INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE

3 - Avenue Circulaire
B - 1180 BRUXELLES

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In Situ Measurements of Middle Atmosphere Composition

by

M. ACKERMAN

BELGISCH INSTITUUT VOOR RUIMTE-AERONOMIE

3 - Ringlaan
B - 1180 BRUSSEL

FOREWORD

The review paper "In Situ Measurements of Middle Atmosphere Composition" was presented at the International symposium on Solar-Terrestrial Physics held in Innsbruck (May 29 - June 3, 1978). It will be published in the Journal of Atmospheric and Terrestrial Physics with the other Symposium reviews on the Middle Atmosphere.

AVANT-PROPOS

La mise au point "In Situ Measurements of Middle Atmosphere Composition" a été présentée au International Symposium on Solar Terrestrial Physics à Innsbruck (29 mai - 3 juin 1978). Elle sera publiée dans le Journal of Atmospheric and Terrestrial Physics avec les autres articles de revues du Symposium traitant de l'atmosphère moyenne.

VOORWOORD

De tekst "In Situ Measurements of Middle Atmosphere Composition" werd voorgedragen op het International Symposium on Solar-Terrestrial Physics, gehouden te Innsbruck van 29 mei tot 3 juni 1978. Hij zal in het tijdschrift "Journal of Atmospheric and Terrestrial Physics" verschijnen samen met de andere Symposium mededelingen in verband met de gemiddelde atmosfeer.

VORWORT

Die Arbeit "In Situ Measurements of Middle Atmosphere Composition" wurde zum International Symposium on Solar Terrestrial Physics in Innsbruck (29.Mai - 3.Juni 1978) vorgestellt. Sie wird in Journal of Atmospheric and Terrestrial Physics mit den anderen eingeladenen Arbeiten über der mittleren Atmosphäre herausgegeben werden.

IN SITU MEASUREMENTS OF MIDDLE ATMOSPHERE COMPOSITION

by

M. ACKERMAN

Abstract

Experimental data based on aircraft, balloon and rocket measurements of trace species in the middle atmosphere are briefly reviewed. Some ground based observations are also included where no other information is available. The scarcity of values relevant to the vertical distributions is emphasized as well as the lack of knowledge of tome and geographic variabilities necessary to understand the physical and chemical properties of the middle atmosphere as wemm as to monitor its stability over long periods of time.

Résumé

Une mise au point de données expérimentales basées sur des mesures par avions, ballons et fusées sondes est présentée. Quelques observations effectuées depuis le sol sont prises en compte là ou aucune autre information n'est disponible. Le manque de renseignements sur les distributions verticales est mis en évidence ainsi que le manque de connaissance des variabilités géographiques et dans le temps nécessaire à la compréhension des propriétés physiques et chimiques de l'atmosphère moyenne et à la surveillance de la stabilité de celle-ci à long terme.

Samenvatting

Proefondervindelijke gegevens bekomen door middel van metingen met vliegtuigen, ballons en raketten worden in het kort weergegeven. Daar waar geen "in situ" metingen beschikbaar waren werd beroep gedaan op enkele grondwaarnemingen. Het gemis aan informatie met betrekking tot de vertikale verdelingen werd in het daglicht gesteld alsook het gebrek aan kennis betreffende de geografische veranderingen en deze in functie van de tijd. Deze gegevens zijn onmisbaar voor het begrijpen van de fysische en chemische eigenschappen van de gemiddelde atmosfeer en voor het stabiliteitstoezicht op lange termijn.

Zusammenfassung

Experimentelle Daten über Minderheitsteilchen der mittleren Atmosphäre, die miet Hilfe Flugzeugen, Ballonen und Raketten erreicht wurden, sind kurz vorgestellt. Einige Beobachtung, die vom Grund erreicht wurden, sind einbegriffen wenn es keine andere Informationen gibt. Der Mangel an Daten über senkrechte Ausbreitungen und über Zeit- und Geographische Veränderungen um die physikalische und chemische Eigenschaften der mittleren Atmosphēre sowie seine Stabilität über langen Zeitperioden zu verstehen, wird klargestellt.

INTRODUCTION

In Situ measurements in the stratosphere, mesosphere and lower thermosphere are now emphasized as a part of the middle atmosphere measurements as a result of various motivations related to the uncertainties about the ozone budget to which trace species contribute. A review on such measurements in the altitude range between 10 and 100 kilometers altitude, as defined in a recent planning document on the Middle Atmosphere Program (1976), is necessarily limited to observations made from high flying aircrafts, balloons and rockets. These platforms have, of course, played a major role in this field but past and future roles of spacecraft and ground based observations should not be neglected since all data complement each other.

Measurements on the stratosphere have been stimulated for the last seven years. The limitation in number and accuracy of the results despite the effort made confirms the challenging character of the undertaken work. The extension to the so called middle atmosphere by adding the mesosphere and lower thermosphere to which D Region ionospherists and aeronomers have already devoted so much work constitutes an even more challenging task. This article will only be a limited summary of experimental data intended to point out the definincies of the measurements which are essentially devoted to the verification and improvement of theoretical models.

Atmospheric trace species can be divided in various categories depending on the type of discussion to be supported. For a general discussion, a classification as follows seems reasonnable : a) the oxygen species O, O_2, O_3 ; b) the hydrogen species : CH_4, H_2O, OH, H_2, H ; c) the carbon species : CO_2, CO ; d) the nitrogen species : NO, NO_2, HNO_3, NO_3, N_2O_5, N_2O, NH_3 ; the halogen species : HCl, HF, ClO, Cl, chloro-fluorocarbons and eventually, sulfur, the alcali-metals.

The ions will not be considerd here. Reviews have been devoted to the subject in 1973 and in 1974 by Narcisi. The first measurements of ions in the stratosphere have been reported recently by Arnold *et al.* (1977), Olson *et al.* (1977) and by Arijs *et al.* (1978). The two last groups of authors using balloon platforms for this type of measurements for the first time observed ion masses 73,91 and 109 that were attributed to protons 4,5 and 6 times hydrated. The rocket data of Arnold *et al.* (1977) showed evidence for unidentified ions (masses 29, 42, 60 and 80) some of which seem to be part of a serie of hydrates to which Arijs *et al.* (1978) have added the very abundant mass 96 ion.

Several trace species have been observed for the first time in recent years. If the determination of the vertical distribution of a newly measured molecule even over a small altitude range is an important step, it is only a first order information which has to be brought up to the geophysical standards. These require the determination of time and geographic variabilities in correlation with other relevant parameters.

THE MEASUREMENTS

a) The oxygen species

Molecular oxygen is accepted to be in constant mixing ratio up to the upper edge of the middle atmosphere where it begins to leave its role of major oxygen constituent to atomic oxygen measured in situ by straight forward and unambiguous methods by Dickinson *et al.* (1974) using the absorption process of the 130 nm O radiation over a path length of 40 cm and by Scholtz and Offerman (1974) using mass spectrometers with cryogenically cooled ion sources flown over Sardinia in 1972. More recently atomic oxygen has been measured by resonance fluorescence observed by means of a balloon dropped sonde.

Vallance Jones and Harrison (1958) detected the presence of excited O_2 ('Δ) in the mesosphere twenty years ago. Since then, many ground based and rocket observations have been made and reviewed by Llewellyn *et al.* (1972).

Ozone, since its detection by Van Marum in 1785 has been much investigated as it appears from a recent introduction to its study by Nicolet (1975). Since then Krueger and Minzner (1976) have published for the 1976 U.S. Standard atmosphere a mid-latitude ozone model mainly based on rocket data. Variations from this model can be found in Nasa

Reference Publication 1010 (Hudson, 1977). Their determination is largely based on situ measurements by means of routinely launched balloons. The world coverage is however far from being satisfactory with most of the soundings taking place over land area in the northern hemisphere as shown in figure 1.

In situ data on O, O_3 and O_2 ($^1\Delta$) are represented in figure 2. Below 85 km atomic oxygen exhibits a large day to night variation as O_3 does above 50 km. Stellar occultation measurements (Riegler *et al.* 1977) indicate larger O_3 densities in the mesosphere than currently predicted in models. On the other hand it has recently been indicated that larger ozone amounts than given by the Krueger and Minzner (1976) model exist in the tropical mesosphere for solar zenith angles smaller than 80° (Frederick *et al.* 1977). Typical values are shown in figure 2.

b) The hydrogen species

Despite of its carbon atom, methane must be categorized in the hydrogen species due to its low concentration relative to carbon dioxide and in respect of its appreciable contribution to the hydrogen content in the stratosphere when it is compared with water vapor. Methane has been measured by infrared spectroscopy from balloon platforms as well as by laboratory analysis of in situ collected samples. Reasonnable agreement has been found (Ackerman *et al.* 1977, 1978) at 30 km between the spectrometric measurements after reanalysis of some of them. Rocket sampling has provided determinations up to the stratopause (Ehhalt *et al.* 1975). A discrepency exists between the remote sensing and sampling determinations. The latter ones indicate larger concentrations. The present status of our experimental knowledge of CH_4 in the middle atmosphere is represented in figure 3. No large variation of the stratospheric content of CH_4 has been observed versus latitude from aircraft flying in the low stratosphere (Lowe and McKinnon (1972), Farmer (1974)).

The presently available data on the vertical distribution of H_2O in the stratosphere as reviewed by Harries (1976) show a small range of mixing ratios around 3 parts per million in volume. An increase of H_2O in the stratosphere appears possible from experimental data

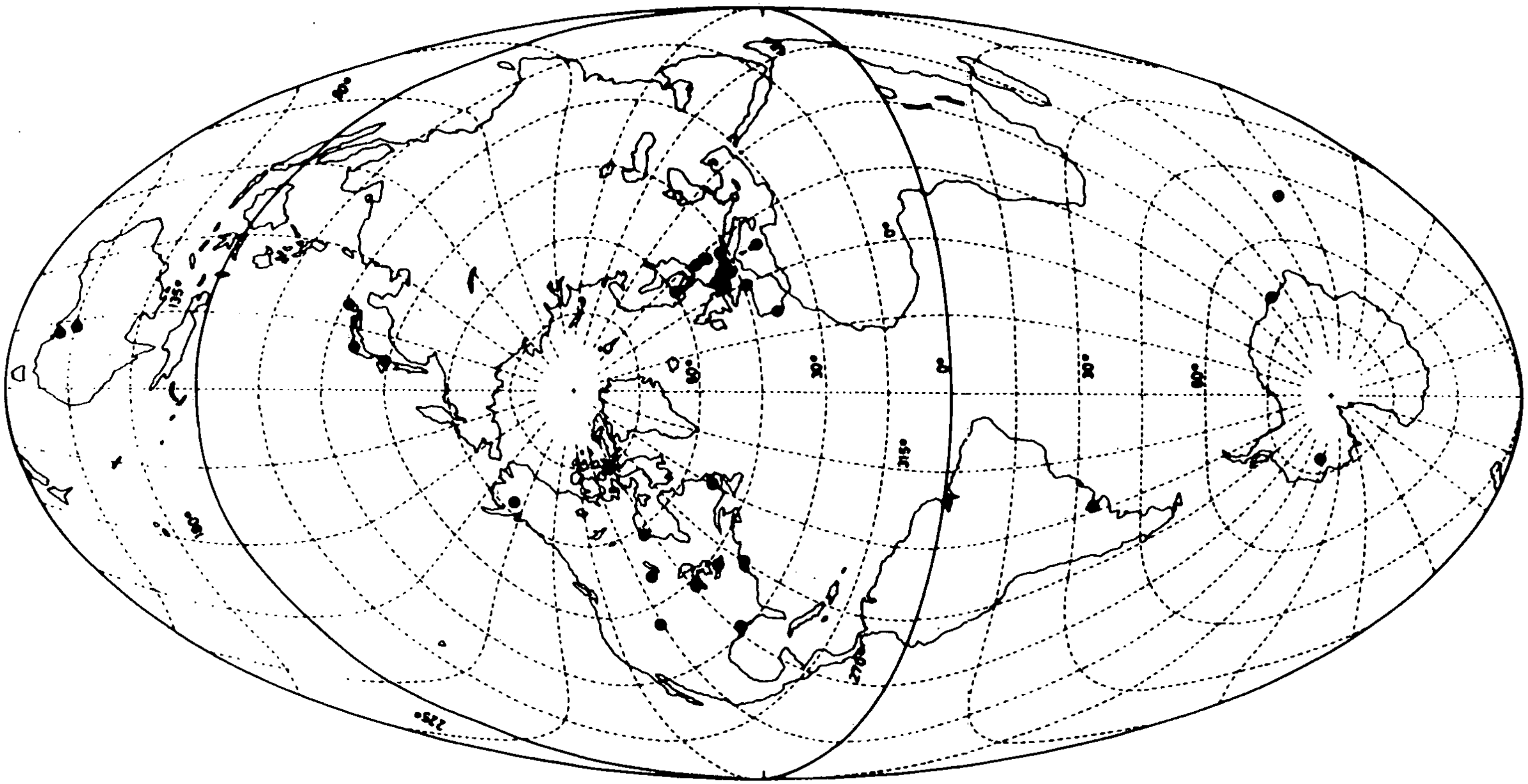

Fig. 1.- Distribution of in situ routine ozone balloon soundings according to the Ozone Data for the World Catalogue (1971-1976) - AES-WMO-Downsview - Ontario - Canada. The area covered appears very limited compared with the earth surface and the distribution versus latitude and longitude seems to be very little organized to taken into account the known variations. The network contributes however much to the study of stratospheric ozone. In particular the correlation of the observed fine structure of the vertical distribution with other air properties is of much use to understand atmospheric air motions up to 20 km altitude.

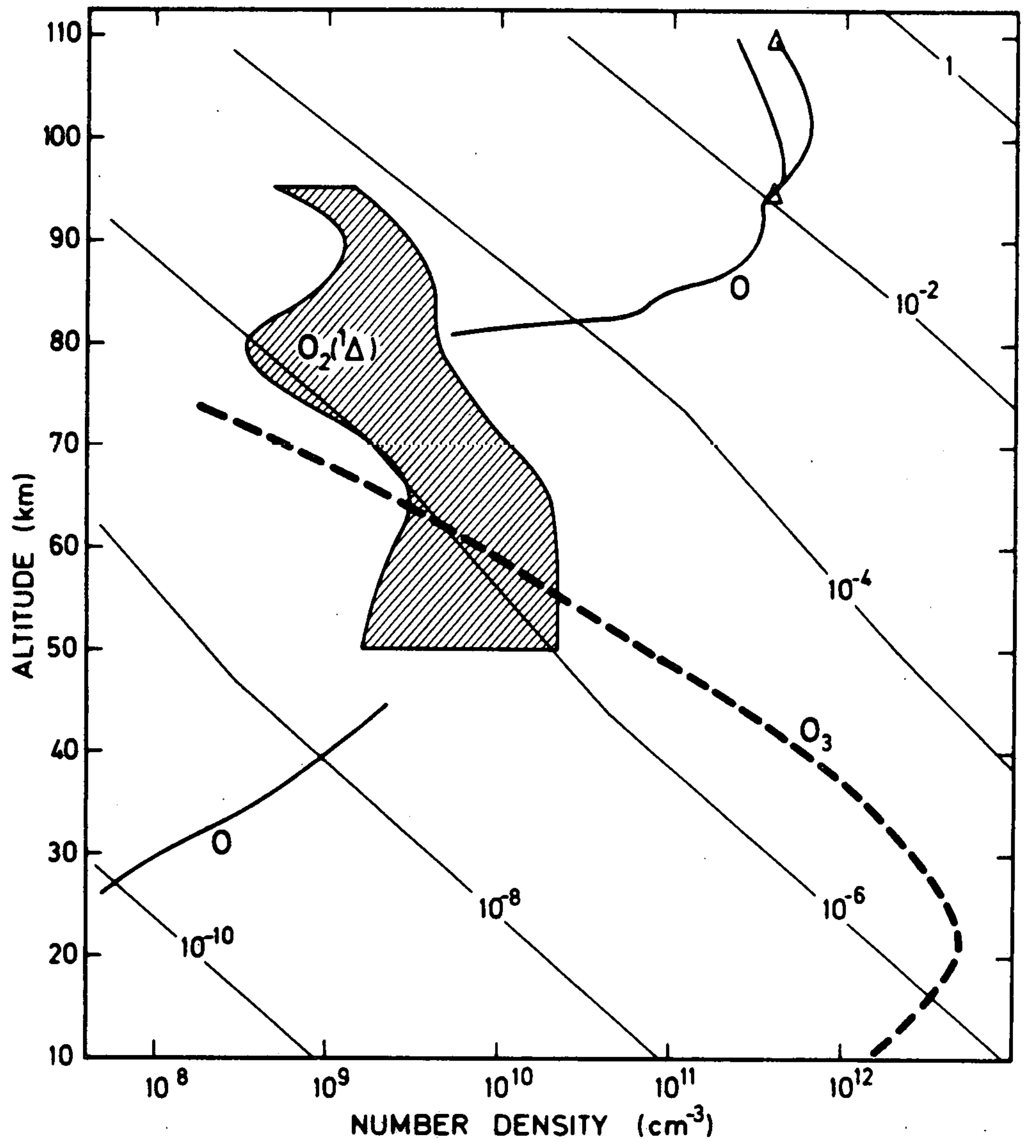

Fig. 2.- Measured abundances of oxygen species in the middle atmosphere : atomic oxygen in the stratosphere (Anderson, 1975) and in the low thermosphere (Dickinson *et al.* 1974; Scholz and Offerman, 1974); electronically excited molecular oxygen (Llewellyn *et al.*, 1973); ozone (Krueger and Minzer, 1976). As in all subsequent figures the volume mixing ratios are indicated.

over the last thirty years. An annual cycle is superposed over this trend. H_2O is more abundant at low latitudes in the lower stratosphere than at high latitudes. Rogers *et al.* (1977) have deduced a range of possible mixing ratio values for the mesosphere from infrared emission measurements taken by means of a rocket borne photometer. Indirect determinations of H_2O have been obtained above 70 km from ion chemistry models applies to rocket mass spectrometric measurements of ions. As show in figure 4, the volume mixing ratio of H_2O in the middle atmosphere does not depart much from 3×10^{-6}.

The volume mixing ratio of molecular hydrogen is almost constant versus altitude and equal to 5×10^{-7} in the low stratosphere. At 100 km altitude, the top of the middle atmosphere, similar abundances of H and H_2 exist with a value close to 1×10^7 cm^{-3} according to Tinsley (1974). This corresponds roughly to a doubling of the volume mixing ratio from the stratosphere to the low thermosphere.

Anderson (1971) has observed the resonantly scattered solar radiation by OH in the 45 to 70 kilometer altitudes of the upper stratosphere and mesosphere by means of a rocket borne spectrophotometer. He deduced number densities equal to $(5 \pm 3) \times 10^6$ cm^{-3} while values ranging from 3×10^7 to 4×10^6 cm^{-3} were observed from 45 to 30 kilometers by means of a balloon dropped scatterometer using the same OH band at 306 nm (Anderson, 1976). No experimental data are yet available on two important species such as HO_2 and H_2O_2.

c) The carbon species

CO_2 is the main carbon containing molecule in the middle atmosphere where it is believed to exhibit the same volume mixing ratio as in the troposphere (3.2×10^{-4}). This value has been observed to drop above the turbopause by Scholz and Offermann (1974) using a mass spectrometer with a cryocooled ion source.

From a volume mixing ratio value of the order of 10^{-7} in the troposphere, carbon monoxide exhibits a decrease above the tropopause (Warneck *et al.* 1973). A similar decrease is also observed by Goldman *et al.* (1972). Farmer (1974) reports a variation of the low stratosphere content with latitude : the mixing ratio decreasing from 31° to 76° latitude. The observation of solar microwave absorption from the ground at 2.6 millimeters by Waters *et al.* (1976) indicates a stratospheric volume mixing ratio equal to 5×10^{-8}. This is in agreement at 44 km with the value determined by Ehhalt *et al.* (1975) from the analysis of cryosamples. An increase is indicated at higher altitudes with a value reaching 4×10^{-5} at 90 km altitude.

d) The nitrogen species

Multiple sources of odd nitrogen have been considered for the stratosphere and the mesosphere. Ascending molecules from the troposphere have been considered such as NH_3 and N_2O which cannot be formed in the stratosphere. From infrared spectra taken from the ground (1600 m altitude) Kaplan (1973) has shown that the tropospheric mixing ratio is less than 8×10^{-11}. However, recently Murcray *et al.* (1978) have observed NH_3 infrared absorptions in solar spectra taken from Denver, Colorado. From a comparison with in situ chemical data which show higher abundances and from the dayly variability they conclude that ammonia is confined to the atmospheric boundary layer. Its observation is most probably limited to the vicinity of biological sources and no direct impact on the middle atmosphere is expected.

N_2O is observed in the whole troposphere at a mixing ratio value found equal to 3.3×10^{-7} by Pierotti and Rasmussen (1977) who have reviewed all previous measurements. The same authors have observed a decrease of volume concentration above the tropopause confirming previous stratospheric measurements by Schütz *et al.* (1970) Murcray *et al.* (1973), Toth *et al.* (1977) and Ehhalt *et al.* (1978). According to these two sets of measurements, the N_2O number density decreases from the tropopause to 35 km altitude following with a good approximation a scale height equal to 3.8 km. This also holds rather well for the measurements made by Schmeltekopf *et al.* (1977) at various latitude from the Antarctic to 50° North except for those performed at Panama and in Sakatchewan.

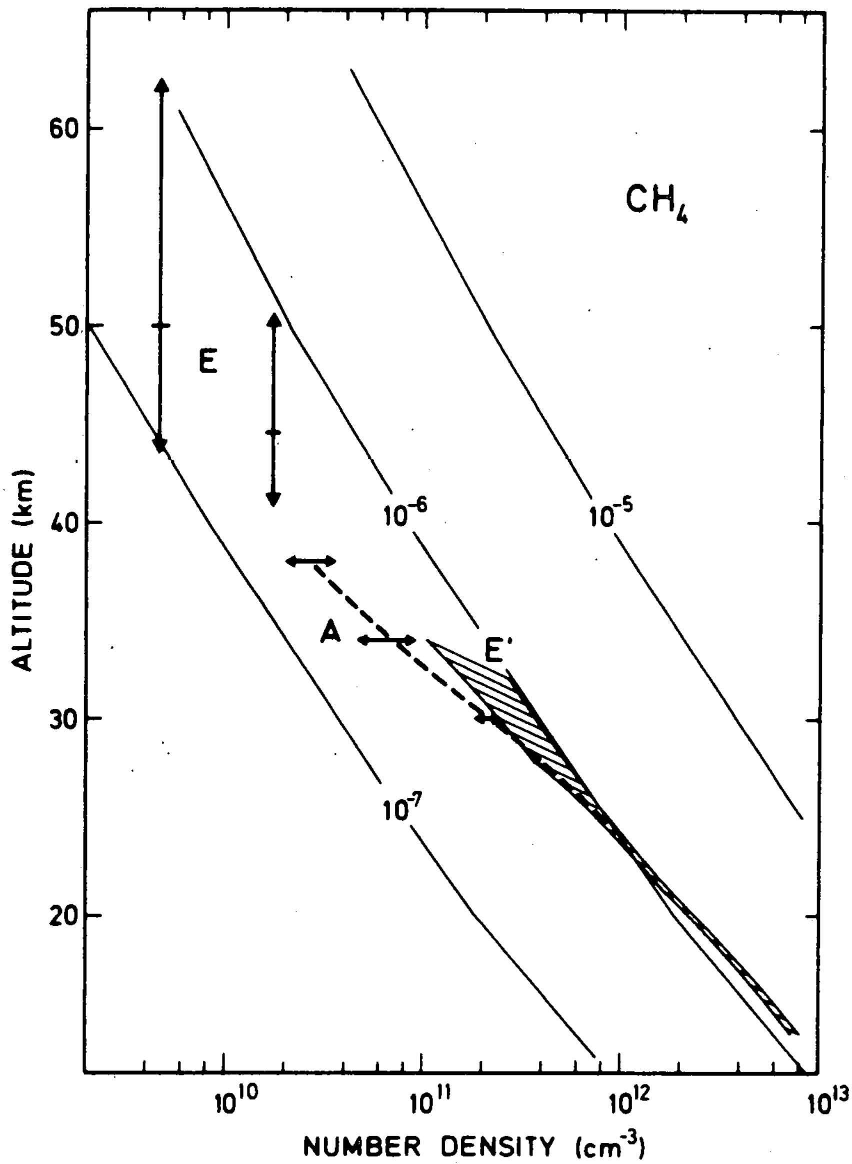

Fig. 3.- Most recent spectroscopic, A (Ackerman *et al.* 1977, 1978) and in situ measurements, E' (Ehhalt *et al.* 1978) on methane from balloon flights and from rocket flights E (Ehhalt *et al.* 1975).

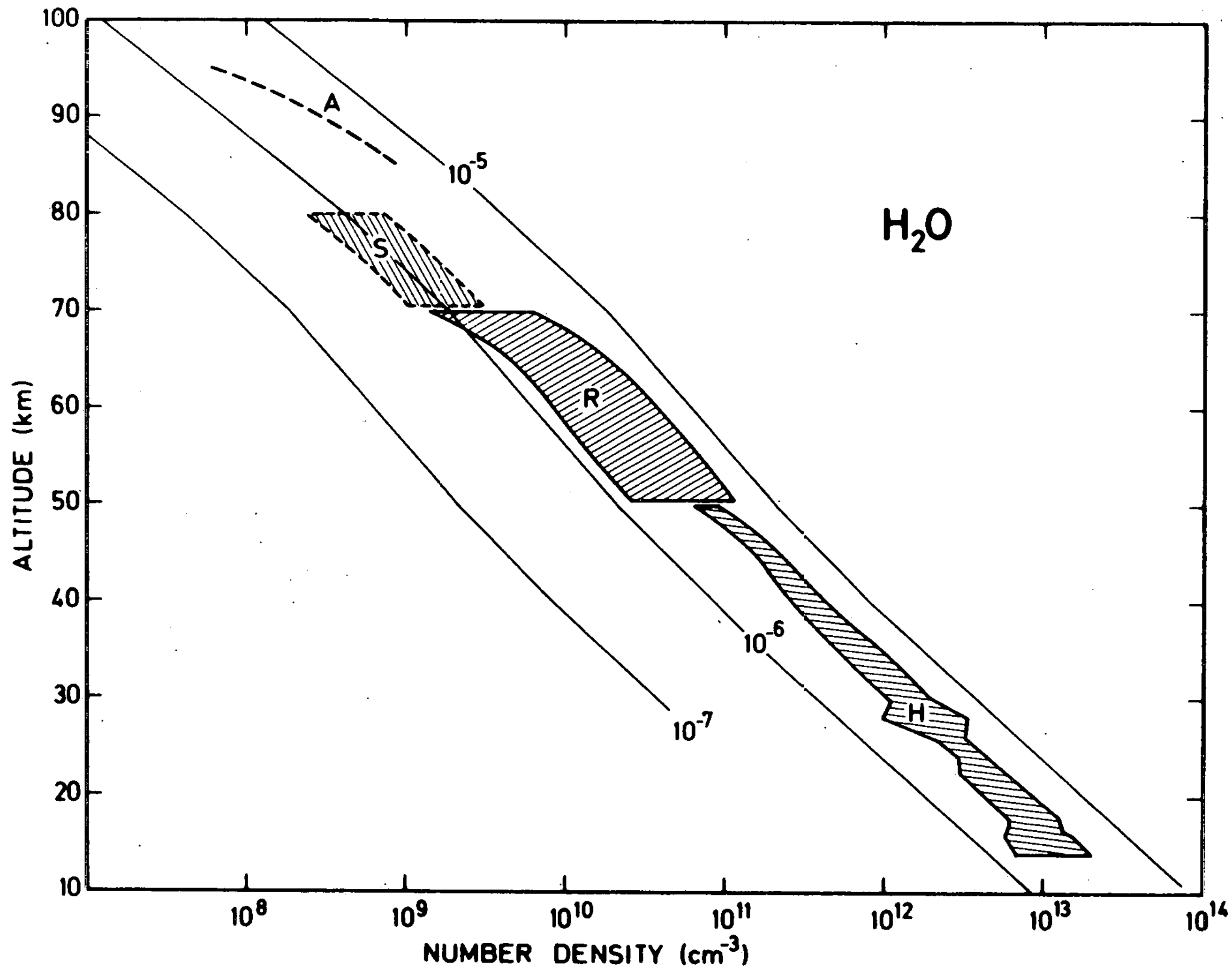

Fig. 4.- In situ observations have provided data on the abundance of H_2O in the middle atmosphere; many balloon and a few rocket measurements in the stratosphere, H, have been reviewed by Harries (1976); infrared emission measurement, R, by Rogers *et al.* (1977) and hydrated ions determinations, S, A, exist for the mesosphere (Swider and Narcissi, 1975, Arnold and Krankowsky, 1977a).

The production of mesospheric odd nitrogen compounds is due to the direct reactions of nitrogen atoms with molecular oxygen. It is thus not a surprise to find nitric oxyde at all altitudes in the middle atmosphere as shown in figure 5. A large variability with time of NO is now recognised. Short term and seasonal variations have been observed, the latter ones exhibit a maximum in summer (Lowenstein *et al.* 1975) based however only on aircraft measurements in the lower stratosphere. NO is in close photochemical equilibrium with NO_2 which has only been measured up to 40 km altitudes as shown in figure 6. While NO has been measured by observation of in situ chemiluminescence with O_3, by infrared absorption and emission in the stratosphere, the mesospheric values are due to the observation of the resonantly scattered solar radiation and to mass spectrometric analysis. Data on NO_2 are only due to remote sensing in the infrared and in the visible from aircraft from balloon and from the ground (Brewer *et al.*, 1973; Kulkarni, 1975 and Noxon, 1975). A seasonal variation with a maximum in summer has been deduced from a latitude survey covering both hemispheres (Girard *et al.* 1978) and from a year of observation (Noxon, 1977). Very little information is however known on the variability versus altitude since the presently available data are related to the total vertical amount.

HNO_3 is the third odd nitrogen molecule produced in the middle atmosphere which is present in appreciable quantity. It has only been observed in the stratosphere from infrared absorption and emission spectra and from sampling followed by chemical analysis. A strong latitude variation with a minimum in equatorial regions has been demonstrated (Lazrus and Gandurd, 1975, Murcray *et al.*, 1975; Girard *et al.* 1978).

Other odd nitrogen species have not been observed. Upper limits have been set for NO_3, 2 percent of NO_2, by Noxon (1975) and for N_2O_5.

e) The halogen species

Concerns about the possible effect of man made halogen compounds on the ozone balance have prompted measurements of fluorocarbons in the stratosphere. Most data are based on in situ sampling during balloon ascents followed by gas chromatographic analysis.

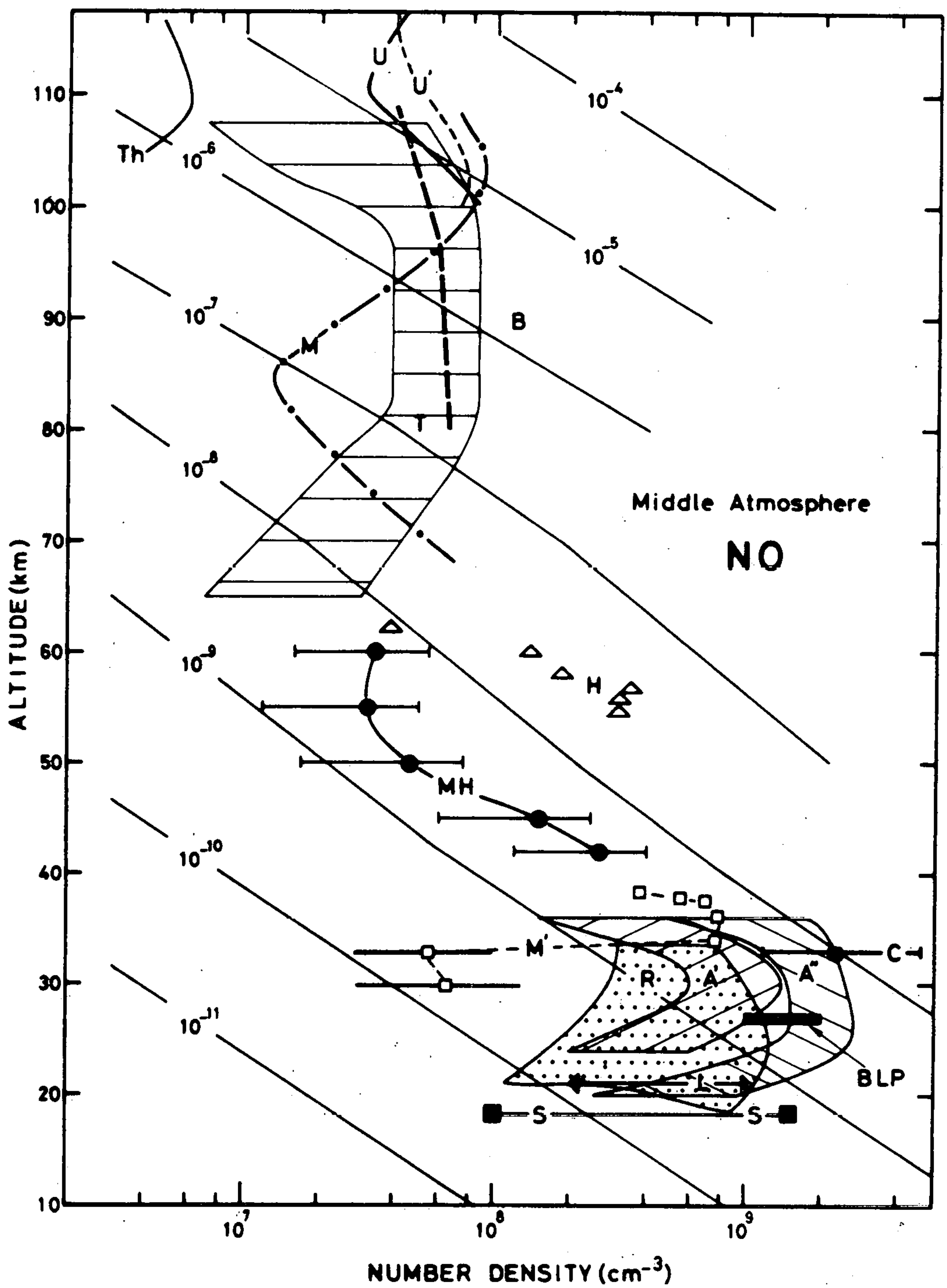

Fig. 5.- Number density of nitric oxide has been measured in the middle atmosphere by Thomas (1978), Th, Thrinks *et al.* (1978), U and U' , by Barth (1964), B, Meira (1971), M, Tisone (1973), T, Hale (1972), H, Mason and Horvath (1976), MH, Maier *et al.* (1978) M'. Ackerman *et al.* (1975) A',A'', Chaloner *et al.* (1975), Ridley *et al.* (1976), T, Burkhardt *et al.* (197R), Loewenstein *et al.* (1974, 1976), L, S. The data show a large variability at all altitudes.

Many measurements have been performed on $CFCl_3$ and on CF_2Cl_2. Both are photo-dissociated by solar UV radiation penetrating in the atmosphere through the 200 nm atmospheric window. Sundararaman (1976) has reviewed several data sets. Infrared absorption spectra have provide the longest time base showing an increase of the stratospheric content by comparison of spectra observed in 1968 and in 1975 (Williams *et al.* 1976). As HNO_3 is considered as a sink for stratospheric odd nitrogen through rainout in the troposphere, HCl and HF should play this role for chlorine and fluorine. The determinations of HCl by observation of the 3 micron infrared band from balloon platforms (Ackerman *et al.* 1976, Williams *et al.* 1976, Eyre and Roscoe 1977 and Raper *et al.* 1977) agree and constitute an important data base to monitor a possible increase in the future.

HF has been detected first by Zander (1975) and measured in the stratosphere by Zander *et al.* (1977). Farmer and Raper (1977) have simultaneously obtained stratospheric data on HF and HCl and found a ratio of abundance equal to 0.1. As for HNO_3 the HCl concentration measured by sampling on filter paper (Lazrus and Gandmol, 1976) are slightly lower than those found by the infrared spectrophotometric method.

Atomic chlorine and chlorine monoxide, the two active species reacting with odd oxygen in the middle atmosphere have been measured by Anderson (1977) using a balloon dropped reactor in which Cl resonantly scatters the 119 nanometers ultraviolet radiation.

f) Miscalleneous species

In relation with the stratospheric aerosols SO_2 has been mass spectrometrically measured in the low stratosphere by Jaeschke *et al.* (1976). In the 90 km altitude region sodium (Megie *et al.* 1978, Thomas *et al.*, 1977) and potassium (Megie *et al.* 1978) have been measured by means of ground based lidar. Typical maximum number densities are equal to 2000 and 300 cm^{-3} respectively.

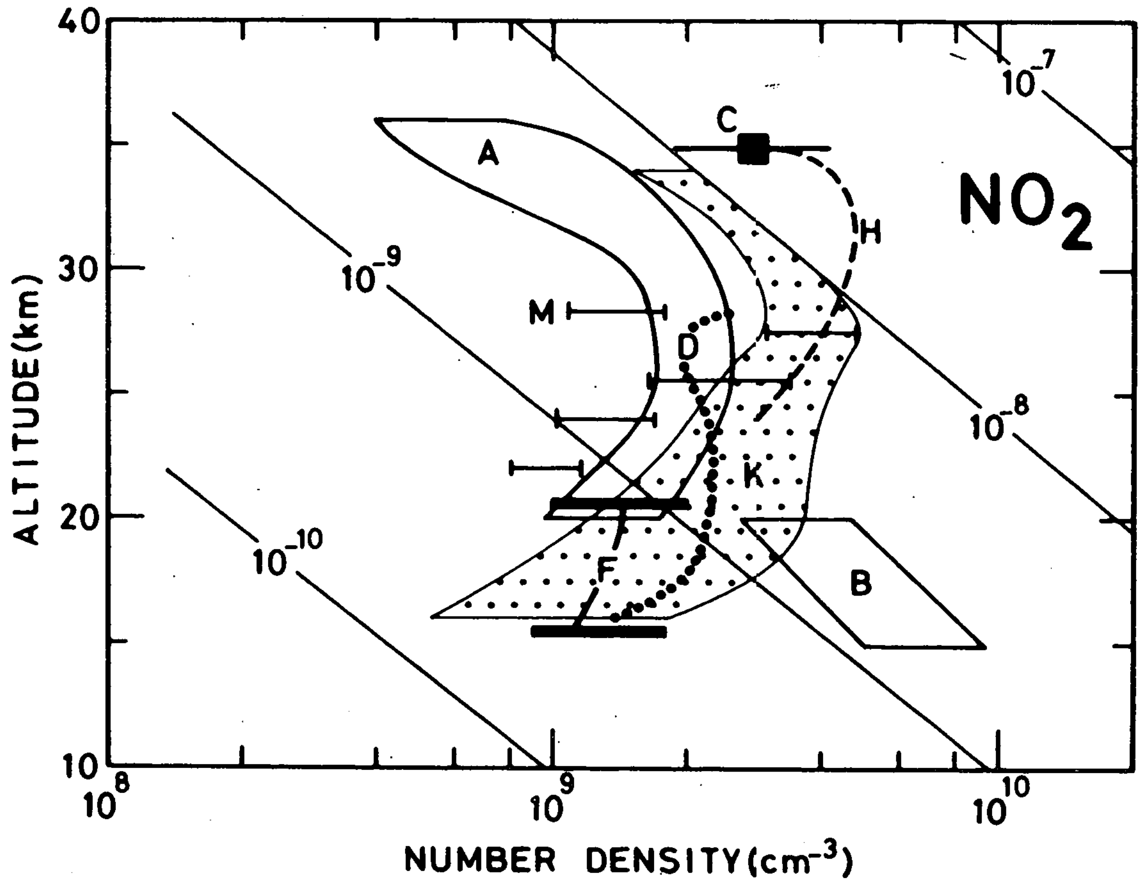

Fig. 6.- The abundance of nitrogen dioxide has only been determined in the low middle atmosphere. Most of the information is due to infrared absorption spectroscopy by Ackerman and Muller (1972), M, Farmer (1974), B, Fontanella *et al.* (1975), F, Murcray *et al.* (1974), D, Chaloner *et al.* (1975), C. The values obtained by Kerr and McElroy (1976) in the visible are also shown, K.

DISCUSSION AND CONCLUSION

In situ measurement in the middle atmosphere have grown considerably for the last five years with a particular emphasis on the stratosphere. Data on the vertical distribution of neutral trace species give a broad picture of their typical abundances as shown in figure 7. Recent theoretical analysis of the experimental data on trace species have been published by Crutzen *et al.* (1978) and by Wofsy (1978). The most versatile measuring method appears to be the infrared limb sounding which has been applied to O_3, $O_2(^1\Delta)$, H_2O, CH_4, CO, NO, NO_2, HNO_3, N_2O, HCl, HF and halocarbons. Its main disadvantages are the limited altitude resolution due to the integration of emission or absorption feature over a long atmospheric path. Even if the highest spectral resolution was used, the detection limit would most probably not be better than 10^6 molecules per cm^{-3} in the best cases where spectral lines are the most intense. It has on the other hand the avantages to be quite free from contamination and of very high specificity. Eventually, it can be used from orbiting vehicles to give global coverage. The gas sampling method used in association with chromatography or other analytical methods is almost as versatile with the potentiality of measuring non infrared active species such as H_2. Special care has to be taken to avoid contamination.In particular cases, the in situ use of specific chemiluminescent reactions has provided much information. This has been the case for O_3, CO and NO. Low stability reactants at very low concentration have often to be used for calibration purposes.

A large fraction of the constituents has not been measured in the mesosphere. Middle atmosphere programs will most probably emphasize data collection in the altitude range between the stratosphere and the low thermosphere. Simultaneous measurements of various species interacting closely in chemical or thermal processes will be required. Eventually, long time series of observation, continuous in some cases, will be necessary to study variability with time and geographic location in order to establish the possible mechanism of interaction of solar terrestrial character already potulated at present on statistical basis.

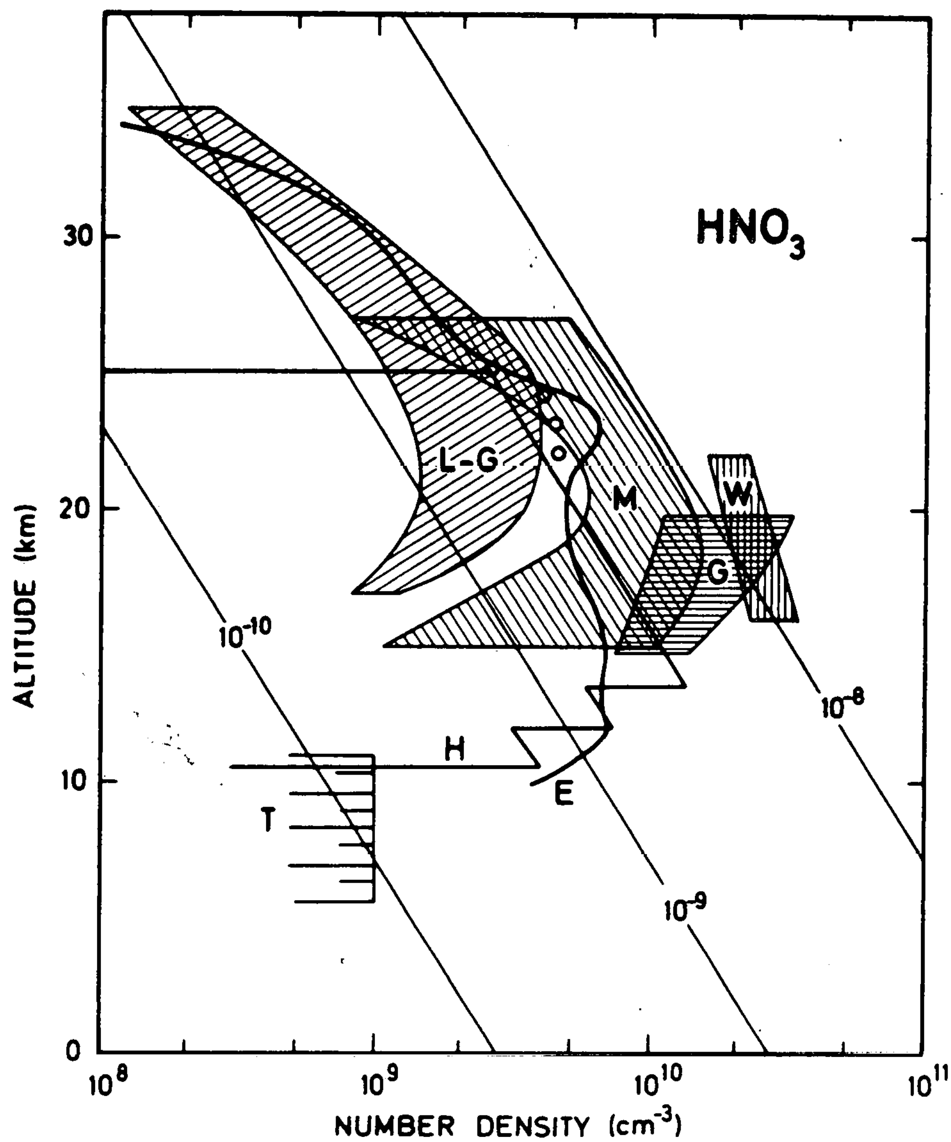

Fig. 7.- The various vertical distributions of nitric acid in the stratosphere are due to Lazrus and Gandrud (1975) L.G., Murcray *et al.* (1974) M, Fontanella *et al.* (1975), G, Harries *et al.* (1976), H, and Evans *et al.* (1976), E. The upper limit, T, in the upper troposphere is an evaluation by Ackerman (1975).

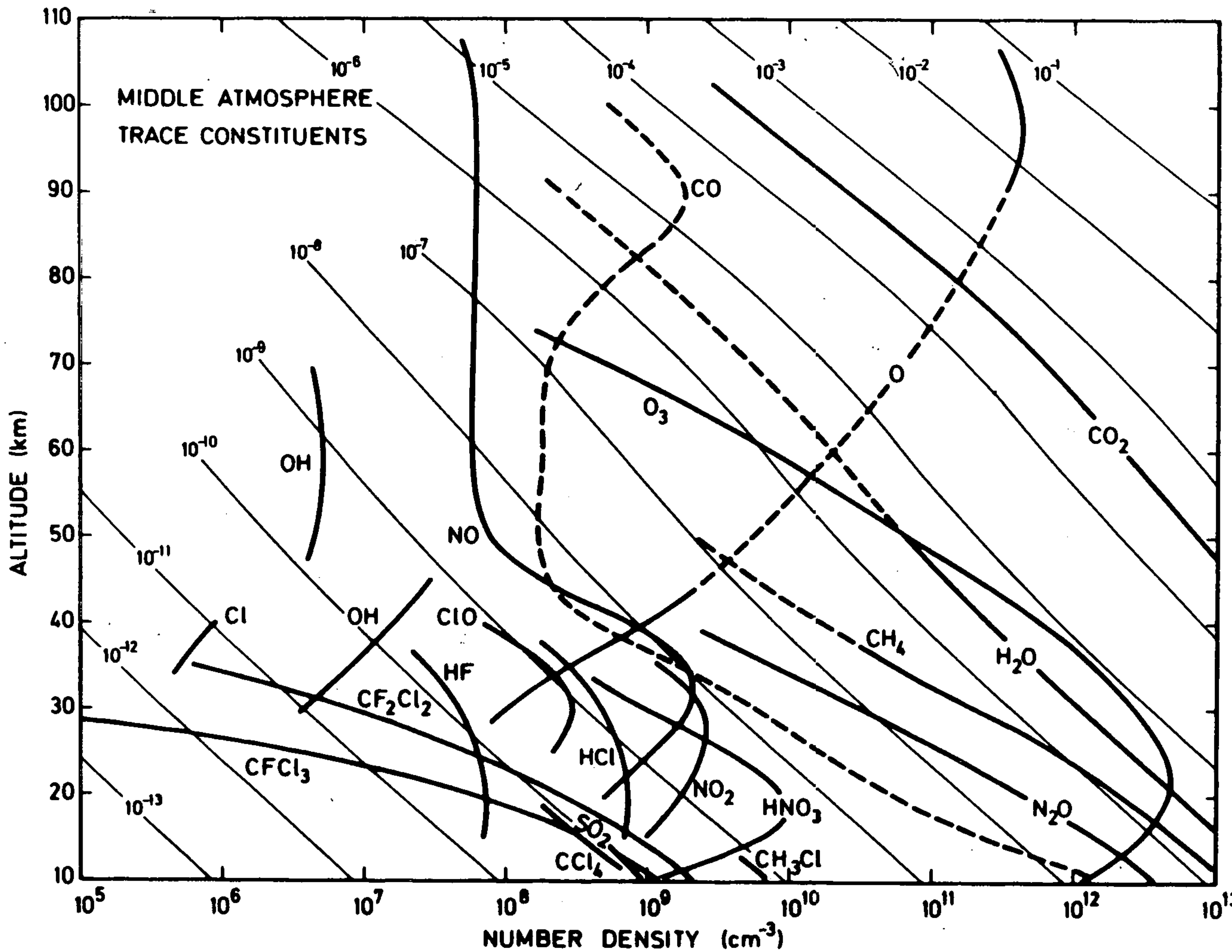

Fig. 8.- Typical number density versus altitude of middle atmosphere trace constituents. Volume concentrations are indicated from 10^{-1} to 10^{-13}.

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