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Characteristics of the atmosphere

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The atmosphere (and ocean) are thin films of fluid on the spherical Earth under the influence of gravity, Earth’s rotation, and differential heating by solar radiation. In this chapter we describe the chemical composition of the atmosphere and key physical properties of air. We discuss the equation of state of air (the connection between pressure, density, and temperature) and key properties of moist air. In particular, we will learn that warm air is generally more moist than cold air, a fact that has enormous implications for the climate of the planet.

1.1. GEOMETRY

The Earth is an almost perfect sphere with mean radius $a = 6370$ km, a surface gravity field $g = 9.81 \text{ ms}^{-2}$, and a rotation period of $\tau_{\text{Earth}} = 24$ h, equivalent to an angular velocity $\Omega = 2\pi / \tau_{\text{Earth}} = 7.27 \times 10^{-5} \text{ s}^{-1}$ (see Table 1.1).

The atmosphere which envelops the Earth is very thin; it fades rapidly away

TABLE 1.1. Some parameters of Earth.

| | | |
|------------------------------|------------|--------------------------------------|
| Earth’s rotation rate | Ω | $7.27 \times 10^{-5} \text{ s}^{-1}$ |
| Surface gravity | g | 9.81 ms^{-2} |
| Earth’s mean radius | a | $6.37 \times 10^6 \text{ m}$ |
| Surface area of Earth | $4\pi a^2$ | $5.09 \times 10^{14} \text{ m}^2$ |
| Area of Earth’s disc | πa^2 | $1.27 \times 10^{14} \text{ m}^2$ |

with altitude and does not have a definite top. As we shall see in Chapter 3, its density decreases approximately exponentially away from the surface, falling by a factor of e about every 7 km. About 80% of the mass of the atmosphere is contained below 10 km altitude. Fig. 1.1 shows, to scale, a shell of thickness 10 km on a sphere of radius 6370 km.

The thinness of the atmosphere allows us to make some simplifications. For one thing, we can take g to be constant (the fractional decrease in gravity from the Earth’s surface to 10 km altitude is about 10^{-4} and so is negligible in most applications). We will see that we can often neglect the Earth’s

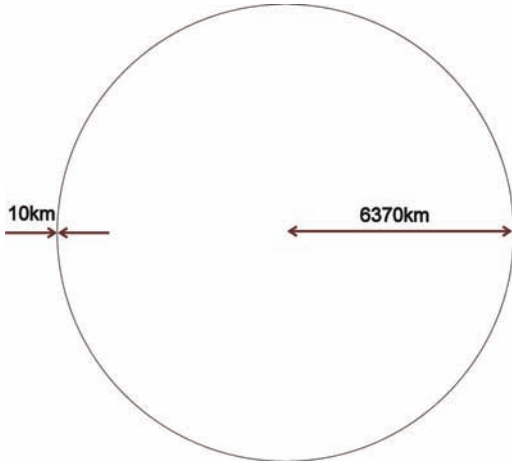


FIGURE 1.1. The thinness (to scale) of a shell of 10 km thickness on the Earth of radius 6370 km.

curvature and assume planar geometry. But there are of course (as we will also see) some aspects of spherical geometry that cannot be neglected.

Land covers about 30% of the surface of the Earth and, at the present time in Earth's history, about 70% of Earth's land is in the northern hemisphere (see Fig. 9.1). As Fig. 1.2 illustrates, the height of mountains rarely exceeds 2 km and so is a relatively small fraction of the vertical decay scale of the atmosphere. Thus, unlike the ocean, the atmosphere is not confined to basins. As it flows around the globe, air is deflected by topography but never completely blocked.

1.2. CHEMICAL COMPOSITION OF THE ATMOSPHERE

Air is a mixture of “permanent” gases (N_2 , O_2) in constant ratio together with minor constituents (see Table 1.2). The molecular weight of the mixture that makes up air is 28.97, so that 22.4 liters of air at standard temperature and pressure (STP; $T = 273\text{ K}$ and $p = 1013\text{ hPa}$) weighs 28.97 g.

The composition of air is a direct consequence of the supply of elements from the Earth's interior and the presence of life on the surface. Photosynthesis by plants makes O_2 ; nitrogenous compounds from living organisms are returned to the atmosphere as N_2 from metabolism. Lightning converts N_2 into usable molecules for life. Two of the most important minor constituents are H_2O and CO_2 ; they play a central role in controlling the temperature of the Earth's surface (see Chapter 2) and sustaining life (living material is primarily composed of C, H and O).

Atmospheric water vapor is present in variable amounts (typically 0.5% by volume). It is primarily the result of evaporation from the ocean's surface. Unlike N_2 and O_2 , water vapor—and to a lesser degree CO_2 —is of great importance in radiative transfer (the passage of radiation through the atmosphere), because it strongly absorbs and emits in the infrared, the region of the spectrum (wavelengths about $10\ \mu\text{m}$)

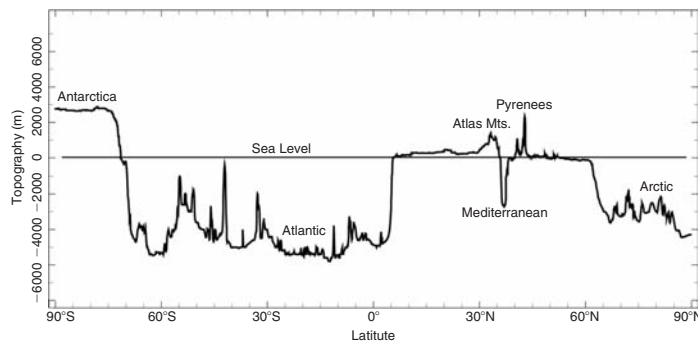


FIGURE 1.2. A north-south section of topography relative to sea level (in meters) along the Greenwich meridian (0° longitude) cutting through Fig. 9.1. Antarctica is over 2 km high, whereas the Arctic Ocean and the south Atlantic basin are about 5 km deep. Note how smooth the relief of the land is compared to that of the ocean floor.

TABLE 1.2. The most important atmospheric constituents. The chlorofluorocarbons (CFCs) CCl_2F_2 and CCl_3F are also known as CFC-12 and CFC-11, respectively. [N.B. (ppm, ppb, ppt) = parts per (million, billion, trillion)] The concentrations of some constituents are increasing systematically because of human activity. For example, the CO_2 concentration of 380 ppm was measured in 2004 (see Fig. 1.3); CFCs are now decreasing in concentration following restrictions on their production.

| Chemical species | Molecular weight (g mol^{-1}) | Proportion by volume | Chemical species | Molecular weight | Proportion by volume |
|------------------------------|--|----------------------|--------------------------|------------------|----------------------|
| N_2 | 28.01 | 78% | O_3 | 48.00 | ~500 ppb |
| O_2 | 32.00 | 21% | N_2O | 44.01 | 310 ppb |
| Ar | 39.95 | 0.93% | CO | 28.01 | 120 ppb |
| H_2O (vapor) | 18.02 | ~0.5% | NH_3 | 17.03 | ~100 ppb |
| CO_2 | 44.01 | 380 ppm | NO_2 | 46.00 | ~1 ppb |
| Ne | 20.18 | 19 ppm | CCl_2F_2 | 120.91 | 480 ppt |
| He | 4.00 | 5.2 ppm | CCl_3F | 137.37 | 280 ppt |
| CH_4 | 16.04 | 1.7 ppm | SO_2 | 64.06 | ~200 ppt |
| Kr | 83.8 | 1.1 ppm | H_2S | 34.08 | ~200 ppt |
| H_2 | 2.02 | ~500 ppb | AIR | 28.97 | |

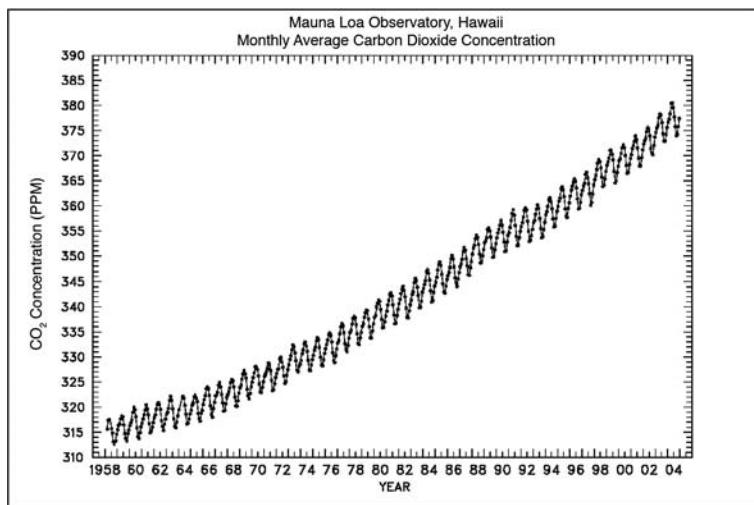


FIGURE 1.3. Atmospheric CO_2 concentrations observed at Mauna Loa, Hawaii (19.5°N , 155.6°W). Note the seasonal cycle superimposed on the long-term trend. The trend is due to anthropogenic emissions. The seasonal cycle is thought to be driven by the terrestrial biosphere: net consumption of CO_2 by biomass in the summertime (due to abundance of light and heat) and net respiration in wintertime.

at which Earth radiates energy back out to space (see Chapter 2). The CO_2 concentration in the atmosphere is controlled by such processes as photosynthesis and respiration, exchange between the ocean and the atmosphere, and, in the modern world, anthropogenic activities.

It is important to note that the proportion of some constituents (especially chemically or physically active species, such as H_2O) is variable in space and time. Moreover, several crucially important constituents (e.g., H_2O , CO_2 , O_3) are present in very small concentrations, and so are

sensitive to anthropogenic activity. For example, Fig. 1.3 shows the CO₂ concentration measured at the Hawaiian island of Mauna Loa. Atmospheric CO₂ concentration has risen from 315 ppm to 380 ppm over the past 50 years. Preindustrial levels of CO₂ were around 280 ppm; it is thought that over the course of Earth's history, CO₂ levels have greatly fluctuated. Atmospheric CO₂ concentrations were probably markedly different in warm as opposed to cold periods of Earth's climate. For example, at the last glacial maximum 20,000 years ago, CO₂ concentrations are thought to have been around 180 ppm. Reconstructions of atmospheric CO₂ levels over geologic time suggest that CO₂ concentrations were perhaps five times the present level 220 million years ago, and perhaps 20 times today's concentration between 450 and 550 million years ago, as we shall see in Section 12.3 and Fig. 12.14. If the curve shown in Fig. 1.3 continues its exponential rise, then by the end of the century, CO₂ concentrations will have reached levels—perhaps 600 ppm—not seen since 30 million years ago, a period of great warmth in Earth history.

1.3. PHYSICAL PROPERTIES OF AIR

Some important numbers for Earth's atmosphere are given in Table 1.3. Global mean surface pressure is 1.013×10^5 Pa = 1013 hPa. (The hecto Pascal is now the official unit of atmospheric pressure [1 hPa = 10^2 Pa], although the terminology "millibar" [1 mbar = 1 hPa] is still in common use and will also be used here.)

The global mean density of air at the surface is 1.235 kg m^{-3} . At this average density we require a column of air of about 7–8 km high to exert pressure equivalent to 1 atmosphere.

Throughout the region of our focus (the lowest 50 km of the atmosphere), the mean free path of atmospheric molecules is so short and molecular collisions so frequent that the atmosphere can be regarded as a *continuum fluid in local thermodynamic equilibrium* (LTE), and so the "blackbody" ideas to be developed in Chapter 2 are applicable. (These statements break down at sufficiently high altitude, $\gtrsim 80$ km, where the density becomes very low.)

1.3.1. Dry air

If in LTE, the atmosphere accurately obeys the perfect gas law,¹ then

$$p = \rho \frac{R_g}{m_a} T = \rho RT, \quad (1-1)$$

where p is pressure, ρ , density, T , absolute temperature (measured in Kelvin), R_g , the universal gas constant

$$R_g = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1},$$

the gas constant for dry air

$$R = \frac{R_g}{m_a} = 287 \text{ J kg}^{-1} \text{ K}^{-1},$$

and the mean molecular weight of dry air (see Table 1.2, last entry), $m_a = 28.97$ ($\times 10^{-3} \text{ kg mol}^{-1}$).



¹ Robert Boyle (1627–1691) made important contributions to physics and chemistry and is best known for Boyle's law, describing an ideal gas. With the help of Robert Hooke, he showed among other things that sound did not travel in a vacuum, proved that flame required air, and investigated the elastic properties of air.

TABLE 1.3. Some atmospheric numbers.

| | | |
|---------------------------------|----------|----------------------------|
| Atmospheric mass | M_a | 5.26×10^{18} kg |
| Global mean surface pressure | p_s | 1.013×10^5 Pa |
| Global mean surface temperature | T_s | 288 K |
| Global mean surface density | ρ_s | 1.235 kg m ⁻³ |

TABLE 1.4. Properties of dry air at STP.

| | | |
|------------------------------------|----------------------------|--|
| Specific heat at constant pressure | c_p | 1005 J kg ⁻¹ K ⁻¹ |
| Specific heat at constant volume | c_v | 718 J kg ⁻¹ K ⁻¹ |
| Ratio of specific heats | γ | 1.40 |
| Density at 273K, 1013mbar | ρ_0 | 1.293 kg m ⁻³ |
| Viscosity at STP | μ | 1.73×10^{-5} kg m ⁻¹ s ⁻¹ |
| Kinematic viscosity at STP | $\nu = \frac{\mu}{\rho_0}$ | 1.34×10^{-5} m ² s ⁻¹ |
| Thermal conductivity at STP | K | 2.40×10^{-2} W m ⁻² K ⁻¹ |
| Gas constant for dry air | R | 287.05 J kg ⁻¹ K ⁻¹ |

From Eq. 1-1 we see that it is only necessary to know any two of p , T , and ρ to specify the thermodynamic state of dry air completely. Thus at STP, Eq. 1-1 yields a density $\rho_0 = 1.293$ kg m⁻³, as entered in Table 1.4, where some of the important physical parameters for dry air are listed.

Note that air, as distinct from liquids, is compressible (if p increases at constant T , ρ increases) and has a relatively large coefficient of thermal expansion (if T increases at constant p , ρ decreases). As we shall see, these properties have important consequences.

1.3.2. Moist air

Air is a mixture of gases, and the ideal gas law can be applied to the individual components. Thus if ρ_v and ρ_d are, respectively, the masses of water vapor and of dry air per unit volume (i.e., the partial densities) then the equations for the partial pressures (that is the pressure each component would exert at the same temperature as the mixture, if it

alone occupied the volume that the mixture occupies) are:

$$e = \rho_v R_v T; \quad (1-2)$$

$$p_d = \rho_d R_d T, \quad (1-3)$$

where e is the partial pressure of water vapor, p_d is the partial pressure of dry air, R_v is the gas constant for water vapor, and R_d is the gas constant for dry air. By Dalton's law of partial pressures, the pressure of the mixture, p , is given by:

$$p = p_d + e.$$

In practice, because the amount of water vapor in the air is so small (see Table 1.2), we can assume that $p_d \gg e$, and so $p \simeq p_d$.

Now imagine that the air is in a box at temperature T , and suppose that the floor of the box is covered with water, as shown in Fig. 1.4. At equilibrium, the rate of evaporation will equal the rate of condensation, and the air is said to be *saturated* with water vapor. If we looked into the box, we would see a mist.² At this point, e has reached

² This is true provided there are plenty of *condensation nuclei*—tiny particles—around to ensure condensation takes place (see GFD Lab I).

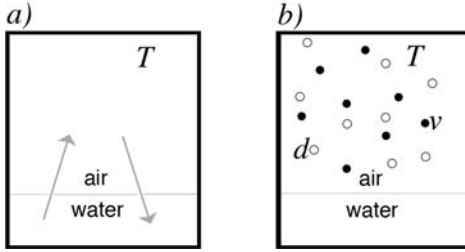


FIGURE 1.4. Air over water in a box at temperature T . At equilibrium the rate of evaporation equals the rate of condensation. The air is saturated with water vapor, and the pressure exerted by the vapor is e_s , the saturated vapor pressure. On the right we show the mixture comprising dry 'd' and vapor 'v' components.

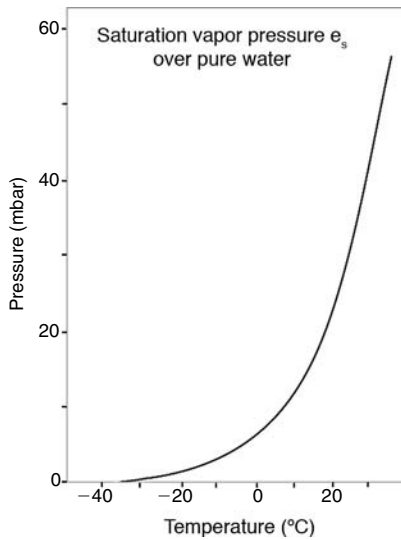


FIGURE 1.5. Saturation vapor pressure e_s (in mbar) as a function of T in $^{\circ}\text{C}$ (solid curve). From Wallace & Hobbs, (2006).

the saturated vapor pressure, e_s . In fact, saturation occurs whenever the partial pressure of water exceeds the saturation vapor pressure e_s . As shown in Fig. 1.5, e_s is a function only of temperature and increases very rapidly with T . To a good approximation at typical atmospheric temperatures, $e_s(T)$ is given by:

$$e_s = Ae^{\beta T} \quad (1-4)$$

where $A = 6.11 \text{ hPa}$ and $\beta = 0.067^{\circ}\text{C}^{-1}$ are constants and T is in $^{\circ}\text{C}$, a simplified statement of the Clausius-Clapeyron relationship. The saturated vapor pressure

increases *exponentially* with temperature, a property which is enormously important for the climate of the planet.

From Eq. 1-4 (see also Fig. 1.5) we note that $e_s = 16.7 \text{ hPa}$ at $T = 15^{\circ}\text{C}$. From Table 1.2 we deduce that $R_v = R_g/m_v = 461.39 \text{ J kg}^{-1} \text{ K}^{-1}$ and so, using Eq. 1-2, at saturation $\rho_v = 0.0126 \text{ kg m}^{-3}$. This is the maximum amount of water vapor per unit volume that can be held by the atmosphere at this temperature.

The $e_s(T)$ curve shown in Fig. 1.5 has the following very important climatic consequences:

- The moisture content of the atmosphere decays rapidly with height, because T decreases with height, from the Earth's surface up to 10 km or so. In Chapter 3 we will see that at the surface the mean temperature is about 15°C , but falls to about -50°C at a height of 10 km (see Fig. 3.1). We see from Fig. 1.5 that $e_s \rightarrow 0$ at this temperature. Thus most of the atmosphere's water vapor is located in the lowest few km. Moreover, its horizontal distribution is very inhomogeneous, with much more vapor in the warm tropics than in cooler higher latitudes. As will be discussed in Chapter 2, this is crucially important in the transfer of radiation through the atmosphere.
- Air in the tropics tends to be much more moist than air over the poles, simply because it is warmer in the tropics than in polar latitudes; see Section 5.3.
- Precipitation occurs when moist air is cooled by convection, and causes H_2O concentrations to be driven back to their value at saturation at a given T ; see Section 4.5.
- In cold periods of Earth's history, such as the last glacial maximum 20,000 years ago, the atmosphere was probably much more arid than in warmer periods. Conversely, warm climates tend to be much more moist; see Section 12.3.

1.3.3. GFD Lab I: Cloud formation on adiabatic expansion

The sensitive dependence of saturation vapor pressure on temperature can be readily demonstrated by taking a carboy and pouring warm water into it to a depth of a few cm, as shown in Fig. 1.6. We leave it for a few minutes to allow the air above the warm water to become saturated with water vapor. We rapidly reduce the pressure in the bottle by sucking at the top of the carboy. You can use your lungs to suck the air out, or a vacuum cleaner. One might expect that the rapid adiabatic expansion of the air would reduce its temperature and hence lower the saturated vapor pressure sufficiently that the vapor would condense to form water droplets, a “cloud in the jar.” To one’s disappointment, this does not happen.

The process of condensation of vapor to form a water droplet requires condensation



FIGURE 1.6. Warm water is poured into a carboy to a depth of 10 cm or so, as shown on the left. We leave it for a few minutes and throw in a lighted match to provide condensation nuclei. We rapidly reduce the pressure in the bottle by sucking at the top. The adiabatic expansion of the air reduces its temperature and hence the saturated vapor pressure, causing the vapor to condense and form water droplets, as shown on the right.

nuclei, which are small particles on which the vapor can condense. We can introduce such particles into the carboy by dropping in a lighted match and repeating the experiment. Now on decompression we do indeed observe a thick cloud forming which disappears again when the pressure returns to normal, as shown in Fig. 1.6 (right).

In the bottom kilometer or so of the atmosphere there are almost always abundant condensation nuclei, because of the presence of sulfate aerosols, dust, smoke from fires, and ocean salt. Clouds consist of liquid water droplets (or ice particles) that are formed by condensation of water vapor onto these particles when T falls below the dew point, which is the temperature to which air must be cooled (at constant pressure and constant water vapor content) to reach saturation.

A common atmospheric example of the phenomenon studied in our bottle is the formation of fog due to radiational cooling of a shallow, moist layer of air near the surface. On clear, calm nights, cooling due to radiation can drop the temperature to the dew point and cause fog formation, as shown in the photograph of early morning mist on a New England lake (Fig. 1.7).

The sonic boom pictured in Fig. 1.8 is a particularly spectacular consequence of the sensitive dependence of e_s on T : just as in our bottle, condensation of water is caused by the rapid expansion and subsequent adiabatic cooling of air parcels induced by the shock waves resulting from the jet going through the sound barrier.

1.4. PROBLEMS

1. Given that the acceleration due to gravity decays with height from the centre of the Earth following an inverse square law, what is the percentage change in g from the Earth’s surface to an altitude of 100 km? (See also Problem 6 of Chapter 3.)



FIGURE 1.7. Dawn mist rising from Basin Brook Reservoir, White Mountain National Forest, July 25, 2004. Photograph: Russell Windman.



FIGURE 1.8. A photograph of the sound barrier being broken by a US Navy jet as it crosses the Pacific Ocean at the speed of sound just 75 feet above the ocean. Condensation of water is caused by the rapid expansion and subsequent adiabatic cooling of air parcels induced by the shock (expansion/compression) waves caused by the plane outrunning the sound waves in front of it. Photograph was taken by John Gay from the top of an aircraft carrier. The photo won First Prize in the science and technology division of the World Press Photo 2000 contest.

2. Compute the mean pressure at the Earth's surface given the total mass of the atmosphere, M_a (Table 1.3), the

acceleration due to gravity, g , and the radius of the Earth, a (Table 1.1).

3. Express your answer to Problem 2 in terms of the number of apples per square meter required to exert the same pressure. You may assume that a typical apple weighs 0.2 kg. If the average density of air is 5 apples per m^3 (in apple units), calculate how high the apples would have to be stacked at this density to exert a surface pressure equal to 1000 hPa. Compare your estimate to the scale height, H , given by Eq. 3.6 in Section 3.3.
4. Using (i) Eq. 1-4, which relates the saturation vapor pressure of H_2O to temperature T , and (ii) the equation of state of water vapor, $e = \rho_v R_v T$ (see discussion in Section 1.3.2), compute the maximum amount of water vapor per unit volume that air can hold at the surface, where $T_s = 288 \text{ K}$, and at a height of 10 km where (from Fig. 3.1) $T_{10 \text{ km}} = 220 \text{ K}$. Express your answer in kg m^{-3} . What are the implications of your results for the distribution of water vapor in the atmosphere?