INFRA-RED ABSORPTION BY CARBON DIOXIDE, WITH SPECIAL REFERENCE TO ATMOSPHERIC RADIATION

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SUMMARY

Recent additions to our knowledge of the structure of the water vapour spectrum (Elsasser 1940), and the atmospheric transmission of infra-red radiation (Adel 1939), have tended to emphasise the importance of atmospheric radiation as a fundamental factor in meteorological processes.

Normally the greater part of this radiation comes from the large quantities of water vapour present in the air, but there are certain important regions of the atmosphere where the amount of water vapour is extremely small and where a large part of the radiation comes from the carbon dioxide always present.

It is probable that measurements of carbon dioxide absorption and radiation have been more numerous and extensive than for most other gases, but these observational data are scattered through the scientific literature of many decades and in several languages; also they are usually presented in a form which cannot be applied to atmospheric conditions and which requires much coordination and simplification before it can be used for the calculation of energy exchanges. In the following pages these measurements are reviewed and the different sets of observations are compared with the aid of a simple function which will give the absorption by any quantity of CO_2 in the different wave bands.

The measurements of carbon dioxide absorption

Nearly all the heat radiation of matter at temperatures below about 300° abs. (81°F.) takes place in wave lengths greater than 5μ, with a maximum intensity at 10μ, and most of the radiation in wave lengths greater than 10μ. In this spectral region absorption by carbon dioxide is mainly concentrated in the wave band from $12\cdot5$ to $17\cdot5\mu$, which carries about one quarter of the total radiation; there is also weak CO_2 absorption in the band from 9 to 11μ.

The following is a brief summary of the principal measurements of carbon dioxide absorption in the wave lengths of normal temperature radiation.

(1) J. Koch (1901) made extensive measurements of the CO_2 absorption of the whole beam of radiation from a black body at $373°$ abs. These observations have been fully discussed, and an attempt made to apply them to atmospheric conditions, by N. Elkholm (1902). This type of whole energy measurement is not very useful alone, but gives a valuable check on totals calculated from spectrum observations.

(2) S. Arrhenius (1901) made observations similar to those by Koch and confirmed the latter's values. He also attempted to measure the absorption by CO_2 at 200° abs., but these values appear to be much too large.

(3) H. Rubens and E. Ladenberg (1905) observed the absorption by CO_2 in columns from 1 mm. to 4 m. long at normal temperature and pressure, in successive wave bands from about 5 to 18μ. On account of the extensive range covered by these observations and their consequent value for atmospheric conditions, they have been examined closely in relation to the more precise wave lengths obtained by some modern measurements, and it will be shown that the agreement of absorption values is excellent, provided that the wave lengths they originally gave are slightly corrected as follows :—

R. & L. μ	12·1	12·8	13·4	14·0	14·6	15·2	15·7	16·2	16·7	17·4	17·7
Corrected μ	12·5	13·1	13·7	14·3	14·9	15·4	15·9	16·3	16·7	17·2	17·4

It appears that each set of values they gave at one wave length is the mean absorption in a band of approximately $0·6\mu$ in width.

(4) G. Hertz (1911) measured the effect of pressures from 0·05 up to one atmosphere upon the absorption in the principal CO_2 bands ; his measurements were comprehensive and the mean values obtained for the main CO_2 band agree well with the other observations.

(5) C. Schaefer and B. Philipps (1926) made extensive measurements which covered the range from 1 to $13·2\mu$. Large quantities of CO_2 were used and numerous weak absorption bands were discovered. They found that 8 metre-atmospheres of CO_2 were transparent in wave lengths from 5 to 9 and from 11 to $12·4\mu$.

(6) P. Martin and E. Barker (1932) made many observations of high definition in the main CO_2 band from 13 to 17μ. These are the most accurate measurements which have been made in this band, and they have revealed its complex but symmetrical structure (Fig. 1) ; they have also greatly assisted in the study of the vibrational structure of the CO_2 molecule.

(7) E. Barker and A. Adel (1933) used extremely high definition to examine the CO_2 absorption lines between 9 and 11μ. They found two double bands of lines, all of weak intensity.

(8) G. Falckenberg (1938) used a new method (Hottel and Mangelsdorf 1935), to observe the total radiation from small quantities of CO_2 at normal temperatures and pressures. Kirchoff's law states that the emission (radiation) and absorption are equivalent for the same conditions, so that Flackenberg's observations give the whole energy absorption of the CO_2 he used.

Other CO_2 absorption measurements, where less precision was attempted, are not referred to here. In wave lengths below 5μ there are numerous CO_2 bands ; for information concerning these the reader is referred to Schaefer and Philipps, to Hertz, and to Martin and Barker. In wave lengths greater than 18μ no CO_2 absorption has been found (Rubens and Wartenberg 1911).

Observed and calculated absorption by carbon dioxide

The *relative* quantities of a gas required for different degrees of absorption are not necessarily the same for any two wave bands, because they depend upon the variation of line intensity within the band; if, however, the bands cover a very narrow range of wave lengths and of line intensity the relative quantities should be approximately the same for all bands, and the only additional factors required would be the absorption intensities for each band.

Fortunately the observations with CO_2 are so extensive and complete that the actual intensity of absorption is known with considerable certainty in all the required wave lengths. These observations have been examined carefully and it was found that the observed variation of absorption can be represented by a very simple relation,* as follows :—

$$I_\lambda = I_{0\lambda}/(1 + k_\lambda c) \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where $I_{0\lambda}$ is the original intensity of the radiation in wave length λ, and I_λ the intensity after passing through a thickness c of CO_2; k_λ is the absorption coefficient for the wave band or wave length. In all cases c refers to the equivalent thickness of CO_2 in cms. at N.T.P.

From (1),

$$A = 1 - 1/(1 + kc) \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where A is the fraction of the energy absorbed by a thickness c of CO_2. Since A always refers to the same wave length or wave band as the coefficients, the suffix λ is omitted as unnecessary.

From equation (2) it follows that kc is equal to a series in ascending powers of A,

$$kc = A + A^2 + A^3 + A^4, \text{ etc. } = A/(1 - A) \qquad . \qquad . \qquad (3)$$

By substituting the observed values of A and c in this relation the absorption coefficient k is quickly obtained for the wave length to which the measurements refer.

These coefficients are shown in Fig. 1, where the scale for k is *logarithmic; they refer to the absorption in small groups of lines,* or bands of about 0.1μ. The line spacing in 9 to 11 was 0.2μ, so that the bands to which k refers should contain about five separate lines if the line spacing in the main band is similar.

As the main CO_2 absorption region is approximately symmetrical about the central maximum at 15μ, each k value will refer to two wave lengths, one on each side of the centre and at equal distances from it; these wave lengths form the horizontal scale of Fig. 1. The actual values of this coefficient are derived as follows : up to 1.2μ from the centre of the band they are the mean

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* It will be noticed that (1) is not the same as the relation for continuous absorption :—

$$I = I_0 e^{-kc}$$

where I/I_0 is the fraction of the radiation transmitted through thickness c of the gas. It is probable that the absorption by a single spectral line would be approximately continuous if it could be observed at very low gas pressure, but this type of absorption is not given by a group of lines, and is not found even if very narrow bands are observed, in wave lengths where the gas has numerous spectral lines as in the CO_2 bands. (See also Elsasser 1940, p. 41.)

values taken from Martin and Barker's first series of curves, at
more than 1·2 from the centre they were obtained graphically by
plotting Rubens and Ladenberg's measurements, and from 13·2
to 12·5μ, also those by Schaefer and Philipps. In general they
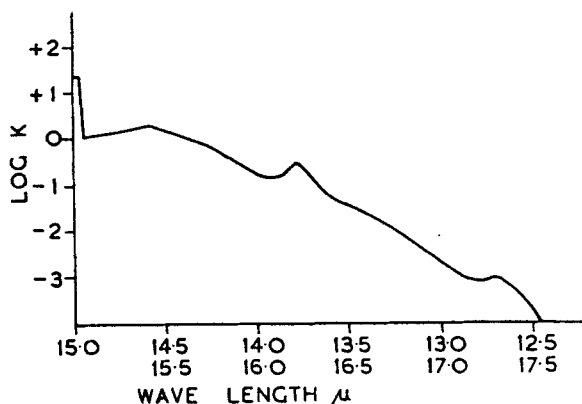represent a smoothed appraisal of the best observations in this
band.

FIG. 1.—The CO_2 absorption coefficient k in equation (1).

The mean absorption by CO_2

For most purposes it is necessary to consider the *mean* absorp-
tion in wave bands covering a definite interval of wave length,
because the computation of mean absorption values from detailed
coefficients, such as those given in Fig. 1, is very tedious; the
observed values also refer, except for some modern measurements
where high definition was used, to the mean absorption in bands of
appreciable width; thus Rubens and Ladenberg's values are means
for widths of about 0·6μ, those by Hertz for widths of about 0·3μ,
and so on.

As the fall of intensity from the centre to the edges of the
main CO_2 band is broken by several subsidiary maxima, the
intensity coefficient k in (1) is not a simple function of the distance
from the centre of the band, and the integral of the equation will
not give the mean absorption in a wave band covering a considerable
range of line intensity.* The mathematical relations between mean
absorption and the variation of intensity within the band are
complex if the latter is not a simple function of wave length, but it
will not be necessary to discuss these relationships because the
actual development of mean absorption in the CO_2 bands is known
with considerable accuracy from the extensive measurements on
this gas.

The latter have been examined carefully, and it was found that
the mean absorption in bands of width about 1 to 2μ is represented
accurately by the following quantity function :—

$$A = 1 - 1/(1 + nc^x) \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

* It will be realised that the *average* of the coefficients within a wave band
    is *not* the same as the coefficient for the mean absorption in the band.

where A is the fractional absorption of the energy in a wave band by thickness c of CO_2, and n and x are constants for the band.

Clearly the equation (2) is a special case of (4); thus when the variation of line intensity is very small, $x = 1$. Comparison of the observed mean absorption in the different bands shows that the index coefficient x is a function of the variation of intensity within the band.*

The coefficients n and x are obtained directly from the observed values of the mean absorption, and the validity of (4) depends upon the accuracy with which it gives the observed development of absorption in the different bands; comparisons are given in Table I over a wide range of band intensity. The observations in the strong absorption between 14 and 16μ are most extensive and accurate, they cover the entire range of absorption with a quantity range of 100,000. Owing to the large quantities of CO_2 required, the weak absorption near the edges of the main band, and between 9 and 11μ, has only been observed up to a small degree, but there is no reason to suppose that its further development follows a different course from that in the stronger bands.

It will be realised that *mean* observed values, such as those shown in Table I, are considerably more accurate than any single reading observed at a particular wave length, because the former tend to smooth out the chance irregularities so difficult to avoid in this type of measurement. These observations, which represent many thousands of single readings, are probably more comprehensive in extent and variety of observing method than those values made for any other gas in these wave lengths, and they are in unusually good agreement with one another; the values computed from equation (4) also agree very well with the observed values throughout a wide range of intensity.

In the region between 9 and 11μ, Table I, where there are four groups of lines giving a fairly even intensity throughout the band, the CO_2 absorption is too weak to be of much importance for present atmospheric conditions. This region, however, is interesting from the point of view of climates in earlier geological epochs, when the air may have been rich in carbon dioxide (Callendar, 1939), because it lies in the centre of the spectral region where the present atmosphere is nearly transparent.

The percentages of the total radiation at normal temperatures, included within the wave bands chosen to sub-divide the CO_2 absorption regions, are shown in Table II, together with the co-efficients for equation (4). A convenient measure of the intensity of the mean absorption in a wave band is the reciprocal of the quantity of gas required for 50 per cent absorption; (4) shows

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* On page 42 Elsasser (1940) states that . . . for small values the absorption . . . (in groups of spectral lines) . . . is proportional to the square root of the quantity of gas. . . . From equation (2) the absorption in small groups of CO_2 lines is nearly proportional to the square root of the quantity over the middle range from about 30 to 70 per cent absorption. The mean absorption in large groups of CO_2 lines, (4), changes more slowly and in this general case it approximates to Elsasser's definition, but the precise relation will depend upon the range of line intensity within the group.

that this measure of the band intensity is equal to the xth root of n, and values for the bands are included in Table II.

TABLE I.—The mean absorption by CO_2 in wave bands of varying intensity. Observed and calculated values compared

Observations by: M=Martin and Barker; R=Rubens and Ladenberg; S=Schaeffer and Philipps; B=Barker and Adel; n and x=coefficients for wave band, equation (4); c=thickness of CO_2 used for observation in cms. at N.T.P.; A_0=observed mean absorption in band, per cent; A_c=calculated absorption, from (4), per cent.

Wave band μ		14-16		13-14 & 16-17		12·5-13 & 17-17·5		9-11	
n		0·9		0·08		0·0055		0·00017	
x		0·84		0·67		0·67		1·0	
Obs. by	c	A_0	A_c	A_0	A_c	A_0	A_c	A_0	A_c
M	0.004	1	0·9						
M	0·05	8·0	7·0						
M	0·23	20·0	20·7						
M	0·68	38·7	39·4						
R	1·00	48·0	47·4	8	7·4				
M	1·58	57·7	57·0	—	—				
R	4	73·3	74·2	17	17·0	2	1·4		
R	20	91·2	91·8	39	37·1	5	4·0		
M	25	—	—	40	40·5	—	—		
R	100	98·0	97·8	63	63·3	12	10·6	2	1·7
R	400	100	99·4	83	81·3	23	23·0	—	—
B	550	—	—	—	—	—	—	8	8·5
S	800	—	—	—	—	32	32·1	12	11·8

TABLE II.—The percentage of the total radiation in the CO_2 bands, and the mean absorption coefficients for the bands

| $T°$ Abs. | Percentage total energy at | | | Constants in (4) | | Rel. intensity |
	230°	265°	300°	n	x	$n^{1/x}$
Bands 14-16 μ . . .	9·9	9·7	9·2	0·9	0·84	0·88
13-14 & 16-17 . .	9·8	9·8	9·3	0·08	0·67	0·023
13-17	19·7	19·5	18·5	0·35	0·55	0·155
12·5-13 & 17-17·5 .	4·9	4·8	4·8	0·0055	0·67	0·0004
12·5-17·5. . . .	24·6	24·4	23·5	0·40	0·36	0·078
9-11	9·4	11·6	13·7	0·00017	1·0	0·00017

Table II shows that the fractions of the total radiation in the different CO_2 bands vary a little in the temperature range between 230 and 300° abs., but in most cases only the radiation in the main band 12·5 to 17·5μ need be considered, and the changes here are so slight that they are unimportant except for extreme temperatures. . It should be noted that these temperatures refer to the radiating surface when the gas absorption is being considered and the temperature of the gas when its radiation is being considered. The effect of the gas temperature only upon its absorption has been discussed by Schnaidt (1939), Elsasser (1938), and others; it is slight and may be neglected, as a rule, in relation to the uncertainty of the absorption coefficients.

To obtain the percentage of the whole energy in a parallel beam of radiation from a " black " surface absorbed by any quantity of CO_2 up to about 20 metres at N.T.P., we calculate from (4), using the values of n and x given in Table II, the fractions of the energy in the bands absorbed by the given quantity of CO_2; the sum of the products of these fractional absorptions and the per-

centage of the energy in the respective bands is the required absorption expressed as a percentage of the total energy.

If the quantity of CO_2 exceeds 20 cms. much computation may be saved by using the coefficients given for the whole band $12\cdot5$ to $17\cdot5\mu$; for smaller quantities the separate band coefficients lead to a more accurate mean.

The following figures show the mean absorption in the band $12\cdot5$ to $17\cdot5\mu$ for three amounts of CO_2 calculated in three ways: (a) from (2), using the values of k given in Fig. 1 and band-widths of only $0\cdot1\mu$; (b) from (4), using the values of n and x given in rows 5 and 6 of Table II; and (c) from (4), using the mean values of n and x given in Table II. The observed values of the mean absorption are given for comparison, and show the great value of the simple relation (4), which agrees very closely both with observation and with the values calculated, with great labour, by method (a):—

Computed mean absorption in band $12\cdot5$ to $17\cdot5$ μ.

Thickness of CO_2 cms. c . . .	1	10	100
Method (a)	$21\cdot3$	$47\cdot5$	$67\cdot0\%$
,, (b)	$22\cdot0$	$45\cdot9$	$66\cdot6\%$
,, (c)	21	48	68%
Best mean observed = . . .	22	46	67%

The effect of pressure

At low pressures the absorption by gases falls off considerably, and it is necessary to correct values observed at normal pressure if they are required for the conditions in the upper atmosphere. The theoretical aspects of this correction have been discussed by numerous investigators (E. von Bahr 1913, Schnaidt 1939, and others). Briefly the effect is as follows: disturbance of the gas molecule, by impact with others, slightly displaces the wave length of its absorption lines; hence the greater number of impacts at higher pressures spread the lines shown by a large number of molecules and enable them to absorb more of the radiation. At some moderate pressure, which may be anything from about $\frac{1}{4}$ to 10 atmos., the lines spread into each other and further increase of pressure has little effect.

The effect of pressures between $0\cdot05$ and 1 atmos. upon the absorption by CO_2 was the subject of an extensive investigation by G. Hertz (1911), who made about 200 observations in the main band from 13 to 17μ. These values have been examined carefully in relation to the CO_2 absorption in this band as determined by other measurements at 1 atmosphere pressure, and it was concluded that at pressures up to 1 atmosphere the quantity of CO_2 required for a given degree of absorption in band 13 to 17μ is inversely proportional to the square root of the total pressure.

This conclusion agrees with the most recent measurements of the effect of total pressure upon the absorption by water vapour (Elsasser 1940).

When this pressure correction is included in relation (4) it becomes:—

$$A = 1 - 1/[1 + n\,(c\,\sqrt{p})^x] \qquad . \qquad . \qquad . \qquad (5)$$

where c is the equivalent thickness of CO_2 in cms. at N.T.P., and p is the total pressure in atmospheres (x and n as before).
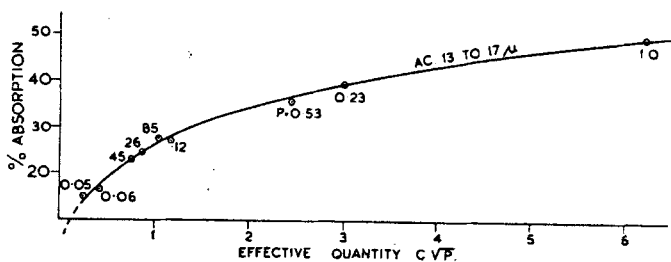

Fig.2.—Mean absorption by CO_2 in the band 13 to 17μ. Observations by G. Hertz. at pressures from 1/20 to 1 atmos.

In Fig. 2 Hertz's observations of the effect of total pressure on the CO_2 absorption in the band 13 to 17μ are plotted against the curve given by (5) with the coefficients for this band in Table II. Agreement is surprisingly good considering that the coefficients, n and x, are derived from quite independent observations.

Although the effect of pressures above 1 atmos. is not important for atmospheric conditions, it may be noted that the increase of CO_2 absorption at higher pressures appears to be very slight; presumably the line spacing is such that they spread into each other when some pressure near to 1 atmos. is reached. Comparable observations at higher pressures are few, and, in the case of CO_2 absorption, the square root law must be understood to apply only for pressures *below* 1 *atmos.*

Hertz also investigated the effect on CO_2 absorption of dilution with large quantities of dry air or hydrogen, at constant total pressure. The mean values given by his extensive measurements in the band 13 to 17μ are summarised in Table III, which shows that dry air has practically no effect on the absorption by a given quantity of CO_2. This means that the *partial* pressure of the gas does not affect its absorption. The dilution with hydrogen, however, appears to have caused a definite though slight increase of absorption by the CO_2, for hydrogen itself does not absorb in these wave lengths; this increase might be caused by the greater number of impacts from the light hydrogen molecules.

TABLE III.—THE EFFECT OF DILUTION AT CONSTANT TOTAL PRESSURE, WITH DRY AIR OR HYDROGEN, UPON THE MEAN ABSORPTION BY CO_2 IN BAND 13 TO 17μ

Observations by G. Hertz

Quantity c cms.	Total pressure atmos.	CO_2 only % A	Ratio CO_2/gas	% Absorption of mixture CO_2/air	CO_2/H
1·12	0·45	—	1/8	23·1	24·2
1·12	0·85	—	1/16	27·1	28·1
1·66	0·26	24·2	2/9	25·0	25·2
3·33	0·53	35·1	2/9	34·8	37·0
4·00*	1·00	45·1	1/25	44·3	—
6·20	1·00	49·2	2/9	49·8	51·2

* Observations by Rubens and Ladenberg.

The partial pressure of CO_2 in the atmosphere is now close to 0·00032 (Callendar 1940), and for h metres of air at total pres-

sure p atmos. and absolute temperature $T°$, the equivalent thickness of carbon dioxide, c, in cms. at N.T.P. is given by :—

$$c = 8·7 \, hp/T.$$

Whole energy absorption

In this type of measurement the whole of a parallel beam of radiation from a black body is passed through the gas, and the fractions absorbed by various quantities of the latter are observed. A disadvantage of such measurements is that they do not give any useful information about the absorption of two gases when mixed together, unless, of course, they are made on a large number of mixtures; no measurements on mixtures of CO_2 and water vapour appear to have been published.

As regards the relative accuracy of whole energy observations in these wave lengths, compared with that of values calculated from the spectrum measurements, my own opinion, from a study of the data and methods used, is that the latter are considerably more accurate, mainly because they allow the use of much higher radiation intensity with all its attendant advantages; it is also very hard to avoid differential losses in the long waves when using the whole of a weak beam of radiation.

TABLE IV.—THE PERCENTAGE ABSORPTION BY CO_2 OF THE WHOLE ENERGY IN A PARALLEL BEAM OF RADIATION FROM A BLACK BODY AT NORMAL TEMPERATURES

c cms. of CO_2	2	4	7	10	20	50	100	200	400	1000
				Observed						
Koch	5·6	7·4	9·0	10·1	11·9	13·2	14·6	16·5	17·6	20·9
Arrhenius	—	—	—	—	—	13·0	15·0	17·1	19·5	(23)
Flackenberg	6·0	7·6	8·8							
				Calculated						
Schnaidt	7·0	9·0	11·2	12·6	15·4	18·7	19·8	20·2	—	—
Callendar	6·8	8·6	9·9	10·6	12·2	14·2	15·7	17·1	18·7	21·0

Hottel (1935) obtained 15·8 % absorption by 50 cm. of CO_2.

The observed values by Koch and by Arrhenius, Table IV, have been corrected from a source temperature of 373° abs., which they used, to one of 283° abs., in order to make them comparable with the others. Schnaidt's calculated values appear to be based on reliable theory, but give too rapid an increase of absorption for small quantities. The last line shows the values given by the coefficients in Table II for a source temperature of 283° abs.; they are based on the accurate spectrum measurements referred to in the text. Agreement between the values by Koch and Falckenberg must be accepted with caution on account of the large corrections applied to the former values.

The absorption by CO_2 probably continues up to at least one kilometre of the gas at normal pressure, but the total for such large quantities is very uncertain on account of absorption in other wave lengths besides those of the well known bands; the coefficients for the latter give 34 per cent A for 1 km. of CO_2, but the actual total may be much greater than this. An interesting example of the finding of additional absorption regions with large quantities of CO_2 is provided by the case of the well known " Venus " bands

between 0·8 and 0·9μ; these bands were seen in the spectrum of the planet Venus, but could not be attributed to any common gas until Adel and Slipher (1934), using over 2,000 metre-atmospheres of CO_2, found that they were due to large quantities of this gas in the planet's atmosphere. These bands gave no measurable absorption when 120 m.-atmos. of CO_2 were used.

The absorption by mixtures of CO_2 and water vapour

In the spectral region between about 8 and 18μ the absorption by water vapour is weak, without any well marked lines, but if there are large quantities of water vapour in the path of the radiation it gives a considerable amount of continuous absorption, especially in the longer wave lengths (Elsasser 1938).* As this type of absorption is equivalent to a simple reduction of the intensity, without the selective filtering caused by bands of spectral lines, the effect of superimposing it upon the line absorption by CO_2 is easily obtained from:—

$$A_{cw} = A_w. + A_c (1 - A_w) \qquad . \qquad . \qquad . \qquad (6)$$

where A_{cw} is the fractional absorption by a mixture of CO_2 and water vapour, and A_c and A_w are the absorptions for the quantities of the respective gases which are present in the mixture. All values refer to a particular wave band.

In the wave lengths 8 to 27μ the continuous, or exponential, absorption by water vapour is given by Elsasser:—
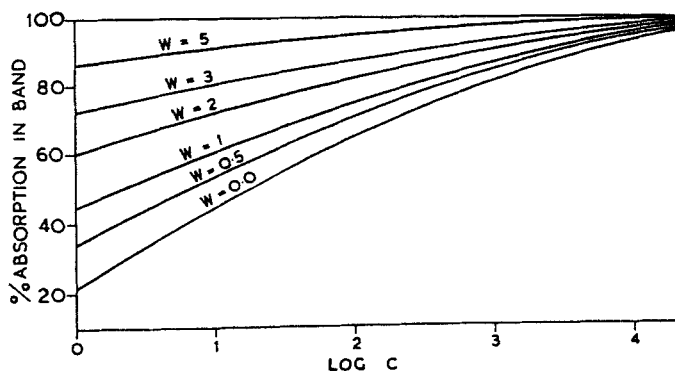
$$A_w = 1 - e^{-aw} \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

Fig. 3.—The mean absorption in the band 12.5 to 17.5μ by mixtures of CO_2 and water vapour; C=cm.—atmos. of CO_2; W=water vapour, cms. equivalent liquid.

* This important conclusion regarding the absorption by water vapour in wave lengths from 8 to 27μ, which carry over two-thirds of the normal temperature radiation, has been advanced by Elsasser on certain theoretical grounds; observational support is given by Adel's measurements of atmospheric transmission in wave lengths 8 to 13μ. If the atmosphere contains a mixture of weak line absorptions from minute traces of ammonia, hydrocarbons, cyanogen, etc., the effect might be that of weak continuous absorption in spectral regions where water vapour and CO_2 are transparent, but Elsasser's water vapour coefficients do in fact give good agreement with the available observational data in these wave lengths, and it may be assumed that they are substantially correct.

where A_w is the fractional absorption by w cms. of liquid equivalent to the vapour, and a, the logarithmic absorption coefficient, is a constant for the wave band.

The following are the mean water-vapour absorption coefficients for the CO_2 bands here considered :—

Wave band μ	9-11	12·5-13	13-14	14-16	16-17	17-17·5
% Energy, 265°	11·6	2·9	5·4	9·7	4·4	1·9
a	0·12	0·22	0·25	0·34	0·45	0·52

From these coefficients, and those in Table II for carbon dioxide, the absorption in the CO_2 bands by mixtures of the gases may be calculated from the equations (4), (6), and (7). Some typical curves for the band 12·5 to 17·5μ are shown in Fig. 3.

Atmospheric transmission

Of late years A. Adel (1939) has made a number of valuable observations on the transmission of solar radiation through the atmosphere in the wave lengths from 7 to 14μ. Although it is not the purpose of this paper to venture into the field of atmospheric absorption, it will be of interest to compare the values calculated from the coefficients given here with those actually observed in the atmosphere.

From a number of observations at 12·8 and 13·4μ,, with different amounts of water vapour in the path, Adel obtained the following mean values for a wave length of 13·1μ.

Cms. pp. water, equivalent to water vapour at 1 atmos.	1·3	3·2
Cms. of CO_2, equivalent at 1 atmos.	130	320
Observed atmospheric absorption, %	45	76

From the CO_2 and water vapour coefficients for wave length 13·1μ ($K=0·003$, and $a=0·24$), the calculated absorption values for these quantities are 47 and 76 per cent respectively, showing excellent agreement with the observed.
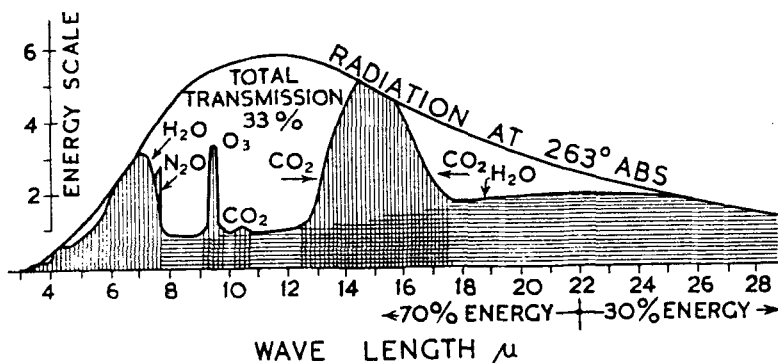

Fig. 4.—The approximate distribution of atmospheric absorption for 1 cm. pp. water.

This close agreement between the observed and calculated values of atmospheric transmission at 13·1μ must be accepted with caution on account of the uncertainty of the absolute intensity of solar radiation in these wave lengths, and also of the equivalent

amounts of CO_2 and water vapour in the air at the time; it does show, however, that the absorption coefficients give values approximating to those actually found in the atmosphere.

The generalised atmospheric spectrum in these wave lengths is shown in Fig. 4 to illustrate the position of the CO_2 absorption regions.

I hope to reconsider the difficult problem of the effect of changes in the amount of carbon dioxide on the temperature of the atmosphere (Callendar 1938), with the aid of the much more accurate absorption values given here.

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DISCUSSION

Prof. S. CHAPMAN said that Mr. Callendar had done extremely valuable work and that people working on this subject ought to be very glad to have the opportunity of reading the paper.

Prof. D. BRUNT thought that the paper brought out very clearly the fact that CO_2 absorption was rather more important than had been thought in the past. Most writers had regarded this absorption as limited to a narrow band, so that only a small fraction of the range of wave lengths within the solar band was affected. Mr. Callendar's paper supplied data which would make it possible to estimate with increased accuracy the effects of CO_2 absorption and radiation on the heat balance of the atmosphere.

Sir GEORGE SIMPSON (President) said that further advance in solving the problems of the radiative balance of the atmosphere depended on more complete knowledge of the absorption coefficient of water absorption; we must know the absorption in the different wave lengths of both water vapour and CO_2. It was not sufficient to know the total absorption

only, for the total energy was distributed differently amongst the different wave lengths, according to the temperature of the source of radiation. No advance had been made in this problem until just after the last war when in conversation with Sir Robert Robertson, the Government Chemist, Sir George mentioned the need for information on the absorption of water vapour and was referred to Hettner's paper. This paper had been entirely overlooked by meteorologists and gave information which led immediately to further advances in the radiation problem. Hettner's absorption coefficients were now being questioned and revised values were required and until they were provided the advance had come to a stop.

Prof. S. CHAPMAN said that the polyatomic gases in the atmosphere were the chief absorbers and emitters of radiation. The most important among them were CO_2, H_2O, O_3 and N_2O. It now appeared that there was more N_2O than O_3. When one considered the vast quantities of money spent on meteorology, not only in the world but in this country alone, one would have expected that meteorologists would not have waited on the chance of spectroscopists and other physicists investigating them, but instead would have actually planned and organised the acquisition of the necessary data. This was essential before the temperature balance of the atmosphere could be estimated on a satisfactory basis.

Mr. G. S. CALLENDAR in reply (communicated): I was very pleased to find that experienced meteorologists considered the absorption values given in my paper would be valuable in the study of atmospheric radiation, because I took great care to find out from the observational data the actual intensity of CO_2 absorption in the required wave lengths, and especially the variation of this intensity with gas thickness. The discovery of just the required set of observations in some ancient volume of the *Deutscher Physiker,* taken with the meticulous care of the older German scientists, has more than once provided compensation for the pursuit of a rather difficult subject.

I agree with Sir George Simpson and Professor Brunt that the water vapour spectrum presents a more formidable problem than that of CO_2, but think that Elsasser's interpretation of the recent observations by H. Randall and others gives values which appear to agree with direct observations of atmospheric radiation and absorption.

Professor Chapman's suggestion that meteorologists might consider an organised research on atmospheric radiation is interesting. The problem of improving on existing data is rather formidable and would require strong financial support on a five or ten year basis; but it would be well worth while in providing a greater understanding of fundamental processes.

Howard Prize

Owing to the difficulties under which the Training Schools whose cadets usually compete for the Howard Prize are now working, no entries have been received for 1940. The Council have therefore decided to suspend this award for the time being.