Vertical Transport and Photochemistry in the Terrestrial Mesosphere and Lower Thermosphere (50–120 km)

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The coupled effects of kinetics, solar cycle flux variations and vertical transport on the distribution of long-lived hydrogen-carbon-oxygen compounds in the terrestrial mesosphere and lower thermosphere are studied using a one-dimensional aeronomy model. The calculations account for the important chemical reactions and use rocket measurements of the solar flux at solar minimum and maximum. Photodissociation rates appropriate for the mesosphere are determined with a spherical shell atmosphere formalism; detailed corrections for the O_3 Schumann-Runge bands and the temperature dependence of the CO_2 cross sections are used. Then an eddy diffusion profile is derived which gives agreement with the Aladdin 74 mass spectral measurements of atomic O, O_2, CO_2, and Ar in the lower thermosphere and observations of the O_3 minimum at ~80 km. The 115 GHz CO radio emission line computed for the CO mixing ratio profile predicted with the new eddy diffusion profile compares well with recent observations of W. J. Wilson. Differences between the calculated CO mixing ratio profile and previous theoretical and observational determinations are discussed. Our derived eddy diffusion profile has a sudden decrease at 92 km which is necessary to produce the atomic O peak at 98 km that appears in the Aladdin 74 measurements. This stagnant region apparently is a recurrent or persistent feature of the upper atmosphere since an atomic O peak around 98 km has been seen by different techniques in different seasons over several years. Slow eddy diffusion in the lower thermosphere through the homopause was also the conclusion of earlier Ar/N_2 rocket measurements studies. The analytic approach of this paper could be used in the future to monitor variations in middle atmosphere dynamics, if regularly conducted simultaneous observations of various groups of species were available.

INTRODUCTION

The chemical composition of the terrestrial mesosphere and lower thermosphere (~50–120 km altitude) reflects the coupled effects of solar radiation, chemical kinetics, and mass transport. An understanding of the relative importance of each of these factors will improve our knowledge of what changes in the middle atmosphere might result from variations in these driving forces and in turn will enable observations of changes in the chemical composition to be used to monitor the variability of the solar radiation field and mass transport rates (the kinetic rate constants being ‘invariable’).

Mount et al. [1980] report the results of rocket measurements of the solar spectrum near solar maximum and compare them with similar observations taken around solar minimum. At certain wavelengths below 1900 Å, the intensity variation over the 11-year solar cycle is as much as a factor of two. Frederick [1977] has shown that smaller scale solar variation (over a 28-day cycle) causes perturbations in the abundances of odd-oxygen compounds in the mesosphere. Changes due to the 11-year solar cycle therefore will be very significant. High altitude observations of the solar radiation field, in principle, could be done sufficiently frequently so that correct values would be available for model comparisons with atmospheric data.

As will be seen in this paper, the chemistry of the neutral atomic and molecular species containing hydrogen, carbon, and oxygen can be well described by ~35 reactions. (The photochemistry of nitrogen has not been included.) This is to be compared with stratospheric models that require 150 or more reactions for an adequate description. The fewer reactions in the mesospheric model allow more straightforward analyses of the dependence of model results on the rate constants.

Least well known is mass transport in the mesosphere and lower thermosphere. The altitude profiles of species with chemical lifetimes close to the timescales for vertical transport will directly reflect the magnitude of the dynamical processes. In turn, the vertical profiles of species strongly coupled to these long-lived constituents will also reflect transport processes. Since the radiation field and the chemistry are or can be known with reasonable confidence, the model results for transport-sensitive species can be compared with observations to place constraints on the transport parameters.

Given the limitations of current computers, one-dimensional numerical models are best able to explore the coupling of transport and a complex chemical reaction network. In a one-dimensional photochemical model, the effect of vertical transport is conveniently parameterized by a set of eddy diffusion coefficients K(z). Eddy diffusion rates may be directly connected to the nature of turbulence generated by the breakdown of gravity waves and tides [Lindzen, 1980]. The magnitude of K(z) can be deduced from the study of long-lived tracer species [e.g., Hunten, 1975]. Between the tropopause and 40 km, our knowledge of K(z) is based on studies of the distribution of radioactive nuclei, CH_4, N_2O, and chlorofluorocarbons [Wofsy and McElroy, 1973; Hunten, 1975; Johnson et al., 1976; NAS, 1976; Schmeltekopf et al., 1977]. Until recently, experimental difficulties limited the amount of tracer observations in the mesosphere and our knowledge of K(z) between 40 and 100 km. Analyses of rocket mass spectral data for the thermosphere have used (1) the O/O_2 concentration ratio at 100 km to yield a value for K(z) of 4 × 10^6 cm^2 s^{-1} [Colegrove et al., 1965]; (2) the Ar/N_2 ratio at 120 km to deter-
mine the turbopause altitude [von Zahn, 1970] which in turn results in a value of $4 \times 10^{13} \text{ cm}^2 \text{s}^{-1}$ for $K(z)$ [Huntten, 1975]; and (3) the helium density at 500 km to get a value of $1.8 \times 10^{4} \text{ cm}^2 \text{s}^{-1}$ for $K(z)$ in the lower thermosphere. In most studies, the magnitude of $K(z)$ above 80 km is assumed to be constant. Huntten [1975], for example, reviews the $K(z)$ determinations just enumerated and suggests a value of $1 \times 10^{6} \text{ cm}^2 \text{s}^{-1}$ for $K(z) \geq 80$ km.

The different values reported for $K(z)$ in the lower thermosphere may reflect real variations in $K(z)$ since the different analyses used measurements made at different places and times. Moreover, the various tracer species are driven by slightly different transport processes, the normalization of such differences being somewhat difficult. However, a mass spectrometer rocket flight during the Aladdin 74 program simultaneously measured density profiles of $N_2$, $O_2$, $O$, Ar, and $CO_2$ in the lower thermosphere [Trinks et al., 1978; Trinks and Fricke, 1978], which can be used to determine $K(z)$ consistent with many species. Microwave measurements of the mesospheric distribution of CO [Waters et al., 1976; Goldsmith et al., 1979; W. J. Wilson, private communication] and $H_2O$ [Radford et al., 1977; Waters et al., 1980; S. Deguchi and D. O. Muhlemann, private communication. 1980] also allow the derivation of $K(z)$ for the mesosphere. Having compiled an updated model of hydrogen-carbon-oxygen upper atmosphere chemistry and having accounted for solar cycle flux variations, we used a one-dimensional computer model to explore the consequences of a range of eddy diffusion profiles to find a profile that would be consistent with the previously mentioned observations of tracer species in the mesosphere and lower thermosphere.

**Mesosphere/Lower Thermosphere Model**

We have developed a general one-dimensional planetary atmosphere computer program that solves the continuity equation for a species $i$,

$$\frac{\partial n_i}{\partial t} + \frac{\partial \Phi_i}{\partial z} = P_i - L_i$$

(1)

where $n_i$, $\Phi_i$, $P_i$, and $L_i$ are the concentration, vertical flux, production and loss rates of species $i$ at altitude $z$. Both steady state calculations ($\partial n_i/\partial t = 0$, in which case $P_i$ and $L_i$ can be diurnally averaged quantities) and time-dependent calculations ($\partial n_i/\partial t \neq 0$, in which case $P_i$ and $L_i$ may follow the diurnal variation of the solar radiation field) can be performed. The transport terms include eddy, molecular, and thermal diffusion [Banks and Kockarts, 1973]. The calculations use numerical techniques similar to those described by Logan et al. [1978].

For the results reported in this paper, background atmospheres appropriate for 30°N July and midlatitude spring/fall were used to be consistent with the time and location of different observations. Below 80 km the profiles for total density, molecular nitrogen, and temperature were taken from the U.S. Standard Atmosphere Supplements (1966). The background atmosphere above 90 km is critically important. The results of in situ observations of the thermosphere (for example, Trinks et al. [1978]) usually differ from the theoretical profiles since theoretical models do not account for atmospheric dynamic disturbances such as tides and gravity waves. Therefore we used the Aladdin 74 total density and molecular nitrogen mass spectrometer measurements of Trinks et al. [1978] to define the background atmosphere above 90 km. The background atmosphere between 80 and 90 km was chosen to smoothly match the 80 and 90 km values. A derivation of the temperature profile used above 80 km is described in the appendix.

Our chemical model includes the chemistry and transport of the major nonnitrogen chemical species in the altitude range 50–120 km: O, $O^+$, $O_2$, $O_3$, H, $H_2$, OH, $H_2O$, $H_2O_2$, $CO$, $CO_2$, $CH_4$, and Ar. Listed in Table 1 are the important reactions governing the chemistry of these species. In most cases, the kinetic rate constants are taken directly from the sources referenced. However, in another of our middle atmosphere studies (M. Allen and Y. L. Yung, in preparation, 1981), we found that, to better fit the observed $O_3$ minimum at $\sim 80$ km, the values for $k_{S16}$, $k_{S17}$, $k_{S18}$, $k_{S28}$, and $k_{S30}$ needed to be adjusted within the reported estimated uncertainty range of the laboratory values. Those adjusted values were used here. Since Klais et al. [1980] and others show that the rate constant for three-body recombination of $O_3$ and $O_2$ to form $O_3$ depends on the nature of the third body, we include separately recombination with $O_3$ and $N_2$ as 'third bodies.' Since atomic O becomes more abundant than $O_3$ above $\sim 106$ km, a separate reaction in which atomic O is the third body is included and the rate constant $k_{S13}$ is set equal to that for $O_3$-mediated recombination.

The model used a solar flux adjusted for the season, latitude, and phase of the solar cycle appropriate for each set of measurements which we analyzed. The solar maximum and minimum flux values reported by Mount et al. [1980] were used. The radiative transfer calculations are for a spherical shell atmosphere with the optical opacity due to the photodissociation of molecular oxygen and ozone. Radiative transfer in the $O_3$ Schumann-Runge bands (1750–2000 Å) is complicated and, if not handled properly, will result in errors in the photodissociation rates of species sensitive to radiation in this range. A number of papers, most recently, Frederick and Hudson [1980a, b] and Nicolet and Peeleman [1980], have done detailed studies of this problem. We used a simple parametrization of $O_3$ Schumann-Runge band cross sections that yield Schumann-Runge band transmission and $O_3$ photodissociation values in good agreement with those from more complicated calculations of Frederick and Hudson [1980a, b]. The $H_2O$ Lyman alpha dissociation rate has been modified in accordance with Frederick and Hudson [1980a]. We account for the reported wavelength-dependent temperature variation of $CO_2$ photodissociation cross sections [DeMore and Patatoff, 1972] as follows (W. B. DeMore, private communication, 1979):

$$\sigma(\lambda, T)/\sigma(\lambda, 298) = (1 - [P(\lambda)/100])^{298-T}$$

(2)

$$P(\lambda) = 0.5 + 5 \times 10^{-5}(\lambda - 1740 \text{ Å}) \quad \lambda \geq 1640 \text{ Å}$$

where $\sigma(\lambda, T)$ is the cross section at temperature $T$ and wavelength $\lambda$ and the wavelength-dependent percentage change $P(\lambda)$ is an increasing function of wavelength and is assumed to be zero for $\lambda < 1640$ Å.

The numerical calculations were performed for the altitude range 40–130 km. Below 50 km, however, $ClO$ and $NO_x$ are important in the chemistry of odd oxygen [Frederick, 1980], so our results apply only above 50 km since we do not include such chemical cycles. The lower boundary for the calculations was set at 40 km because of the availability of upper stratosphere observational results for the more abundant species.
TABLE 1. Reactions and Chemical Rate Constants Used in Model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant*</th>
<th>Reference†</th>
<th>Reference‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $O_2 + h\nu \rightarrow 2O$</td>
<td>$6.6 \times 10^{-10}$, $3.3 \times 10^{-8}$</td>
<td>Watanabe [1958]; Hudson [1974]; Prather [1981]; see text</td>
<td>$1775 \leq \lambda \leq 2560$ Å</td>
</tr>
<tr>
<td>2. $O_2 + h\nu \rightarrow O + O(^1D)$</td>
<td>$1.5 \times 10^{-12}$, $1.6 \times 10^{-7}$</td>
<td>Watanabe [1958]; Ackerman [1971]; Corver et al. [1977]</td>
<td>$\lambda \leq 1775$ Å</td>
</tr>
<tr>
<td>3. $O_3 + h\nu \rightarrow O_2 + O$</td>
<td>$2.5 \times 10^{-4}$, $2.5 \times 10^{-4}$</td>
<td>Ackerman [1971]; Hudson and Reed [1979]</td>
<td>$3000 \leq \lambda \leq 3550$ Å</td>
</tr>
<tr>
<td>4. $O_3 + h\nu \rightarrow O_2 + O(^1D)$</td>
<td>$4.3 \times 10^{-3}$, $4.5 \times 10^{-3}$</td>
<td>Ackerman [1971]; Hudson and Reed [1979]</td>
<td>$1675 \leq \lambda \leq 3200$ Å</td>
</tr>
<tr>
<td>5. $H_2O + h\nu \rightarrow H + OH$</td>
<td>$1.5 \times 10^{-6}$, $3.7 \times 10^{-6}$</td>
<td>Watanabe [1958]; Hudson [1971]; CIAP [1975]; Prather [1981]; see text</td>
<td>$\lambda \leq 2025$ Å</td>
</tr>
<tr>
<td>6. $H_2O_2 + h\nu \rightarrow H_2O(^1D)$</td>
<td>$8.3 \times 10^{-12}$, $6.7 \times 10^{-7}$</td>
<td>Schürgers and Welge [1968]; CIAP [1975]; Hudson and Reed [1979]</td>
<td>$\lambda = 1215.7$ Å</td>
</tr>
<tr>
<td>7. $H_2O_2 + h\nu \rightarrow 2OH$</td>
<td>$5.8 \times 10^{-5}$, $6.6 \times 10^{-5}$</td>
<td>CIAP [1975]; Hudson and Reed [1979]</td>
<td>$1200 \leq \lambda \leq 3500$ Å</td>
</tr>
<tr>
<td>8. $O(^1D) + O_3 \rightarrow O_2 + O_2$</td>
<td>$2.9 \times 10^{-11} e^{0.7T}$</td>
<td>Logan et al. [1978]</td>
<td>See text</td>
</tr>
<tr>
<td>9. $O(^1D) + N_2 \rightarrow O + N_2$</td>
<td>$2.0 \times 10^{-11} e^{0.7T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>10. $O(^1D) + O_2 \rightarrow 2O_2$</td>
<td>$2.3 \times 10^{-10}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>11. $O(^1D) + H_2 \rightarrow H + OH$</td>
<td>$9.9 \times 10^{-11}$</td>
<td>Klatis et al. [1979]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>12. $2O + M \rightarrow O_2 + M$</td>
<td>$9.59 \times 10^{-10} e^{400T}$</td>
<td>Klatis et al. [1979]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>13. $O + O_3 + O \rightarrow O_3 + O_2$</td>
<td>$2.15 \times 10^{-6} e^{0.11T}$</td>
<td>Klatis et al. [1979]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>14. $O + O_3 + O_2 \rightarrow O_3 + O_2 + O_2$</td>
<td>$2.15 \times 10^{-6} e^{0.11T}$</td>
<td>Klatis et al. [1979]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>15. $O + O_3 + N_2 \rightarrow O_3 + N_2 + O$</td>
<td>$8.82 \times 10^{-6} e^{0.11T}$</td>
<td>Klatis et al. [1979]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>16. $O + O_2 \rightarrow 2O$</td>
<td>$1.5 \times 10^{-11} e^{121T}$</td>
<td>Klatis et al. [1979]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>17. $O + OH \rightarrow O_2 + H$</td>
<td>$1.7 \times 10^{-11} e^{317T}$</td>
<td>R. T. Watson (unpublished data, 1979)</td>
<td>See text</td>
</tr>
<tr>
<td>18. $O + HO_2 \rightarrow OH + O_2$</td>
<td>$3.5 \times 10^{-11} e^{200T}$</td>
<td>Hampson and Garvin [1978]</td>
<td>See text</td>
</tr>
<tr>
<td>19. $OH + HO_2 \rightarrow OH + H + O_2$</td>
<td>$2.8 \times 10^{-11} e^{121T}$</td>
<td>Hampson and Garvin [1978]</td>
<td>See text</td>
</tr>
<tr>
<td>20. $OH + H_2 \rightarrow OH + H + O_2$</td>
<td>$3.0 \times 10^{-11} e^{400T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>21. $OH + O_3 \rightarrow HO_2 + D_2$</td>
<td>$1.6 \times 10^{-12} e^{904T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>22. $2OH + H_2O \rightarrow 2O + 2H_2O$</td>
<td>$1.0 \times 10^{-12} e^{500T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>23. $OH + HO_2 \rightarrow HO_2 + O_2$</td>
<td>$4.0 \times 10^{-11}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>24. $OH + HO_2 \rightarrow OH + O + HO_2$</td>
<td>$1.0 \times 10^{-12} e^{750T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>25. $OH + H_2 \rightarrow OH + O + H_2$</td>
<td>$1.0 \times 10^{-12} e^{750T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>26. $H_2O_2 + OH \rightarrow H_2O + H_2$</td>
<td>$1.0 \times 10^{-12} e^{2200T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>27. $H_2O_2 + HO_2 \rightarrow H_2O + O_2$</td>
<td>$1.0 \times 10^{-12} e^{2200T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>28. $H + 2O_2 \rightarrow H_2O + O_2$</td>
<td>$1.14 \times 10^{-12} e^{1053T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>29. $H + O_2 \rightarrow H + O_2$</td>
<td>$1.76 \times 10^{-12} e^{28T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>30. $H + HO_2 \rightarrow H + O_2$</td>
<td>$1.4 \times 10^{-12} e^{70T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>31. $H + HO_2 \rightarrow H_2 + OH$</td>
<td>$7.8 \times 10^{-12}$</td>
<td>Baulch et al. [1980]; see text</td>
<td>See text</td>
</tr>
<tr>
<td>32. $H + H_2O \rightarrow H + H_2 + O$</td>
<td>$3.2 \times 10^{-11}$</td>
<td>Baulch et al. [1980]</td>
<td>See text</td>
</tr>
<tr>
<td>33. $H + H_2O \rightarrow H + H_2 + O$</td>
<td>$9.3 \times 10^{-13}$</td>
<td>Baulch et al. [1980]</td>
<td>See text</td>
</tr>
<tr>
<td>34. $CO_2 + h\nu \rightarrow CO + CO_2 + M$</td>
<td>$1.8 \times 10^{-10} e^{10T}$</td>
<td>Hampson and Garvin [1978]</td>
<td>See text</td>
</tr>
<tr>
<td>35. $CO_2 + h\nu \rightarrow CO + OH + H_2O$</td>
<td>$6.7 \times 10^{-10}$, $2.3 \times 10^{-7}$</td>
<td>Inn et al. [1953]: Hudson [1971]; CIAP [1975]; see text</td>
<td>$\lambda \leq 2225$ Å</td>
</tr>
<tr>
<td>36. $CH_4 + OH \rightarrow CO + CH_4 + OH + H_2O$</td>
<td>$2.4 \times 10^{-12} e^{1110T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>37. $CH_4 + O(^1D) \rightarrow CO + 2OH + H_2O$</td>
<td>$3.5 \times 10^{-12} e^{1455T}$</td>
<td>See text</td>
<td>See text</td>
</tr>
<tr>
<td>38. $CO + OH \rightarrow CO_2 + H$</td>
<td>$1.44 \times 10^{-10}$</td>
<td>See text</td>
<td>See text</td>
</tr>
</tbody>
</table>

*Photodissociation constants are in units of s⁻¹, two body rate constants in units of cm³ s⁻¹, three body rate constants in units of cm⁶ s⁻¹.
†Rate constants come from Hudson and Reed [1979], unless otherwise noted.
‡Diurnally averaged photodissociation values for 60 and 100 km, respectively, at summer solstice, 38°N latitude, using solar minimum flux. Indicated also is the wavelength range in which the cross sections are significant.

The lower (40 km) boundary conditions for $O_2$, $CO_2$, and $Ar$ are the tropospheric mixing ratios of 0.21, 3.3 × 10⁻⁴, and 9.34 × 10⁻³, respectively [McCleary, 1976], and for $H_2$, $CO$, and $CH_4$ are mixing ratios of 5 × 10⁻⁶ [Ehnhalt et al., 1975], 1 × 10⁻⁸ [Farmer et al., 1980], and 3 × 10⁻⁷ (an average of Ehnhalt et al. [1972], Ehnhalt et al. [1975], and Farmer et al. [1980]), respectively. Model calculations were run with mixing ratios for $H_2O$ of 5 and 7 ppm, a range of values that is consistent with Farmer et al. [1980] and Waters et al. [1980]. All other species, being short lived, are in local photochemical equilibrium, so their vertical fluxes at 40 km were set equal to zero. The upper boundary at 130 km was chosen to allow for accurate modeling of the region of the homopause. Molecular oxygen flows upward through the 130 km boundary, is photodissociated, and returns below 130 km as atomic oxygen. A velocity boundary condition for $O_2$ was calculated assuming that the
upward flux (velocity times abundance of O$_3$ at 130 km) is
equal to the column O$_3$ photodissociation rate above 130 km.
The downward flux of atomic O was set equal to twice the up-
ward O$_3$ flux. The upward flow of carbon in the form of CO$_2$
and its downward return as CO are similar; a velocity bound-
ary condition was set for CO$_2$ and the downward flux of CO
was equated to the column CO$_2$ photodissociation rate. A ve-
celity boundary condition for H$_2$O was used assuming that an
upward flux of H$_2$O at 130 km is needed to compensate for its
loss above. The boundary conditions for H and H$_2$ were the
maximum diffusion velocities [Banks and Kockarts, 1973]. All
other species are in local photochemical equilibrium, so their
vertical fluxes were set equal to zero.

The transport processes incorporated in the model are eddy,
molecular, and thermal diffusion. Derivation of the altitude
dependence of the eddy diffusion coefficients is a goal of this
work. A systematic tabulation of the available measurements
of molecular diffusion is presented by Mason and Marrero
[1970]. When air is the background gas, the diffusion coeffi-
cients for a variety of species of different mass are inversely
related to the H$_2$ diffusion coefficient by the square root of
mass. This generalization is used in our model. The thermal
diffusion parameters are −0.27, −0.39, and −0.31 for O, H,
and H$_2$, respectively, and zero for all other species [Keneshea
et al., 1979].

**Derivation of Eddy Diffusion Profile**

A number of different models were used in the calculations
to be discussed (see Table 2). The standard case, model 1, is a
diurnally averaged calculation with a 7 ppm H$_2$O mixing ratio
at 40 km and a background atmosphere and radiation field
chosen to simulate the circumstances of the Aladdin 74 mea-
surements. One diurnal calculation, model 2, was performed
to compare with the standard case. A drier atmosphere for
which the H$_2$O mixing ratio at 40 km was fixed at 5 ppm was
tried in one calculation, model 3. The effect of increasing the
solar flux to solar maximum values was investigated (model
4). Finally, there was a calculation appropriate for the time
and place of W. J. Wilson’s CO measurements (model 5).

The calculated chemical lifetimes (model 1) of the major
neutral nonnitrogen-containing species are shown in Figure 1.
Since argon is chemically inert, its lifetime is infinite and
therefore not shown. The lifetimes of all species are longer
than a day, except for atomic O below 86 km. This permits ac-
curate calculations of their abundances using a diurnally aver-
ged model, using properly diurnally averaged photodissocia-
tion rate constants and assuming that the diurnally averaged
production and loss rates (due to diurnally averaged concen-
trations) are equal to daily averages of rates using diurnal
concentrations. A comparison of midnight and noon results of
model 2 and the model 1 results for these long-lived species
reveals, at most, 2% differences among these sets of data.

Also in Figure 1, the time scale for species-independent
transport by eddy diffusion

$$\tau(z) = H^2(z)/D(z)$$  (3)
is compared with molecular diffusion time scales

$$\tau(i, z) = H^2(z)/D(i, z)$$  (4)

where $H(z)$, $K(z)$, and $D(i, z)$ are the mean atmosphere scale
height, eddy diffusion coefficient, and molecular diffusion co-
efficient for species $i$, respectively, at altitude $z$. The $K(z)$ used
is the best fit profile (Figure 2) whose derivation is described
later.

Below ~100 km, eddy diffusion dominates mass transport.
Then the mixing ratio of a species will remain constant over
an altitude range in which its chemical lifetime $\tau(z)$ is more
than a factor of five larger than the transport time scale $\tau(z)$.
But above ~100 km, the various molecular diffusion time
scales become less than $\tau(z)$, thus resulting in different verti-
cal abundance profiles because of the different diffusion veloci-
Atures of each species. Therefore the 100 km level is the homopa-
use, below which the ‘chemically inert’ species have constant mixing ratios and above which separation occurs due
to different molecular diffusion rates. This explains the pro-
files of O, CO, and Ar in the lower thermosphere. The homopause altitudes individually derived from these different
species may differ due to the molecular diffusion variability
and the resulting sampling of eddy diffusion rates at different
altitude levels.

Below the homopause, when the chemical lifetime of a spe-
cies is within a factor of five of $\tau(z)$, the eddy diffusion profile
strongly influences the abundance profile of the species. Such
is the case for atomic O and H$_2$O in the lower thermosphere
and CO and H$_2$O in the mesosphere. At the mesopause (~80
km), O$_3$ is in photochemical equilibrium $\tau(O_3, 80) \ll \tau(O_2)$,
but its concentration is directly proportional to the mesopause
atomic O abundance which is controlled by eddy diffusion.
Thus O$_3$ at the mesopause is an indirect monitor of vertical
mass transport.

The eddy diffusion profile in model 1 was varied to give re-
sults which fit the measured profiles of O, O$_3$, CO$_3$, and Ar
above 90 km [Trinks et al., 1978; Trinks and Fricke, 1978]. As
the O$_3$ minimum at 80 km is affected by the downward trans-
port of atomic O and the upward transport of H$_2$O (M. Allen
and Y. L. Yung, in preparation, 1981), the eddy diffusion pro-
file was adjusted to minimize the calculated value for O$_3$ at

**TABLE 2. Models Used in Calculations**

<table>
<thead>
<tr>
<th>Model</th>
<th>Background Atmosphere*</th>
<th>Solar Cycle Phase</th>
<th>Earth Latitude</th>
<th>Season</th>
<th>H$_2$O Mixing Ratio 40 km</th>
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<td>38°N</td>
<td>July</td>
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<tr>
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<td>minimum</td>
<td>38°N</td>
<td>July</td>
<td>5 ppm</td>
<td>diurnal average</td>
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<td>minimum</td>
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<td>July</td>
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<td>diurnal average</td>
</tr>
<tr>
<td>5</td>
<td>midlatitude spring/fall</td>
<td>maximum</td>
<td>32°N</td>
<td>May</td>
<td>7 ppm</td>
<td>diurnal average</td>
</tr>
</tbody>
</table>

Fig. 1. A comparison of the model 1 results for the chemical lifetimes (dashed line) of major middle atmosphere species and the timescales for transport due to eddy diffusion (dotted line) and molecular diffusion (solid line). The species-dependent chemical lifetime and molecular diffusion curves are labeled with the appropriate species and, in the latter case, are shown only when they are less than the eddy diffusion values.

the mesopause to bring it into better agreement with the Aladdin 74 observations [Weeks et al., 1978].

In the lower thermosphere, the results of model 1 using the best fit eddy diffusion profile (Figure 2) agree well with the observations as is seen in Figure 3. As shown in Figure 4a, above 90 km the production of atomic O due to O2 photodissociation (reactions 1 and 2, Table 1) is significantly larger than the chemical loss of odd oxygen (atomic O being the most abundant species) due to reactions 12 and 17 (Table 1). This results in an increasing downward flux of atomic O (Figure 4b). On the other hand, the profiles of O2 and CO2 reflect the upward motion of these species. The derived value of K(z) at the homopause is thus constrained by two opposing effects: if K(z) is significantly reduced, the downward flow of atomic O is reduced and its concentration at 120 km is increased, but the upward flow of O2, CO2, and Ar is also reduced and their values at 120 km decrease. Complementary profile variations will occur if K(z) is significantly increased instead. Thus the resulting K(z) profile gives the best agreement between measured and calculated thermospheric O2, CO2, and Ar profiles and the atomic O profile above 105 km. The model results systematically lie on the high side of the uncertainty range for all the species above 110 km. This may be explained by dynamical perturbations of the atmosphere—tidal and internal gravity waves—that our numerical model does not account for, but which may influence the atmospheric structure [Trinks et al., 1978]. Atomic O may be particularly sensitive to tidal effects as demonstrated by the model calculations of Forbes [1978], which show significant tidal variability for all species around 120 km. But in the case of atomic O there is a maximum variation of ~20% in both diurnal and semi-diurnal modes that both peak in mid to late afternoon (precisely the time of the Aladdin 74 observations).

The atomic O peak at 98 km is an important feature resulting from transport in the lower thermosphere. If K(z) were constant above 90 km at a value of $1 \times 10^6$ cm$^2$ s$^{-1}$, all species (including atomic O) would monotonically decrease above this level. The only way to produce the atomic O peak with the right magnitude at the right altitude is to introduce a small K(z) for the range 92–98 km. The atomic O which otherwise would flow down to the mesopause is stopped at 98 km and accumulates. The observed rapid decrease in atomic O below the peak fixed the value of K(90).

The magnitude of eddy diffusion below 90 km has no effect on the O2, CO2, and Ar profiles in the lower thermosphere. However, the flow of atomic O down to the mesopause (as reflected in the abundance of O2) and the upward transport of H2O will be affected by the value of K(z) for the range 80–90 km. The chemical lifetime of H2O is only a little longer than $\tau_d(z)$, so the gradient of the H2O mixing ratio at the mesopause (Figure 5b) is sensitive to the values of $\tau_d(z)$. The eddy diffusion profile was chosen to minimize the O3 concentration at the mesopause minimum (M. Allen and Y. L. Yung, in preparation, 1981), but at the same time the resulting value for H2O at 90 km remaining consistent (which it does) with the unpublished result of H. Trinks from the Aladdin 74 flight (Figure 5b). The Trinks measurement marginally excludes the result for a drier atmosphere. The difference between the profiles for solar minimum and maximum conditions demonstrates the need for precise model simulation of observing conditions when a good theoretical fit to measurements is being attempted.

The mesospheric portion of the derived eddy diffusion profile was constrained to intersect the stratospheric eddy diffusion profile recommended by Hudson [1977] at the stratosopause (50 km). Since the magnitude of the O3 minimum at the mesopause is inversely related to the rate of upward transport of H2O in the mesosphere (M. Allen and Y. L. Yung, in preparation, 1981), the derived eddy diffusion coefficient increases with altitude to maximize the upward flux of H2O to the mesopause. The chemical lifetime of H2O places a maximum value on K(z) above which the rate of H2O transport cannot be effectively increased [Hunten, 1975]. In Figure 5b, the H2O profile of model 1 is seen to lie between the data of Waters et al. [1980] and Radford et al. [1977].

Observations of upper atmosphere CO can be used to check the K(z) profile derived for the mesosphere. The chemical lifetime of CO below 80 km is sufficiently close to the transport timescales so that the CO vertical profile reflects the magnitude of mesospheric eddy diffusion. Above ~55 km, the primary source of CO is the photodissociation of CO2 (reaction 34, Table 1). At the stratosopause, the dominant local production source becomes the oxidation of methane by odd oxygen species (OH, O, O(1D), reactions 35–37 in Table 1). (Addi-

Fig. 2. The best fit eddy diffusion profile derived in this paper (solid line) and a range of values (shaded area) for which the model results are still in relatively good agreement with the observations.
Fig. 3. A comparison of model 1 calculations (solid lines) and Aladdin 74 mass spectral observations with uncertainties included (shaded area) for (a) atomic O and O₂ and (b) CO₂ and Ar.

tional destruction of CH₄ by Cl is minimal and has not been included.) There are a number of intermediate steps in each oxidation sequence [Wofsy et al., 1972; Wofsy, 1976] but the net result for the conditions of the upper atmosphere can be well represented by the reaction sequences in Table 1 (with the assumption that the initial reaction with CH₄ is the rate-determining step). There is only one chemical loss mechanism known to be important for CO in the upper atmosphere: oxidation by OH to CO₂ (reaction 38, Table 1). The production and loss rates for CO due to these reactions are shown in Figure 6a. Above the mesopause, chemical loss is negligible, resulting in a downward flux of CO (Figure 6b). Below 75 km, CO is also not in photochemical equilibrium, but in this region the chemical loss rate is larger than the production rate. The magnitude of this chemical loss is proportional to the abundance of OH. The only available measurements of mesospheric OH (Anderson [1971], updated by Hudson and Reed [1979]) are shown in Figure 5a. The OH profiles from models 1–4 are presented to demonstrate the sensitivity of the OH profile to the phase of the solar cycle and the amount of mesospheric H₂O. The model 1 diurnally averaged profile is seen to be close to the profile of the model 2 diurnal calculation for 1816 local time, the time of Anderson’s observations. The fact that all the OH profiles are approximately the same demonstrates that the OH distribution depends most on the model kinetics. So the agreement with the Anderson measurements confirms the basic reaction scheme.

As the mesosphere is a sink for CO, the magnitude of the downward transport of CO strongly controls the mesospheric CO profile. One way of testing the best fit eddy diffusion profile is by comparing the model mesospheric CO profiles with observational results. W. J. Wilson has kindly communicated to us his accurately calibrated measurement of mesospheric CO emission at 115 GHz (J = 1–0 transition) made in May 1979 at Kitt Peak, Arizona (32°N). We used the CO results of model 5, which best simulates the circumstances of his observation, to calculate a CO emission profile for comparison with his observations. The results are shown in Figure 7. Figure 8 shows the CO mixing ratio profile from model 5. Considering

Fig. 4. Model 1 odd oxygen results. (a) Odd oxygen production (solid line) and loss rates (dashed line). (b) Atomic O vertical flux.

Fig. 5. (a) The altitude profiles of OH calculated in model 1 (solid line), model 2 for 1816 LST (dashed line), model 3 (dotted line), and model 4 (crosses) compared with the measurements of Anderson [1971] as updated in Hudson and Reed [1979] (A). (b) The altitude profiles of H₂O calculated in models 1, 3, and 4 (same symbols as in Figure 5a) compared with the observations of Radford et al. [1977] (R), Waters et al. [1980] (W), and H. Trinks (private communication, 1979) (T). Recent observations by S. Deguchi and D. O. Muhleman (private communication, 1980) yield a constant mixing ratio in accord with the Waters et al. [1980] result, but can be better explained by a varying mixing ratio profile close to that of model 3.
the estimated calibration uncertainty and the peak-to-peak noise in Wilson's observational data of ~0.08K, the CO emission line synthesized from the model 5 results and the observed emission line agree to within the observational uncertainty. The CO mixing ratio reported by Waters et al. [1976] is plotted in Figure 8 and is seen to be a factor of 2–3 higher than the model 5 profile for altitudes below 90 km. As a result, a synthetic CO emission profile calculated with the Waters et al. [1976] mixing ratio is twice as large as the observed profile. Since the emission at line center is most sensitive to the CO abundance in the 70–90 km range, the agreement between the observed and model 5 emission suggests that the eddy diffusion profile below 90 km as derived from early summer 1974 (solar minimum) observations is not significantly different from that in late spring 1979 (near solar maximum).

The best fit eddy diffusion profile which we have derived is shown as a solid line in Figure 2 and is summarized in Table 3. The shaded area in Figure 2 defines a range of values for the eddy diffusion profile which still would result in model profiles in reasonable agreement with the observational data.

**DISCUSSION**

Considering that the vertical profiles of several of our tracer species reflect chemistry in addition to transport, it is remarkable that a single set of species-independent variables—K(z)—could be determined which allows the model profiles to match observations so well. This is indeed surprising since many speculate that one-dimensional models cannot be expected to be accurate, that there are important dynamical processes which are not included, therefore limiting the validity of the models. Frederick [1979] shows how winds and internal gravity waves could result in large horizontal variations in the abundances of trace thermospheric species, which certainly would be seen in observations deviating from mean values predicted by the one-dimensional models. However, if the net effect of all of these short-term dynamical perturbations systematically remains constant over the lifetime of the measured species, this net effect may still be validly parametrized as eddy diffusion.

Out best fit eddy diffusion profile above 90 km is close to the value of Hunten [1975] derived from the homopause altitude obtained from Ar measurements von Zahn, 1970). The profile below 80 km is actually twice the values of Hunten [1975], as was suggested for the stratosphere by Hudson [1977].

In Figure 9, the best fit eddy diffusion profile is compared with eddy diffusion coefficients derived from direct observations of atmospheric motions. Below 60 km, our eddy diffusion profile is in good agreement with the 40°N summer values of Nastrom and Brown [1978], who analyzed rocketsonde data. Keneshea et al. [1979] calculated a minimum eddy diffusion profile for below 90 km using turbulent heat transfer theory. As such, there is no conflict between their profile and our derived profile, for below 80 km the slopes are the same but ours is offset by a factor of two. The magnitude (2 x 10^6 cm^2 s^-1) and altitude (80 km) of the maximum eddy diffusion coefficient is in surprising agreement with the independently calculated theoretical value of Lindzen [1980] for a summer atmosphere. Above 90 km, the eddy profile of Keneshea et al. [1979] was determined from observations of chemical trails [Zimmerman and Trowbridge, 1973]. Eddy diffusion coefficients for above 95 km have also been derived from radio and radar observations of ionospheric turbulence [Egel, 1978; Alcyade et al., 1979]. Where seasonal variations were reported, the summer observations were chosen for Figure 9. These latter 'direct' measurements of K(z) are much higher than our derived values, but are in some agreement with the widely varying numbers of Keneshea et al. [1979]. As this is the region in which molecular diffusion comes to dominate mass transport, our model calculations become less useful for deriving K(z), but model 1 runs using such high values for K(z) at the homopause yield results that do not agree well with observations. It should be noted that the K(z) deduced from direct observations refer to instantaneous values, whereas the K(z) of the current study is averaged over the lifetime of the tracer species.

A very interesting feature in our best fit eddy diffusion profile is the 'stagnant' layer extending from 92 to 98 km, which does not affect the O_2, Ar, and CO_2 concentrations at 120 km but is needed to produce the atomic O peak at 98 km. The large precipitous decrease of our profile at 92 km and the chemical trail result of Keneshea et al. [1979] are in very good agreement. Because this stagnant layer exists in our eddy diffusion profile, the model results of Keneshea et al. [1979] also yield an atomic O peak around 95 km. As the chemical trail data used by Keneshea et al. [1979] came from the Aladdin 1 experiment in November 1970 and the observational data we used from Aladdin 4 (June 1974), a stagnant layer in this part of the thermosphere appears to be a frequently recurrent, if not persistent, feature. It may indeed be a persistent feature, independent of season or solar cycle, since the mass spectra of Scholz and Offermann [1974] (March 1972), the resonance lamp observations of Dickinson et al. [1974] (April 1974), Thomas et al. [1979] (September 1975), and Howlett et al. [1980] (December 1975), and the airglow measurements of Watts et al. [1979] (July 1969) and Witt et al. [1979] (March 1975) all show an atomic O peak around this altitude. Moreover, Donahue and Carignan [1975] in their analysis of OGO 6 atomic O nightglow photometric data suggest a low value for K(z) in the lower thermosphere. The elucidation of a detailed physical mechanism that would generate this thermospheric structure is beyond the scope of this paper. Various theoretical dynamics models do exist in the literature, for example, Lindzen [1971]. However, this stagnant layer may simply reflect a stable atmosphere due to the small positive temperature gradient at the base of the thermosphere, analogous to the situation in the lower stratosphere.
Table 3. Best Fit Eddy Diffusion Profile

<table>
<thead>
<tr>
<th>Altitude Range, km</th>
<th>$K(z)$, cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$50 \leq z &lt; 70$</td>
<td>$2 \times 10^6 [z^{(-50/9.9)}]$</td>
</tr>
<tr>
<td>$70 \leq z &lt; 80$</td>
<td>$1.5 \times 10^6 [z^{(-70/34.8)}]$</td>
</tr>
<tr>
<td>$80 \leq z &lt; 90$</td>
<td>$7 \times 10^5 [z^{(-80/29.0)}]$</td>
</tr>
<tr>
<td>$90$</td>
<td>$1 \times 10^6$</td>
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<tr>
<td>$92-98$</td>
<td>$3 \times 10^5$</td>
</tr>
<tr>
<td>$z \geq 100$</td>
<td>$2 \times 10^5$</td>
</tr>
</tbody>
</table>

Discrepancy between their O/$O_2$ model results and the Aladdin 1 observations is most likely due to measurement error.

The earlier thermospheric models of Hunt [1971, 1973] and Thomas and Bowman [1972] yield values of ~1 for the 120 km O/$O_2$ concentration ratio and no atomic O peak at ~98 km. This is due to a systematic use of a large $K(z)$ above 100 km and a smoothly varying $K(z)$ profile below. Thomas and Bowman [1972] do note the need for a slower eddy diffusion profile if they were to produce a large O/$O_2$ ratio at 120 km to be consistent with the results of more accurate thermospheric mass spectroscopy just becoming available at the time of their paper. However, an atomic O peak at ~100 km is seen in the results of Koshelev [1976] when the eddy diffusion profile that decreases rapidly at ~95 km is used (i.e., the atmosphere is stagnant above), but he does not state any causal relationship. Moreels et al. [1977] produce an atomic O peak at ~90 km, but they do not discuss the significance of this feature and the $K(z)$ profile used in generating this result is not clearly stated.

The decrease in the H$_2$O mixing ratio from the stratopause to the lower thermosphere reflects the intensity of the solar radiation field (see Figure 5b for an illustration of the difference due to the phase of the 11-year solar cycle) and the magnitude of eddy diffusion in the upper mesosphere. The H$_2$O gradient in the Keneshea et al. [1979] model is similar to ours since the mean transport time at the relevant altitude in both cases is similar. On the other hand, Hunt [1971, 1973] has too sharp a gradient, which is probably due to his slow eddy diffusion profile at 80 km (upward transport not being able to replenish the H$_2$O lost due to photodissociation). The mesospheric H$_2$O gradients of Thomas and Bowman [1972], Koshelev [1976], and Moreels et al. [1977] are approximately the same as ours, but the combinations of solar flux and transport differ among the papers so the explanation of the results is not clear.

Figure 7 demonstrates that the differences between our model CO mixing ratio profile and that of Waters et al. [1976] (see Figure 8) would result in significantly different rotational line spectra. (The CO microwave line measured by Waters et al. [1976] is almost twice as strong as the recent unpublished measurement by W. J. Wilson; the difference may be due to long-term variations in the mesospheric CO profile.) The results of Goldsmith et al. [1979] would also produce CO spectra different from what W. J. Wilson observed. An intercomparison of the results of our models 1–5 reveals that this discrepancy cannot be accounted for by seasonal, solar cycle, or H$_2$O content effects. So the variance between our CO mixing ratio profile and the profiles derived from published observations may be due to measurement errors, errors in the post-observation deconvolution analysis, or differences in the transport rates at the times of the observations.

A major difference between our CO model calculations and previous work, besides the use of different eddy diffusion rates, is the temperature dependence of our CO$_2$ cross sections. In the thermosphere, as the temperature increases rap-
ignore, some CO₂ cross sections will increase, resulting in a larger CO production rate than would occur otherwise. At the mesopause, where the temperature is as much as 100° below the temperature at which the cross sections were measured, the CO production rate will be reduced by this effect. In the thermosphere, this CO production rate temperature dependence, along with the choice of appropriate CO and CO₂ boundary conditions, results in the CO profile crossing the CO₂ profile at 109 km (model 1). The crossing point in the solar maximum calculation (model 4) is 2 km lower.

Most of the previously published mesospheric carbon chemistry models yield CO profiles quite different from ours. The pioneering model of Hays and Olivo [1970] gives too much CO in the lower mesosphere by a factor of 10–100. The fact that they find CO to be in photochemical equilibrium below 70 km (cf. our Figure 6) must mean that their CO₂ photodissociation rate is too large (as described above) and/or their OH concentrations too small, both effects leading to an increase in the predicted CO abundance. The Wofsy et al. [1970] CO profile is smaller than ours above the mesopause, which may result from their using a k(2) = 5 × 10⁴ cm³ s⁻¹ above 70 km, causing CO to be moved too rapidly through this region. As the CO peak brightness temperature is most sensitive to the 70–90 km CO distribution, the Wofsy et al. [1972] profile would yield a 115 GHz CO microwave emission line much weaker than observed (the microwave line calculated for the Wofsy et al. [1972] CO profile is given by Waters et al. [1976]). Since the models of Hunt [1973], Whitten et al. [1973], and Shimazaki and Cadle [1973] have less mesospheric OH than ours, their mesospheric CO is systematically greater. Also, their temperature, independent CO₂ cross sections contribute to this result. In addition, the CO-CO₂ crossing altitude is too high in Hunt [1973] and Shimazaki and Cadle [1973].

**Conclusions**

The vertical distributions of long-lived species in the terrestrial mesosphere and lower thermosphere are controlled by several factors: kinetics, solar radiation, and vertical transport. We have shown that an eddy diffusion profile can be derived that will give good agreement between predicted and observed distributions for various species if the solar flux values for the appropriate phase of the 11-year solar cycle and the kinetics are carefully modeled. This eddy diffusion profile provides information on the mean dynamical structure of the middle atmosphere.

Since we utilized only a limited number of observations, the eddy diffusion coefficients presented in this paper may only be appropriate for midlatitudes in late spring and early summer, but are possibly independent of the phase of the solar cycle. Other sets of rocket mass spectrometer data are available (C. R. Philbrick, private communication, 1980; D. Offermann, private communication, 1980), which could be analyzed by the approach used in this paper to yield eddy diffusion profiles for various seasons and latitudes. Indeed, extensive analysis of OGO 6 OI green line nightglow photometer data [Was-

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>Hydrostatic Calculation, K</th>
<th>Millstone Hill Data, K</th>
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*Trinks et al. [1978] total density and mass density data used.
†Average of Millstone Hill observations at 2002 and 2035 UT, June 29, 1974 (W. Oliver, private communication, 1980).
‡Below 90 km, close to the tabulations in the 1966 U.S. Standard Atmosphere Supplements.
ser and Donahue, 1979, and references therein] suggests significant latitudinal variation in thermospheric transport.

In addition, it would be valuable to have a long-term program of regularly conducted simultaneous observations of trace species profiles which would allow monitoring of variations in the chemical and dynamical nature of the mesosphere and lower thermosphere. The O/NO group is important for measuring \( K(z) \) at the homopause and in the lower thermosphere region just below. If measurements sensitive to the thermospheric CO could be made, variations in the vertical profile of the CO/CO\(_2\) ratio would also reflect thermal structure and radiation field changes. As mesospheric O\(_3\) concentrations reflect the magnitude of the downward flux of atomic O from the thermosphere and the upward transport of H\(_2\)O from the stratopause, simultaneous radio observations of H\(_2\)O, O\(_3\), and CO could be used to separate the effects of diurnal chemistry and systematic changes in the radiation field and eddy diffusion rate below 90 km. Of these various group measurement programs, the last set of observations can be instituted most easily since the necessary technology is currently available.

**APPENDIX: DERIVATION OF TEMPERATURE PROFILE ABOVE 80 KM**

We calculated a temperature profile for the atmosphere above 90 km at the time of the Trinks et al. [1978] rocket flight using the total density and mass density reported by Trinks et al. and assuming that the atmosphere was hydrostatic. The results of this calculation are presented in Table 4 along with the incoherent scatter radar data obtained at Millstone Hill simultaneous with the Aladdan 74 rocket flight (W. Oliver, private communication, 1980). Above 110 km, the Millstone Hill temperature profile is much closer to the 1966 U.S. Standard Atmospere Supplements (USASS) 30°N July profile than is the profile derived from the hydrostatic calculation. Below 105 km there are no radar results; the hydrostatic temperatures show wavelike structure and are significantly cooler than the 1966 USASS profiles. This probably reflects the perturbed nature of the atmosphere at the time of the rocket flight [Trinks et al., 1978]. Since the lifetimes of the species we are considering in this paper are longer than the diurnal period, their profiles reflect the long-term average atmospheric temperature. Therefore we chose a thermospheric temperature profile that follows the Millstone Hill data above 110 km, below which altitude we then guess at a smoothly varying profile that fits with the 1966 profile below 90 km.

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