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THE MIDDLE ATMOSPHERE

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Content

Note on bibliography

Basic textbooks on the topics covered by these lectures are:

" Aeronomy of the Middle Atmosphere" by G. Brasseur and S.Solomon; D. Reidel Publishing Company, Dordrecht, Holland, 1986.

" Middle Atmosphere Dynamics" by D.G. Andrews, J. R. Holton and C. B. Leovy; Academic Press, Inc. London, UK, 1987

" Minor constituents in the middle atmosphere" by T. Shimazaki; Terra Scientific Pub. Company and D. Reidel Pub. Company, Tokyo, Japan, 1985.

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1.- Characteristics of the middle atmosphere

The intermediate region of the earth atmosphere between the height of the *tropopause* , located at 6-16 km above the sea level, and that of the upper limit of the homogeneously mixed atmosphere, around 85-100 km (Fig. 1, from Shimazaki, 1985) is called MIDDLE ATMOSPHERE .

The region below the middle atmosphere has been investigated in the past, and is studied at present time by a large number of research programs in the fields of *Meteorology* and *Climatology*. The ionized component of the upper atmosphere, the *ionosphere*, has been studied since about 1930 by means of radio soundings with frequencies below 30 MHz, but the later introduction of space and other radio techniques, from 1950 on, made possible a very intensive investigation of the physical characteristics of both the neutral and ionized components of the upper layers of the atmosphere.

The middle atmosphere, on the contrary, is a height region less accessible to experimental observations and its systematic study only began about 15 years ago.

The investigation of the upper and middle atmosphere gave rise to a new discipline in the realm of atmospheric sciences: *Aeronomy*. This is a word that is not really well known and also its meaning is not clear to everybody. Brasseur and Solomon (1986) adopt the definition given by the Chambers Dictionary of Science and Technology:

> " Aeronomy- The branch of science dealing with the atmosphere of the Earth and the other planets with reference to their chemical composition, physical properties, relative motion, and reactions to radiation from outer space."

In practice, aeronomy deals with the atmospheric properties above the height of the tropopause, being the *troposphere* the domain of meteorology and climatology. However, it must be said that a clear cut between meteorology and climatology from one side and aeronomy from the other is not possible because of the effective interactions and coupling of the different regions of the atmosphere.

The thermal structure of the middle atmosphere is controlled by a minor constituent of great importance for the survival of life on earth: the ozone. This allotrope of oxygen is the only effective absorber of lethal ultraviolet radiation from the sun in the spectrum range 250-300 nm. Its height distribution shows a peak at about 25 km .

The vertical variation of temperature that could be expected in absence of ozone is shown in Fig. 1. In such a case the two main processes that will define the temperature variation with height would be: convection, that produces a decrease of temperature with height, and heating by the solar radiation of wavelength below 100 nm absorbed above about 100 km, that produces the increase of temperature in the *thermosphere* .

In the presence of ozone the temperature variation with height is determined by the radiative equilibrium between heating by O_3 absorption of solar radiation and cooling by emission of infrared radiation, mostly by CO_2 (Fig. 1). Above the *tropopause* the combination of both processes causes an increase of temperature with height up to about 50 km in the *stratosphere*, followed by a decrease with height to values below 200 K at around 85 km in the *mesosphere*. Above this height the temperature again rises due to the absorption of the solar radiation by molecular oxygen .

The dominant variations of temperature in the middle atmosphere, that greatly affects the wind system in that atmospheric region, are seasonal and latitudinal (Fig.2, from Shimazaki, 1985)). The main features of these variations are : 1) the latitudinal variation of the tropopause height, of about 16 km at low latitudes and about 8 km at high latitudes, with a sudden jump in middle latitudes , 2) the lower temperature at the tropopause height (8-16 Km) observed at lower latitudes than at higher latitudes , and 3) the presence of a winter mesosphere warmer than the summer mesosphere.This last characteristic is due to the large atmospheric circulation in the upper part of the middle atmosphere.

Diurnal and longitudinal variations of middle atmosphere temperature are less important.

The physical state of the middle atmosphere is determined also by its pressure , density and mean molecular weight. The density variation follows the ideal gas law, that can be written as:

$$p = n k T, \qquad (1)$$

were n is the number density of the atmospheric gas, k is the Boltzman constant and T is the temperature in degrees K.

The pressure decreases with height following reasonable well the hydrostatic equation:

$$p = p_0 \exp (- \int_0^z dz \,/ H) \qquad (2)$$

Where p is the pressure at height z, p_0 is the pressure at a reference height and H represents a characteristic height over which the pressure decreases by a factor e^{-1}. This height is called *scale height* and is given by:

$$H = kT / mg \qquad (3)$$

were: m is the main molecular mass in the atmosphere and g is the acceleration due to gravity.

Because at middle atmosphere heights the variation of g and m is negligible, H varies essentially with T. Table 1 gives typical values of the main physical parameters of the atmosphere below 120 km.

The mixing ratios of the main species in the middle atmosphere - molecular nitrogen (78.088 % per volume), molecular oxygen (20.949 %) and argon (0.93 %) - is almost constant with height but this region is characterized by a large number of minor constituents, many of them very active, that make it a true natural laboratory of gaseous matter chemistry. These constituents are molecular and atomic, neutral and ionized, and at ground or exited levels. These species, of very little concentration when compared with the main constituents of the atmosphere, also play an important role in radiative processes like atmospheric heating and cooling.

A primary process that originate the very complex minor constituents chemistry in the middle atmosphere is the photoionization of molecular oxygen. Other photodissociation processes of importance involve species like N_2, H_2O, CO_2 and CH_4. At the same heights, primary ionization processes from both photons and particles initiate also chains of chemical reactions that produces a large series of positive and negative ions .

The middle atmosphere plays an important role as the region of the atmosphere that links together the more dense and energetic troposphere to the upper atmosphere, less dense but more sensitive to the external space energy input . Planetary waves forced in the lower atmosphere propagate upward trough the middle atmosphere and are believed to play an important role in the behaviour of the D-region of the ionosphere. Gravity waves originated in the troposphere propagate to higher regions and represent the coupling mechanism of the dynamics of the lower to that of the upper atmosphere. At the same time changes of ozone in the middle atmosphere can affect tropospheric temperatures by altering the amount of radiation that reaches those lower levels. Fig. 3 (from SCOSTEP, 1988) shows a pictorial scheme of the interactions of the middle atmosphere with the adjacent regions.

From the viewpoint of radiopropagation the importance of middle atmosphere studies is related to the ionospheric absorption effects on the field strength of long distance propagated high frequencies radio waves and to the propagation conditions of low and very low frequencies in the earth-lower ionosphere waveguide.

2.-Elementary chemical kinetics

It has been mentioned already that the middle atmosphere is a complex chemistry laboratory where a series of primary and secondary reactions give rise to a large number of minor constituents of great importance for the structure and energy budget of the atmosphere. It is then convenient to refresh same basic concepts of chemical kinetics.

The principle governing the reactivity of chemical substances is to be found in the thermodynamical properties of the species involved. The *enthalpy* of the reaction considered (the energy needed to make or break chemical bonds among elements which compose the substance) must be examined in order to estimate the possible occurrence of a given reaction.

Let us consider a general reaction:

$$A + B \longrightarrow C + D \qquad (4)$$

The enthalpy change associate to the reaction is given by the difference between the enthalpy of formation of the products C and D and the enthalpy of formation of the reactants A and B:

$$\Delta H_R^o = \Delta H_f^o(C) + \Delta H_f^o(D) - \Delta H_f^o(A) - \Delta H_f^o(B) \qquad (5)$$

Where the superscript o refers to the standard state taken at 298.15 K by convention. If ΔH_R^o is negative, heat is released and the reaction is called *exothermic*. If it is positive, heat must be supplied to allow the reaction to occur and it is then called *endothermic*.. Exothermic reactions can proceed spontaneously in the atmosphere while endothermic processes need additional energy. This energy can be provided by an external source like a photon. Its energy is given by:

$$E = h\nu = hc/\lambda \qquad (6)$$

where ν and λ are the frequency and the wavelength of the photonic radiation, h is the Planck's constant and c is the speed of light in vacuum.

As an example two very important processes in the middle atmosphere can be considered: the photodissociation and recombination of molecular oxygen with the formation of ozone.

The photolysis of molecular oxygen to form two atoms of oxygen is :

$$O_2 + h\nu \longrightarrow 2\,O\,(^3P) \qquad (7)$$

The enthalpy of a stable element like O_2 is assumed to be zero and the enthalpy for the formation of an oxygen atom is 59.55 in kcal/mole. Equation (5) is then:

$$\Delta H_R = 2(59.55) - hc/\lambda = 119.10 - hc/\lambda \qquad (8)$$

Relation (8) tells that the process requires an external energy of 119.10 kcal/mole to be provided by the photon in order to proceed. This energy corresponds to a $\lambda \leq 240$ nm. This is the lowest wavelength able to dissociate molecular oxygen.

Atomic oxygen produced by reaction (7) will recombine, in the presence of a third arbitrary molecule M, to produce a new molecule: ozone:

$$O + O_2 + M \longrightarrow O_3 + M \qquad (9)$$

The enthalpy change associated to this reaction will be:

$$\Delta H_R^o = \Delta H_{O_3}^o + \Delta H_M^o - \Delta H_O^o - \Delta H_{O_2}^o - \Delta H_M^o \qquad (10)$$

that reduces to:

$$\Delta H_R^o = \Delta H_{O_3}^o - \Delta H_O^o \qquad (11)$$

Because $\Delta H_{O_3}^o$ is 34.1 and ΔH_O^o is 59.5 kcal/mole, the value of ΔH_R^o is -25.4. Reaction (9) is then an exothermic process liberating 25.4 kcal/mole.

The process represented by the equation (9) is an important source of heat in the mesosphere.

The following question that can be addressed is about the velocity of the reaction under study. In fact, if transport processes are ignored for the moment, the concentration of a chemically active atmospheric constituent depends upon the balance of its rates of production and destruction. This is the realm of *chemical kinetics*.

Reactions involving the transformation of a single molecule are called first order or unimolecular, those involving two particles are called two body or bimolecuaiar reactions and processes involving three particles are called three body or termolecular.

The rate of a first order reaction of the type:

$$A \longrightarrow C + D \qquad (12)$$

is given by:

$$\text{Rate} = -[d(A)/dt] = d(C)/dt = d(D)/dt = k_u\,(A) \qquad (13)$$

where k_u is the reaction rate constant given in sec^{-1} for a first order process and the parenthesis indicates the concentration of the constituent given in particles per cm^3 (or cm^{-3}).

Rearranging (13) a new expression can be obtained:

$$d(A)/(A) = -k_u\,dt \qquad (14)$$

Integrating (14), and assuming the initial value of (A) as $(A)_o$ for t = 0, is:

$$(A) = (A)_o\,e^{-k_u t} \qquad (15)$$

The time required to reduce, through process (12), the concentration of A to 1/e of its initial value - called *chemical lifetime* -, is:

$$\tau_A = 1/k_u \qquad (16)$$

This concept plays an important role in atmospheric studies. It allows, for example, to compare the chemical lifetime of a reaction involving a given constituent to the time scale of transport processes affecting that constituent, in order to determine in a first approximation if transport is affecting its concentration.

The rate of a two body reaction of the type:

$$A + B \longrightarrow C + D \qquad (17)$$

is written:

$$\text{Rate} = d(C)/dt = d(D)/dt = -[d(A)/dt] = -[d(B)/dt] = k_r\,(A)(B) \qquad (18)$$

where the reaction rate constant k_r is now given in $cm^3\ sec^{-1}$. The rate constant k_r is found to be often temperature dependent.

Two body and three body reactions can be reduced to pseudo first order reactions in order to define the chemical lifetime of the species involved. For reaction (17):

$$(A) = (A)_0\, e^{k_r (B) t} \qquad (19)$$

and the lifetime is:

$$\tau_A = 1 / k_r (B) \qquad (20)$$

Expression (20) can be used only if the concentration of B can be considered constant over the time τ_A. This is not always the case.

In practice the analysis of the lifetime and rate of change of a constituent must consider all of the processes involved in its production and destruction.

Assuming the following reactions scheme:

$$\left.\begin{array}{ll} (k_1) & A + B \longrightarrow \text{Products} \\ (k_2) & A + C + M \longrightarrow \text{Products} \\ (k_3) & A + F \longrightarrow \text{Products} \\ (k_4) & G + H \longrightarrow A + \text{Products} \end{array}\right\} (21)$$

the rate of change of the concentration of A, i.e. the continuity equation for the constituent A, and its lifetime can be written:

$$d(A)/dt = -k_1(A)(B) - k_2(A)(C)(M) - k_3(A)(F) + k_4(G)(H) \qquad (22)$$

$$\tau_A = 1/\{k_1(B) + k_2(C)(M) + k_3(F)\} \qquad (23)$$

If this lifetime is short compared with transport time and if the concentrations of B, C, F, G, and H are not changing over the time scale considered, then stationary state or *steady state* can be assumed. In such a case the concentration of A is in instantaneous equilibrium and is determined by its sources and sinks, i.e. its production and destruction processes.

In actual unimolecular processes or two and three body interactions, intermediate species are formed. These are called *activated complexes*.. As an example , reaction (12) can be considered as an effective representation of a two steps process including the formation, by collision with a third body, of an activated molecule A^* and its deactivation by another collision, and its decomposition into B and C.

This type of reactions is present in the middle atmosphere. One of it is the thermal decomposition of N_2O_5:

$$N_2O_5 = NO_2 + NO_3, \qquad (24)$$

a very important process in the stratosphere.

Photolysis processes can also produce unstable electronic excited molecular species that can decompose into their constituent atoms:

$$XY + h\nu \longrightarrow XY^* \qquad (25)$$

$$XY^* \longrightarrow X + Y \qquad (25')$$

Often the products X and Y are also electronically excited. Rate constant of photolitic reactions like (25) are normally designated with j instead of k .

An important example of these reactions in the middle atmosphere is the photodissociation of ozone:

$$O_3 + h\nu \longrightarrow O^*$$

$$O_3 \longrightarrow O(^1D) + O_2(^1\Delta_g) \qquad (26)$$

$$O(^1D) + H_2O \longrightarrow 2\,HO \qquad (27)$$

Reaction (26) provides the major source of free radical OH of high reactivity in the stratosphere. On the other hand, process (27) is important in the negative ions chemistry of the D region of the ionosphere at mesospheric heights.

The basic concepts of chemical kinetics summarized above, in particular with the help of expressions (12) to (23) are valid for both neutral and ionic chemistry. The main reactions of ions, positive and negative, are charge exchange reactions of the type:

$$XY^{+or-} + ZW \longrightarrow XY + ZW^{+or-} \qquad (28)$$

or:

$$XY^{+or-} + ZW + M \longrightarrow XY^{+or-}\ XY + M \qquad (29)$$

These reactions are very effective in controlling ion and electron concentration in the middle atmosphere. Primary positive ions are formed in photoionization processes or energetic particle collisions with neutrals. Negative ions originate in attachment processes like:

$$e + XY + M \longrightarrow XY^- + M \qquad (30)$$

That can give rise to large chains of charge exchange reactions.

3.- Solar radiation and its atmospheric effects

The atmosphere is a mixture of gases under the effect of the photon and particle energy of the sun. Both the chemical kinetics and the dynamics of the atmospheric gases are controlled by this external source of energy.

Most of the solar energy reaching the Earth's atmosphere is originated in the thin layer that defines and limits the visible sun: the *photosphere* . From the energy viewpoint this layer behaves as a black body with a temperature of about 6000 K. Transient phenomena in the photosphere, known as sunspots and faculae, influence the variability of the solar emissions. The sunspots are generally grouped defining *active regions* in the solar disk. In most cases faculae are also associated to active regions.

The appearance of active regions in the sun shows a fairly regular behaviour with a periodicity close to 11 years in average. This periodicity define the *solar cicle* .

Photospheric emission is characterized by a continuum with superimposed dark lines called the *Fraunhofer lines* (Fig. 4, from Brasseur and Solomon, 1986)). The *chromosphere*, the hotter solar layer above the photosphere, seen only sometimes during total solar eclipses, radiates in discrete emission lines. Also the corona, which extends outward for several solar radii, radiates in several emission lines.

Solar flares are intense transient phenomena, originated in the active regions of the chromosphere, that produce bursts of enhanced emissions of ionizing radiation lasting for periods ranging from few minutes to one hour or so.

The chromosphere and the corona also radiates at radio waves wavelengths. These emissions are easily recorded on Earth and are very sensitive to solar changes being good indicators of solar activity.

The solar corona radiates also continuously a fully ionized and electrically neutral plasma that streams outward from the sun carrying a magnetic field: the *solar wind* . It consists of protons, doubly charged helium ions, a small number of other positively charged particles, and enough electrons to maintain the electrical neutrality. The solar wind is highly variable with the solar activity.

Other particles are also emitted from the sun at the time of solar flares. These transient phenomena are called Solar Cosmic Rays events (SCR), Solar Proton events, Solar Electron events, and Polar Cap Absorption events (PCA). They are important sources of energy that affects particularly the middle atmosphere.

Units more commonly used to measure the energy flux of the solar photonic irradiance, and their equivalence are:

$$1 \text{ erg cm}^{-2} \text{ sec}^{-1} = 1 \text{ mw m}^{-1} = 5.0324 \times 10^{15} \lambda \text{ photons cm}^{-2} \text{ sec}^{-1}$$

or:

$$1 \text{ photon cm}^{-2} \text{ sec}^{-1} = 1.9871 \times 10^{-16} / \lambda \text{ erg cm}^{-2} \text{ sec}^{-1}$$

where λ represents the wavelength of the solar radiation .

Fig. 5 (from Brasseur and Solomon, 1986) shows the solar irradiance, including the fluxes of photonic emissions during solar flares, and the solar regions responsible for the emission.

The theory of the absorption of the solar radiation by the atmosphere was first presented by Chapman (1931) . It describes both the ionization and the absorption processes in the atmosphere. A complete discussion of the theory has been given earlier in this College. The theory allows to define the depth of penetration or penetration height as the height where the maximum absorption of the given wavelenght occurs.

For an isothermal atmosphere the equation for the penetration height z_m can be written as:

$$z_m = H \ln (\sigma \sec \chi) \qquad (31)$$

where σ is the absorption cross section and χ the solar zenith angle.

At the level z_m the intensity of the radiation is reduced to e^{-1} times the value at the top of the atmosphere.

Fig. 6 (from Brasseur and Solomon, 1986) shows the depth of penetration of the solar radiation in the atmosphere . It can be seen that the middle atmosphere is the height region where the radiation between 100 and 320 nm is absorbed by O_2 and O_3 .

According to equation (31) the penetration height is lowest at vertical incidence and increases with increasing χ . An important consequence of this fact is that the solar radiation can penetrate deeper in summer than in winter, at lower latitudes than at higher latitudes, and closer to noon time that near sunrise or sunset.

The absorption of ultraviolet solar radiation by ozone is the principal source of heat in both the stratosphere and the mesosphere.

Another process of importance, at those height in the atmosphere where density is still high, is multiple scattering of solar radiation by air molecules and aerosols. Scattering occurs when a particle attracts energy from the incident wave and reradiate that energy in all directions. Atmospheric particles responsible for scattering cover from gas molecules ($\approx 10^{-8}$ cm) to large raindrops and hail ($\approx$ cm). Fig. 7 (from Brasseur and Solomon, 1986) shows the ratio between scattered and direct solar radiation at different wavelenghts at 40 km.

Taking into account this process it can be shown that the attenuation of radiation in the atmosphere is the result of two contributions: absorption and scattering. Through complex theoretical treatments it is possible to show, as an example, that an increase in aerosol content always increases the effective photodissociation of ozone at higher levels and reduces it at low levels in the middle atmosphere.

Solar radiation is also reflected from the Earth surface. The total radiation reflected by it plus the upward diffracted one is called the planet *albedo* .

The radiation reemitted from the Earth, observed above the atmosphere, is equivalent to that emitted by a black body with an average temperature of about 256 K, as seen in Fig. 8 (from Wayne, 1985). The figure shows a huge temperature deep in the wavelength region between 12 and 17 µm. This correspond to the infra-red active band region of the atmospheric carbon dioxide. This is to say that CO_2 has effectively trapped the radiation coming from the surface of the Earth. In fact, CO_2 absorbs and emits infra-red radiation with an effective cooling of the stratosphere and lower mesosphere and an increase of temperature of the Earth surface. This is the *greenhouse effect.* of carbon dioxide. The presence of O_3 and H_2O in the middle atmosphere also contribute to this effect, but to a lesser degree.

The photodissociation of the main component of the atmosphere, N_2, plays a very little role in the middle atmosphere. The absorption of molecular oxygen, with the production of the very active atomic oxygen that in turn produces ozone, which is also photodissociated, dominate instead the chemical kinetics of the neutral middle atmosphere.and is an important factor in the ion chemistry of the region.

At mesospheric heights, the photodissociation of H_2O and CH_4 by the solar radiation below 200 nm is the source of two active minor constituents: H and OH. This species link the chemistry of oxygen with the chemistry of water in the middle atmosphere.

In recent years, middle atmosphere photodissociation processes involving chlorine compounds of natural and anthropogenic origin have been widely studied because they represents a source of free Cl, a very effective destroyer of ozone.

Solar photon energy plays also an important role as a source of ionization in the mesosphere. The radiation involved includes extreme ultraviolet , X-rays and Lyman- α .

During large solar flares protons of high energies (10-300 MeV) are ejected from the sun and produces intense ionization in the middle atmosphere at high latitudes. This events are known as PCA events, and affects also the chemical kinetics of the neutral middle atmosphere through the increased ionization of molecular nitrogen. The molecular nitrogen ions are capable to generate neutral NO_x and HO_x free radicals that play an important riole in the destruction of ozone in the stratosphere and mesosphere respectively. Fig. 9 (from Brasseur and Solomon, 1986) shows the effect of a proton event, at high latitudes, on the total ozone content above about 38 km (4 mb).

<u>4.- Minor neutral constituents</u>

It has been mentioned already that the middle atmosphere is characterized by the presence of a large number of minor constituents that are generated by photochemical processes. These initial process produces very active species that originate, through chains of reactions, long lasting constituents of low concentration but of great importance to the understanding of the middle atmosphere behaviour.

Fig. 10 (Shimazaki, 1985) shows, in an illustrative manner, the height variation of some of the neutral minor constituents observed in the middle atmosphere. The curves marked 10^{-1}, 10^{-2}, etc. represent the variations of the concentrations for the case of constant mixing ratio with height. So that if a given species is completely mixed the slope of its concentration should follow one of those lines.

The figure is adequate to give a general idea about the behaviour of minor species with altitude and to differentiate between two types. One corresponds to constituents which concentration decreases monotonously with height, indicating a tendency toward constant mixing, the other shows a maximum concentration in the middle atmosphere.

The first group includes water vapor carbon dioxide, methane, sulfur dioxide and various chlorofluoromethanes. These compounds have their origin , natural or anthropogenic, near the surface of the Earth and are transported by dynamical processes into the middle atmosphere. They can be called *primary minor constituents.*

The second group contains: ozone, nitrogen oxides, free radicals, including chlorine, etc. They are produced at middle atmosphere heights by photochemical reactions and chain of reactions. They can be named *secondary minor constituents.*

It is outside the scope of these lectures to give a detailed description of the behaviour of the minor neutral components of the middle atmosphere. However it appears important to briefly outline the chemistry of one these species: ozone. The reason for this choice is the importance of atmospheric ozone as a screen for solar radiations that would be lethal to life on Earth if they could reach the surface without being absorbed. Ozone plays also an important role as the starter, by charge exchange, of the main chain of reactions in the negative ions chemistry in the middle atmosphere.

The solar ultraviolet radiation of biological interest can be divided into three bands: UV-A (320-400 nm), UV-B (280-320 nm) and UV-C (< 280 nm). Fig. 11(from Shimazaki, 1985) shows the intensity of the solar radiation at the Earth surface at various levels of total ozone content in the atmosphere. The radiation that reaches the lower atmospheric regions and is more critically variable as a function of ozone is the UV-B. This band of radiation is capable to destroy or alter deoxyiribonucleic (DNA) molecules that are essential components of all living matter, being a basis material for the chromosomes.

It is well known the fact that in recent years unusual decrease of ozone content in the atmosphere have been observed, in particular at high latitudes in the southern hemisphere. In a recent paper, Heath (1988) studied the non seasonal changes of the ozone content , using data from satellite and ground observations. He found that the decrease is observed all over the globe, but more pronounced at the southern pole region. Fig. 12 taken from his paper shows the behaviour of ozone content from ground data, as a function of climate zones. The same trend is also observed in the data obtained by satellite observations, as is seen in Fig. 13, taken from the same paper.

The basic reactions of the ozone chemistry are shown in Fig. 14 (from Shimazaki, 1985). It can be seen that the oxygen chemistry starts with the photodissociation of O_2 to form atomic oxygen, and the following recombination to produce ozone. This, in turn, is photodissociated and reacts with atomic oxygen to produce back molecular oxygen.

The simple picture of Fig. 14 is actually complicated by the complex interactions with: 1) the family of hydrogen compounds, originated by the photodissociation of water vapor and methane in the middle atmosphere; 2) the family of nitrogen compounds , produced by the destruction of N_2O, transported by vertical motions from the Earth surface level into the stratosphere, in the reaction with atomic oxygen; 3) chlorine compounds of natural and athropogenic origin that are produced at the Earth surface and are transported toward the stratosphere and react with other species or are photodisocciated, generating free chlorine.

Making an attempt to give a simplified picture of the reactions involved, the following continuity equations can be given for the two odd allotropes of oxygen, O and O_3 (Brasseur and Solomon, 1985):

$$d(O_3)/dt = k_2(M)(O_2)(O) - j_{O3}(O_3) - k_3(O)(O_3) - a_2(H)(O_3) - a_6(OH)(O_3) - a_{6b}(HO_2)(O_3) - b_4(NO_2)(O_3) - d_2(Cl)(O_3) \quad (32)$$

$$d(O)/dt = 2\, j_{O2}(O_2) + j_{O3}(O_3) + j_{NO2}(NO_2) - 2k_1(M)(O)^2 - k_2(M)(O_2)(O) \quad k_3(O)(O_3) - a_5(OH)(O) - a_7(HO_2)(O) - b_3(NO_2)(O) - d_3(ClO)(O) \quad (33)$$

The letters j_i, k_i, a_i, b_i and d_i indicate reaction rate constants for the given reaction, with the same meaning adopted for equation (22) above.

Fig. 15 (from Brasseur and Solomon, 1986) give a model of the relative importance of each of the terms of (32) and (33) as a function of height. It can be seen, as an example, that the relative importance of a given reaction and component in the destruction of ozone varies with height.

Fig. 16 (from Shimazaki, 1985) shows the variation of the chemical time constants of oxygen odd allotropes in the case of a pure oxygen atmosphere and in the presence of other species. It shows also an estimate of the dynamical time constant. It is important to note that the ozone concentration is dominated by chemical processes from 30 to 75 km. Transport processes can affect ozone in the lower stratosphere and in the troposphere.

Kinnison et al(1988) have recently analyzed the combined effect of the nitrogen oxides, chlorine compounds and hydrogen compounds in the ozone chemistry by means of a one- dimensional chemical-radiative-transport model. They found that the nitrogen and hydrogen families almost completely suppress the effect on ozone of a reasonable high concentration of chlorine , but the absence of those compounds make chlorine a powerful destroyer of ozone. These results show the complexity of the study of the effect of very minor species of natural or anthropogenic origin on key species like ozone.

A brief mention is necessary also due to a minor neutral constituent of importance to the ion chemistry in the upper mesosphere: NO. This species is formed in the thermosphere and in the upper mesosphere by dissociation of molecular nitrogen and reaction with molecular oxygen. Most of the stratospheric NO is originated in the tropospheric N_2O. The source of this compound is biological.

NO transport appears to play a role in the winter anomaly of D-region high frequency radiowave absorption (Garcia et al, 1987).

5.-Minor ionized species

Solar radiation, both photonic and corpuscular, galactic cosmic rays and precipitated particles from the magnetosphere into the more dense atmosphere, are sources of ionization in the middle atmosphere.

Fig. 17 (from Brasseur and Solomon, 1986) shows typical values of the ionization rates produced by different sources during daytime and at night, in the mesosphere. It can be seen that the main source of solar origin are Lyman-α ionization of nitric oxide and hard x-rays ionization of the main components above 90 km. Galactic cosmic rays ionization is important below 60 km.

Nighttime ionization is mainly due to precipitated energetic particles, scattered solar Lyman-α and cosmic rays. X-rays emitted from certain stars can also contribute but to a lesser extent.

Sporadic sources of ionization like increased fluxes of x-rays during solar flares and precipitation of particles at high latitudes during solar proton events can modify substantially the ionization rates shown in Fig. 17. Under these conditions the resulting increase of electron density can alter the radiopropagation condition to a great extent. The increased ionospheric absorption will lower the field strength of high frequency signals. Also the height of reflection of low and very low frequencies will be reduced by the increased ionization.

Fig. 18 (from Brasseur and Solomon, 1986) shows the ionization rate associated to some solar proton events.

Mesospheric ion chemistry, i.e. the ion chemistry of the D-region of the ionosphere, is characterized by the presence of a large family of both positive and negative ions.

The initial positive ions are: O_2^+ generated by direct ionization of O_2 and $O_2\,(^1\Delta_g)$ and by charge exchange with N_2^+, and NO^+ generated by ionization of Lyman-α . A very complex family of positive ions follows from charge exchange reactions. It includes hydration processes that give rise to cluster ions that contains water molecules. Fig. 19 (from Brasseur and Solomon, 1986) shows a schematic diagram of the positive ion chemistry in the D-region. Fig. 20 shows model calculations of daytime positive ions concentration in the D-region (Rstbergs and Radicella , 1988) .

Experimental observations have shown that free electrons are absent below 65-70 km during daytime and below 75-80 km at night. However, electrical neutrality implies that the free electrons produced by primary ionization present at all heights in the mesosphere must be attached to molecules to produce negative ions. In fact, two initial negative ions, O_2^- and O^-, generate a large number of negative ions by charge exchange with several minor neutral species like ozone. Fig. 21 gives a schematic diagram of the complex negative ion chemistry in the mesosphere. Fig. 22 (Restbergs and Radicella, 1988) shows a model calculation of the daytime main negative ions concentration in the region. It is clear that the free electron density in the D-region is controlled by the presence of negative ions. It has been shown (Restbergs and Radicella, 1981) that atomic oxygen plays a decisive role in the balance between electron density and negative ions concentration, in the transition region where electrons are rapidly converted into negative ions.

Another feature that can be noted in the negative ions chemistry of the D-region is the presence of hydration processes similar to those acting in the positive ions chemistry.

The variability of the electron density in the D-region will be given in other lectures of this College, when studying ionospheric absorption.

6.- Fundamentals of atmospheric dynamics

The study of the dynamical properties of the middle atmosphere is essential to the understanding of the complex behaviour of the atmospheric gas in that region. This cannot be done without considering the interactions between radiation, chemistry and dynamics.

The temperature distribution in the middle atmosphere varies with latitude following the balance between the net radiative drive, due to the sum of solar heating and infrared heating and cooling, and heat transport plus the local temperature changes produced by the air motions.

The net radiative heating distribution is maximum at the summer pole and minimum at the winter pole. The maximum equinoctial heating is at the equator and the minima at the poles.

This differential heating must be dynamically balanced by motions of the atmospheric gas. This is obtained by a circulation in the meridional plane called *diabatic circulation* . At the solstice this circulation consists of rising motions at the summer pole region, a meridional drift toward the winter hemisphere, and sinking near the winter pole. Typical averaged observed values of meridional winds in the mesosphere at a fixed location are given in Fig. 23 (from Brasseur and Solomon, 1986) .

The Coriolis torque exerted by the meridional circulation tends to generate mean zonal westerlies winds in the winter hemisphere and easterly in the summer hemisphere. At the equinoxes the radiative drive generate a weak diabatic circulation that rises the air in the equatorial region and drift it poleward in the meridional plane of the spring and autumn hemispheres. The Coriolis force thus generates only weak mean zonal winds westerlies in both hemispheres.

Fig. 24 and Fig. 25 (from Andrews et Al., 1987) give the schematic variations of temperature and mean zonal winds as a function of height and latitude for solstice conditions.

Both the mean zonal wind and the temperature distributions in the middle atmosphere are maintained by the competing effects of the radiative heating and the forcing of motions of scales that range from global -scale tides to microscale turbulence. Although this last type of motions is of importance the dominant dynamical phenomena in the middle atmosphere are due to coherent wave motions of various classes.

Inertia and restoring forces acting over parcels of air, removed from their equilibrium conditions in height or latitude, generate the wave motions that affects the middle atmosphere. When the restoring force is provided by gravity the motions will be of the internal *gravity waves* type. If the origin of the force is the poleward gradient of planetary vorticity, the motions will be of of the *planetary* or *Rossby waves* class.

A qualitative indication of the velocities of the different motions, as a function of height , is given in Fig. 26 (from Andrews et Al., 1987).

Another type of motion is represented by the global-scale daily oscillations of the atmosphere of thermal origin, due to the diurnal variations of the absorption of solar radiation by water vapor and ozone. These are the *atmospheric tides* .

7.- Interactions between the middle atmosphere and the lower atmosphere

The middle atmosphere is strongly linked with the adjacent atmospheric regions. With the lower atmosphere the interaction is dynamical, radiative, chemical and also electromagnetic. The complexity of these interactions is shown in Fig. 27 (from Shimazaki, 1985).

Planetary waves generated by orography and heat sources in the troposphere influence substantially the circulation in the stratosphere. Internal gravity waves generated in the lower atmosphere propagates upward to the middle and upper atmosphere. Their influence is seen clearly in the ionosphere being observed as electron density perturbations of the type of Travelling Ionospheric Disturbances (TID) (Waldock and Jones, 1987). The effect of gravity waves in the mesospheric ion distribution has been modelled showing their influence on the main structure and irregularities of the electron density profiles in the D-region. (Sugiyama, 1988).

Also atmospheric tides excited in the lower atmosphere propagate into the middle and upper atmosphere, and recent modeling effort have been successful in simulate upward tide propagation (Forbes, 1987).

It is now accepted that stratospheric temperature is strongly affected by changes in the concentration of ozone and carbon dioxide, and the effect of dynamics on temperature is very significant . This is particularly so in the case of the *sudden stratospheric warmings* which occurs usually in the northern winter latitudes and last to few days. The increase of temperature starts generally at the upper stratospheric heights and propagates downward to the lower stratosphere. These events are accompanied by temperature decrease in the mesosphere. The sudden stratospheric warmings are caused by the interaction between gravity waves and the mean wind system. Fig. 28 (from Shimazaki, 1985) illustrates the temperature behaviour at the level of 30 mb (25 km), during a winter event.

In turn, winter stratospheric warmings appears to have an effect on the electron concentration in the D-region, as it has been shown by early works summarized by Kazimirovsky (1985). The International Middle Atmosphere Program (MAP) have organized a multidisciplinary and multinational project called Winter In Northern Europe (WINE) that comprised study of structure, dynamics and composition of the middle atmosphere in northern winter. A complex set of coordinated experiments were performed during the winter season 1983-84. The results of many aspects of this effort were published in a special issue of the Journal of Atmospheric and Terrestrial Physics in 1987 (Vol. 49, Nos 7/8). Among these outcomes one regarding the interaction of sudden stratospheric warmings with D- region electron density shows that minor warmings correlate with minima in ionospheric absorptions; another one was the nighttime depletion of ionization in the upper mesosphere observed in the presence of stratospheric warmings (Williams et al. 1987).

To show the degree of complexity of the atmospheric interactions it can be mentioned that the increase of D-region electron density observed in winter, that give rise to the well known *winter anomaly* of the ionospheric absorption, is due to the downward transport of excess NO from the polar night thermosphere (Taubenheim, 1983). This process is an example of the interactions existing between the middle and the upper atmosphere.

To end this topic it can be also pointed out that the middle atmosphere acts also as the electromagnetic link between between the lower and the upper atmosphere. Electromagnetic energy generated near the ground by both natural and athropogenic sources (thunderstorms, earthquakes, power lines etc.) are coupled to the upper regions of the atmosphere by the transmission line-like lower and middle atmosphere from the ground to about 85 km (Volland, 1987).

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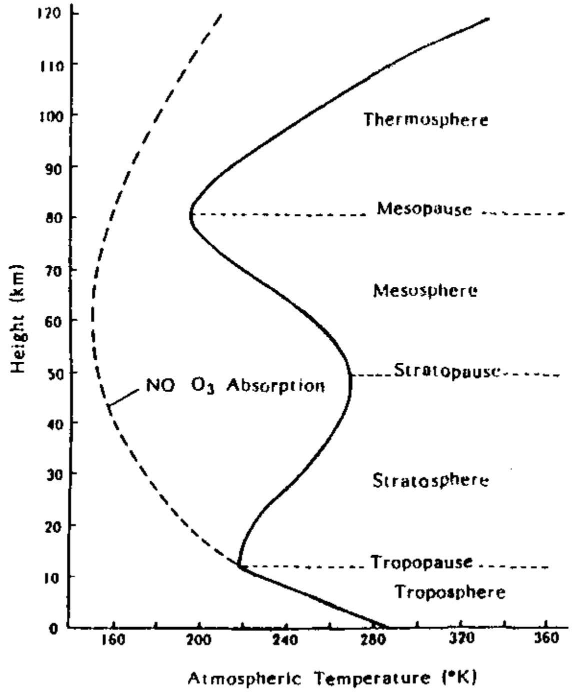

FIG. 1 Schematic illustration of a vertical profile of atmospheric temperature and names of subdivisions of the atmosphere. Dashed curve indicates a profile when there were no ozone absorption.

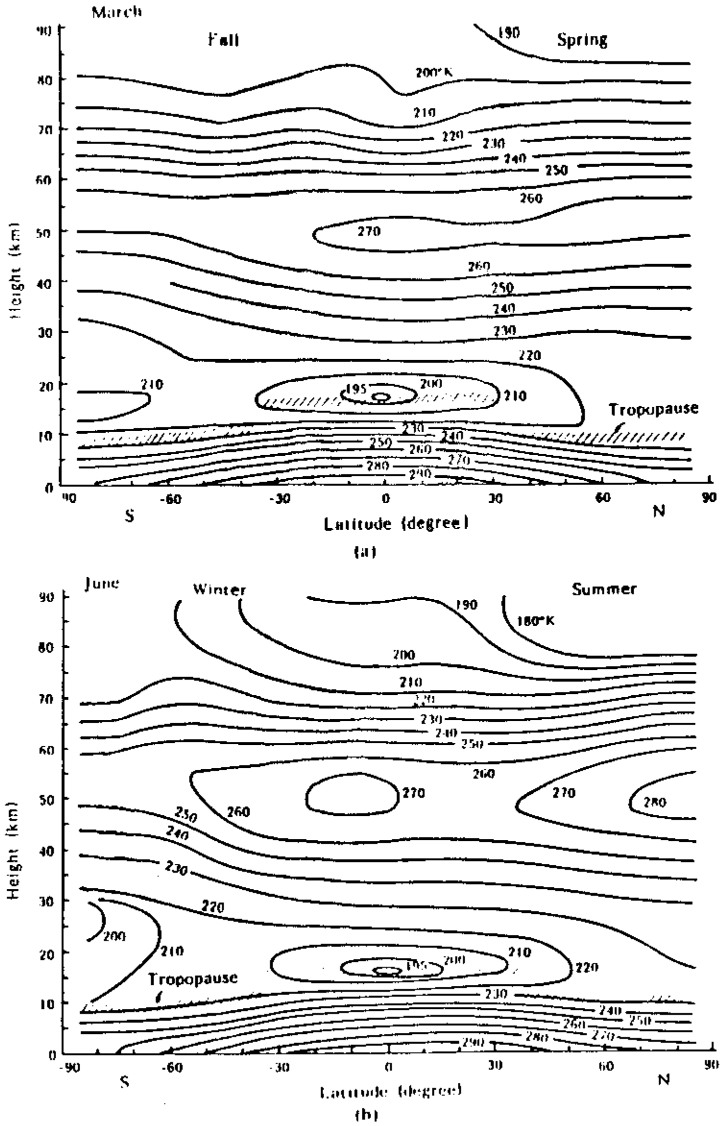

FIG. 2 (a) Contour plots of the atmospheric temperature in the meridional plane for March. Shaded area indicates the tropopause. (b) The same as Fig. 2.2

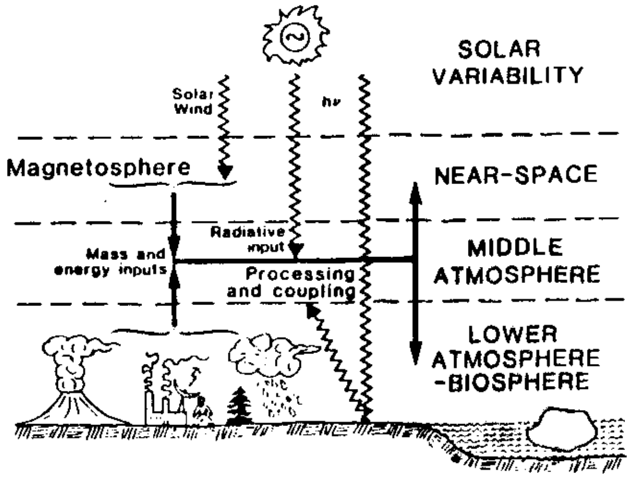

Fig. 3 Sketch of middle atmosphere interactions with adjacent regions and responses to energy and mass inputs (from SCOSTEP 1986b).

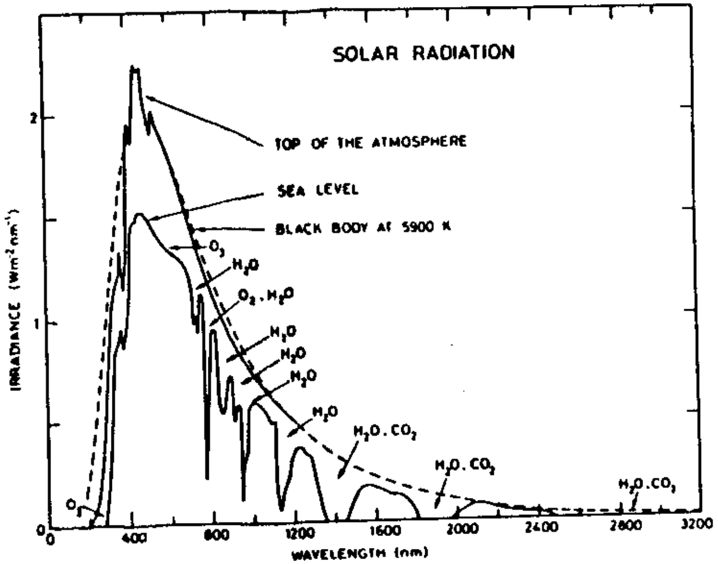

Fig. 4 Spectrum of solar radiation (UV, visible, IR) outside the earth's atmosphere and at sea level. (Adapted from Coulson, 1975).

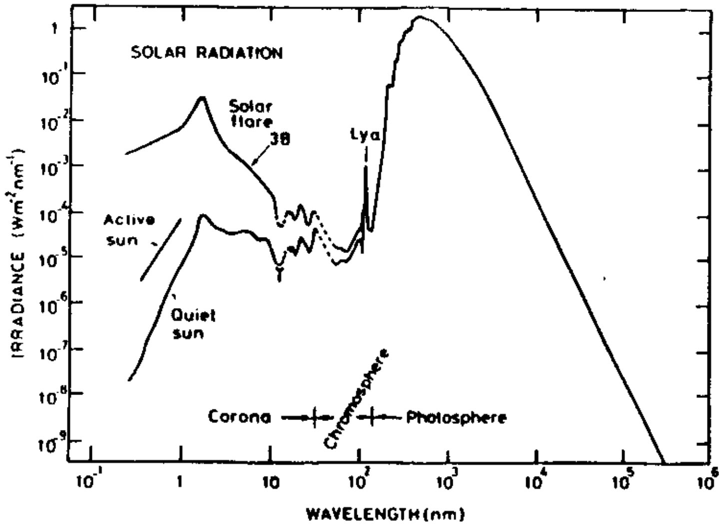

Fig. 5 Spectral distribution of the solar irradiance, and its variation with solar activity. The logarithmic representation emphasizes the contribution of x-rays and extreme ultraviolet radiation. After Smith and Gottlieb (1974).

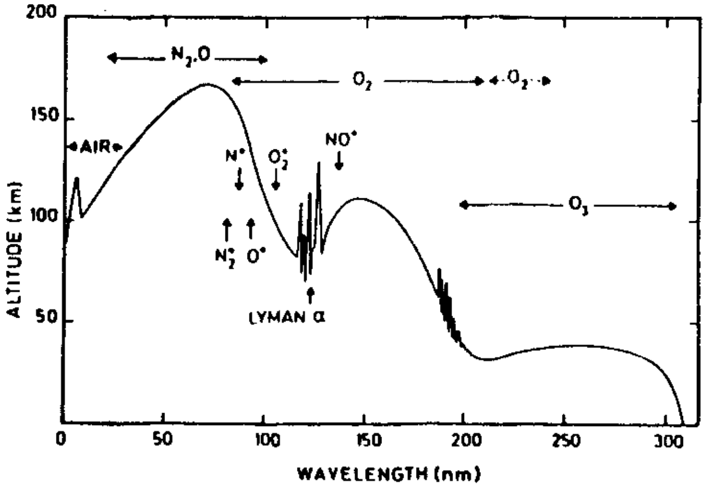

Fig. 6 Depth of penetration of solar radiation as a function of wavelength. Altitudes correspond to an attenuation of 1/e. The principle absorbers and ionization limits are indicated.

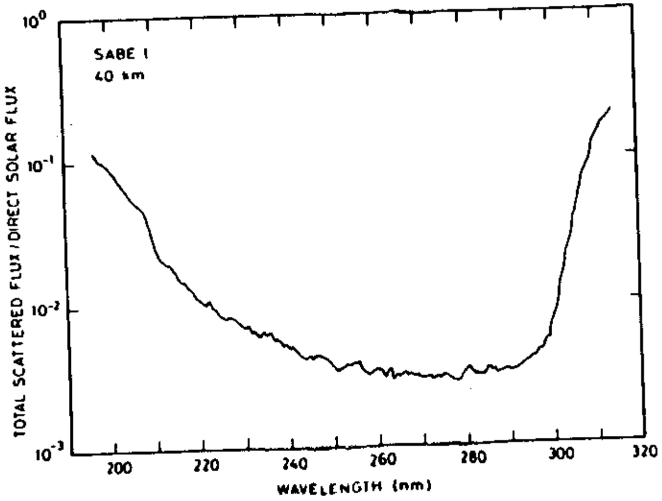

Fig. 7 Observed ratio of scattered to direct solar flux as a function of wavelength at 40 km. From Herman and Mentall (1982). (Copyright by the American Geophysical Union).

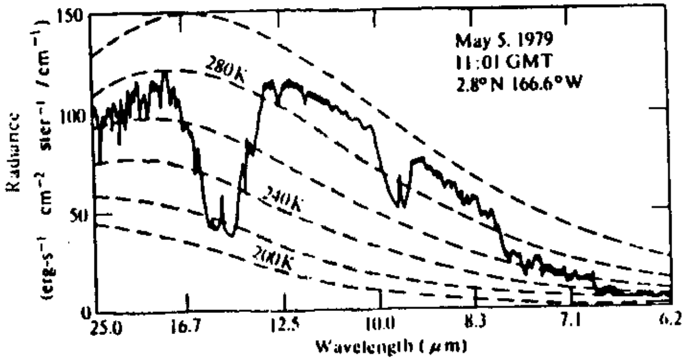

Fig. 8 Spectrum of infra-red emission escaping to space, as observed from outside the Earth's atmosphere by the Nimbus 4 satellite. Dashed lines represent the spectrum expected from a black body at different temperatures. Atmospheric absorbers cause the escaping radiation to come from different altitudes at different wavelengths, so that the effective temperature of the Earth's spectrum is wavelength dependent. (Figure reproduced from Dickinson, R. E., in Clark, W. C. (ed.), *Carbon dioxide review: 1982*, Oxford University Press, Oxford, 1982.)

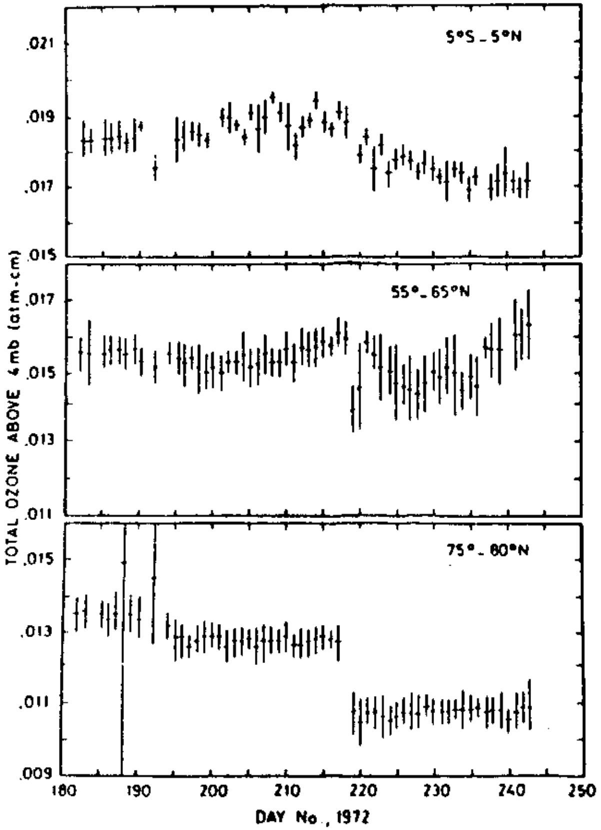

Fig. 9 . Ozone density changes during the August, 1972 solar proton event observed by the Nimbus 4 BUV experiment. From Heath et al. (1977). (Copyright by the American Association for the Advancement of Science).

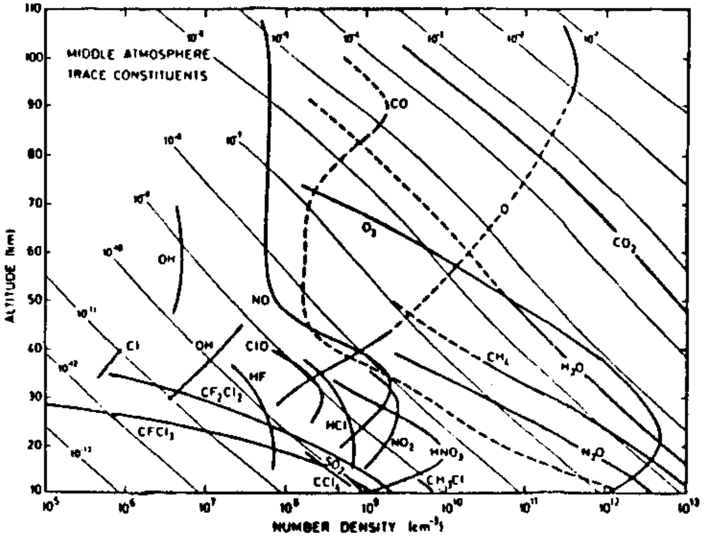

FIG. 10 Vertical profiles of observed number densities of the typical trace constituents in the middle atmosphere (ACKERMAN, 1979).

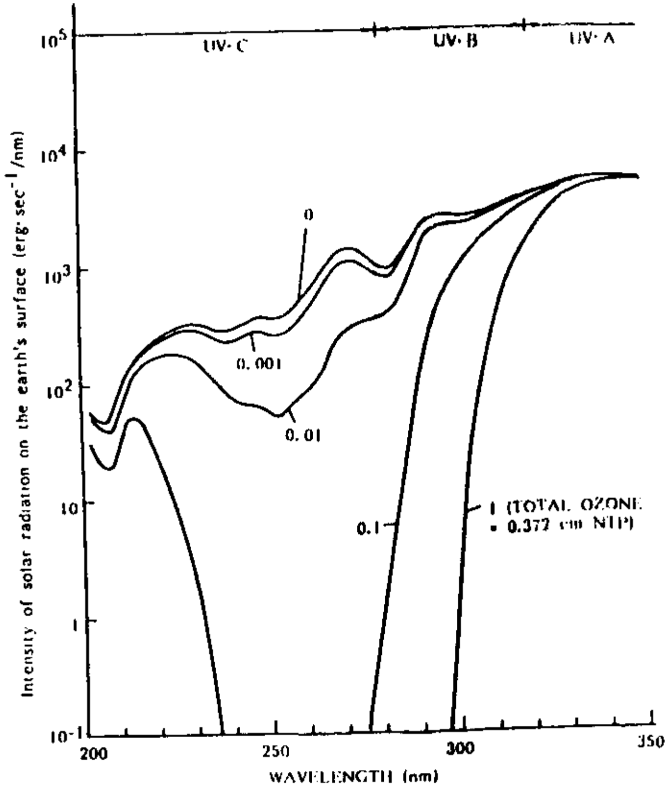

FIG. 11 Intensity of solar radiation in the spectrum range 200–350 nm predicted on the earth's surface for equinoxes and for various levels of total ozone. Effects of diurnal variation is included.

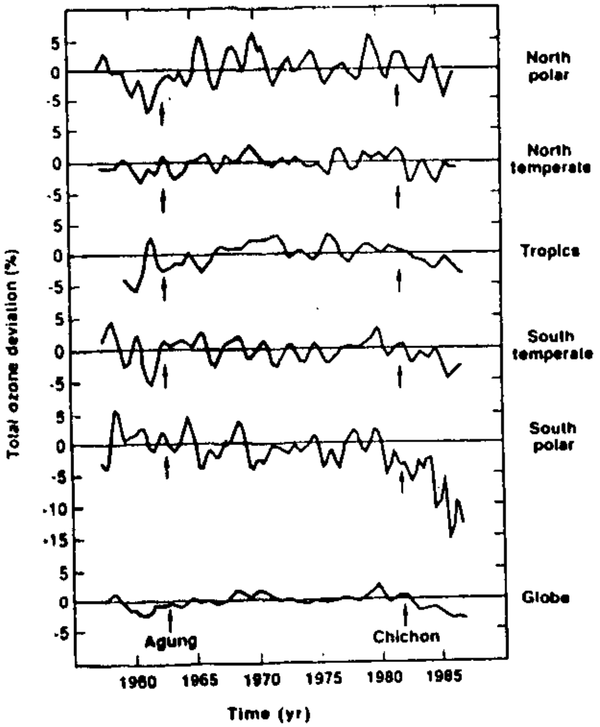

Fig. 12 Climate zone and global average of seasonal deviations from a long-term mean of Dobson network total ozone data (courtesy of J. K. Angell).

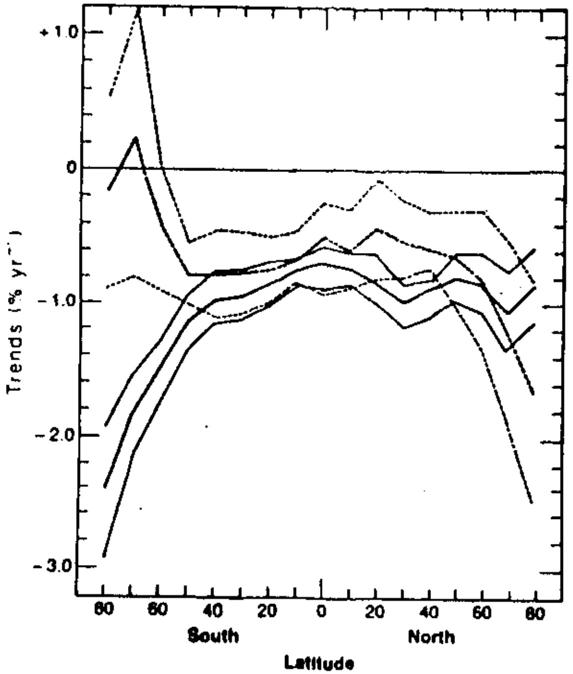

Fig. 13 Linear trends of total column ozone from the Nimbus 4 BUV instrument (heavy broken line) with 95% confidence limits (light broken lines) and the Nimbus 7 instrument (heavy solid line) and 95% confidence limits (light solid lines). No correction applied for possible instrument drift relative to Dobson network.

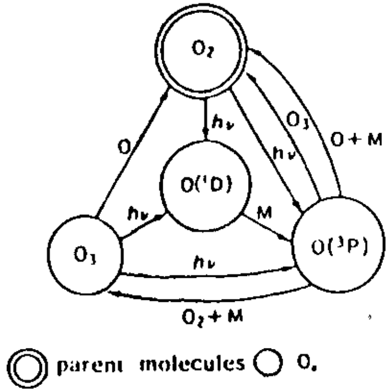

FIG. 14 Diagram for chemical reactions of odd oxygens (O_x).

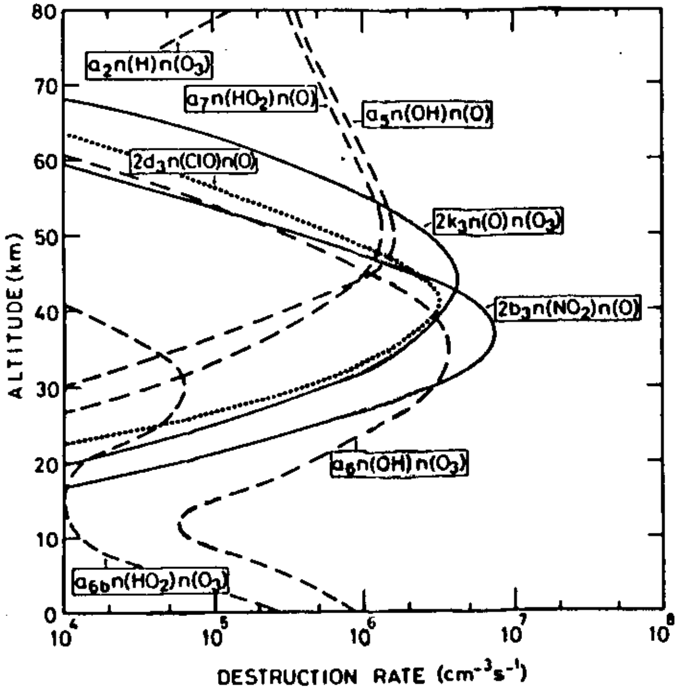

Fig. 15 Contribution of different reaction to the atmospheric odd oxygen balance. Nitrogen, oxygen, hydrogen and chlorine reactions are indicated. (From the model of Brasseur et al., 1983).

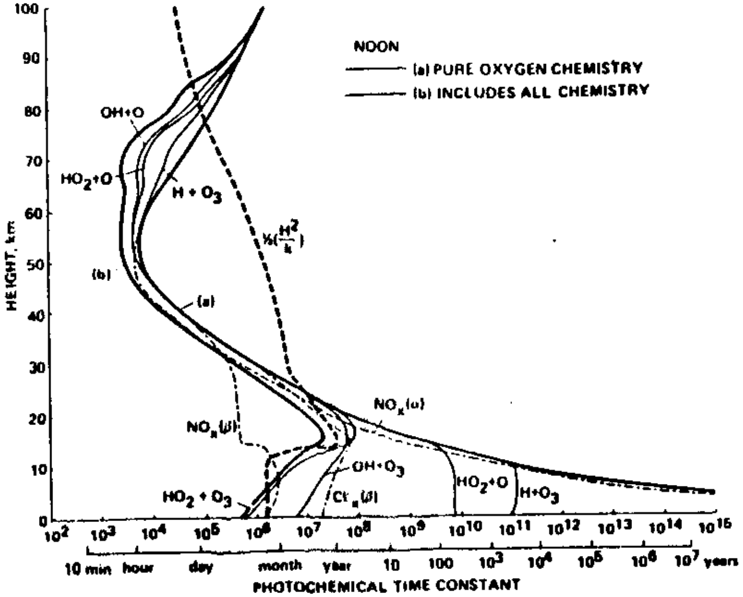

FIG. 16 Height profiles of photochemical time constants for odd oxgen (O_x) families at noon, due to major reactions affecting ozone densities. Heavy broken curve indicates the dynamical time constant due to the vertical eddy mixing.

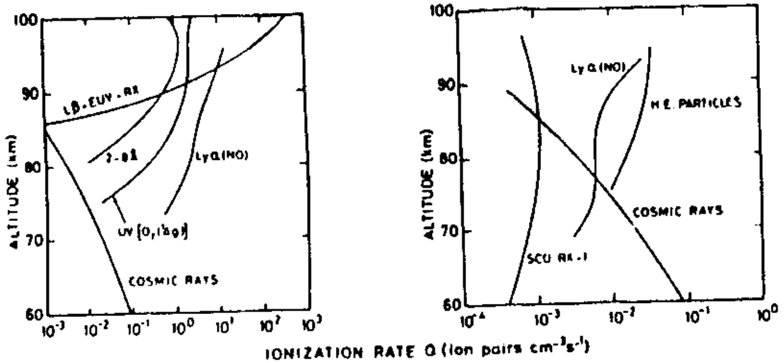

Fig. 17 Ionization rates produced by various sources in the region from 60 to 100 km, during the day and at night. From Thomas, (1974). (Copyright by the American Geophysical Union).

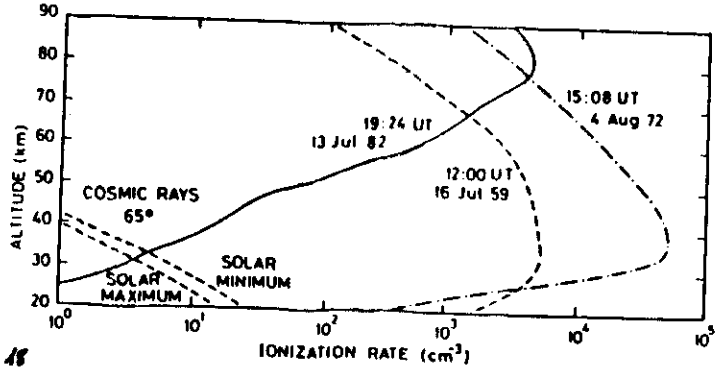

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Fig. Ionization rates associated with some solar proton events, compared to that due to cosmic rays. Adapted from Solomon et al. (1983).

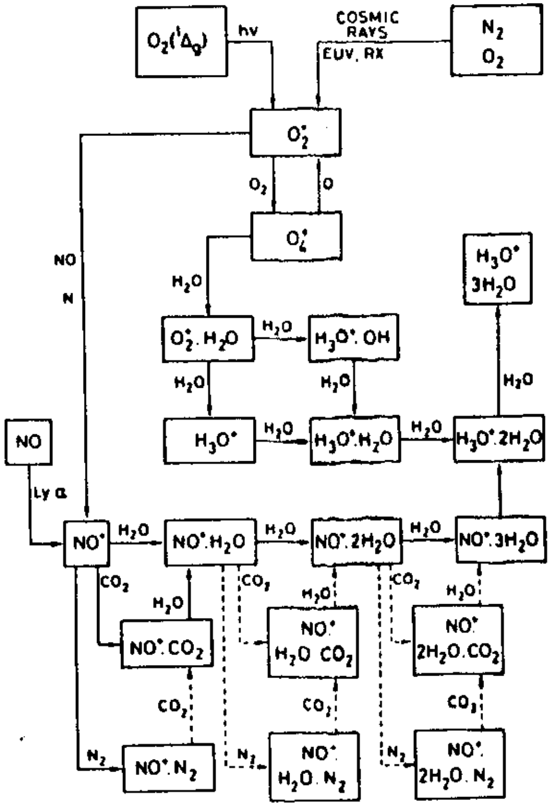

Fig. 19 Schematic diagram of D-region positive ion chemistry. From Ferguson (1979). (Copyrighted by Plenum).

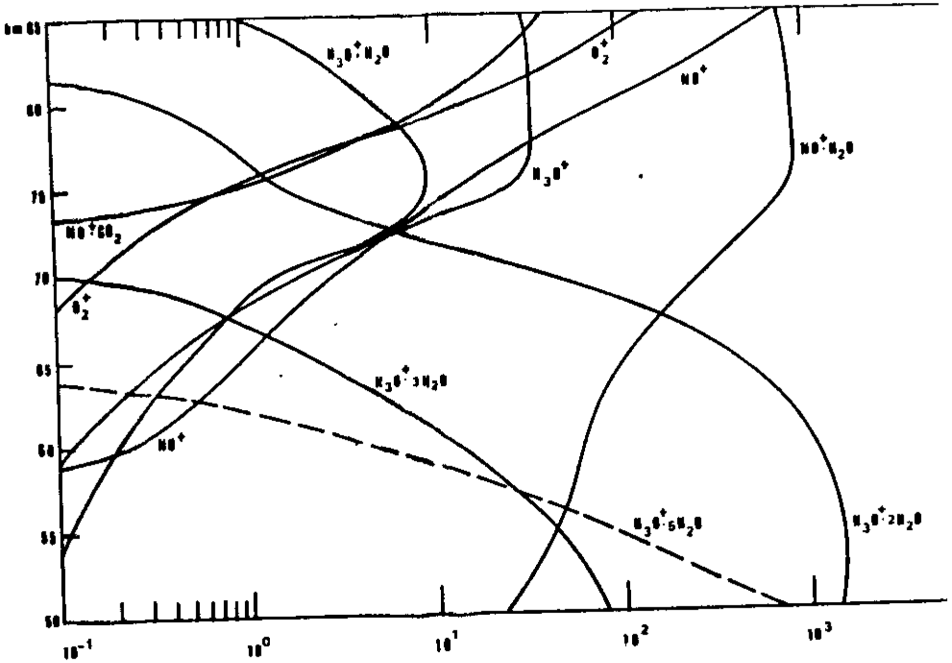

Fig. 20

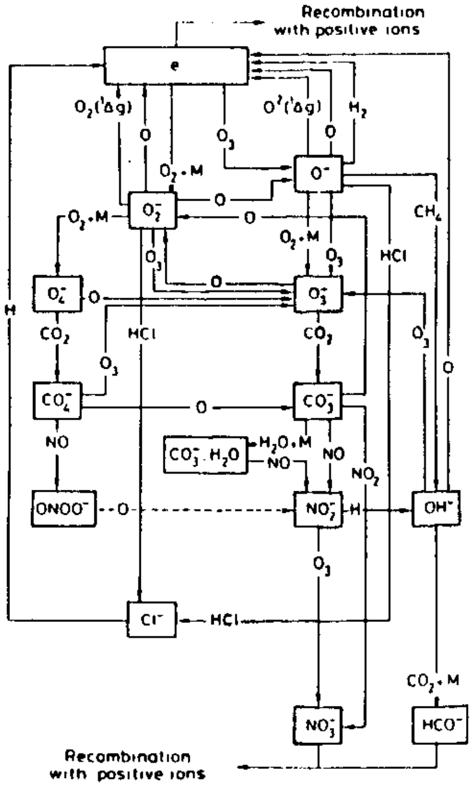

Fig. 21 Schematic diagram of the negative ion chemistry of the D-region. From Ferguson (1979). (Copyrighted by Plenum).

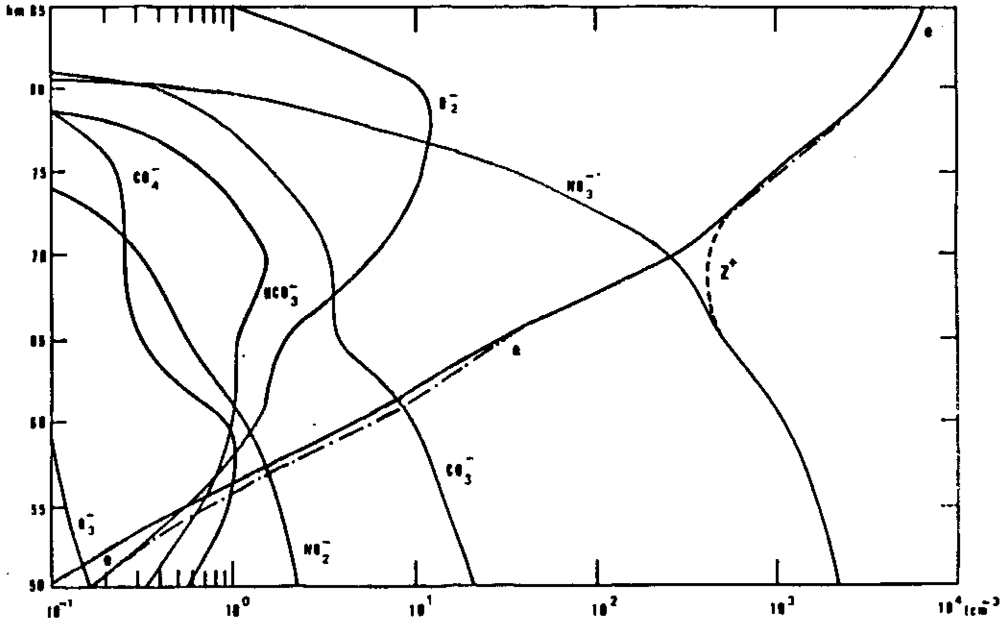

Fig. 22

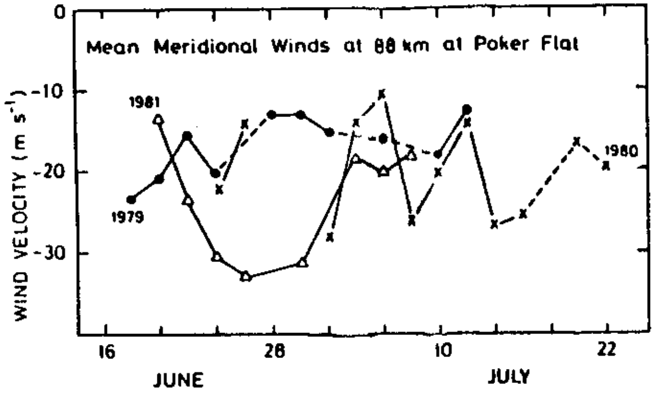

Fig. 23 Meridional winds in the mesosphere. From Nastrom et al. (1982). (Copyright by the American Geophysical Union).

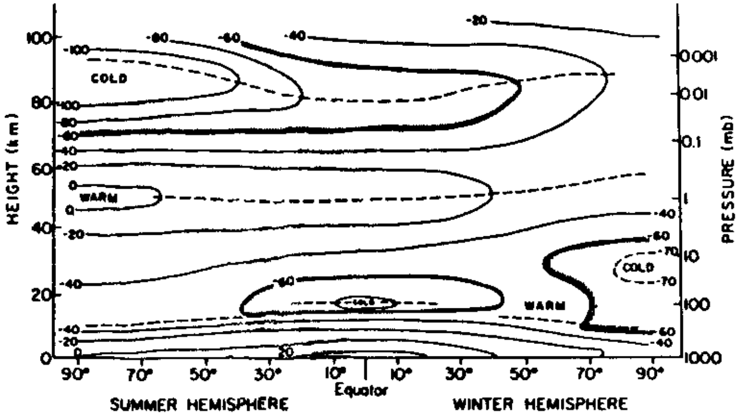

Fig. 24 Schematic latitude-height section of zonal mean temperatures (°C) for solstice conditions. Dashed lines indicate tropopause, stratopause, and mesopause levels. (Courtesy of R. J. Reed.)

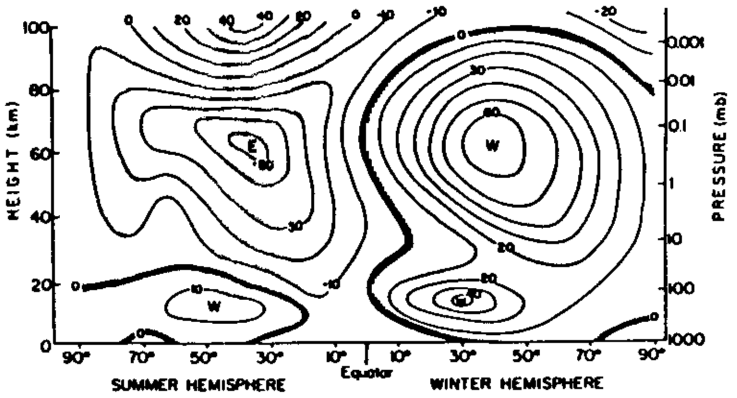

Fig. 25 Schematic latitude-height section of zonal mean zonal wind (m s^{-1}) for solstice conditions; W and E designate centers of westerly (from the west) and easterly (from the east) winds, respectively. (Courtesy of R. J. Reed.)

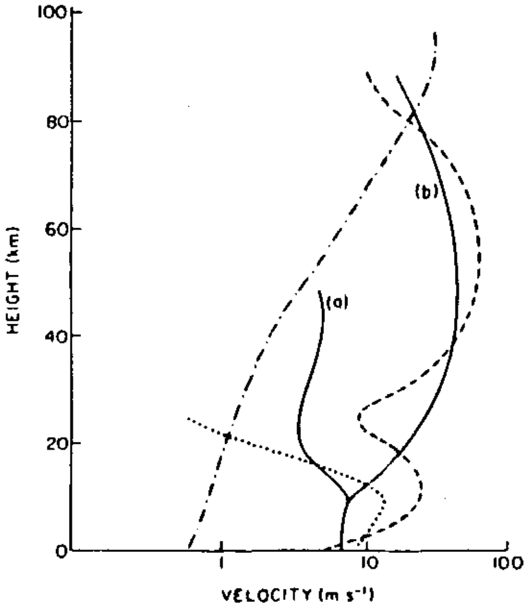

Fig. 26 Schematic vertical profiles of horizontal wind amplitudes corresponding to various types of atmospheric motions. Solid line: planetary waves (a) summer, (b) winter; dashed: zonal mean; dotted: synoptic scale; dotted-dashed: gravity waves. (Courtesy of Professor T. Matsuno.)

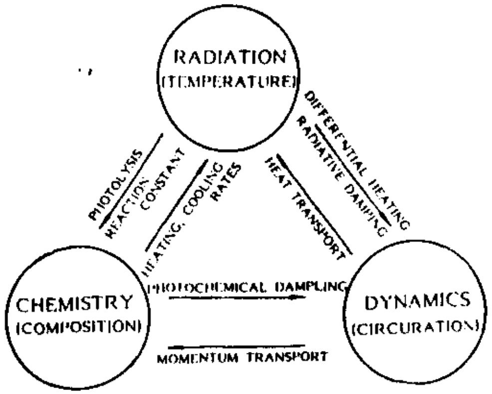

Fig. 27 Schematic diagram illustrating coupling among radiation, photochemistry and dynamics.

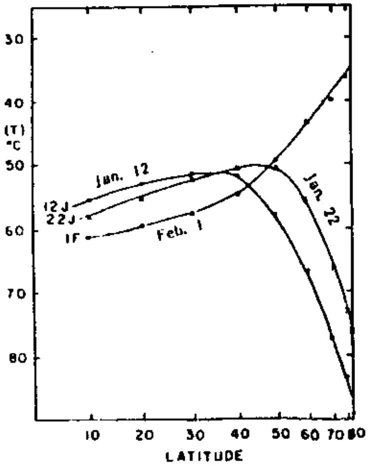

FIG. 28 The zonally averaged temperature at 30 mb as a function of latitude during and after a strong, sudden warming (JULIAN and LABITZKE, 1965).

Table 4 Example of typical values of physical parameters below 120 km at middle latitudes. From the U. S. Standard Atmosphere (1976).

Altitude (km)	Temperature (K)	Scale height (km)	Pressure (mb)	Concentration (cm^{-3})
0	288	8.4	1013.3	2.55(19)*
5	256	7.5	540.5	1.53(19)
10	223	6.5	265.0	8.61(18)
15	217	6.4	121.1	4.04(18)
20	217	6.4	55.3	1.85(18)
25	222	6.5	25.5	8.33(17)
30	227	6.6	12.0	3.83(17)
35	237	6.9	5.7	1.74(17)
40	250	7.3	2.3	6.67(16)
45	264	7.7	1.5	4.12(16)
50	271	7.9	8.0(-1)	2.14(16)
55	261	7.6	4.3(-1)	1.19(16)
60	247	7.2	2.2(-1)	6.45(15)
65	233	6.8	1.1(-1)	3.42(15)
70	220	6.4	5.2(-2)	1.71(15)
75	208	6.1	2.4(-2)	8.36(14)
80	198	5.8	1.1(-2)	4.03(14)
85	189	5.5	4.5(-3)	1.72(14)
90	187	5.5	1.8(-3)	6.98(13)
95	188	5.5	7.6(-4)	2.93(13)
100	195	5.7	3.2(-4)	1.19(13)
105	209	6.1	1.5(-4)	5.20(12)
110	240	7.0	7.1(-5)	2.14(12)
115	300	8.8	4.0(-5)	9.66(11)
120	360	10.5	2.5(-5)	5.03(11)

*read 2.55(19) for example, as 2.55×10^{19}.