The influence of the 9·6 micron ozone band on the atmospheric infra-red cooling rate

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SUMMARY

The upward and downward radiation flux and the heating and cooling rate in the atmosphere have been determined for the 9·6 μ band of ozone from the absorption measurements of Summerfield. Three different ozone distribution curves as well as three different temperature-height curves have been used for these calculations. The radiations that interact with the 9·6 μ ozone band always act to cool the atmosphere from the earth's surface to a height of several kilometres and to heat the region from there to approximately 20 km. The heating or cooling rate is never larger than a few tenths of a degree Celsius per day in this region. On the other hand, from 35 to 60 km the usual order of magnitude of the cooling is 2 to 3°C/day, but the cooling rate can be considerably larger if the upper layers have a higher temperature than normal. An increase in the ozone amount at the lower altitudes may cause the surface temperature of the earth to rise several degrees Celsius in order to restore infra-red equilibrium, if no other factors change that produce an effect upon the heat balance. The pressure broadening and overlapping of the spectral lines have been taken into account in these calculations together with all other physical phenomena that are known to be of importance to the problem. An estimate is given for the accuracy of the results.

1. INTRODUCTION

This study is concerned only with the influence of the 9·6 μ ozone band on the infra-red radiation flux and the heating and cooling rates in the atmosphere. The upward and downward flux and the cooling rates are calculated here for three different ozone distributions and for three different temperature-height curves. The results are obtained from the absorption measurements of Summerfield (1941). Such effects as the pressure broadening and overlap of the spectral lines are taken into account. The atmosphere is not divided into homogeneous layers for the purpose of the calculation, as this procedure may introduce large errors in the determination of cooling rates. At each stage a careful estimate is made of the accuracy of the calculation.

The many aspects of the ozone problem have been discussed in the excellent survey articles by Craig (1950, 1951); these contain references to earlier work. Special mention should be made of the long study of ozone cooling rates by Gowan, of which the most recent was published in 1947. Recent articles by Wexler (1950), Craig (1951), Johnson (1953, 1954) and Pressman (1955) have made interesting contributions to the ozone problem and have summarized more recent work.

2. METHOD OF CALCULATION OF ATMOSPHERIC TRANSMISSION FROM LABORATORY DATA

Laboratory measurements of the transmission of infra-red bands as a function of pressure and path length can be used for the calculation of the radiation flux in the atmosphere. The method used in this article has been described by Plass (1952a). From various types of graphs of the laboratory absorption measurements, it is possible to find the regions of validity of several different approximations for the transmission function and to estimate the accuracy of the approximation in each case. It is then possible to calculate the infra-red radiation flux and cooling rates in the atmosphere directly from the laboratory data.

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When these calculations were first made in 1952 the most accurate absorption measurements for the 9·6 μ band of ozone were those of Summerfield (1941). His results have been analysed by a different procedure by Elsasser and King (1953). More recent ozone measurements have recently been discussed by Goody and Walshaw (1954) and by Walshaw and Goody (1954). However, the calculations were completed using Summerfield's results, as they appear to be sufficiently accurate and complete for this purpose.

All Summerfield's measured points at pressures less than atmospheric are shown in Fig. 1, where the logarithm of the fractional absorption, A, is plotted against the logarithm of the product of the pressure, p, and the path length, w, used in the laboratory. It is seen that all the measured points fall on a single universal curve within the experimental error of about 5 per cent. Thus the experimental results show that the ozone absorption can be represented by this single universal curve for the range of pressure and path length used in the experiment (this includes a large portion of the relevant range in the atmosphere). The physical meaning of this result can be shown to be (Plass, 1952a) that most of the absorption is caused by the wings of the strong lines for this range of pressure and path length. Less than 5 per cent of the absorption can come from the centres of weak lines; there would be noticeable departures from the universal curve if this were not true.

From this universal curve, representing the laboratory measurements, Plass (1952a) has shown that the transmission along the variable path conditions found in the atmosphere can be obtained by replacing the variable pw by $g^{-1} \sec\theta \int_{p_0}^{p_1} c\, p\, dp$, where g is the

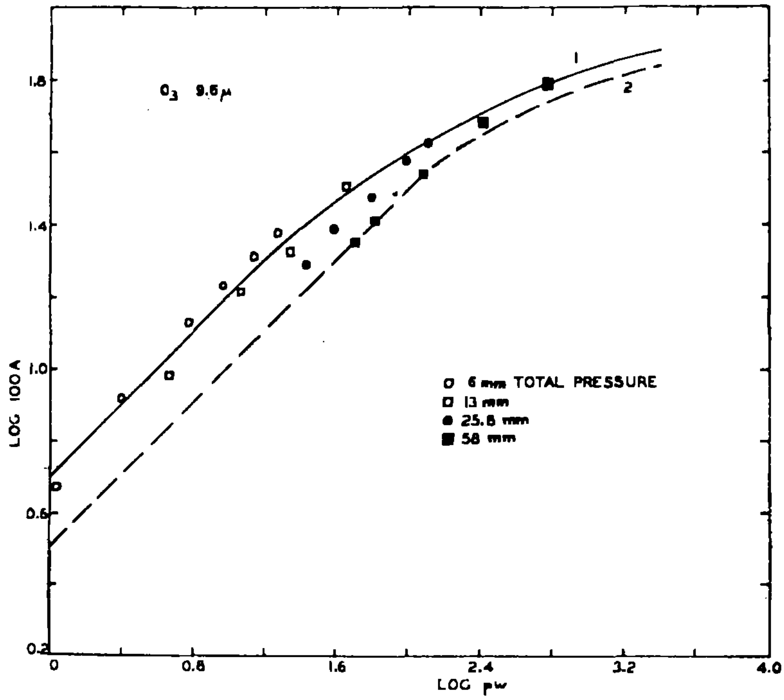

Figure 1. The fractional absorption of the 9·6 μ ozone band as measured by Summerfield (1941). A is the fractional absorption measured in the laboratory; p is the pressure in mm; w is the path length through the ozone in mm at STP. Absorption curve 1 was taken as giving the best fit of the experimental data. Absorption curve 2 was drawn to lie outside the experimental limits of error; its use provided a check of the sensitivity of the results to changes in the absorption curve.

acceleration of gravity, θ is the angle that the beam makes with the vertical, c is the ratio of the density of the radiating gas, ρ_T, to the total density, ρ, and p_0 and p_1 are the pressures at the two levels between which one wishes to calculate the transmission.

This substitution of variables gives a result for the transmission along the variable atmospheric path that is as accurate as the original laboratory measurements. This substitution is valid regardless of how irregularly the line spacing, intensity, or half-width may vary throughout the band, and of whether or not the lines overlap, provided that the range of pressure and path length is in the experimentally determined region of validity of the universal curve. This result is also valid for any line shape which has an absorption coefficient proportional to the pressure in the wings of the line, as is true for the Lorentz line shape or any other collision-broadened line shape that has been proposed.

It is also assumed for the ozone calculation that the measured absorption for the entire band is independent of the temperature. Such an assumption of temperature independence would not be justified, for example, for the 15 μ band of carbon dioxide, since this must be divided into several regions about 1 μ wide for a calculation of this type. In order to use this same method for carbon dioxide, a procedure has been developed for correcting the universal curve by using the Boltzmann factor and an effective temperature between the levels of the atmosphere in question. This method will be discussed in detail when we present the results of our carbon dioxide calculations. When this method is applied to ozone, we find that the temperature correction does not change the absorption for the entire band by more than the experimental error in Summerfield's measurements for the range of temperatures in the atmosphere. Since this result agrees with theoretical predictions for the temperature dependence of the absorption from an entire band, we do not present further details here. Laboratory measurements of the absorption of atmospheric gases should ideally be taken over the range of temperatures that occurs in the atmosphere. This would eliminate any uncertainties that may be connected with the theoretical estimates for this correction. However, to our knowledge, no suitable measurements have yet been made at temperatures below room temperature.

When the logarithm of the absorption is plotted against the logarithm of pw, as in Fig. 1, the slope of the curve is zero for virtually complete absorption. As the absorption decreases, the slope increases to the value one-half when the square-root absorption region is reached. In between these regions the slope gives a convenient measure of the degree to which the spectral lines overlap. If still smaller values of the absorption were measured, the slope would increase to unity in the linear absorption region. In the latter region, there would be no single absorption curve valid over a wide range of the variables p and w as in Fig. 1. Here another procedure described by Plass (1952a) can be used. Since the smaller absorptions shown in Fig. 1 are still above the linear region, it follows that the absorption curve must have a slope of one-half in this region.

The upward and downward flux of infra-red radiation, $I^{\downarrow}$ and $I^{\uparrow}$ respectively, can be obtained from the transmission function, τ, from the well-known solutions of Kirchhoff's equations

$$I^{\downarrow}(u) = I_b(u) + \int_u^{u_1} \tau(u, u') \frac{d\,I_b(u')}{du'}\,du' \qquad (1)$$

$$I^{\uparrow}(u) = I_b(u) - I_b(u_0)\,\tau(u_0, u) - \int_{u_0}^{u} \tau(u', u) \frac{d\,I_b(u')}{du'}\,du' \qquad (2)$$

where

$$\tau(u, u') = \exp\left\{-\sec\theta \int_u^{u_1} k(u)\,du\right\} \qquad (3)$$

$$du = -c\,\rho\,dz = -\rho_T\,dz,$$

$I_b(u)$ is the black-body intensity at the level u, θ is the angle the radiation makes with the vertical, u_0 and u_1 are the upper and lower boundaries in the atmosphere ($u_0 < u_1$), and k is the absorption coefficient. It is assumed that the temperature of the atmosphere at the lower boundary ($u = u_1$) is the same as the temperature of the surface and that the surface emits as a black body. This is the case if the lower boundary is at the surface of the earth or at the upper surface of a cloud. It is also assumed that no appreciable flux is incident on the atmosphere from outside the earth at 9·6 μ.

The time rate of change of the temperature due to the flux of infra-red radiation in the interval $\Delta\nu$ is given by :

$$\frac{\partial T}{\partial t} = \frac{c\,\Delta\nu}{c_p}\frac{d}{du}(I^{\downarrow} - I^{\uparrow}) \qquad (4)$$

where c_p is the specific heat at constant pressure of the air. Thus the cooling or heating rate can be obtained from the derivative of the difference of the upward and downward flux.

Although the upward and downward flux can probably be calculated to a reasonable accuracy by the division of the atmosphere into a number of homogeneous layers, numerical examples convinced us that this procedure can introduce large errors in the derivatives that are needed to obtain the heating and cooling rates from Eq. (4). Further, such calculations showed that large additional errors can be introduced in the final results if intervals larger than 1 km are taken for the numerical evaluation of Eqs. (1), (2) and (4).

The actual procedure adopted for the evaluation of Eqs. (1) and (2) was to perform the indicated integrations numerically by the choice of intervals of 1 km or less, depending on the rate at which the function varied. In the calculations, all atmospheric quantities were taken to have their actual continuous variation with height and were not averaged over layers. The transmission functions were obtained from the data of Summerfield and corrected where necessary by the methods described below. As the calculation of each curve shown in the following sections required well over 10,000 arithmetic operations, the problem was finally set up for an IBM electronic calculator.

Although the straightforward procedure for the calculation of the flux and cooling rates outlined above could be used for most of the intervals, there were certain, usually small, corrections that had to be made between certain levels in the atmosphere. At the highest elevations for which these calculations were made (up to 70 km), it was necessary to consider the importance of Doppler broadening to the line shape in addition to the Lorentz broadening. This correction can be made without difficulty from the equations given by Plass and Fivel (1953). A small correction was made to the transmission data to account for the fact that Summerfield did not include the lines at the extreme edges of the ozone band in his measurements. This correction was made by the method outlined by Elsasser and King (1953).

When the path length is quite short, particularly at the higher altitudes, the equivalent product of the pressure and path length is so small that a large extrapolation has to be made beyond the measured values in Fig. 1. For a sufficiently short path length, the transmission is determined by the total line intensity of the band (Plass 1952a), which can be obtained in the usual manner (Elsasser and King 1953). Because of the lack of experimental evidence in this case for the region of validity of the linear approximation, this was estimated from the equations given by Plass (1954). Although there is a larger uncertainty associated with the points that had to be corrected in this manner, a careful examination of the results of a number of trial runs has shown that this correction influences the final results only at the highest altitude. This uncertainty has been taken into account in estimating the accuracy of these results. Thus, the universal curve is not used for short path lengths.

The measurements of Summerfield show that the absorption cannot be represented by a single universal curve when the pressure is near one atmosphere and for a moderate path length. Since the cooling rate for ozone does not need to be known accurately for the first few kilometres above the earth's surface, no correction was made in this calculation for this departure from the universal curve at pressures near one atmosphere.

In order to compute the total diffuse infra-red radiation for the band, it is necessary to integrate not only over the frequency, but over the solid angle of the hemisphere. This latter integration has often been taken into account approximately by multiplying the path length by some constant factor near 1·67. Because this factor does vary between one and two, as the transmission in an interval changes from one to zero, certain errors can be introduced in calculations of this type by using such a constant factor (Plass 1952b). However, even with the aid of an electronic computor to perform the final integrations, it appeared to be prohibitively complicated to calculate the integrals over the hemisphere for each of the curves given here. It was therefore decided to multiply the path lengths by a numerical factor to convert into radiation over a hemisphere. In order to improve the accuracy of the usual procedure of using a constant numerical factor, a numerical factor was chosen that depended on the transmission between the levels in question.

The relationship between these two quantities was calculated from the results of Plass (1952b). This procedure was checked by actually performing the numerical integration over the hemisphere in several cases. These calculations, together with the results of Plass (1952b), show that the procedure adopted here of using a numerical factor that depends on the transmission in the interval, cannot introduce an error as large as one per cent in the transmission function.

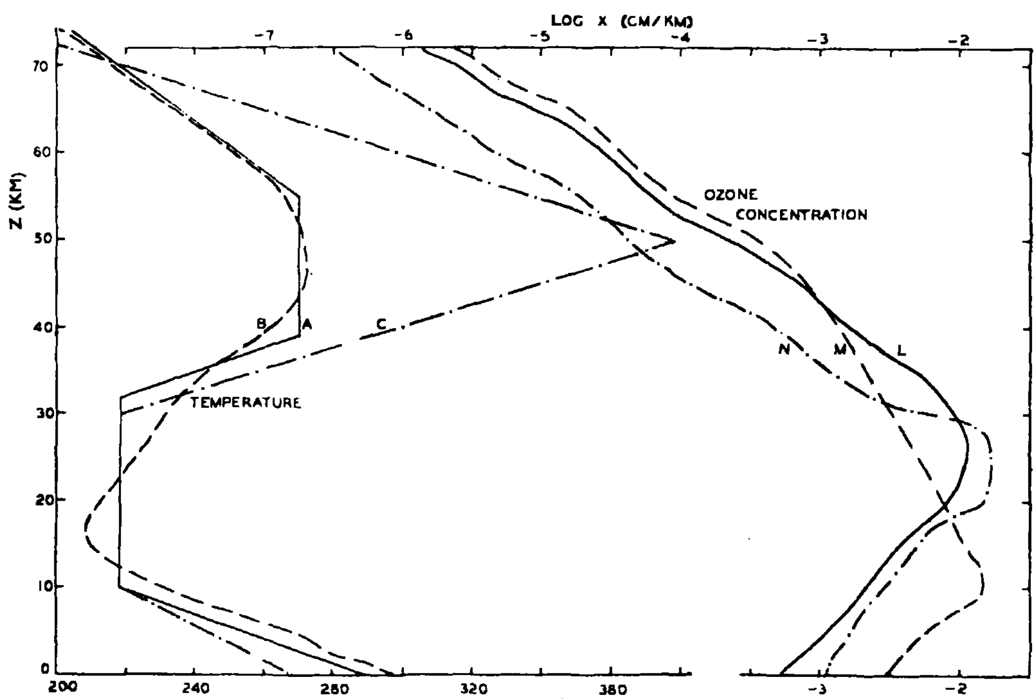

Figure 2. Assumed variation with height of the ozone concentration (curves L, M, N) and of the temperature (curves A, B, C). T is the absolute temperature; x is the ozone amount in cm/km at STP; z is the height in kilometres.

3. Assumed ozone and temperature distributions

Various combinations of the three different ozone distribution curves and of the three temperature-height curves shown in Fig. 2 were used in the six different calculations reported here. The ozone distribution curve L agrees with the NRL rocket measurements of 14 June 1949 above 20 km (Craig 1950, Johnson 1954). This is believed to represent the average ozone concentration at middle latitudes with reasonable accuracy. The curve was extended to lower altitudes from the average of other measurements.

The APL rocket measurements of 25 Jan. 1951 were used to determine the ozone distribution curve M above 20 km. This curve represents larger ozone concentrations above 45 km than curve L. At lower altitudes curve M gives the smallest ozone amounts that have ever been measured at these altitudes. For the total ozone amount to be reasonable, the maximum of this curve must be at a very low altitude. The curve has been continued below 20 km in such a manner. A careful analysis shows that this distribution probably existed at the time of the experiment, possibly owing to convergence and subsidence at the lower altitudes. It would be difficult to explain this result as due to instrumental failure. In any case, we have assumed the ozone distribution curve M in order to study the influence on the infra-red flux and cooling rates of a larger ozone concentration at high altitudes and of a maximum in the ozone distribution at a relatively low altitude.

The NRL measurements of 10 Oct. 1946 are the basis for ozone distribution curve N. This curve has been extended to high altitudes and to the surface of the earth to give a reasonable total amount of ozone according to other measurements. This measurement showed a very much smaller ozone amount above 30 km than is usually found. Further-

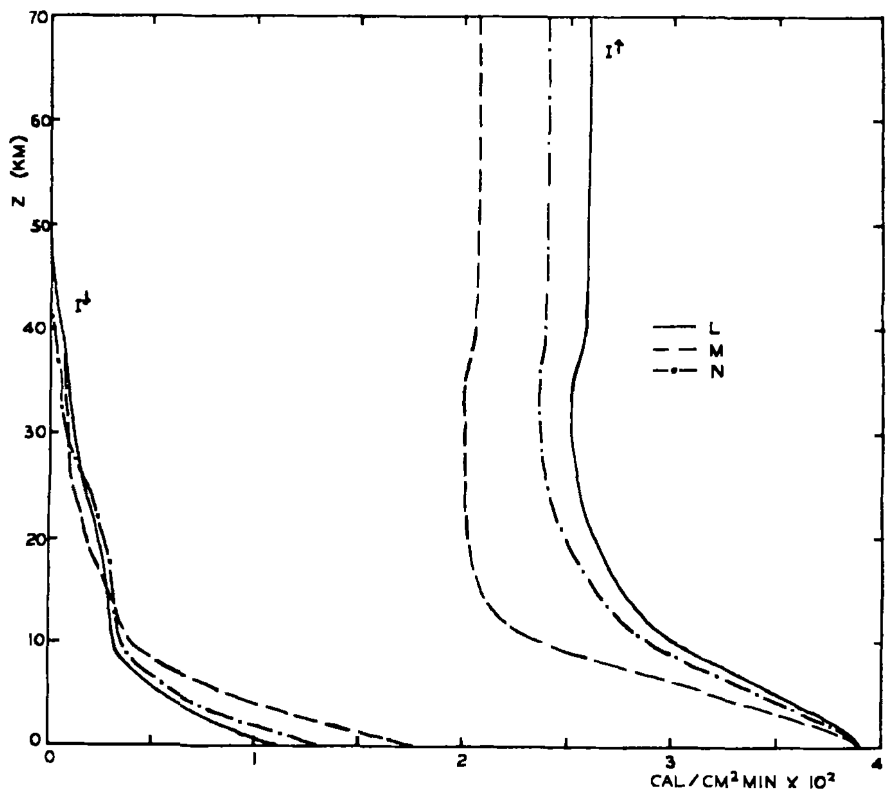

Figure 3. The upward and downward radiation flux ($I^{\downarrow}$ and $I^{\uparrow}$ respectively) in the region of the 9·6 μ ozone band for ozone-distribution curves L, M, N, temperature curve A, and transmission curve 1.

more, the maximum around 23 km is relatively narrow and shows one of the highest ozone amounts (0·17 cm/km) that has been measured. We have assumed the ozone distribution curve N in order to study the effect of greatly reducing the ozone amount at high altitudes and of having a narrow, intense maximum in the distribution. The total ozone amounts for curves L, M and N are 0·213, 0·267 and 0·254 cm respectively at standard temperature and pressure. The curves in Fig. 2 have been plotted against the logarithm of the concentration as abscissa and not against the concentration directly as is customary.

Temperature curve A, the first of the three temperature-height curves used in this study, was chosen to give a reasonably accurate representation of the variation of the average temperature with height at middle latitudes. The calculations are considerably simplified if the temperature-height curve is composed of a number of straight-line segments, since the number of arithmetical operations required to obtain a given accuracy is then reduced. Curve A was taken as our standard temperature curve and curves B and C were introduced in order to study the effect of temperature variations from those given by curve A.

Temperature curve B agrees with the values adopted by the Rocket Panel (1952) as the best average temperatures that can be given at the present time. We repeated the calculations using curve B in order to study the effects of the discontinuities of slope in curve A on the cooling rate.

Temperature curve C was arbitrarily drawn to study the effect of a sudden heating in the upper atmosphere (to a maximum of 378°K at 50 km) and of somewhat lower temperatures near the surface of the earth than are given by curve A. All of the densities used in this calculation are those given by the Rocket Panel (1952) corrected where necessary for our assumed variation of the temperature.

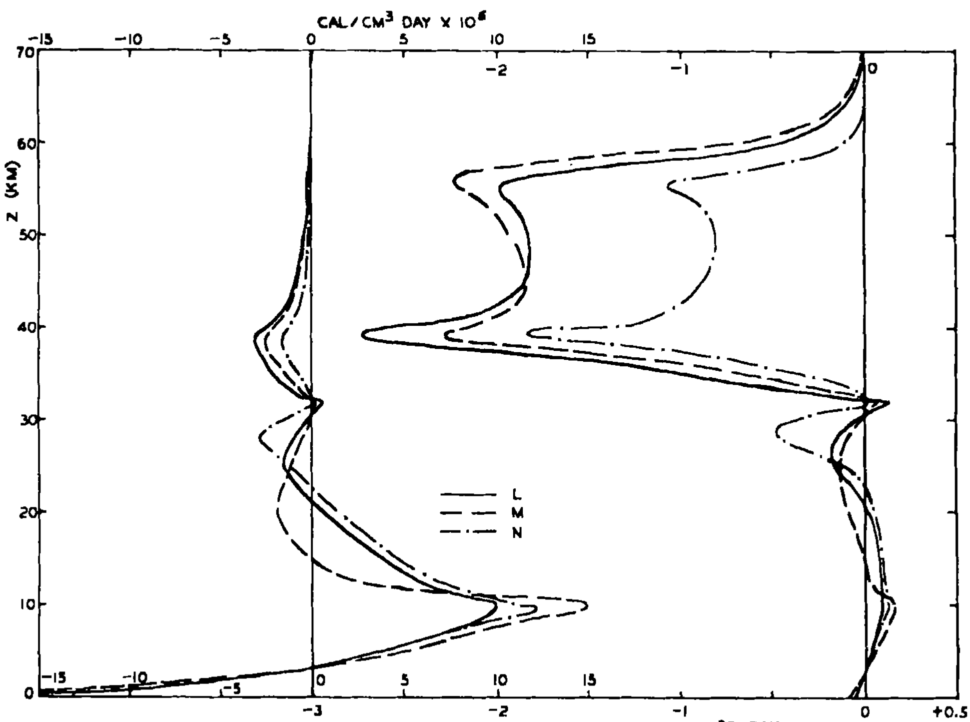

Figure 4. The heating or cooling rates for ozone-distribution curves L, M, N, temperature curve A, and transmission curve 1. The three curves at the left-hand side of the figure give the energy absorbed in units of cal cm^{-3} day^{-1}. The three curves at the right-hand side of the figure give the heating rate in °C/day.

4. Influence of ozone concentration on infra-red flux and cooling

In order to determine the influence of changes in the ozone concentration alone, all calculations reported in this section were made with the temperature curve A. The upward and downward infra-red flux in the region of the 9·6 μ ozone band is shown in Fig. 3 for ozone distribution curves L, M and N. All values of the flux have been reduced to an interval 1·07 μ wide centred at 9·6 μ. Curve M has the highest ozone concentration at low altitudes and therefore the upward flux is more nearly able to follow the decrease in the black-body intensity with height up to 10 km. For this reason the values of the upward flux are less for curve M at all heights than for N and L. The transmission is so near unity above 30 km that the temperature rise in this region causes only a small increase in the upward flux. The variations in the downward flux shown in Fig. 3 can be explained by similar considerations.

It is not apparent from Fig. 3 that the slopes of these curves can be determined with sufficient accuracy to calculate the heating and cooling rates from Eq. (4). However, the original results are sufficiently accurate for the numerical calculation of the derivative. This procedure was checked in several different ways and is discussed further in a later section.

The rate of heating or cooling due to the absorption and emission of infra-red radiation by the ozone is plotted in Fig. 4. Any gas must cool the atmosphere by the action of infra-red radiation in the layer next to the earth's surface, if it is assumed that the atmospheric boundary layer is at the same temperature as the earth's surface. This layer of cooling is found to exist for each ozone distribution curve in Fig. 4. If the mixing ratio is constant, or decreases with height, (as is usually the case for carbon dioxide and water vapour), the action of the infra-red radiation can only cool the atmosphere at all levels. However,

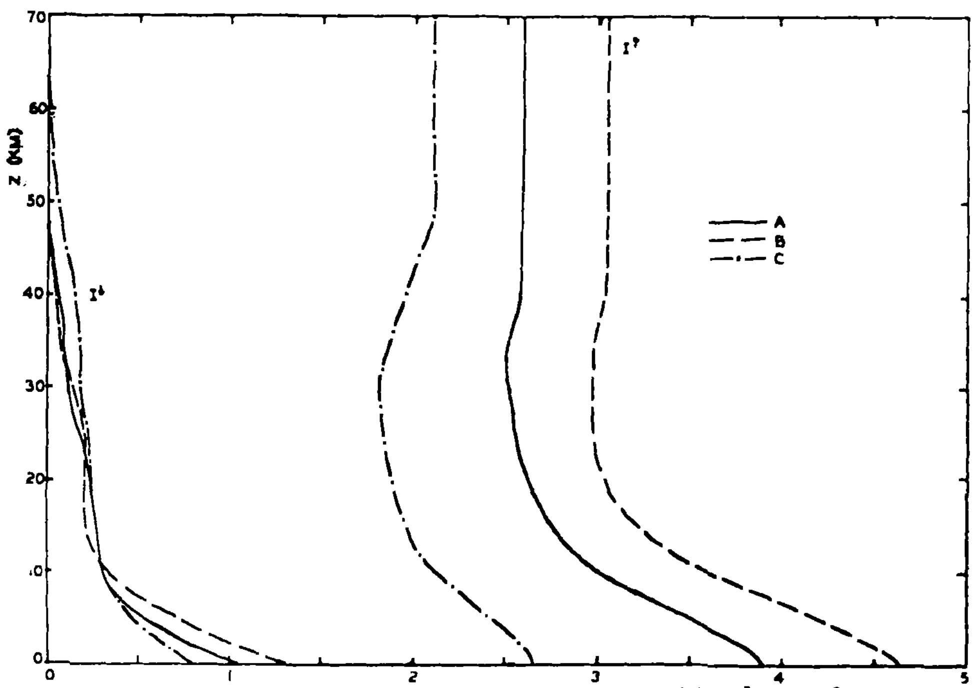

Figure 5. The upward and downward radiation flux ($I^\uparrow$ and $I^\downarrow$ respectively) in the region of the 9·6 μ ozone band for ozone-distribution curve L, temperature curves A, B, C, and transmission curve 1.

if the mixing ratio increases with height (as is the case with ozone up to heights of 10 to 30 km), then the infra-red radiation can cause a net heating of the atmosphere over a range of heights. Fig. 4 shows that this effect is most pronounced at moderate altitudes for curve M which has the highest ozone concentration at low altitudes. The ozone distribution M causes cooling above 13 km, whereas ozone distributions L and N continue to warm the atmosphere to heights of 20 km and above. The reason for this difference is the greater altitude at which the maximum of the ozone distribution occurs for curves L and N than for M. The heating rates are quite small, never exceeding 0·2°C/day at these altitudes.

The cooling rates begin to become large around 35 km for all three curves and are appreciable up to 60 km. The maximum cooling shown for any of these curves is 2·7°C/day. The cooling rate for curve N is roughly one-half that of the other curves above 40 km, because of the very small ozone concentration assumed at these altitudes for this curve. The double maximum is caused by the discontinuities in the assumed temperature curve and is discussed in the next section.

The normal variations in ozone amount in the atmosphere at a given altitude are probably represented by the three rather different values for the ozone concentrations given by curves L, M and N at each altitude. Thus the results of Figs. 3 and 4 show the approximate variation in infra-red flux and cooling rate that might be expected to occur in the atmosphere owing to reasonable variations in the ozone amount. It appears that variations in the ozone amount can change the cooling rate by as much as a factor of two. However, if the temperature remains unchanged, the qualitative features of the cooling curve, including the positions of the maxima, do not vary appreciably with changes in the ozone concentration.

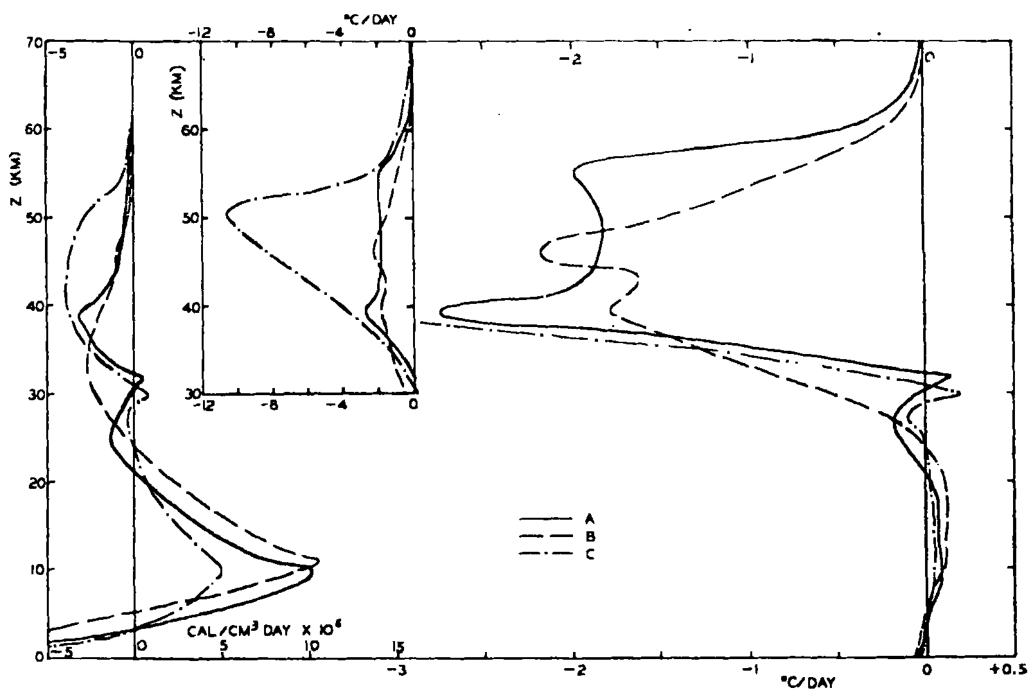

Figure 6. The heating or cooling rates for ozone-distribution curve L, temperature curves A, B, C, and transmission curve 1. The three curves at the left-hand side of the figure give the energy absorbed in units of cal cm^{-3} day^{-1}. The three curves at the right-hand side of the figure give the heating rate in °C/day. The insert in the upper part of the figure gives the heating rate in °C/day at the higher altitudes plotted on a different scale.

5. Influence of temperature distribution on infra-red flux and cooling

In order to separate the effects due to temperature variation with height from those due to changes in the ozone distribution curve, the calculations were repeated using the single ozone distribution curve L, with the three different temperature curves A, B and C (Fig. 2).

The corresponding upward and downward flux of radiation is shown in Fig. 5. Since the temperature in the atmospheric layers close to the ground is the principal factor that determines the magnitude of the upward flux for a given ozone distribution, it follows that, at all heights, the upward flux corresponding to the temperature curve C is less than that from curve A, which in turn is less than that from curve B. The assumed ground temperatures increase in the same sequence. The upward flux corresponding to curve C continues to increase at higher altitudes (up to 50 km) than for the other curves due to the very high assumed temperature at 50 km for curve C. Similarly the downward flux is considerably greater for curve C than for the other two at all altitudes above 30 km. Near the surface of the earth, the downward flux is mainly determined by the temperature of the lowest atmospheric layers. Below 7 km, the three values for the downward flux are in the same numerical sequence as the corresponding assumed temperatures.

In Fig. 6 the heating and cooling rates are shown for these three temperature curves. The region of cooling is seen to extend from the earth's surface to a few kilometres with a region of heating from there to above 20 km. The magnitude of the heating or cooling is again less than a few tenths of a degree per day in this region.

The effect introduced by use of a temperature curve composed of regions with a linear variation of temperature with height and discontinuities in the derivative (curve A), compared with a temperature distribution with a continuous derivative (curve B), is shown in Fig. 6. The points at which the derivative of the temperature with respect to height are discontinuous, appear in Fig. 6, curve A, as maxima in the cooling curve at 39 and 55 km and a narrow maximum of heating at 32 km. In order to obtain these differences, it is necessary to take quite narrow intervals for the calculation of the integrals in Eqs. (1) and (2). It is possible that our maxima would be even sharper had we used still smaller intervals in our calculation. However, it was not felt worth while to do this, since such discontinuities do not actually occur in the atmosphere. Thus a somewhat smoothed curve is closer to reality.

However, in order to check our numerical results further, we have obtained analytic solutions to similar problems by the method of Plass and Fivel (1955), where a discontinuous temperature derivative is assumed and the variation of the Lorentz line shape with pressure is taken into account. The results of these calculations confirm the conclusion that such maxima and minima are always to be expected at points of discontinuity of the derivative of the temperature distribution.

The double maximum near 40-45 km in the cooling curve for temperature distribution B, appears to be real for our assumed data. However, it may be due entirely to small variations in our assumed temperature and density curves. Otherwise curves A and B are qualitatively similar, except that curve B does not have the variations at 32, 39 and 55 km due to the discontinuities in the derivative of the temperature for curve A.

The high assumed temperatures near 50 km for curve C give such a high cooling rate above 40 km that it has been plotted on another scale as an insert to Fig. 6. There is a narrow region of heating near 30 km and a maximum cooling rate at 50 km; these are the positions of the discontinuities in temperature curve C. The cooling rate is 10·6°C/day at 50 km where the assumed temperature is 105°C compared with a maximum of 2·7°C/day for curve A at 39 km where the assumed temperature is − 3°C. Above

30 km the results of Fig. 6 agree qualitatively with the earlier calculations of Gowan (1947) (see also the discussion by Wexler 1950).

Thus if some process, such as increased ultra-violet radiation from the sun, increases the temperature of the upper layers of the atmosphere, the infra-red radiation immediately acts to cool these layers. The influence of the carbon dioxide and possibly also of the water vapour on the infra-red radiation at these levels would considerably increase the cooling rate which has been calculated here only for ozone. Thus the infra-red radiation would allow the atmosphere to return to its equilibrium temperature at a relatively rapid rate. These calculations show that the infra-red cooling rate is more sensitive to temperature variations in the atmosphere than to changes in the ozone concentration that might reasonably be expected to occur.

6. Accuracy of results

At every stage of these calculations, various checks have been made of the accuracy of the results. In the first place, from an estimate of the experimental error for the laboratory determination of the transmission function, τ, it is possible to determine directly from Eqs. (1) and (2) the corresponding error in the calculated values for the upward and downward flux. A liberal estimate of the experimental error of Summerfield's measurements is 5 per cent. The corresponding error in the upward and downward flux is about 3 per cent. This is smaller than the original experimental error since the black-body flux that enters into Eqs. (1) and (2) is known exactly. However, it is more difficult to estimate the error in the cooling rates since these depend essentially on the determination of the derivative of the transmission function.

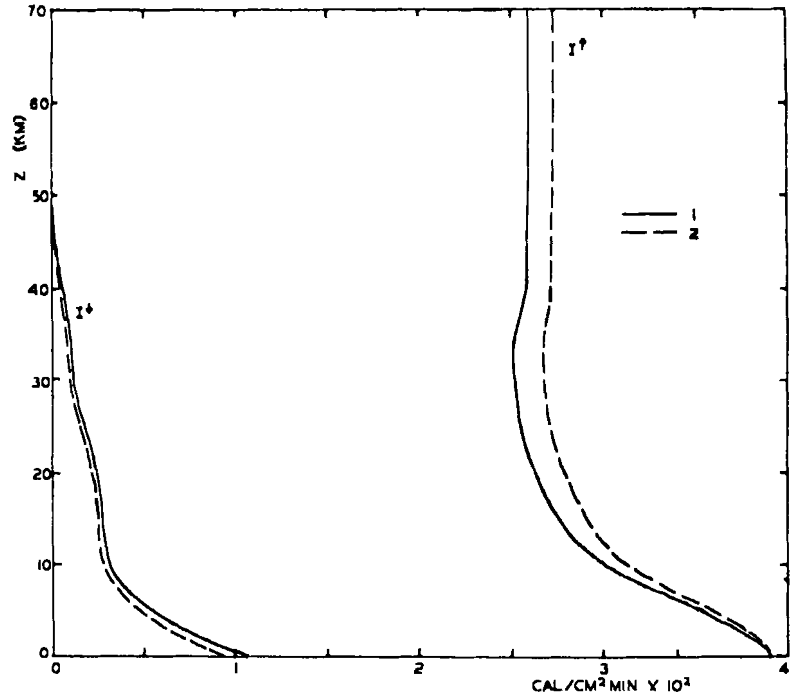

Figure 7. The upward and downward radiation flux ($I^{\downarrow}$ and $I^{\uparrow}$ respectively) in the region of the 9·6 μ ozone band for ozone-distribution curve L, temperature curve A, and transmission curves 1 and 2.

For this reason the calculations were repeated using the ozone distribution curve L and the temperature curve A with two different absorption curves, 1 and 2. Absorption curve 1 (Fig. 1) was used in all the previous sections of this article and is the best fit to the laboratory data. Curve 2 was drawn farther from curve 1 than the limits of the experimental error. The slope of both curves must be one-half near the left-hand side of Fig. 1 because this is the square-root region where the lines do not overlap. The slope of one-half was continued to larger path lengths for curve 2 than for curve 1. These curves also have different slopes for all path lengths beyond the square-root region. For large absorptions curve 2 gives 5 per cent less absorption than curve 1. This difference between the curves increases as the absorption become smaller and the difference is about 30 per cent when the absorption is 10 per cent. It is felt that the difference between the results computed for curves 1 and 2 gives an upper limit to the possible error in the final results that can be caused by errors in the determination of the transmission function.

The upward and downward flux is shown in Fig. 7. The differences between these two curves are relatively small. For example, the error in the determination of the upward flux is nowhere greater than 6 per cent, even though the transmission curves differ over part of their range by much more than this amount.

The heating and cooling rates are shown in Fig. 8. These are more sensitive to the transmission function, as was to be expected. At the upper levels, the results from curve 2 are as much as 30 per cent below those of curve 1. However, it is interesting to note that both curves have the same qualitative shape with their maxima and minima at the same altitude, even though their magnitudes are somewhat different. These features of the cooling curve are primarily determined by the temperature distribution and so are not sensitive to the values adopted for the transmission function.

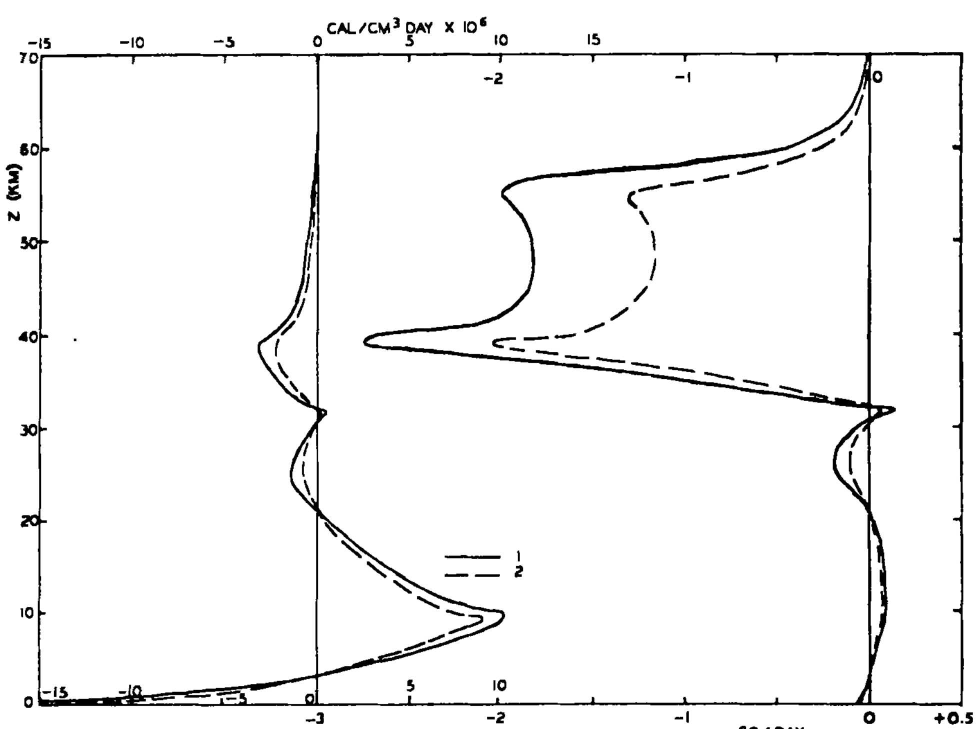

Figure 8. The heating or cooling rates for ozone-distribution curve L, temperature curve A, and transmission curves 1 and 2. The three curves at the left-hand side of the figure give the energy absorbed in units of cal cm^{-3} day^{-1}. The three curves at the right-hand side of the figure give the heating rate in °C/day.

Further tests to determine the accuracy of these results, in addition to those described above, have been made with the aid of the electronic computor. The estimated error deduced from all of these tests and based on the assumption that Summerfield's measurements are accurate to within 5 per cent is that : (a) the curves for the upward and downward flux are accurate to within 5 per cent; (b) the heating and cooling curves have an estimated error of 10 per cent below 20 km with the error increasing to 30 per cent at 50 km. Above 60 km the absolute value of the cooling rate in °C/day is rather uncertain. However, it is believed that the relative values of the different curves have been determined with considerably greater accuracy than this, since all the corrections have been made in the same manner for each of the curves.

7. Temperature changes at the surface of the earth

The temperature change at an absorbing surface at a given height in the atmosphere as the ozone concentration or temperature curves change can be many times larger than the corresponding change in the free atmosphere. The change in the equilibrium temperature at the surface of the earth, as the ozone concentration changes from curve L to M, can be calculated from the results shown in Fig. 3. The difference in the upward and downward flux of the radiation for these two curves is 0·0068 cal cm^{-2} min^{-1} at the surface of the earth. An appropriate calculation that makes allowance for the carbon dioxide and water vapour absorption in the infra-red, shows that the surface emits an additional 0·0033 cal cm^{-2} min^{-1} to space for each degree that the surface temperature rises. Thus the equilibrium temperature would rise 2·1°C if the ozone distribution changed from curve L to M and nothing else changed in the atmosphere. It is assumed that this small temperature rise does not introduce any new physical factors that can remove heat from the surface.

If the ozone distribution changed from curve L to N, the corresponding rise in the equilibrium temperature at the ground is 0·7°C. A temperature rise of the same order of magnitude is obtained for the top of cloud banks. Thus, if the ozone concentration increases in the troposphere owing to convergence and subsidence, or from other causes, the equilibrium temperature at the surface of the earth can increase by as much as several degrees Celsius through the action of the infra-red radiation processes alone. It would be difficult to observe this effect, since larger temperature changes would usually be caused by other meteorological factors in situations where the ozone concentration changes by a large amount. It is interesting to speculate that the average surface temperature would have to rise by a small, but measurable amount, if a change in the circulation pattern or some other factor should change the ozone distribution curve so that, on the average, its maximum would occur at lower altitudes. The temperature changes calculated here, which are caused by radiative processes, would be superposed on those from other meteorological factors; the latter factors may be considerably larger than the former but any complete discussion of climatic change must include the radiative factors. The possibilities of interrelation of solar phenomena with ozone distribution and the circulation pattern are very numerous (Craig 1950, 1951).

A similar, but opposite effect exists for water vapour. Since the concentration of water vapour usually decreases rapidly with height, convergence and subsidence would reduce the water vapour at lower levels. Thus the equilibrium temperature at the surface of the earth would be reduced owing to infra-red radiation effects. The change due to water vapour would oppose the ozone effect calculated above, and might on occasions be considerably larger. Too little attention has been given, as yet, to the changes in the infra-red flux as the water vapour mixing ratio changes with height.

8. Absorption of solar radiation; the 14 μ band

In order to obtain a complete picture of the action of ozone on the cooling rate in the atmosphere, the direct absorption of solar radiation by ozone and the influence of the 14 μ band must be considered. There are, as yet, no extensive laboratory measurements of the absorption due to the 14 μ band and it is not possible to make calculations similar to those given here for the 9·6 μ band. The effect of this additional band would be to increase somewhat the magnitude of the cooling rates given here. However, this increase would probably be small, since the total intensity of this band is several orders of magnitude smaller than the intensity of the 9·6 μ band and since it is shielded to some extent by carbon dioxide. However, it should be determined whether the carbon dioxide does effectively shield this band at all altitudes. At the higher altitudes where the ozone concentration is large and the carbon dioxide band is no longer opaque at its centre, the 14 μ ozone band may make a small contribution to the cooling rate.

Recent calculations of the direct absorption of ultra-violet light from the sun by the ozone (Johnson 1953; Pressman 1955) show that the maximum diurnal temperature change is from 5°C to 10°C at heights of 40 to 50 km. Johnson's Fig. 5 is very similar to the results given here for the infra-red cooling above 35 km. His heating rates are approximately twice the infra-red cooling rate for ozone curve L and temperature curve A. The heating due to ultra-violet absorption could be balanced by the cooling due to infra-red radiation from 40 to 60 km for a temperature curve with values intermediate between our curves A and C. Since carbon dioxide can contribute to the cooling rate at these altitudes, it did not seem worth while to make such a calculation until the carbon dioxide cooling rates are better known.

Recent calculations of the cooling rate due to water vapour (Möller 1951, London 1954) indicate that its maximum value is about 5°C/day and that such large values can only be obtained within a few kilometres of the earth's surface, or near the top of a cloud. Above 15 km the cooling rate due to water vapour is less than ½°C/day and decreases with altitude. Thus the influence of water vapour on the cooling rate, is considerably more important than that of ozone below 15 km. At greater altitudes, the ozone becomes more important than the water vapour. Above 30 km, the water vapour can possibly be neglected, unless it is found to occur in unexpectedly large concentrations at these altitudes.

9. Conclusions

The variation of the upward and downward infra-red radiation flux and cooling rate has been determined for three different ozone distributions and for three different temperature distributions. In all cases the infra-red radiation interacting with the 9·6 μ band acts to cool the atmospheric layer from the ground to several kilometres and to heat the atmosphere from there to approximately 20 km. The heating and cooling rates are never larger than a few tenths of a degree per day at these altitudes. The radiation cools the atmosphere by amounts of the order of 2°C to 3°C/day from 35 to 60 km. If this portion of the atmosphere is heated above its normal temperature, this cooling rate is greatly increased. The overlapping of the spectral lines together with the variations of their intensities and half-widths with pressure and temperature have been taken into account in this calculation. For a normal temperature and ozone distribution, the calculated infra-red cooling rate for ozone is approximately one-half the heating rate from ultra-violet absorption.

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