On the spatial distribution of some hydrogen components in the mesosphere and lower thermosphere

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ABSTRACT

On the basis of a photochemical oxygen–hydrogen atmosphere model the concentrations of OH, HO_2, H_2, H_2O and H were computed as a function of height, latitude and season. The computations were made for two values of the hydrogen/air mixing ratio, differing by a factor of about 100. Atomic hydrogen was found to be the major hydrogen constituent above about 85 km, while water vapor takes up almost all hydrogen at levels below about 75 km. In the shallow layer between these two regimes molecular hydrogen enters as the major hydrogen component. The seasonal and latitudinal variation was found to be relatively small. The effect of the air motion is discussed. An ascent of 1 cm/s near the high latitude summer mesopause seems to be necessary to keep the moisture content high enough for ice clouds to form.

1. Introduction

Only a few successful attempts have been made to measure the concentrations of the major hydrogen components, H, H_2 and H_2O, in the upper atmosphere. The results obtained are by far insufficient to make it possible to draw even a sketch of the spatial distribution of these components. At present the only way to approach this problem seems to be construction of theoretical atmosphere models. In such models a set of chemical reactions is prescribed and if the recombination rates and the necessary radiation data are known, the use of meteorological data such as pressure, temperature and wind makes it possible to compute the concentrations of the various components.

A photochemical oxygen–hydrogen atmosphere model was first constructed by BATES & NICOLET (1950). This model has later been used by other authors. However, improved knowledge of the recombination rates and radiation data, as well as more detailed meteorological informations makes it desirable to recompute the concentrations from time to time. Such a revision has been made by HESSTVEDT (1964, 1965). The present work may be regarded as an extention of these papers. Recent data for the recombination and dissociation rates have been used, and the influence of the choice of total amount of hydrogen is discussed.

2. The oxygen–hydrogen atmosphere model

As mentioned above, the atmosphere model proposed by BATES & NICOLET was adopted. The concentrations of the pure oxygen components are, at most levels, determined by the five reactions from the pure oxygen atmosphere model:

$O + O + M \rightarrow O_2 + M$	$k_1 = 2.8 \times 10^{-33}$ cm^6 sec^{-1}
$O + O_2 + M \rightarrow O_3 + M$	$k_2 = 2.8 \times 10^{-34}$ cm^6 sec^{-1}
$O + O_3 \rightarrow 2O_2$	$k_3 = 8 \times 10^{-12} \times e^{-3.26/RT}$ cm^3 sec^{-1}
$O_2 + h\nu \rightarrow 2O$	$J_2 = 5.71 \times 10^{-6}$ sec^{-1} for zero optical depth
$O_3 + h\nu \rightarrow O + O_2$	$J_3 = 9.85 \times 10^{-3}$ sec^{-1} for zero optical depth.

In most cases the introduction of reactions involving hydrogen causes only an unimportant revision of the results from the pure oxygen atmosphere model. But in the vicinity of the mesopause atomic oxygen is destroyed by recombination with OH and HO_2 to form O_2.

The values of the recombination rates k_1 and k_2 seem to be fairly well established. Recent laboratory experiments by REEVES, MANNELLA & HARTECK (1960), MORGAN & SCHIFF (1963) and KAUFMAN & KELSO (1961) resulted in the k_1-value given above, whereas BARTH (1961)

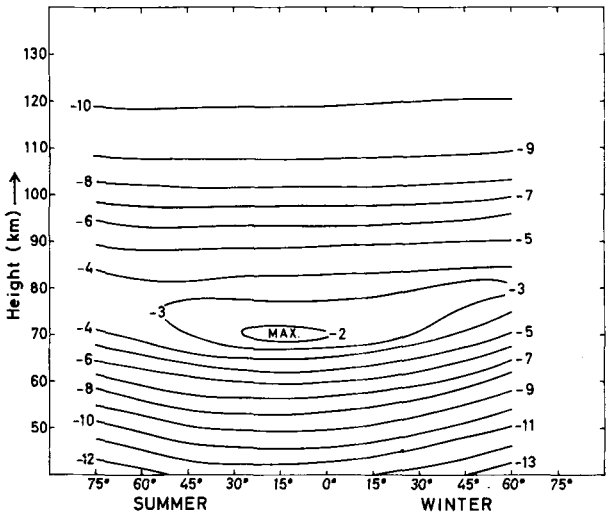

FIG. 1. Relative concentration of OH, defined as the ratio $[OH]/\Sigma_H$ where Σ_H denotes the total number of hydrogen atoms per cm^3, for the "dry" case (i.e. for a water vapor mixing ratio of 1.8×10^{-6} g/g).

mentions a value almost three times higher. k_2 has recently been determined by ELIAS, OGRYLZO & SCHIFF (1959). Their value, indicated above, was used in the present paper. A somewhat different value, lower by a factor of about 2, was obtained by KAUFMAN & KELSO (1961).

The determination of a representative value for k_3 seems to be much more difficult, and the results obtained by various authors differ often by orders of magnitude. The value adopted in this paper was calculated by CAMPBELL & NUDELMAN (1960) on the basis of experiments by LEIGHTON, URBACH, WOJTOWICZ & ZASLOWSKY (1960). One reason for selecting this value was that, in combination with the selected k_2-value, it gives a good agreement between theoretical determination and observed values of the ozone content at about 30 km, where photochemical equilibrium should be expected.

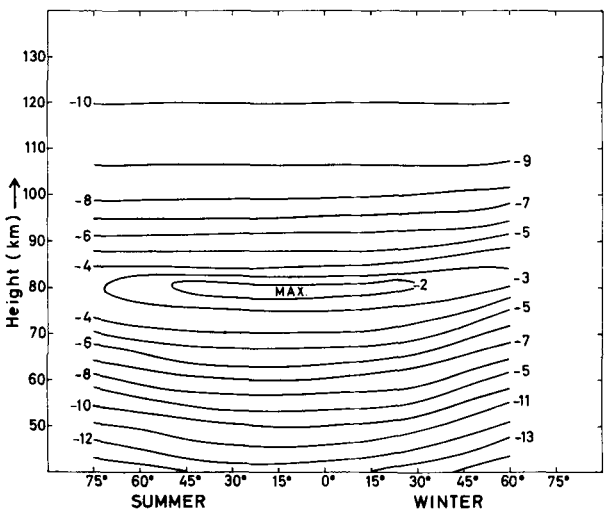

FIG. 2. Relative concentration of OH, defined as the ratio $[OH]/\Sigma_H$ where Σ_H denotes the total number of hydrogen atoms per cm^3, for the "moist" case (i.e. for a water vapor mixing ratio of 1.5×10^{-4} g/g).

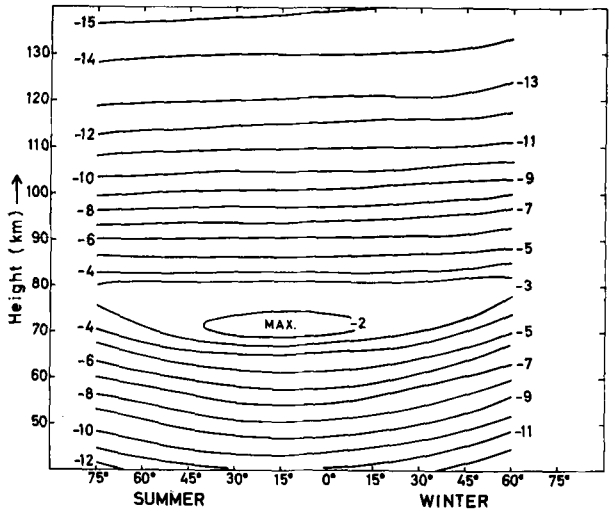

FIG. 3. Relative concentration of HO_2, defined as the ratio $[HO_2]/\Sigma_H$ where Σ_H denotes the total number of hydrogen atoms per cm^3, for the "dry" case (i.e. for a water vapor mixing ratio of 1.8×10^{-6} g/g).

For the dissociation rates J_2 and J_3 the values recently computed by DÜTSCH (private communication) have been used.

The reactions involving hydrogen used in the present paper are the same as those used in earlier works by the author. These reactions and the recombination rates will not be reproduced here; reference is made to earlier works (HESSTVEDT, 1964, 1965).

Meteorological data were taken from the temperature and density profiles, for every 15 degrees of latitude, summer and winter, published by COLE & KANTOR (1963).

Most likely the greatest uncertainty in the results rests upon the choice of value for the total amount of hydrogen. During the last fifteen years a series of measurements of water vapor have been made up to about 30 km, most of them indicating a considerable increase with height of the mixing ratio from about 20 km.

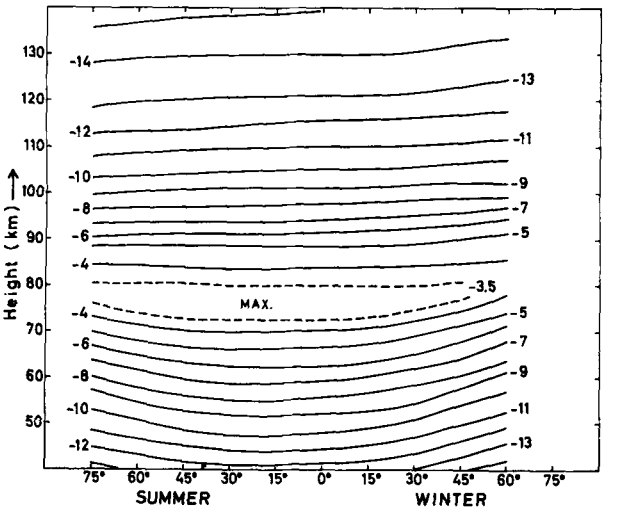

FIG. 4. Relative concentration of HO_2, defined as the ratio $[HO_2]/\Sigma_H$ where Σ_H denotes the total number of hydrogen atoms per cm^3, for the "moist" case (i.e. for a water vapor mixing ratio of 1.5×10^{-4} g/g).

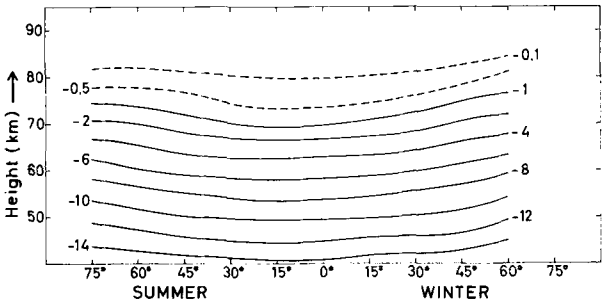

FIG. 5. Relative concentration of H, defined as the ratio $[H]/\Sigma_H$ where Σ_H denotes the total number of hydrogen atoms per cm³, for the "dry" case (i.e. for a water vapor mixing ratio of 1.8×10^{-6} g/g).

The mean value at 30 km was found to be 1.5×10^{-4} g/g (GUTNICK, 1962). Later, much doubt has been thrown on the validity of these measurements, and measurements by MASTENBROOK (1963) and by GOLDSMITH (1964) do not show any increase in the mixing ratio with height. Their values for the mixing ratio lie very close to 1.8×10^{-6} g/g, constant for all levels.

Although the general opinion seems to return to the "dry" stratosphere again, we cannot say that the problem of stratospheric humidity has been conclusively solved. Consequently it is of interest to compute the concentrations of the atmosphere for two different cases, using the two values for the water vapor mixing ratio mentioned above. (These two cases will be referred to as the "dry" and "moist" case.)

3. Results of the computations

The dissociation rates J_2, J_3 and J_{H_2O} depend on the optical depth of molecular oxygen and ozone along the path of the sun's rays. If we want to compute the equilibrium concentrations of the eight components in the model atmosphere, we must specify the elevation of the sun. Similarly, if we want to study the diurnal variation of the concentrations we must consider the elevation of the sun as a function of time for the latitude and season in question. For most purposes it is sufficient to use a mean elevation for the day and no dissociation during the night. However, the aim of this paper is not to study such diurnal variations but rather the daytime conditions and their dependence on latitude, season, height and total amount of hydrogen. For this purpose it may be regarded as sufficient to compute daytime equilibrium conditions modified as follows: the dissociation rates corresponding to the mean elevation of the sun during the day was determined. These values were used for the components having characteristic times shorter than a day (for instance for ozone). For the components having characteristic times longer than a day the dissociation rate was multiplied by $t_d/24$, t_d being the length of the day in hours. If the characteristic time is about a day, this procedure presents a conflict as to whether we shall choose the first or the second way of approximation. This will

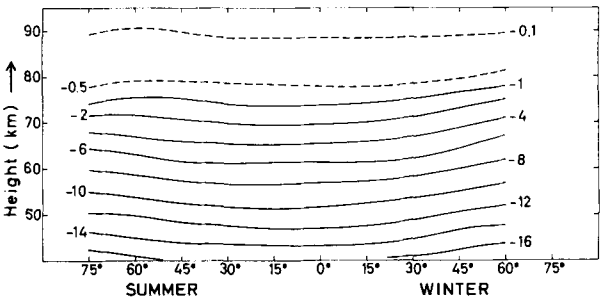

FIG. 6. Relative concentration of H, defined as the ratio $[H]/\Sigma_H$, where Σ_H denotes the total number of hydrogen atoms per cm³, for the "moist" case (i.e. for a water vapor mixing ratio of 1.5×10^{-4} g/g).

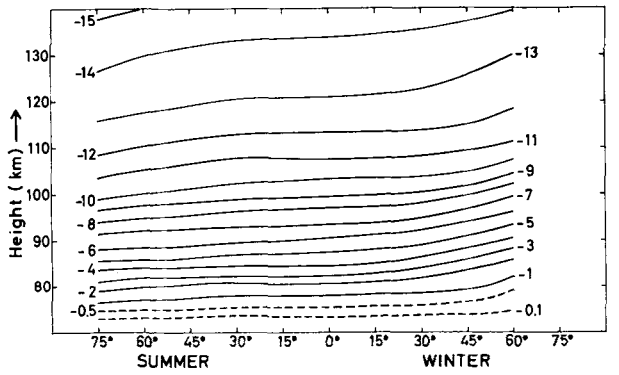

FIG. 7. Relative concentration of water vapor, defined as the ratio $2[H_2O]/\Sigma_H$, where Σ_H denotes the total number of hydrogen atoms per cm³, for the "dry" case (i.e. for a water vapor mixing ratio of 1.8×10^{-6} g/g).

be the case for atomic oxygen near the mesopause, where the characteristic time drops from about 100 hours at 85 km to a couple of hours at 80 km. Thus the transition takes place within a shallow layer and the uncertainty in the computations is by no means disturbing.

The BATES & NICOLET model atmosphere contains OH, HO_2, H_2, H_2O and H in addition to the three pure oxygen components. For each of these components the daytime equilibrium concentration, modified as above, is determined by an equation of the type $A_i x_i = B_i$, expressing that the formation and destruction of a component are equal. (Here x_i denotes the concentration of component i and A_i and B_i are polynomials containing the concentrations of some of the other components but not x_i.) In addition we have the continuity equations for oxygen and hydrogen, expressing that the total amount of oxygen and of hydrogen at a given level is a constant fraction of the air particle concentration. This gives ten equations (not independent) to find the concentrations. In most cases the equations are solved by an iterative method.

The concentrations of the pure oxygen components are not seriously effected by the presence of hydrogen. On the other hand, the concentrations of the hydrogen components depend very strongly upon the choice of value for the mixing ratio total hydrogen/air. In order to be able to compare the results obtained for the "dry" and "moist" atmosphere, the relative concentrations $k_i x_i/\Sigma_H$ were computed (Σ_H denotes the total concentration of hydrogen atoms; the factor k_i is 1 for OH, HO_2 and H,

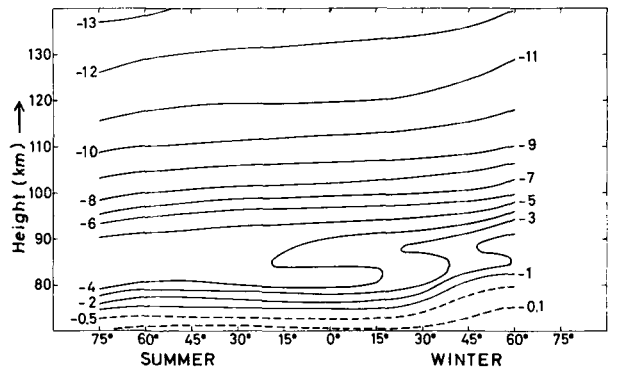

FIG. 8. Relative concentration of water vapor defined as the ratio $2[H_2O]/\Sigma_H$, where Σ_H denotes the total number of hydrogen atoms per cm³, for the "moist" case (i.e. for a water vapor mixing ratio of 1.5×10^{-4} g/g).

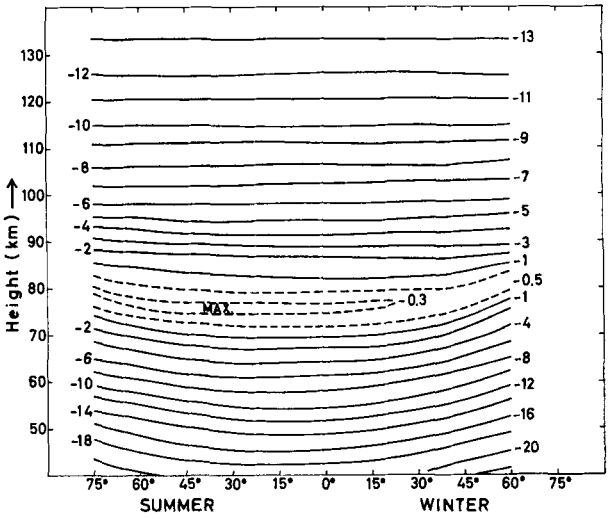

FIG. 9. Relative concentration of H_2, defined as the ratio $2[H_2]/\Sigma_H$, where Σ_H denotes the total number of hydrogen atoms per cm^3, for the "dry" case (i.e. for a water vapor mixing ratio of 1.8×10^{-6} g/g).

and 2 for H_2 and H_2O). The results are shown in Figs. 1–10. The relative concentrations are given by their logarithmic values.

The similarity between the results for the "dry" and the "moist" case is striking. It is further of interest to note that the meridional and seasonal variations are relatively small. Consequently, the relative concentrations of the hydrogen components are primarily functions of height.

The components OH and HO_2 are minor hydrogen constituents at all levels. The highest concentrations are found just below the mesopause, where they take up to about 1 % of the hydrogen. Above and below the maximum level the concentrations of OH and HO_2 decrease rapidly towards exceedingly small values.

The relative concentrations of H, H_2 and H_2O show remarkable variations with height. At the highest levels the hydrogen budget is largely

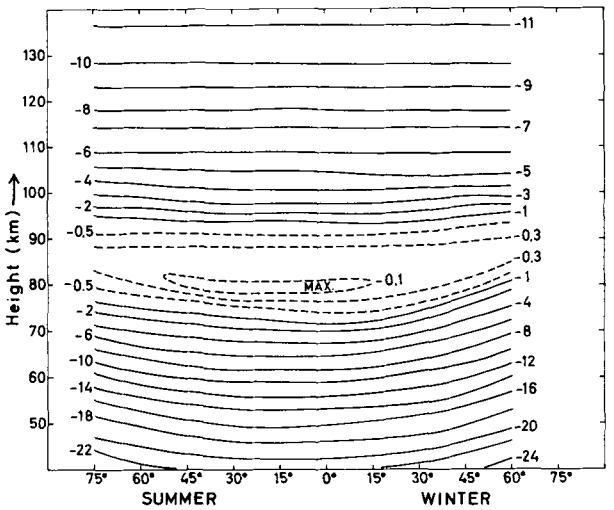

FIG. 10. Relative concentration of H_2, defined as the ratio $2[H_2]/\Sigma_H$, where Σ_H denotes the total number of hydrogen atoms per cm^3, for the "moist" case (i.e. for a water vapor mixing ratio of 1.5×10^{-4} g/g).

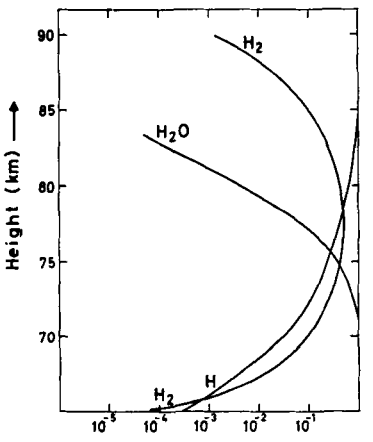

FIG. 11

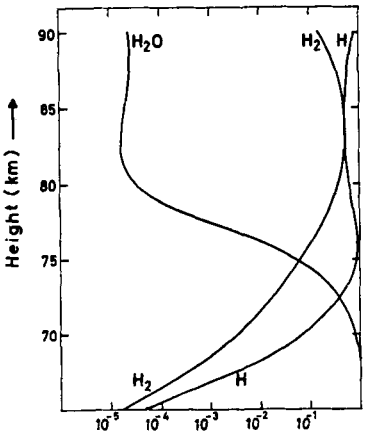

FIG. 12

FIG. 11. Relative concentration of H, H_2 and water vapor for latitude 45°, summer, "dry" case (atmospheric motion neglected).

FIG. 12. Relative concentration of H, H_2 and water vapor for latitude 45°, summer, "moist" case (atmospheric motion neglected).

dominated by H. As we descend through the upper atmosphere, this dominance lasts down to about 85 km, where H_2 enters the picture. From 85 km the concentration of H decreases rapidly as we descend and from about 70 km H becomes a minor hydrogen constituent. The reason for this is that the main production source of atomic hydrogen ($O + OH \rightarrow H + O_2$) becomes unimportant due to the rapid decrease in O and OH.

In the stratosphere and lower mesosphere the hydrogen budget is completely dominated by water vapor. Even as high as 65 km the sum of hydrogen taken up by the other components is less than 10^{-4} times the water vapor concentration. The break-down of water vapor is due to photodissociation. For zero optical depth the dissociation rate was found to be 1.5×10^{-5} sec^{-1}. The absorption of radiation in the interval 1475–1900 A is mainly due to O_2, and for an optical depth of about 15 cm O_2 (corresponding to a height of about 75 km) the dissociation rate becomes seriously reduced. Accordingly the roof of atmospheric water vapor should be at about 75 km. (The influence of vertical motion will be discussed briefly in the following section). For optical depths much larger than 15 cm O_2 the values obtained for the dissociation rate of water vapor becomes increasingly uncertain. For this reason the results obtained for low levels should be regarded as advisory only.

Between the H- and the H_2O-regimes molecular hydrogen enters the picture as the dominating component. It is seen that the H_2-regime is much more pronounced in the "moist" than in the "dry" case. On the whole the mesopause region provides a very complicated photochemistry: we have the transitions (see Figs. 11–14) from H_2O-regime to H_2-regime and further to the H-regime, we have the maximum occurrence of OH and HO_2, and we have the only layer where hydrogen reduces the O and O_3 concentrations by consuming O (through the process $O + OH \rightarrow H + O_2$ and $O + HO_2 \rightarrow OH + O_2$).

4. Modification of the results by atmospheric motions

It has been pointed out earlier (HESSTVEDT, 1964, 1965) that the results obtained for a rigid atmosphere may be considerably modified by atmospheric motions. In order to estimate the importance of this influence we must know the vertical and horizontal wind components and the characteristic times for the eight components of our model atmosphere. Of principal interest for the present study is the following question: to what extent will the atmospheric circulation modify the conditions in the vicinity of the mesopause?

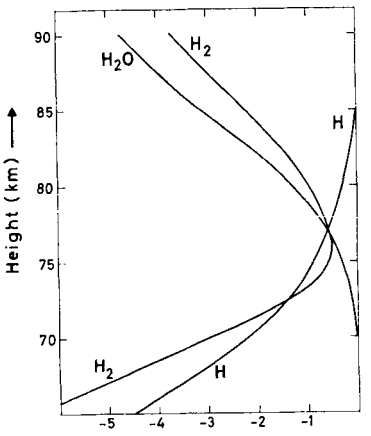

FIG. 13

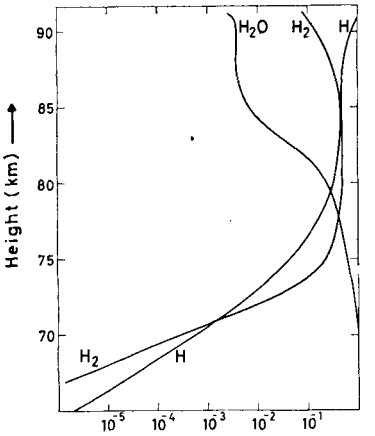

FIG. 14

FIG. 13. Relative concentrations of H, H_2 and water vapor for latitude 45°, winter, "dry" case (atmospheric motion neglected).

FIG. 14. Relative concentrations of H, H_2 and water vapor for latitude 45°, winter "moist" case (atmospheric motion neglected).

Theoretical computations of the vertical and horizontal velocity field have been made by MURGATROYD & SINGLETON (1961) and LEOVY (1964). The results of these authors are in a qualitative agreement: near the mesopause we have the ascending motion over the summer pole, nearly horizontal motion in lower latitudes, directed from the summer pole towards the winter pole, and finally descent over the winter pole. But as to the magnitude of the velocities the disagreement is substantial. For this reason it is difficult to consider the influence of the air motion upon the results in Figs. 1–10. Nevertheless, it is of some interest to make some estimates on the basis of the circulation models of LEOVY and of MURGATROYD & SINGLETON.

Since water vapor is the component which calls upon the greatest interest we shall start with the lifting of the H_2O-regime in polar regions during the summer due to the ascending

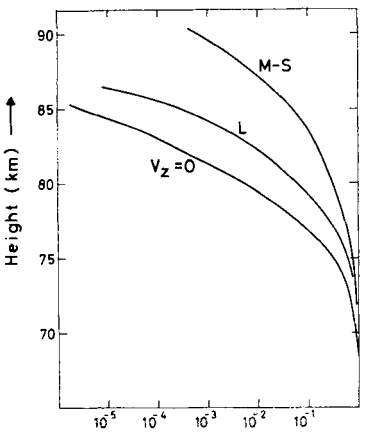

FIG. 15

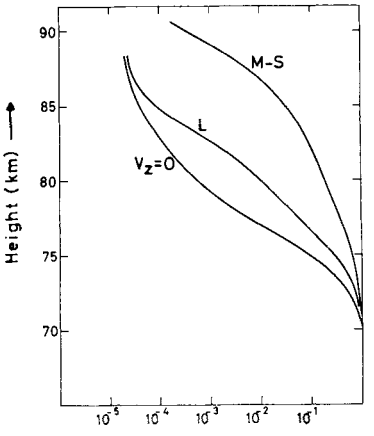

FIG. 16

FIG. 15. Relative concentration of water vapor, high latitude summer, for vertical velocity profiles according to LEOVY (*L*) and MURGATROYD & SINGLETON (*M–S*), "dry" case.

FIG. 16. Relative concentration of water vapor, high latitude summer, for vertical velocity profiles according to LEOVY (*L*) and MURGATROYD & SINGLETON (*M–S*), "moist" case.

air motion. A typical value for the vertical velocity at about 75 km for this season and latitude is, according to MURGATROYD & SINGLETON, 1 cm/s, while LEOVY found about 0.25 cm/s for his model. On the basis of their velocity profiles the lifting of the H_2O-regime was computed for the "dry" and the "moist" case. The results are shown in Figs. 15–16. It is seen that a vertical velocity as computed by LEOVY will raise the water vapor regime by 1–2 km, i.e. the computations for the static atmosphere model remains almost unaffected by such small velocities. On the other hand, a vertical velocity as computed by MURGATROYD & SINGLETON will raise the water vapor regime by as much as 5–7 km, which would ensure a sufficient amount of water vapor at the mesopause to form noctilucent clouds.

A similar computation for the meridional transport from the summer pole across the equator towards the winter pole gave as result that a meridional velocity as computed by LEOVY (about 0.5 m/s) would have very little effect upon the water vapor distribution. Any departure from photochemical equilibrium would be eliminated during a travel of less than 5 degrees of latitude. On the other hand, a meridional velocity of about 4 m/s, as obtained by MURGATROYD & SINGLETON, will result in a displacement of 15–20 degrees of latitude during the characteristic time. Consequently the high water vapor content at the polar mesopause which is a result of the ascent, will not be seriously reduced before we reach latitude of about 50–60 degrees. In equatorial regions and in low and middle latitudes in the winter hemisphere photochemical equilibrium seems to be a fair approximation. In polar regions the descending motion during the winter tends to lower the water vapor regime, very little for LEOVY's model, about 3–5 km for MURGATROYD & SINGLETON's model.

We started in this section with a question. The discussion above has shown that it is at the present time not possible to give a conclusive answer. Concerning water vapor more accurate values for the dissociation rate are desirable and our knowledge about the circulation of the stratosphere is not sufficient to establish the influence of the air motion.

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