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The Earth's Atmosphere

1.0.1 Atmospheric Dissipation

The distribution of speeds $f(v)$ for a molecule in thermal equilibrium is

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/(2k_B T)} dv \quad (1.1)$$

The most probable speed of a molecule, v_{\max} is the maximum of $f(v)$ and is found from setting $df/dv = 0$ to be

$$v_{\max} = \sqrt{\frac{2k_B T}{m}} \quad (1.2)$$

The escape velocity is

$$v_{\text{esc}} = \sqrt{\frac{2GM}{R+z}} \quad (1.3)$$

The escape parameter λ_{esc} is the ratio of a molecule's potential to kinetic energy and has the value

$$\lambda_{\text{esc}} = \frac{GMm}{R+z} \frac{2}{mv^2} = \left(\frac{v_{\text{esc}}}{v} \right)^2 \quad (1.4)$$

The number of molecules lost from the exosphere is given by ■ Sort out working ■

$$\Phi = \frac{Nv_{\max}}{2\sqrt{\pi}} (1 + \lambda_{\text{esc}}) e^{-\lambda_{\text{esc}}}$$

The exobase is that level in the atmosphere above which collisions between molecules are so infrequent as to be negligible and below which collisions are sufficiently frequent to maintain a Maxwellian distribution of molecular velocities. Since collisions are negligible above the exobase, the molecules in this region, called the exosphere, move along ballistic trajectories under the action of the Earth's gravitational field. Some of the upward-moving molecules have sufficient velocities to carry them on hyperbolic trajectories away from the Earth, into space.

Jean's escape is a lower limit of atmospheric loss further processes that contribute include

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The evolution of the Sun will place the Earth outside the habitable zone in about 1 billion years *Schröder and Smith* [2008]. This is far sooner than the projected loss of atmosphere, about 10^{313} years, at its current dissipation rate (see Problem 1.3).

1.1 Atmospheric Structure

1.1.1 An Ideal Gas

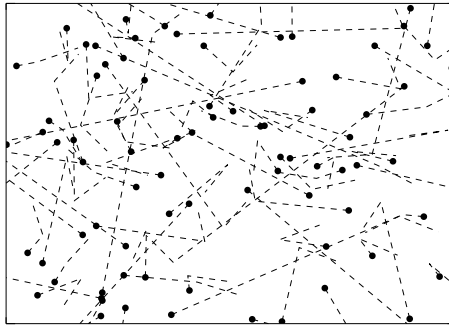


FIGURE 1.1

An ideal gas composed of a set of randomly-moving, point particles whose only interaction is through collision with the container walls or other particles.

In an ideal gas atoms or molecules move independently and interact with each other through random collisions. The volume of the atoms or molecules is negligible compared with the volume they occupy. A single cubic centimetre of air contains about 10^{19} molecules. These molecules collide with their neighbours billions of times per second moving on average about 10 nm (~ 100 molecular radii) between collisions. Therefore a particle-by-particle description of the evolution of an air volume would involve a prohibitively large number of values. Advances in kinetic theory in the 19th century (ref Blundell & Blundell ???) allowed the description of the macroscopic properties of a gas without the need to describe the motion of the gas particles themselves. A gas contained within a volume, V , can be described by two fundamental macroscopic properties: the temperature T , which is proportional to the kinetic energy, and the pressure p , which is the force per unit area exerted on a surface by the collisions of the gas particles. For a gas comprised of N particles the pressure and temperature are related by the ideal gas law

$$pV = Nk_{\text{B}}T, \quad (1.5)$$

where k_{B} is Boltzmann's constant. The number density n of a gas is the number particle per unit volume (i.e. $n = N/V$) so that an alternate form of the ideal gas law is

$$p = nk_{\text{B}}T. \quad (1.6)$$

The ideal gas law also is expressed using moles of material. The mole is the amount of substance which contains as many elementary entities as there are atoms in 12 grams of carbon-12, where the carbon-12 atoms are unbound, at rest and in their ground state [BIPM, 2006]. The number of atoms in a mole is known as the Avogadro constant, and is determined empirically. The currently accepted value is $6.02214179 \times 10^{23}$ [Mohr *et al.*, 2008]. The ideal gas law can be written using moles as

$$pV = n_m RT \quad (1.7)$$

where n_m is the number of moles and R is the universal gas constant.

If the mass of each gas particle is m_m then the mass density ρ of the gas is

$$\rho = nm_m \quad (1.8)$$

Although air is comprised of a number of different gases it is often convenient to treat it as a homogeneous quantity comprised of 'air' molecules whose mass is equivalent to the weighted average of the composite molecules. As nitrogen comprises 80 % of the atmosphere it is unsurprising that the mean molar mass of air, $M = 28.97 \text{ g mol}^{-1}$ is very close to that of a N_2 (28.01 g mol^{-1}). This leads to another form of the ideal gas law

$$pV = mR'T \quad (1.9)$$

where m is the mass within the volume and R' is a constant found by dividing the universal gas constant by the molecular weight of the gas being considered. For dry air $R' = 287 \text{ J kg}^{-1} \text{ K}^{-1}$.

It is also useful to define an *air parcel* as a hypothetical volume of gas whose properties can be considered independently from those of the surrounding air parcels.

1.1.2 Pressure & Density

The dominating change with in the atmosphere is that of atmospheric pressure which covers over five orders of magnitude between the surface and space. The variation of atmospheric pressure and density with altitude can be found by considering a column of gas subdivided into layers between height z and $z + dz$. If each gas molecule has mass m_m and the density of molecules is n then the layer exerts a force per unit area (i.e. a pressure) that is the sum of the weights of the molecules so that the change in pressure dp over dz is

$$dp = -(m_m g) \times (n dz) \quad (1.10)$$

(change in pressure = weight of a molecule \times molecules per unit area)

The negative accounts for the fact that pressure scale runs in the opposite sense to the height scale i.e. pressure reduces as z increases. Substituting in Equation 1.8 ($\rho = nm_m$) gives the hydrostatic equation

$$dp = -\rho g dz \quad (1.11)$$

which is extremely useful as it forms the basic relation between height and pressure.

Using the ideal gas law in the form $p = nk_B T$ we can write

$$dn = -\frac{m_m g n}{k_B T} dz \quad (1.12)$$

which is integrated to give the change in molecular density

$$n(z) = n(0)e^{-m_m g z / k_B T} \quad (1.13)$$

Alternatively we can use the ideal gas law in the form $pV = n_m RT$ and the hydrostatic equation to determine the variation of pressure with altitude

$$p(z) = p(0)e^{-Mg z / RT} \quad (1.14)$$

The vertical change in pressure is approximately logarithmic and can be re-expressed as

$$p(z) = p(0)e^{-z/H} \quad (1.15)$$

where $H = RT/Mg$ is called the scale height of the atmosphere. Assuming an average atmospheric temperature of 240 K gives the scale height of the Earth's atmosphere as about 7 km. The thickness of the atmosphere is remarkably small compared to the size of the Earth — equivalently thinner than the thickness of the peel of an apple.

1.1.3 Temperature

Atmospheric temperature is much less variable than pressure as a function of height however it is still a function of altitude as shown in Figure 1.2. The naming conventions for the various atmospheric layers relates to temperature as follows:

- The troposphere is the lowest layer of the atmosphere starting at the surface going up to between 8-9 km at the poles and 15-16 km at the Equator. Generally temperature decreases with height in the troposphere with a region of temperature increase called a temperature inversion. The troposphere contains 80 % of the Earth's atmosphere and is characterised by strong vertical mixing. This is driven by surface solar heating which warms the air near the surface giving it buoyancy.
- The stratosphere starts above the troposphere and extends to about 50 km. It is the region where shortwave solar radiation is absorbed giving active chemical processes including the formation of ozone. Temperature increases with altitude so that there is weak vertical mixing and long residence times for gases and particles.
- The mesosphere extends from about 50 km to 80–85 km where temperatures again decrease with height.

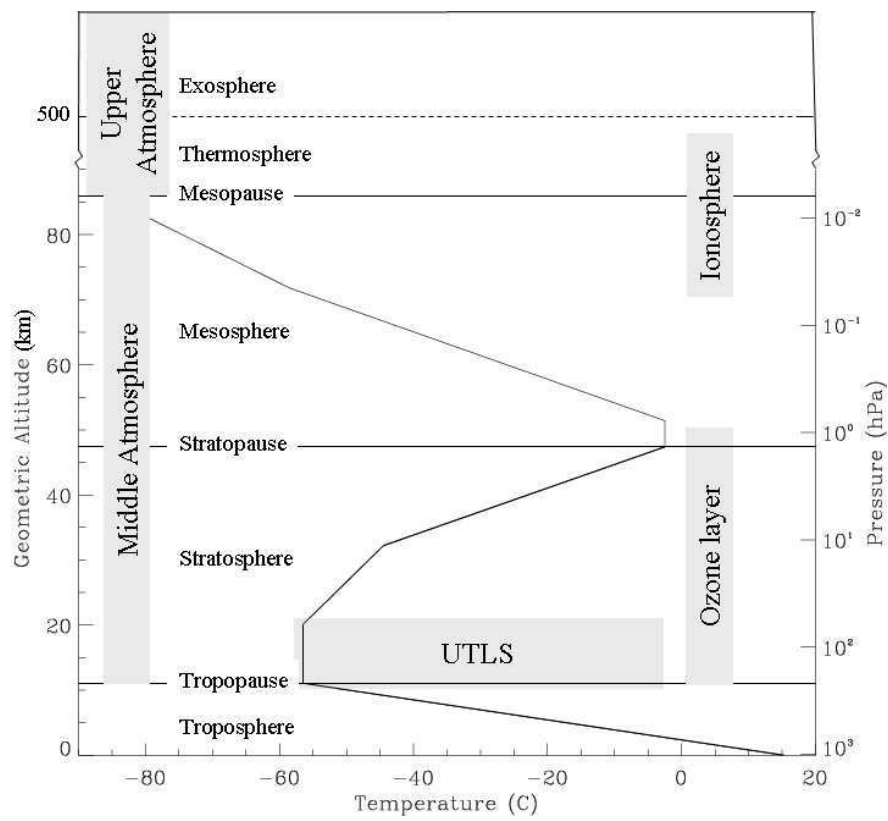


FIGURE 1.2

Vertical regions of the atmosphere and the international standard atmosphere temperature profile. Use measured temperature and variation but keep labels add ozone profile to right + electron density

- The thermosphere extends from 80–85 km to about 500 km, and is characterized by high temperatures as a result of the absorption of short wavelength radiation by nitrogen and oxygen. Temperature increases with height although at these altitudes the air is very tenuous.
- The exosphere refers to altitudes above about 500 km where the atmosphere thins out into space. In this region it is possible for energetic gas molecules to escape the Earth's gravitational attraction.

Atmospheric regions are also named in other ways:

- The upper troposphere - lower stratosphere (UTLS) is approximately that part of the atmosphere between 5 and 20 km. It is a transition zone between the convectively dominated and therefore unstable troposphere and the stable, stratified stratosphere. The UTLS contains strong gradients in many trace constituents of tropospheric or stratospheric origin (such as water vapour and ozone).
- The ozone layer or ozonosphere, approximately 10–50 km, where stratospheric ozone is found. Note that even within this region, ozone is a minor constituent by volume.
- The ionosphere the region containing ions: approximately the upper mesosphere and thermosphere.
- The magnetosphere the region where the Earth's magnetic field interacts with the solar wind from the Sun as shown in Figure 1.1.3. It extends for tens of thousands of kilometres, with a long tail away from the Sun.

■ Redraw/obtain figure ■ ■ horizontal variation of pressure and temperature
■

1.2 Composition

1.2.1 Terms Used to Describe Amounts of a Gas

There are several ways of describing the amount of trace gas X (say) in an air parcel:

- The partial pressure of the gas p_X .
- The gas density which comes in three forms:
 - The number density or molecules per unit volume, typically molecules per cubic centimetre, which is denoted by n_X
 - The moles per unit volume which is denoted c_X

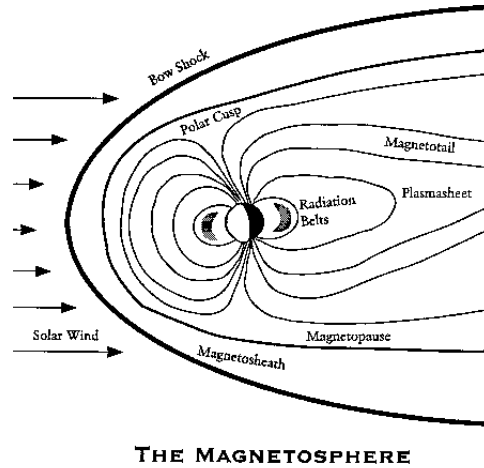


FIGURE 1.3
The magnetosphere where the solar wind interacts with the Earth's magnet field.

- The mass per unit volume which is denoted ρ_X .

These terms are all interrelated through

$$n_X = A c_X = A \rho_X / M_X \quad (1.16)$$

where A is Avogadro's constant and M_X is the molar mass of X.

- The volume mixing ratio (VMR) x_X which is the ratio of the number density of X to the total number density of molecules in an air parcel, i.e.

$$x_X = \frac{n_X}{n_{\text{total}}} \quad (1.17)$$

The VMR is a useful quantity as it is conserved as an air mass changes temperature or pressure. The VMR is usually small so it is often multiplied by 10^6 , 10^9 or 10^{12} to give parts per million by volume (ppmv), parts per billion by volume (ppbv) or parts per trillion by volume (pptv).

- The mass mixing ratio, w_X , which is the ratio of the mass of gas X to the remaining mass in the air parcel.

$$w_X = \frac{m_X}{m_{\text{parcel}} - m_X} \quad (1.18)$$

There are additional ways of representing the amount of water vapour, these are:

- The specific humidity q which is the ratio of the mass of water vapour to the mass of moist air

$$q = \rho$$

- The relative humidity RH which is the ratio of the partial pressure of water vapour to the partial pressure of water vapour for saturated air (expressed in percent)

$$RH = 100 \frac{e}{e_s}$$

Another useful measure of the loading of a gas in the atmosphere is the vertically integrated amount of a gas called the *column amount*. This too can be expressed in a number of ways, the principal being

- The molecules per unit area, N_a , is found by integrating the vertical profile of volume mixing ratio, x_X , to get

$$\sigma_N = \frac{1}{m_m^{\text{air}} g} \int_0^{p_0} x_X dp \quad (1.19)$$

- The mass per per unit area, σ , which is given by

$$\sigma = \frac{1}{g} \int_0^{p_0} x_X dp \quad (1.20)$$

- The Dobson unit is the thickness of a layer formed when a gas is compressed to standard pressure and temperature.

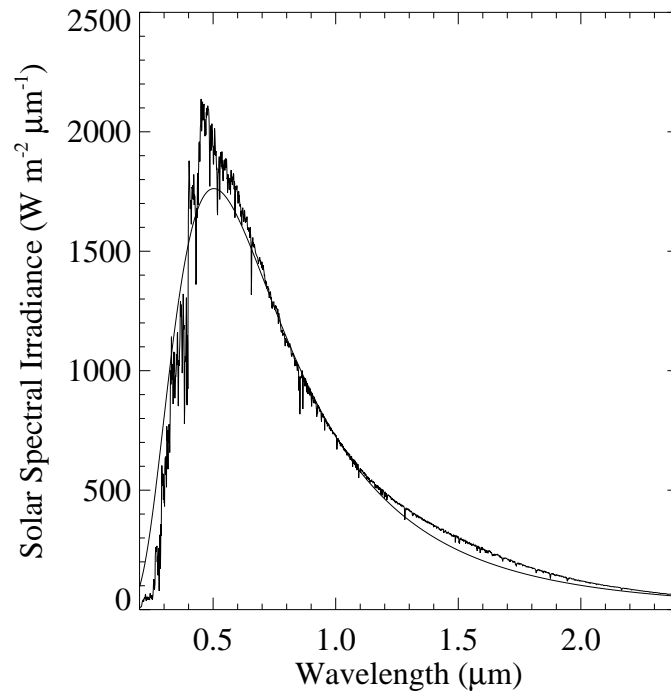
$$\text{D.U.} = \frac{10^5 k_B T_0}{m_m^{\text{air}} g p_0} \int_0^{p_0} x_X dp = 7.89 \times 10^3 \int_0^{p_0} x_X dp \quad (1.21)$$

The thickness is expressed in units of 10^{-5} m so that this unit is sometimes described as a milli-atmosphere-centimetre.

1.3 Solar Radiation

The Sun is a middle aged star around 4570 million years old. The Sun has a radius of 6.96×10^5 km much larger than that of the Earth (6356 km) and on average the centre of the Earth and Sun are separated by 1.496×10^8 km. The Sun consists mostly of hydrogen and helium and these gases becomes denser and hotter as depth into the Sun increases. Despite its large size compared to the Earth the Sun the density of the Sun is 1.4 g cm^{-3} compared to that of the Earth which is 5.5 g cm^{-3} .

Virtually all the radiant energy generate by the Sun starts out as gamma rays in the core. As the gamma rays move out from the solar interior most of them are absorbed heating the outer solar layers. The Sun emits radiation primarily from the outer 500 km of the Sun's atmosphere - the photosphere. Some 99 % of solar radiative output — that at wavelengths from 275 to 4900 nm — emerges from the

**FIGURE 1.4**

Solar spectrum at the average Earth-Sun distance [data from *Thuillier et al.*, 2003]. The smooth curve is that for a black body at a temperature of 5759 K.

photosphere [*Fröhlich and Lean*, 2004]. The solar spectrum is shown in Figure 1.4. The temperature of this layer varies but comparing the solar spectrum to the theoretical spectrum given by Planck's Law gives a best match at about 5800 K. The maximum radiance is emitted at about 500 nm in the red portion of the electromagnetic spectrum. Most solar radiation arises from non-quantised transitions so that radiation spectrum emitted by the photosphere is continuous. However specific absorption transitions by gases (H, He, C, N, O, Mg, Al, Si, Ca and Fe in various states of ionization) in the Sun's outer atmosphere introduce absorption and emission line structure. Prominent emission and absorption lines at 121 nm and 656.3 nm, respectively are attributable to hydrogen, while helium produces strong line emission at 30.4 nm and 58.4 nm and absorption at 1083 nm.

The integral of the spectral solar irradiance at the top of the atmosphere is the superterrestrial solar irradiance and has an accepted value of $1366 \pm 3 \text{ W m}^{-2}$ (REF Lean ???) for an Earth-Sun separation of 1 a.u.

Problem 1.1 Assuming the surface pressure is 1 atm what is the mass of the atmosphere?

Problem 1.2 What was the mass of CO₂ in the atmosphere in the year 2000 when its mixing ratio was 370 ppmv? What is the mass of CO₂ in the atmosphere now?

Problem 1.3 Estimate the time for all molecules to escape the Earth's atmosphere.

Problem 1.4 How long does sunlight take to travel from the surface of the Sun to the surface of the Earth?

Problem 1.5 What would be the thickness of the atmosphere if it were compressed so that it was entirely at standard temperature and pressure? What is the respective contribution to this thickness of atmosphere oxygen and ozone?

Problem 1.6 Starting from the value of the solar constant calculate the area on the surface of the Sun that emits radiation with the same power as a 100 MW gas turbine power plant?

Problem 1.7 Calculate the energy received by the Earth in one day and so estimate how many cups of tea that could be prepared with this energy. Assume that to make one cup of tea 1/4 l of water needs to be heated from 20 to 100 °C.

Problem 1.8 The worldwide energy consumption of energy is estimated in 2008 at 1.3×10^{18} J day⁻¹. If this grows at a compound rate of 1.6 % per year, in what year will the use of energy equate to all available solar energy incident on the Earth?

Additional Reading