

I. INTRODUCTION

1. INTRODUCTION TO THE ATMOSPHERE

VÍCTOR J. HERRERO
Instituto de Estructura de la Materia (CSIC)

1. SOME FEATURES OF ATMOSPHERES

The word *atmosphere* was introduced into the western languages in the course of the 17th century. It is an adaptation of the New Latin word *atmosphæra*, which in turn derives from the Greek roots ἀτμός, vapour, and σφαῖρα, ball. The term defines the gaseous envelope surrounding a celestial body and retained to it by gravity.

Gravity imposes a roughly exponential decline of atmospheric pressure (or density) with growing height. A common expression for this decline is (Milone & Wilson, 2008, Visconti, 2001):

$$p(z) = p(0) \exp\left(-\frac{mgz}{kT}\right) = p(0) \exp\left(-\frac{z}{l}\right) \quad (1)$$

where $p(z)$ is the pressure at a height z , $p(0)$ is the pressure at a given origin $z=0$ (e.g. the surface of a planet), m is the average molecular mass of the gas, k is the Boltzmann constant, g the acceleration of gravity, and T the absolute temperature. Equation (1) is called *barometric formula* and is easily derived using the ideal gas law and assuming that pressure is only hydrostatic (Berberan-Santos et al, 1997). The formula contains crude approximations (it assumes that g and T do not depend on z), but provides a simple view of the pressure dependence on the mass of a given body and performs reasonably well for a limited z stretch. The magnitude $l=(kT/mg)$ provides a characteristic scale height.

With dropping pressure the collision frequency decreases and atoms or molecules can leave the upper part of an atmosphere if their kinetic energy exceeds their gravitational potential energy. This mechanism is called *Jeans escape*. The escape velocity can be expressed as:

$$v_{es} = \sqrt{2gr} \quad (2)$$

where r is the distance to the body centre. Collisions become negligible when the mean free path of the molecules equals the local scale height. This condition is usually taken as the definition of the *exobase*, the altitude from which escape is possible.

For the low densities implied here, viscosity is not large enough to overcome gravitational separation and the different molecular species must be considered separately. The flux of molecules of species i escaping the atmosphere can be expressed as (Milone & Wilson, 2008, Visconti, 2001, Chamberlain, 1963):

$$\phi_{esc}(i) \approx \frac{1}{2\sqrt{\pi}} n_e(i) v_s(i) (1 + \lambda_e) \exp(-\lambda_e) \quad (3)$$

where n_e is the molecular density at the exobase, v_s is the corresponding most probable thermal velocity and λ_e is an escape parameter relating the gravitational and the thermal energy of the molecule:

$$\lambda_e = \frac{GMm_i}{kTr_e} \quad (4)$$

where G is the gravitational constant, M is the mass of the body, m_i the mass of molecules of species i and r_e the distance of the exobase to the body centre. As intuitively expected, lighter species are more likely to leave the atmosphere and the escape will be favoured by higher temperatures. Sometimes fast moving light species will drag heavier molecules with them (*hydrodynamic escape*) and on many occasions the actual escape flux will be determined by diffusion from the lower atmosphere, which can limit the value of the molecular density at the exobase.

In the lower part of an atmosphere, density and viscosity are higher. Friction and convective movements can become important and winds can establish an atmospheric circulation. This atmospheric circulation can in turn be affected by the rotation of the celestial body. A convenient measure of the influence of rotation on atmospheric circulation is given by the *Rossby number* (Visconti, 2001, Milone & Wilson, 2008):

$$R_o = \frac{U\tau}{kTr_e} \quad (5)$$

where τ is the rotational period of the body and U/L is a characteristic time relating the typical length L at which an air parcel will be transported and the typical wind velocity U in the atmosphere. A small value of the Rossby number ($R_o < 1$) corresponds to a strong influence of rotation in the atmospheric motions through Coriolis forces. The Rossby number can vary strongly with latitude and altitude.

Thus far we have only considered a few general concepts relating basic physical characteristics, like gravity (mass) and rotational period of a celestial body, to properties of its atmosphere. Each atmosphere is however different. Perhaps the most significant differences between atmospheres reside in their chemical composition, which is in general peculiar to a given celestial body and carries most valuable information about its origin and evolution. In the following we will look at specific atmospheres in some more detail. We will centre our attention on the atmosphere of the Earth, but will also consider the atmospheres of other planets and satellites, and will briefly mention the Sun's heliosphere.

2. THE EARTH'S ATMOSPHERE

2.1. Composition, layers and bounds

The atmosphere of the Earth consists of a mixture of gases called «air», together with some particulate matter of different kinds. By volume, dry air close to the surface is composed of N_2 (78.084 %), O_2 (20.946 %), Ar (0.934 %), CO_2 (0.038 %), and a number of other trace gases in smaller concentrations. In addition, there is a variable concentration of water vapour, ranging from less than 1% to roughly 4%. Trace gases include CH_4 , nitrogen and sulphur oxides, O_3 , NH_3 and the rest of the noble gases, as well as other inorganic and organic compounds. Typical concentrations of trace gases are in the parts per million by volume (ppmv) or less, and exhibit a great local variability. Many of these trace gases have natural origin and are produced through volcanic eruptions, thunderstorms, fires or biological processes; in recent times, human activities have begun to contribute appreciably to the production of some trace gases (Finlayson-Pitts & Pitts, 2000, Wayne, 2000). Unstable reactive species like ions, atoms and radicals are also present in very small amounts. Their relative concentrations increase with growing height.

Small particles in suspension are present throughout the atmosphere in the form of clouds and aerosols (in principle clouds are also aerosols, but they are usually treated apart). Their sizes range from a few nm to some μm . Clouds are mostly made of water droplets or small ice particles. Atmospheric aerosols can be either primary (emitted directly to the atmosphere) or secondary (formed by «gas to particle conversion»). Typical primary aerosols are dust, sea salt, volcanic ashes or soot, whereas sulphuric acid, sulphates, nitrates and organic matter are examples of secondary aerosols. As in the case of trace gases, recent human activities are releasing increasing amounts of aerosols to the atmosphere (Finlayson-Pitts & Pitts, 2000, Wayne, 2000).

In the vertical direction, the Earth's atmosphere is conventionally divided in a series of layers, which delimit characteristic properties (see Figure 1.1). The most conspicuous atmospheric layer structure is that associated with temperature, which shows a non-monotonic evolution with altitude. The lowest and most dense part of the atmosphere is called the *troposphere*.

In the troposphere, which is in contact with the Earth's surface, temperature decreases steadily with height. The average rate of decrease (normal *lapse rate*) is 6.5 K per km, but its actual value can be very variable. The upper limit of the troposphere is called the *tropopause*. At the tropopause, the lapse rate decreases to very low values and beyond it the temperature trend inverts. The position of the tropopause depends on latitude and varies with the season. It is lowest at the poles (≈ 9 -12 km) and increases in altitude at the equator (15-18 km). Its temperature can be typically 210 K. The average atmospheric pressure at sea level is 101.3 kPa (1013 mbar), which corresponds to a molecular density of $\approx 2.5 \times 10^{19} \text{ cm}^{-3}$ at 298 K. At an altitude of 10 km pressure drops to about 25% of its sea level value. The evolution of pressure in the troposphere is described reasonably well by equation 1, with a scale height of 8.5 km. The troposphere contains approximately 80% of the mass of the atmosphere; in fact 50% of the total atmospheric mass is located below 5.6 km. It contains also 99% of

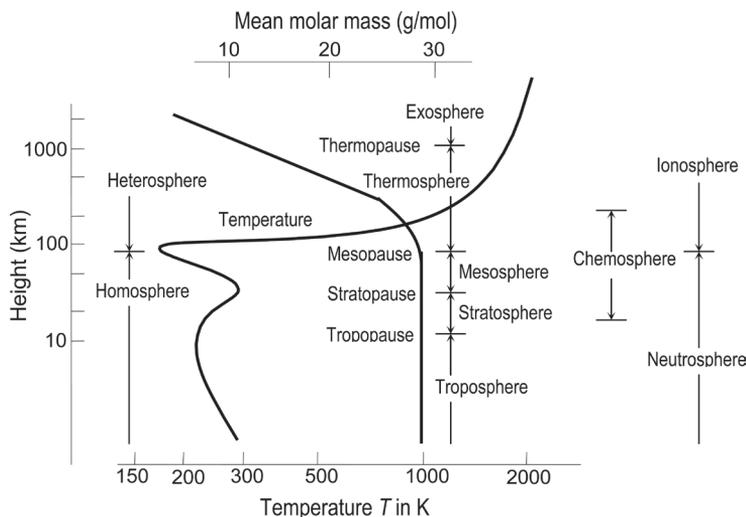


Figure 1.1. Characteristic atmospheric layers.

the water vapour and particulate matter. The troposphere is often divided into two parts with distinct characteristics: the boundary layer, in contact with the Earth's surface, and the free troposphere, between the boundary layer and the tropopause. The free troposphere is a turbulent and well mixed region with high speed winds. The *boundary layer*, affected by friction near the surface, is a much more quiescent region extending from a few hundred meters to about 1 km in height. Its physical properties are conditioned by the particular characteristics of the nearby surface and can be very variable. It is the atmospheric region with the highest chemical complexity and with the largest proportion of particulate matter.

Above the tropopause starts the **stratosphere**. This layer is characterized by a temperature increase with altitude which is caused by the absorption of ultraviolet (UV) radiation from the Sun in a series of exoergic reactions associated with the formation and destruction of O_3 molecules. Typical stratospheric temperatures vary between 210 K at the tropopause and 270 K at its upper limit, the *stratopause*, located at a height of about 50 km. The temperature inversion at the stratosphere hampers vertical air movements and favours a horizontal stratification without appreciable convection or turbulence. Due to these properties, the tropopause acts as an effective, though not completely impermeable, barrier for the transport of materials from the troposphere. Occasionally giant thunderstorm clouds or volcanic eruptions can inject particles into the lower stratosphere, but in general the stratosphere is free from particulate matter and very dry. At high latitudes, thin characteristic clouds, termed *polar stratospheric clouds* (PSC) can form during the winter.

Beyond the stratopause ozone chemistry ceases and temperature drops again with altitude. This layer is called the **mesosphere**, and stretches to a height of 80-90 km until the *mesopause*, which is the coldest place in the atmosphere, with typical temperatures of ≈ 170 K. Although the water vapour content is very low in this region,

polar clouds (*noctilucent clouds*) can still form. These are the highest clouds known in the atmosphere. Typical pressures in the mesosphere range from 1 to 0.1 Pa, which is enough to vaporize most meteorites entering the atmosphere. As a consequence, a relatively high proportion of iron and other atoms is encountered in this region (Wayne, 2000).

Above the stratopause, the temperature rises again, due mostly to the dissociation of O_2 and, to a lesser extent, N_2 molecules by short wavelength ($\lambda < 200$ nm) ultra-violet photons from the solar radiation. This region is called the **thermosphere**, and in it temperatures, which are very dependent on the Sun's activity, rise again and can reach values of ≈ 2000 K (Mueller-Wodarg, 2008, Milone & Wilson, 2008). Note that this high temperature corresponds to a very rarefied atmosphere and that, in spite of the high T, the density of thermal energy is very low. Appreciable ionization of atoms and molecules also takes place in this region. The upper limit of the thermosphere, called the **thermopause**, is considered the outer boundary of Earth's energy system. Below the thermopause the atmosphere is sensitive to the insolation received, due to the appreciable presence of heavy components, especially O atoms, that can interact efficiently with the solar radiation. The altitude of the thermopause can vary within the ≈ 400 -1000 km interval. Its lower range coincides roughly with that of the exobase (Mueller-Wodarg *et al.*, 2008, Milone, 2008) mentioned in the previous section, which is the level where collisions become negligible and marks the beginning of the **exosphere**.

Besides the thermal structure just commented on, other atmospheric properties determine also characteristic layers. Below ≈ 100 km, the composition of the atmosphere is homogeneous, with an average molecular mass close to 29. This layer is called **homosphere** and its upper limit is the homopause. At 100 km the approximate pressure is 0.03 Pa and above this height, viscosity is too low to counter gravitational separation. In addition, the increasing level of UV radiation leads to extensive photofragmentation. As a consequence of these two effects, the mean molecular mass decreases with growing height and the region above the homopause is termed **heterosphere**. Between ≈ 10 and 150 km, photochemical reactions have a great influence on the properties and composition of the atmosphere, and the corresponding layer is often called **chemosphere**. At about 60 km, ionic concentrations begin to be relevant and this altitude corresponds to the approximate beginning of the **ionosphere**, an electrically conducting region that plays a key role in radio wave propagation, and in the screening of the planet from the solar wind. The ionosphere is a cold, low density, weakly ionized plasma. The maximum ion concentrations ($\approx 10^6$ cm $^{-3}$) are found at ≈ 300 km, but, even there, the fraction of charged species is of the order of 10^{-3} . The ionosphere is broadly divided in three layers with distinct electrical properties, termed D, E and F, in order of increasing altitude. Layers E and F reflect low frequency radio waves. At night, layers D and E disappear largely in the absence of ionizing radiation, and radio wave reflection is effected only by the upper part of layer F. The ionic composition also varies with height within the ionosphere. At the lower altitudes molecular ions (O_2^+ , NO^+) are prevalent. Above 150 km O^+ is the major ion and beyond 1000 km the lighter ions He^+ and H^+ begin to dominate.

The Earth's atmosphere has no clear upper limit; its density and composition approach gradually that of interplanetary space, but in some cases atmospheric bounds are defined with different criteria. The magnetic field of the Earth, which controls the motions of the ions in the low density upper ionosphere (*magnetosphere*) overlaps the magnetic field associated with the solar wind. The region of interaction defines a neat (though variable) limit (*magnetopause*), which can be taken in some sense as the border of the Earth's atmosphere. The magnetopause is not spherical, but elongated with a long tail in the «shadow» side. At the side of Earth facing the Sun its distance to the planet's surface is ≈ 60000 km. From the point of view of aeronautics and spacecraft re-entry, the boundary of «outer space» is often placed at ≈ 100 km (Kármán line), which corresponds to the approximate location of the homopause, below which viscous effects become relevant.

2.2. Radiation budget, circulation and chemistry

At the thermopause (i.e. the limit of effective thermal interaction), the global radiation incident on a surface element perpendicular to the Sun-Earth direction is $S = 1360 \text{ W m}^{-2}$. This quantity is defined as the *solar constant*. The solar spectrum corresponds roughly to that of a blackbody at ≈ 5800 K (see Figure 1.2), with a maximum in the visible region.

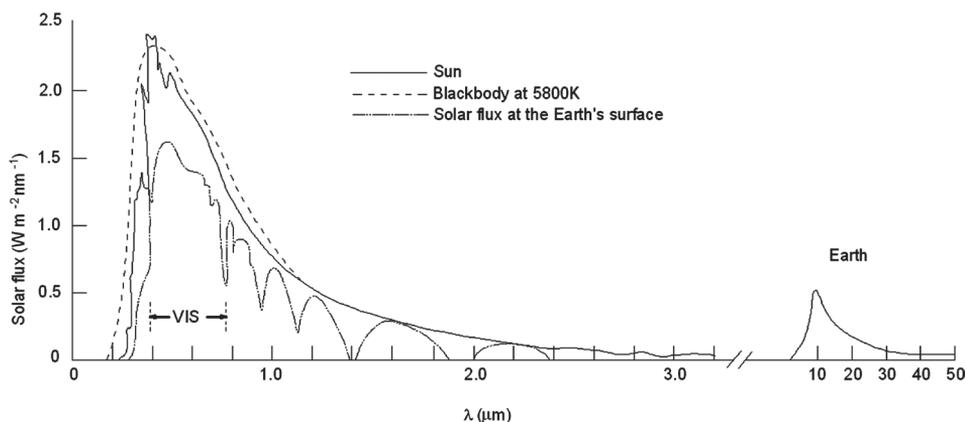


Figure 1.2. Comparison of solar and terrestrial radiation (The curve for the Earth's radiation is just schematic and not to scale). Atmospheric absorptions of the Sun's radiation, which correspond mostly to O_2 , O_3 and H_2O , reduce significantly the solar flux reaching the surface.

Approximately 30% of the incident radiation is reflected back to space; roughly 50% is absorbed by the Earth's surface and most of the remaining 20% is absorbed by the atmosphere. Considering that the average temperature of the Earth is approximately constant, a steady state condition must exist between incoming and outgoing radiation. The average incoming radiation absorbed by the Earth can be expressed as:

$$F_s = \frac{S}{4} (1 - A) \quad (6)$$

where S is the solar constant and A the average reflectivity (*albedo*) of the planet. For the derivation of equation 6, the amount of solar radiation intercepted by the Earth (with a cross section of πR^2 , where R is the planet's radius) has been redistributed over the entire Earth surface ($4\pi R^2$). The approximate value of the reflectivity, which includes both surface and atmosphere, is $A \approx 0.3$. Assuming that the Earth behaves globally as a blackbody, the average energy radiated at the top of the atmosphere can be estimated using the law of Stefan-Boltzmann:

$$F_e = \sigma T_e^4 \quad (7)$$

where $\sigma = 5.7 \times 10^{-8} \text{ Wm}^2\text{K}^{-4}$ is the Stefan-Boltzmann constant and T_e the effective radiative temperature of the Earth. Neglecting the heat from the interior of the Earth, which amounts to less than 0.001 of the energy of the incident radiation, equations 6 and 7 can be combined to estimate this temperature:

$$T_e = \left[\frac{(1 - A)S}{4\sigma} \right]^{1/4} \quad (8)$$

Substituting in equation (8) one gets $T_e = 254 \text{ K}$, which is very close to the effective radiative temperature ($\approx 256 \text{ K}$) measured by satellites outside the Earth. This value is, however, appreciably lower than the average temperature at the Earth's surface ($\approx 288 \text{ K}$) due to the fact that the gases in the atmosphere absorb part of the energy radiated by the Earth and retain it as heat. The atmosphere is relatively transparent to the incoming solar radiation, which has a maximum spectral density in the visible at a wavelength of $\approx 0.5 \mu\text{m}$, but absorbs efficiently most of the infrared (IR) radiation from the Earth's surface, whose emission spectrum peaks at about $10.5 \mu\text{m}$. A significant part of the absorbed energy is then transferred back to the surface. This phenomenon is known as *greenhouse effect*. Atmospheric gases contribute differently to greenhouse warming depending on their specific IR absorptivities and on their concentration. Table 1 summarizes the contribution of the various atmospheric species to the global greenhouse effect. Note that water vapour is the major greenhouse gas, due to its high atmospheric abundance. In fact, water plays a key role not only in the greenhouse effect, but also in the global redistribution of energy. Through a cycle of evaporation, condensation and precipitation, H_2O provides the most important non-radiative mechanism of energy transport in the atmosphere.

The radiation of the Sun does not heat the Earth's surface in a uniform way. There can be strong local variations depending on latitude, season, cloud coverage, etc. This uneven distribution of heat gives rise to a displacement of large air masses known as atmospheric circulation (Hidore, 1993, Visconti, 2001). The largest flow of radiant energy reaches the Earth close to the equator, where the heated air expands and rises. At the upper troposphere (remember that the tropopause acts as a barrier for vertical movements) the ascending air column diverges and heads toward the poles. In this poleward motion the air cools and eventually descends at a latitude of

about 30° , where it flows again at low altitude towards the equator thus closing a convection cell (Hadley cell). This vertical cell structure is repeated three times between the equator and each of the poles. Other air circulation cells associated with surface temperature gradients are also found in the atmosphere (Hidore, 1993). The tropospheric Rossby number relating characteristic speed and length of wind with planetary rotational period (equation 5) takes a value of ≈ 0.1 at mid-latitudes, indicating that Coriolis forces play an important role in atmospheric circulation. As a consequence of the superposition of the convective circulation and Coriolis forces, air masses at low altitude move frequently in rotating spiral structures associated with low and high pressure systems. In the northern hemisphere the sense of rotation of high pressure systems is clockwise and that of low-pressure systems counter-clockwise and the opposite is true in the southern hemisphere. In the upper troposphere there is also an air circulation characterized by high speed winds (*jet streams*).

**TABLE 1.1. CONTRIBUTIONS TO THE GREENHOUSE EFFECT
(DATA FROM SCHÖNWIESE, 1995)**

Gas	Contribution to the temperature increase (K)	Contribution to global greenhouse effect (%)
H ₂ O	20.6	62.0
CO ₂	7.2	22.0
O ₃ (tropospheric)	2.4	7.0
N ₂ O	1.4	4.0
CH ₄	0.8	2.5
Others	≈ 0.6	2.5
Sum	33.0	100.0

The small UV component of the solar spectrum induces a rich photochemistry with distinct characteristics for the various atmospheric layers (Finlayson-Pitts & Pitts, 2000, Wayne, 2000).

Tropospheric chemistry is dominated by oxidation processes, in which CO, methane and other hydrocarbons and organic substances of biological origin are transformed in a series of complex chain reactions propagated by radicals. The main oxidizing radical during the day is OH, produced from the photolysis of tropospheric ozone:



Tropospheric ozone is one of the few simple molecules that can be appreciably photolyzed by the $\lambda > 290$ nm photons reaching the troposphere (most radiation with shorter wavelengths is filtered at higher altitudes). The steady state concentrations of OH at ground level are very low, of the order of 10^5 cm^{-3} (as compared with the total molecular density of $\approx 2.5 \times 10^{19} \text{ cm}^{-3}$), given its extreme reactivity. Other important

daytime oxidizing species are O_3 molecules, OH_2 radicals and O atoms. At night, oxidation reactions are mainly brought about by NO_3 , which is produced in the reaction:



Nitrogen oxides (NO and NO_2 , denominated globally as NO_x) and sulphur compounds also play an active role in the oxidation chain reactions.

The tropospheric boundary layer is the site of the most complex atmospheric chemistry, due to the large variety of gas phase species and particulate matter entering the atmosphere from the surface of the oceans and continents. Over the continents, volatile organic compounds (VOCs), carbonaceous particles and dust aerosols are particularly important, whereas dimethylsulphide (DMS), released by phytoplankton, and sea-salt aerosol are determinant for chemical processes above the oceans. The chemical complexity is especially increased in the neighbourhood of industrial or densely populated areas. Substances released by human activities can give rise to health hazardous air pollution. Characteristic pollution episodes take the form of *urban smog*, a mixture of smoke and fog, that can have different origins. Carbonaceous particles and H_2SO_4 droplets produce the so called «London smog», chemically reductive and associated with the burning of sulphur-containing coal. An increased concentration of NO_x and VOCs, trapped by a thermal inversion and irradiated by sunlight, leads to photochemical smog («Los Angeles smog») which has an oxidizing character and is often related to motor vehicle traffic.

Stratospheric chemistry is dominated by the photochemical reactions of the ozone cycle (Finlayson-Pitts & Pitts, 2000, Wayne, 2000, Solomon, 1999). The simplest processes of ozone formation involving only reactive oxygen species is given by:



where M is a third body, usually N_2 or O_2 .



Ozone production (R4 + R5) and destruction (R6 + R7) processes are exothermic by 106 kJ mol^{-1} and 392 kJ mol^{-1} , respectively. Other mechanisms of ozone loss involve catalytic cycles with the participation of different species (OH, NO, Cl...). The neat result of ozone chemistry is the above mentioned heating of the stratosphere and the build-up of an ozone layer with a maximum concentration of $\approx 5\text{-}8 \times 10^{12} \text{ cm}^{-3}$ at an approximate height of $\approx 15\text{-}25 \text{ km}$, depending on latitude, that prevents virtually all radiation with $\lambda < 290 \text{ nm}$ (hazardous for living beings) from reaching the Earth's surface. Most ($\approx 90\%$) of the O_3 existing in the atmosphere is concentrated within this stratospheric layer. During much of the 20th century human activities have increased stratospheric concentrations of NO_x and

halogen containing compounds, mostly in the form of chlorofluorocarbons (CFCs), that have led to an appreciable destruction of O_3 . This effect has been most dramatic at the end of the polar winter at high latitudes (*ozone hole*), where heterogeneous reactions on polar stratospheric clouds provide additional loss mechanisms for O_3 . The phasing out of CFCs, following international agreements, is expected to lead to a gradual recovery of O_3 levels over the next decades (Solomon, 1999).

At higher altitude, shorter wavelength radiation is available and this leads to ionization and to dissociation of the major atmospheric components N_2 and O_2 . The distinct ionospheric layers have specific chemical characteristics (Tanarro, 2001, Wayne, 2000) and, although neutral molecules are predominant, it is instructive to have a short look at the chemistry of charged species. In the D layer between ≈ 60 and 90 km the collision frequency is still relatively high and allows a variety of chemical processes. Below ≈ 80 km, protonated water aggregates, $H^+(H_2O)_n$, and negative molecular ions are present in significant amounts. Above this height the ion distribution is dominated by the positive molecular species NO^+ , formed by ionization of NO with Lyman- α (121.6 nm) photons, and by O_2^+ . In the E region (≈ 90 -120 km) the primary ionization products, N_2^+ and O_2^+ undergo a series of ion molecule reactions that favour the formation of NO^+ . The ions NO^+ and O_2^+ are again prevalent in this layer. In the F layer, (between ≈ 120 and 1000 km) the dissociation of O_2 molecules is very efficient, and extensive formation of O^+ becomes possible. The O^+ ion can still be transformed to O_2^+ and NO^+ in ion molecule reactions, but with growing height, collisional mechanisms lose relevance and O^+ is by far the dominant ion in this layer, where the maximum concentrations of atmospheric ions (and electrons) are found.

The light He and H atoms (and their respective ions) prevail in the atmosphere above ≈ 1000 km. Hydrogen atoms can be formed, for instance, in the upper F layer through reactions of hot O atoms with H_2 molecules, and H^+ ions can be produced through charge exchange between O^+ and H atoms. Hydrogen atoms in the upper thermosphere (with T up to ≈ 2000 K) above the exobase, can leave the atmosphere through the Jeans escape mechanism commented on above (equation 3), but there is also an important non-thermal mechanism for escape, based on charge exchange between thermal H atoms and fast H^+ ions from the magnetosphere, that leads to neutral H atoms with very high velocities. Irrespective of the final escape mechanism, hydrogen loss is limited by upward diffusion (Chamberlain, 1963, Visconti, 2001). The Magnetosphere acts as an effective shield deflecting most of the solar wind away from the Earth, but close to the poles, open magnetic field lines allow some exchange of matter between the solar wind and the atmosphere. A neat outflow of plasma from the upper ionosphere into the magnetosphere along geomagnetic field lines is observed at high latitudes (*polar wind*) (Ganguli, 1996). This flow is mostly composed of H^+ , He^+ and O^+ ions. Particles from the solar wind can also enter the atmosphere at high latitudes. When the magnetic field of the Sun is favourably oriented these particles (mostly electrons) get trapped in the magnetosphere and can be accelerated towards the Earth. At an altitude of ≈ 100 km, where the density is already appreciable, characteristic light emissions (*polar aurorae*) are produced by

the collisions of these energetic particles with atoms and molecules. Green and red colours, corresponding to atomic and molecular emission systems of oxygen and nitrogen predominate in these phenomena.

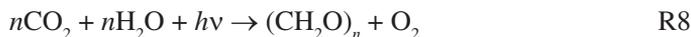
2.3. Origin and evolution of the atmosphere

The Earth was formed about 4500 millions of years ago by accretion of bodies (first *grains*, then *planetesimals*) in the *solar nebula*, during the gravitational collapse of gas and dust that gave rise to the *Solar System* (Mc Bride & Gilmour, 2004, Milone & Wilson, 2008). Little is known about the conditions of the planet in this early age, but it can be hypothesized that, during its formation, the *proto-Earth* might have collected an atmosphere of volatile species from the surrounding nebular material. This primeval atmosphere should have reflected the original composition of the nebula, dominated by hydrogen and He and containing a much smaller proportion of noble gases and hydrogenated chemical compounds of light elements (CH_4 , NH_3 , H_2O). Given its mass, it is unlikely that the Earth, with an escape velocity $v_{es} = 11.3 \text{ km s}^{-1}$, could have retained a large amount of compounds with molecular weights smaller than 10 and thus, this original atmosphere should have been depleted of hydrogen and He and enriched in the other volatile species. Likely remnants of this primordial atmosphere would be the noble gases, which being unreactive should not have been chemically transformed in later stages of atmospheric evolution. However, the relative abundance of noble gases in the Earth is smaller, by many orders of magnitude, than that in the Solar System, indicating that the conjectured primeval atmosphere disappeared at some point. Astronomic observations on protostars and models of stellar evolution suggest that an enhanced solar wind from the young Sun should have blown away most of the gas and dust, and thus much of the planetary atmospheres, in the inner Solar System during the early phases of its formation. The heat derived from the gravitational energy liberated in the accretion process could have contributed also to the loss of the original atmosphere.

Once the crust of the Earth solidified, a secondary atmosphere was generated through outgassing, a process that is continued in present-day volcanism. Although no ices of volatile elements could condense in the relatively hot region of the original nebula, where the Earth was formed, volatile species could get trapped during accretion or be part of the composition of a number of minerals in the grains and planetesimals. It is assumed that the gases emitted by the planet were mainly H_2O and CO_2 with small amounts of N_2 , NH_3 , CH_4 , and other minor species, but virtually no O_2 . The actual origin and the amount of the various gases is still a matter of debate (Mc Bride, 2004, Mueller-Wodarg et al, 2008, Milone & Wilson, 2008). It has been suggested, for instance, that hydrous compounds must have been rare in the minerals that formed the Earth and that most of the H_2O reached the planet in collisions with comets, which were frequent during an early period of the existence of the Solar System. In an atmosphere devoid of an O_2 filter for the UV radiation, NH_3 and CH_4 would be readily photolyzed. In fact it is believed that a large amount of the atmospheric N_2 was formed from NH_3 through photolysis and subsequent chemical reactions. Further cooling of

the planet led to the condensation of most of the H_2O to form the oceans. In the presence of liquid water most of the CO_2 was precipitated as carbonate in sedimentary rocks. The oldest sedimentary rocks are dated ≈ 3800 millions of years (Myr) before present (bp); by that time the atmosphere must have been already largely depleted of H_2O and CO_2 and its most abundant component was probably the chemically inert gas N_2 . Some O_2 could be generated through photochemical reactions of H_2O or CO_2 , but once formed, a comparatively small amount of the gas would filter UV radiation below ≈ 240 nm and would inhibit a further photolysis of its precursors. Photochemical models and geologic data constrain the amount of photochemically produced O_2 to a very small fraction of the present concentration. There are many evidences from different sources indicating that oxygen, the second gas in importance in today's atmosphere, is essentially of biological origin.

Chemical and biological evolution on Earth are assumed to have started in an anoxic environment protected from UV radiation, most likely under water. The first living beings were single cells without a nucleus (*prokaryotes*) and with an anaerobic metabolism. At a certain time some of these prokaryotes developed a photosynthetic apparatus that allowed the incorporation of energy from the Sun's radiation into a more efficient metabolism. Chemical transformations associated with photosynthesis can be schematically written:



The oldest fossil remains (*stromatolites*) attributed to photosynthetic cyanobacteria are dated ≈ 3500 Myr bp, and, at least since that time, biogenic oxygen was released to the atmosphere. Initially this oxygen was largely removed from the atmosphere through chemical reactions of oxidation of Fe^{2+} ions, very abundant in the crust minerals and in the oceans, to Fe^{3+} . The dating of iron containing rocks shows that the oxidation process must have been complete by about 1500 Myr ago. From that time on, O_2 began to accumulate rapidly in the atmosphere. The increasing amount of oxygen, which was a poison for most of the existing anaerobic prokaryotes, accelerated the evolution of those life forms who could incorporate it into their metabolism (respiration). An oxygen-based metabolism, more efficient than its anaerobic counterpart, facilitated the surge of more complex organisms (*eukaryotes*). Chemical models and considerations about the oxygen requirements for the various stages of the evolution of life derived from the fossil record provide an approximate timeline for the increase of the O_2 concentration in the atmosphere (Wayne 2000). It is believed that 1% of the present concentration was reached ≈ 2000 My bp. A 10% value was attained ≈ 700 Myr bp and allowed the existence of soft bodied metazoans in the oceans. The present concentration of oxygen, and of its photochemical derivative, ozone, was reached ≈ 350 Myr ago. At that time, thanks to the effective UV filter provided by O_2 and O_3 , land plants had become widespread and highly evolved animals like the amphibians began to populate the land's surface. Since then, biogenic production has balanced loss processes and kept the concentration of O_2 essentially constant. Estimations suggest that in the absence of photosynthesis the existing atmospheric

oxygen would be lost in about 4 Myr through weathering reactions at the surface and in the oceans.

3. A BRIEF LOOK AT OTHER ATMOSPHERES IN THE SOLAR SYSTEM

A broad divide can be made between the atmospheres of the rocky (terrestrial) planets and those of the gaseous giant (Jovian) planets located beyond *the frost line*, which delimits the nebular region where temperature drops below ≈ 150 K and ices can form. This dividing line is presently located between the orbits of Mars and Jupiter at ≈ 3 AU from the Sun (1 AU = 1 Astronomic Unit is $\approx 1.5 \times 10^8$ km, which corresponds to the average Sun-Earth distance).

The rocky planets formed in the hot central part of the nebula, where volatile species could not condense. Grains and planetesimals were mostly made of substances with high melting points like silicates and metals. These compounds constitute less than 1% of the mass of the original solar nebula, and consequently the rocky planets could not grow to large sizes. Given their low masses they were unable to retain gravitationally significant amounts of He or hydrogen. In addition, the increased solar wind of the young Sun probably depleted the rocky planets from their primordial atmospheres. Volatiles trapped in the accreted material were then outgassed from the interior of the planets and accumulated to form secondary atmospheres when the strong solar wind subsided in the course of the Sun's evolution. Asteroid and comet impacts, which were frequent during the first hundreds of millions of years of existence of the Solar System, may also have contributed to the present inventory of volatiles. The resulting atmospheres are thin (remember that 90% of the mass of the Earth's atmosphere is concentrated in the first 15 km; as compared with the Earth's radius of 6371 km) and their properties are specific for the distinct planets.

Figure 1.3 shows the values of pressure and temperature for Venus (0.72 AU from the Sun), the Earth, and Mars (1.52 AU from the Sun) over the first 100 km of altitude. Note the marked differences between the three planets. The peculiar thermal inversion characteristic of the Earth's stratosphere is absent in the other two planets. Venus has a denser atmosphere than the Earth and a surface pressure 90 times higher. Mars has a much thinner atmosphere, with a typical pressure of 600 Pa at the surface. Coriolis forces, associated with planetary rotation, are important on the Earth and Mars. For the lowest 10 km at a latitude of 45° the Rossby number (equation 5) has a value $R_o \approx 0.1$ for both planets. In contrast, under the same conditions, $R_o \approx 10$ -50 for Venus (Milone & Wilson, 2008), where Coriolis forces are weak due to the slow planetary rotation ($\tau = 243$ terrestrial days).

The *atmosphere of Venus* is composed of CO_2 (96%), N_2 (3%) and a series of minor gases (SO_2 , H_2O , CO, noble gases). Thick layers of H_2SO_4 clouds, located between 45 and 70 km of height, cover the whole planet and screen the surface from the Sun's radiation. The clouds have been observed to move rapidly around the planet in a direction parallel to the equator (super-rotation). The velocity of circulation on top of the clouds is of the order of 100 m s^{-1} , 50 times faster than the planets' ro-

tation. The high amount of atmospheric CO_2 gives rise to a very pronounced greenhouse effect that leads to surface temperatures above 700 K. A noteworthy feature of Venus is the scarcity of H_2O , at first sight a singular trait for a planet which is otherwise very similar to Earth in size and density, and that was formed in a nearby region of the solar nebula (its present orbit is at 0.72 AU). Current models cannot decide whether the planet was formed without water, or lost it afterwards (Feigley, 2008). In any case, the absence of liquid water prevented the precipitation of CO_2 as carbonate and allowed the runaway greenhouse effect characteristic of the planet.

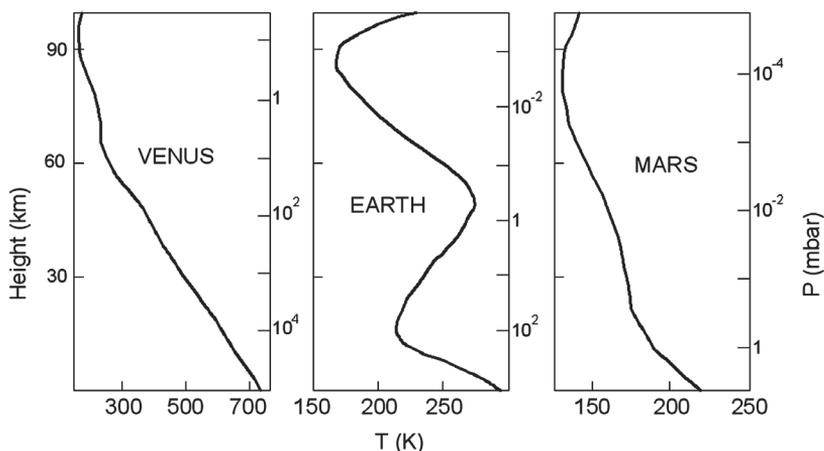


Figure 1.3. Temperature and pressure as a function of altitude, for the rocky planets.

The *atmosphere of Mars*, with an average pressure of 600 Pa (6 mbar), is thinner than that of the Earth. In analogy with Venus it is made of CO_2 (96%) and N_2 (3%) with trace amounts of other gases like O_2 , H_2O and CH_4 . Although water ice and some CO_2 are trapped in the polar caps, the proportion of volatiles in Mars is small in comparison of that of Venus and the Earth. The larger distance of Mars to the Sun (1.52 AU) results in a lower surface temperature, that cannot be countered by the small greenhouse effect provided by the thin CO_2 atmosphere. As a result, the average surface temperature is just 227 K. Geochemical data and models suggest that volatiles were much more abundant in the beginning of the planet's history and point even to the early presence of liquid water (maybe only sporadically), but impact erosion and hydrodynamic escape must have largely depleted the volatile inventory more than 3800 Myr ago (Catling, 2008). In spite of its low pressure, dust in suspension and dust storms are common features of Mars' atmosphere.

There are many other small-sized rocky objects in the solar system, including a planet (Mercury), many satellites, asteroids, and trans-neptunian objects from the Kuiper belt, but, as far as we know, none of them sustains an appreciable atmosphere, with the notable exception of Titan, the largest moon of Saturn. Titan, with a mean radius of 2576 km (slightly larger than Mercury), has a significant atmosphere with a pressure of ≈ 1.5 bar and a temperature of ≈ 94 K at the surface. It is located at

9.54 AU from the Sun. The Cassini-Huygens Mission has recently provided most valuable first hand information about the characteristics of its atmosphere (Coustenis, 2007). The Huygens probe, that descended on the moon's surface in January 2005 is, to date, the furthest man-made spacecraft ever to have landed on a celestial body. The main constituent of ***Titan's atmosphere*** is N_2 (98%). The second most abundant gas is CH_4 ; it reaches a concentration of 5% at the surface, but its proportion diminishes with growing height due to photolysis. There are also smaller amounts of other gases like CO, CO_2 , H_2O , hydrocarbons, and nitriles. The photochemistry of methane yields hydrocarbons and other nitrogen rich organic compounds (*tholins*), that produce an orange coloured haze. This haze, together with methane and ethane clouds, covers much of the moon's surface. The intense solar heating of the optically thick photochemical aerosol layer gives rise to a temperature inversion that creates a stratosphere. Studies of isotopic composition indicate that the present N_2 was originally incorporated as NH_3 , which was much more abundant in the saturnian subnebula, and then photolyzed. The persistence of the photolytically labile CH_4 suggests that it is replenished from the interior. It is believed that the atmosphere of Titan may bear some resemblance with early stages of the Earth's atmosphere, but at a much lower temperature.

The ***atmospheres of the gaseous planets*** (Jupiter, Saturn, Uranus and Neptune) are very different from those of the rocky bodies. These planets, with orbits situated between 5 and 30 AU from the Sun, formed originally beyond the frost line. Volatile species, much more abundant in the nebula than metals and silicates, could condense there to icy grains that accreted and led to much larger planetary cores capable to capture and retain He and hydrogen, the most abundant nebular materials. The atmospheres, very thick and large as compared to the total size of the planet, are made essentially of He and hydrogen in a proportion consistent with that found in the solar nebula. Minor gases, mostly small volatiles (H_2O , NH_3 , CH_4) are also found. The giant planets have probably no definite liquid or solid surface, but have different layers of gaseous, icy and rocky materials. Uranus and Neptune are much smaller in size than Jupiter and Saturn and have higher densities indicating a larger proportion of icy vs gaseous materials. The temperature profile of the jovian atmospheres shows a structure with troposphere, mesosphere and thermosphere, but no stratosphere (Mc Bride, 2004). Clouds and photochemical aerosols are also present in these atmospheres. The outermost cloud layer in Jupiter and Saturn is made of NH_3 , whereas methane clouds have been identified in Uranus and Neptune. The four planets rotate very fast (with rotational periods smaller than a terrestrial day) and atmospheric circulation is characterized by high speed east-west (*zonal*) winds and by a series of alternating dark and light bands parallel to the equator called *belts* and *zones* respectively and associated with downward and upward convective motions.

4. THE HELIOSPHERE

The ***heliosphere*** is the vast region of Space pervaded by the solar wind. It extends a long stretch beyond the orbits of the outer planets and can be viewed as a sort

of thin atmosphere for the whole Solar System. The *solar wind* is a stream of highly energetic particles, mostly electrons and protons, emitted from the solar corona. It expands in all directions and submerges all bodies located within its region of influence. Planets and satellites possessing a magnetic field deflect most of the solar wind around them, but those without magnetic activity are directly exposed to it and can suffer enhanced losses of atmospheric material. A significant fraction of Mars' atmosphere may have been depleted this way.

The solar wind expansion ends in a shock wave structure caused by the interaction with the interstellar medium. The flow should first become subsonic at the *termination shock* and then travel with decreased velocity and increased temperature and density through the *heliosheath* until the *heliopause*, the point where the pressures of the solar wind and interstellar medium equilibrate. In spite of its name, the heliosphere is not spherical, but has an elongated shape due to its interaction with the local galactic magnetic field.

The boundary of the heliosphere, which had long been just the object of models and conjectures, has been recently reached by human spacecraft. In 2005 and 2007 respectively, Voyager 1 and Voyager 2, after a 30 year journey, crossed the termination shock, which was found to lie between 84 and 94 AU (the two spacecraft crossed at different latitudes). Data from Voyager 2 indicated surprisingly that the shock was weaker than expected. The flow, although with reduced velocity, moves still supersonically into the heliosheath (Richardson et al, 2008). At present, Voyager 1 and 2 are the furthest man-made objects sending information to the Earth.

ACKNOWLEDGMENT

I am indebted to my wife, Margarita Fernández, for her careful reading of the manuscript and for the preparation of the figures.

REFERENCES

- BERBERAN-SANTOS, M. N., BODUNOV, E. N. & POGLIANI, L. (1997), «On the barometric formula», *Am. J. Phys.* 65, 404.
- CATLING, D. (2008), «Atmospheric Evolution of Mars» in *Encyclopedia of Paleoclimatology and Ancient Environments*, edited by V. Gorniz, Springer, Dordrecht, The Netherlands.
- CHAMBERLAIN, J. W. (1963), «Planetary Coronae and Atmospheric Evaporation», *Planet. Space. Sci.* 11, 901.
- COUSTENIS, A. (2007), «What Cassini-Huygens has revealed about Titan», *Astron. and Geophys.* 48, 2.14.
- FEIGLEY, B. jr. (2008), «Atmospheric evolution on Venus» in *Encyclopedia of Paleoclimatology and Ancient Environments*, edited by V. Gorniz, Springer, Dordrecht, The Netherlands.
- FINLAYSON-PITTS, B. J. & PITTS, J. N. (2000), *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, California.

- GANGULI, S. B. (1996), «The Polar Wind», *Rev. Geophys.* 34, 311.
- HIDORE, J. J. & OLIVIER, J. E. (1993), *Climatology*, Mc Millan. New York.
- MC BRIDE, N. & GILMOUR, I. (eds). (2004), *Introduction to the Solar System*, Cambridge University Press. Cambridge, UK.
- MILONE, E. F. & WILSON, W. (2008), *Solar System Astrophysics: Planetary Atmospheres and the Outer Solar System*, Springer. New York.
- MUELLER-WODARG, I. C. F., STROBEL, D. F., MOSES, J. I., WAITE, J. H., CROVISIER, J., YELLE, R. V., BOUGHER, S. W. & ROBLE, R. G. (2008), «Neutral Atmospheres» *Space Sci. Rev.* 139, 191.
- RICHARDSON, J. D., KASPER, J. C., WANG, C., BELCHER, J. W. & LAZARUS, A. (2008), «Cool heliosheath plasma and deceleration of the upstream solar wind at the termination shock», *Nature*, 454, 63.
- SCHÖNWIESE, C. (1995), *Klimaänderungen*, Springer. Berlin-Heidelberg.
- SOLOMON, S. (1999), «Stratospheric Ozone Depletion: A Review of Concepts and History», *Rev. Geophys.* 37, 275.
- TANARRO, I. (2001), «Ionosfera» in *Físico-Química de la Atmósfera* edited by Rafael Escribano, Comité de Espectroscopía. Sociedad Española de Óptica, Madrid.
- VISCONTI, G. (2001), *Fundamentals of Physics and Chemistry of the Atmosphere*, Springer. Berlin-Heidelberg.
- WAYNE, R. P. (2000), *Chemistry of Atmospheres*, Oxford University Press, Oxford, UK.