Abstract—The dependence of the atmospheric distributions of CO$_2$ and CO upon the combined effects of photochemical production and loss, and transport is examined. It is found that, for CO$_2$, deviations from complete mixing are possible in the mesosphere and upper stratosphere. Further, sufficient quantities of CO may be maintained, as a product of CO$_2$ photodissociation, to be aeronomically significant.

The role of carbon dioxide as a major participant in the transfer of infrared radiation through the Earth's atmosphere has been apparent for many years (Gold, 1909). Moreover, both the recent suggestion of using the 4.3 $\mu$m and 15 $\mu$m bands of CO$_2$ as means by which to measure remotely atmospheric temperature (Kaplan, 1959), and the recognition of the role played by CO$_2$ in the thermal budget of the mesosphere (Curtis and Goody, 1956) have greatly increased our understanding of its importance. Ultimately, the accuracy of such studies must depend upon a knowledge of the distribution of CO$_2$ in the upper atmosphere. This discussion briefly considers the factors which influence the distribution of CO$_2$ in the stratosphere, mesosphere, and lower thermosphere.

Carbon monoxide has been measured at concentrations of between 0.1 and 0.2 ppm in the troposphere (Robinson and Robbins, 1967). Thought to be chiefly the product of automobile exhausts, it has become a major air pollutant in this century. Little is known of its abundance in the upper atmosphere and the proximity of its molecular mass to that of N$_2$ precludes mass spectrometric identification.

Carbon dioxide is continuously produced at or near the Earth's surface by combustion and biological decay, and is also released from the oceans (Robinson and Robbins, 1967). Turbulent mixing within the troposphere should be sufficiently rapid that complete mixing is a valid assumption. In the past it has been assumed that this is true for the stratosphere, mesosphere, and lower thermosphere as well. However, in both the mesosphere and thermosphere CO$_2$ is dissociated and/or ionized by solar (u.v.) radiation. Thus, either a vertical flux must be maintained or the resulting CO must recombine locally in order to balance this loss. Recombination is thought to occur both by the three body process:

\[(a) \quad \text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M} \quad K_a = 10^{-24} \text{ cm}^3/\text{sec at } 300^\circ\text{K} \quad (\text{Kaufman, 1968}).\]

and by the two body process:

\[(b) \quad \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad K_b = 1.5 \times 10^{-13} \text{ cm}^3/\text{sec at } 300^\circ\text{K} \quad (\text{Kaufman, 1968}).\]

Estimates of process (a) suggest a significant effect on the vertical flux below about 60 km. The effect of process (b) is much less clear due to the present state of uncertainty in the OH distribution. Using the time constants for transport and recombination as a basis for comparison, and assuming an OH concentration as large as given by Hestvedt (1967), as an upper limit, one finds that above 70 km transport dominates but local photochemical equilibrium will prevail below that level. Because of the uncertainties the following

*On leave from NASA-Langley Research Center.
two limiting cases were considered: (1) no recombination; and (2) full recombination of CO below 70 km and none above. These cases should encompass the possible variations of CO₂ and CO in the atmosphere.

The general method employed here in calculating the distributions of CO₂ and CO is similar to that used by Colegrove, Hanson and Johnson (1965, 1966), where both molecular and eddy diffusion as well as photochemical production and loss are considered. It is found that the problem can be simplified by introducing a parameter, $\zeta$, which equals the ratio of the actual mixing ratio of a species to that for the zero flux case. A brief discussion of the formulation is contained in the Appendix.

The dissociation rate for CO₂ used in these calculations is a global average obtained from CO₂ cross sections as listed in Table 1, with values for solar u.v. flux and total absorption cross sections taken from Hinteregger, Hall, and Schmidtke (1965). An atmospheric model essentially the same as the CIRA-1965 model is used.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>165–580 Å</td>
<td>Romand (1966)</td>
</tr>
<tr>
<td>Solar lines: 303-8 Å, 765-1 Å, 708-7 Å, etc.</td>
<td>Cairns and Samson (1965)</td>
</tr>
<tr>
<td>580–1675 Å (except solar lines)</td>
<td>Nakata, Watanabe and Matsunaga (1965)</td>
</tr>
<tr>
<td>1675–1775 Å</td>
<td>Thompson, Harteck and Reeves (1963)</td>
</tr>
</tbody>
</table>

The molecular diffusion coefficients for CO₂ and CO were taken from Chapman and Cowling (1939) and Lettau (1951). The eddy diffusion coefficients, $K_T$, used in this study fall naturally into the categories of stratospheric and upper atmospheric values. In the stratosphere, the maximum, minimum and global averages of the seasonal-latitude values of $K_T$, given by Gudiksen et al. (1968) were adopted. These three mixing profiles were extrapolated from 27 to 50 km. to match the upper atmospheric value; they are shown in Fig. 1, labelled C, D and E. Between 50 and 120 km an equilibrium eddy diffusion coefficient was determined from an earth-averaged thermal model (Olivero, 1970) in a manner similar to Johnson and Wilkins (1965) and Johnson (1968). Above 120 km $K_T$ was allowed to decrease exponentially. The eddy diffusion profile adopted as well as the range of values associated with the uncertainties in the inputs to the thermal model are shown in Fig. 1. Thus three models of eddy diffusion were chosen and used in all calculations corresponding to maximum, minimum and average mixing in the stratosphere and average mixing above 50 km.

The time independent continuity equation was integrated between the tropopause (12 km) and 200 km for each of the combinations of the three eddy diffusion profiles and two characterizations of recombination. The CO₂ volume mixing ratio was set at $3.145 \times 10^{-4}$, the average sea level value (Bolin and Keeling, 1963) at the tropopause and the CO volume mixing ratio was set at $1 \times 10^{-7}$ (Robinson and Robbins, 1967) at the tropopause.

The results of the calculations for CO₂ and CO are shown in Fig. 2. It is apparent that the question of recombination is not significant for CO₂ within the limits of eddy diffusion considered. On the other hand, the CO mixing ratio is critically dependent upon
recombination. The limits of eddy diffusion and recombination used in these calculations lead to more than two orders of magnitude uncertainty in the CO mixing ratio in the upper stratosphere and lower mesosphere. However, in the thermosphere the uncertainty is reduced to less than a factor of two, and CO is shown to be a significant minor constituent. Because of the importance of these results to aeronomical studies confirming experimental evidence would be highly desirable.
Any measurement of CO in our atmosphere will be quite difficult in practice to accomplish. One might observe the Cameron or the fourth positive bands which arise from transitions to the $^3\Delta_T$ and $^5\Pi_T$ levels respectively. But these transitions are either forbidden or hidden by nitric oxide and molecular oxygen bands in the same region of the spectrum. However, if actual measurements of the carbon monoxide concentration in the mesosphere and thermosphere could be made and were to give results significantly below the minimum profile of Fig. 2 the assumed CO$_2$ dissociation rate would be seriously questioned. Such a result would suggest that the apparent CO$_2$ absorption continua above the 903 Å ionization threshold are partially made up of unresolved band systems which do not lead to appreciable dissociation. This conclusion might shed new light on the low atomic oxygen concentration in the Martian atmosphere.

Acknowledgement—This work was supported by National Aeronautics and Space Administration Grant NASr-54 (03) and National Science Foundation Grant GA-1025.

REFERENCES


APPENDIX

The CO$_2$ and CO distributions are described by the following equations, respectively:

\[
\frac{\partial \gamma_2}{\partial z} = \frac{\partial \gamma_1}{\partial z} = \frac{\varphi_{\text{dis}} + \varphi_{\text{ion}}}{N(D_4 + K_T)}
\]

\[
\frac{\partial \gamma_1}{\partial z} = \frac{\varphi_{\text{dis}}}{N(D_4 + K_T)} - \frac{\gamma_1 D_1}{(D_4 + K_T)} \frac{H - H_1}{HH_1}
\]

where: $\gamma_1$ is the actual CO$_2$ mixing ratio
$\gamma_2$ is the zero flux CO$_2$ mixing ratio
$\gamma_2 = \gamma_2 \exp \left\{ -\int_0^t \frac{D_4 (H - H_4)}{HH_4} \right\}$
\( \varphi_{\text{dis}} \) is the photochemical induced flux from dissociation

\[
\varphi_{\text{dis}} = \int_z^\infty \tilde{\gamma}_0 N \zeta J_{\text{dis}} \, dz
\]

\( J_{\text{dis}} \) is the dissociation rate, per molecule

\( \varphi_{\text{ion}} \) is the photochemical induced flux from ionization

\[
\varphi_{\text{ion}} = \int_z^\infty \tilde{\gamma}_0 N \zeta J_{\text{ion}} \, dz
\]

\( J_{\text{ion}} \) is the ionization rate, per molecule

\( N \) is the total number density

\( D_0 \) is the effective molecular diffusion coefficient for CO

\( K_\gamma \) is the eddy diffusion coefficient

\( H \) is the atmospheric scale height

\( H_\gamma \) is the specific scale height for CO

\( \gamma_i \) is the actual CO mixing ratio

\( D_i \) is the effective molecular diffusion coefficient for CO

\( H_i \) is the specific scale height for CO.

Both equations were integrated between the tropopause (12 km) and the arbitrary upper boundary at 200 km for each of the combinations of mixing and recombination. The following boundary conditions were employed:

(a) \( \gamma_i^p = 3.145 \times 10^{-4} \) at \( z = 12 \) km.

(b) \( \gamma_i^p = 1.0 \times 10^{-7} \) at \( z = 12 \) km.