CARBON DIOXIDE AND MONOXIDE
ABOVE THE TROPOSPHERE

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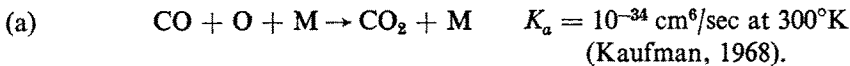University of Michigan, Ann Arbor, Mich. 48105, U.S.A.

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 $4\cdot3\ \mu$ and $15\ \mu$ 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) $\qquad CO + O + M \rightarrow CO_2 + M \qquad K_a = 10^{-34}\ cm^6/sec$ at $300°K$
$$\text{(Kaufman, 1968).}$$

and by the two body process:

(b) $\qquad CO + OH \rightarrow CO_2 + H \qquad K_b = 1\cdot5 \times 10^{-13}\ cm^3/sec$ at $300°K$
$$\text{(Kaufman, 1968).}$$

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 Hesstvedt (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

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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 CO_2 and CO in the atmosphere.

The general method employed here in calculating the distributions of CO_2 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, ζ, 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 CO_2 used in these calculations is a global average obtained from CO_2 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 1. SOURCES OF CARBON DIOXIDE CROSS SECTIONS

Wavelength	Reference
165–580 Å $\left(\begin{array}{c}\text{except } 303 \cdot 8 \text{ Å}\\ \text{solar line}\end{array}\right)$	Romand (1966)
Solar lines: 303·8 Å, 765·1 Å, 708·7 Å, etc.	Cairns and Samson (1965)
580–1675 Å $\left(\begin{array}{c}\text{except solar}\\ \text{lines}\end{array}\right)$	Nakata, Watanabe and Matsunaga (1965)
1675–1775 Å	Thompson, Harteck and Reeves (1963)

The molecular diffusion coefficients for CO_2 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-latitudinal 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 CO_2 volume mixing ratio was set at $3 \cdot 145 \times 10^{-4}$, the average sea level value (Bolin and Keeling, 1963) at the tropopause and the CO volume mixing ratio was set at 1×10^{-7} (Robinson and Robbins, 1967) at the tropopause.

The results of the calculations for CO_2 and CO are shown in Fig. 2. It is apparent that the question of recombination is not significant for CO_2 within the limits of eddy diffusion considered. On the other hand, the CO mixing ratio is critically dependent upon
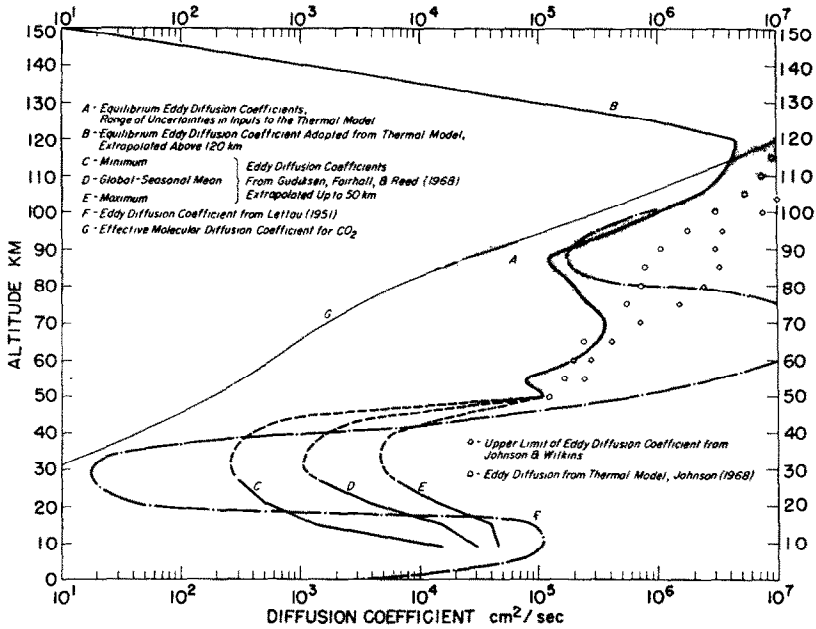
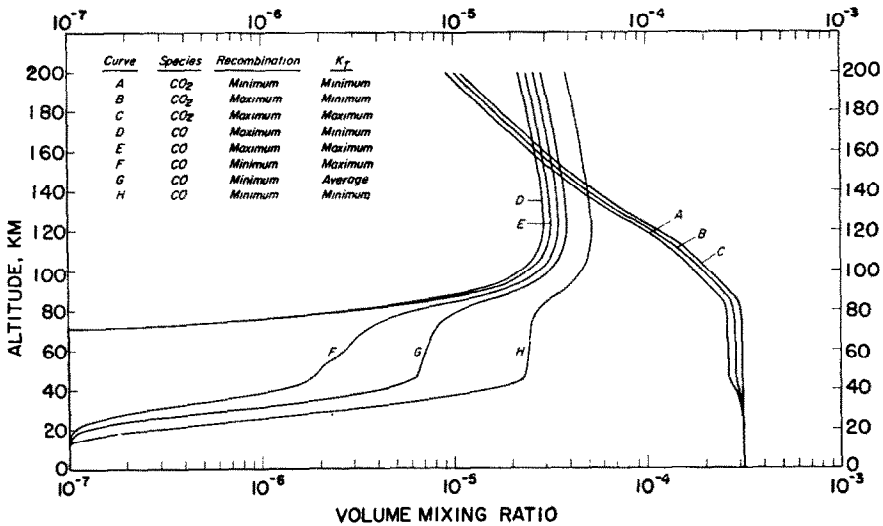FIG. 1. EDDY DIFFUSION COEFFICIENTS USED ALONG WITH OTHER ESTIMATES.

FIG. 2. CALCULATED PROFILES OF THE VOLUME MIXING RATIOS OF CO_2 AND CO.

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 $\frac{3}{a}\pi$ and $\frac{1}{a}\pi$ 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.

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APPENDIX

The CO_2 and CO distributions are described by the following equations, respectively:

$$\frac{d\zeta}{dz} = \frac{d}{dz}\frac{\gamma_2}{\bar{\gamma}_2} = -\frac{\varphi_{dis} + \varphi_{ion}}{\bar{\gamma}_2 N(D_2 + K_T)} \tag{1}$$

$$\frac{d\gamma_1}{dz} = \frac{\varphi_{dis}}{N(D_1 + K_T)} - \frac{\gamma_1 D_1}{(D_1 + K_T)}\frac{H - H_1}{HH_1} \tag{2}$$

where: $\zeta = \gamma_2/\tilde{\bar{\gamma}}_2$
γ_2 is the actual CO_2 mixing ratio
$\bar{\gamma}_2$ is the zero flux CO_2 mixing ratio

$$= \bar{\gamma}_2{}^0 \exp\left\{-\int_{z_0}^z \frac{D_2}{(D_2 + K_T)}\frac{(H - H_2)}{HH_2}\,dz\right\}$$

φ_{dis} is the photochemical induced flux from dissociation

$$= \int_z^\infty \bar{\gamma}_2 N \zeta J_{\text{dis}} \, dz$$

J_{dis} is the dissociation rate, per molecule
φ_{ion} is the photochemical induced flux from ionization

$$= \int_z^\infty \bar{\gamma}_2 N \zeta J_{\text{ion}} \, dz$$

J_{ion} is the ionization rate, per molecule
  N is the total number density
  D_2 is the effective molecular diffusion coefficient for CO_2
  K_r is the eddy diffusion coefficient
  H is the atmospheric scale height
  H_2 is the specific scale height for CO_2
  γ_1 is the actual CO mixing ratio
  D_1 is the effective molecular diffusion coefficient for CO
  H_1 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) $\gamma_2{}^0 = 3 \cdot 145 \times 10^{-4}$ at $z = 12$ km.

(b) $\gamma_1{}^0 = 1 \cdot 0 \times 10^{-7}$ at $z = 12$ km.