

THE TEMPERATURE DEPENDENCE OF OZONE RADIATIONAL HEATING RATES IN THE VICINITY OF THE MESOPEAK

By Richard A. Craig and George Ohring

Geophysics Research Directorate, Air Force Cambridge Research Center

(Manuscript received 18 July 1957)

ABSTRACT

Radiational heating of the mesosphere results principally from absorption of ultraviolet radiation by ozone. For conditions of photochemical equilibrium, the amount of ozone present near the mesopeak depends critically on the temperature. Relatively high temperature results in less ozone and less heating. Calculations presented herein show that this effect has a strong stabilizing influence on the temperature values near the mesopeak.

1. Introduction

The photochemical-equilibrium ozone concentration at a particular level in the atmosphere depends upon the temperature at that level. Ozone is destroyed by the two-body collision

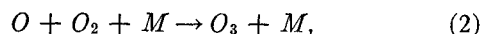


the rate at which the destruction proceeds being proportional to the product of the densities of ozone and atomic oxygen. The factor of proportionality, k_{13} , depends markedly on the temperature. The relationship is such that there is a greater equilibrium concentration at low temperatures than at high temperatures. Since the ozone absorption of solar energy and resulting solar-heating rate at a particular level depend directly upon the ozone concentration at that level, it is obvious that the ozone heating rate is a function of temperature.

The present article deals with this variation of ozone heating rates with temperature in the region of the mesopeak (about 50 km) and the tendency for this variation to act as a stabilizing force for the temperature in this region. At these heights the actual ozone concentrations are presumably close to equilibrium values (see, for example, Johnson *et al.*, 1952) so that the results apply to the real atmosphere.

2. Methods

As ozone is being destroyed by the two-body collision (1) it is being formed by the three-body collision,



where M is an arbitrary third body (either nitrogen or oxygen). The collision coefficient for this reaction is called k_{12} . The expression for the equilibrium ozone concentration at a particular level, which takes into

consideration collisions (1) and (2) as well as the reactions involving dissociation of ozone and oxygen by ultraviolet light, can be written as follows:

$$n_3 = \frac{n_2 J_2}{2J_3} \left[\left(1 + \frac{4kn_m J_3}{J_2} \right)^{\frac{1}{2}} - 1 \right], \quad (3)$$

where n_2 , n_3 , and n_m (molecules cm^{-3}) represent the concentrations of O_2 , O_3 and the third body M , respectively, J_2 and J_3 (quanta $\text{sec}^{-1} \text{cm}^{-2} \text{molecule}^{-1}$) are the rates of dissociation per unit concentration of O_2 and O_3 , respectively, and k ($\text{cm}^3 \text{molecule}^{-1}$) is the ratio k_{12}/k_{13} . Equation (3) does not include the effects of the oxygen recombination reaction, $O + O + M \rightarrow O_2 + M$, which, according to sample calculations, can be neglected below 60 km. Except for a slight change in notation, this equation is the same as that derived by Craig (1950).

The molecular concentrations, n_2 and n_m , depend only upon the density at the level in question. J_2 and J_3 depend upon the solar spectrum, the absorption coefficients of O_2 and O_3 , and the O_2 and O_3 path lengths, N_2 and N_3 , above the level. The solar spectrum and absorption coefficients given by Craig (1950) were used to construct graphs of J_2 and J_3 as functions of path length. Measurements of the temperature dependence of k (Eucken and Patat, 1936) indicate that $k \sim e^{1/t}$. Since Eucken and Patat's measurements were made in a mixture of oxygen and ozone, their values had to be corrected in order to apply to the actual atmosphere. There are indications that a nitrogen molecule is about 0.6 times as effective as an oxygen molecule in a three-body collision (Penndorf, 1949). Since, in the atmosphere, the third body will be nitrogen 79 per cent of the time and oxygen 21 per cent of the time, Eucken and Patat's values were multiplied by 68 per cent.

Once the ozone concentration has been determined,

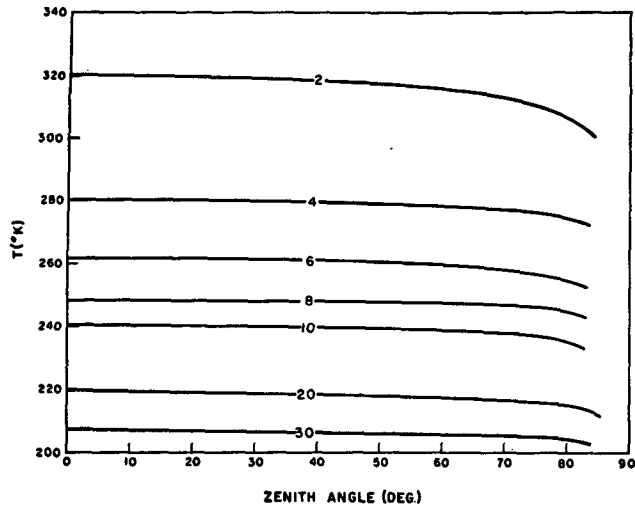


FIG. 1. Isopleths of equilibrium ozone concentration at 45 km as a function of temperature and zenith angle (10^{-4} cm km $^{-1}$).

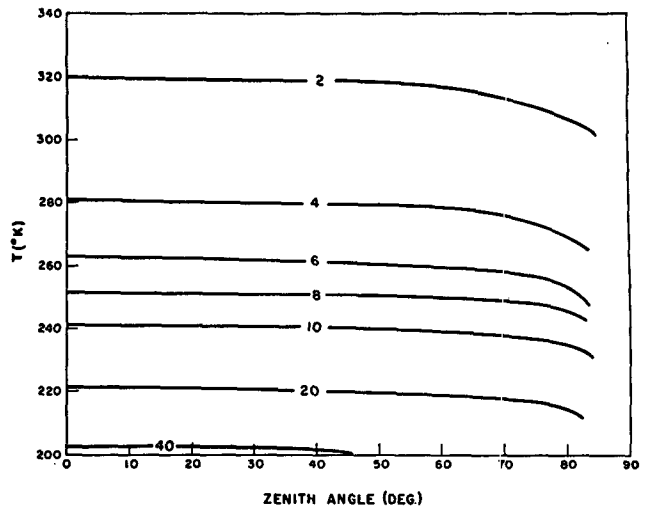


FIG. 4. Isopleths of equilibrium ozone concentration at 60 km as a function of temperature and zenith angle (10^{-8} cm km $^{-1}$).

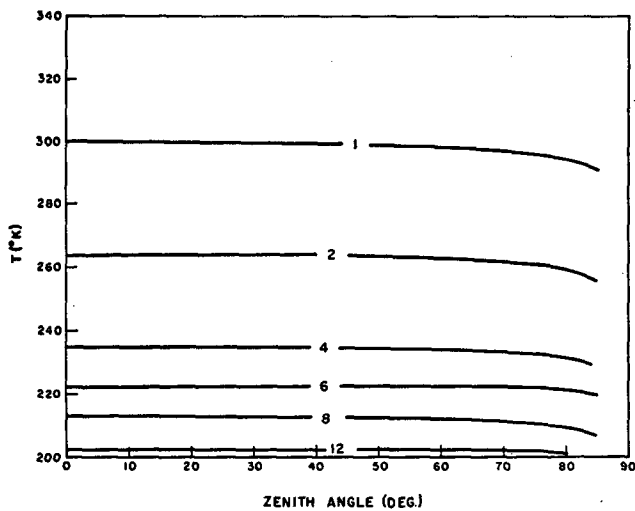


FIG. 2. Isopleths of equilibrium ozone concentration at 50 km as a function of temperature and zenith angle (10^{-4} cm km $^{-1}$).

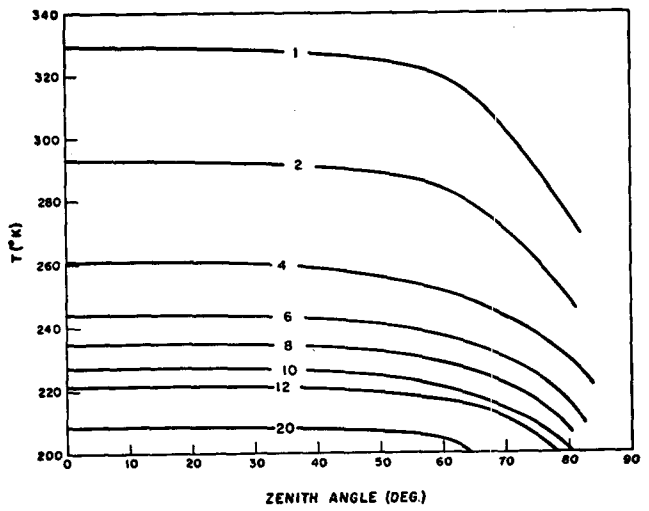


FIG. 5. Isopleths of ozone heating rate at 45 km as a function of temperature and zenith angle ($^{\circ}$ C per 3 hr).

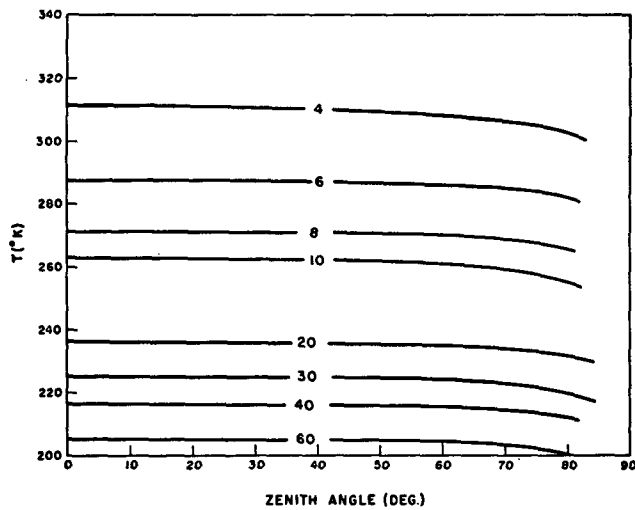


FIG. 3. Isopleths of equilibrium ozone concentration at 55 km as a function of temperature and zenith angle (10^{-8} cm km $^{-1}$).

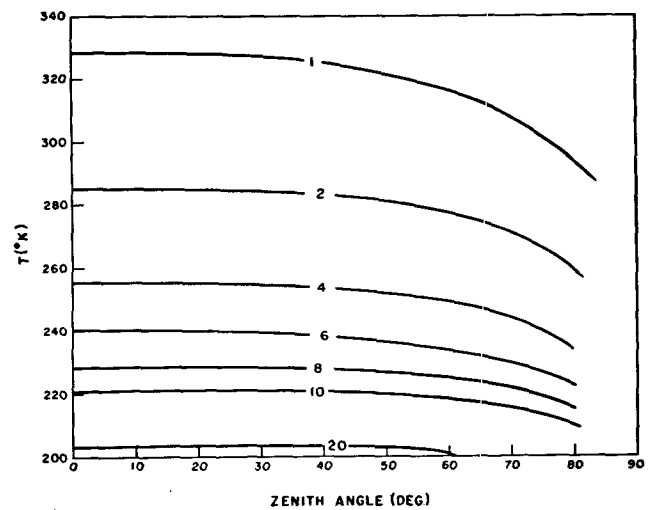


FIG. 6. Isopleths of ozone heating rate at 50 km as a function of temperature and zenith angle ($^{\circ}$ C per 3 hr).

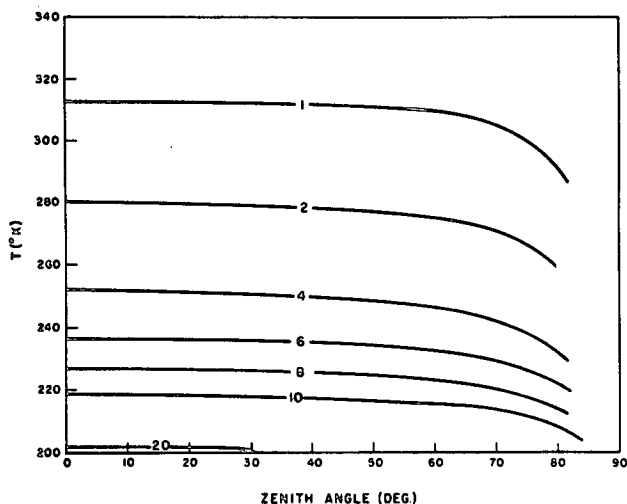


FIG. 7. Isopleths of ozone heating rate at 55 km as a function of temperature and zenith angle ($^{\circ}\text{C}$ per 3 hr).

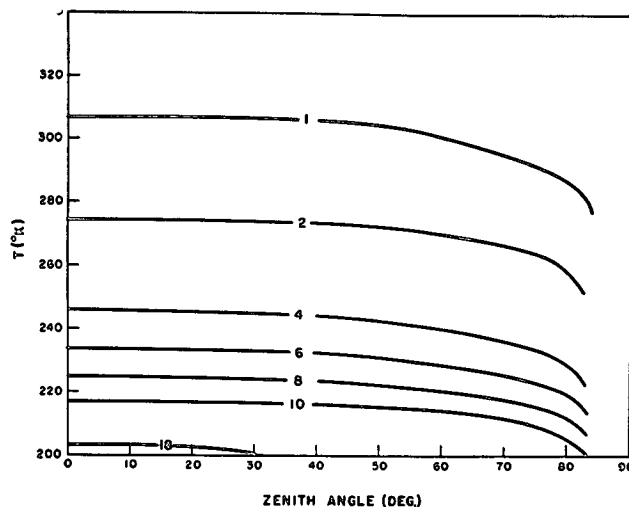


FIG. 8. Isopleths of ozone heating rate at 60 km as a function of temperature and zenith angle ($^{\circ}\text{C}$ per 3 hr).

the absorption of solar energy can be computed from

$$E_z = n_3 \int I_{0\lambda} \alpha_{\lambda} \exp(-\alpha_{\lambda} N_3) d\lambda, \quad (4)$$

where E_z is the total energy absorbed per unit volume per unit time at the level z ($\text{cal cm}^{-3} \text{sec}^{-1}$), $I_{0\lambda}$ is the intensity of incident solar radiation at wavelength λ outside the atmosphere ($\text{cal cm}^{-2} \text{sec}^{-1} (\Delta\lambda)^{-1}$), α_{λ} is the ozone absorption coefficient at wavelength λ (cm^{-1}), and N_3 is the total ozone path length above z passed through by the oblique solar beam (cm). The integral in (4) has been computed as a function of N_3 (Craig, 1951) for the solar spectrum and absorption coefficients used by Craig (1950).

The heating rate can then be expressed as

$$\frac{\partial T}{\partial t} = \frac{E_z}{\rho c_p}, \quad (5)$$

where ρ is the air density, and c_p is the specific heat of air at constant pressure.

Actually, if one lets ρ represent the height variable, the ozone heating rate at a height z depends only upon the temperature at z , and the ozone path length above z . For zenith angles less than 80 deg, the ozone path length, N_3 , can be written as $N_3 = N_3(o) \sec \zeta$, where $N_3(o)$ is the total amount of ozone in a vertical column above z , and ζ is the zenith angle. In order to simplify matters and to isolate the temperature dependence of the heating rates, mean values of ρ and $N_3(o)$ were used at the various levels. For the present purpose of showing the temperature dependence of

the heating rate, this is an excellent approximation for zenith angles less than about 60 deg and levels above 40 km. The mean values of ρ and $N_3(o)$ used at the various levels are shown in table 1. With these values, the ozone heating rate at the level z is a to good approximation specified by the temperature at z and the zenith angle.

3. Discussion of results

Computations of equilibrium ozone concentrations and resulting solar heating rates were made for a wide range of temperatures and zenith angles at 45, 50, 55, and 60 km. The results are presented in the form of isopleths of ozone concentration (figs. 1-4) and heating rate (figs. 5-8) on graphs with temperature as ordinate and zenith angle as abscissa.

The exponential increase of ozone concentration and heating rate as the temperature decreases is due to the exponential character of the temperature dependence of k . If the temperature decreases by 30 deg, the ozone concentration and heating rate are approximately doubled; if the temperature increases by 30 deg, the ozone concentration and heating rate are approximately halved. The variation of ozone concentration with zenith angle at these heights is quite small, at least for zenith angles less than 70 deg to 75 deg. The variation of ozone heating with zenith angle is also small up to zenith angles of about 50 deg. With increasing zenith angle the heating rate decreases since more of the solar energy is absorbed before it reaches the level. This effect becomes more pronounced at the lower levels and, in the present calculations, is largest at 45 km. The reader who wishes to assess the effect on these calculations of a change in $N_3(o)$ may inspect the variation of heating rate with zenith angle, since N_3 is directly proportional to $N_3(o)$ and $\sec \zeta$.

The temperature variation of the ozone heating rates for the different levels can be seen more clearly

TABLE 1. Values of ρ and $N_3(o)$ assumed at various levels.

Ht (km)	ρ (g cm^{-3})	$N_3(o)$ (cm)
45	2×10^{-6}	1.7×10^{-3}
50	1×10^{-6}	6.75×10^{-4}
55	6×10^{-7}	3.75×10^{-4}
60	4×10^{-7}	2.22×10^{-4}

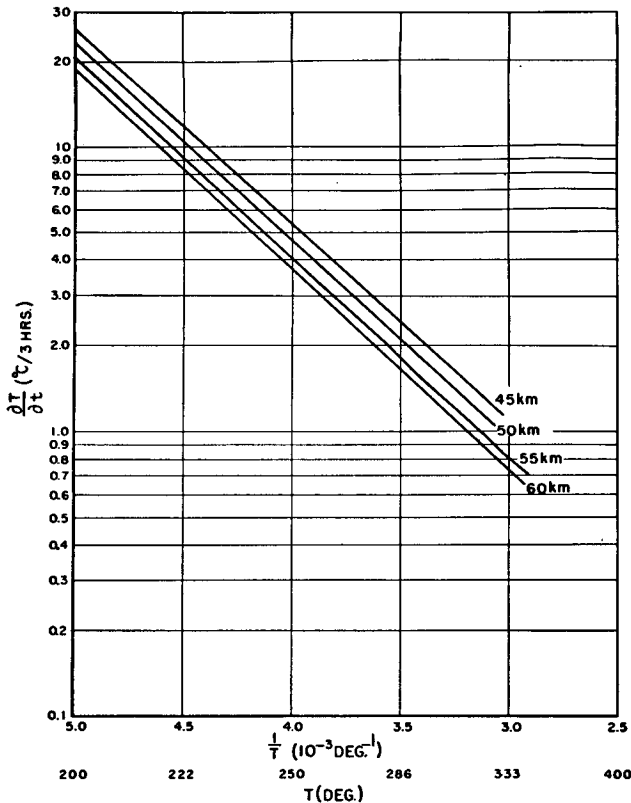


FIG. 9. Ozone heating rates at various levels as a function of temperature for a zenith angle of zero degrees ($^{\circ}\text{C}$ per 3 hr).

from fig. 9. Here, the heating rates, on a logarithmic scale, are plotted against the reciprocal of the temperature, for zero zenith angle. Since, at these levels, the second term under the square root in (3) is much larger than one, the ozone concentration and resulting heating rate are proportional to $k^{\frac{1}{2}}$. But k is proportional to $e^{1/T}$ so that in a graph such as fig. 9, the heating rate curves appear as straight lines. If the 45- to 60-km region were isothermal the heating rate would decrease with height in this layer.

This type of heating rate-temperature relationship should result in a stabilizing effect upon the mesopeak temperatures. If, for example, during the day, the 50-km level is in radiative equilibrium at a temperature of 270K, a sudden increase in temperature of about 30 deg would result in a 50 per cent decrease in the solar heating rate, from 3C per 3 hr to about 1.5C per 3 hr. Moreover, because of the higher temperature, the infrared cooling would increase. There would be a state of radiative unbalance with more emission than absorption. The temperature would drop until the equilibrium temperature of 270K is once again attained. Analogously, a decrease of 30 deg would result in more solar heating than infrared cooling, and the temperature would seek to return to its equilibrium value. Because the temperature dependence is of exponential character, the "restoring force" will be an exponential function of the departure from equilibrium. Even if this level is

not in radiative equilibrium the same type of argument holds except that the radiative equilibrium temperature would now be replaced by the mean temperature of the level. Thus, only for rather short periods of time should the mesopeak temperatures vary markedly from their mean values.

Below 45 km, however, these arguments are not valid. In the first place, the equilibrium ozone concentration and ozone heating rate depend much more critically upon N_3 . Therefore, they are influenced markedly by conditions at other, higher levels. In the second place, probably at 30–40 km and increasingly so at lower levels, the ozone concentration is not necessarily at its equilibrium value. Thus, the ozone concentration predicted by equation (3) is much less likely to represent the actual concentration at a given time and place at lower levels than at the higher levels near the mesopeak.

Another point to be emphasized is that the mechanism described herein does not provide for any significant net increase or decrease of ultraviolet absorption in the mesosphere. An increase in temperature at the mesopeak, which decreases the amount of ozone present at that level, simply allows more ultraviolet radiation to penetrate, most of which is absorbed at a lower level. Conversely, a decrease in temperature at the mesopeak, which increases the ozone concentration at that level, increases the absorption and thus decreases the amount of energy available for absorption at a lower level.

There is certainly some doubt about the absolute value of k , and indeed, about other factors (such as the solar intensity in the ultraviolet), so that the absolute values presented herein are somewhat uncertain. Neither is it possible to estimate quantitatively the infrared cooling rate as a function only of temperature at the level in question. Both factors, however, act to stabilize the temperature near the mesopeak and prevent prolonged sizable deviations from the mean value. This interesting state of affairs may have application to the problem of solar-weather relationships and to the question of resonance in connection with the solar semi-diurnal tide.

REFERENCES

- Craig, R. A., 1950: The observations and photochemistry of atmospheric ozone and their meteorological significance. *Meteor. Monogr.*, 1, No. 2, 50 pp.
- , 1951: Radiative temperature changes in the ozone layer. *Compendium Meteor.*, Boston, Amer. meteor. Soc., 292–302.
- Eucken, A., and F. Patat, 1936: Die temperaturabhängigkeit der photochemischen ozonbildung. *Z. phys. Chem.*, B, 33, 459–474.
- Johnson, F. S., J. D. Purcell, R. Tousey, and K. Watanabe, 1952: Direct measurements of the vertical distribution of atmospheric ozone to 70 kilometers altitude. *J. geophys. Res.*, 57, 157–177.
- Penndorf, R., 1949: The vertical distribution of atomic oxygen in the upper atmosphere. *J. geophys. Res.*, 54, 7–38.