (a)*) we must assume the atmosphere to be constant during the interval over which observations are taken, and if the conditions are changing regularly we obtain a result which would be true when the sun was on the horizon. Moreover the values of  $\log I_0$  found by the long method observations are so changed that when the amount of ozone is calculated by the short method (*see § 2 (c)*) the value would again always be equal to the true value at sunrise or sunset, whatever time the actual observation was made. We have thus no evidence that diurnal variation does not take place.

Table VI.—1925—*continued.*

Day.	October.			November.		
	Average Time.	Ozone.	Surface Pressure. Mb.	Average Time.	Ozone.	Surface Pressure. Mb.
1	—	—	1031	—	—	1009
2	—	—	1031	N.	0.258	1005
3	N.	0.221	1027	N.	0.221	997
4	—	—	1029	N.	0.222	1011
5	N.	0.207	1029	—	—	1009
6	N.	0.200	1024	N.	0.237	1013
7	—	—	1021	N.	0.228	983
8	N.	0.228	1030	—	—	986
9	N.	0.230	1034	N.	0.264	1000
10	p.m.	0.224	1027	N.	0.250	1009
11	—	—	1021	N.	0.281	1026
12	—	—	1017	N.	0.240	1030
13	—	—	1009	—	—	1022
14	—	—	1016	N.	0.205	1020
15	N.	0.224	1018	N.	0.236	1020
16	—	—	1018	N.	0.223	1025
17	p.m.	0.190	1013	N.	0.200	1027
18	a.m.	0.197	1010	N.	0.192	1031
19	—	—	1016	N.	0.198	1033
20	—	—	1005	N.	0.191	1032
21	a.m.	0.210	999	—	—	1027
22	a.m.	0.237	982	—	—	1016
23	a.m.	0.243	976	—	—	1017
24	N.	0.244	984	N.	0.251	1020
25	a.m.	0.257	1001	N.	0.237	1011
26	—	—	1003	N.	0.244	1020
27	N.	0.238	998	N.	0.263	1008
28	N.	0.235	1013	N.	0.235	1004
29	—	—	1009	—	—	1007
30	N.	0.220	1006	—	—	994
31	N.	0.226	1010	—	—	—

§ 7 (d) *Connection with Atmospheric Pressure.*—The most interesting result obtained from this series of observations is the relation shown between the variations of the amount of ozone and the pressure of the atmosphere. Since there is reason to suppose that the ozone is situated above the troposphere, one would expect the variations in the ozone to be related—if at all—to the conditions in the upper air rather than to conditions near the earth's surface. Unfortunately the information relating to the upper atmosphere is very scarce. However, the figures of Table VI show clearly that a very definite connection exists between the variations in the amount of ozone and surface pressure. Considering that it is highly probable that this connection only exists through the pressure at great heights, the agreement is as close as could be expected,

for W. H. Dines\* has shown that the correlation coefficient between the surface pressure and that at 9 km. is only 0·68. High values of ozone are associated with cyclonic, and low values with anticyclonic, conditions. Further, if instead of using the absolute surface pressure at Oxford, one takes the general pressure distribution in the neighbourhood, a closer connection is observed, and it is possible to see that, with very few exceptions, almost all changes in the amount of ozone are associated with changes in the surface pressure distribution. There appears to be a tendency for the changes in the amount of ozone to reach a maximum a day or two after the extremes of pressure, and this is quite as marked with anticyclones as with cyclones. Did this lag occur in the case of cyclones only one would suspect that it was connected with the different origins of the air currents usually found in the front or rear of a cyclone, but the fact that it occurs in anticyclones also is against this supposition.

It is of interest to note that while Fabry and Buisson's results in 1920 were mostly made in anticyclonic conditions, yet it is possible to trace the variation of ozone with pressure even in these few early observations.

There is reason to suppose that secondary depressions are frequently confined to the lower atmosphere, and that they do not extend to the stratosphere, as in the case of cyclones. In view of this it is important to notice that when well-marked secondary depressions have crossed southern England, the ozone has shown little variation, while when cyclones have followed the same course large effects in the amount of ozone have almost always been observed.

§ 7 (e) *Connection with Upper Air Conditions.*—We are greatly indebted to the Director of the Meteorological Office and Mr. L. H. G. Dines for supplying us with all the information obtained from British balloon-sondes ascents, and giving us all possible assistance. The full data are set out in Table VII. There are 19 days when comparison can be made, but unfortunately there is often considerable difference of time between the two observations, and since the balloon-sonde ascents were made from either Kew or Sealand (Chester) there is also a large difference of locality.

In fig. 6 (a) the values of the pressure at 12 kms. ( $P_{12}$ ), the pressure at the base of the stratosphere ( $P_c$ ), and the height of the base of the stratosphere ( $H_c$ ) are plotted as ordinates, while the values of the ozone are plotted as abscissæ. A diagram giving a similar comparison for the surface pressure at Oxford ( $P_s$ ) on the same days that upper air data are available is also added for comparison.

\* W. H. Dines, 'Geophysical Memoirs,' No. 18.

Table VII.—Upper Air Data.

Date.	Place.	Time.	$P_s$	$P_9$	$P_{12}$	$P_{14}$	$P_{16}$	$P_{18}$	$T_{14}$	$T_{16}$	$T_{18}$	$H_c$	$P_c$	$P_c$	Ozone
1924.		G.M.T.	mb.	mb.	mb.	mb.	mb.	mb.	°a.	°a.	°a.	Km.	mb.	°a.	cm.
Sept. 3	S	7.22	1023	320	203	148	108	—	215	217	—	12.7	181	217	0.247
1925.															
March 17	S	17.40	1032	310	193	140	102	74	215	213	213	11.4	212	208	0.250
" 19	S	7.25	1032	310	195	143	105	—	221	222	—	10.9	230	216	—
" 21	S	8.00	1018	282	179	133	97	—	223	223	—	7.5	353	221	0.320
April 14	S	17.50	1012	303	—	—	—	—	—	—	—	10.5	238	219	—
" 15	S	7.50	1004	292	187	—	—	—	—	—	—	8.9	296	227	0.307
" 16	S	17.59	1001	297	187	138	—	—	225	—	—	10.5	236	222	0.327
" 21	K	15.34	1024	308	192	—	—	—	—	—	—	11.0	227	213	0.286
May 13	S	17.50	1024	311	194	141	—	—	219	—	—	11.8	202	211	0.283
" 14	S	7.43	1023	313	197	143	106	—	222	223	—	11.5	214	215	0.272
" 15	S	7.55	1017	311	195	143	105	—	221	223	—	11.1	223	215	0.283
June 18	S	18.30	1020	310	193	140	103	75	217	217	218	11.5	210	209	0.285
" 19	S	17.45	1021	312	197	—	—	—	—	—	—	11.2	221	219	0.293
" 27	S	16.30	1018	315	199	145	107	—	221	222	—	12.0	199	215	0.287
July 18	K	11.49	1006	313	199	147	109	—	225	229	—	11.6	213	221	0.263
Aug. 14	S	7.50	1026	319	203	150	111	82	225	225	225	10.8	244	223	0.252
" 14	S	13.3	1026	320	203	150	110	81	221	222	224	10.7	248	222	0.252
" 15	S	7.55	1027	325	207	150	110	80	221	219	215	12.5	190	211	0.254
" 15	K	18.00	1027	322	205	149	109	79	216	217	219	12.9	177	209	0.254
" 16	K	7.00	1025	322	205	149	109	80	216	220	222	13.0	176	210	0.246
" 17	S	8.00	1019	321	206	152	113	83	225	227	231	12.1	204	221	0.249
" 19	K	7.10	1012	311	198	147	—	—	230	—	—	10.4	253	223	—
" 20	S	8.00	1011	309	196	145	107	79	227	225	226	10.3	254	221	—
" 22	K	7.00	1001	301	193	143	—	—	228	—	—	8.5	327	229	0.283
Sept. 17	S	7.55	1013	308	194	143	105	—	221	221	—	10.9	229	217	0.236

Places of ascent: S = Sealand (Chester), K = Kew.

It is at once evident that there is a close connection between the amount of ozone and the pressure in the upper air. A diagram for the pressure at 9 km. is very similar to that for 12 km., and the connection is as well marked up to 16 km., above which there are very few results.

There is, of course, an annual variation in the various characteristics of the upper atmosphere, and, as has been shown above, there appears to be a marked annual variation in the amount of ozone. If these annual variations are eliminated, the range of pressure variation is reduced to about two-thirds of its former value, though it happens that the range of ozone values is not much affected. Fig. 6 (b) shows the connection between upper air data and ozone values when both annual variations have been eliminated by using the differences from monthly means ( $P_s$  has no annual variation).

We have estimated that the standard error of the mean ozone value found for any day is about 0.005 cm., and Mr. L. H. G. Dines informs us that the standard error of measurements of pressure at, say, 10 km. is about 1.5 mb. Making an estimate of the standard error involved in measuring the ozone and

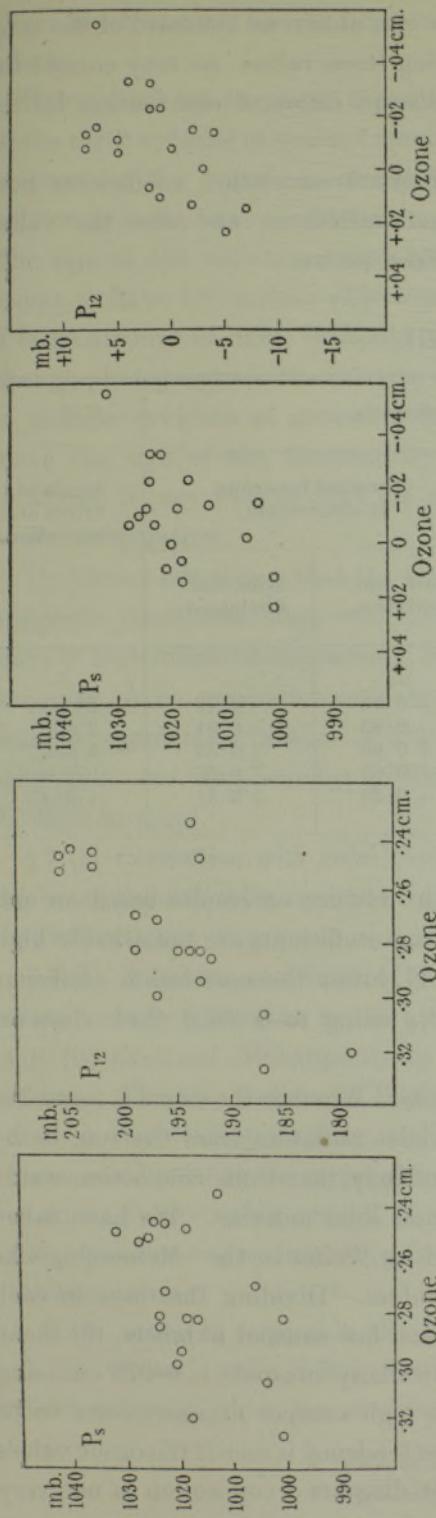


Fig. 6 (a).—Annual Variations not eliminated.

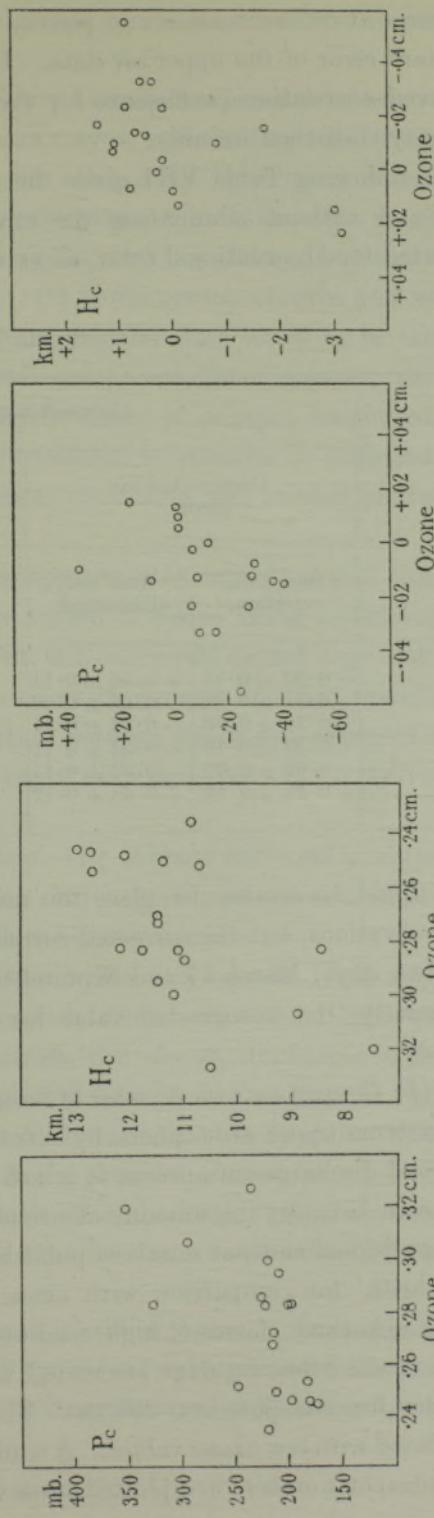


Fig. 6 (b).—Annual Variations eliminated.

pressures at different times and places, we can obtain an estimate of the total standard error of the upper air data. Using these values, we may correct the observed correlation coefficients for the known errors of observation by the ordinary statistical formula.

The following Table VIII gives the observed correlation coefficients both with and without eliminating the annual variations, and also the values corrected for observational error, as explained above.

Table VIII.

	Correlation coefficients.				Assumed errors of observation.	
	Uncorrected for errors.		Corrected for errors of observation.			
	Incl. ann. variation.	Ann. var. eliminated.	Incl. ann. variation.	Ann. var. eliminated.		
P <sub>s</sub> .....	-0.50 ± 0.12	-0.56 ± 0.11	*	—	—	
P <sub>9</sub> .....	-0.71 ± 0.08	-0.66 ± 0.09	-0.75	-0.73	2½ mb.	
P <sub>12</sub> .....	-0.78 ± 0.06	-0.53 ± 0.11	-0.83	-0.81	2 mb.	
P <sub>c</sub> .....	+0.59 ± 0.10	+0.52 ± 0.11	+0.60	+0.53	4 mb.	
H <sub>r</sub> .....	-0.62 ± 0.09	-0.52 ± 0.11	-0.62	-0.52	0.2 km.	
T <sub>c</sub> .....	+0.28 ± 0.14	+0.49 ± 0.12	+0.29	+0.51	1.0° C.	

It would be unwise to place too much reliance on results based on only 19 observations, but the corrected correlation coefficients are remarkably high. The two days, March 17 and September 17, lower the correlation coefficient enormously, the uncorrected value for P<sub>12</sub> rising to 0.88 if these days are omitted.

§ 7 (f) *Connection with Number of Sunspots.*—Whether the ozone is formed in the extreme upper atmosphere by ultra-violet radiation from the sun, or by electrical discharges in auroræ, it is not unlikely that some connection would be shown between the amount of ozone and solar activity. We have taken the provisional sunspot numbers published by Wolfer in the 'Meteorologische Zeitschrift,' for comparison with ozone values. Dividing the days in each month into three classes of high, medium and low sunspot numbers, the mean value of the ozone on days associated with many sunspots is 0.275 cm., and that for few sunspots is 0.298 cm. Thus high sunspot numbers seem to be associated with low ozone values. A similar tendency is seen if the ozone values and sunspot numbers are plotted on a dot diagram; connection is not very

close, but this could not be expected in view of the large barometric pressure effect.

Humphries\* has suggested that the lower average temperature of many parts of the earth at times of sunspot maximum may be explained by smaller amounts of ozone in the upper air, owing to the ultra-violet light being reduced by scattering in the corona, which is more extensive at times of sunspot maximum. The sign of the variation found here agrees with his theory, but the theory seems to have two serious objections : (1) if the corona absorbs and scatters a large amount of light, it should appear brighter than seems to be the case, though photographs in the extreme ultra-violet would be of interest ; (2) there is definite evidence of greater rainfall at times of sunspot maximum, and, since the sign of the temperature correlation is positive in extremely dry localities, it may well be that the greater cloudiness and rainfall produce the lower temperature.

Dr. Chree† has shown that the ozone appears to be connected with terrestrial magnetic conditions, days with large values of ozone being associated with days of high magnetic character. From this one would expect days with many sunspots to be associated with days of much ozone. It may, therefore, be well to regard the existence of a relation between ozone and sunspots as still uncertain, and the possibility of the errors discussed above in § 5 (b) (iv) must be kept in mind.

§ 7 (g) *Connection with Solar Constant.*—Dr. Abbott has kindly supplied us with provisional solar constant values, but a preliminary examination does not indicate any close connection with the ozone values.

§ 7 (h) *Formation and Height of the Ozone.*—The only agencies likely to produce ozone in large quantities in the atmosphere are (i) ultra-violet light from the sun, (ii) electrical discharges in the aurora, (iii) electric discharges in thunderstorms. The observations of Rayleigh and Götz show that there is very little ozone in the lower atmosphere, and, indeed, one would hardly expect that much ozone could exist in the troposphere in the presence of atmospheric dust, some of which is oxidisable and all of which affords a large surface on which the ozone will decompose into oxygen, so that the ozone can hardly be formed by thunderstorms.

If the ozone be formed in the aurora it will probably be formed at heights above 100 km., while if it is formed by the wave-lengths of the sun's ultra-violet radiation which are absorbed by oxygen, it must be formed at heights

\* 'Physics of the Air.'

† See an adjacent paper.

above 40 km. Recent observations by Cabannes and Dufay\* give an effective height of 50 km., but the close connection with the pressure at about 10 km. indicates that a considerable portion must be at a much lower level, for there is good evidence that the pressure changes due to cyclones and anticyclones do not extend above about 20 km. It has been shown that oxygen is transformed into ozone by wave-lengths in the oxygen absorption band ( $<1800 \text{ \AA}$ ), and that ozone is decomposed again by (at least some of) the wave-lengths which it absorbs.

If the ozone be formed by the action of ultra-violet light, there will probably be a region at about 40 to 50 km. where the concentration of ozone will be governed by the equilibrium between the rate of formation by the shorter wave-lengths and the rate of decomposition by the longer wave-lengths. From this level it will probably sink down owing to its high molecular weight.

§ 7 (i) *Cause of the Connection between Atmospheric Pressure and Ozone.*—In the present limited state of our knowledge, it is not very profitable to speculate on this subject. Prof. Lindemann pointed out some time ago that the presence of ozone must raise the radiation equilibrium temperature of the earth's atmosphere, and that if the amount of ozone varied, the resulting temperature changes would cause variations in the pressure of the air below them. Again, if the ozone be formed at great heights and slowly sinks through the stratosphere, until it comes into the troposphere, where it is decomposed by dust, etc., then the greater the amount of air in the stratosphere, the greater will be the amount of ozone. Against this view is the fact that the correlation is closer with pressure at any fixed height than with either the height of the tropopause or the pressure at this level. Again, it is not unlikely that the origin of the air current has a large effect. When more observations are available, we shall be able to test such hypotheses with greater certainty.

In the meantime, in view of the interest of the pressure-ozone relation, arrangements are being pushed forward for making simultaneous daily measurements of the ozone at six widely distributed stations in N.W. Europe during 1926. From these measurements it should be possible to determine the distribution of ozone round various types of pressure distribution. By the kindness of the Smithsonian Institution measurements are also to be made at Montezuma, Chili, which will give an indication of the variation of ozone in tropical regions, and at a place where weather conditions are almost invariable. Thus real or apparent changes (*cf.* § 5 (b) (iv)) in the amount of ozone, due to

\* 'Comptes Rendus,' August, 1925.

changes in the sun, should be separated from those due to local pressure variations.

In conclusion we wish to express our thanks to Prof. F. A. Lindemann, F.R.S., for the help he has afforded us throughout the whole of this work, and the many valuable criticisms and suggestions which he has given. The work was made possible by a grant to one of us from the Department of Scientific and Industrial Research, which we desire gratefully to acknowledge.

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*Atmospheric Ozone and Terrestrial Magnetism.*

By C. CHREE, Sc.D., LL.D., F.R.S.

(Received December 29, 1925.)

It is now generally believed that magnetic disturbance is primarily due to the special development or modification of electrical currents in the upper atmosphere. During magnetic disturbance the regular diurnal variation is enhanced, which suggests a general increase of electrical conductivity. It is not a far step to suppose that a decided change of electrical conditions in the upper atmosphere may be associated with some change at lower levels. In a presidential address\* to the Royal Meteorological Society I made the suggestion that something might result from a comparison of meteorological or electrical phenomena on days of high and low magnetic disturbance. The idea so far recommended itself to the meteorologists on the National Committee of Geodesy and Geophysics as to lead them to propose at the meeting of the International Union held in October 1924, at Madrid, that international funds should be applied to an investigation on these lines. This suggestion was not, however, approved.

On seeing the data contained in a preliminary account of the earlier of the ozone observations now discussed by Messrs. D. N. Harrison and G. M. B. Dobson, which was given to the Royal Meteorological Society, it occurred to me that they afforded suitable material for the kind of comparison I had suggested. On mentioning this to Dr. Dobson, he sent me the data obtained up to June 14.

For the investigation contemplated the most suitable magnetic data would have been the international magnetic character figures assigned at De Bilt.

\* 'Quarterly Journal Roy. Met. Soc.,' vol. 50, p. 96.