Estimates of eddy diffusion coefficient
in the Mars' atmosphere

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RESUMEN

Se presentan nuevos cálculos para determinar el perfil con la altura del coeficiente de difusión turbulenta en la atmósfera de Marte basados en la integración de las ecuaciones de continuidad y movimiento acopladas para el oxígeno atómico y el monóxido de carbono. Se obtienen valores en el intervalo 2×10^7 - 4×10^8 cm^2 s^{-1} capaces de explicar los perfiles observados de estos compuestos. El perfil del coeficiente de difusión turbulenta deducido es compatible con otros publicados y se discute su efecto sobre la concentración de los diferentes constituyentes atmosféricos. La turbopausa se encuentra localizada entre 130 y 140 km, siendo la difusión molecular el proceso de transporte más rápido a alturas superiores a 160 km.

ABSTRACT

New calculations are presented on the eddy diffusion coefficient profile in the height range 30-200 km in Mars' atmosphere based on the integration of the coupled continuity and motion equations for atomic oxygen and carbon monoxide. Values in the range 2×10^7 - 4×10^8 cm^2 s^{-1} are determined and are able to explain the observed altitude profiles of these compounds. The eddy diffusion coefficient altitude profile deduced is compatible with others reported in the literature and we discuss its effect upon the concentration of the different atmospheric constituents. The turbopause level is located between 130 and 140 km, the molecular diffusion being the fastest transport process at altitudes above 160 km.

1. Introduction

Vertical transport of the atmospheric constituents is mainly produced by turbulent and molecular diffusion. The different processes able to produce and propagate turbulence have been studied by several authors (see e.g., Ebel, 1980 and references therein). It is essential to understand the nature of the eddy turbulence in the middle atmosphere, since it is a predominant controlling factor for both the composition and thermal structure of this region. Unfortunately, a global theory for turbulence allowing a simple calculation of the strength of turbulence related to basic geophysical parameters is not yet available. Following the early works of Lettau (1951) and Colegrove *et al.* (1965, 1966), it is usual to describe the turbulence using the concept of eddy diffusion. In this way, when one-dimensional models of the atmosphere are developed, the turbulent diffusion is parameterized by means of a factor called eddy diffusion coefficient, K. The adoption of an effective eddy diffusion coefficient and the corresponding eddy flux, analogous to molecular diffusion coefficient, D, and molecular flux, allows us to study the effect of eddy turbulence on the atmospheric composition. The considerable influence exerted by the height variation of the eddy diffusion coefficient profile on the altitude distribution of the concentration of certain compounds at mesospheric levels in the martian atmosphere is well known. Although in the last few years considerable efforts have been made to determine the temporal, seasonal and height

variation of the eddy diffusion coefficient, it still remains the least known factor when it comes to constructing models of the atmosphere. Nevertheless, a great number of studies, mainly on the role of turbulence in the terrestrial atmosphere, have contributed to our knowledge on turbulence and its influence on minor compounds. Kong and McElroy (1977a, b), Izakov (1978), von Zahn *et al.* (1980) and von Zahn and Hunten (1982), have presented a critical analysis of the eddy diffusion coefficient profiles used in different martian atmosphere models. In most of these, an eddy diffusion coefficient was chosen to adjust the abundance of certain compounds (see e.g., Nier and McElroy, 1977). Other indirect methods have been used to estimate the values of the eddy diffusion coefficient in the middle and upper atmosphere. Anderson and Leovy (1978) provide, by means of observations with TV cameras in the planetary limbs of aerosol layers from the Mariner 9 orbiter and assuming a particle radii of 1 μm, a value for $\dot{K}$ of 2×10^6 and 7×10^6 cm^2 s^{-1} at 35 and 45 km, respectively, after a dust storm, and a value of $(2\text{-}14) \times 10^7$ cm^2 s^{-1} at 50-60 km during the storm. In the lower atmosphere, Zurek (1976) estimated, from atmospheric tides theory, an upper limit for the value of K equal to 5×10^7 cm^2 s^{-1} in the 30-80 km altitude region. From dayglow measurements, Krasnopolsky (1975) derived a value for K equal to 2×10^8 cm^2 s^{-1} at 160 km with a CO_2 concentration of 5×10^9 cm^{-3} which agrees well with Viking landers data, from which a value of $(1.3\text{-}4.4) \times 10^8$ cm^2 s^{-1} was deduced with the same concentration of CO_2, but at an altitude of 140 km. Later, Krasnopolsky and Parshev (1977, 1979) obtained a value of 3×10^6 cm^2 s^{-1} in the lower troposphere (up to $\sim$ 30 km), based on the analysis of diurnal variation of water vapour content and its rotational temperature. Similar values for heights of about 30 km were obtained using the data on the aerosol distribution at these heights (Krasnopolsky, 1979). In order to adjust the O_3 concentration, these authors assumed a gradual variation of K within the 30-40 km region up to a value 3×10^7 cm^2 s^{-1}. The scarcity of reliable data on K and their scatter together with the expected high seasonal and latitudinal variation, reveal that there is still considerable uncertainty about the values of K in the middle and upper martian atmosphere.

We have developed a new Mars' atmosphere theoretical non-steady model for middle latitudes in equinox conditions with moderate solar activity in the 30-200 km region to compute the height and temporal variation of the carbon, oxygen and hydrogen compounds: CO_2, CO, $O(^3P)$, $O(^1D)$, O_2, O_3, H, H_2, H_2O, OH, H_2O_2 and HO_2. In this model, which will be published elsewhere, a new eddy diffusion coefficient was used. The aim of this paper is to present these new calculations on the eddy diffusion coefficient altitude profile based on the integration of the coupled continuity and motion equations for certain minor constituents to determine which value of K explains the observed altitude profiles of these compounds. We also present a discussion of the influence of the eddy diffusion coefficient on the altitude distribution of the minor compounds in the 30-200 km altitude range.

2. Derivation of K

The continuity and momentum equations for each constituent may be expressed as (Stubbe, 1973)

$$\frac{\partial n_i}{\partial t} = P_i - n_i l_i - \frac{\partial}{\partial z}(n_i v_i) \tag{1}$$

$$\phi_i = n_i V_i - D_i \left(\frac{\partial n_i}{\partial z} + \frac{n_i(1 + \alpha_i)}{T} \frac{\partial T}{\partial z} + \frac{n_i}{H_i} \right)$$

$$-K\left(\frac{\partial n_i}{\partial z} + \frac{n_i}{T}\frac{\partial T}{\partial z} + \frac{n_i}{H}\right) \tag{2}$$

where: i is the ith constituent; t is local time; n_i is concentration; P_i is photochemical production; l_i is specific photochemical loss; z is altitude; v_i is mean vertical velocity; ϕ_i is vertical flux; V_i is friction velocity; D_i is molecular diffusion coefficient; α_i is thermal diffusion coefficient; T is temperature; H_i is individual scale height; K is eddy diffusion coefficient; and H is atmospheric scale height.

The second term on the right hand side in equation (2) represents the flux due to molecular diffusion. If molecular diffusion predominates in an atmospheric region, this flow acts rapidly and continues until a situation of diffusive equilibrium is reached. The third term represents the net flux resulting from eddy diffusive mixing. This flux will be 0 if the relative abundance of the ith constituent remains constant with the altitude, i.e., the atmosphere is uniformly mixed. The vertical eddy diffusion coefficient is considered as a parameter controlling the intensity of the vertical mixing effect and this is stronger for larger values of K. In this case, the distribution of the constituents is in accordance with the average atmospheric scale height H.

Turbulent and molecular diffusion are processes very competitive. It is known that turbulent diffusion predominates in lower regions and thus, the relative concentration of the the constituents with a large photochemical characteristic time remains constant with altitude. At higher altitudes, the characteristic time of molecular diffusion is smaller than that of turbulent diffusion and the atmospheric compounds are distributed, at different velocities, according to their individual scale heights, H_i. In general, there is a broad transition region, in which both processes act simultaneously and thus the constituents cannot be considered to be either well mixed or in a diffusive equilibrium situation. This region is usually called *turbopause*. As explained above, K is a parameter representing the mean vertical atmospheric motion and its values do not depend on the constituent considered. On the other hand, each compound has its own associated molecular diffusion coefficient so that, it is better to consider a turbopause for each compound rather than a global atmospheric turbopause.

In stationary conditions, the introduction of equations (2) into equations (1) and the integration over altitude results in the expression

$$\phi_t = \int_z^\infty \left(P_i - n_i l_i - \frac{\partial}{\partial z}\phi_m\right)dz \tag{3}$$

where ϕ_t and ϕ_m are the turbulent and molecular fluxes, respectively. It is assumed that the turbulent flux is zero at the infinity.

As Krasnopolsky and Parshev (1979) claimed, the study of the distribution of the atmospheric minor compounds is the most reliable procedure for the determination of K. To derive a time-independent profile for K, we have used the method described by Battaner (1975). Basically, the procedure consists of the integration of the coupled continuity and motion equations for atomic oxigen and carbon monoxide to determine which value of K explains the experimental O- and CO-profiles. We have chosen O and CO because their abundances are found to be very much affected by turbulent transport. This could explain the great observed abundance of CO_2 and the low densities of O and CO against the rapid CO_2 photodissociation caused by UV solar radiation (McElroy and Donahue, 1972; Parkinson and Hunten, 1972).

We have adopted the O- and CO-profiles recommended by COSPAR in its Mars reference atmosphere (McElroy *et al.*, 1977; Stewart and Hanson, 1982) on the basis of the mass spectrometer measurements taken by the Viking 1 and 2 landers during descent. P_i and l_i for O, and CO in equation (3) are computed taking into account the photochemical processes listed in Table I, which can be considered as the main chemical sources and sinks for these compounds when constructing martian atmosphere models (see e.g., Lindner, 1988). The photodissociation coefficients were calculated following the same method described in the Rodrigo *et al.*'s (1986) model, and the values at the top of the atmosphere are given in Table I. To compute ϕ_m it is also necessary

TABLE I. Photochemical scheme

No.	Reaction	Coefficient†	Reference*
1	$CO + O + CO_2 \rightarrow CO_2 + CO_2$	$k_1 = 2 \times 10^{-37}$	Slanger *et al.* (1972)
2	$CO + OH \rightarrow CO_2 + H$	$k_2 = 6.0 \times 10^{-13}(0.25 + A[M]/(1 + A[M]))$ $A = 1.82 \times 10^{-20}$	
3	$O(^3P) + O_2 + CO_2 \rightarrow O_3 + CO_2$	$k_3 = 6.0 \times 10^{-34}(T/300)^{-2.3}$	
4	$O(^3P) + O_3 \rightarrow O_2 + O_2$	$k_4 = 8.0 \times 10^{-12} \exp(-2060/T)$	
5	$O(^3P) + O(^3P) + CO_2 \rightarrow O_2 + CO_2$	$k_5 = 9.4 \times 10^{-34} \exp(484/T)$	Hampson (1980)
6	$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$	$k_6 = 7.4 \times 10^{-11} \exp(117/T)$	
7	$O(^3P) + OH \rightarrow O_2 + H$	$k_7 = 2.2 \times 10^{-11} \exp(117/T)$	
8	$O(^3P) + HO_2 \rightarrow OH + O_2$	$k_8 = 3.0 \times 10^{-11} \exp(200/T)$	
9	$H + HO_2 \rightarrow H_2O + O$	$k_9 = 2.96 \times 10^{-12}$	
10	$O(^3P) + H_2O_2 \rightarrow H_2O + O_2$	$k_{10} = 1.4 \times 10^{-12} \exp(-2000/T)$	
11	$CO_2 + h\nu \rightarrow CO + O(^1D)$	$J_\infty = 5.6 \times 10^{-8}$	see text
12	$CO_2 + h\nu \rightarrow CO + O$	$J_\infty = 5.6 \times 10^{-9}$	see text
13	$O_3 + h\nu \rightarrow O_2 + O$	$J_\infty = 3.6 \times 10^{-3}$	see text
14	$O_2 + h\nu \rightarrow O + O(^1D)$	$J_\infty = 3.1 \times 10^{-8}$	see text
15	$O_2 + h\nu \rightarrow O + O$	$J_\infty = 1.1 \times 10^{-6}$	see text
16	$HO_2 + h\nu \rightarrow OH + O$	$J_\infty = 2.6 \times 10^{-4}$	see text

† All values are quoted in the molecule cm s system

* Except as noted, reaction rate constants are those recommended by DeMore *et al.* (1985)

to know the temperature profile and the diffusion coefficients. Two different temperature profiles were adopted. The first (see Fig. 1) has been taken from the same COSPAR reference model and the second is that obtained experimentally by the Viking 2 lander. The altitude profiles of other constituents, mainly O_2 and CO_2 are also necessary for the computations, and again they were taken from the COSPAR model.
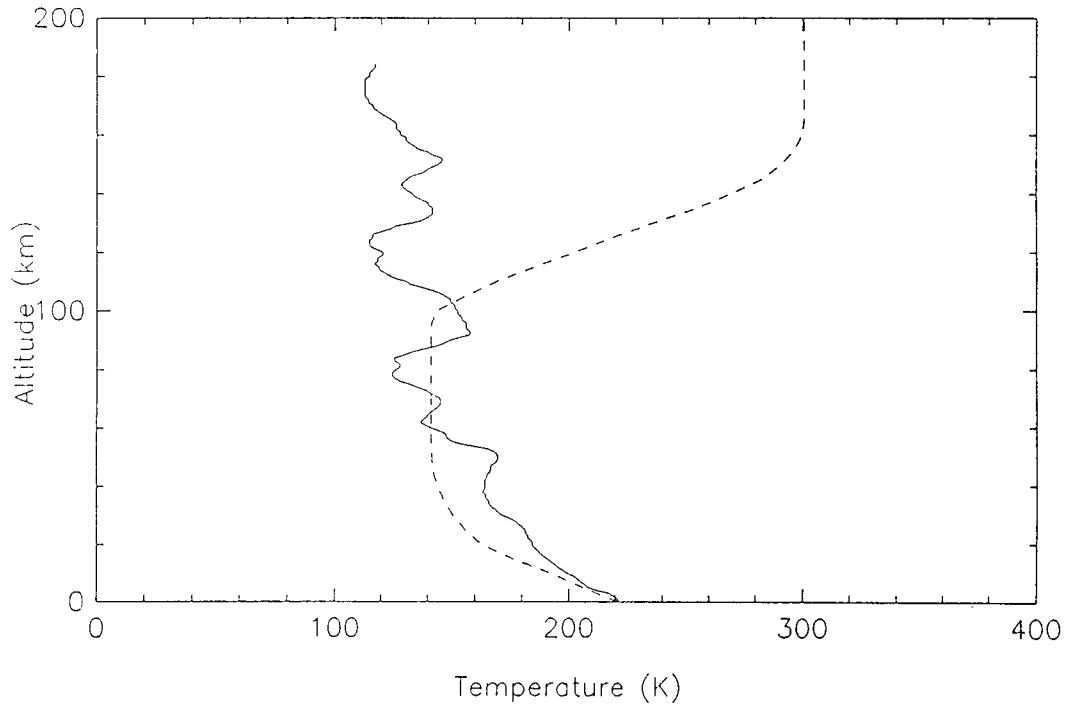
Fig. 1. Temperature profiles of the martian atmosphere considered in the model. Solid line: from Viking 2 entry science data (Seiff and Kirk, 1977); Dashed line: COSPAR reference model.

The molecular diffusion coefficients were calculated, according to Stubbe's (1973) formulation, by means of

$$D_i = \frac{H_i g}{\sum_{j \neq i} n_j S_{ij}} \qquad (4)$$

where g is the gravity acceleration and S_{ij}, for gases consisting of rigid sphere molecules with a Maxwellian distribution function are given by

$$S_{ij} = \frac{16}{3} \frac{\mu_{ij}}{m_i} \sigma_{ij}^2 \{\frac{\pi k T}{2\mu_{ij}}\}^{1/2} \qquad (5)$$

where σ_{ij} is the sum of the colliding gas kinetic radii, m_i is the mass, μ_{ij} is the reduced mass, and k is the Boltzmann constant.

The values obtained for D_i at noon have been plotted in Fig. 2. The diffusion coefficient corresponding to atomic hidrogen is the largest, as it corresponds to the lightest mass, and reaches a value of 3.7×10^9 cm^2 s^{-1} at 170 km. Molecular hidrogen also has a higher diffusion coefficient at 170 km (2.7×10^9 cm^2 s^{-1}) than that corresponding to the other compounds, which take values of about 9×10^8 cm^2 s^{-1} at the same altitude.
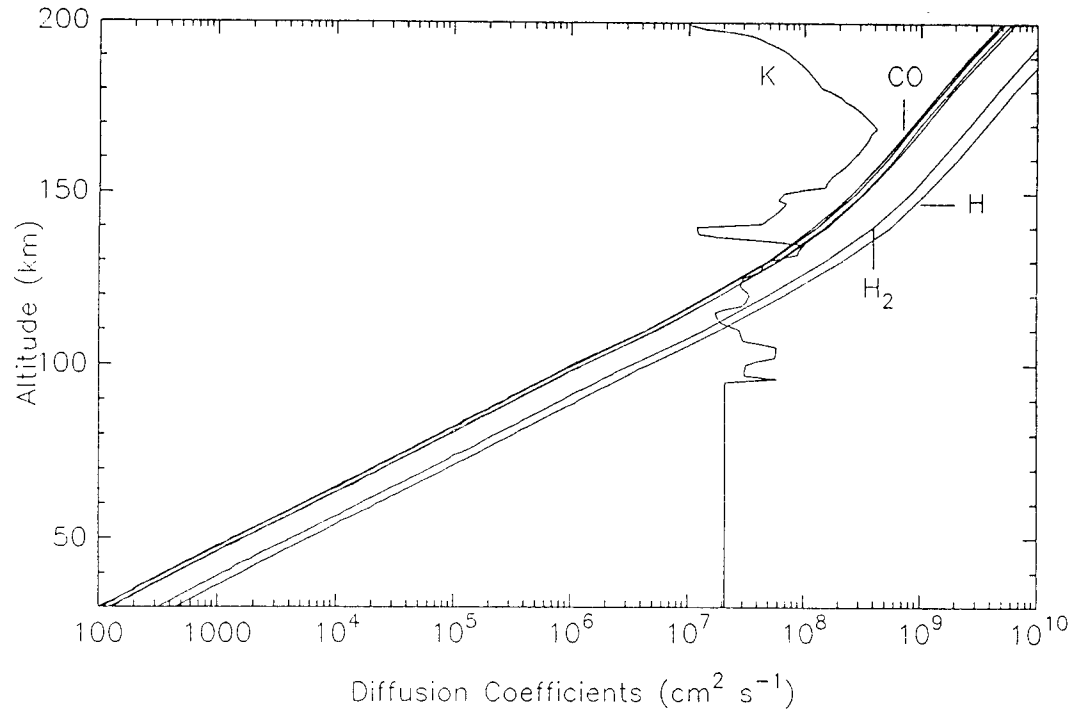
Fig. 2. Eddy and molecular diffusion coefficients profiles at noon, as defined in the text.
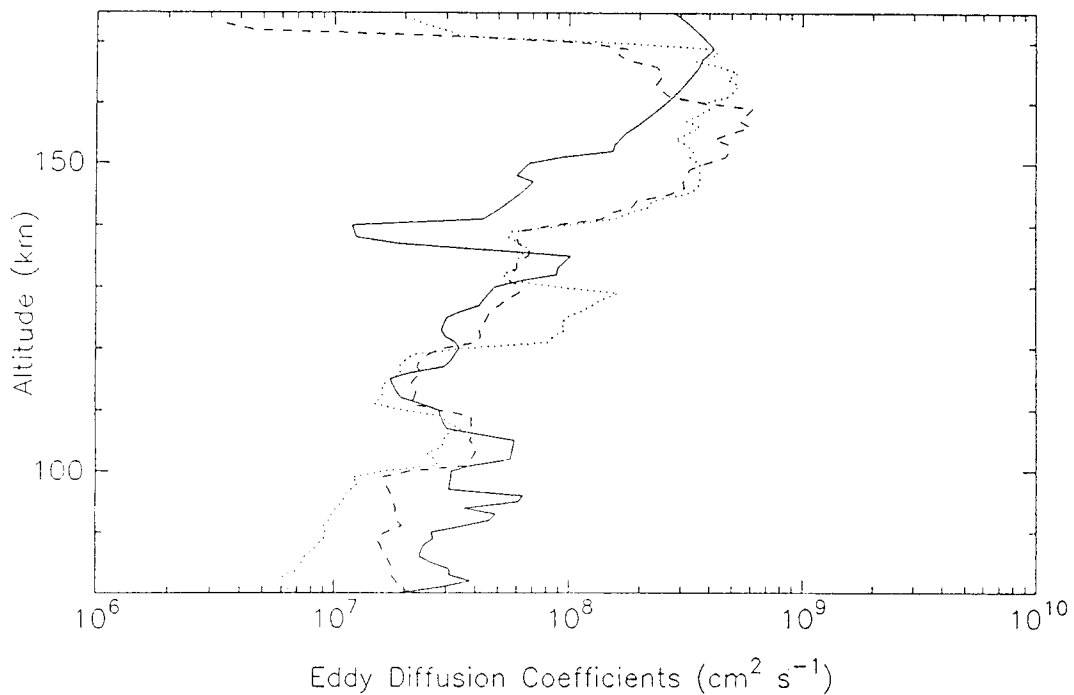

Fig. 3. Different calculated eddy diffusion coefficient profiles. Solid line: considering CO-abundances and temperature profile from COSPAR reference model; Dotted line: considering CO-abundances and temperature profile from Viking 2 entry science data; Dashed line: considering O-abundances and temperature profile from Viking 2 entry science data.

Once ϕ_t is computed, K can be calculated making use of Lettau's (1951) classic expression

$$K = \frac{\phi_t}{n\frac{d}{dz}(\frac{n_i}{n})} \tag{6}$$

where n is the total number of molecules.

The K profiles obtained using equations (3) and (6) for both O- and CO-profiles and considering the two temperature profiles mentioned above are shown in Fig. 3. The results are very similar, with values for the eddy diffusion coefficient somewhat higher in the 140-160 km range when the Viking 2 experimental profile for T is used.

The method described here to compute K is reliable when turbulent diffusion predominates or, at least, competes on more or less equal terms with either molecular diffusion (in the upper region) or chemical processes (in the lower region), but not otherwise. The integral in equation (3) is computed by means of a summation and considering a height step of 1 km. The partial derivatives in equations (3) and (6) at a determined altitude are substituted by their corresponding finite differences taking into account the values of the variables at 1 km above and below the considered altitude. On the other hand, the numerator in equation (6) is approximately constant between 120 and 170 km. Its values depend very much on the O_2 and CO_2 concentration profiles and the magnitude of K is very sensitive to this choise. Moreover, if in this region ϕ_t is approximately constant, the shape of the K-profile will be given by the denominator in equation (6), which in turn depends exclusively on the O- or CO-abundances. Thus, it is possible to obtain the shape of the K profile more reliably than its absolute value, by using a realistic O- or CO-profile. The K-profiles obtained, using both O and CO concentration profiles, agree very well both qualitatively and quantitatively, and this gives us confidence in the computed absolute values for K.

3. Discussion

In the development of the atmosphere theoretical non-steady model we have adopted the K-profile obtained by using CO concentrations because experimental results on CO abundances are available and because CO is a constituent chemically less active than the atomic oxygen. Below 90 km, where the method is not applicable, a constant value equal to 2.1×10^7 cm^2 s^{-1} was chosen for K in accordance with different theoretical and semi-experimental results indicating that values for K around 10^7 cm^2 s^{-1} are required to explain the aeronomy of the lower martian atmosphere. In Fig. 4, the K-profile proposed is plotted, together with others reported in the literature for comparison. Our profile shows a typical shape with different turbulent layers and its absolute values are, in general, in good agreement with those obtained by other authors.

Up to $\sim$ 130-140 km, eddy diffusion dominates transport processes, as can be seen in Fig. 2. At about 160 km the molecular diffusion is the fastest process, ensuring diffusive equilibrium at 200 km, where the upper boundary of the model was placed. The turbopause level, between 130 and 140 km, is also in agreement with other determinations.

Nier *et al.* (1976) and Nier and McElroy (1977) in their analysis of the Viking data, obtained a K-profile by correlating the altitude profiles of constituents with different molecular masses, N_2, Ar, CO and O_2, measured by the Viking landers. The turbopause was located at 120-125 km with a CO_2 concentration equal to 5×10^{10} cm^{-3}. These authors concluded that the eddy
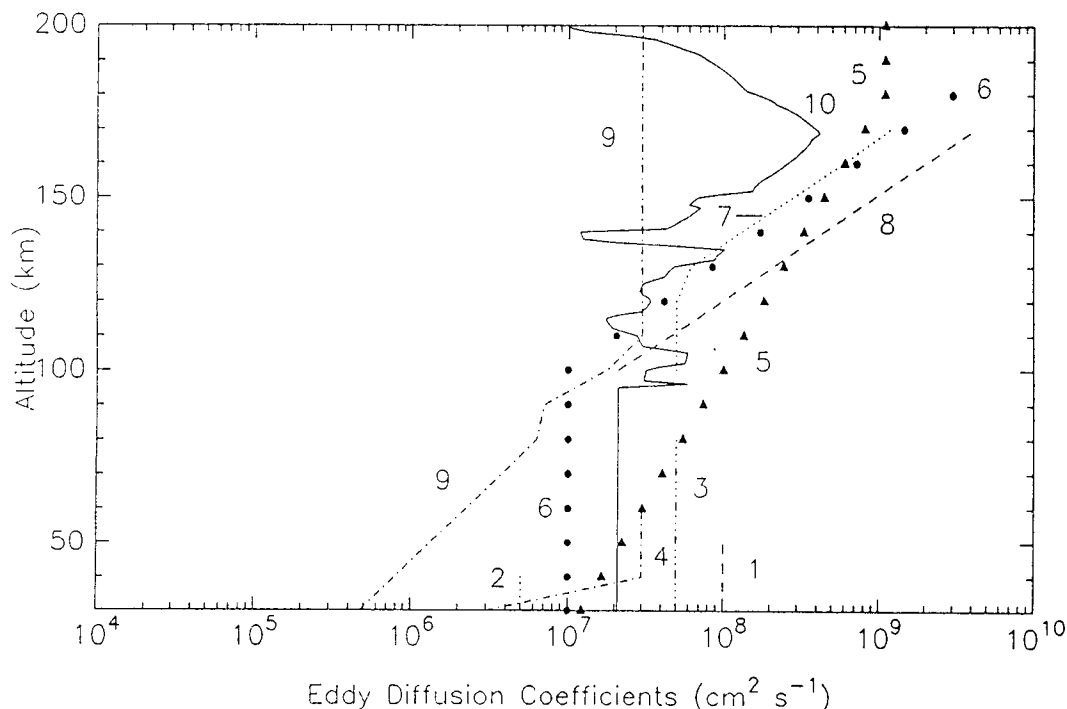
Fig. 4. Different eddy diffusion coefficient profiles. 1. McElroy and Donahue (1972); 2. Parkinson and Hunten (1972); 3. Zurek (1976); 4. Krasnopolsky and Parshev (1979); 5. Shimazaki (1981); 6. Shimazaki and Shimizu (1979); 7. Nier *et al.* (1976); 8. Nier and McElroy (1976); 9. Krasitskii (1978) and 10. This model.

processes cannot play a primary role in the martian atmosphere at altitudes above 140 km, while the martian atmosphere must be mixed to heights greater than 130 km, and this implies an eddy diffusion coefficient of at least 5×10^7 cm^2 s^{-1}. The same data were later analyzed by Izakov (1978), who made a critical analysis of the retrieval method for atmospheric temperature, and, consequently, for the eddy diffusion coefficient profile, carried out by McElroy *et al.* (1976) and Nier and McElroy (1976, 1977). He found that the use of a value for K equal to 5×10^7 cm^2 s^{-1} constant in the range 100-150 km and $K(z)$ values rapidly decreasing at altitudes higher than 150-170 km, yields a better agreement between theoretical predictions and measurements of the altitude profiles of minor compounds in the altitude range between 110 and 200 km.

Figures 5a and 5b show the concentration profiles at noon of the different compounds obtained in the theoretical model using the K-profile calculated in this paper. A detailed analysis of the temporal variation of the concentrations of the atmospheric constituents and their altitude profiles will be given elsewhere. Here we shall just analyse the influence of the eddy diffusion coefficient profile on the altitude distribution of the compounds summarily. It is well known that the altitude profile of the eddy diffusion coefficient has a negligible influence on the CO_2- and O_2-concentration profiles throughout the altitude range considered here. In the same way, photochemical models of the martian middle atmosphere are relatively insensitive to values assumed for K between 0 and 30 km (Kong and McElroy, 1977a). It is clear, however, that dynamic mixing acts very rapidly at altitudes above 90 km and the effective eddy diffusion coefficient must be in excess of 10^7 cm^2 s^{-1}. In the lower atmosphere, a lower intensity of turbulent mixing corresponds to higher values of the CO and O_3 concentration. Atomic oxygen is the compound most affected and its concentration increases in the 70-110 km region up to one order of magnitude, when a value 5 times greater for
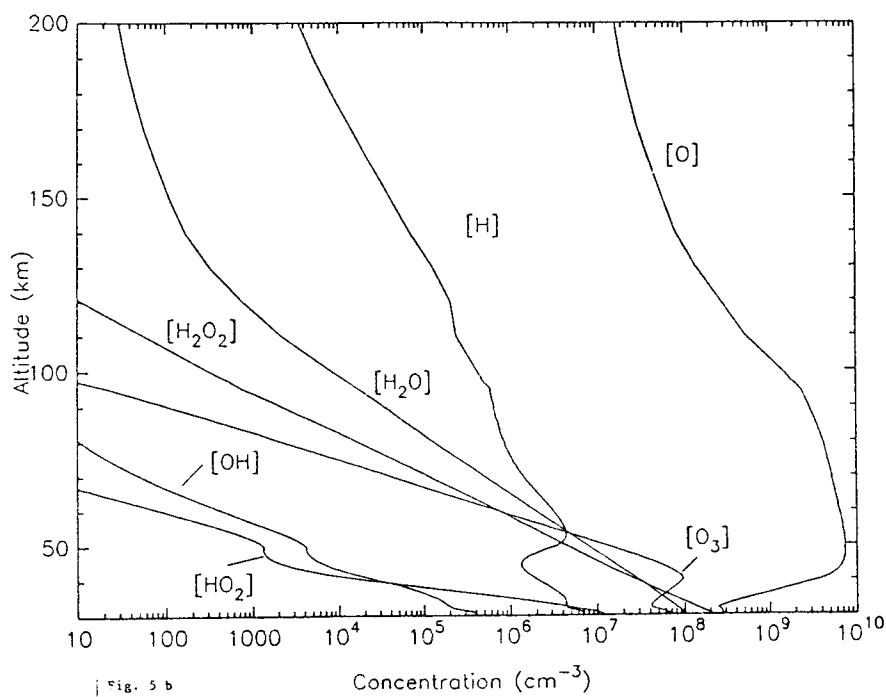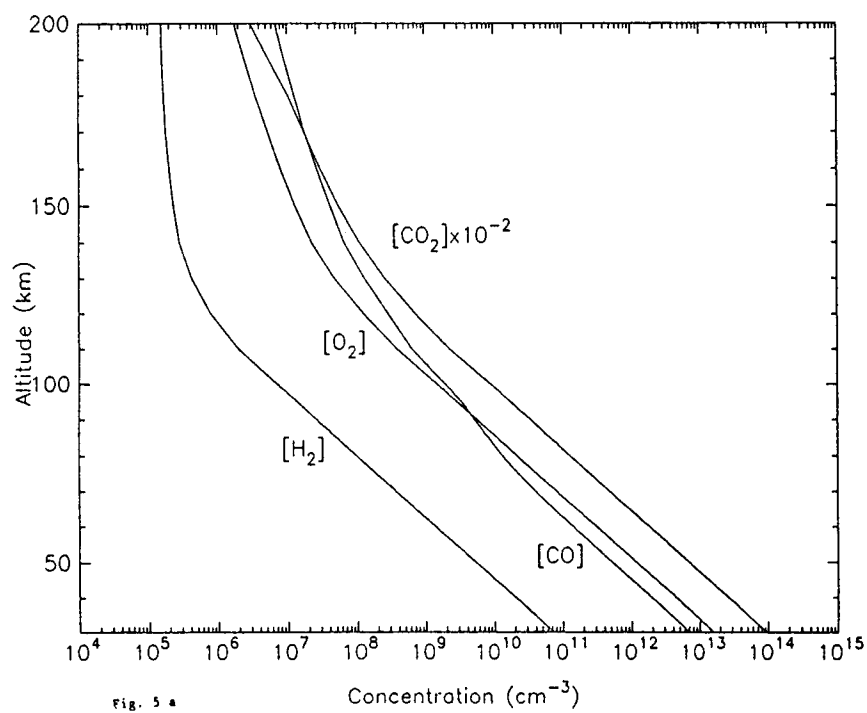
Fig. 5. Noon concentration profiles (30-220 km) for the atmospheric compounds considered in the model.

K is used. In this way, measurements of diurnal variations of O concentration at these heights would enable us to assess the intensity of turbulent mixing (Krasitskii, 1978). Moreover, H_2 and H concentrations decrease as a consequence of smaller values for K in the lower atmosphere, and this decrease is more dramatic at the upper boundary of the model. In the thermosphere, however, as K increases, the total abundances of H_2 and H are seriously affected at altitudes above 90 km, the H_2 concentration increasing up to almost two orders of magnitude at 200 km, if K increases by a factor of 5. In general, higher values of K at altitudes above 100 km produce lower abundances of O, CO and H in this region down to values incompatible with the experimental results. The use of lower values of K in the middle atmosphere leads to a dry thermosphere, since the upward transport of H_2O is affected by the values of K in the 80-110 km altitude range.

Von Zahn *et al.* (1980) argued that the K-profiles derived from the Viking 1 and 2 results of Nier and McElroy (1977) as well as the eddy diffusion coefficient profile measured in the venusian thermosphere at 130-170 km and in the Earth's atmosphere from 30 to 85 km may be represented by the relationship $K = A \, n^{-1/2}$, having A the value 1.4×10^{13}. Individual properties of the planets are revealed via the range of number density, n, which is valid for this expression. In the martian atmosphere this range is 10^{12} - 10^9 cm^{-3} or, in other words, between 100 and 170 km approximately. The dependence between K and n reflects the increase of amplitudes of gravity waves with altitude. The fact that constant A is the same for the three planets is, however, very surprising and has not been yet explained. We have run the theoretical composition model through the computer using a K-profile derived from the von Zahn *et al.*'s (1980) relationship in the 100-170 km altitude range with a constant value equal to 1.5×10^7 $cm^2 \, s^{-1}$ from 30 to 100 km. As we have seen, CO_2 and O_2 concentrations show similar distributions to those obtained in the model using the K-profile proposed here. The atomic oxygen concentration, however, has higher values in all the altitude range, being the maximum variation up to a factor of 4. The concentration profile of carbon monoxide is practically unaffected by using this K-profile as compared with that obtained using the K-profile adopted in the general model. Hydrogen compounds are the compounds most affected by the adoption of the K-profile derived from the relationship proposed by von Zahn *et al.* (1980). Molecular hydrogen concentration reaches extremely high values, up to four orders of magnitude (especially at altitudes above 120 km), which are not compatible with the observations. The same occurs for the atomic hydrogen concentration, when the K-profile recommended by von Zahn *et al.* (1980) is used. The values obtained for $[H]$, 2×10^7 cm^{-3} at 200 km, are up to three orders of magnitude higher than those predicted by the general model and those determined from airglow measurements by Mariner 6, 7 and 9 and by Mars 3 and 5 spacecraft (see e.g., Anderson and Hord, 1971; Anderson, 1974; Bertaux *et al.*, 1975; Krasnopolsky and Krysko, 1976). Ozone concentration presents a maximum near 40 km in the martian atmosphere. Great seasonal and latitudinal variation has been detected by satellite (Barth *et al.*, 1973; Lane *et al.*, 1973; Krasnopolsky *et al.*, 1979) and ground-based measurements (Noxon *et al.*, 1976; Traub *et al.*, 1979). Considerable diurnal variability of the O_3 maximum is to be expected (Shimazaki, 1981) and this is predicted in the model with midnight values up to a factor of 20 higher than noon values. From a general point of view, as K increases at altitudes above 40 km, the O_3 maximum is higher in absolute value, but lower in altitude and the ozone layer is narrower. Moreover, when the K-profile derived from the relationship $K = A \, n^{-1/2}$ is adopted, the same values of the ozone concentration at noon and at midnight at altitudes above 50 km are obtained, and this does not agree with the expected higher values of O_3 concentration during the night because of not only the absence of photodissociation of O_3 but also the rapid interchange of odd-oxygen species.

4. Conclusions

We have tried to estimate values for the eddy diffusion coefficient profile capable of explaining the observed abundances of atomic oxygen and carbon monoxide in the martian atmosphere. The method described here is in line with the previous work of Battaner (1975), Rodrigo *et al.* (1981) and Battaner and Rodrigo (1981) for the computation of the eddy diffusion coefficient altitude profile in the terrestrial atmosphere. The results show that turbulence plays a primary role in the distribution of the atmospheric compounds at altitudes below 130-140 km, where the turbopause can be placed. Vertical mixing is stronger than in the terrestrial atmosphere, reaching K values up to two orders of magnitude greater at levels of the same atmospheric densities. Values as high as 4×10^8 cm^2 s^{-1} are obtained in the thermosphere, which are compatible with other estimations. The results on the neutral composition of the atmosphere obtained in a non-steady theoretical model using the K- profile computed in this paper agree very well with the observed abundances of the atmospheric constituents and their diurnal variation. Measurements of the altitude distribution of some minor constituents, especially atomic oxygen, could allow a more accurate determination of the vertical mixing.

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