

~~H-07537~~  
N71-33732  
036350-2-T  
NASA CR-121469

*Radiation Processes and the  
Distribution of Radiative Sources  
and Sinks*

Technical Report

WILLIAM R. KUHN

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May 1971

National Aeronautics and Space Administration  
Contract No. NASr-54(03)  
Washington, D.C.



High Altitude Engineering Laboratory  
Departments of Aerospace Engineering  
Meteorology and Oceanography

This report was also a review paper presented at the Symposium on the Dynamics of the Mesosphere and Lower Thermosphere of the AMS, June 15-18, 1970, Boulder, Colorado.

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COLLEGE OF ENGINEERING  
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RADIATIVE SOURCES AND SINKS

William R. Kuhn

ORA Project 036350

under contract with:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NO. NASr-54(03)

WASHINGTON, D. C.

administered through

OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

May 1971



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## Introduction

Since the equations necessary to represent the dynamical state of the atmosphere include the first law of thermodynamics it is entirely appropriate for a conference on dynamics of the mesosphere and lower thermosphere to include a radiation section. The content of this report therefore, represents a review of our present state of knowledge of radiative processes and radiative sources and sinks primarily in the mesosphere and lower thermosphere in the height range of 50 to 100 km. This division is somewhat arbitrary although one might argue that the stratopause represents a logical boundary for dynamical considerations; the upper boundary has been chosen from a practical standpoint in that, I believe, it represents the upper limit for which our knowledge of radiative effects are known with any degree of certainty. In this review I shall discuss the contributions of the various gases to the radiative problem as well as uncertainties in the results.

Before examining the radiative sources and sinks in this region of the atmosphere, it is instructive to compare the radiative contributions of the more important gases to the region as a whole, as well as the non-radiative components. Figure 1 indicates this comparison. The gas primarily responsible for cooling the mesosphere and lower thermosphere is carbon dioxide. In the region of the mesopause, carbon dioxide produces a slight heating whose magnitude is somewhat uncertain, as well as the cooling in the lower thermosphere. The influence of ozone is only significant in the mesosphere where its contribution is about one-half that of carbon dioxide. Similarly, water vapor is only significant in cooling the mesosphere,



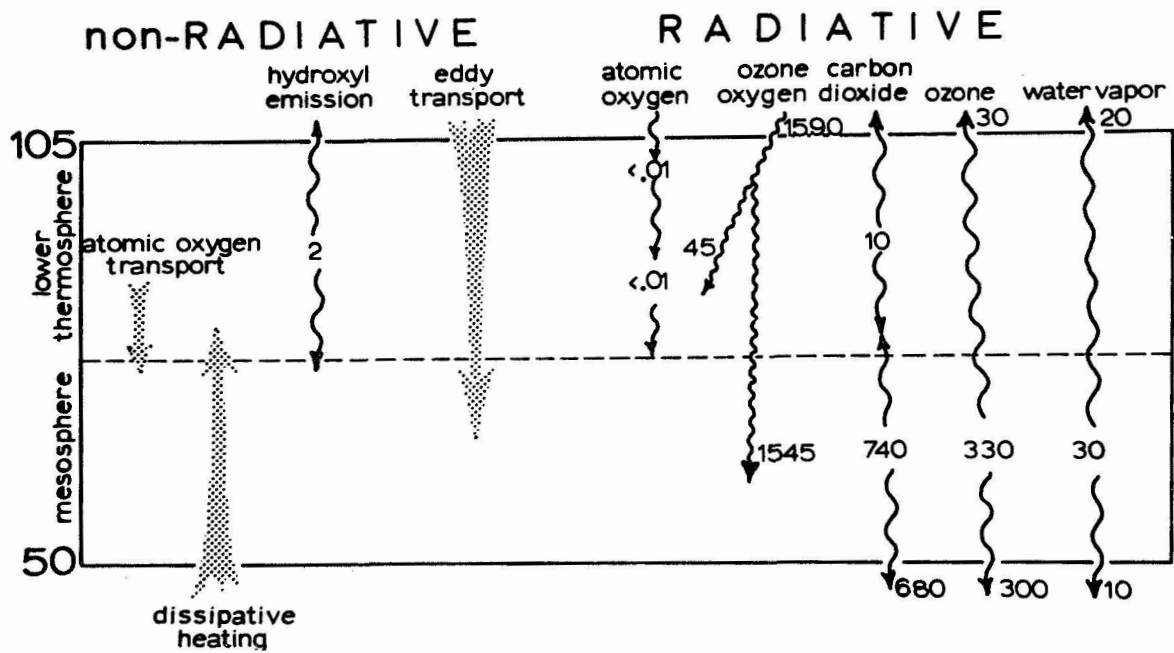


Figure 1. Radiative and non-radiative contributions to the heat budget in the height range 50 to 105 km. Units of  $\text{ergs}/\text{cm}^2/\text{sec}$ .

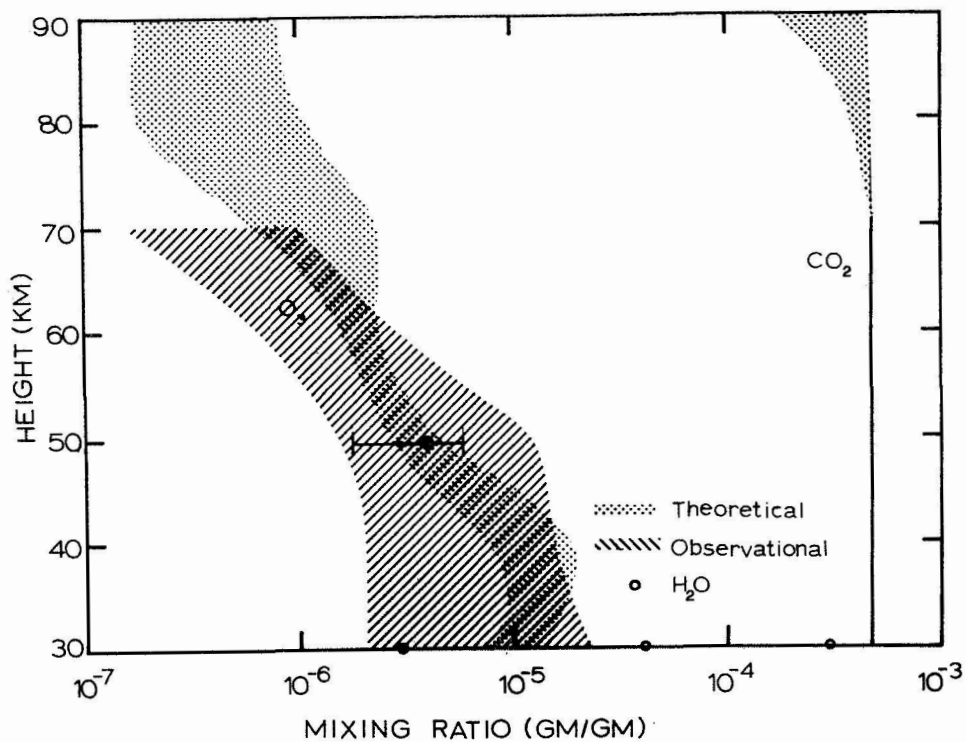


Figure 2. Variations in height concentrations of carbon dioxide, ozone, and water vapor.

and is only about one-tenth as important as ozone. The primary gases tending to heat this region by absorption of solar radiation are ozone and molecular oxygen. The values depend on latitude and season, but for 30 deg N summertime, approximately three times as much energy is absorbed in the mesosphere as in the region from about 80 to 105 km. Contributions from atomic oxygen emission in the  $62\mu$  line are also shown, but these are negligible in comparison to the gases previously discussed.

Included in Figure 1 are also the important non-radiative contributors to the heat budget. Eddy transport downward is rather uncertain, with Johnson and Wilkins (1965) finding a cooling of about 30 units from 105 to 80 km and about 150 units from 80 to 50 km. Webb (1970), on the other hand, has indicated that the cooling in the lower thermosphere could be as large as the radiative heating, and that eddy transport in the mesosphere could conceivably produce a heating comparable to heating from solar radiation. Of primary concern is our lack of knowledge of the eddy diffusion coefficient (if one accepts the validity of the mathematical formulation!) and this represents a major problem to heat budget studies in this region of the atmosphere. Dissipative heating values are also rather uncertain. Tidal effects (Lindzen, 1966) contribute less than 10 units, and Charney and Drazin (1961) indicate that synoptic effects should also be small. Dissipation of gravity waves may contribute significantly to the heating; according to Hines (1965) heating of 30 units may occur in the mesopause - lower thermosphere region, increasing to possibly a few hundred in the mesosphere. Downward transport of atomic oxygen (Craig and Gille, 1970) probably produces a heating of about 3 units in the vicinity of the mesopause. Hydroxyl emission (Wallace,

1962) is also rather small (Listed as a non-radiative component since the source of this energy is not from the radiation field but from the internal energy of the ozone-water vapor collision. ), Thus although the non-radiative effects are relatively uncertain, nevertheless the radiative contributions are large enough so that they are certainly important and probably of major importance in thermodynamic calculations of the mesosphere and lower thermosphere.

#### Gases of Importance to the Mesosphere-lower Thermosphere Radiation Problem

The importance of an atmospheric constituent to the radiation problem depends not only on the concentration of the gas but also on the ability of the gas to absorb and emit radiation in regions of the spectrum where the boundary fluxes are significant. In this section we briefly examine this problem.

Concentrations expressed in terms of mixing ratio (gm/gm) of the more important radiatively active gases are given in Figure 2.\* The distribution of carbon dioxide is the best known of these gases. Measurements by Glueckauf (1944) indicated a mixing ratio of  $3.8 \times 10^{-4}$  in the lower stratosphere, while Hagemann et al (1959) measured values from  $4.72$  to  $4.73 \times 10^{-4}$ . Recently Martell (1970) used a cryogenic sampler at White Sands and found values of  $4.87$  to  $4.9 \times 10^{-4}$  in the altitude range of 43.6 to 62.3 km. It would thus appear that our knowledge of carbon dioxide concentrations is rather good at least up to mid-mesospheric elevations. Recently, Hays and Olivero (1970) studied the dissociation of carbon dioxide with the inclusion of vertical mixing. Their values fall generally in the dashed region shown. Radiation calculations to date have not included this possible variation of carbon dioxide concentration

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\*The units for concentration in the papers cited are generally ppm, or a volumetric mixing ratio. They have been converted in this review to mass mixing ratios.

with height, although S. R. Drayson at the University of Michigan is presently working on this problem. Observations and theoretical calculations of the ozone distribution are also shown. The dashed region represents the results of ozone measurements as summarized by Leovy (1967). Concentrations above 35 km represent results of measurements of the attenuation of ultraviolet radiation from rockets and satellites. Leovy attributes approximately one-half of this variation to uncertainties in measurement or interpretation of results. For comparison we have included theoretical calculations of the ozone distribution for a "wet atmosphere" by London (1968). The variation shown is due to latitudinal and seasonal changes in concentration. The largest values correspond to 30 deg and 60 deg summer below and above 70 km respectively. Minimum values correspond to 60 deg winter above about 45 km; below this elevation they correspond to 90 deg summer. One can observe the disparity in theoretical and observational results, and it is this uncertainty which is the major source of error in radiative transfer calculations in the upper stratosphere and mesosphere.

Water vapor is another constituent whose concentration is rather uncertain. Results of earlier studies (Gutnick, 1962) were not in general agreement for the mid-stratosphere. Japanese results showed a much higher concentration (mixing ratio  $3 \times 10^{-4}$ ) than those of the British group ( $4 \times 10^{-5}$ ). Houghton (1963), from measurements of solar radiation in the  $6.3 \mu$  region, found a value of  $1.5 \times 10^{-6}$  in the lower stratosphere, increasing to  $5 \times 10^{-5}$  in the upper stratosphere. Williamson and Houghton (1965) measured the downward planetary radiation in the  $6.3 \mu$  band, and they found a value of  $3 \times 10^{-6}$  for the lower stratosphere. Scholz, et al (1970) recently published results from

his cryogenic sampling method and he finds in the vicinity of the stratopause values of  $1.9$  to  $6 \times 10^{-6}$ . Very little is known about latitudinal (Mastenbrook, (1968) and possibly temporal variations. Thus it would appear the mesosphere-upper stratosphere values are uncertain by approximately one order of magnitude. Even with the relatively large uncertainties in the stratospheric concentrations of water vapor, the contributions to the radiative problem are probably quite small (Drayson and Kuhn, 1968), being on the order of a one degree per day cooling.

For the height range indicated, molecular oxygen can be considered as uniformly mixed so that the mixing ratio is about 0.23 and is not shown in this diagram.

The strengths and locations of the more important spectroscopic transitions of the above mentioned gases are given in Figure 3. The numerical area of the shaded regions is equal to the strength of the band and is expressed in  $\text{cm}^2/\text{gm}$ . The solid line curves to the right and left in the diagram indicate the boundary fluxes incident on the atmosphere for temperatures of 250K (planetary) and 6000K (solar) respectively. For wave numbers less than about  $2000 \text{ cm}^{-1}$  ( $5 \mu$ ), molecular transitions are influenced primarily by the planetary radiation field which can either heat or cool the atmosphere, i. e. the  $9.6 \mu$  ozone band, the  $15 \mu$  carbon dioxide band, and the  $80 \mu$  water vapor band. At wavenumbers greater than  $2000 \text{ cm}^{-1}$ , molecular transitions are influenced primarily by solar radiation which can only heat the atmosphere. Major atmospheric bands for molecular oxygen are the Schumann-Runge bands from  $51300$  to  $57100 \text{ cm}^{-1}$  ( $1950$ - $1705 \text{ \AA}$ ), which merge into a dissociation continuum extending to  $76900 \text{ cm}^{-1}$ . The Herzberg bands extend from about  $38400$  to  $41400 \text{ cm}^{-1}$  ( $2600$ - $24200 \text{ \AA}$ ) merging into the weak dissociative continuum.

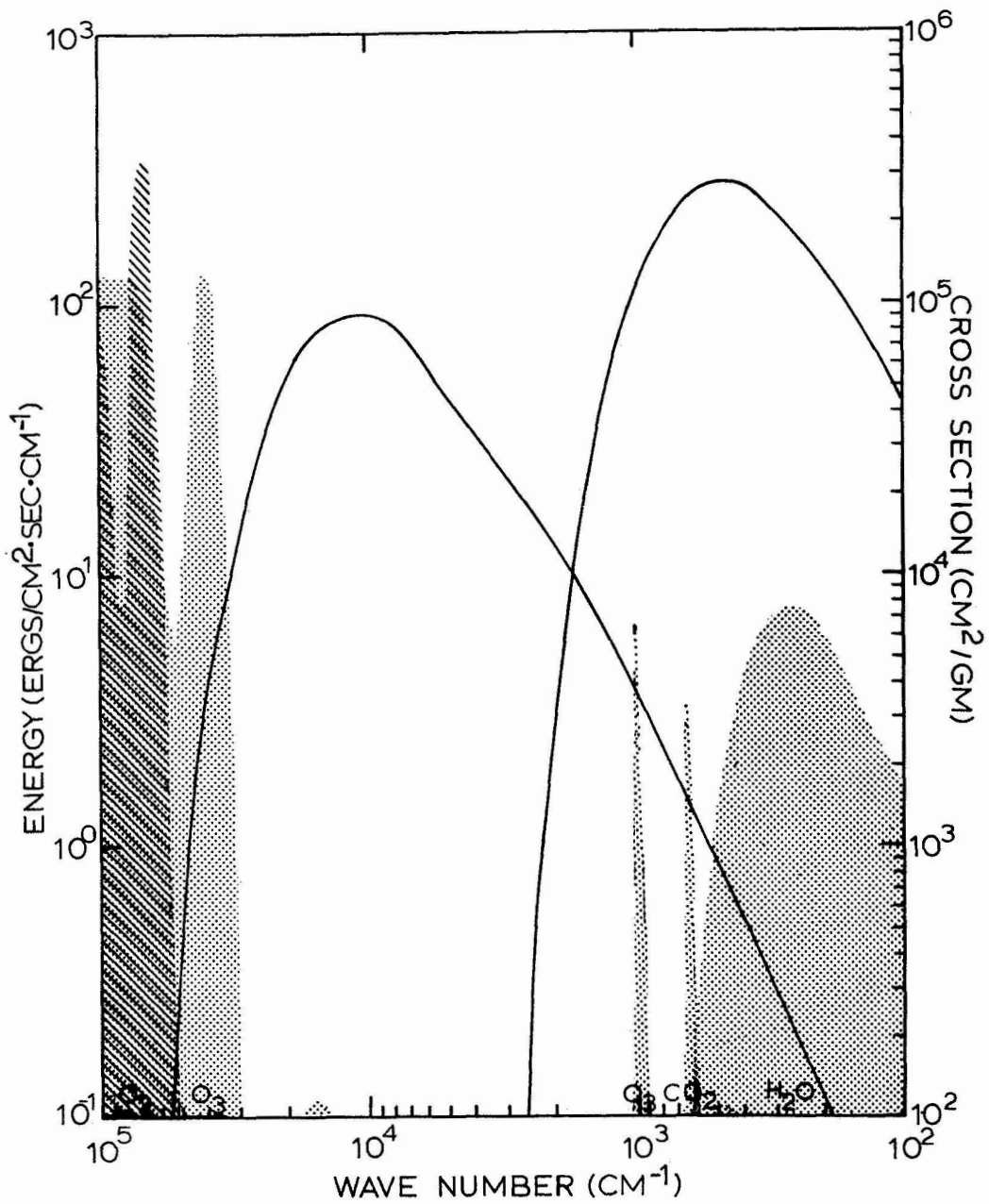


Figure 3. Absorption cross sections for CO<sub>2</sub>, O<sub>3</sub>, and H<sub>2</sub>O (shaded regions), and boundary fluxes for planetary (250K) and solar (6000K) radiation (solid curves to the left and right respectively)

Ozone bands are: the Hartley bands centered at  $39200 \text{ cm}^{-1}$ ; the rather weak Huggins bands from  $32200$  to  $29400 \text{ cm}^{-1}$  ( $3100\text{-}3400 \text{ \AA}$ ) and the Chappius bands between  $22200$  and  $13500 \text{ cm}^{-1}$  ( $4500\text{-}7400 \text{ \AA}$ ).

### Theoretical Formulation of the Radiative Transfer Problem

The theoretical treatment of the radiative transfer problem is decidedly different in the mesosphere than in the thermosphere. Throughout the mesosphere, for those gases thought to be of major importance to a radiative study, the atmospheric density is still large enough so that collisional transitions determine the population densities of the energy states of the molecules. When this distribution of densities prevails (Boltzmann distribution), one can use a local thermodynamic equilibrium formulation (LTE) for the transfer equation, and represent the source function as a Planck function. For this case the solution to the transfer equation can easily be determined, the major problems being of a numerical nature such as accurately representing the transmission function (see, e. g., Goody, 1964). A summary of this formulation is shown in Figure 4.

In the vicinity of the mesopause, the collisional rates become comparable to the radiative rates, which then influence the population densities of the energy levels. The source function is dependent on the radiation field and an additional equation must be introduced which expresses the population densities in terms of the radiation fields. This additional equation is the statistical equilibrium equation, for which one assumes the total collisional and radiative rates into a particular energy level equals the total rate of transition from that level. The population densities appearing in the source function are expressed from the statistical equilibrium equation in terms of the radiation fields. One can then substitute for the radiation field from

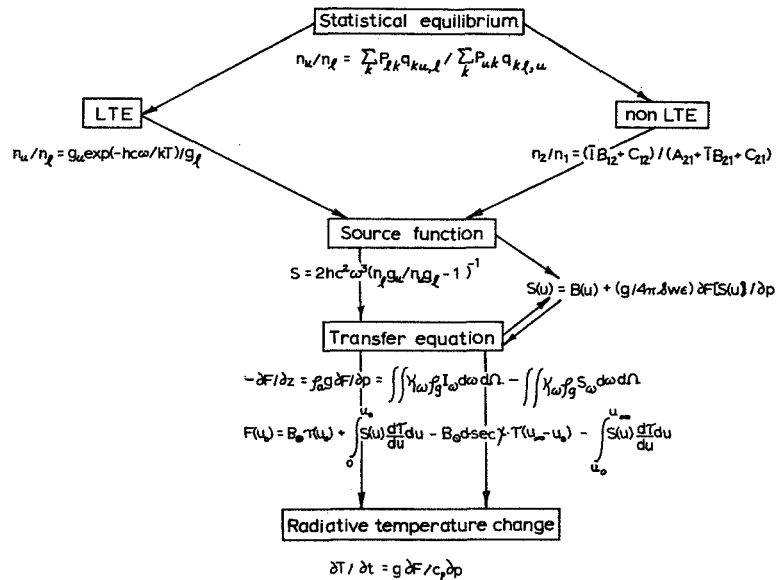


Figure 4. Summary of theoretical formulation of radiative transfer problem

Statistical equilibrium (Jefferies, 1960):

$n_u, n_l$  = number of molecules in upper and lower energy states respectively.

$P_{lk}$  = rate of transition (collisional plus radiative) from energy state  $l$  to state  $k$ .

$q_{kl, u}$  = probability for all transitions from state  $k$  to  $l$  but excluding  $u$ .

LTE (Goody, 1964):

$g_u, g_l$  = statistical weights of the upper and lower energy states respectively.

$h, c, k, T, \omega$  = Planck's constant, speed of light, Boltzmann's constant, temperature, and wave number

Non LTE (Kuhn and London, 1969):

$\bar{I}$  = specific intensity averaged over a wave number interval

$B_{ul}, A_{ul}, B_{lu}$  = Einstein coefficients for stimulated emission, spontaneous emission, and absorption.

$C_{ul}$  = collision transition rate from state  $u$  to  $l$ .



Source function (Kuhn and London, 1969):

- S = source function
- B = Planck function
- g = acceleration due to gravity
- $\mathcal{I}$  = band strength
- w = mass mixing ratio
- $\epsilon$  = ratio of collisional to radiative rate for the u- $\ell$  transition
- F = flux of radiation
- p = pressure

Transfer equation (Goody, 1964):

- $\delta F / \delta z$  = flux divergence
- $\rho_a, \rho_g$  = density of air and absorbing gas respectively
- $\kappa_\omega$  = absorption coefficient
- $\Omega$  = solid angle
- u = mass path of the absorbing gas
- $\oplus, \odot$  = designation for earth and sun respectively
- $\tau$  = transmission function
- d = dilution factor for solar radiation
- $\chi$  = solar zenith angle
- $\infty-o$  = top of the atmosphere and a reference level respectively

Radiative temperature change (Goody, 1964):

- t = time
- $c_p$  = specific heat of air at constant pressure

the transfer equation which gives an expression for the local source function in terms of the source functions throughout the atmosphere. If one assumes the atmosphere to be divided into layers, the source functions being constant in each, one then has a closed set of simultaneous linear equations in terms of the source functions. The source functions, in turn, yield the heating or cooling rates from the equation of transfer. Details of this method can be found in the paper by Kuhn and London (1969), and an analytical summary is given in Figure 4.

An example of the variation of the source function (S) and Planck function (B) with height or mass path for the  $\nu_2$  band ( $15\mu$ ) of carbon dioxide is shown in Figure 5.  $\lambda$  refers to the collisional relaxation time (reciprocal of the collisional rate) and the chosen values represent probable extremes of our uncertainty in this parameter. Note that for this band the LTE formulation is adequate throughout the mesosphere, i. e.,  $S \approx B$ . Above this region however, the Planck function deviates from the source function so that in the thermosphere most of the radiative energy is not converted to thermal energy. Note that in the lower thermosphere ( $\sim 95$  km) the source function has a slight maximum which, analogously to a peak in the Planck function (or temperature maximum) should give a maximum or peak in the cooling rate. This is indeed the case as will be seen later.

As mentioned earlier, when one can consider a LTE formulation, the solution to the transfer equation is straightforward, the major difficulty, in most cases, being the calculation of the transmission function, defined as the fractional amount of energy transmitted through a known thickness of gas (excluding emission of the gas). This transmission function  $\tau_\omega$  at wavenumber  $\omega$  can be given as,

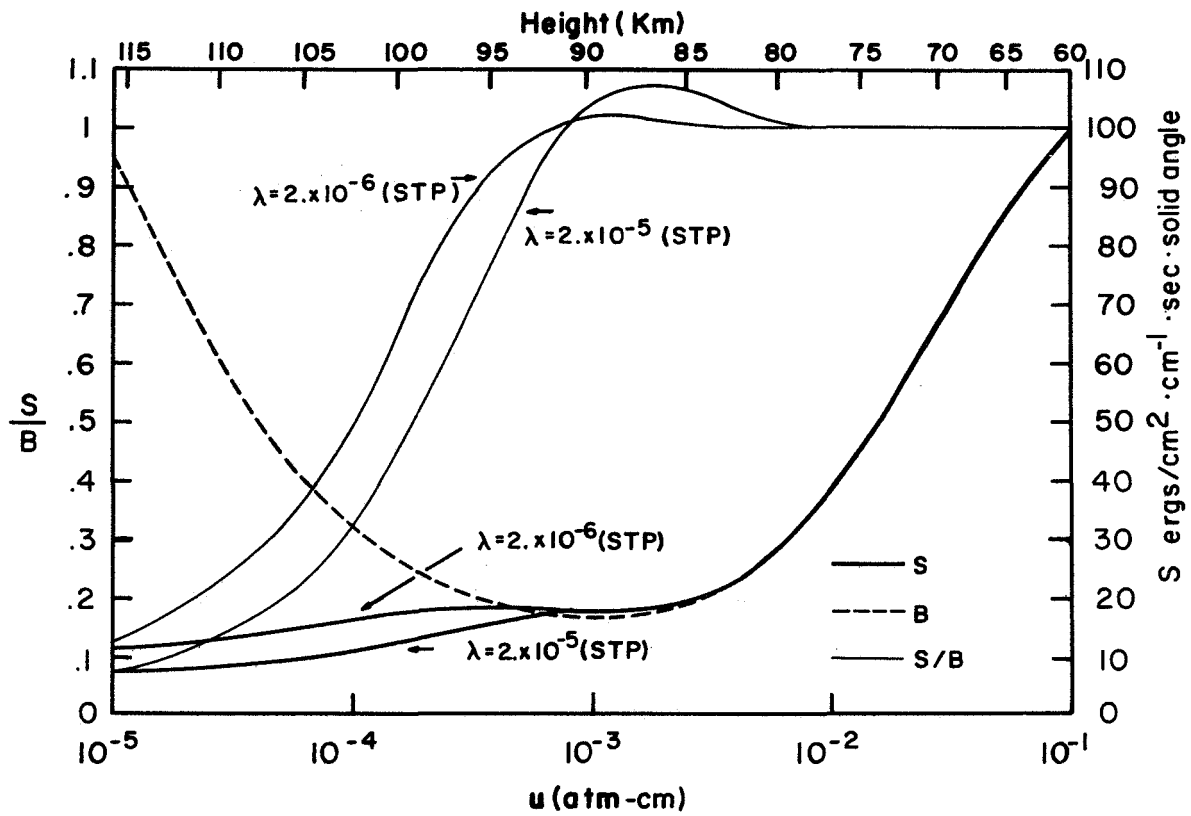


Figure 5. Variation of the source function (S) and Planck function (B) for the  $15\mu$  band of  $\text{CO}_2$  in the mesosphere and lower thermosphere.

$$\tau_{\omega} = \exp \left( - \int \kappa_{\omega} \sec \theta \, du \right)$$

where  $\kappa_{\omega}$  is the absorption coefficient,  $\theta$  the zenith angle, and  $u$  is the zenith mass path, or the amount of absorbing gas in a square centimeter column through which the radiation passes. The absorption coefficient for a particular transition can be represented as the product of a line strength, which represents the ability of the molecule to absorb and emit radiation, and a profile function giving the "distribution" of this line strength in the wave number domain. Although the line strength changes slowly with temperature for the strong lines which are most important for upper atmospheric radiative calculations, the profile function varies rapidly with wave number, and also with pressure and temperature. This profile function is determined by the collisions between the absorbing molecule and ambient molecules (Lorentz broadening), by Doppler shifts due to line of sight velocity components of the absorbing molecules (Doppler broadening), or by a combination of both broadening mechanisms (Voigt profile). Examples of these broadening mechanisms are shown in Figures 6 and 7. Note for conditions of temperature and pressure corresponding to elevations above 50 km the Doppler profile represents reasonably well the profile function. For a quantitative discussion of these profile functions, the reader is referred to Penner (1969).

The absorption coefficients for planetary radiation consist of vibrational-rotational ( $15\mu$   $\text{CO}_2$ ,  $9.6\mu$   $\text{O}_3$ ) and pure rotational ( $80\mu$   $\text{H}_2\text{O}$ ) transitions in the infra-red region of the spectrum, and the transmission function is determined for these bands. Because of the large number of transitions involved in each band and the strong dependence of the absorption coefficient on wave

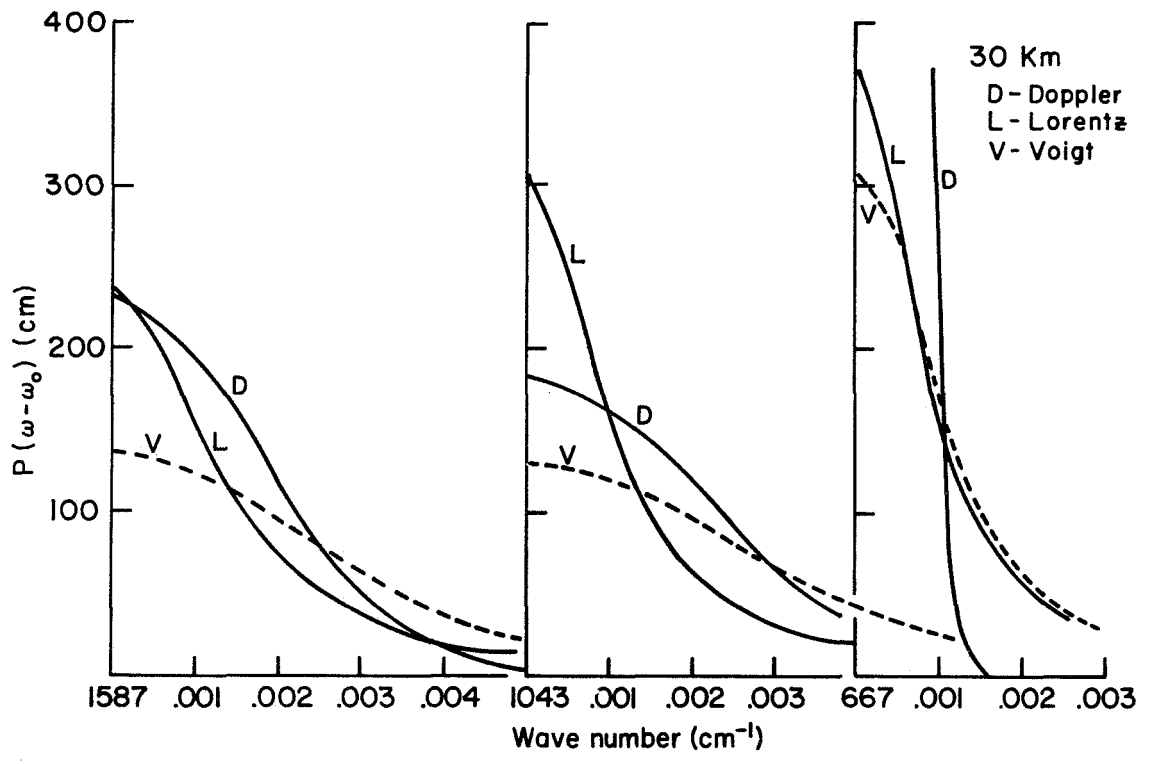


Figure 6. Profile functions for Lorentz, Doppler, and Voigt broadening corresponding to conditions at the 30 km. height.

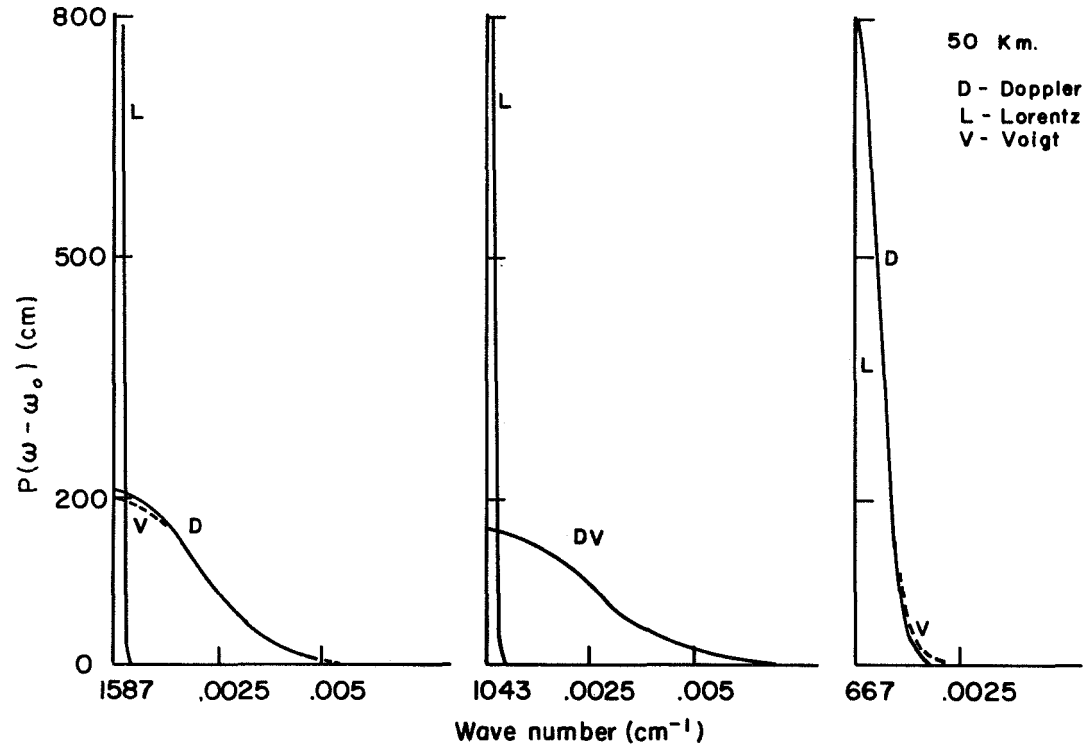


Figure 7. Profile functions for Lorentz, Doppler, and Voigt broadening corresponding to conditions at the 50 km. level.

number, detailed calculations of these transmission functions for use in the transfer equation would require an evaluation of the absorption coefficient for many wave numbers in the spectrum. These calculations are very time consuming, and even for present day computers this is not practical for direct incorporation into heat budget calculations. Usually a transmission for an equivalent homogeneous part is determined for a spectral interval by assuming a band model for the transitions within that interval. Numerous band models have been used and most of these have been summarized by Goody (1964). For a discussion of the quasi-random model, see Wyatt, Stull, and Plass (1962).

Solar radiation is absorbed by electronic and vibrational-rotational transitions primarily in the visible and ultraviolet regions of the spectrum. The absorption spectra are very complex and rather than considering a band model for the transmission, such as is done for vibrational-rotational bands, one defines a cross section over a selected wave number interval which is taken to represent an averaged absorption coefficient. The cross section and absorption coefficient are related through the expression,  $\sigma_{\omega} = \kappa_{\omega} m$ , where  $\sigma_{\omega}$  is the cross section,  $\kappa_{\omega}$  is the absorption coefficient, and  $m$  is the mass of the molecule. The concept of the cross section is also used when one considers the more slowly varying dissociation continua. Cross sections for absorption of solar radiation by ozone and molecular oxygen are discussed by, e. g., Goody (1964).

### Primary Contributors to Radiative Heating and Cooling Rates

#### i. Carbon Dioxide ( $15\mu$ )

The major contributors to long wave heating and cooling rates are the  $15\mu$  bands of carbon dioxide. Results of a number of investigations are

shown in Figure 8. Major features of these calculations are a maximum cooling near the stratopause, a region of minimum cooling or slight heating near the mesopause, and a slight maximum of cooling again in the lower thermosphere. These results show reasonable agreement when one considers that the calculations were made with different formulations for the transmission - both theoretical and empirical - various vertical (height resolutions, and utilizing different forms of the transfer equation. Unfortunately, the temperature distributions were also somewhat different but one can approximately correct for this effect.

In the mid-stratosphere, the results of Kuhn and London (1969) are approximately 1 deg/day smaller than those of Plass (1956). Much of this difference is due to assumed temperature distributions in the mid-stratosphere. Plass' temperature is about 10 K higher than that of Kuhn and London (USSA, 1962). When the latter used Plass' temperature structure, indeed the cooling rates were increased by about 1 deg/day. The agreement between these results is quite exceptional when one considers that Plass used the experimental data of Cloud (1952) and extrapolated to appropriate mass depths and pressures. The band from  $12\mu$  to  $18\mu$  was also subdivided into  $1\mu$  intervals. Kuhn and London used a quasi-random band model with spectroscopic data from Stull et al (1963) and a spectral interval of  $570$  to  $780\text{ cm}^{-1}$  with averages taken over  $5\text{ cm}^{-1}$  intervals. Although one might argue that the agreement between these results is somewhat fortuitous, nevertheless I believe it does indicate that very precise values of the transmission function are not critical for reliable heat budget calculations at least in the stratosphere. The double maximum near the stratopause shown in Plass' calculations is due to discontinuities in his temperature gradient at 43 and 54 km. Plass estimates

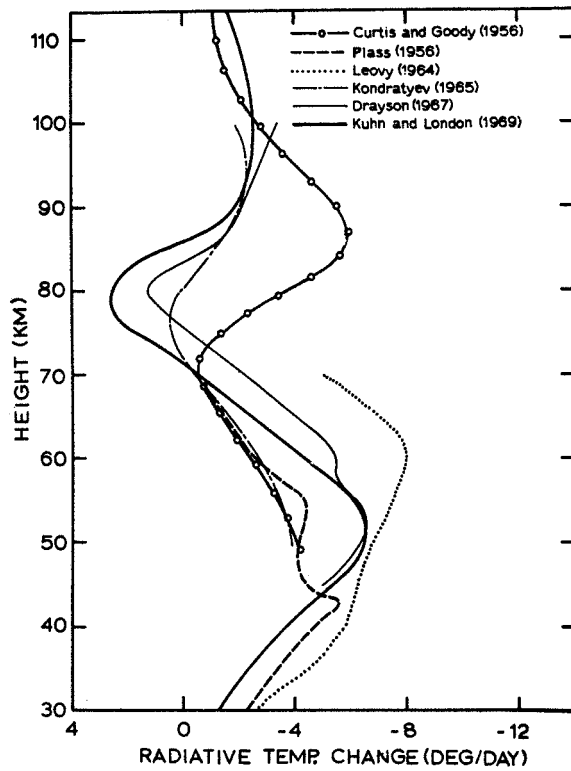


Figure 8. Comparisons of heating and cooling rates for the  $15\mu$  bands of carbon dioxide.

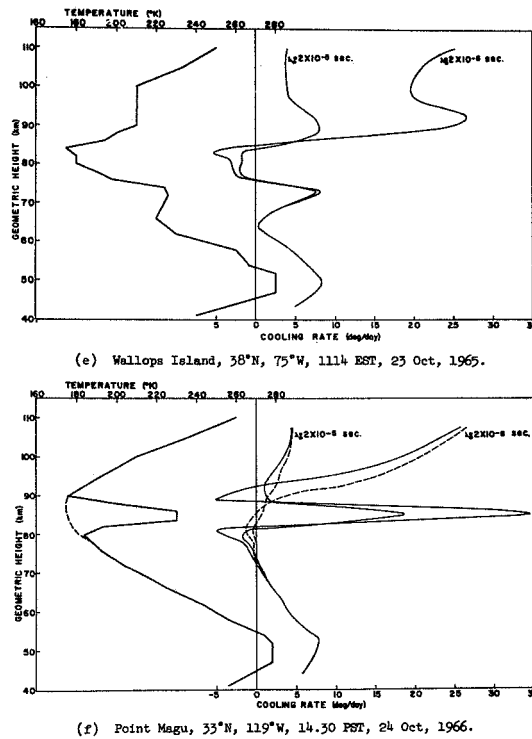


Figure 9. Influence of temperature perturbations on radiative temperature change (Drayson and Epstein, 1969)



the probable error in his calculations to be 30% at 50 km and rather uncertain above 60 km.

Calculations for the mesosphere and lower thermosphere are also in good agreement with the exception of those of Curtis and Goody (1956). Again a major discrepancy is due to the different temperature distributions. Curtis and Goody used the Rocket Panel profile which gives a lower, more broad mesopause with temperatures some 35 K higher than the USSA (1962) which was used by Kuhn and London, and Drayson (1967). Drayson determined transmission functions by integrating directly over the band; he also permitted the source function to vary linearly with pressure over a specified height range; thus a slab approximation was not necessary. The discrepancy of about 1 deg/day in the mesosphere between these calculations and those of Kuhn and London has not been resolved. Part of the discrepancy may be that Drayson considered not only the  $\nu_2$  fundamental but additional sub-bands, including isotopes in the 15  $\mu$  region, treating each as a separate "two level" problem. Both calculations are subject to some uncertainty since Kuhn and London did not exclude those transitions of the subbands in computing their transmission functions for the fundamental, while Drayson, in treating each sub-band as a separate "two level" problem has not demonstrated that the various transitions can be uncoupled from one another.

Details of the calculation by Kondratyev et al (1966) are not given; they exhibit heating and cooling rates for different temperature distributions, and the one reproduced in Figure 8 is for the CIRA (1961) atmosphere. In the region from 90 to 100 km, the CIRA (1961) and USSA (1962) temperature distributions differ by less than about 6K and results of Kondratyev et al, Kuhn and London, and Drayson are in good agreement.

In the mesosphere, the CIRA 1961 temperature is uniformly lower (~10-15K) and the mesopause less prominent than the USSA (1962). These features, especially the latter, explain the smaller heating which Kondratyev finds in this region.

As shown in Figure 5, the collisional and radiative rates are comparable near the mesopause, and a non LTE formulation must be used above this elevation. The mesosphere and lower thermosphere calculations in Figure 8 were made with a surface collisional relaxation time of  $2 \times 10^{-5}$  sec, with the exception of Curtis and Goody who used a value of  $1.5 \times 10^{-5}$  sec. The actual value of the relaxation time is uncertain and depends primarily on pressure, temperature, and the colliding species. Houghton (1969) has calculated for a temperature of 210K and collisions of excited ( $\nu_2$ ) carbon dioxide molecules with nitrogen and oxygen, that the relaxation time is  $6 \times 10^{-6}$  sec. There is no experimental verification for this value and since heating and cooling rates in this part of the atmosphere depend strongly on the collisional relaxation time, there is a need for further work in this area. For a review of problems involved and experimental techniques used in determining these relaxation times, the reader is referred to Read (1965).

As is well known, the temperature in the region of the mesopause is oftentimes highly structured and the question arises as to whether one can average these temperature profiles, compute a net radiative temperature change and then expect this radiative temperature change to be representative of the average of the radiative temperature change as calculated from the structured profiles, i. e., can one consider the problem as being linear. An example of the type of heating and cooling rates one gets from a structured

atmosphere is shown in Figure 9. Drayson and Epstein (1969) investigated this problem and found that for temperature perturbations not exceeding 20K, use of an average temperature profile gives results within 0.2 deg/day.

ii Ozone and Molecular Oxygen (ultraviolet bands,  $9.6\mu$ )

Major contributors to the radiative temperature change in the mesosphere and lower thermosphere are ozone and molecular oxygen, which absorb large amounts of solar ultraviolet radiation. As is shown below, uncertainties in the ozone distribution are responsible for much of the uncertainty in net radiative heating and cooling rates in this section of the atmosphere.

Ozone also absorbs and emits terrestrial radiation primarily in the  $9.6\mu$  region, which produces a cooling of at most 4 deg/day near the stratopause and lesser amounts at higher and lower elevations. Uncertainty in this cooling rate is probably less than about 1 deg/day (see Figure 10). Calculations by Plass (1956) were made from absorption data of Summerfield (1941) while those of Kuhn and London (1969) from theoretical transmissivities based on corrected line strengths and positions from Kaplan, Migeotte, and Neven (1956). Plass' temperature distribution had a somewhat broader and slightly lower stratopause than Kuhn and London (USSA, 1962) but the former used a slightly larger ozone concentration in the upper stratosphere and a somewhat smaller concentration in the mesosphere. These two effects will drive the cooling rate in opposite directions so that a reasonable comparison between the two calculations can be made and is seen to be quite good. The two peaks in Plass' profile are due to the temperature gradient discontinuities at 38 and 55 km; he estimates the uncertainty in his cooling rate to be less than 30% at 50 km with larger uncertainties above this elevation.

The important contribution to the heating rate made by ozone and oxygen (assuming local deposition of the absorbed solar radiation) is also shown in Figure 10. The maximum near the stratopause is produced by ozone while in the lower thermosphere the major contributor is molecular oxygen. The secondary maximum at 70 km in the calculation by Kuhn (1969) is formed from the secondary maximum in the assumed ozone distribution.

Comparison of calculations for ozone and oxygen heating from Murgatroyd and Goody (1958) and Kuhn (1969) give an estimate of uncertainties in the heating rate produced by variations in ozone concentrations. Although some of the discrepancy is due to the different absorption coefficients used (Murgatroyd and Goody used the Ny and Choong (1933) coefficients while Kuhn used those of Vigroux (1953)), much of the difference is due to the different assumed distributions for ozone. Kuhn used the theoretical ozone values of London (1968) which at about 40 km are twice as large as those used by Murgatroyd and Goody (ozone distributions from calculations of Bates and Witherspoon (1952)) and in the mesosphere they are about four times larger. This produces a heating rate nearly twice as large in the upper stratosphere and five times as large in the mesosphere as the rates given by Murgatroyd and Goody. Since, as noted previously, the mesospheric ozone distribution is very uncertain, upper stratospheric and mesospheric heating rates will remain very much in doubt until more definitive concentrations are available.

### iii Water Vapor ( $6.3\mu$ , $80\mu$ )

The contribution of water vapor to radiative cooling in the stratosphere and mesosphere has the same uncertainty associated with it as does that of ozone. As discussed previously, only one preliminary measurement of

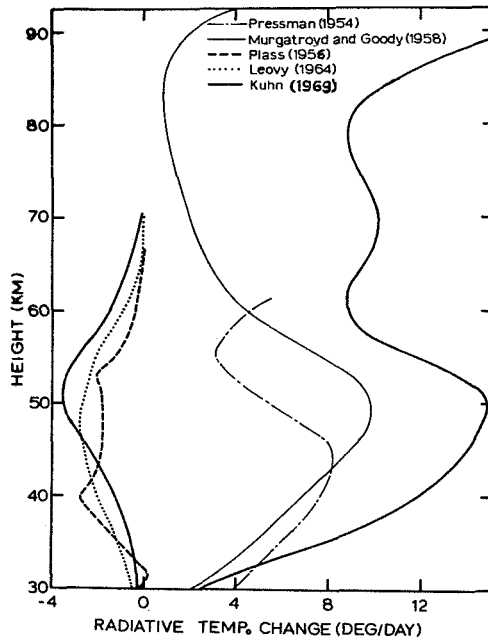


Figure 10. Comparisons of heating and cooling rates for ozone and molecular oxygen. Planetary and solar contributions are given in the left and right of the diagram respectively.

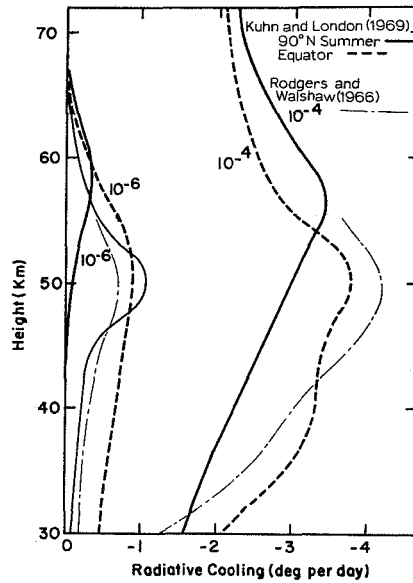


Figure 11. Comparisons of cooling rates for water vapor. Calculations by Kuhn and London refer to the  $80 \mu$  band, with the exception of the unlabeled solid curve which corresponds to the  $6.3 \mu$  band (mixing ratio of  $10^{-4}$ ). Rodgers and Walshaw's calculations include both the  $80 \mu$  and  $6.3 \mu$  bands.

water vapor at altitudes of 50 km or above has been made (Scholz, et al.1970) and the distribution with height is virtually unknown. Extreme mixing ratios are taken as  $10^{-6}$  and  $10^{-4}$  with the actual values thought to lie within these limits, probably nearer to  $10^{-6}$ . In Figure 11 are shown the cooling rates (Kuhn and London, 1969) for equatorial and polar temperature distributions for the extreme mixing ratios. If the mixing ratio is constant with height with a value of  $10^{-6}$ , the water vapor contribution to radiative cooling is less than about 10% of the total stratosphere-lower mesosphere cooling rate. The rather unlikely mixing ratio of  $10^{-4}$  produces a cooling, however, which approaches 40% of the net cooling. One should keep in mind that the variation of mixing ratio with height can be as important as the total amount of vapor present, and our knowledge of the water vapor distribution is too inadequate to take into account this possible effect. This problem has been discussed in the report of Drayson and Kuhn (1969) for the lower stratosphere. A comparison of cooling rates for the  $80\mu$  band for the work of Kuhn and London (1969) and Rodgers and Walshaw (1966) can be made from Figure 11. Rodgers and Walshaw used the ARDC (1959) temperature distributions which have stratopause temperatures 10K (equatorial) and 20 K (polar) higher than those used by Kuhn and London. Transmissions in both cases were calculated from the line strengths and positions of Benedict and Kaplan (unpub) for a random band model. For the "dry case", Rodgers and Walshaw assumed a mixing ratio of  $2 \times 10^{-6}$  as opposed to a value of  $10^{-6}$  chosen by Kuhn and London. Results for the two sets of calculations are in qualitative agreement. A single calculation for the  $6.3\mu$  band (Kuhn and London 1969) indicates that it contributes to the cooling at most 25% of the  $80\mu$  band cooling near the stratopause.

### Latitudinal Distributions of Radiative Temperature Change (rtc)

The only apparent latitudinal distributions of rtc for carbon dioxide in the mesosphere and lower thermosphere are those from Murgatroyd and Goody (1958) and Kuhn and London (1969); these results are shown in Figures 12 and 13. Only a qualitative comparison is possible since Murgatroyd and Goody used a computing scheme described by Curtis (1956) which "... is only a preliminary attempt and has a number of sources of inaccuracy". The more important inaccuracies in this method are: the assumption that the lines do not overlap and thus an overestimation of the cooling from the Q branches, primarily below 50 km; the Voigt profile was only taken into account in an approximate way; the volume concentration of carbon dioxide was assumed to be  $2.4 \times 10^{-4}$ , which is only about 80% of the presently accepted value; and the calculations extended to only 90 km, which means their results are unreliable above about 80 km. There is a region of maximum cooling near the stratopause and heating in the mesopause region. Murgatroyd and Goody's values near the stratopause for the high latitudes are somewhat larger than those of Kuhn and London since they assumed a polar summer stratopause temperature of 290K while Kuhn and London used 270K. Also their high latitude winter stratopause temperature distribution is more peaked than that of Kuhn and London. A comparison of these temperature distributions can be made from Kuhn and London (1969) and Murgatroyd (1957). The relatively large cooling near the winter mesopause in Figure 12 is produced by the high temperature ( $\approx 240$ K). These calculations were made for a relaxation time of  $2 \times 10^{-5}$  sec. (STP) (Kuhn and London) and  $1.5 \times 10^{-5}$  sec (Murgatroyd and Goody). For a relaxation time of  $2 \times 10^{-6}$  sec, the cooling rate in the mesopause-lower thermosphere region increases by about a factor of four.

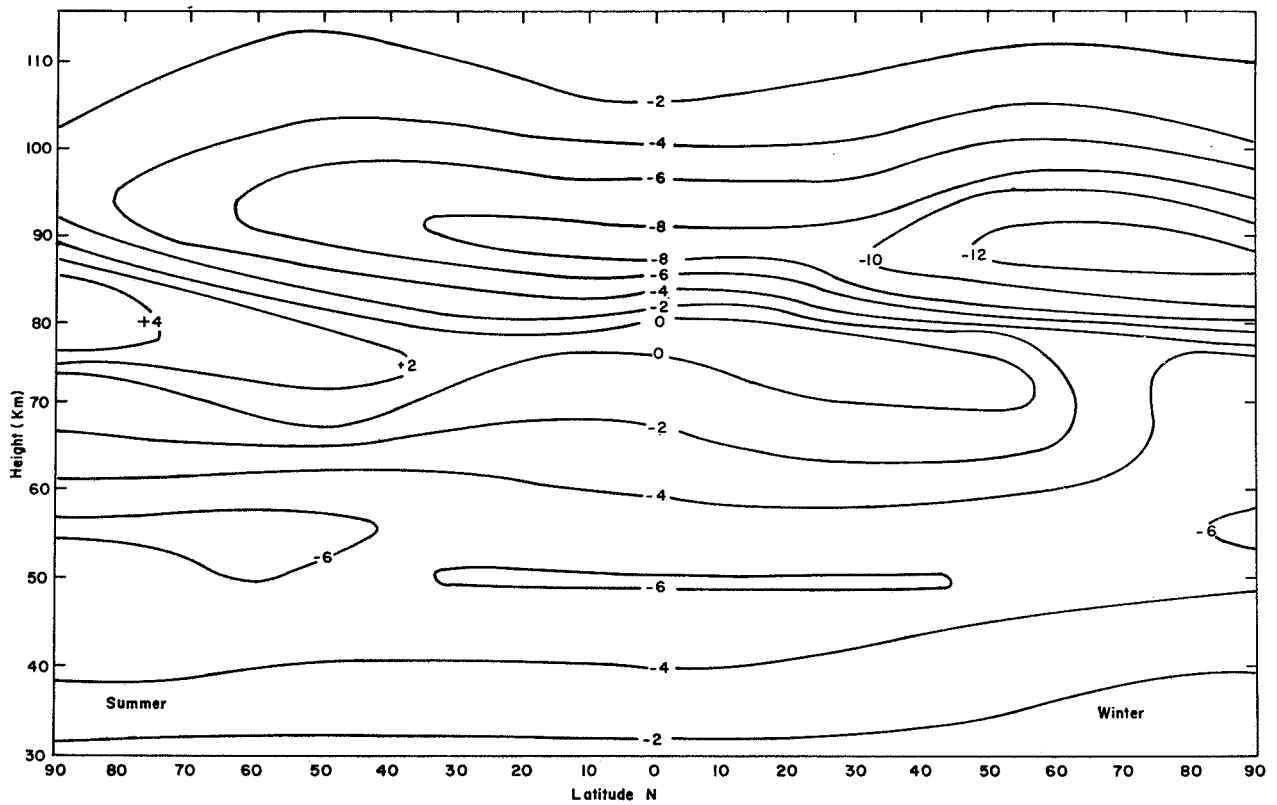


Figure 12. Latitudinal distribution of  $r_{tc}$  for summer and winter by carbon dioxide for a  $15 \mu$  ( $\nu_2$ ) relaxation time of  $2 \times 10^{-5}$  sec(STP) (Kuhn and London, 1969).

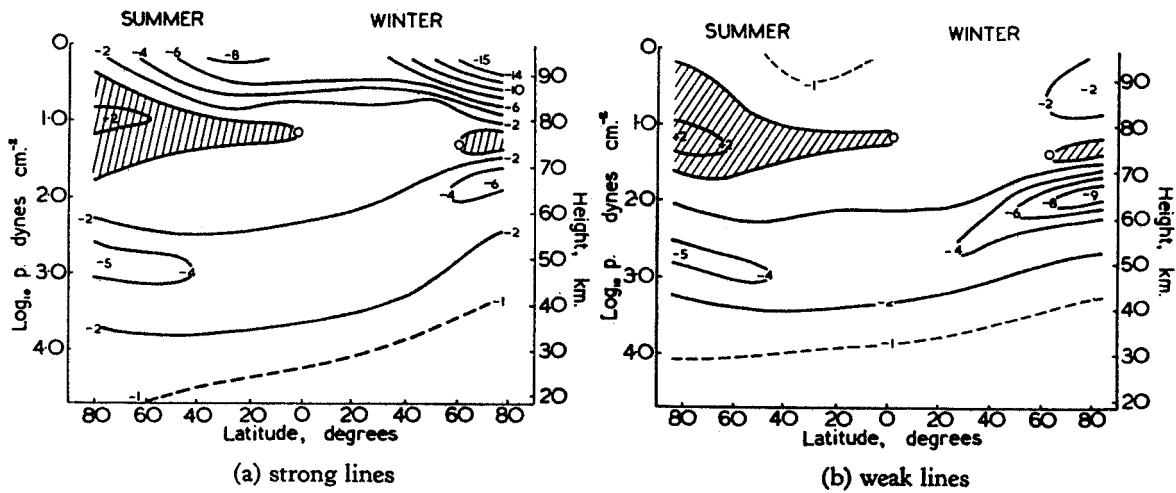


Figure 13. Temperature change caused by the  $15 \mu$  carbon dioxide band ( $^{\circ}\text{K day}^{-1}$ ). After Murgatroyd and Goody (1958).



Similar calculations for the rtc of ozone and oxygen are shown in Figures 14 through 17. The cooling rates for the  $9.6\mu$  band are quite similar (Figures 14, 15), although the methods of calculation were decidedly different. Murgatroyd and Goody (1958), using Plass' (1956) ozone and temperature distributions, assumed that the cooling rate could be expressed as a linear function of the Planck function for each height in the atmosphere, while Kuhn and London (1969) determined the cooling rate by solving numerically the radiative transfer equation. The largest discrepancy appears in the winter stratosphere, where the cooling rates of Kuhn and London are somewhat larger than those of Murgatroyd and Goody. This is probably due to the higher temperatures assumed by Kuhn and London in this region of the atmosphere. The close agreement between these two calculations which differ greatly in their degree of sophistication indicates that the rtc from the  $9.6\mu$  band in this portion of the atmosphere is very strongly locally controlled.

With the exception of the polar summer stratopause region, the ozone and oxygen heating rates of Kuhn (1969) (Figure 16) are larger than those of Murgatroyd and Goody (Figure 17), primarily because of the smaller ozone distributions used by the latter. Only in the lower stratosphere are the results in general agreement. The discrepancy is particularly apparent in the upper mesosphere where the calculations of Kuhn show a heating rate some five times larger than those of Murgatroyd and Goody.

The net rtc for the two calculations are shown in Figures 18 and 19 (Kuhn) and Figure 20 (Murgatroyd and Goody). Figures 18 and 19 apply to a relaxation time for the  $15\mu$  band of carbon dioxide of  $2 \times 10^{-5}$  and  $2 \times 10^{-6}$  sec respectively, while Murgatroyd and Goody assumed a value of  $1.5 \times 10^{-5}$  sec. Even qualitatively, the results are quite dissimilar; Murgatroyd

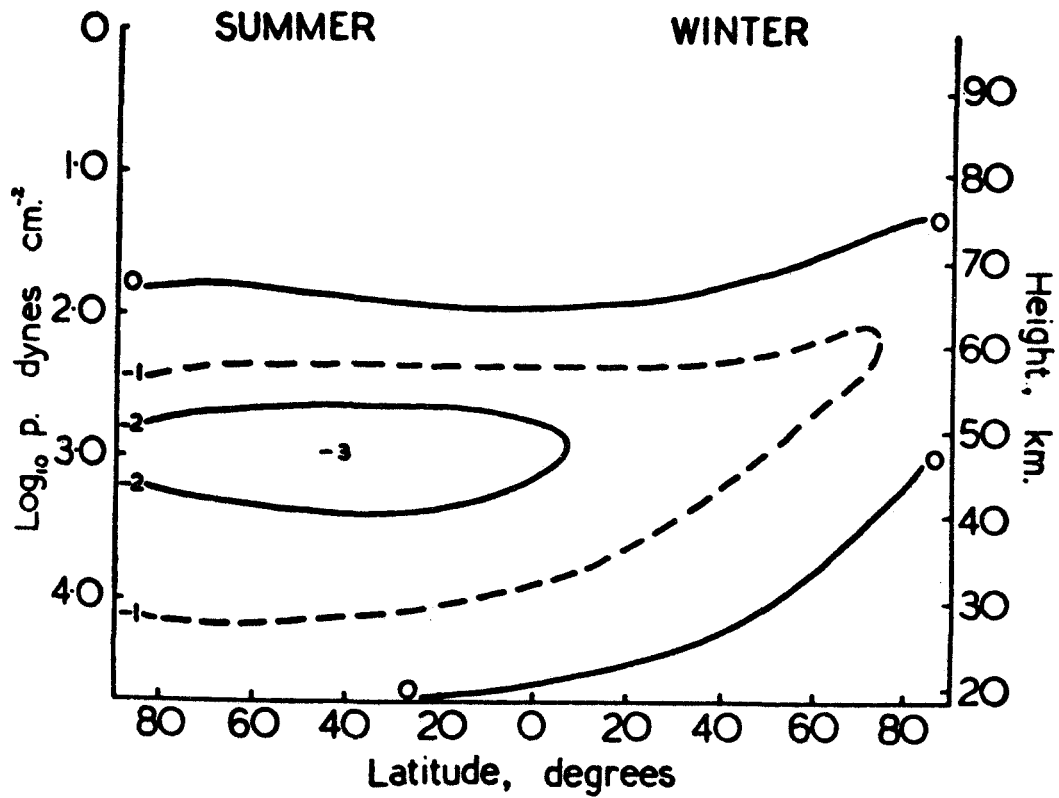


Figure 14. Temperature changes caused by the 9.6 μ ozone band ( $^{\circ}\text{K day}^{-1}$ ). From Murgatroyd and Goody (1958).

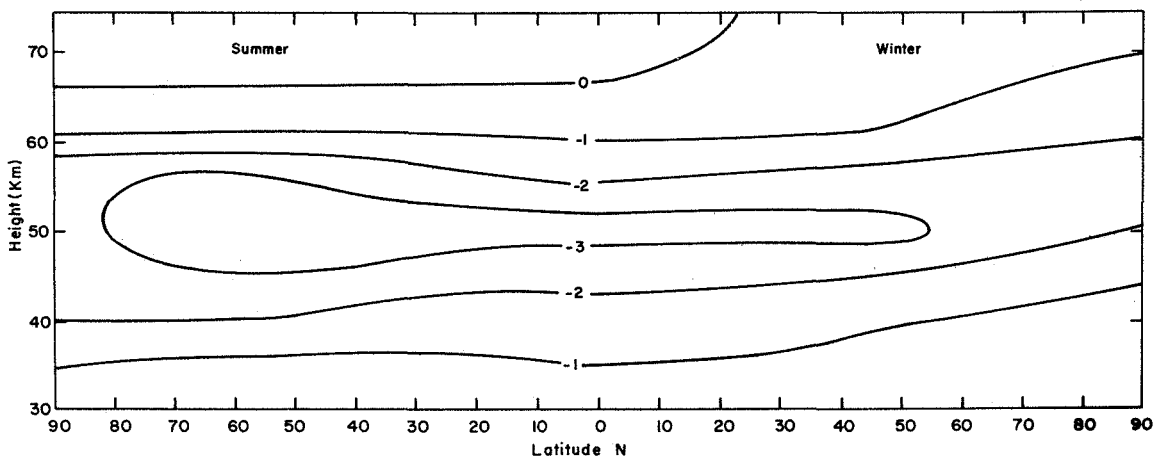


Figure 15. Latitudinal distribution of rtc for the 9.6 μ band of ozone (Kuhn and London, 1969).

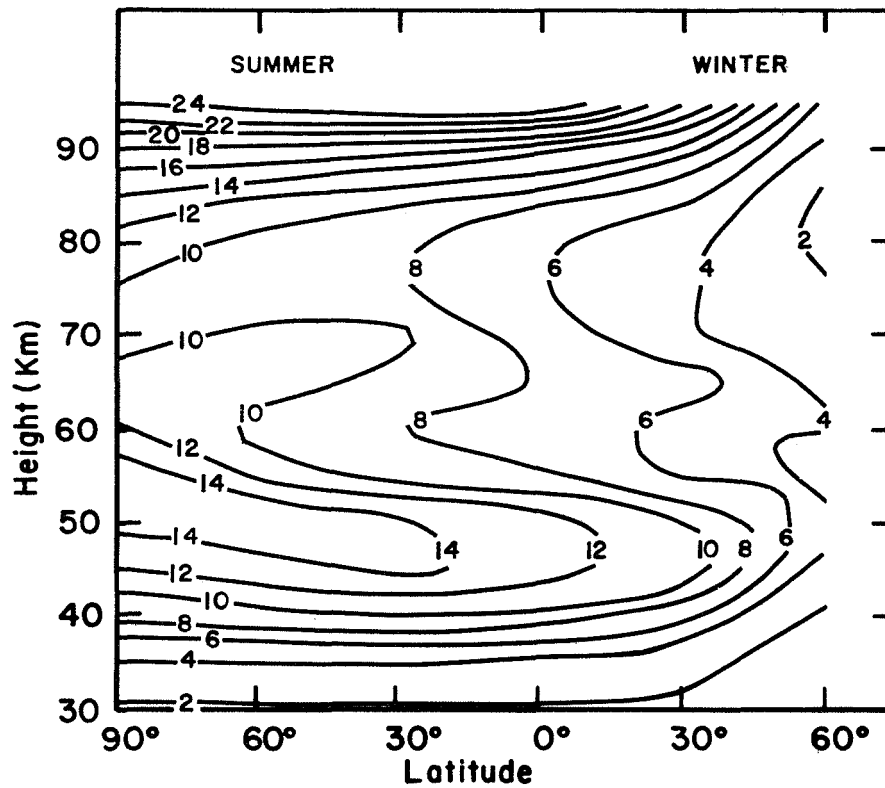


Figure 16. Latitudinal distribution of solar heating by ozone and molecular oxygen.

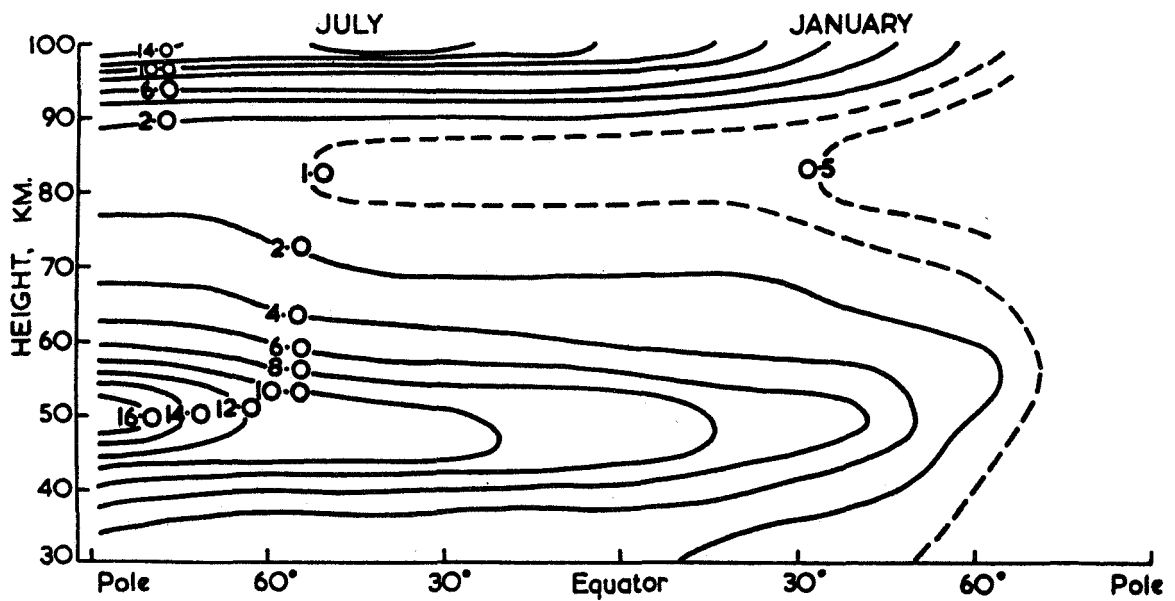


Figure 17. Latitudinal distribution of solar heating by ozone and molecular oxygen. From Murgatroyd and Goody (1958).

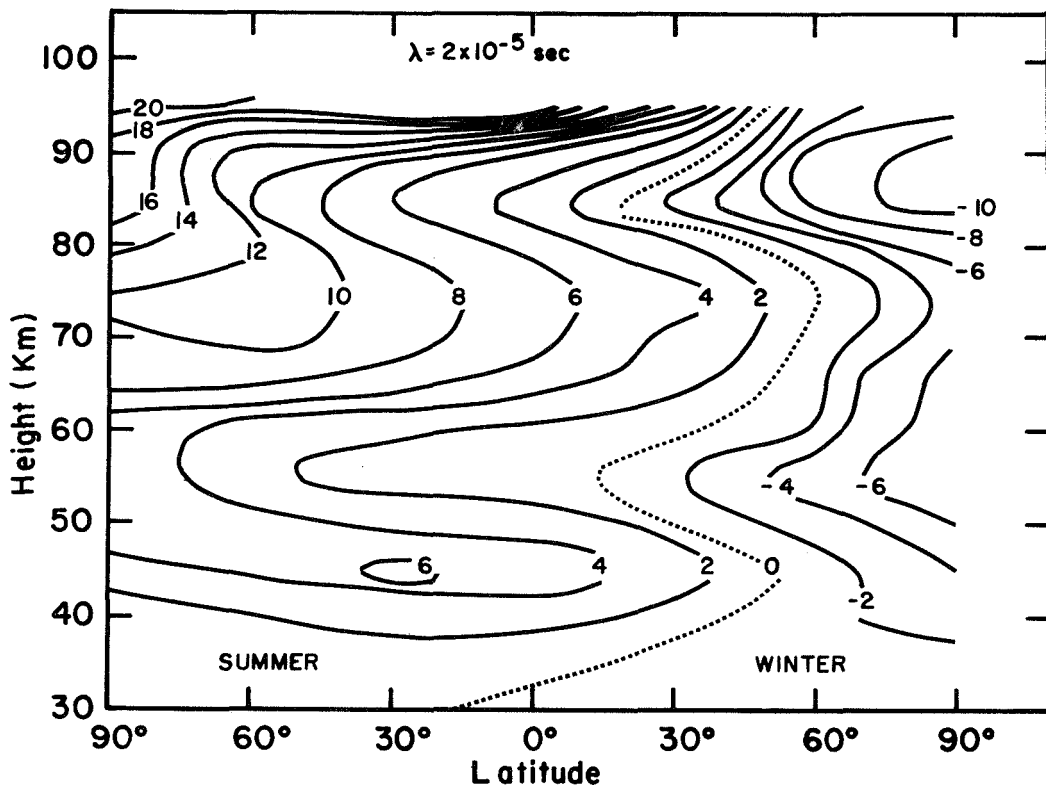


Figure 18. Latitudinal distribution of net rtc (CO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub>) for a CO<sub>2</sub> (ν<sub>2</sub>) relaxation time of 2 × 10<sup>-5</sup> sec (STP).

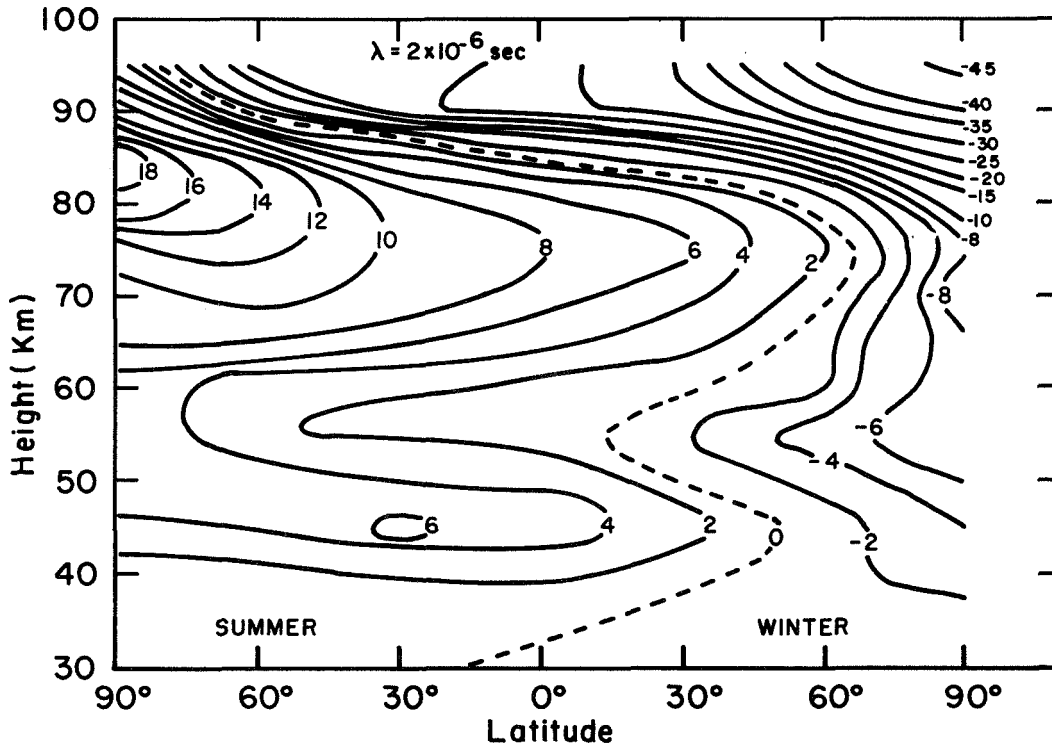


Figure 19. Latitudinal distribution of net rtc (CO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub>) for a CO<sub>2</sub> (ν<sub>2</sub>) relaxation time of 2 × 10<sup>-6</sup> sec (STP).

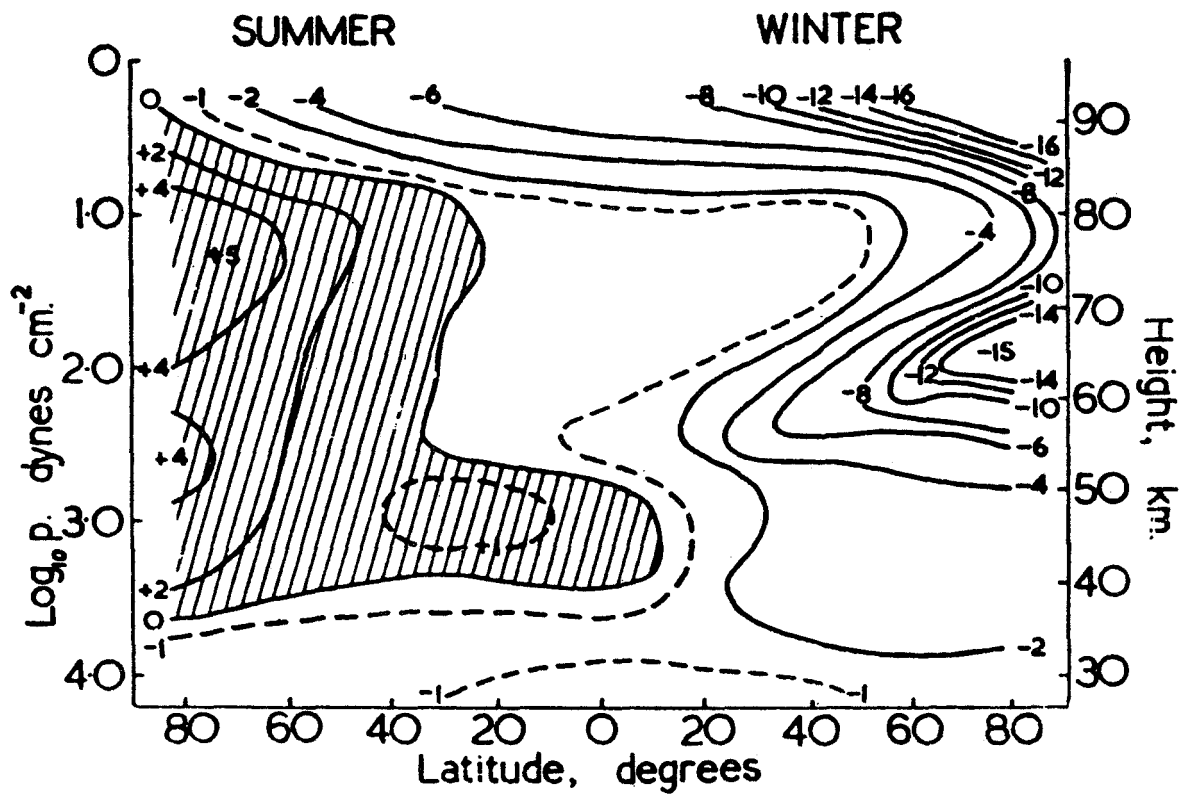


Figure 20. Latitudinal distribution of net rnc ( $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ) for a  $\text{CO}_2$  ( $\nu_2$ ) relaxation time of  $1.5 \times 10^{-5}$  sec. (STP). From Murgatroyd and Goody (1958).

and Goody find that a condition of near radiative equilibrium exists in the mid and low latitude stratosphere and mesosphere, while Kuhn and London find much larger heating and cooling rates. In the polar latitudes during the wintertime, the cooling rates of Murgatroyd and Goody are about a factor of two larger than those of Kuhn and London, while during the summertime, the low and mid-latitude stratospheric, and polar mesopause heating rates of Kuhn and London are about four times larger than those of Murgatroyd and Goody. The major cause of these discrepancies is the different ozone distributions used by the authors; until these distributions are better known, the radiational contribution to the heat budget in this part of the atmosphere will remain uncertain.

#### Contributions to the rtc from the minor atmospheric bands

Little effort has been devoted to a study of the minor bands which may contribute to the rtc in the upper stratosphere and mesosphere. Calculations by Houghton (1963) showing the absorption by solar radiation on a mid-summer day by the near infrared bands of  $H_2O$ ,  $CO_2$ ,  $O_2$ ,  $CH_4$ , and  $N_2O$  in the stratosphere are shown in Figure 21. These gases may contribute a heating up to about 0.4 deg/day, which is well within the range of our uncertainty of rtc in this region of the atmosphere, primarily because of the uncertainty in the ozone distribution.

The importance of the minor bands of carbon dioxide to rtc in the mesosphere has been investigated by Kaplan (1966), Kuhn (1968) and Houghton (1969). In Figure 22 is shown the heating rates from planetary and solar radiation for certain of these minor bands with the assumption that local thermodynamic equilibrium prevails. However, in the upper mesosphere,

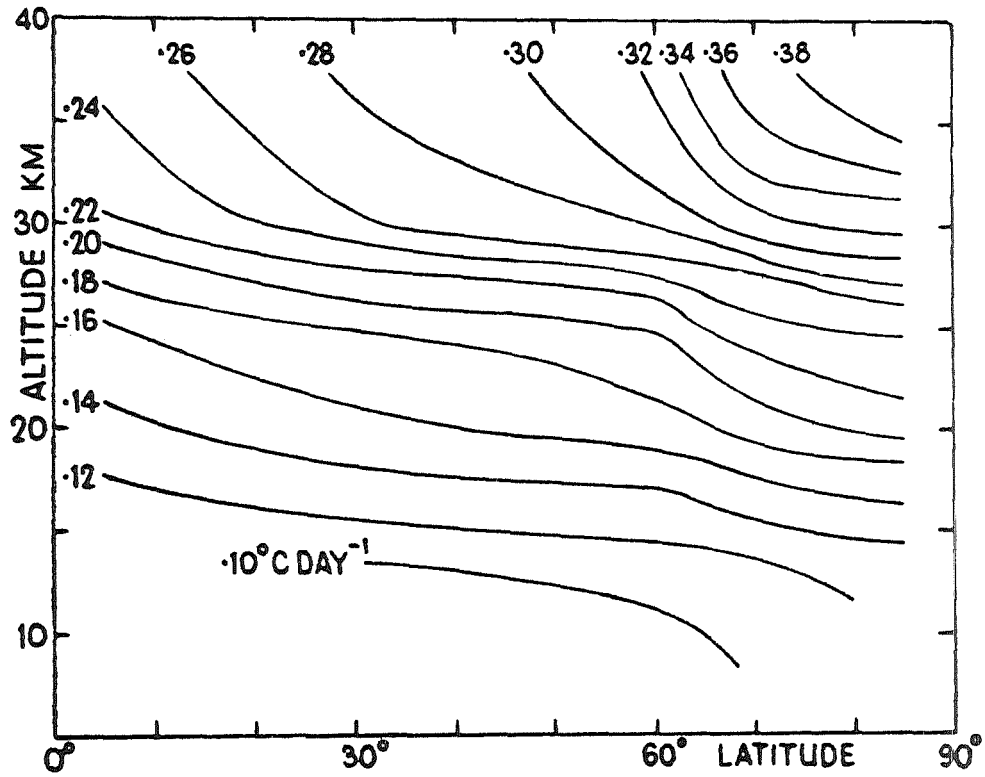


Figure 21. Heating rate in the stratosphere due to the absorption of solar radiation for a midsummer day. Gases considered are  $H_2O$ ,  $CO_2$ ,  $O_2$ ,  $CH_4$ , and  $N_2O$ . From Houghton (1963).

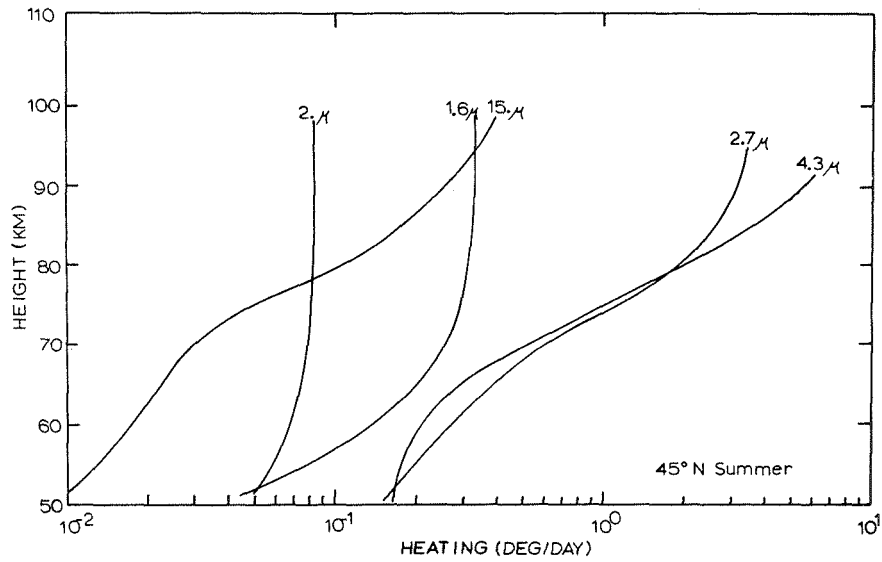


Figure 22. LTE calculations for the heating rates of the minor  $CO_2$  bands.

the Planck function does not approximate to the source function as is seen in Figure 23. Thus the results in Figure 22 are only valid up to a height of approximately 60 to 70 km, and the contributions from these minor bands are quite insignificant when compared with the  $15\mu$  band (see Figure 8). Non LTE calculations for the  $4.3\mu$  band are shown in Figure 24 (Kuhn, 1969). For these calculations, vibrational excitation to other molecular species through collisions was not considered, and for this case the  $\nu_3$  transition can be treated as a two level problem. Note that only in the mid-mesosphere does the rtc approach 1 deg/day, representing approximately 10% of the net rtc (see Figure 18). Houghton (1969) has considered vibrational transfer from the  $\nu_3$  transition to molecular nitrogen and oxygen, and his results are shown in Figure 25. Curves b, c, d, show the effects of water vapor on the rtc. Some of the energy from the excited vibrational state of oxygen is transferred through collision to the  $\nu_2$  state of the water molecule where a portion of this energy returns spontaneously to the radiation field. These calculations also include radiation from the  $\nu_2$  transition of carbon dioxide through collisional coupling with the excited oxygen molecule. Heating rates are on the order of 1 deg/day in the upper mesosphere which again show the relative unimportance of these minor bands.

The contribution to the rtc from the  $62\mu$  transition of atomic oxygen is also negligible throughout the mesosphere. This problem was first investigated by Bates (1951) who demonstrated that atomic oxygen in the  $^3P_2$  ground state can be collisionally excited to the  $^3P_1$  state, where the internal energy can be lost in the form of a spontaneous emission, leading to a cooling. Craig



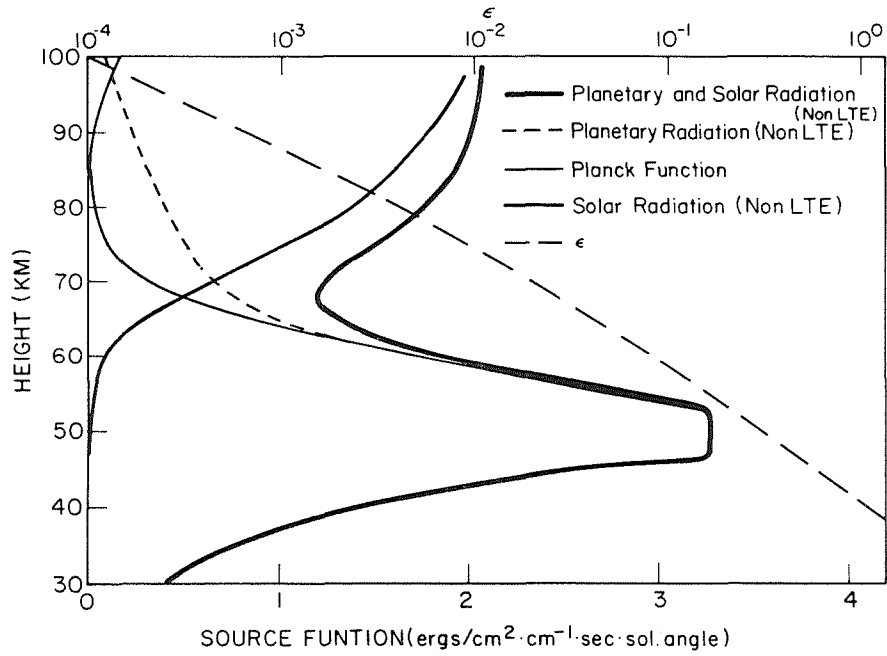


Figure 23. Variation of the source functions with height for the  $4.3 \mu$  transition of  $\text{CO}_2$ .  $\epsilon$  is the ratio of the collisional to the radiative rate (Kuhn, 1969).

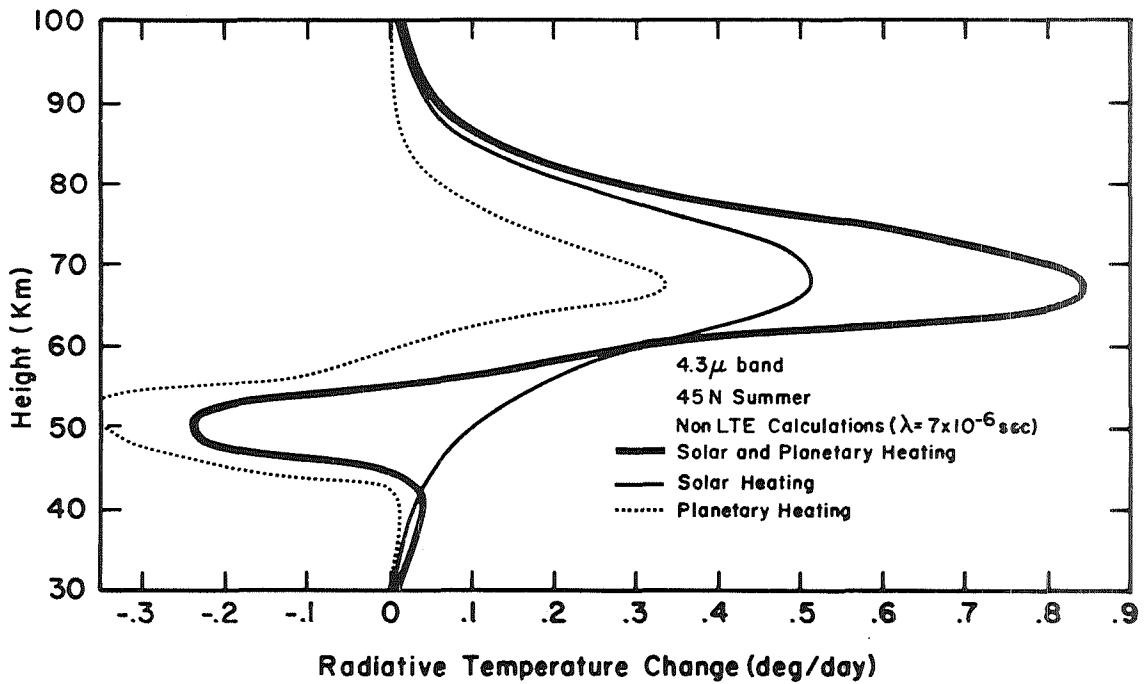
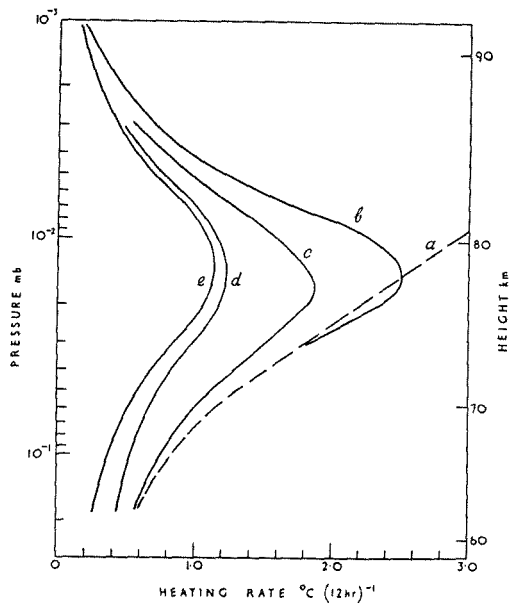


Figure 24. Radiative temperature change for the  $4.3 \mu$  band of  $\text{CO}_2$  From Kuhn (1969).



Heating rate due to absorption of solar radiation by  $\text{CO}_2$  in the  $\nu_3$  band at  $4.3\ \mu$  and the combination bands at  $2.7\ \mu$  with  $P_s = 9\ \text{mb}$  and  $\Delta p = 0.26 \times 10^{-3}\ \text{mb}$ . Curve (a) is on the assumption that all the energy absorbed goes directly into kinetic energy. Curve (b) is for a very dry atmosphere (water-vapour mass mixing ratio  $\tau < 10^{-6}$ ), (c) for  $\tau = 3 \times 10^{-6}$ , (d) for  $\tau > 10^{-4}$ , and (e) is on the assumption that none of the energy which goes into vibrationally excited oxygen goes into kinetic energy.

Figure 25. Heating rate due to absorption of solar radiation by  $\text{CO}_2$  in the  $\nu_3$  band at  $4.3\ \mu$  and the combination bands at  $2.7\ \mu$ . From Houghton (1969).

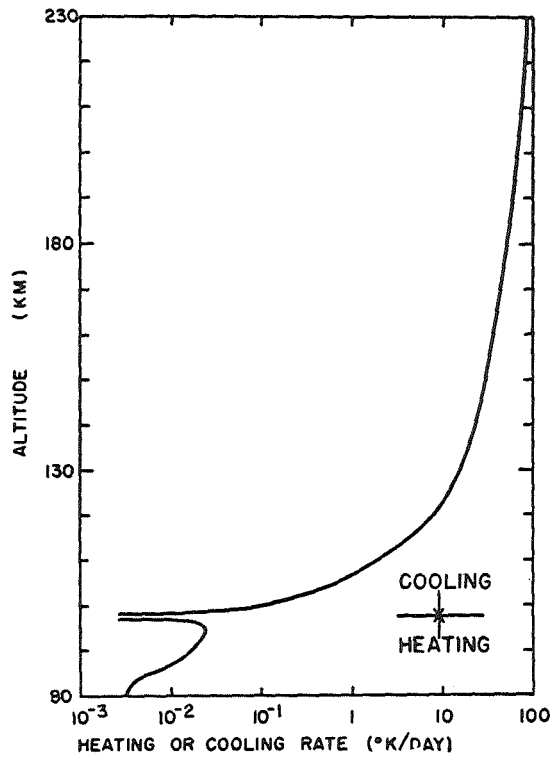


Figure 26. Rate of change of temperature due to transfer in the  $62\ \mu$  line plotted logarithmically as a function of altitude. From Craig and Gille (1969).

and Gille (1969) recently solved the transfer equation for this problem and found that in the mesosphere there is a slight heating (Figure 26) but only on the order of a few hundredths of a degree per day, which is certainly negligible in comparison to the other contributors.

### Conclusions

The basic theory for treating the radiative transfer problem in the mesosphere is generally well known, and the problems are primarily computational in nature as well as a lack of data, especially the ozone distribution; near the mesopause non LTE effects become important for the infrared transitions, but these transitions generally can be considered as two level problems for which the formulation is well known.

Comparisons for calculations of  $r_{tc}$  for the  $15\mu$  carbon dioxide band with band models and integration directly over the band show only minor differences and are therefore not of major concern in radiative calculations applicable to heat budget studies.

Mesospheric  $r_{tc}$  will remain very uncertain until better data on the temperature structure and especially on the ozone distribution are available. In addition, there is a need for better measurements for the collisional relaxation time for the  $15\mu$  band of carbon dioxide.

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