

KEY ATMOSPHERIC PHOTOCHEMICAL PROCESSES

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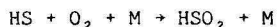
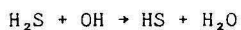
ABSTRACT

Homogeneous and heterogeneous physical and chemical processes are shaping our immediate environment at ground level and in the troposphere. All are related with the incoming actinic and thermal solar radiation. The tropospheric radiation field is mostly determined by the properties of the upper layers of the atmosphere, namely the stratosphere, the mesosphere and even the thermosphere. The composition of these regions is determined by photochemical processes among which some play the most important role. Its global change, inevitably leads to changes in our immediate environment. The ozone filtering 300 nm radiation is of paramount importance by initiating all reactions with the free radical OH in the troposphere. "Global change" is thus not only a surface or tropospheric question as far as chemistry is concerned.

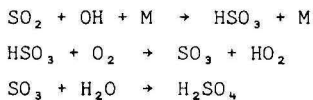
INTRODUCTION AND TROPOSPHERIC ASPECTS

Trace constituents in the tropospheric air determine its aggressivity towards man, animals, plants and constructions. Some of them lead to the formation of aerosols modifying the visibility. Others dissolve in water, changing its properties for living organisms as in the so called "acid rain" case.

The chemical elements involved are mainly nitrogen, oxygen, carbon, hydrogen and sulfur. The principal naturally emitted atmospheric sulfur compounds, H₂S and CH₃S CH₃, react to produce SO₂¹. The proposed reaction path for H₂S is



and for SO_2 is

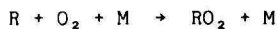


In the case of dimethyl sulfide, the OH reaction leads to the formation of sulfur dioxide and of methyl sulfonic acid. Acids lower the pH of water droplets which determines further photo-sensitized reactions in the liquid phase.

The OH radical is also of fundamental importance in the transformation of hydrocarbons through



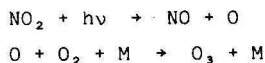
The alkyl radical can easily form peroxy radicals



In polluted areas the role of nitric oxide becomes here dominant with the formation of nitrogen dioxide



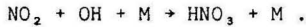
and of odd oxygen through photodissociation by blue light and subsequently of ozone



Ozone can thus be photochemically formed in the troposphere in absence of the direct photodissociation of molecular oxygen



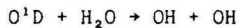
this latter reaction being only possible in the stratosphere. Nitrogen dioxide also contributes to the tropospheric acidification since again the hydroxyl radical can lead to nitric acid through



If partly formed in situ, tropospheric ozone is also transported from the stratosphere where its main atmospheric production takes place. Ozone is the precursor molecule of tropospheric oxidation. Its photodissociation by sunlight at wavelengths equal to or shorter than 310 nm produces atomic oxygen excited in the ^1D state



which through reaction with water vapor and with methane is the source of the hydroxyl radical initiating all reaction sequences described previously



The quantum yield of reaction (2) assumed to be unity below 303 nm is shown in figure 1 versus wavelength². Figure 2 shows the extinction cross sections of the most optically active atmospheric constituents for actinic radiation : O_3 and O_2 absorption and air Rayleigh scattering³. The abrupt variation of the O_3 extinction near 300 nm leads to the cut off of solar ultraviolet radiation. Atmospheric transmission plotted versus wavelength in figure 3 appears mostly controlled by ozone with important effects due to scattering by air and by aerosols⁴. The tropospheric chemistry is thus strongly dependent on the total ozone column which in addition protects life on earth. The wavelength response displayed on figure 4, of skin and of various biological molecules demonstrates the other importance of the 300 nm solar light⁵.

STRATOSPHERIC ASPECTS

The weak absorption of oxygen in the Herzberg continuum and the ozone minimum near 200 nm (figure 3) allow the solar radiation to penetrate in the stratosphere and reaction (1) to take place followed by the ozone forming reaction



The ozone abundance is maintained at stationary values, as illustrated in figure 5, by loss reactions



Due to the photodissociation in the visible the lifetime of an ozone molecule in daylight is only three hours below 20 km altitude and 100 seconds at 50 km and above this altitude, reformation taking place by reaction (3). If only reaction (4) is taken into account as odd oxygen destruction step, the computed ozone number density is larger than observed. Catalytic odd oxygen destruction cycles have been introduced involving hydrogen, nitrogen and halogen containing species. They can be summarized by



equivalent to reaction (4) and where X may be OH, NO and Cl.

For standard conditions at 35 km altitude, the reaction cycle (6) - (7) can destroy some 4×10^4 odd oxygen molecules before the breaking reaction



intervenes and is ten times more efficient than the Chapman reaction (4). The odd nitrogen active species are thus apparently as abundant as carbon dioxide from their reactivity point of view. Odd oxygen has thus a lifetime of the order of three hours. As shown in figure 6 at the altitudes of its largest abundance ozone losses are mostly due to catalytic cycles⁷ interacting mutually and thus leading to the complexity of atmospheric chemical models where radiative and dynamical aspects including feedbacks have to be accounted for as well as heterogeneous aspects which come into play in the rainout of HNO₃ and HCl in stratospheric-tropospheric exchanges. For instance, the rate of reaction (3) varies by a factor of 2 when the temperature changes from 222 to 240 K. The mid-latitude stratospheric air between 12 and 35 km is replaced by tropospheric air within 1.5 to 2.5 years.

The sources of H, N, Cl containing trace species are numerous. Odd nitrogen is formed in the thermosphere by EUV solar radiation and auroral activity and is there the source of nitric oxide which has been considered as predissociated in the Schumann-Runge bands spectral region which precludes thermospheric NO to reach the stratosphere. Recent satellite observation of NO₂ during the polar night indicate however a possibility for an odd nitrogen thermospheric source for the stratosphere. Middle atmospheric nitric oxide and nitrous oxide vertical distributions observed from Spacelab One indicate the presence of thermospheric NO down to low mesospheric levels. In addition to the low cosmic radiation influence, stratospheric odd nitrogen is due to the reaction



as proposed by Nicolet. N₂O in the stratosphere is of biological origin and linked to agriculture.

An important fraction of the chlorine source gases are now of industrial origin with a common great chemical stability. They are however and fortunately photodissociated by sunlight in the 200 nm atmospheric window, thus in the stratosphere. They would otherwise grow and induce large climatic effects by blocking the 10 μm earth thermal radiation window. The photolytic products lead to free chlorine as X in reactions (6) and (7).

The key stratospheric chemical reactions mentioned in this paragraph are essential for modelling purposes and for trend evaluation. Comprehensive chemical models take into account some 200 reactions of secondary importance but necessary for a proper representation of observations. Heterogeneous reactions with stratospheric aerosols have up to recently been considered as negligible since the collision rate is of the order of $10^{-4} \text{ sec}^{-1} \text{ per cm}^3$. High accommodation coefficients would be required for appreciable effects to take place.

The discovery⁹ of a growing antarctic spring ozone minimum, the "ozone hole", cannot be explained by current chemical processes. The simultaneous occurrence of this phenomenon with the seasonal appearance of mother of pearl stratospheric clouds already photographed in 1908 by Carl Störmer has lead to envisage heterogeneous processes at the very low (- 90°C) antarctic temperatures in that season. Much work remains to be done, particularly satellite observation since large stratospheric balloons operation is practically not feasible now in Antarctica.

MESOSPHERIC ASPECTS

In the low mesosphere and upper stratosphere, namely near the stratopause the ozone formation time from molecular oxygen by reactions (1) and (3) is about 3 hours. Photochemical equilibrium exists in daylight allowing for a check on the chemistry modelling which gives smaller amounts of ozone than observed by 50 to 100%. This is presently an important pending question about atmospheric ozone. It has been suggested¹⁰ that reaction (2) exhibiting a quantum yield smaller than unity, vibrationnally excited ground state O_2 would be formed and

dissociated by sunlight at wavelengths larger than 242 nm, up to 400 nm. An additional source of odd oxygen would thus exist and an other excited specie would lead to a key chemical atmospheric process.

Due to few observations the mesosphere is still poorly known. Infrared observations of H₂O and CO from Spacelab¹¹ have shown negative correlations between these two species and large latitudinal-seasonal variations (by a factor of 100) of CO near 70 km altitude. This is partly explained by the dominant role of the reaction



important at stratospheric levels too.

Both H₂O and CO₂ are photodissociated in the upper mesosphere and low thermosphere by sunlight at the H Lyman alpha wavelength and in the Schumann region. The fragments CO, O, H, OH have first to diffuse towards higher density altitudes before recombining, introducing dominant vertical transport terms.

DISCUSSION AND CONCLUSION

A more comprehensive description of atmospheric chemical reaction schemes is out of the scope of this session. In addition the ionic chemistry has been omitted. Enough facts have however been presented here to make a most important point. The immediate environment of man is strongly dependent on chemical reactions not only at ground level but also at higher altitudes. Fundamental processes including biochemical ones are extremely sensitive to the solar radiation penetrating in the atmosphere in the 300 nm range. We can thus only reemphasize the role of stratospheric ozone and of the upper atmosphere which can easily induce global changes even if only minutes alterations are made in its chemical stationary state.

Belgium has traditionnally much contributed to the development of many of the above mentionned aspects.

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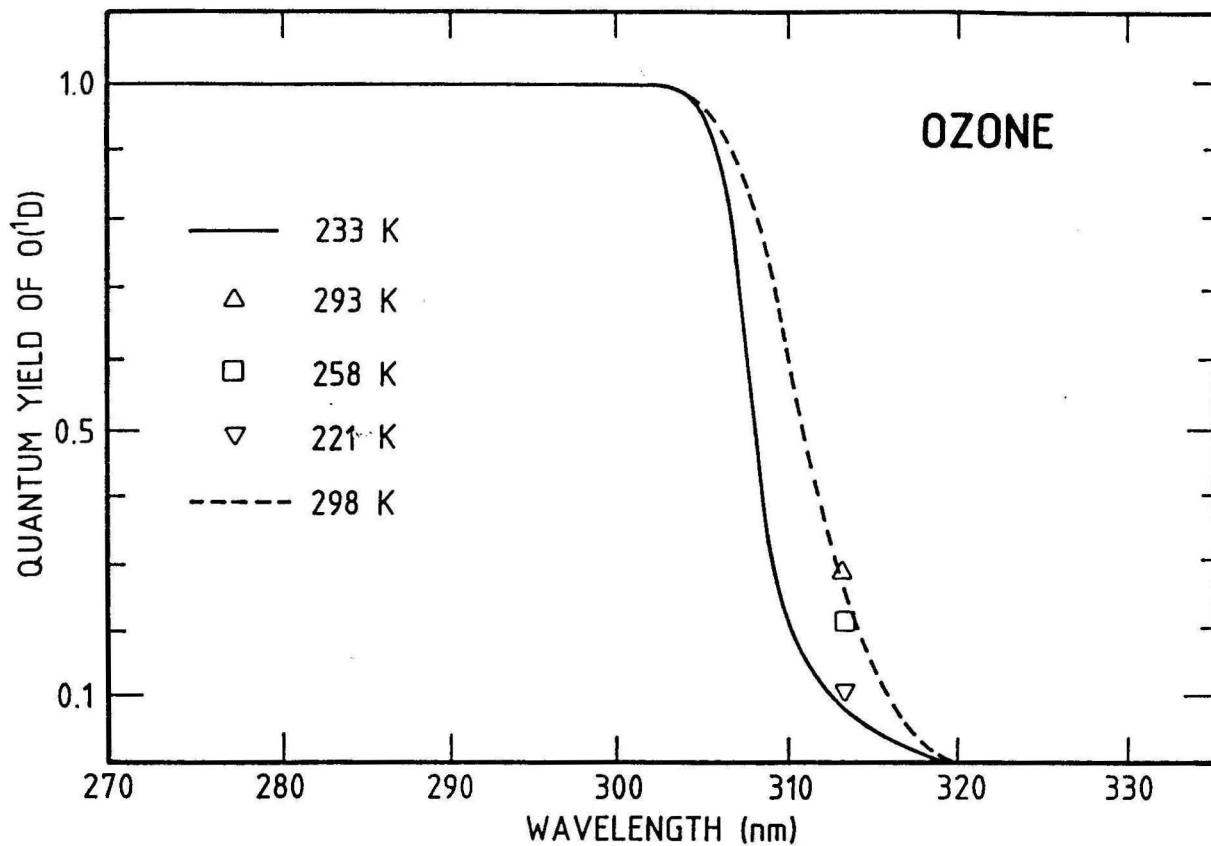


Figure 1.- Production efficiency of atomic oxygen in the excited 1D state versus wavelength by ozone photodissociation.

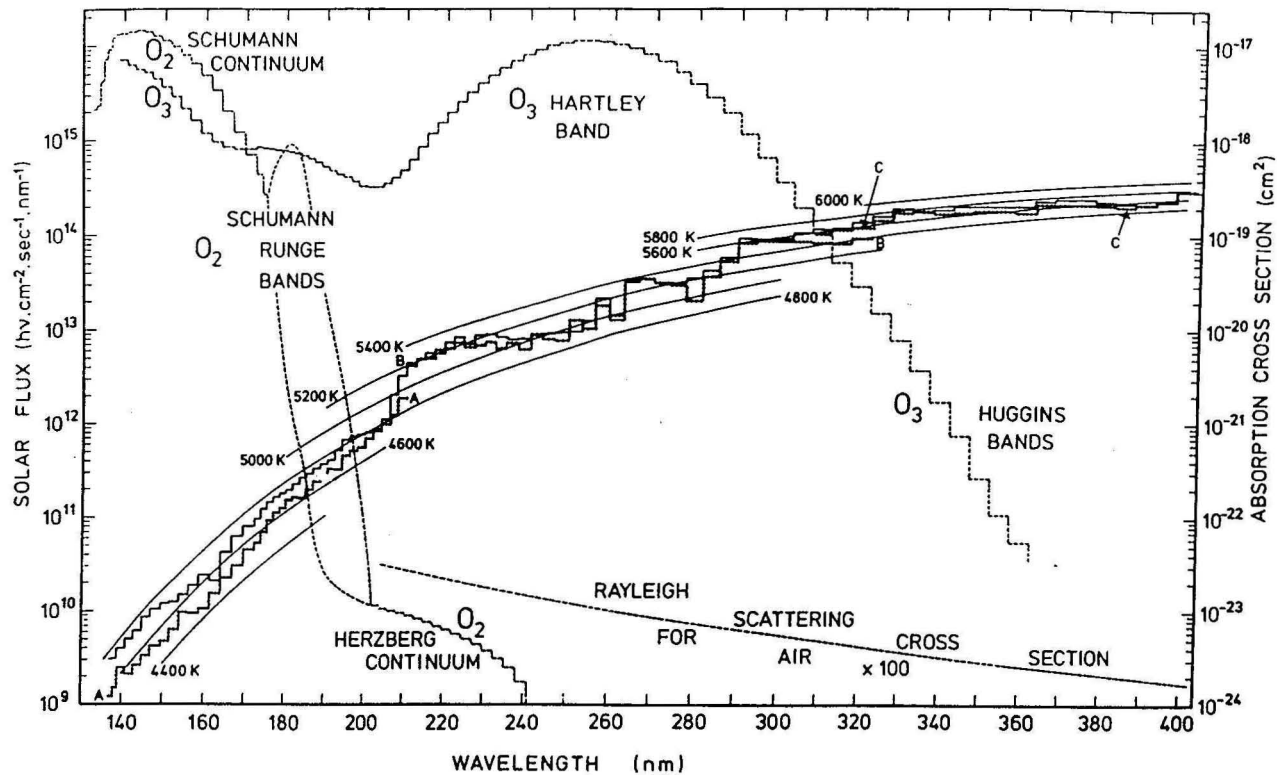


Figure 2.- Distribution versus wavelengths from 140 to 400 nm of solar irradiance at one A.U., of O₃ and O₂ extinction cross sections and of air Rayleigh scattering cross section.

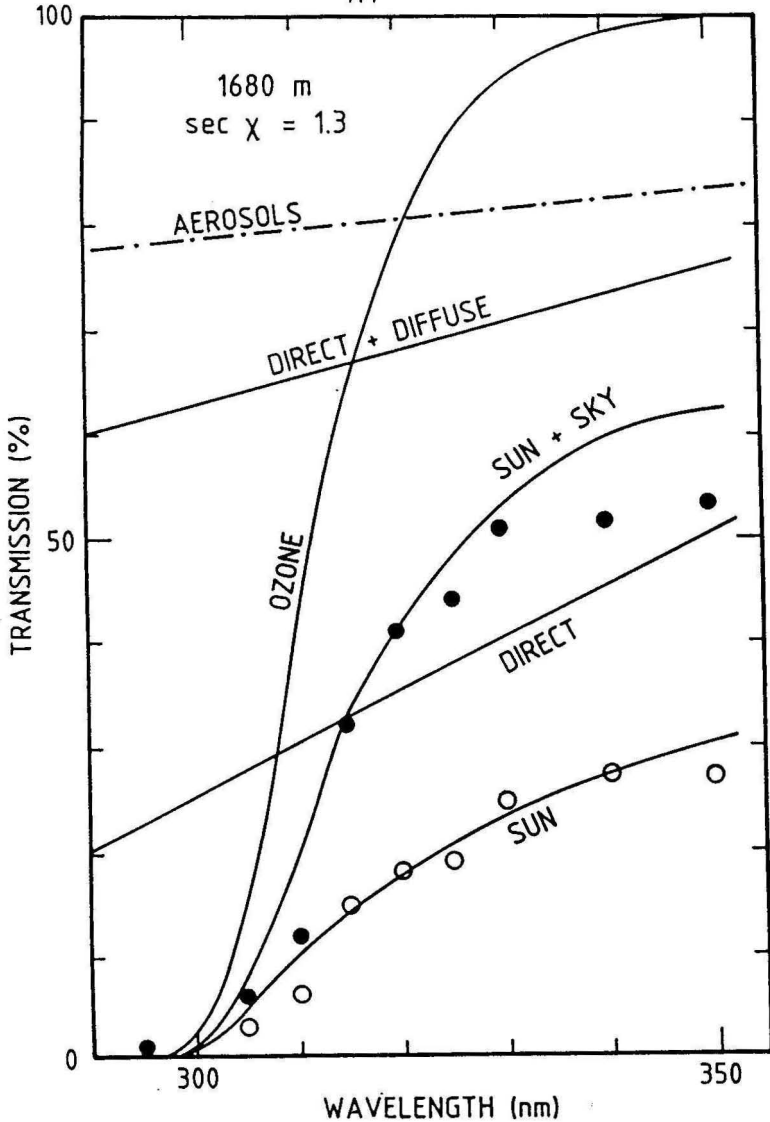


Figure 3.- Atmospheric optical transmission at an altitude of 1680 m, for a solar zenith angle of 40° and a total vertical ozone reduced thickness of 0.25 cm. The ozone contribution is represented by the line marked "ozone". The dot and dash line marked "aerosols" represents their contribution for average conditions. The transmission computed from the air column and from the scattering cross section is represented by the line marked "direct", while an apparent transmission in a two streams approximation is marked "direct + diffuse". The curve "sun" indicates the transmission of the direct solar radiation which can be compared with Bener's values⁸ represented by open circles. The curve "sun + sky" shows the effective "transmission" taking scattering into account. Here also Bener's data allow the comparison.

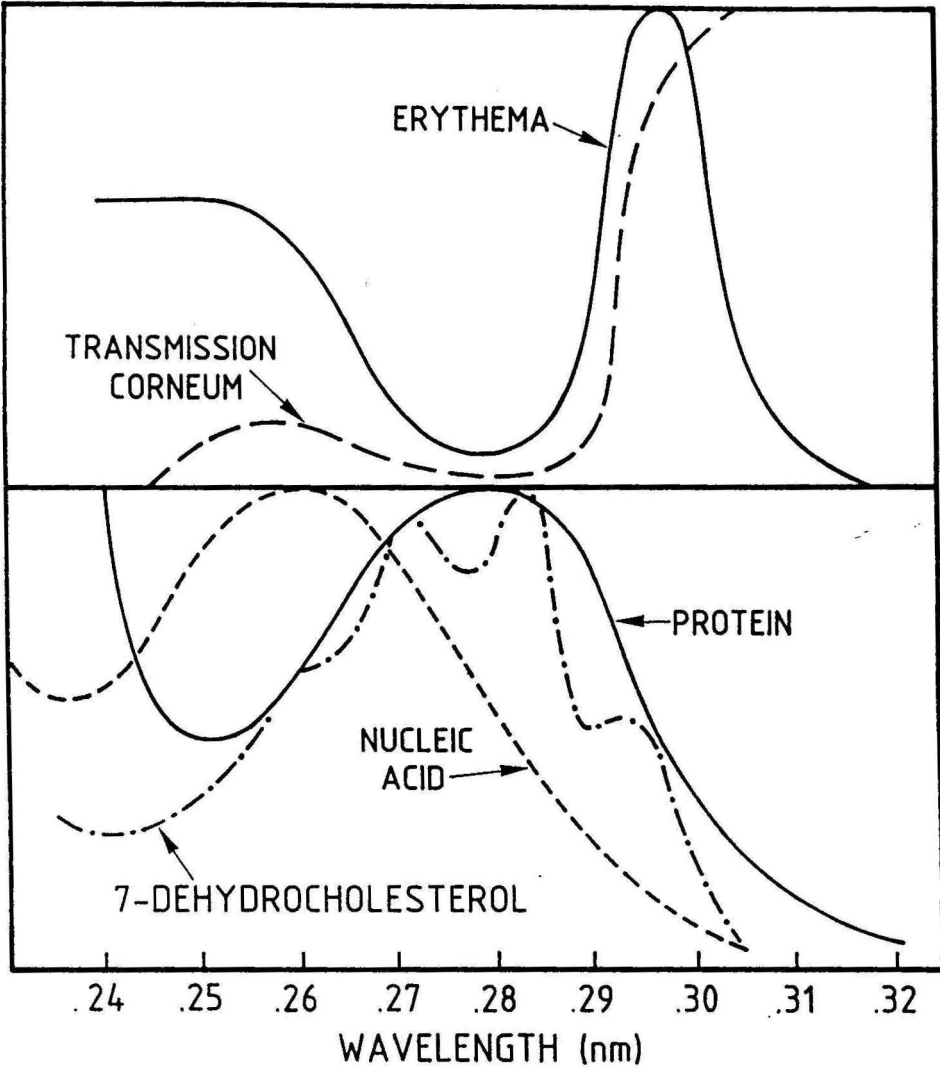


Figure 4.- Spectral relationship between erythema response and other factors. Ordinate units are arbitrary. Above, transmission corneum represents measured transmission of a sample of human corneum. Below, absorption spectra of three photoreactive substances in skin (7 - dehydrocholesterol is the precursor of Vitamin D).

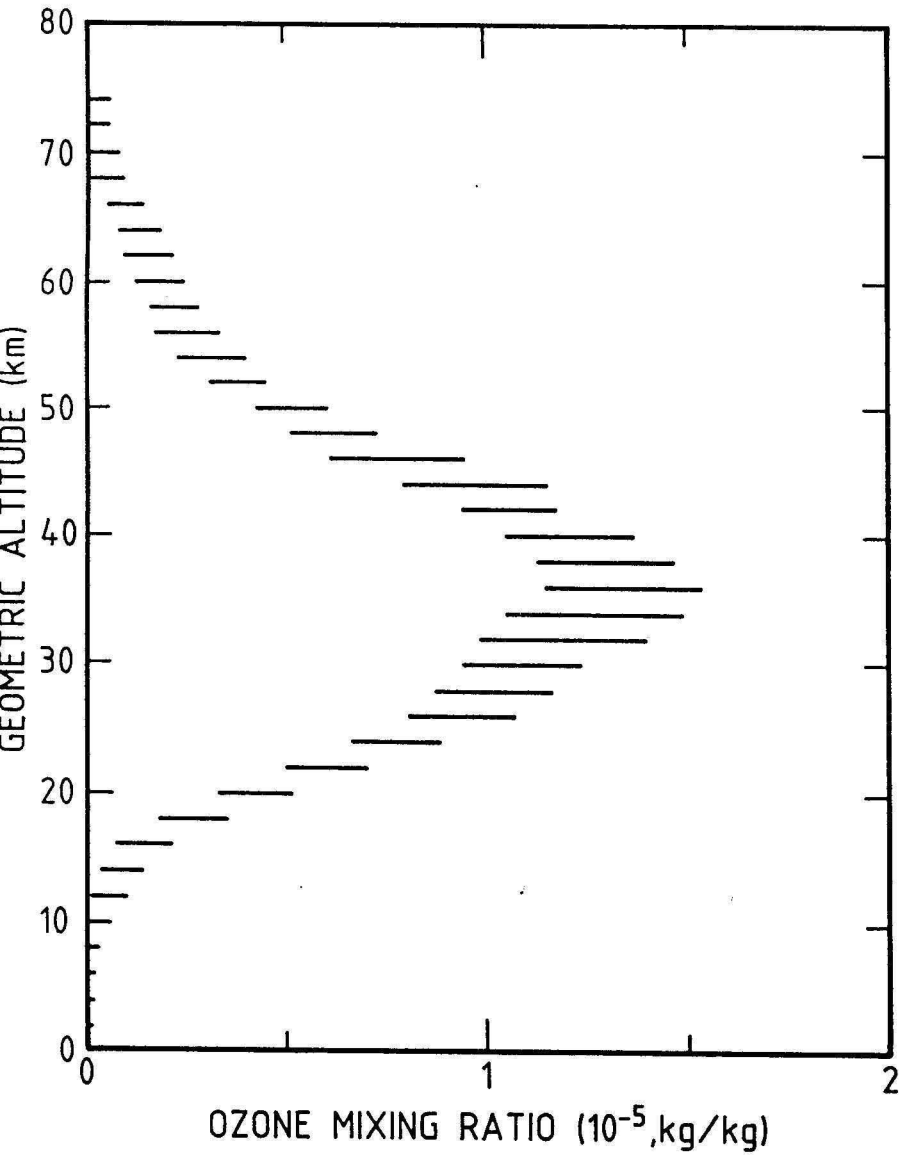


Figure 5.- Ozone mixing ratio as a function of height from mid-latitude ozone model.

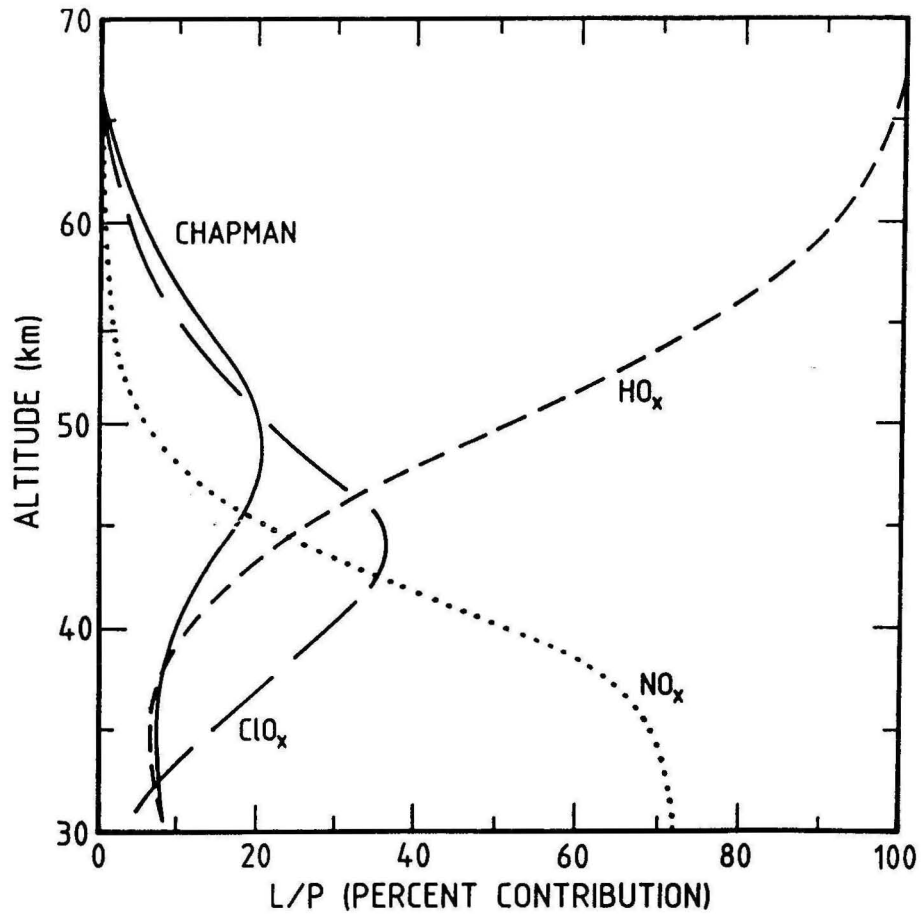


Figure 6.- Ratio (in percent) of odd oxygen loss rates due to the atomic oxygen, hydrogen, nitrogen and chlorine mechanisms to the odd oxygen production rate for typical conditions. L and P are the odd oxygen loss and production rates respectively.