Thermal physics (and some chemistry) of the atmosphere

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Abstract An exploration of how the temperature of the atmosphere varies with altitude can serve as a useful means of illustrating some important principles relating to the behavior of gases and to the absorption and transformation of radiant energy.

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Life as we know it on the Earth is entirely dependent on the tenuous layer of gas that clings to the surface of the globe, adding about 1% to its diameter and an insignificant amount to its total mass. And yet the atmosphere serves as the earth's window and protective shield, as a medium for the transport of heat and water, and as source and sink for exchange of carbon, oxygen, and nitrogen with the biosphere.

On the scale of cubic meters the air is a homogeneous mixture of its constituent gases, but on a larger scale the atmosphere is anything but uniform. Variations of temperature, pressure, and moisture content in the layers of air near the earth's surface give rise to the dynamic effects we know as the weather. Vertical gradations in these same variables and also in chemical composition describe the structure of the atmosphere as a whole, and will be the focus of our attention here.

We commonly think of gas molecules as moving about in a completely random manner, but the Earth's gravitational field causes downward motions to be very slightly favored so that the molecules in any thin layer of the air collide more frequently with those in the layer below. This gives rise to a pressure gradient that is the most predictable and well known structural characteristic of the atmosphere. This gradient is described by an exponential law[2] which predicts that the atmospheric pressure should decrease by 50% for every 6 km increase in altitude. This law also predicts that the composition of a gas mixture will change with altitude, the lower-molecular weight components being increasingly favored at higher altitudes. However, this gravitational fractionation effect is completely obliterated below about 160 km owing to turbulence and convective flows (winds). The variations in composition that characterize the upper parts of the atmosphere are mainly due to chemical reactions of the various species that result from absorption by atmospheric gases of the intense short-wavelength solar ultraviolet radiation present at high altitudes.

Although the pressure of the atmosphere decreases more or less uniformly with altitude, the temperature does not; the temperature gradient dT/dh (known as the *lapse rate*) undergoes three reversals that divide the atmosphere into four major sections: the troposphere, stratosphere, mesosphere, and thermosphere. Although these regions correspond roughly to the altitude ranges shown in Fig. 1, the actual boundaries between them are defined by the gradient reversals whose altitudes can vary from time to time.

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[2] The partial pressure of a gas of molecular weight M at elevation h in a column is given by $P_h = P_o \exp(-Mgh/RT)$ where Po is the pressure at the bottom of the column and g is the acceleration of gravity.

In order to explain the thermal structure of the atmosphere, it is necessary to understand that there are three sources of heat available to the air: direct absorption of ultraviolet solar radiation, exothermic chemical reactions, and absorption of long-wave infrared radiation emitted by the Earth (1). Each of these mechanisms predominates in a different range of altitudes.

Tropospheric heating

Very little of the Sun’s “heat” (i.e., electromagnetic radiation in the infrared region of the spectrum) that penetrates to the lower portion of the atmosphere can be absorbed by the atmospheric gases directly; homonuclear molecules such as N_2 and O_2 are not capable of absorbing the visible and mid-range infrared frequencies that are the sun’s main emission. This radiation passes through the atmosphere and is absorbed by the surface of the earth which re-radiates this energy in the long-wavelength infrared region (Fig. 2). Long-wavelength radiation is efficiently absorbed by water vapor, CO_2 and N_2O (the major “greenhouse gases” of the atmosphere) and transformed into kinetic energy which is quickly dispersed to the other atmospheric gases. Thus the troposphere is heated from the bottom up and the temperature of the lower atmosphere decreases with elevation.

This is only the beginning of the story, however. Any fluid that expands with temperature is inherently unstable when heated from below; the density of the bottom-most layer decreases as it is heated, causing it to be displaced by and rise through the cooler fluid above. Thus in the lower atmosphere, those parcels of air in contact with the warmer spots on the surface move up through the surrounding air and undergo expansion as the atmospheric pressure decreases. As the parcel expands, it pushes the surrounding air out of the way, doing work on it at the expense of its own thermal energy, and thus suffers a fall in temperature. Because convective ascent takes place far too rapidly for thermal equilibrium with the surrounding air to be restored, the expansion and compression processes are effectively adiabatic. The decrease in temperature with altitude in the lower troposphere is usually dominated by this process which defines the *adiabatic lapse rate* whose value is about $-9.8\ \mathrm{K\ km^{-1}}$ for dry air and is somewhat less for moist air owing to release of heat as water condenses out of it.

The thermosphere

As we move higher in the atmosphere, Chemistry begins to play a more significant role. While the lower troposphere can be regarded as a repository of largely unreactive gases[1], the uppermost part, the thermosphere, is a roiling chemical reactor. The intense ultraviolet radiation that bathes the outer atmosphere has an energy equivalent in the range of common bond energies, and thus produces a complex mixture of atoms, ions, and fragmented molecules. Because the wavelengths actually absorbed are governed by the spacing of electronic energy states rather than by bond dissociation energies, absorption of light having an energy equivalent greater than the bond energy is very common; the

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[1] Here we disregard reactive species such as HO and those related to photochemical air pollution. Although these are important to humans, their concentrations are too low for them to play significant roles in the overall thermal physics of the atmosphere.

excess appears as kinetic energy of the resulting fragments, and thus as the very high temperatures that give the thermosphere its name (2,3).

One might think that the dissociation products of a diatomic molecule such as O_2 or N_2 would quickly recombine, but in fact this is not an efficient process at low pressures. The reason is that in order to conserve both energy and momentum, nonradiative recombination must always involve a third body, which can be any atomic or molecular species. Three-body collisions are not likely processes at the very low pressures encountered at these altitudes.Thus through a complex web of reactions, atomic oxygen emerges as the principal chemical species of the thermosphere. Although O is almost as strong an oxidizing agent as F, the high temperatures tend to drive any possible oxidation reactions in the reverse direction, making the thermosphere a “reducing” environment in which species such as N_2, CO, and H are favored over NO, CO_2, and H_2O.

Some of the photodissociation processes lead to atoms and ions in excited electronic states that emit the excess energy as visible light when they finally decay to their ground states. In some cases the decay process is so slow that it continues long after darkness, resulting in the nighttime airglow that produces about as much light as the stars on a moonless night.

The high thermospheric temperatures have several other interesting consequences. During local daytime the thermosphere bulges out on its heated side, giving rise to winds that transport the heat around to the night side, so that the temperature of the thermosphere remains fairly uniform. Owing to the increase in viscosity that gases undergo at higher temperatures, the winds in the upper thermosphere (above about 300 km) tend to move as a single unit[1].

There is one additional source of thermospheric heating that occasionally becomes important: this is the solar wind, a flux of electrons and protons that continually streams from the Sun. Under normal conditions the Earth’s magnetic field deflects this flux of charged particles so that they strike only the polar regions, where they can heat the upper thermosphere more than does the solar radiation. However, during periods of intense sunspot activity, the solar wind is deflected to lower latitudes where it can penetrate down to 150 km, giving rise to a variety of new ionized and excited species whose radiative decay produces auroral displays. The high ion densities increase the conductivity of the atmosphere, resulting in the high circulating currents (of the order of a million amperes) which disrupt terrestrial power distribution and communications systems. The extra heating causes the entire outer atmosphere to expand; one consequence of this is to increase the drag on artificial satellites that often penetrate this region, sometimes causing them to re-enter the lower atmosphere and disintegrate sooner than expected.

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[1] The viscosity of a gas, unlike that of a liquid, increases with temperature owing to transport of momentum in directions normal to the flow as a result of random thermal motions of the molecules. There is no larger-scale consequence of this than the thermospheric circulation.

The stratosphere and ozone

Nearly all of the solar radiation below 170 nm is totally absent at the bottom of the thermosphere, mainly due to absorption by O_2. There is, however, an important exception having immense environmental significance: a strong peak in the solar emission due to the intense Lyman-α hydrogen emission line at 121.57 nm is able to penetrate into the upper stratosphere. This wavelength is strongly absorbed by O_2 and results in its dissociation. The resulting O atoms react with undissociated oxygen molecules to form ozone:

$$O_2 + O \rightarrow O_3 \qquad \Delta H = -105 \text{ kJ mol}^{-1}$$

This process gives rise to the celebrated *ozone layer* which extends from about 10 to 80 km, and has a peak at 30 km (Fig. 4). It is also the source of heat responsible for the rise in temperature in the upper stratosphere; ozone formation is highly exothermic, providing as it does a route for the release of solar energy stored in the dissociation of O_2.

Ozone is a thermodynamically unstable molecule having a small bond dissociation energy (101 kJ/mol, 1180 nm); absorption of light in any region of the spectrum from the near-infrared on down will dissociate ozone with unit quantum yield: $O_3 \rightarrow O_2 + O$. The first strong absorption band of ozone occurs in the so-called Hartley continuum which starts at about 320 nm and continues to shorter wavelengths. It is this absorption that shields the earth from the short-wave uv radiation which is damaging to both plants and animals. In humans, there is an approximately logarithmic relationship between the incidence of skin cancers and the intensity of radiation in the 320-nm region.

The chemical processes in the mesosphere and stratosphere include both oxidations and reductions, some of which involve products of the biosphere. Methane, which is mostly of biological origin, diffuses into the stratosphere where it is decomposed into H_2, formaldehyde, CO, and CO_2. That portion of the H_2 that diffuses upward accounts for the major loss of hydrogen from the earth; thus rice paddies and cattle farming, which are major agricultural sources of methane, also contribute to the loss of hydrogen from the Earth. Another important component of the stratosphere is HNO_3, which is formed by direct reaction of OH and NO_2; most of the latter derives from biologically-produced NO. Any NH_3 that diffuses up into the stratosphere is either oxidized or reacts with nitric acid to produce solid NH_4NO_3 which eventually falls back to the surface.

The “ozone hole”

In the mid 1980s, it was noticed that stratospheric ozone in the antarctic regions from about 70°S was greatly reduced during the local winters. Average depletions in excess of 50% were noted, and in 1987, virtually all of the ozone seemed to be removed over some regions. In the worst years, normal ozone concentrations were not restored until local summer, and less pronounced depletions were observed in the arctic as well. The finding that periods of ozone depletion were accompanied by heightened concentrations of chlorine monoxide suggested that chlorine chemistry played an essential role in the process. ClO can dimerize to Cl_2O_2 which photolyzes to Cl and ClOO, initiating a chain process in which Cl converts O_3 to O_2 and regenerates ClO.

A key step in the process appears to be adsorption of otherwise unreactive chlorine species (including HCl) onto ice crystals that form in the extremely cold stratospheric air during the polar night. This air tends to circulate in a pattern known as the polar vortex that minimizes heat transfer from warmer regions, and generally isolates the local concentration changes from the neighboring regions of the stratosphere. The active intermediates are believed to form on the ice crystal surfaces, and possibly on frozen aerosol particles of sulfuric acid and nitric acid trihydrate. All of this would remain rather esoteric chemistry if it were not for the discovery, in the mid-1980s, that chloroflurocarbons, manufactured for use as refrigerants, aerosol propellants and other uses, were the most likely source of stratospheric chlorine, but that's another story.

The ionosphere

This is a region containing a high concentration of electrons and ions. The ionosphere starts in the upper mesosphere at about 60 km, and extends through the lower half of the thermosphere. Historically, the ionosphere was known before the structure of the other parts of the atmosphere was studied. This is due to its important role in the transmission of radio signals over long distances. Around-the-world radio communication depends on successive reflections of radio waves between the ionosphere and the earth, which together act as a sort of waveguide.

The various subdivisions of the ionosphere were originally based on their effects on radio propagation. When radio-frequency electromagnetic waves enter the ionosphere, their interaction with the charged particles causes them to change direction slightly. The degree of refraction depends on the density of charge and on the wavelength. If the angle of incidence and degree of refraction are large enough, the wave will be reflected back toward the earth; if not, it will be "absorbed" by the ionosphere. The first to be identified was the E- (electric) layer. In this region the mean free path is sufficiently low to facilitate rapid recombination of ions and electrons, so this layer is present only during the day and disappears at night. An even lower layer, the D-layer, is a region of diminishing charge density even during the day, low-frequency (< 3 Mhz) radio waves entering the D-layer tend to get absorbed before they can pass through to be reflected off the E-layer. This is the reason that distant broadcast-band radio stations can only be received at night. Higher-frequency (3–30 Mhz) communications depend on reflections off the F-layer, a region of higher ion density above the E-layer. Here the mean free paths are sufficiently long that ion recombination is relatively slow, so this layer remains intact after sunset, declining slowly through the night.

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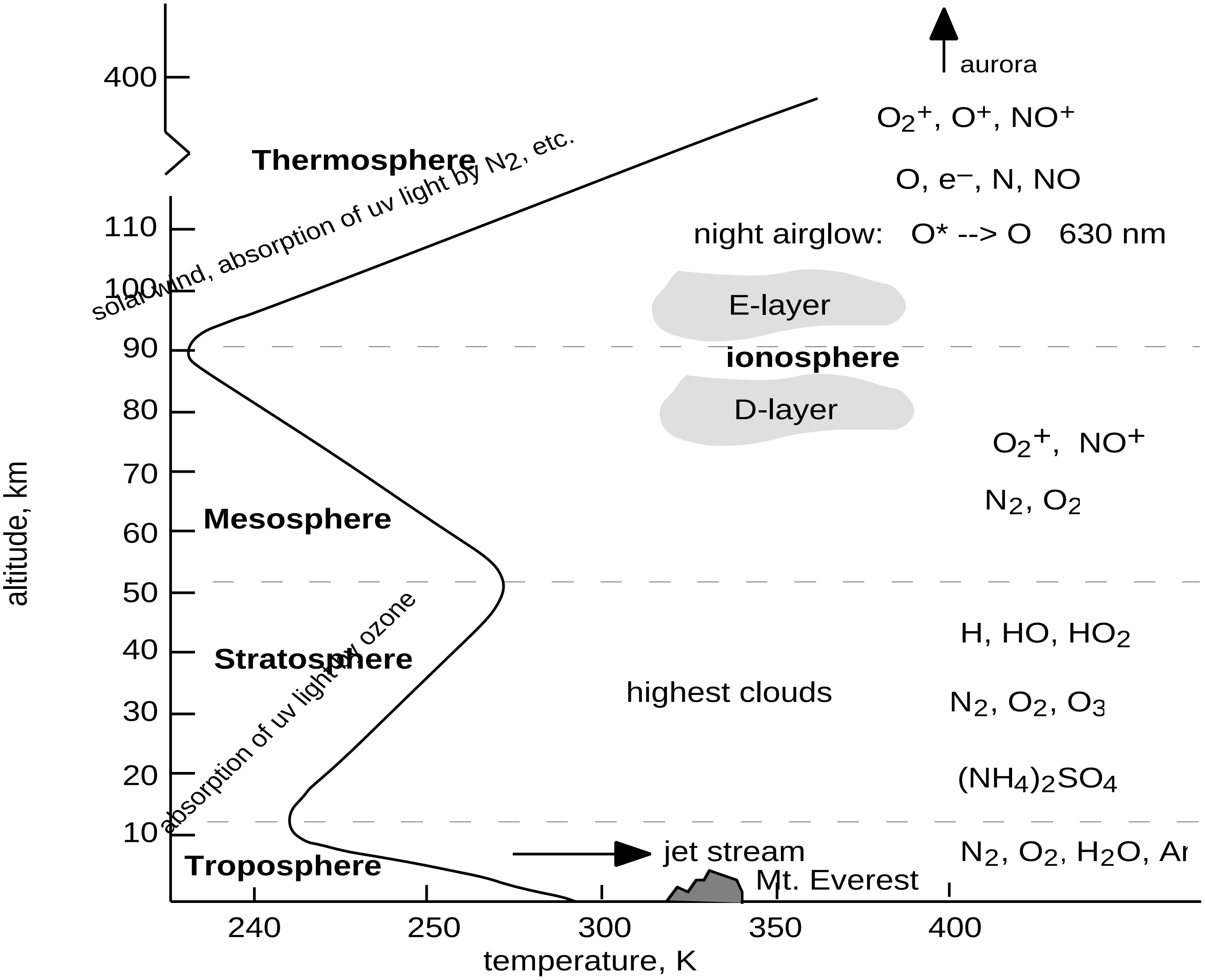

Figure 1. Temperature profile and principal chemical components of the atmosphere

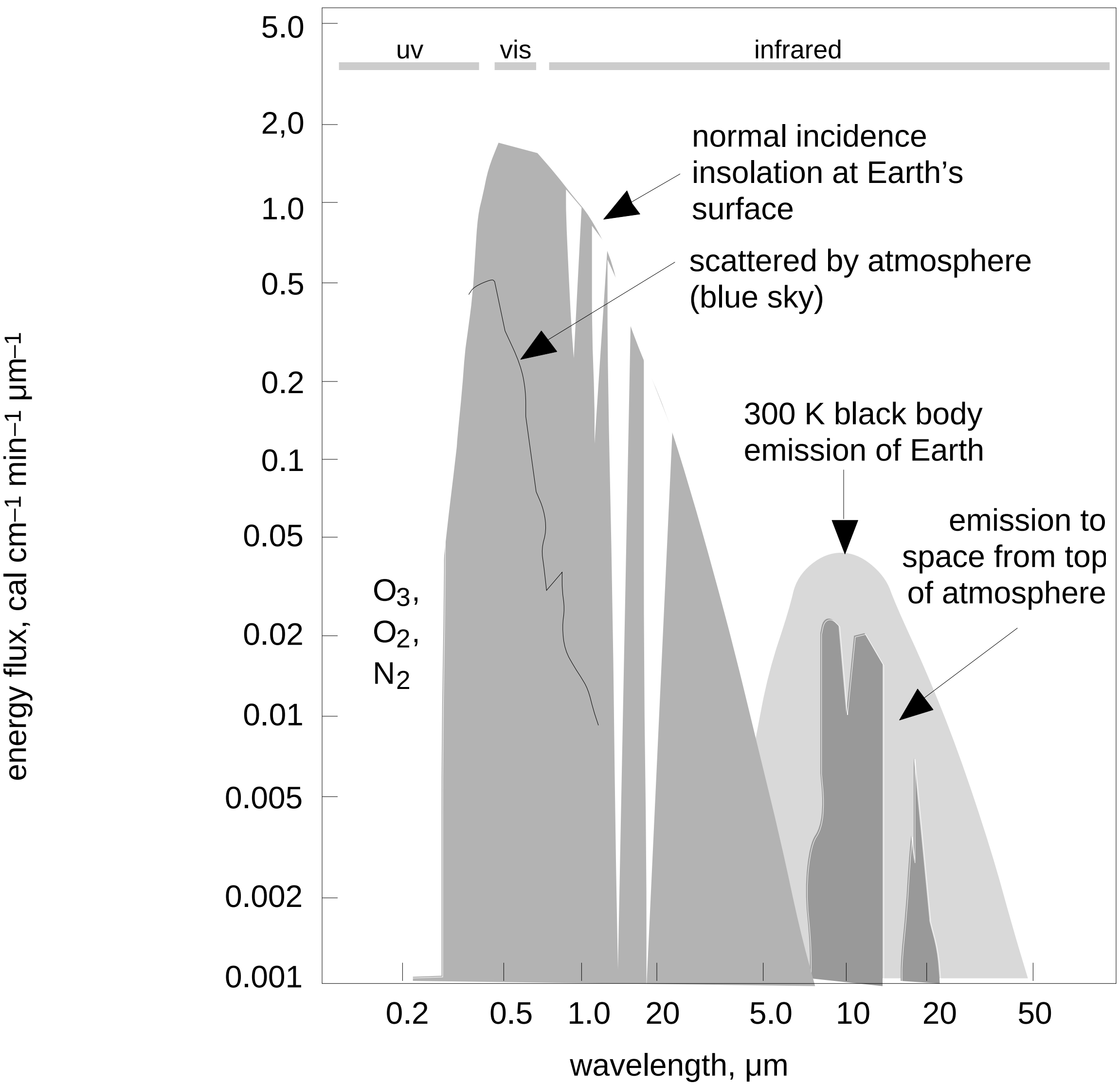

Figure 2. Spectrum of solar radiation at the Earth's surface, and of the Earth's emission to space. The narrow "windows" of the latter, relative to Earth's black body emission, are the basis of the greenhouse effect. (This diagram was adapted from one in Reference (1).)

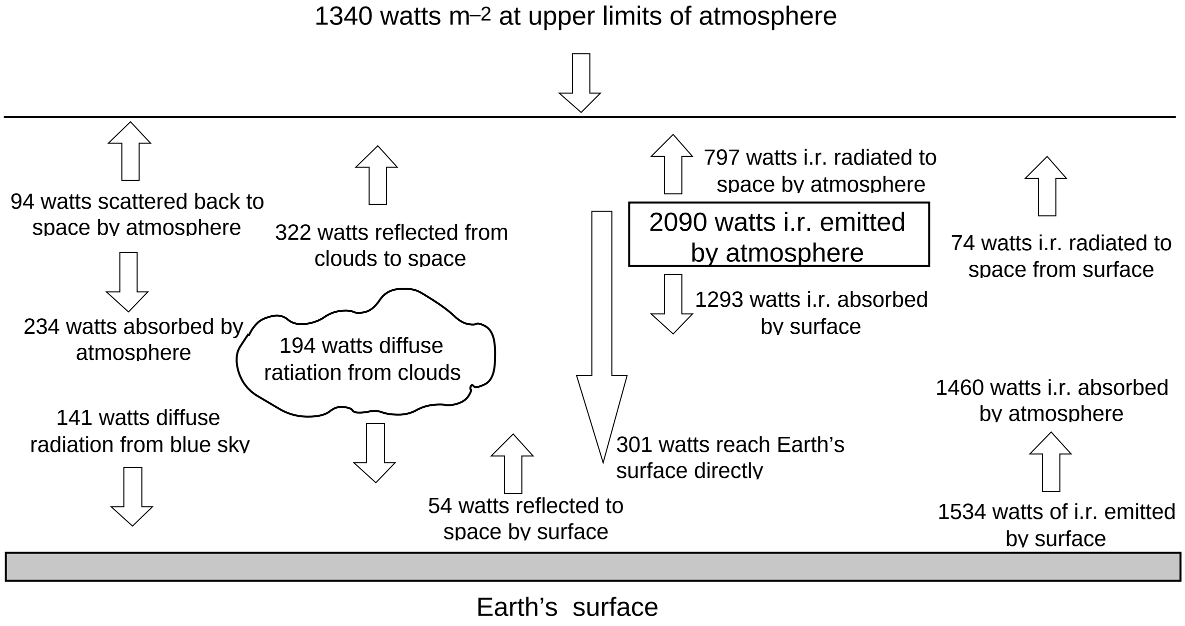

Figure 3. Thermal balance of the atmosphere.

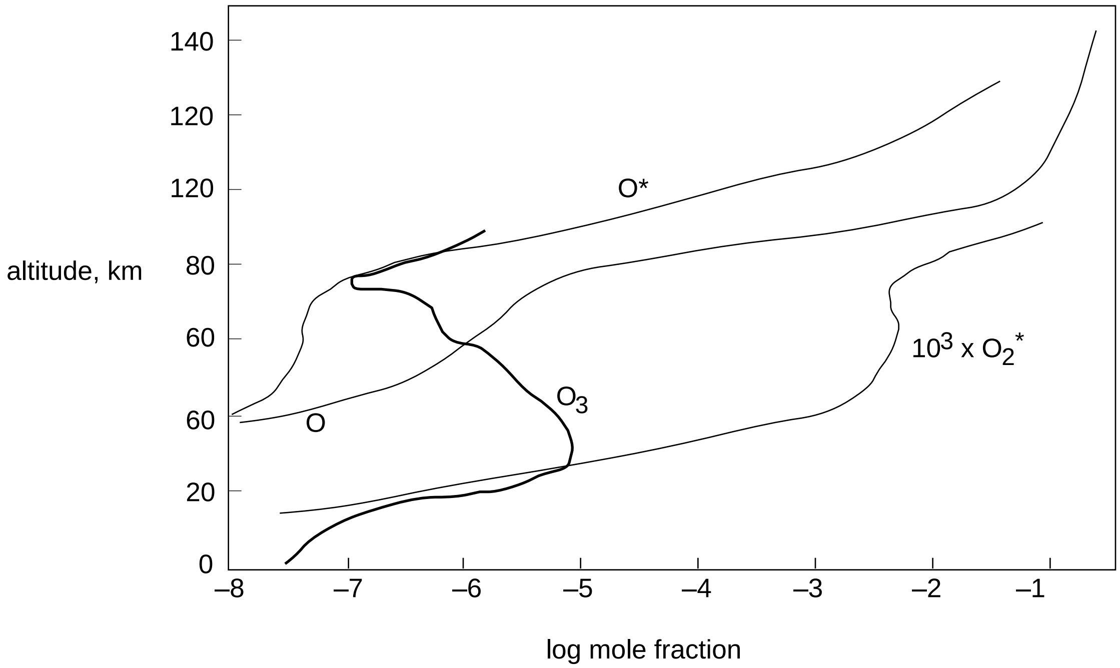

Figure 4. Concentration profiles of ozone and some other oxygen species (3). The asterisks refer to electronically-excited states.