

I The Structure of Planetary Atmospheres

Interactions between the atmosphere, ocean, solid planet, biosphere, and space are responsible for the evolution of the Earth's atmosphere. Other planets have simpler global systems that merely consist of an atmosphere surrounding a rocky surface without a liquid ocean, or, in the case of gas giants, atmospheres that thicken inwards towards higher-density layers and cores. In the first five chapters, we describe general physical and chemical principles that apply to all or most atmospheres. There are many excellent introductory texts on atmospheric physics and chemistry, e.g., Walker (1977), Hartmann (1994), Houghton (2002), Hobbs (2000), Wallace and Hobbs (2006), and Andrews (2010). These books focus on Earth's atmosphere. Our approach here is to discuss the fundamentals of atmospheres using examples from a variety of planetary atmospheres. Thus, Chapters 1–5 are an introduction to the concepts of planetary atmospheres, often with a view to how the basics apply to issues of atmospheric evolution. We refer back to these fundamentals in subsequent chapters.

Some other books also discuss planetary atmospheres. Ingersoll (2013) is an excellent readable primer. Chamberlain and Hunten (1987) has a particular emphasis on upper atmospheres, Yung and Demore (1999) focus on photochemistry, Pierrehumbert (2010) has broad insightful coverage with an emphasis on radiation, while Sanchez-Lavega (2010) is a valuable general reference text for planetary atmospheres.

The key uniqueness of this book is that we emphasize atmospheric evolution, which, needless to say, we consider the most interesting aspect of planetary atmospheres!

1.1 Vertical Structure of Atmospheres

1.1.1 Atmospheric Temperature Structure: An Overview

A planet's atmosphere, through its composition and greenhouse effect, controls climate, which is weather that

has been averaged over some period of time such as a month, season, year, or longer. The mean surface temperature is a key parameter of importance for habitability. If the surface temperature is not suitable for liquid water, life as we know it will probably not exist there, except possibly hidden in the subsurface.

The same principle applies to extreme places on the Earth. For example, the coldest place on Earth's surface is Vostok, Antarctica, with temperatures ranging from $-14\text{ }^{\circ}\text{C}$ (259 K) to a record extreme of $-89.2\text{ }^{\circ}\text{C}$ (184 K) (Turner *et al.*, 2009). Consequently, Vostok is frozen and lifeless. In part, the coldness of Vostok arises from its height of 3450 m above sea level. How the air temperature varies with altitude is one of the most basic features of planetary atmospheres, the *atmospheric structure*, which is our starting point for this book.

The Earth's atmosphere provides the nomenclature for describing vertical regions of planetary atmospheres. Terminology for Earth's atmospheric layers was developed in the early 1900s (Lindemann and Dobson, 1923; Martyn and Pulley, 1936). Because of this historical origin, the same terminology only approximately applies to other planetary atmospheres.

Earth's atmosphere consists of five layers of increasing altitude (Fig. 1.1). Going upwards, new layers begin where there is a temperature inflection.

(1) The *troposphere* goes from the surface to the *tropopause*, which lies at a height of 11 km (0.2 bar) in the US Standard Atmosphere but varies in altitude from ~ 8 km at the poles to ~ 17 km in the tropics. The global average tropopause pressure is 0.16 bar (Sausen and Santer, 2003), varying 0.1 to 0.3 bar from tropics to pole (Hoinka, 1998). *Tropos* is ancient Greek for the 'turning' of convection and *pause* is Greek for "stop."

(2) The *stratosphere* (from Greek *stratus* for "layered") goes from the tropopause to the *stratopause* at ~ 50 km altitude, where the air pressure is about 100 Pa (1 mbar).

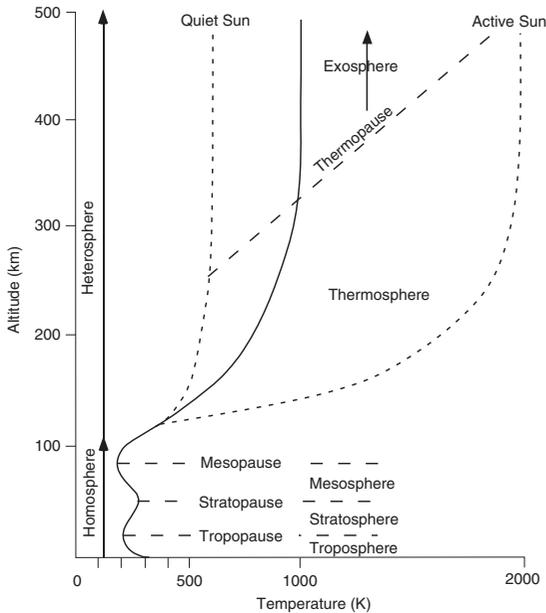


Figure 1.1 The nomenclature for vertical regions of the Earth's atmosphere, shown schematically.

(3) The *mesosphere* extends from the stratopause to the *mesopause* at ~ 85 km altitude, where the air pressure is about 1–0.1 Pa (0.01–0.001 mbar)

(4) The *thermosphere* goes from the mesopause to the *thermopause* at about ~ 250 – 500 km depending on varying ultraviolet from the Sun. Above the thermopause, the atmosphere becomes isothermal.

(5) The *exosphere* lies above the thermopause and joins interplanetary space. Unlike the other layers that are defined by the temperature profile, the exosphere is where collisions between molecules are so infrequent that they can usually be neglected. The *exobase* is the bottom of the exosphere and nearly coincides with the thermopause.

The terminology developed for Earth's lower atmosphere depends upon the presence of the ozone layer in the stratosphere. Ozone absorbs ultraviolet (UV) sunlight, which causes temperature to increase with height above the troposphere and defines the stratosphere. Other planets, such as Mars, do not have UV absorbers to induce a stratosphere, so the geocentric nomenclature for atmospheric layers breaks down (Fig. 1.2). However, we generally find analogs in other planetary atmospheres for a troposphere, mesosphere, thermosphere, and exosphere. On Titan and the giant planets, absorbers of shortwave sunlight (UV, visible, and near-infrared) produce stratospheres.

Convection is the key process in tropospheres. On Earth, radiation heats the surface, so air is warmed near

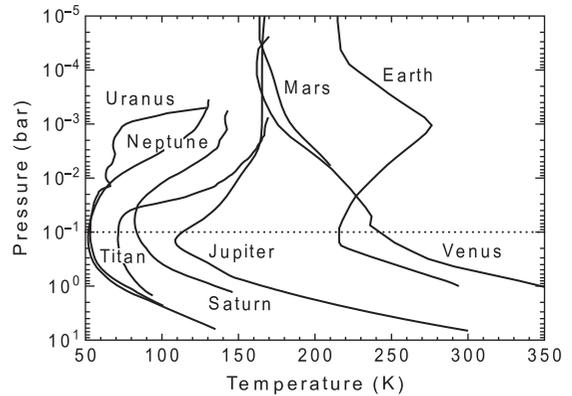


Figure 1.2 Thermal structure of the atmospheres of various planets of the Solar System. The dashed line at 0.1 allows you to see the feature of a common tropopause near ~ 0.1 bar for the thick atmospheres, despite the differences in atmospheric composition. See Robinson and Catling (2014) for sources of data.

the ground and lifted upwards by buoyancy. Consequently, air parcels convect to places of lower pressure where they expand and cool. The net effect of lofted parcels that cool, and sinking ones that warm, is to maintain an annual average temperature decrease from Earth's warm surface to the cold upper troposphere of about 6 K km^{-1} when globally averaged (see Sec. 1.1.3).

Earth's troposphere contains $\sim 80\%$ of the mass of the atmosphere and this mass, along with the composition of the air, renders the troposphere fairly opaque to thermal-infrared (IR) radiation emanating from the planet's surface. In general, somewhat below the tropopause, atmospheres become semi-transparent to thermal-IR radiation. Consequently, transfer of energy by radiation in the upper troposphere replaces convection as the means of upward energy transfer at a *radiative-convective* boundary. Efficient emission of thermal-IR radiation to space accounts for the temperature minimum at the tropopauses of many planetary atmospheres, which occurs above the radiative-convective boundary for atmospheres with stratospheres.

For planets with thick atmospheres, the tropopause temperature minimum occurs where the air has thinned to roughly ~ 0.1 bar pressure (Fig. 1.2). Remarkably, this rule applies to Earth, Titan, Jupiter, Saturn, Uranus, and Neptune, and the mid-to-high latitudes of Venus (Tellmann *et al.*, 2009), despite vast differences in atmospheric composition. This commonality occurs because the broadband opaqueness to thermal-IR in upper tropospheres is pressure-dependent with similar scaling – varying approximately with the square of the pressure – despite the differences in atmospheric composition. Since all these atmospheres have strong and roughly similar

opaqueness (within the same order of magnitude) to thermal-IR at moderately deep pressures, such as 1 bar, the weak square-root dependence of pressure on the upwardly decreasing opacity ensures that the tropopause minima are all near 0.1 bar, within a factor of 2 or so (Robinson and Catling, 2014). Thus, a “0.1 bar tropopause minimum rule” could apply to exoplanet atmospheres, provided that they have temperature minima at the base of stratospheres. Of course, such a rule can’t apply to atmospheres without stratospheric absorbers and tropopause temperature minima.

In Earth’s stratosphere, ozone (O_3) warms the air by absorbing solar UV over a wavelength range of about 200–300 nm. Stratospheric warming also occurs on the giant planets and Titan because aerosols (fine, suspended particles) and methane absorb in the UV, visible, and near-IR. Warming creates an *inversion* – a vertical region of the atmosphere where temperature increases with height (Fig. 1.2). Cooler air is inhibited from rising into warmer air, so the air becomes stratified and mixes slowly in the vertical. Mars and Venus, which have atmospheres containing 96% CO_2 , do not have strong shortwave absorbers above their tropospheres and so lack inversions in the global average. However, an inversion is not required to prevent convection. We will see later that convection effectively ceases when the rate at which temperature decreases with altitude becomes smaller than a critical value (Sec. 1.1.3). For example, the atmosphere on the early Earth, which lacked oxygen and an ozone layer, would still have had relatively slow mixing above a troposphere, with a stratosphere of more stable air.

The terrestrial stratosphere is very dry. Atmospheric motions control the entry of tropospheric water vapor into the stratosphere, and only ascending air in the tropics can break through into the stably stratified stratosphere. The tropical tropopause is the coldest part of the troposphere and freezes out most of the water that passes through it. This tropical tropopause “*cold trap*” limits stratospheric water vapor to about 3–4 *parts per million by volume* (ppmv), meaning that water makes up 3–4 molecules out of every million air molecules.

Earth’s mesosphere has the lowest air temperature. Here ozone concentrations have declined while CO_2 still radiates to space efficiently. The mesopause forms the lower boundary of the *thermosphere* and generally occurs at or a little below the ~ 0.1 Pa pressure level in all planetary atmospheres in the Solar System. Mesopauses are extremely cold because the atmospheric density becomes sufficiently low around this altitude ($< 10^{14}$ molecules cm^{-3}) that energy-exchanging collisions between molecules become less frequent than emission of photons.

Consequently, a molecule excited by absorption of a photon or a rare collision loses internal energy by radiation rather than kinetic energy through collisions. The altitude where this happens is the level of *radiative relaxation* (Curtis and Goody, 1956; López-Puertas and Taylor, 2001).

Above the mesopause, Earth’s thermosphere is extremely thin (e.g., $< 10^{12}$ molecules cm^{-3} above 120 km, compared to $\sim 10^{19}$ cm^{-3} at the surface) and responds rapidly to variations in solar radiation shorter than ~ 100 nm in wavelength – the extreme ultraviolet (EUV). Daily temperature changes are very large here. Similar EUV absorption occurs high up in all planetary atmospheres, where EUV, x-rays, and chemical reactions break up molecules into atoms. The mean free path (which is inversely proportional to density) becomes so big that the combination of a continuous flux of ionizing radiation and infrequent collision between ions and electrons produces an *ionosphere* – on Earth, a layer of electrons and ions from the mesosphere into the exosphere.

The rate of heating of the thermosphere is about one millionth that of Earth’s surface but the average temperature is ~ 1000 K at 250 km altitude versus 288 K at the Earth’s surface (Fig. 1.1). Temperature measures the average kinetic energy or velocity of atoms or molecules and in the thermosphere the high energy of UV photons absorbed is converted to kinetic energy. Atoms and ions cannot vibrate or rotate and thus are not good radiators in the infrared, unlike the molecules of the lower atmosphere. So kinetic energy generated by absorption of UV or collisions with hot (i.e. fast-moving) electrons cannot be transferred to molecular vibrations. Consequently, the high thermospheric temperature reflects the inefficiency of removing heat. Energy must be removed somehow, however, and this is achieved by conduction when atoms and ions infrequently collide and transfer heat downwards from the hot thermosphere to the cold mesopause.

Atmospheric composition makes a large difference to the temperature of a thermosphere. Because the atmospheres of Venus and Mars have much more CO_2 (96%) than Earth’s atmosphere (0.04%), radiative cooling of their upper atmosphere is more pronounced. Despite heating from EUV, the upper atmospheres are relatively cold: ~ 270 K for Mars and ~ 250 K for Venus. To explain Venus’ cold thermosphere despite its location much closer to the Sun, we must also consider the effect of photochemical reactions, which are described in Ch. 3.

At the exobase, collisions are so infrequent that energetic atoms can escape into space. Today, only H and He escape from Earth significantly. The other molecules and atoms are sufficiently massive that they are bound by

Earth's gravity and only a negligible fraction of them ever attain escape velocity. However, fast escape from past, present and future atmospheres is extremely important in understanding the evolution of planetary atmospheres in our own Solar System and those of exoplanets (Ch. 5).

In Fig. 1.1, we also divide the Earth's atmosphere into two basic compositional layers, a *homosphere* below ~ 100 km altitude, where the bulk constituents of the atmosphere are homogeneously mixed, and a *heterosphere* above this level. This nomenclature is based on vertical mixing rather than on temperature. The air in the heterosphere is sufficiently thin that molecular diffusion becomes important compared to mixing by turbulence or large-scale winds. In this diffusive regime, molecules separate in altitude according to mass. Gravity, of course, exerts the same acceleration on heavy objects, or atoms, as it does on light ones, as proved by Galileo. But pressure increases downward in the gravitational field, and lighter atoms tend to diffuse toward lower pressure, so the net effect is that in the heterosphere the abundance of heavy species decreases more rapidly with altitude than light ones.

As a result of diffusive separation, atomic oxygen becomes the most abundant constituent between ~ 250 – 1000 km altitude, helium becomes the most abundant species between ~ 1000 – 2500 km, and atomic hydrogen dominates above that. The tendency for species to separate diffusively according to mass exists at all altitudes, but in the homosphere the timescale for diffusive separation is longer than the timescale of turbulent mixing, so the latter dominates. For example, near-surface air has a diffusive separation timescale $\sim 10^5$ years, compared to mixing by weather in a few days.

The diffusive timescale decreases exponentially with altitude as the mean free path increases, and the *homopause* is the transition from turbulent to diffusive mixing, i.e., on Earth at ~ 100 km height,

diffusive separation time = mixing time

Consequently, above the homopause, where diffusive separation is faster than mixing, concentrations of O, H₂, and He increase relative to CO₂, N₂, O₂, and Ar, and the mean molar mass of air decreases.

Diffusive separation occurs in all planetary atmospheres at low pressure. It can be measured by monitoring the distribution of some relatively heavy gas and finding where it drops off relative to lighter gases. Typically, diffusive separation begins to occur within a few orders of magnitude of 0.01 Pa (or 0.1 μ bar), as shown in Table 1.1, noting that characteristic motions of each atmosphere are influential in controlling the homopause level (Leovy, 1982b).

1.1.2 Atmospheric Composition and Mass

The vertical structure of atmospheric pressure and density determine where physical and chemical processes take place by affecting the vertical distribution of thermal radiation, which emanates from the planet's surface, and incoming sunlight through wavelength absorption and scattering. The three-dimensional distribution of temperature determines the distribution of pressure, which drives an atmosphere's circulation or wind system. To connect distributions of pressure, temperature, and density, we use two equations: (1) an *equation of state* that relates the three variables, and (2) a *hydrostatic equation* that links pressure to the mass per unit area of overlying atmosphere. The latter equation is, by definition, always approximate, as no atmosphere is ever truly without motion in the vertical direction. But it is an excellent approximation in the lower atmospheres of all known planets and in the upper atmospheres of most of them. We now describe these two fundamental equations.

Table 1.1 Homopause levels. (Sources: Atreya *et al.* (1991), p. 145; Atreya *et al.* (1999).)

Planet	Altitude (km)	Pressure (μ bar)	Number density (molecules cm ⁻³)
Venus	130–135	0.02	7.5×10^{11}
Earth	~ 100	0.3	10^{13}
Mars	~ 130	0.002	10^{10}
Jupiter	~ 385 above 1 bar level	1	1.4×10^{13}
Saturn	~ 1140 above 1 bar level	0.005	1.2×10^{11}
Titan	800–850	~ 0.0006	2.7×10^{10}
Uranus	~ 354 – 390 above the 1 bar level	~ 20 – 40	1 – 2×10^{15}
Neptune	~ 586 – 610 above the 1 bar level	~ 0.02	10^{13}

1.1.2.1 The Ideal Gas Equation

The equation of state applicable to common atmospheric situations is the ideal gas law,

$$p = nkT = (n\bar{m})\left(\frac{k}{\bar{m}}\right)T = \rho\bar{R}T \quad (1.1)$$

Here k is Boltzmann's constant ($k = 1.381 \times 10^{-23} \text{ J K}^{-1}$), \bar{m} is the mean mass of molecules in the atmosphere, n is the number of molecules per unit volume or *number density*, $\rho = n\bar{m}$ is the mass density, and $\bar{R} = k/\bar{m}$ is the specific gas constant. The universal gas constant R ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) is related to the *specific gas constant* by $\bar{R} = R/\bar{M} = k/\bar{m}$, where we have introduced \bar{M} , the mean molar mass of the atmosphere (in kg mol^{-1}). In turn, \bar{M} is related to the mean molecular mass, \bar{m} , of individual molecules by $\bar{M} = N_A\bar{m}$, where

N_A is Avogadro's number, 6.022×10^{23} molecules mol^{-1} . The ideal gas law can be written in a variety of forms given in Box 1.1. Deep in the atmospheres of gas giant planets, the ideal gas law will fail because gas molecules are so close together that they begin to attract or repel each other so the gas is no longer "ideal." A modified equation of state is then needed.

The mean molar mass is defined as follows. Planetary atmospheres consist of mixtures of gases, which obey Dalton's Law of partial pressures. Dalton's Law says that each gas exerts a partial pressure p_i proportional to its number density n_i ,

$$p_i = n_i kT \quad (1.2)$$

The total pressure of the gas is made up of the sum of partial pressures, $p = \sum p_i$, so it follows that in eq. (1.1)

Box 1.1 Different Forms of the Ideal Gas Law

(1) One basic form of the gas law is:

$$pV = n_m RT \quad (B1)$$

Here, n_m = number of moles in volume V at pressure p and temperature T . $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ = **universal gas constant**. Equation (B1) incorporates **Boyle's Law** ($pV = \text{const.}$), **Charles' Law** ($V/T = \text{const.}$), and **Avogadro's hypothesis** ($n_m = pV/RT$, i.e., gas samples at the same p and T contain same number of moles n_m).

(2) Rather than moles, we can use the total number of molecules, N . The number of molecules per mole is Avogadro's number, N_A , so $N = n_m N_A$. The equation of state is then

$$pV = \frac{N}{N_A} RT, \quad \text{or} \quad pV = NkT \quad (B2)$$

Here we have introduced $k = R/N_A$ = Boltzmann's constant = $1.381 \times 10^{-23} \text{ J K}^{-1}$.

(3) A third way of expressing the ideal gas law is to use molecules per unit volume:

$$p = nkT \quad (B3)$$

where $n = N/V$ is the number density of molecules. (In SI units, n is in molecules m^{-3} , but frequently molecules cm^{-3} is used in atmospheric science, which requires other consistent units.)

(4) A fourth expression uses mass density rather than number density. Density = mass/volume = $\rho = M/V = N\bar{m}/V$, where \bar{m} = mean molecular mass and N = number of molecules in volume V . Hence

$$p = \frac{\rho kT}{\bar{m}} \quad (B4)$$

(5) A fifth expression (commonly used in studies of planetary atmospheres) can be derived from eq. (B4), by substituting for $k = R/N_A$ and noting that $N_A \bar{m} =$ molar mass, \bar{M} . This gives:

$$p = \frac{\rho RT}{\bar{m} N_A} \Rightarrow p = \frac{\rho RT}{\bar{M}} \Rightarrow p = \rho \bar{R}T \quad (B5)$$

Note that \bar{M} , the *mean molar mass*, is sometimes called the *mean molecular weight*. Frequently, \bar{R} is described as the *gas constant*, and should not be confused with the *universal gas constant*, R [$\text{J K}^{-1} \text{ mol}^{-1}$]. The *specific gas constant* \bar{R} is per unit mass [$\text{J K}^{-1} \text{ kg}^{-1}$] and depends on the gas composition, unlike R .

$$\rho = \sum_i m_i n_i, n = \sum_i n_i, \bar{m} = \frac{\sum_i m_i n_i}{n} \quad (1.3)$$

where m_i is the mass of the i th molecule. In Earth's lower atmosphere, the mean molar mass, \bar{M} , of dry air of $0.02897 \text{ kg mol}^{-1}$ and $\bar{R} = R/\bar{M} = 287 \text{ J K}^{-1} \text{ kg}^{-1}$.

To show how we use the equations, given Earth's global mean temperature of 288 K and sea-level pressure of $1.013 \times 10^5 \text{ Pa}$, eq. (1.1) gives the air density as 1.2 kg m^{-3} to which we can compare the air density on Mars. If the Martian atmosphere were pure CO_2 , we would expect $\bar{M} = 0.044 \text{ kg mol}^{-1}$, the molar mass of CO_2 . But the atmosphere is 96% CO_2 by volume, with

N_2 and Ar making up most of the remainder (Table 1.2), and since N_2 and Ar are lighter molecules than CO_2 , $\bar{M} = 43.5 \text{ mol}^{-1}$, which gives $\bar{R} = R/\bar{M} = 191 \text{ J kg}^{-1} \text{ K}^{-1}$. The global average barometric pressure and temperature on the surface of Mars are $\sim 610 \text{ Pa}$ and $\sim 215 \text{ K}$, respectively, so eq. (1.1) gives the average air density on the Martian surface as 0.015 kg m^{-3} , approximately 1% of that on Earth.

1.1.2.2 The Composition of Planetary Atmospheres

We express the amount of a gas in a planetary atmosphere as a *mixing ratio*, f_i , which usually means *volume mixing ratio* (Table 1.2). This is the mole fraction of a gas in a

Table 1.2 Properties of Venus, Earth, and Mars and their atmospheric compositions. Note the large disparity in the atmospheric pressures of the planets when interpreting their atmospheric composition. For example, 3.5% N_2 in the atmosphere of Venus represents 3.3 bars of N_2 (considerably more than the Earth), indicating a planet that is either more volatile-rich than the Earth or (more likely) much more efficiently outgassed. Abbreviation: ppm = parts per million by volume. (Sources: Krasnopolsky and Lefevre (2013); Lodders and Fegley (1998); Pollack (1991); Franz *et al.* (2015).)

Parameter	Venus	Earth	Mars			
Mean surface pressure (bar)	95.6 at a modal radius	1.0 at sea level	0.006			
Mean surface temperature (K)	740	288	215			
Mass relative to Earth ($5.97 \times 10^{24} \text{ kg}$)	0.815	1.0	$0.107 \approx 1/9$			
Mean radius relative to Earth (6371 km).	0.950	1.0	$0.532 \approx 1/2$			
Key gases in atmosphere (by volume)	CO_2	$96.5 \pm 0.8\%$	N_2^*	78.084%	CO_2	$95.7 \pm 1.6\%$
	N_2	$3.5 \pm 0.8\%$	O_2^*	20.946%	N_2	$2.03 \pm 0.03\%$
	SO_2^\ddagger	• $150 \pm 30 \text{ ppm}$ (22–42 km)	H_2O	0.1 ppm–4% (varies)	Ar	$2.07 \pm 0.02\%$
		• $25 \pm 150 \text{ ppm}$ (12–22 km)	Ar	9340 ppm	O_2	$0.173 \pm 0.006\%$
	Ar	$70 \pm 25 \text{ ppm}$	$\text{CO}_2^{*\S}$	• $\sim 280 \text{ ppm}$ (pre-industrial)	CO	$749 \pm 3 \text{ ppm}$
	$^{36+38}\text{Ar}$	$75 \pm 35 \text{ ppm}$		• 400 ppm (year 2015)	H_2O	$\sim 0.03\%$ (varies)
	$\text{H}_2\text{O}^\ddagger$	30–70 ppm (0–5 km)	Ne	18.18 ppm	He	10 ppm
	CO^\ddagger	• $45 \pm 10 \text{ ppm}$ (cloud top)	^4He	5.24 ppm	H_2	$15 \pm 5 \text{ ppm}$
		• $17 \pm 1 \text{ ppm}$ (12 km)	CH_4^*	1.8 ppm	Ne	2.5 ppm
	He	12 (+24/-8) ppm	Kr	1.14 ppm	Kr	0.3 ppm
	Ne	$7 \pm 3 \text{ ppm}$	H_2^*	0.55 ppm	O_3	0–80 ppb
	H_2^\ddagger	$2.5 \pm 1 \text{ ppm}$ (50–60 km)	N_2O^*	$\sim 320 \text{ ppb}$	H_2O_2	0–40 ppb
	HCl	0.4 ppm (70 km)	CO^*	125 ppb	SO_2	$< 0.3 \text{ ppb}^\ddagger$
^{84}Kr	$50 \pm 25 \text{ ppb}$					

* Under varying degrees of biological influence.

† Indicates lack of volcanic outgassing.

§ CO_2 is currently increasing by $\sim 2 \text{ ppm/yr}$ due to fossil fuel use by humans.

¶ Altitude-dependent.

mixture of gases. By Avogadro's hypothesis, the mole fraction is simply the ratio of the number of molecules N_i of a gas to the total number of molecules N . To summarize:

$$f_i = \frac{N_i}{N} = \text{number fraction} = \frac{p_i}{p} = \text{partial pressure} = \frac{V_i}{V} = \text{volume fraction} = \frac{n_i}{n} \quad (1.4)$$

The relations in eq. (1.4) follow from the ideal gas law (eq. (B3)) and Dalton's Law. Here, V_i is the volume occupied by molecules of the gas in total sample volume, V .

We can also define a *mass mixing ratio*, μ_i , which is ratio of the mass of a particular gas to the total mass of the gas mixture sample, or

$$\mu_i = \frac{N_i m_i}{N \bar{m}} = \frac{m_i p_i}{\bar{m} p} = \frac{m_i}{\bar{m}} f_i \quad (1.5)$$

Here, we have used eq. (1.4) to relate the mass mixing ratio to the volume mixing ratio.

An awkward exception to the above relationships is the way that meteorologists describe water vapor in the terrestrial atmosphere. The volume mixing ratio of H_2O is usually given in meteorology as the number of H_2O molecules expressed as a ratio with respect to the total number of air molecules in a sample *excluding* H_2O . Similarly, the mass mixing ratio of H_2O is given as the mass of H_2O with respect to the mass of air in a sample *excluding* H_2O . Fortunately, the differences are minor between these definitions and those in eqs. (1.4) and (1.5) because the H_2O amount is generally small. However, we can imagine atmospheres, for example, the *run-away greenhouse* atmosphere of early Venus, where this is not true. So, it is important to be clear about what we mean by " H_2O mixing ratio" in such cases.

What are the types of chemical composition of planetary atmospheres? Sometimes, atmospheres of Solar System bodies are grouped as follows: (i) N_2 atmospheres (Earth, Titan, Triton, and Pluto), (ii) CO_2 atmospheres (Venus and Mars), (iii) H_2 -rich giant planets, and (iv) extremely tenuous atmospheres. However, a chemically meaningful categorization for relatively thick atmospheres falls into only two broad categories: *reducing* and *oxidizing*. This classification indicates the overall chemical character of an atmosphere and the form in which elements are likely to exist, e.g., CH_4 versus CO_2 for carbon. With this scheme, Solar System atmospheres group as follows (where the values in parentheses are the surface atmospheric pressures in units of bar (1 bar = 10^5 Pa) from Lodders and Fegley (1998)).

(i) *Reducing atmospheres*: Jupiter, Saturn, Uranus, Neptune, and Titan (1.5).

(ii) *Oxidizing atmospheres*: Earth (1.0), Mars (6×10^{-3}), and Venus (95.6 at the modal radius).

Reducing atmospheres are relatively rich in reducing gases, which are typically hydrogen-bearing gases, such

as methane (CH_4), hydrogen itself (H_2), and possibly ammonia (NH_3). An atmosphere with CO would also be reducing and *hot Jupiter* exoplanets (Jupiter-like gas giants that orbit within 0.5 Astronomical Units of their parent stars) can have carbon in the form of CO rather than CH_4 in their upper atmospheres (Moses *et al.*, 2011; Sharp and Burrows, 2007). Billions of years ago, the atmospheres of the very early Earth (Ch. 10) and early Mars (Ch. 12) may also have been reducing, and so these atmospheres have probably switched places in our above classification scheme as they evolved and became oxidizing.

Oxidizing atmospheres are poor in hydrogen-bearing reducing gases and include O_2 -rich Earth's and Mars' atmosphere, which is CO_2 -rich with $\sim 0.1\%$ O_2 and only 15 ± 5 ppmv H_2 (Krasnopolsky and Feldman, 2001). Venus, as often, is a complex case. Its upper atmosphere is oxidizing, and it even has a very tenuous ozone (O_3) layer at 90–105 km altitude on the nightside (Montmessin *et al.*, 2011). However, in the hot dense Venusian atmosphere below ~ 20 km altitude, sulfur can exist in various redox states (Fegley, 2014; Krasnopolsky and Pollack, 1994) and so the air there could legitimately be described as weakly reducing. Unlike Earth and Mars, O_2 is absent on Venus with < 0.3 ppmv abundance.

One useful aspect of classifying atmospheres into reducing versus oxidizing is that the redox character indicates the possible chemistry of aerosols, which are fine particles in atmospheres. In particular, oxidizing atmospheres with sulfur gases tend to produce aerosols of sulfate at altitude (McGouldrick *et al.*, 2011). On Venus, we find clouds of sulfuric acid (H_2SO_4) and there is an analogous but very thin sulfate haze in the Earth's stratosphere at ~ 20 – 25 km altitude called the *Junge layer* (Crutzen, 1976; Robock, 2000). When early Mars was volcanically active, its atmosphere should also have had sulfate aerosols (Settle, 1979; Smith *et al.*, 2014; Tian *et al.*, 2010). The reducing atmospheres in the Solar System generate hydrocarbon aerosols, which we find on the giant planets (Irwin, 2009; Moses *et al.*, 2004; West *et al.*, 2004; West *et al.*, 2009; West *et al.*, 1991) and Titan (Ch. 14) (Krasnopolsky, 2010; Lavvas *et al.*, 2008a, b; Wilson and Atreya, 2004). Hydrocarbon aerosols were also probably present in the anoxic, weakly reducing atmosphere of the early

Earth (Pavlov *et al.*, 2001; Wolf and Toon, 2010; Zerkle *et al.*, 2012) (see Ch. 9).

Some Solar System bodies have very thin atmospheres or even *exospheres*, which are gases so rarefied that they are effectively collisionless. Tenuous atmospheres can be grouped as follows, with surface pressure given in bars in parentheses.

(i) *N₂-rich atmospheres above surfaces covered in N₂ ice* include Triton ($\sim(14\text{--}20)\times 10^{-6}$), the largest moon of Neptune, and Pluto ($\sim 15\times 10^{-6}$). These tenuous N₂-rich atmospheres (with minor CH₄) on Triton and Pluto are essentially at the vapor equilibrium with N₂ (and CH₄) ice at prevailing surface temperatures.

(ii) *O₂-rich exospheres and thin atmospheres above moons covered in water ice* include Jupiter’s moons Europa ($\sim 10^{-12}\text{--}10^{-13}$ O₂) (Smyth and Marconi, 2006), Ganymede ($\sim 10^{-12}$ O₂) (Hall *et al.*, 1998), and Callisto ($\sim 10^{-9}$ bar of O₂ with some CO₂) (Carlson, 1999; Cunningham *et al.*, 2015; Kliore *et al.*, 2002; Liang *et al.*, 2005), and Saturn’s moons Rhea ($\sim 10^{-12}$ O₂ and CO₂) (Teolis *et al.*, 2010) and Dione ($\sim 10^{-12}$ O₂) (Tokar *et al.*, 2012). The O₂ comes from the decomposition of surface water ice by radiolysis and sputtering (Johnson *et al.*, 2009). *Radiolysis* is the chemical alteration of ices by charged particles, and *sputtering* is when charged particles collide and eject atoms or molecules. The faster escape of hydrogen compared to oxygen leaves oxygen lingering behind. Charged particles come from *magnetospheres*,

a mass-mixing ratio that varies from about 0.1 ppmv in Antarctica to about 4% in wet tropical regions. Ozone is an example of a species affected by chemical reactions, so that ozone concentrations vary with altitude.

The specific gas constant \bar{R} varies if there are changes in gas concentrations. Generally, this variation is only important in atmospheres in which some species undergoes phase changes. Because of condensable gases, such as water vapor in the atmosphere of Earth, methane in the atmosphere of Titan, or ammonia in Jupiter’s atmosphere, some atmospheric literature calculations define a *virtual temperature*. This fictitious temperature has the purpose of allowing the ideal gas law to be satisfied using the gas constant for the dry gas alone. The virtual temperature T_v satisfies

$$T_v = \frac{\bar{R}}{\bar{R}_d} T = \frac{T}{[1 - (e/p)(1 - \varepsilon)]}, \text{ where } \varepsilon \equiv m_c/\bar{m}_d \quad (1.6)$$

Here, m_c is the molecular mass of the condensable gas, \bar{m}_d is the mean molecular mass for the dry gas, \bar{R}_d is the gas constant for the dry gas, e is the vapor pressure of the condensable species, and p is total pressure (e.g., see Wallace and Hobbs (2006), p. 67). If we define the *specific gas constant for the condensable species* as $R_c = R/M_c$, we can easily derive eq. (1.6). Using Dalton’s Law of partial pressures $p = p_d + e$, where p_d is the partial pressure of dry air, the ideal gas law gives the total density as:

$$\rho = \frac{(p - e)}{\bar{R}_d T} + \frac{e}{R_c T} = \left(\frac{p}{\bar{R}_d T} - \frac{e}{\bar{R}_d T} \right) + \frac{e}{R_c T} = \frac{p}{\bar{R}_d T} \left[1 - \left(\frac{e}{p} \right) (1 - \varepsilon) \right]$$

which are envelopes of ions around planets controlled by the planetary magnetic fields. The higher density of O₂ on Callisto suggests that its atmosphere is collisional rather than an exosphere (Cunningham *et al.*, 2015).

(iii) *Volcanogenic atmospheres* include SO₂ on Io ($\sim 10^{-7}\text{--}10^{-9}$), a moon of Jupiter, and a water vapor–CO₂ exosphere on Enceladus, a moon of Saturn. See Ch. 14 for details.

(iv) *Exospheres above rocky surfaces* include Mercury ($\sim 10^{-15}$) and the Moon (3×10^{-15}). Both have ballistic exospheres with atoms hopping across rocky surfaces. Of the above thin atmospheres, those of Pluto, Triton, Io, and perhaps Callisto are sufficiently dense to generate characteristic patterns of atmospheric motions or *atmospheric dynamics*.

Atmospheric compositions can vary because of phase changes or chemical reactions. A species affected by phase changes is water vapor in Earth’s atmosphere, with

where $\bar{R}_d/R_c = m_c/\bar{m}_d = \varepsilon$ because $\bar{R}_d = R/\bar{M}_d = k/\bar{m}_d$ and $\bar{R}_c = R/M_c = k/m_c$. The last equality in the equation above may be rearranged and written as

$$p = \bar{R}_d \rho T_v \quad (1.7)$$

where T_v is given by eq. (1.6). Consequently, the gas constant in the ideal gas form of eq. (1.7) remains the same in all cases, provided we replace the temperature with the virtual temperature T_v .

Because water vapor has a molecular mass of 18 atomic mass units (a.m.u.), which is lighter than the mean molecular mass of the dry gas in Earth’s atmosphere of 28.97 a.m.u., the density of moist air is *less* than the density of dry air at the same pressure and temperature. Similarly, “moist” air on Titan with condensable methane is less dense than “dry” Titan air. In contrast, on Jupiter, the condensable gas ammonia is heavier than the mean molecular mass of the dry gas (a mixture of H₂ and He),

so the density of “moist” air is greater than that of the “dry” gas. Consequently, virtual temperature due to H₂O or CH₄, respectively, is slightly *greater* than actual temperature for Earth and Titan, while virtual temperature accounting for variable NH₃ concentration is slightly *less* than actual temperature in the atmosphere of Jupiter.

1.1.2.3 The Hydrostatic Equation and Barometric Pressure

A key property of atmospheres is pressure, which decreases exponentially with height. Pressure declines with altitude because when air settles under gravity, high pressure lower down in the atmosphere pushes upwards against the weight of overlying air. At higher altitudes there is less weight of air above, so pressure is lower. If the weight of overlying air were not balanced in this way, the atmosphere would contract or expand until it reached equilibrium. The balance of forces involved is *hydrostatic equilibrium*, an approximation that on Earth is generally valid over a horizontal scale larger than a few kilometers.

Considering a column of air of unit cross-sectional area and height Δz allows us to derive the equation for hydrostatic equilibrium (Fig. 1.3). The decrease in the pressure Δp over a height increment of Δz arises from the force caused by the weight of air at the base of the column of height Δz . This column of air has volume $1 \text{ m}^2 \times \Delta z$, so its mass is simply $\rho \Delta z$, where ρ is the air density. Pressure is defined as force over area, so

$$\Delta p = \frac{\text{weight}}{\text{area}} = \frac{-(\text{mass of column}) \times g}{1} = -(\rho \Delta z)g$$

where g is gravitational acceleration. In atmospheric science, pressure is given in various units: bar, millibar, atmospheres, or Pascals (the SI unit). The conversion factors are 1 bar = 10⁵ Pa = 1000 mbar, and 1 atm = terrestrial mean sea level pressure = 1.01325 bar = 1013.25 mbar = 1.01325 × 10⁵ Pa. Rewritten in calculus form, the above equation is

$$\frac{\partial p}{\partial z} = -g(z)\rho(z), \quad p(z) = \int_z^\infty g(z)\rho(z)dz \quad (1.8)$$

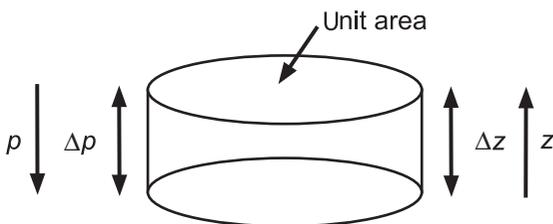


Figure 1.3 Diagram illustrating the pressure decrement Δp across an air column of height increment Δz .

In eq. (1.8), acceleration due to gravity depends on height z , i.e., $g = g(z)$, which could be approximated as $g(z) \approx g_0[r_0/(r_0 + z)]^2$, where r_0 is a reference radius, usually a mean solid surface on a rocky planet or a cloud-top radius on a gas giant, z is the geometric height above that radius, and $g_0 = GM/r_0^2$. This approximation is good for most atmospheric applications on terrestrial planets.

The acceleration in the local vertical also depends on latitude because of planetary rotation. Let us define Ω , the *planetary angular rotation rate* or angular frequency. On Mars, for example, $\Omega = 2\pi/(\text{sidereal rotational period}) = 2\pi/(88\,642.663 \text{ s}) = 7.088 \times 10^{-5} \text{ s}^{-1}$, and on Jupiter, $\Omega = 2\pi/(35\,727.3 \text{ s}) = 1.76 \times 10^{-5} \text{ s}^{-1}$. At any point on the planet, there will be an outward centrifugal acceleration given by $\Omega^2 r_a$, where r_a is the radial distance from the axis of rotation (Fig. 1.4). At the equator, r_a is just the radius of the planet R_p , whereas at the poles r_a is zero. If r is the radial distance from the center of the planet, the centrifugal acceleration at latitude ϕ is $\Omega^2 r \cos \phi$. If we turn this vector through angle ϕ , we get the upward component of this acceleration in the local vertical, $\Omega^2 r \cos^2 \phi$. Hence, a first-order correction to g is to subtract this component. Thus, the corrected gravitational acceleration can be expressed as

$$g(r, \phi) \approx \frac{GM}{r^2} \left[1 - \frac{\Omega^2 r^3 \cos^2 \phi}{GM} + \dots \right] \quad (1.9)$$

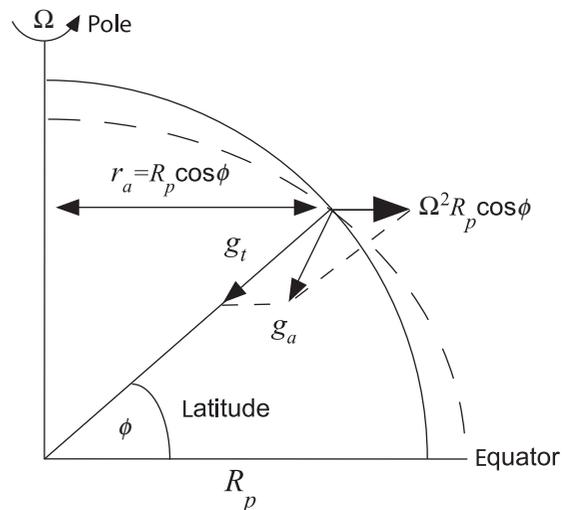


Figure 1.4 The effect of rotation at angular velocity Ω of a spherical planet of radius R_p on the gravity vector at latitude ϕ . In practice, the planet will adjust to an oblate spheroid (dashed); g_t = true gravitational acceleration, g_a = apparent gravitational acceleration = the resultant of the true gravity vector and outward centrifugal acceleration (exaggerated).

where M is the mass of the planet below radius r and $G = 6.674 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$ is the universal gravitational constant. The correction term in eq. (1.9) accounts for the centrifugal acceleration at latitude ϕ . For the terrestrial planets, this term produces correction to the sphericity of gravitational potential surfaces of about a few parts per thousand. Higher-order corrections also appear because of the departure from spherical symmetry of the mass distribution caused by rotation or asymmetric topography (such as on Mars). The correction to g due to rotation reaches as much as 7% on giant planets. The planetary shape of Jupiter, for example, is distinctly deformed from spherical.

Figure 1.4 shows how the addition of gravitational and centrifugal acceleration vectors should produce a gravitational acceleration vector offset from the local vertical on a spherical planet. However, in reality, all planets, even rocky ones, are fluid over geological time-scales and bulge at their equators. The bulge adjusts for the centrifugal acceleration of a planet’s rotation so that the local g -vector becomes perpendicular to the local surface of the planet. With an oblate planet, there is no apparent g offset from the local vertical but the *magnitude* of the gravitational vector must still be corrected.

1.1.2.4 Atmospheric Scale Height

The *scale height* of an atmosphere is the vertical distance over which pressure or density drops by a factor of $1/e = 1/(2.7183) \sim 1/3$. The *pressure scale height* will generally differ slightly from the *density scale height* because they are connected via the ideal gas law through temperature, which varies with height. The pressure scale height equals the density scale height only in an isothermal atmosphere. The hydrostatic equation and the ideal gas equation combine to give us an expression for the pressure scale height, H . From eq. (B4), we can express the air density as $\rho = \bar{m}p/kT$, which can be substituted in eq. (1.8) to produce

$$\frac{\partial p}{\partial z} = -\left(\frac{\bar{m}(z)g(z)}{kT(z)}\right)p \Rightarrow \frac{\partial p}{p} = -\left(\frac{\partial z}{H}\right), \text{ where } H = \frac{kT(z)}{\bar{m}(z)g(z)} = \frac{\bar{R}(z)T(z)}{g(z)} \tag{1.10}$$

Integration of the above equation from the surface ($z = 0$) to an arbitrary altitude z gives

$$p = p_s \exp\left(-\int_0^z \left(\frac{dz}{H}\right)\right) \tag{1.11}$$

where p_s is the surface pressure.

The integral form of the hydrostatic equation (eq. (1.11)) can be simplified further if we assume that the atmosphere is isothermal, well mixed, and that the variation of gravity with height is small. For most planetary atmospheres, these assumptions are not as bad as they seem. For example, the Earth’s atmosphere is well mixed by turbulence to uniform composition of the major gases below the ~ 100 km altitude homopause (Sec. 1.1.1), and over the same vertical distance the temperature lies within 50 K, or 20%, of 250 K. Assuming an isothermal atmosphere at temperature \bar{T} , we obtain,

$$p = p_s \exp\left(-\frac{z}{H}\right), \text{ where } H = \frac{k\bar{T}}{\bar{m}g} = \frac{\bar{R}\bar{T}}{g} \tag{1.12}$$

We can also think of the scale height in terms of a Boltzmann energy distribution. In an isothermal atmosphere the average molecular thermal energy is $\sim k\bar{T}$. If all this energy were used to lift an average molecule to a height H , the gravitational potential energy would be $\bar{m}gH$. However, for a gas at fixed temperature, molecules have a Maxwell–Boltzmann distribution of energies and some will be more energetic. But not many molecules have much more energy than $k\bar{T}$, so the atmosphere thins out above a scale height. Thus the height in $\bar{m}gH \sim k\bar{T}$ defines the top of the first energy level in an exponential Boltzmann distribution.

For most planetary atmospheres, the pressure scale height lies between 5–20 km because the ratio $\bar{T}/\bar{m}g$ is roughly similar for both terrestrial and giant planets, given that small \bar{T} (and large g for Jupiter) compensates for small \bar{m} in hydrogen-rich gas giants. On Earth, if we take a near-surface temperature of 288 K, the pressure scale height is ~ 8.4 km, whereas for a typical mid-tropospheric temperature of 250 K, it is 7.3 km. On Titan, the near-surface temperature $\bar{T} \sim 90$ K, $g = 1.34 \text{ m s}^{-2}$, and $\bar{M} = 28.6 \text{ g mol}^{-1}$, so the pressure scale height is $H = (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 90 \text{ K}) / (0.0286 \text{ kg mol}^{-1} \times 1.34 \text{ m s}^{-2}) \sim 20$ km. This shows how an atmosphere on a small body can be extended vertically because of its small gravity.

1.1.2.5 Geopotential Height and Geometric Height

To avoid dealing with the variation of g with height, a transformation is sometimes used that is analogous to the use of virtual temperature that we encountered earlier. Geopotential height Z , is the height of a given point in

the atmosphere in units proportional to the potential energy of a unit mass at this height relative to some reference altitude. The potential energy per unit mass at height z is the integral of potential energy to that height, which is the *geopotential*, given by

$$\Phi(z) = \int_0^z g dz \quad \text{and} \quad d\Phi = g dz \quad [\text{m}^{-2}\text{s}^{-1} \text{ or } \text{J kg}^{-1}] \quad (1.13)$$

The *geopotential height*, defined by

$$Z = \frac{\Phi(z)}{g_0} = \frac{1}{g_0} \int_0^z g(z, \phi) dz \quad [\text{m}], \quad \text{where } g_0 = \frac{GM}{r_0^2} \quad (1.14)$$

can be used as the dependent variable in place of geometric height, where ϕ is latitude and r_0 is a reference radius. Since $z \ll r_0$, it follows that $g_0 \approx g(z, \phi)$ and $Z \approx z$. For example, Z differs only 1.55% from z at 100 km on Earth. Using the hydrostatic equation in basic form, $dp = -g\rho dz = -\rho d\Phi$, we have, with the ideal gas law:

$$dp = -\left(\frac{p}{RT}\right)d\Phi = -\left(\frac{p}{RT}\right)g_0 dZ \Rightarrow \frac{dp}{p} = -\frac{1}{H} dZ$$

Consequently, the expression for the pressure decrease with geopotential height is

$$p(Z) = p_0 \exp\left(-\int_0^Z \frac{dZ}{H}\right) \quad (1.15)$$

where the scale height is

$$H(Z) = \frac{\bar{R}T(Z)}{g_0} = \frac{\bar{R}_d T_v(Z)}{g_0} \quad (1.16)$$

The difference in geopotential height between two pressure surfaces is called *thickness*:

$$\Delta Z = Z(p) - Z(p_0) = \int_p^{p_0} H(p) \frac{dp}{p} = \bar{H} \ln\left(\frac{p_0}{p}\right) \propto \bar{T} \quad (1.17)$$

where \bar{H} is the log-pressure average scale height between p and p_0 ; it is proportional to \bar{T} , the log-pressure mean temperature.

Equation (1.17) is known as the *hyposometric equation* and has a practical use that one can construct a distribution of heights of isobaric surfaces given the temperature distribution (measured with remote sensing, for example) and the height of one isobaric surface that is measured or assumed. This approach directly relates the temperature distribution to its influence on pressure variations, which, in turn, cause winds in an atmosphere. Equation (1.17) indicates how air expands vertically with increasing temperature. Thus lateral gradients of

temperature cause lateral gradients of pressure to develop at altitude. For example, the 500 mbar surface in Earth’s mid-troposphere (~5–6 km altitude) tends to slope downwards from warm tropics to cold high latitudes. Greater height of a pressure surface is associated with greater pressure below because pressure increases with depth, so there is generally higher pressure towards the tropics. This situation causes strong eastward winds in northern midlatitudes because when account is taken of Earth’s rotation, winds tend to flow such that low pressure is to the left of the flow in the northern hemisphere (Sec. 4.1.2).

In hydrostatic equilibrium, p is a unique function of z for a given distribution of T/\bar{m} from eq. (1.11). So pressure or any function of pressure can be used an alternative vertical coordinate to geometric height z . For example, some dynamical studies use a “log-pressure” vertical coordinate. This approximates height and is defined by

$$z^* = -H_{\text{ref}} \ln\left(\frac{p}{p_{\text{ref}}}\right), \quad \text{where } H_{\text{ref}} = \frac{kT_{\text{ref}}}{gm_{\text{ref}}} \quad (1.18)$$

Here H_{ref} is a reference scale height, p_{ref} is a reference pressure, and T_{ref} and m_{ref} are some global mean reference values.

1.1.2.6 The Relationship Between Surface Pressure and Mass of an Atmosphere

When considering atmospheric evolution, or comparing different planetary atmospheres, it is useful to examine how much material is in an atmosphere. The surface pressure, p_s , integrates the mass, M_{col} , of a column of air per unit area because, by definition, $p_s = \text{weight}/(\text{unit area}) = M_{\text{col}}g$. So the mass of a column of air per unit area is given by

$$M_{\text{col}} = \frac{p_s}{g} \quad (1.19)$$

On Earth, for example, the mass of a column of air above sea level is $\sim(101\,325 \text{ Pa})/(9.8 \text{ m s}^{-2}) \sim 10^4 \text{ kg m}^{-2}$, which compares to 164 kg m^{-2} ($610 \text{ Pa}/3.72 \text{ m s}^{-2}$) above an average location on the surface of Mars.

Highly accurate calculation of the mass of an atmosphere is more involved. This is because eq. (1.19) is a flat Cartesian approximation to a planet that in reality is an oblate spheroid. The surface pressure is actually slightly less than the weight per unit area because curved geometry allows the weight of the atmosphere to be supported by lateral pressure forces as well as the pressure forces at the bottom of the atmosphere (Bannon *et al.*, 1997; Sanudo *et al.*, 1997; Trenberth and Guillemot, 1994).

1.1.2.7 Column Abundance

The column abundance of a gas, which is the number of molecules per unit area above a surface, is commonly used to describe gases that absorb radiation, such as methane or ozone. For a surface at altitude z , the column abundance $N_{\text{col}}(z)$, is given by

$$N_{\text{col}}(z) = \int_z^{\infty} n(z) dz \quad (1.20)$$

where $n(z)$ is the number of molecules of the gas per unit volume at altitude z . The column mass is $N_{\text{col}}(z)\bar{m}$, so the pressure at altitude z , is $p(z) = N_{\text{col}}(z)\bar{m}g$. Thus we can derive an expression for the column abundance in terms of scale height H as follows:

$$N_{\text{col}}(z) = \frac{p(z)}{\bar{m}g} = \frac{n(z)kT(z)}{\bar{m}g} \Rightarrow N_{\text{col}}(z) = n(z)H(z) \quad (1.21)$$

For the last expression on the right-hand side, we recognize the scale height $H(z) = kT(z)/\bar{m}g$.

Column abundance is usually expressed in units of molecules per cm^2 , but the planetary science literature sometimes uses the unit “cm-atm” or “cm-amagat”.¹ This is the number of centimeters of a column produced if the gas were taken to STP (Standard Temperature and Pressure) conditions. The relationship with $N_{\text{col}}(z)$ is a normalization, as follows, by a reference number density:

$$\mathcal{N} \text{ cm-atm} = \frac{N_{\text{col}}(z)}{n_0}, \text{ where } n_0 = \frac{p_{\text{STP}}}{kT_{\text{STP}}} = 2.687 \times 10^{19} \text{ molecules cm}^{-3} \quad (1.22)$$

where $N_{\text{col}}(z)$ is in units of molecules cm^{-2} . Here n_0 is the *Loschmidt number*, the molecular number density in cm^{-3} of an ideal gas at STP conditions of $p_{\text{STP}} = 1 \text{ atm} = 101\,325 \text{ Pa}$ and $T_{\text{STP}} = 273.15 \text{ K}$.

As an example of the use of eq. (1.22), observations of peak ozone levels on Mars by NASA’s *Mariner 9* orbiter spacecraft are reported as a column abundance of $\sim 60 \mu\text{m-atm}$ (Barth, 1974). Application of eq. (1.22) with $\mathcal{N} = 60 \times 10^{-4} \text{ cm-atm}$ gives $N_{\text{col}} = 1.6 \times 10^{17} \text{ molecules O}_3 \text{ cm}^{-2}$. This can be compared to a typical ozone column abundance on Earth of $\sim 8 \times 10^{18} \text{ molecules O}_3 \text{ cm}^{-2}$, some ~ 50 times greater. The large difference with Earth indicates that Mars does not have an ozone layer shield for shortwave ultraviolet radiation,

even when its ozone column abundance is maximal. Consequently, the surface of Mars is sterilized by short-wave ultraviolet (Ch. 12).

A specific unit of column abundance also exists for ozone. This is the Dobson Unit (DU), named after Gordon Dobson, the Oxford professor who built the first spectrometer to measure Earth’s ozone layer in the 1920s. The column abundance in Dobson Units is related to \mathcal{N} and $N_{\text{col}}(z)$ by the following expression:

$$\text{Dobson Units} = 1000 \mathcal{N} \text{ cm-atm O}_3 = \frac{1000 N_{\text{col}}(z)}{n_0} \quad (1.23)$$

One DU refers to a layer of ozone that would be 0.001 cm (or 0.01 mm) thick at STP. Earth’s ozone column abundance varies with latitude and time, but is typically about 300 DU, equivalent to a layer of 3 mm thickness at STP, or 0.3 cm-atm.

Yet another measure of column abundance is used for atmospheric water vapor, which is the depth of water that would result if all the water were condensed out from an atmospheric column onto the surface. This is expressed as *precipitable centimeters* (pr cm) on Earth and as *precipitable microns* (pr μm) on Mars. On Earth, the typical water column abundance is 3 pr cm. In contrast, the Martian atmosphere contains an average 10 pr μm of water. Precipitable water can be readily converted into a columnar mass. The mass of the water per unit area

is (precipitable depth) \times (the density of water). Thus 10 pr μm on Mars is equivalent to $(10 \times 10^{-6} \text{ m}) \times (1000 \text{ kg m}^{-3}) = 0.01 \text{ kg H}_2\text{O m}^{-2}$.

1.1.3 Convection and Stability

Pressure and density must generally decrease with increasing height because of hydrostatics but the way that temperature varies with altitude is less certain *a priori*. Consequently, *atmosphere structure* is usually shorthand for how the temperature changes with height, as mentioned in Sec. 1.1.1. Air temperature can decrease or increase with height depending on the circumstances (Sec. 1.1.1.1), but the dominant physical processes ultimately responsible are radiation and convection. These processes may also interact with other atmospheric motions, e.g., the generation of atmospheric waves can modulate the atmospheric structure (e.g., Sec 4.4.2; Sec. 4.6).

¹ When number density is normalized by the Loschmidt number (i.e., n/n_0) the result is in units of amagat (or “amg”), named after French physicist Emile Amagat (1841–1915).

Convection occurs when air parcels become buoyant, meaning less dense than their surroundings. Several processes can drive buoyancy: radiative heating, contact with a warm planetary surface, release of latent heat when a substance condenses (e.g., water vapor in Earth's atmosphere, see Sec. 1.1.3.5), and heat from the interior of a planet on Jupiter, Saturn, or Neptune. Buoyant air parcels rise and displace adjacent air, causing mixing. Upward-moving air parcels rise into regions of lower ambient air pressure, where they expand and cool. Conversely, sinking parcels contract and warm. In convective equilibrium, we expect atmospheric temperature to decrease with height, as indeed is generally observed above the surfaces of Earth and Mars (during the daytime), Venus and Titan, as well as in the tropospheres of giant planets (Fig. 1.2).

The rate that temperature T , decreases with altitude z , is the *lapse rate*. This is denoted by $\Gamma = -(dT/dz)$ and commonly expressed in units of K km^{-1} . The negative sign convention generally gives a positive number for Γ in tropospheres. For example, on Earth, the global average lapse rate is $\sim 6 \text{ K km}^{-1}$ in the troposphere.

Let us consider a parcel that ascends or descends such that its pressure adjusts to its surroundings. In an idealized case where the temperature of the air parcel warms by contraction or cools by expansion with no exchange of energy with its surroundings either by conduction or radiation, the temperature change is said to be *adiabatic* (from the Greek for “impassable” (to heat)). In this case, the temperature change with altitude is the *adiabatic lapse rate*, $\Gamma_a = -(dT/dz)_a$.

Convection occurs when the ambient lapse rate exceeds the adiabatic lapse rate, $\Gamma > \Gamma_a$. This means that a rising adiabatic parcel will be at a warmer temperature than ambient surroundings after accounting for adiabatic cooling, and so will continue to rise (Fig. 1.5). The result of such an *unstable* atmosphere would be extremely thorough mixing so that the ambient temperature profile would adjust to an adiabatic one. Thus, we think of Γ_a as a limiting lapse rate, so that in nature we expect to find *stable* atmospheres with $\Gamma \leq \Gamma_a$. On average this is observed in planetary atmospheres (Table 1.3).

However, we should be wary that *superadiabatic* conditions can occur, as follows: (i) in Earth's tropics Γ can exceed the *moist adiabatic lapse rate* (see later, Sec. 1.1.3.6), which gives rise to large thunderstorms; (ii) within a few meters of planetary surfaces in daytime, Γ can exceed Γ_a by a factor of hundreds or thousands, especially in deserts. For example, on Mars the atmosphere cannot keep up with the daytime warming of the

surface and so “warm towers” or “thermal vortices” develop that are the convective equivalent of thunderstorms without the clouds or rain. Often such vortices pick up dust and become *dust devils* (reviewed by Balme and Greeley, 2006).

In the cloudless terrestrial atmosphere, the ambient lapse rate is often superadiabatic near the ground and nearly adiabatic at higher levels. Consequently, gases released at the surface travel upwards and are dispersed. However, sometimes an *inversion* arises, meaning that the lapse rate is negative and temperature increases with height. In this case, the atmosphere is highly stable. In urban areas, we commonly experience pollution trapped near the ground when there is a temperature inversion.

1.1.3.1 The Dry Adiabatic Lapse Rate and Observed Lapse Rate

By considering an adiabatic parcel of air, we can derive a formula for the adiabatic lapse rate. We start with the first law of thermodynamics, which is conservation of energy, i.e.,

$$\text{heat input} = (\text{change in internal energy}) + (\text{work done})$$

$$dq = du + dw \quad (1.24)$$

Here dq , du , and dw are energy changes per unit mass, which we indicate in lower case. Now, the definition of specific heat at constant volume is $c_v = (du/dT)_v$, where the v subscript indicates constant volume, from which

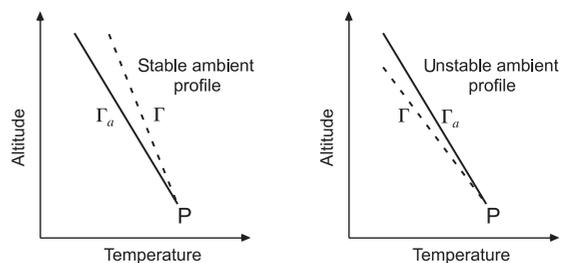


Figure 1.5 Atmospheric profiles showing the adiabatic lapse rate (Γ_a) as a solid line and the ambient lapse rate ($\Gamma = -dT/dz$) as a dashed line. The left-hand profile is stable because $\Gamma < \Gamma_a$, i.e. the decrease of temperature with altitude is smaller than in the adiabatic case. A parcel displaced adiabatically from point P will be colder and denser than its surroundings and so will tend to return to P. In the right-hand graph when $\Gamma > \Gamma_a$, the atmosphere is unstable to convective mixing. A parcel will continue rising from point P. However, the adiabatic assumption will break down, so the parcel will lose its heat to the air aloft such that the ambient profile will move towards adiabatic equilibrium.

Table 1.3 Thermodynamic properties and lapse rates on various planets.

Body	Main gases	Molar mass, M g mol ⁻¹	\bar{R} J kg ⁻¹ K ⁻¹	g m s ⁻²	c_p J kg ⁻¹ K ⁻¹	$\Gamma_a = g/c_p$ troposphere K km ⁻¹	Γ observed in troposphere K km ⁻¹
Venus	CO ₂ , N ₂	43.45	189	8.901	930	9.5	~8.0
Earth	N ₂ , O ₂	28.97	287	9.81	1004	9.8	~6.5
Mars	CO ₂ , N ₂	43.5	191	3.72	850	4.4	~2.5
Jupiter	H ₂ , He	2.22	3745	24.25	10 988	2.1–2.45*	1.9
Saturn	H ₂ , He	2.14	3892	10.0	10 658	0.7–1.1	0.85
Titan	N ₂ , CH ₄	28.67	290	1.36	1044	1.3	1.0–1.4
Uranus	H ₂ , He	2.3	3615	8.80	8643	0.7–1.1	0.75
Neptune	H ₂ , He	2.3	3615	11.1	8643	0.85–1.34	0.95
HD209458b	H ₂	2.0	4160	18.5	14 300	1.3	~0.2 (model)**

* On giant planets, g varies from equator to pole.

** Menou and Rauscher (2009).

we get $du = c_v dT$. Also a small increment of work dw is given by “force \times incremental distance,” which is equivalent to “pressure \times incremental volume change.” If we define specific volume (volume per unit mass) as $\alpha = 1/\text{density} = 1/\rho$, we have $dw = p d\alpha$. (Note that some books use “ $p dV$ ” but then V would have to be in units of m³/kg and in Box 1.1 we defined V as volume (units of m³), so we don’t use V here). Substituting for du and dw , we have

$$\underbrace{dq}_{\text{heat added/kg (zero for adiabatic)}} = \underbrace{c_v dT}_{\text{change in internal heat/kg}} + \underbrace{p d\alpha}_{\text{work done/kg}} \tag{1.25}$$

Here, dq is a small heat input per unit mass (e.g., from contact with a warm surface, or zero if adiabatic), dT is a small rise in temperature, and $d\alpha$ is a small increase in parcel volume per kg. From the ideal gas law $p = \rho \bar{R} T$, it follows that $p\alpha = \bar{R} T$. By applying the product rule [$d(xy) = x dy + y dx$] to T/p , we get

$$d\alpha = (\bar{R}/p) dT - (\bar{R} T/p^2) dp$$

Substituting for $d\alpha$ in the conservation of energy equation (1.25), we have

$$dq = c_v dT + p \left[\frac{\bar{R}}{p} dT - \frac{\bar{R} T}{p^2} dp \right] = (c_v + \bar{R}) dT - \left(\frac{\bar{R} T}{p} \right) dp \Rightarrow dq = c_p dT + g dz \tag{1.26}$$

In the final expression, we’ve used $c_p = c_v + \bar{R}$ from kinetic theory, which connects specific heat at constant pressure (c_p) to that at constant volume. Also, we replaced

$(\bar{R} T/p) dp$ with $-g dz$ by using the hydrostatic equation (eq. (1.8)), i.e., $dp = -\rho g dz$.

Now consider an adiabatic parcel of air that moves up or down. Adiabatic means no exchange of heat with the surroundings. Thus, with $dq = 0$, the last expression in eq. (1.26) gives us the change in air parcel temperature dT , as the parcel moves up or down distance dz and expands or contracts adiabatically. When we rearrange this equation, we get the definition of the *dry adiabatic lapse rate*:

$$\Gamma_a = - \left(\frac{dT}{dz} \right) = \frac{g}{c_p} \tag{1.27}$$

This little equation provides the temperature change with altitude of a dry parcel of air moving up and down through an atmosphere in hydrostatic equilibrium.

Given the specific heat capacities of the atmospheres of Venus, Earth, and Mars as 930, 1004, and 850 J K⁻¹ kg⁻¹, and g values of 8.87, 9.81, and 3.72 m s⁻², respectively, we can readily calculate from eq. (1.27) that Γ_a (K km⁻¹) = 9.8 (Earth), 9.5 (Venus), 4.4 (Mars). However, typical observed lapse rates in the tropospheres of these planets (Table 1.3) are Γ (K km⁻¹) \sim 6 (Earth), \sim 8.0 (Venus), \sim 2.5 (Mars). On average, the atmospheres do not cool as much as expected with height. The explanations are as follows. In Earth’s lower

atmosphere, water vapor condenses, which is an exothermic (heat releasing) process. On Mars, dust absorbs visible sunlight and warms the atmosphere, while on

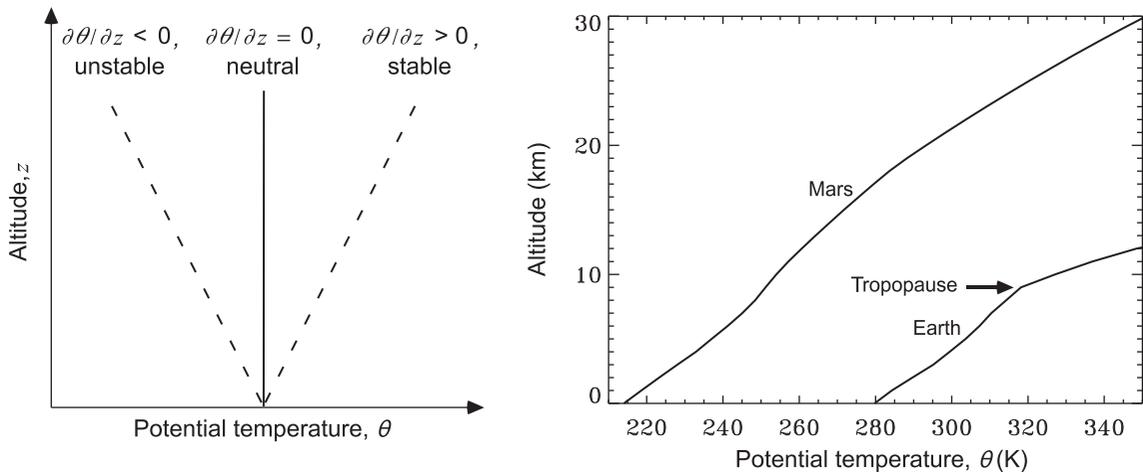


Figure 1.6 Left: The relationship between profiles of potential temperature θ , and stability. Right: Averaged stable potential temperature profiles in midlatitudes of Mars and Earth. Note the marked increase in static stability in the Earth’s stratosphere.

Venus sulfur gases exothermically condense into H_2SO_4 (sulfuric acid) particles.

$$\theta = T \left(\frac{p_{\text{ref}}}{p} \right)^\kappa \tag{1.31}$$

1.1.3.2 Potential Temperature and Generalized Lapse Rates in Tropospheres

Potential temperature is an alternative thermodynamic variable to absolute temperature, and its slope with height gives direct insight into whether an atmosphere is stable or unstable to convection. This variable is easily derived by setting $dq = 0$ in eq. (1.26) and substituting $(\bar{R}T/p)dp$ for gdz from the hydrostatic equation. This gives:

$$\frac{dT}{T} = \left(\frac{\bar{R}}{c_p} \right) \frac{dp}{p} \tag{1.28}$$

This equation indicates that fractional changes in temperature and pressure are in direct proportion for adiabatic processes, with a constant of proportionality given by

$$\frac{\partial \ln T}{\partial \ln P} = \frac{\bar{R}}{c_p} \equiv \kappa \tag{1.29}$$

Integrating eq. (1.29) between a reference pressure p_{ref} and arbitrary pressure p , we get,

$$[\ln T]_{\theta}^T = \kappa [\ln p]_{p_{\text{ref}}}^p \Rightarrow \ln \left(\frac{T}{\theta} \right) = \kappa \ln \left(\frac{p}{p_{\text{ref}}} \right) = \ln \left(\frac{p}{p_{\text{ref}}} \right)^\kappa$$

Thus,

$$T = \theta \left(\frac{p}{p_{\text{ref}}} \right)^\kappa \tag{1.30}$$

and

Equation (1.31) is called *Poisson’s (adiabatic state) Equation* and defines the variable θ , which is *potential temperature*. Mathematically, θ is a constant of integration equivalent to the actual temperature at a reference pressure p_{ref} . Physically, θ is the temperature a parcel of air would have if it were taken to pressure p_{ref} dry adiabatically. Consequently, θ can be regarded as an alternative thermodynamic variable to temperature so that eq. (1.30) is an alternative equation of state.

On Earth, usually $p_{\text{ref}} = 10^5 \text{ Pa}$ and $\kappa = 287 \text{ J K}^{-1} \text{ kg}^{-1} / 1004 \text{ J K}^{-1} \text{ kg}^{-1} = 0.286$. Potential temperature θ is generally greater than actual temperature when the pressure is less than 1000 mbar, and vice versa. The importance of θ is that it is constant with altitude ($\partial\theta/\partial z = 0$) when the lapse rate is adiabatic. Deviations from this constancy indicate conditions of convective stability ($\partial\theta/\partial z > 0$) and instability ($\partial\theta/\partial z < 0$) indicated in Fig. 1.6.

If we invert eq. (1.31), it gives the dry adiabatic temperature variation in the convective part of a troposphere as:

$$T = T_{\text{ref}} \left(\frac{p}{p_{\text{ref}}} \right)^{\bar{R}/c_p} \Rightarrow T = T_{\text{ref}} \left(\frac{p}{p_{\text{ref}}} \right)^{(\gamma-1)/\gamma} \tag{1.32}$$

Here, T_{ref} is a reference temperature at a reference pressure p_{ref} , while γ is the ratio of specific heats c_p/c_v . The exponent in eq. (1.32) is from the relationship of specific heats:

$$\bar{R} = c_p - c_v \Rightarrow \frac{\bar{R}}{c_p} = 1 - \frac{1}{\gamma} = \frac{(\gamma - 1)}{\gamma} \tag{1.33}$$

Kinetic theory allows us to relate the ratio of specific heats γ to the degrees of freedom, N_{dof} , for the primary atmospheric constituent(s), where

$$\gamma = 1 + \frac{2}{N_{\text{dof}}} \tag{1.34}$$

Often atmospheres are dominated by linear diatomic gases, such as H_2 (Jupiter, Saturn, Uranus, and Neptune), N_2 (Titan), or an $\text{N}_2\text{-O}_2$ mixture (Earth). These molecules have three translational and two rotational degrees of

causing oscillations that eventually will be frictionally damped. Atmospheres have a characteristic angular frequency of oscillation, called the *buoyancy frequency* or *Brunt-Väisälä frequency* N_B , which we derive below.

Consider a parcel of air of volume V and temperature T that is displaced by height δz from height z at environmental temperature T to a place where the environmental temperature is T_e (Fig. 1.7). The parcel cools adiabatically to a new temperature $T_p = T - \Gamma_a \delta z$, while the environment cools *less* at the ambient lapse rate as $T_e = T - \Gamma \delta z$. The difference in density between the parcel (ρ_p) and air (ρ_e) drives a buoyancy force, which we can write in the form of Newton’s second law:

$$\underbrace{(\mathcal{Y}\rho_p)}_{\text{mass}} \underbrace{\frac{d^2(\delta z)}{dt^2}}_{\text{acceleration}} = \underbrace{-g(\rho_p - \rho_e)\mathcal{V}}_{\text{buoyancy force}} \Rightarrow \frac{d^2(\delta z)}{dt^2} = g \left(\frac{\rho_e}{\rho_p} - 1 \right) = g \left(\frac{T_e}{T_p} - 1 \right) \tag{1.36}$$

Substituting for temperatures T_p and T_e , we get:

$$\frac{d^2(\delta z)}{dt^2} = g \left(\frac{T - \Gamma_a \delta z}{T - \Gamma \delta z} - 1 \right) = g \left(\frac{\Gamma \delta z - \Gamma_a \delta z}{T - \Gamma \delta z} \right) \approx g \left(\frac{\Gamma - \Gamma_a}{T - \Gamma \delta z} \right) \delta z \Rightarrow \ddot{\delta z} + \frac{g}{T} (\Gamma_a - \Gamma) \delta z = 0$$

freedom, so that $N_{\text{dof}} = 5$ and $\gamma = 7/5 = 1.4$ for these worlds. In the case of the CO_2 -dominated atmospheres of Venus and Mars, there are three translational, two rotational, and ~ 0.3 vibrational degrees of freedom, so $N_{\text{dof}} = 6.3$ and $\gamma = 1.3$ (Bent, 1965). Consequently, the dry adiabatic temperature T (eq. (1.32)) varies with altitude expressed as pressure as $p^{0.3}$ and $p^{0.2}$ for diatomic and CO_2 dominated atmospheres, respectively. Such a relationship for dry adiabats is general and will also apply to dry tropospheres of exoplanets.

In reality, we observe that all the tropospheres we know (in the Solar System) do not follow a dry adiabat because condensation of volatiles during convection releases latent heat and lowers the lapse rate below that of the dry adiabatic lapse rate. The convective part of a tropospheric temperature structure can be modified from eq. (1.32) to

$$T = T_{\text{ref}} \left(\frac{p}{p_{\text{ref}}} \right)^{\alpha_c (\gamma - 1) / \gamma} \tag{1.35}$$

For planets in the Solar System, α_c is an empirical factor, typically around 0.6–0.9, which represents the average ratio of the true lapse rate in the planet’s convective region to the dry adiabatic lapse rate.

1.1.3.3 Static Stability of Atmospheres

In stable conditions, a vertically displaced air parcel will tend to return to its previous height and overshoot,

This is an equation of motion (compare “ $\ddot{x} + \omega^2 x = 0$ ” in elementary physics textbooks), which we may write with an angular frequency N_B , as

$$\frac{d^2(\delta z)}{dt^2} + N_B^2(\delta z) = 0 \tag{1.37}$$

where

$$N_B^2 \equiv \frac{g}{T} (\Gamma_a - \Gamma) \equiv \frac{g}{T} \left(\frac{dT}{dz} + \frac{g}{c_p} \right) \tag{1.38}$$

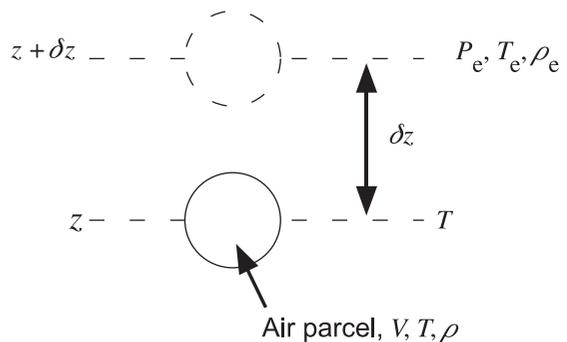


Figure 1.7 Schematic diagram indicating the conditions for a parcel of air of volume V , temperature T , and density ρ that is displaced adiabatically over a vertical distance δz into an environment with air of pressure P_e , temperature T_e , and density ρ_e .

In a statically stable atmosphere, $\Gamma < \Gamma_a$; thus $N_B^2 > 0$ and solutions to eq. (1.37) are simple harmonic motion. The displaced parcel oscillates up and down at a natural angular frequency N_B . For Earth's lower troposphere, $dT/dz \sim -6 \text{ K km}^{-1}$ and $T \sim 270 \text{ K}$ so $N_B^2 = (9.81 \text{ m s}^{-2}/270 \text{ K})(-6 \times 10^{-3} \text{ K m}^{-1} + 9.81 \text{ m s}^{-2}/1004 \text{ J K}^{-1} \text{ kg}^{-1})$, which gives $N_B = 0.0117 \text{ s}^{-1}$, equivalent to a period of oscillation of $2\pi/N_B \approx 9$ minutes.

In a statically unstable atmosphere, $\Gamma > \Gamma_a$ and $N_B^2 < 0$. This means that N_B is imaginary and leads to exponential solutions of eq. (1.37). A displaced parcel would continue to rise with increasing speed. The resulting convection would drive the lapse rate down towards Γ_a by carrying warmer parcels upwards and cooler parcels downward.

The Brunt–Väisälä frequency can also be expressed in terms of potential temperature. First, we take logs of eq. (1.31) to get

$$\ln \theta = \ln T + \kappa(\ln p_{\text{ref}}) - \kappa(\ln p)$$

If we differentiate w.r.t. z , remembering that $d(\ln x) = (1/x)dx$, we have

$$\begin{aligned} \frac{d(\ln \theta)}{dz} &= \frac{d(\ln T)}{dz} + \kappa \frac{d(\ln p_{\text{ref}})}{dz} - \kappa \frac{d(\ln p)}{dz} \\ \frac{1}{\theta} \frac{d\theta}{dz} &= \frac{1}{T} \frac{dT}{dz} - \frac{\kappa}{p} \frac{dp}{dz} = \frac{1}{T} \frac{dT}{dz} + \frac{\kappa \rho g}{p} \end{aligned}$$

In the very last step we have used the hydrostatic equation (1.8) to substitute for dp/dz . Using the definition of $\kappa = \bar{R}/c_p$ and the ideal gas law (B5), $p = \rho \bar{R}T$, we have

$$\frac{1}{\theta} \frac{d\theta}{dz} = \frac{1}{T} \frac{dT}{dz} + \frac{g}{c_p T} \Rightarrow \underbrace{\frac{g}{\theta} \frac{d\theta}{dz}}_{N_B^2} = \frac{g}{T} (-\Gamma + \Gamma_a) \quad (1.39)$$

Comparing eq. (1.38), we see that the square of the Brunt–Väisälä frequency is given by

$$N_B^2 = \frac{g}{\theta} \frac{d\theta}{dz} \quad (1.40)$$

Stable atmosphere solutions are defined by positive N_B^2 and positive $d\theta/dz$. This means that a displaced parcel will experience a restoring force and return to its previous position, albeit with oscillations. When $d\theta/dz = 0$, then $N_B = 0$, and we have neutral stability, where the atmosphere is just stable and the lapse rate equals the adiabatic lapse rate. If $d\theta/dz < 0$, the atmosphere is unstable to free convection (Fig. 1.6).

1.1.3.4 The Planetary Boundary Layer (PBL)

On planets with rocky surfaces, the *Planetary Boundary Layer* (PBL) is a near-surface region where turbulence generated by thermal convection produces an air–ground temperature differential and rapid variation with height of temperature and wind. PBL fluxes of heat, mass and momentum drive the circulation of an atmosphere.

To illustrate the structure of the PBL, consider Mars, shown schematically in Fig. 1.8. Just above the surface, air is so strongly restrained by friction with the ground and by its own intermolecular friction (viscosity), that its motion is nearly nonexistent. This is the *laminar boundary layer* (point A on Fig. 1.8) where momentum, heat and volatiles are transported mainly by molecular diffusion. It has depth ~ 1 cm on Mars compared to a few millimeters on Earth. The next region (marked B) is the turbulent or *surface boundary layer* (or *Prandtl layer*), which on Earth extends up to altitude 5–50 m. On Mars, it reaches a height of a few to a few hundred meters. This is the most turbulent

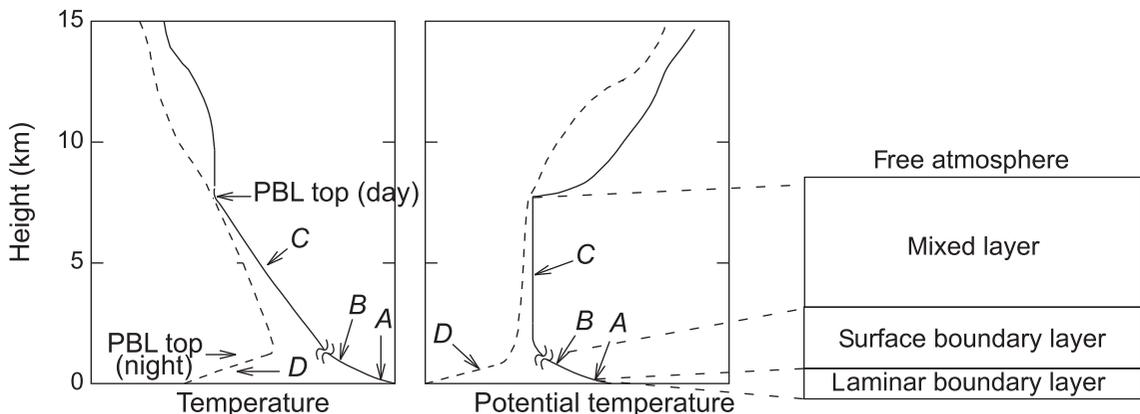


Figure 1.8 Schematic depiction of the planetary boundary layer (PBL) on Mars, indicating day and night conditions. Heights of the top of the laminar boundary layer (A) and surface layer (B) are exaggerated. (Following a schematic by Leovy (1982a).)

part of the atmosphere. Flow is in planes parallel to the surface and strongly shears (i.e. changes direction) with height. After sunset, radiational cooling may lead to a temperature inversion (D). Further up is a much thicker convective layer (C) called the *mixed layer* (or *Ekman layer*) that extends up to the top of the well-mixed (constant θ) zone. In this layer, away from the equator, the local vertical component of the angular momentum of a rotating planet can become important in affecting the direction of flow. Above C, the PBL ends and an increase of potential temperature θ (i.e., static stability) greatly reduces turbulent mixing. The region above the PBL is the *free atmosphere* or *geostrophic level*.

The depth of the PBL varies. On Earth, the PBL typically extends to 0.5–1 km, but can be tens of meters or ~2–4 km in certain circumstances. In early morning on Mars, the PBL may be less than 100 m deep but on a clear, summer afternoon typical thermal convection produces a PBL 5–10 km thick (based on afternoon cumulus cloud shadows, probe entry measurements, dust devil shadows, and atmospheric models). During Martian nighttime, a *nocturnal jet* (10–20 m/s) at a height of ~100 m may form above the inversion layer because the temperature inversion decouples the winds from the surface friction. After sunrise, convection in the PBL destroys the jet.

1.1.3.5 Condensable Species, Entropy, and the Clausius–Clapeyron Equation

In various planetary atmospheres, there are condensable species that affect atmospheric structure through their change of state from vapor to liquid, or vapor to solid: H₂O on Earth, CH₄ and HCN on Titan, H₂O and CO₂ on Mars, H₂SO₄ (SO₃ + H₂O) on Venus, H₂O, NH₃ on Jupiter and Saturn, and N₂ on Triton. Species can also form rain (e.g., water on Earth or CH₄ on Titan), snow (e.g., CO₂ in Mars’ wintertime polar atmosphere), and clouds (all of the aforementioned species). Condensables play a critical role in atmospheric evolution, such as the *runaway greenhouse effect*, which we meet later.

The key concept in understanding the behavior of a condensable is saturation vapor pressure. At any given temperature, the *saturation vapor pressure* (SVP) is the vapor pressure exerted in equilibrium with condensed liquid or solid phase. If we plot the SVP versus temperature, a curve is defined that represents the transition between vapor and liquid phases (or vapor and solid phases) (Fig. 1.9). Once a condensable gas vapor reaches SVP, it must condense into liquid or solid. The *Clausius–Clapeyron equation* defines the curve of Fig. 1.9, or more generally, SVP as a function of temperature for a

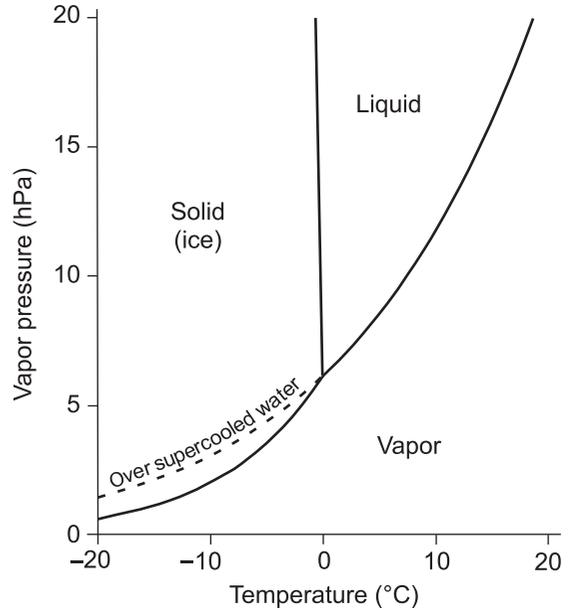


Figure 1.9 The saturation vapor pressure (SVP) for water. The line at the right shows the boundary between liquid and vapor. The dashed line shows the SVP over supercooled water, whereas the solid line beneath it is for SVP over ice. The higher SVP over supercooled water compared to ice causes more rapid evaporation.

condensable gas or a change in the melting point of a solid with pressure, such as CO₂ on Mars. On Earth, we are accustomed to thinking of the Clausius–Clapeyron equation as defining the saturation vapor pressure of water, but an analogous equation can be written for any condensable gas in any atmosphere.

Before quantifying how condensable species affect lapse rates, we must have a slight diversion and discuss *entropy*. Rudolf Clausius (1822–1888) coined the word *entropy*, from the Greek τροπή, meaning *transformation*. The basic motivation for his definition of entropy is that the integral of the quantity dQ/T (= heat absorbed (or lost)/ temperature) along a reversible path between two states A and B is independent of path. This means that you can define a fundamental thermodynamic function S that depends only on the initial and final states of a reversible process. If S_A and S_B are the values of this function in the states A and B, S is defined as

$$S_B - S_A = \int_A^B \frac{dQ}{T} \quad \text{or} \quad dS = \frac{dQ}{T} \quad (1.41)$$

If we define a reference state “O,” the state S can be defined for any state X as:

$$S_X = S_O + \int_O^X \frac{dQ}{T} \quad (1.42)$$

The third law of thermodynamics give us an entropy reference value S_0 as follows: at the absolute zero of temperature (0 K) the entropy of every chemically homogeneous solid or liquid body is zero. In the real world, the transformation from state O to state X involves irreversible processes along a path, as opposed to a reversible path. In idealized thermodynamics, it is often assumed that every irreversible transformation that occurs in nature can also be achieved through a reversible process for which eq. (1.42) is valid.

Although the above seems abstract, entropy is a measurable physical quantity with units of J K^{-1} . For example, when one mole of water ice turns into liquid water the entropy change is $22 \text{ J K}^{-1} \text{ mol}^{-1}$ ($= 6008 \text{ J mol}^{-1}/273.15 \text{ K}$), where we have used a melting temperature of 273.15 K , the latent heat of fusion of water 6008 J mol^{-1} , and eq. (1.41) in the form $\Delta S = \Delta Q/T$.

We can derive the Clausius–Clapeyron equation from basic thermodynamics. We will see that the key concept in understanding where the Clausius–Clapeyron equation comes from is that two phases are in *equilibrium* along the SVP versus T line, so the Gibbs free energy change of the phase transition is zero everywhere along the line. The Gibbs free energy is that available to do useful work and at equilibrium the change of Gibbs free energy is zero.

In order to change unit mass of a condensable from liquid (or ice) to vapor at constant temperature and pressure, a certain amount of energy, called the *latent heat* or, more properly, *enthalpy* l_c , is absorbed. Enthalpy per unit mass has units J kg^{-1} . If the change is from liquid to vapor, l_c is the *enthalpy (latent heat) of vaporization*; from ice to liquid it is the *enthalpy (latent heat) of fusion*, and from ice to vapor it is the *enthalpy (latent heat) of sublimation*. The first law of thermodynamics, eq. (1.24), gives

$$l_c = \int_{q_1}^{q_2} dq = \int_{u_1}^{u_2} du + p \int_{\alpha_1}^{\alpha_2} d\alpha = u_2 - u_1 + p(\alpha_2 - \alpha_1) \\ = (\text{change in internal energy in making vapor}) + (\text{work done in making vapor}) \quad (1.43)$$

Here u is the internal energy per unit mass, $p = e_s$ is the equilibrium or saturation vapor pressure, and α is the specific volume. Subscript 1 refers to the condensed phase and subscript 2 to the vapor phase. The change of phase takes place at constant temperature, so from the definition of entropy (eq. (1.41)), it follows that $l_c = T\delta s = T(s_2 - s_1)$, which can be substituted for l_c on the left-hand side of (1.43) to give

$$T(s_2 - s_1) = u_2 - u_1 + p(\alpha_2 - \alpha_1) \\ \Rightarrow u_1 + p\alpha_1 - Ts_1 = u_2 + p\alpha_2 - Ts_2 \quad (1.44)$$

The combination $u + p\alpha - Ts$ is called the Gibbs function, or G , which, from eq. (1.44), is constant during an isothermal change of phase. (Elsewhere, G is often written as $G = H - Ts$ where H is enthalpy or $H = u + p\alpha$, per unit mass).

Now if the phase change takes place at a higher temperature, $T + dT$, and a correspondingly higher equilibrium vapor pressure, $e_s + de_s$, we can write the Gibbs function as $G + dG$. To obtain dG we take the derivative of $u + p\alpha - Ts$, as follows:

$$dG = du + pda + adp - Tds - sdT \quad ; \text{sub. for } dq = du + pda \\ = dq + adp - Tds - sdT \quad ; \text{sub. for } dq = Tds \\ = adp - sdT \quad (1.45)$$

Since G remains constant during the isothermal change of phase, $G_1 + dG_1 = G_2 + dG_2$ and $dG_1 = dG_2$. So, from eq. (1.45)

$$\alpha_1 dp - s_1 dT = \alpha_2 dp - s_2 dT \\ \Rightarrow dp(\alpha_2 - \alpha_1) = dT(s_2 - s_1) \quad (1.46)$$

Thus, replacing p above with e_s (the saturation vapor pressure), the slope of the Clausius–Clapeyron curve is defined by

$$\frac{de_s}{dT} = \frac{\delta s}{\delta \alpha} = \frac{\text{entropy gained per kg from condensed to vapor}}{\text{volume increase per kg from condensed to vapor}} \quad (1.47)$$

Since enthalpy $l_c = T\delta s$, it follows that we can substitute for δs in eq. (1.47) as follows:

$$\frac{de_s}{dT} = \frac{l_c}{T\delta \alpha} = \frac{l_c}{T(\alpha_{\text{vapor}} - \alpha_{\text{condensed}})} \approx \frac{l_c}{T\alpha_{\text{vapor}}}$$

The specific volume of vapor is much larger than the specific volume of the condensed phase ($\alpha_{\text{vapor}} \gg \alpha_{\text{condensed}}$),

so we can ignore the latter. By substituting $\alpha_{\text{vapor}} = R_c T / e_s$, where R_c is the specific gas constant for the condensable species vapor, we obtain

$$\frac{de_s}{dT} = \frac{l_c e_s}{R_c T^2}, \quad \text{or} \quad \frac{d(\ln e_s)}{dT} = \frac{l_c}{R_c T^2} \quad (1.48)$$

This equation is a differential form of the *Clausius–Clapeyron equation*. We can also obtain an integral form by integrating from a reference temperature T_0 to temperature T , to give saturation vapor pressure as a function of temperature:

$$e_s(T) = e_s(T_0) \exp\left(\int_{T_0}^T \frac{l_c}{R_c} \frac{dT}{T^2}\right) \approx e_s(T_0) \exp\left[\frac{l_c}{R_c} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{1.49}$$

The second expression in eq. (1.49) is approximate because l_c changes slightly with temperature.

What are some properties of the Clausius–Clapeyron equation? Applied to water vapor over liquid water, we take $T_0 = 273.15$ K and $e_s(T_0) = 611$ Pa; $R_c = 461$ J K⁻¹ kg⁻¹ is the gas constant and $l_c = 2.5 \times 10^6$ J kg⁻¹ is the specific enthalpy of vaporization for water. We find that SVP roughly doubles for every 10 K temperature rise. The exponential form of eq. (1.49) indicates that SVP is very sensitive to temperature. Noting that $R_c = km_c$, and given that exponents are additive, we deduce from eq. (1.49) that $e_s \propto \exp(-m_c l_c / kT)$. This is a Boltzmann equation, which gives us the insight that the numerator in the exponent is the energy required to free a water molecule from its neighbors while the denominator is the average molecular energy.

For some bodies, the Clausius–Clapeyron equation gives direct insight into the entire atmosphere. On Mars, CO₂ condenses on the cold poles at a temperature ~148 K, which corresponds to a CO₂ SVP of ~600 Pa. This pressure is the typical surface air pressure on Mars. Consequently, Mars’ CO₂ ice caps may be buffered at a temperature near 148 K (Leighton and Murray, 1966). On Pluto and Triton, the atmospheric pressure is just the SVP of N₂ over N₂ ice at temperatures of 38 K and ~40 K, respectively (Brown and Ziegler, 1979; Lellouch *et al.*, 2011b; Zalucha *et al.*, 2011). Perhaps on some hot exoplanets, rock-vapor atmospheres are similarly in equilibrium with molten surfaces.

To consider the effect of condensable species on atmospheric temperatures, we define the volume mixing ratio, f_c , of the condensable species according to eq. (1.4),

$$f_c = \frac{n_c}{n} = \frac{e_c}{p}$$

where the n s are number densities, e_c is the partial pressure of the condensable species, and p is the total pressure. Similarly, we define a mass mixing ratio by eq. (1.5) as:

$$\mu_{cm} = \epsilon f_c = \epsilon \frac{e_c}{p}, \quad \text{where } \epsilon = \frac{m_c}{\bar{m}} = \frac{\text{molecular mass of condensable}}{\text{mean molecular mass of air}} \approx \frac{m_c}{m_d} \tag{1.50}$$

For water vapor in Earth’s atmosphere, $\epsilon = 0.622$. We can also define saturation mixing ratios as

$$f_{cs} = \frac{e_s(T)}{p}, \quad \mu_{cms} = \epsilon \frac{e_s(T)}{p} \tag{1.51}$$

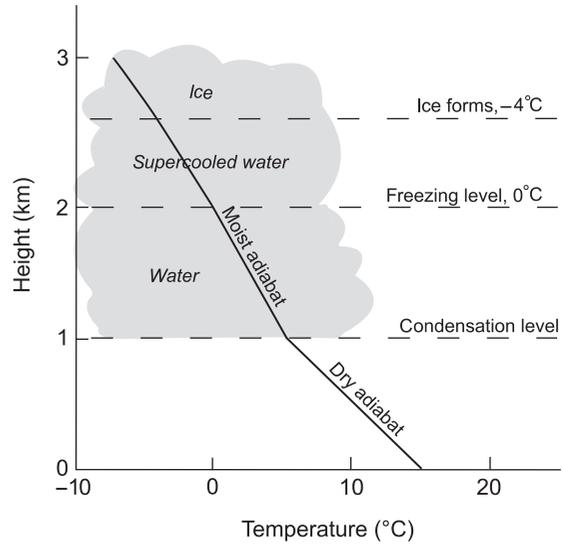


Figure 1.10 A rising air parcel and the lifting condensation level, which forms the base of cloud at 1 km altitude. The cloud is shown schematically as the shaded region.

Now consider a parcel that rises adiabatically from the surface, which is at pressure p_{ref} and temperature T_{ref} . In the adiabatic parcel, potential temperature θ starts out as T_{ref} and remains constant at T_{ref} , while the actual temperature will fall via eq. (1.30) as $T = T_{ref}(p/p_{ref})^\kappa$, or equivalently, $p = p_{ref}(T/T_{ref})^{1/\kappa}$. Substituting for p in eq. (1.50), where e_{parcel} is the partial pressure of the condensable, gives

$$e_{parcel}(T) = \frac{p \mu_{cm}}{\epsilon} \Rightarrow e_{parcel}(T) = \frac{\mu_{cm} p_{ref}}{\epsilon} \left(\frac{T}{T_{ref}}\right)^{1/\kappa} \tag{1.52}$$

The parcel behaves as dry air until it reaches the SVP temperature, when $e_{parcel} = e_s$, at an altitude called the *lifting condensation level*. After this point, cloud particles form from the condensable and the parcel is warmed. Instead of the temperature dropping at the dry adiabatic lapse rate, the temperature drops less sharply with altitude at a *saturated adiabatic lapse rate* on the SVP curve (Fig. 1.10).

SVP also gives us general insight into the formation of clouds (Fig. 1.11). On average, clouds will tend to form where the mean temperature–pressure conditions reach the SVP for particular condensable species (Sanchez-Lavega *et al.*, 2004).

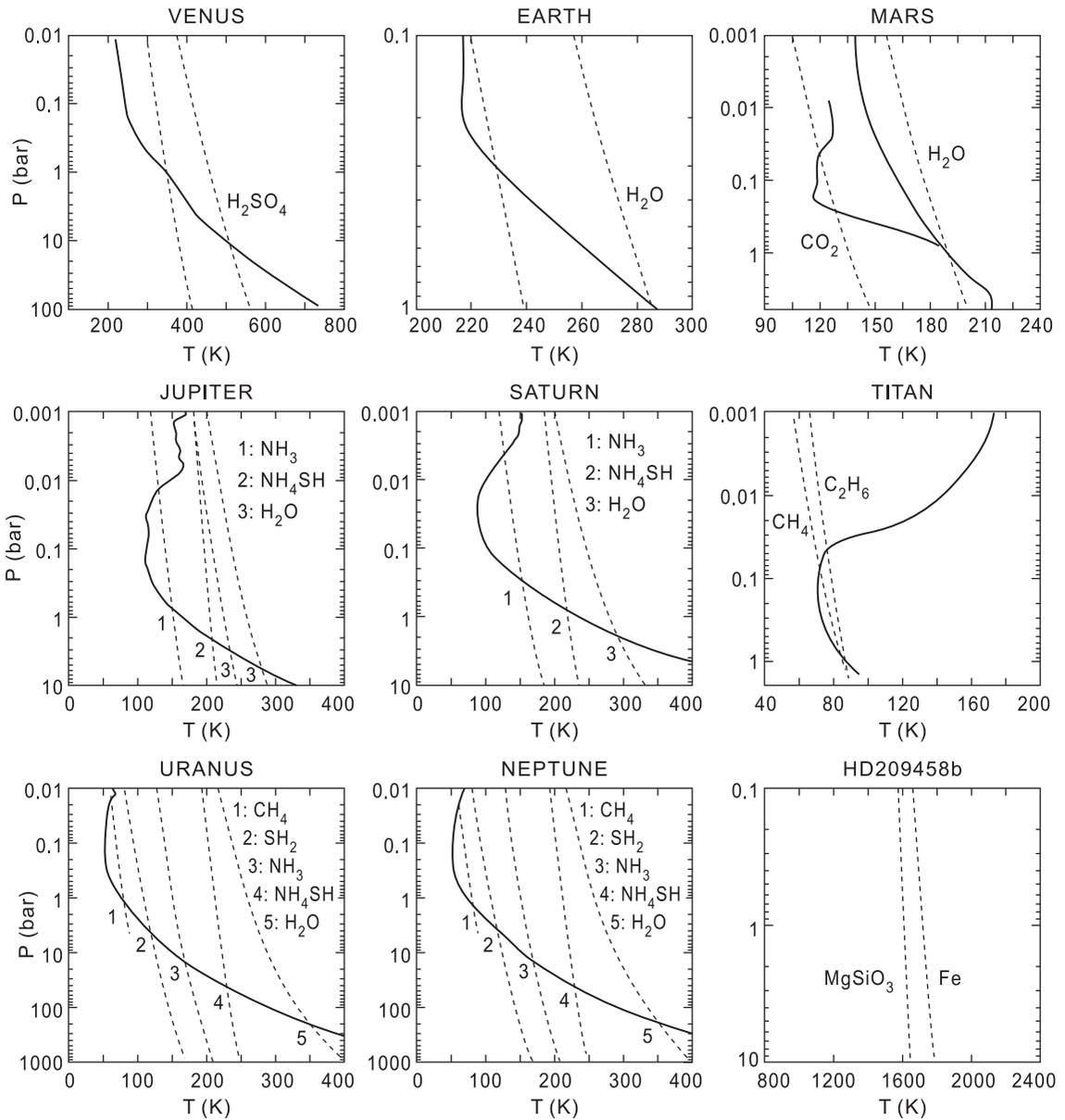


Figure 1.11 Use of vapor pressure and saturation vapor pressure (SVP) to predict cloud formation in Solar System atmospheres and hot Jupiter HD209458b. The solid line is the typical vertical profile of pressure (p) versus temperature (T). For Mars, an annual average p - T profile is shown as well as a colder profile. Dashed lines are the SVP curves for various condensables, assuming a fixed volume mixing ratio of the condensable. It is assumed that particles condense when the partial pressure (e) reaches the saturation vapor pressure (e_s), i.e., where $e = f_c p(T) \geq e_s(T)$, where f_c is the volume mixing ratio of the condensable. Thus, the base of clouds are marked where a dashed line crosses the solid p - T profile. Below this level, the phase is vapor because the ambient air is too hot. Mixing ratios are assumed to calculate the dashed curves: Venus 2 ppm and 2000 ppm H_2SO_4 (where liquid clouds form); Earth 250 ppm and 1.5% H_2O , giving ice and liquid clouds, respectively; Mars 0.95% CO_2 and 300 ppm H_2O giving ice clouds; Jupiter 200 ppm NH_3 , 36 ppm NH_4SH , 50 ppm H_2O , 0.17% H_2O giving solid phase clouds except for the higher water level; Saturn 200 ppm NH_3 , 36 ppm NH_4SH , 0.17% H_2O , giving solid particles; Titan 5% CH_4 , 10 ppm C_2H_6 , giving solid particles; Uranus and Neptune 2% CH_4 , 37 ppm SH_2 , 200 ppm NH_3 , 36 ppm NH_4SH , 0.17% H_2O , giving solid particles; HD209458b 75 ppm $MgSiO_3$ and 68 ppm Fe , giving solid particles. (From Sanchez-Lavega *et al.* (2004) Reproduced with permission. Copyright 2004 American Astronomical Society of Chicago, Physica Scripta 2019, 043) subject to the Cambridge Core terms of use, available at <https://www.cambridge.org/core/terms>. <https://doi.org/10.1017/9781139020558.002>

1.1.3.6 The Saturated Adiabatic Lapse Rate (SALR)

The saturated (or “moist”) adiabatic lapse rate occurs when chilled moist air is held at saturation by warming associated with continual condensation of excess vapor. Textbooks and papers commonly talk of “release of latent heat,” which has been criticized as obscuring the physics (Bohren and Albrecht, 1998, p. 290). Condensation is a warming process because as water vapor molecules approach within a few molecular diameters of liquid water they are attracted to it and increase their kinetic energy.

Recall the equation used in deriving the adiabatic lapse rate in Sec. 1.1.3.1 for a unit mass air parcel,

$$dq = c_p dT + g dz$$

For present purposes, we consider the specific heat capacity c_p , to be that for an air–water vapor mixture. If mass $\delta\mu_{cms}$ condenses then $dq = -l_c \delta\mu_{cms}$, from the definition of the enthalpy (“latent heat”) of phase change. Hence, substitution for dq in the above equation gives,

$$l_c \delta\mu_{cms} + c_p dT + g dz = 0 \tag{1.53}$$

At saturation, the condensable species’ mass mixing ratio is equal to the saturation mass mixing ratio given by eq. (1.51), $\mu_{cms} = \epsilon e_s / p$. Taking logs and differentiating (1.51),

$$\frac{\delta\mu_{cms}}{\mu_{cms}} = \frac{\delta e_s}{e_s} + \frac{\delta\epsilon}{\epsilon} - \frac{\delta p}{p} \tag{1.54}$$

Now, $\delta e_s = (de_s/dT)\delta T$ and from eq. (1.48), $(1/e_s)(de_s/dT) = l_c / (R_c T^2)$. Also $\delta p/p = -g\delta z / (\bar{R}T)$ from the hydrostatic equation (1.10). Putting all of these in eq. (1.54) gives

$$\frac{\delta\mu_{cms}}{\mu_{cms}} = \frac{l_c \delta T}{R_c T^2} + \frac{g \delta z}{\bar{R}T} \tag{1.55}$$

We can substitute $\delta\mu_{cms}$ from (1.55) into eq. (1.53), as follows,

$$c_p \delta T + g dz + l_c \mu_{cms} \left(\frac{l_c \delta T}{R_c T^2} + \frac{g \delta z}{\bar{R}T} \right) = 0$$

$$\Rightarrow \delta T c_p \left(1 + \frac{l_c^2 \mu_{cms}}{c_p R_c T^2} \right) + g \delta z \left(1 + \frac{l_c \mu_{cms}}{\bar{R}T} \right) = 0$$

If we now divide through by δz and rearrange we get

$$\Gamma_{sa} \equiv \text{saturated adiabatic lapse rate (SALR)} = - \left(\frac{dT}{dz} \right)_{sa} = \frac{g}{c_p} \frac{\left(1 + \frac{l_c \mu_{cms}}{\bar{R}T} \right)}{\left(1 + \frac{l_c^2 \mu_{cms}}{c_p R_c T^2} \right)} \tag{1.56}$$

This equation does not allow for the precipitation, suspension or further phase change of the condensate and so is only approximate. However, the mass of the condensate is usually small compared to the gas phase. This lapse rate is also called the *pseudo-adiabatic lapse rate* if condensates are assumed to fall out of the parcel. Static stability is controlled by Γ_{sa} under saturated conditions, i.e., saturated air is stable if $\Gamma < \Gamma_{sa}$. Indeed, in Earth’s tropics, data indicate that moist convection controls static stability up to ~ 0.4 bar (Zelinka and Hartmann, 2011). On Earth, in warm humid air near the ground, $\Gamma_{sa} \approx 4 \text{ K km}^{-1}$, whereas $\Gamma_{sa} \approx 6\text{--}7 \text{ K km}^{-1}$ in the middle troposphere, and Γ_{sa} is close to dry adiabatic near the top of the troposphere where the air is cold and dry.

The assumption that the condensable mass mixing ratio is small enough that we can ignore the condensate is not true for CO₂ on Mars or for H₂O in a runaway greenhouse atmosphere. Also the neglect of precipitation is violated by rain on Earth. Additional limits are as follows. (1) That phase change is an equilibrium process, which should not be true for the partitioning of spin isomers of H₂ in giant planet atmospheres. Hydrogen has *ortho*- and *para*-hydrogen forms where the spins of the two atomic nuclei in the molecule are parallel (*ortho*) or antiparallel (*para*). Exothermic conversion of *ortho*- to *para*-hydrogen increases the temperature of an air parcel and is analogous to latent heat release from condensation. (2) That the latent heat of condensation is approximately constant, which is true for most compounds only over a narrow temperature range. More general formulations of the moist adiabatic lapse rate for major constituent condensation are given by Ingersoll (1969) and Kasting (1988, 1991).

1.2 Condensable Species on Terrestrial-Type Planets

Below we discuss CO₂–H₂O atmospheres. The more exotic atmosphere of Titan, the largest moon of Saturn, has methane as a condensable. Methane rainfall and clouds on Titan are discussed in Sec. 14.4.

1.2.1 Pure Water Atmospheres

We can gain some insight into the behavior of condensable volatiles by thinking about idealized atmospheres.

For example, consider a “water world,” with water as the sole volatile. We imagine an atmosphere consisting of water vapor as the only contributor to the surface pressure, which, for the sake of argument, we take as 10^4 Pa (100 mbar). One might imagine a gas giant exoplanet that has migrated inward toward its parent star so that an ice-covered satellite orbiting the gas giant now resides where sunlight melts its surface. In Fig. 1.12, suppose a parcel of pure water vapor starts at point A with $T = 340$ K and $p = 10^4$ Pa. The parcel is cooled and follows the path A to B, given that the pressure, which is just the weight of atmosphere above, remains constant. At point B, however, the parcel is at the saturation vapor pressure and so the pure water vapor atmosphere will condense into droplets and precipitate. With further cooling, the parcel would follow the line of stability between the liquid and gas phases, until the triple point is reached, whereupon solid precipitates. Further cooling beyond the freezing point would result in equilibrium between gas and solid phases, at least locally. The pressure does not drop this way in Earth’s polar atmosphere in wintertime, where the pressure–temperature combination (10^5 Pa and $T < 0^\circ\text{C}$) lies within the solid phase part of the H_2O phase diagram, because Earth’s atmosphere is not pure water, so even if virtually all H_2O is removed, N_2 , O_2 , Ar, and the other gases maintain a pressure far above the saturation vapor curve. (Note that the freezing point of water is weakly dependent on pressure: 273.16 K and 273.15 K ($\equiv 0^\circ\text{C}$) at 10^5 Pa.)

1.2.2 Atmospheres with Multiple Condensable Species

Let us now consider another hypothetical planetary atmosphere with a mixture of CO_2 , Ar, and H_2O gases. We take 10^3 Pa = 10 mbar as the (Mars-like) total pressure on this planet, which is the sum of the partial pressure of all gases. Now imagine that we cool a parcel of air that starts at an initial temperature of 340 K (Fig. 1.12). Water condenses at the point where the partial pressure contributed by the water vapor reaches the saturation vapor pressure. Subsequently, the partial pressure contributed by water vapor is fixed in equilibrium with liquid water and then ice at colder temperatures. The water partial pressure is small so the total pressure becomes $\approx P_{\text{CO}_2} + P_{\text{Ar}}$. With further cooling, eventually the CO_2 solid–gas phase boundary is reached and CO_2 will begin to precipitate. Locally, the CO_2 partial pressure will fall to a level supported by the solid–gas equilibrium at the local surface temperature. The total pressure will now be P_{Ar}

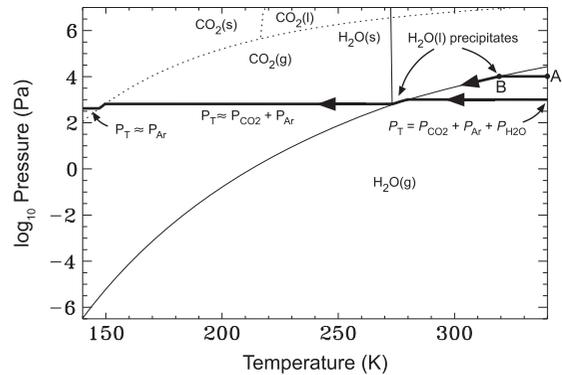


Figure 1.12 Phase diagram of H_2O (solid lines) and CO_2 (dashed). The path from A to B and then along the saturation vapor pressure curve is for cooling a pure H_2O atmosphere starting at a total pressure of 10^4 Pa and temperature of 340 K. The lower path is for a hypothetical Ar– CO_2 – H_2O atmosphere starting at the same temperature and a total pressure P_T of 10^3 Pa. As the mixture is cooled, liquid water condenses when the vapor pressure becomes equal to the saturation vapor pressure. At cooler temperatures, CO_2 ice condenses until the only volatile purely in the gas phase is Ar. (Following a concept from Mutch *et al.* (1976).)

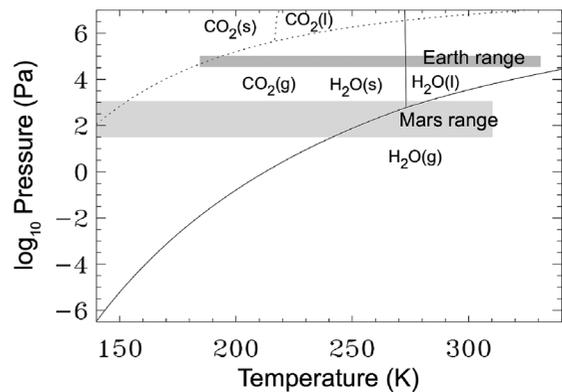


Figure 1.13 Phase boundaries for pure H_2O (solid lines) and CO_2 (dashed). Shaded areas show the range of total surface pressure and temperature on Earth and Mars. Earth’s surface falls below 190 K in Antarctica but CO_2 does not condense because the CO_2 partial pressure of ~ 40 Pa is far below the $\sim 10^5$ Pa CO_2 saturation pressure at such temperatures. In contrast, the Martian atmosphere consists of 96% CO_2 , so CO_2 condenses at the Martian poles. (From Jacob (1999). Reproduced with permission. Copyright 1999, Princeton University Press.)

plus the solid–gas vapor equilibrium of CO_2 at the prevailing surface temperature.

We can apply these ideas to planets. Figure 1.13 shows a plot of the saturation vapor pressure for water and CO_2 . Boxes indicate the range of temperatures and pressures on the surface of Earth and Mars. The “Mars range” box shows that generally the equilibrium for water

is between ice and vapor, while CO_2 condenses at the poles, represented by the top left-hand corner of the box. After N_2 , argon is the second most abundant non-condensable gas on Mars. Analogous to Fig. 1.12, enriched atmospheric Ar has been detected during southern winter as CO_2 frost forms (Sprague *et al.*, 2004; Sprague *et al.*, 2007). This was done using a Gamma-Ray-Spectrometer (GRS) on *Mars Odyssey*. Gamma rays are emitted from ^{41}Ar decay, which is created from neutron capture by atmospheric ^{40}Ar .

1.2.3 Water in the Present-Day Martian Atmosphere

Figure 1.14 shows an expanded pure water phase diagram and limits of pressure and temperature on Mars. The spatially and seasonally averaged surface atmospheric pressure on Mars is ~ 600 Pa (6 mbar), but in low-lying regions such as the Hellas basin, the atmospheric pressure exceeds 1200 Pa. The *boiling point* of a liquid is the temperature at which the saturation vapor pressure equals the total external pressure regardless of the source of that external pressure. For example at 283 K, the saturation vapor pressure of water is ~ 1200 Pa (Fig. 1.14). At this temperature, liquid water will be stable against boiling if the total pressure against it is 1200 Pa or more, even if some gas other than H_2O , such as CO_2 or N_2 , supplies the external pressure. Thus, in principle, liquid water is thermodynamically possible on Mars today in very low-lying locations.

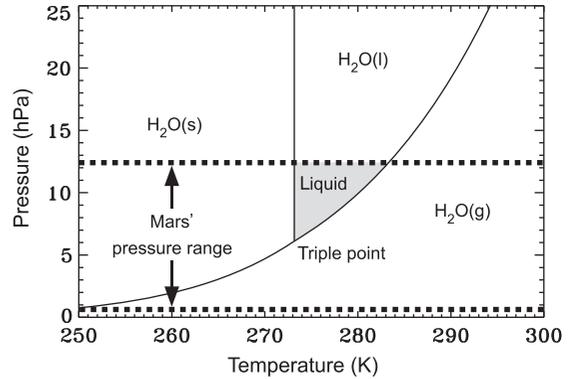


Figure 1.14 Pure phase water diagram showing the range of surface pressures on Mars from the top of Olympus Mons (< 0.5 hPa) to the depths of Hellas basin (> 12 hPa). Liquid water is stable on Mars against boiling in the shaded zone but not against rapid evaporation.

However, such liquid water would not be stable over time against evaporation, which occurs when the actual vapor pressure in the air is less than the vapor pressure of the liquid water. This is generally true on both Earth and Mars, i.e., liquid water evaporates. However, evaporation rates for Mars are very high (Ingersoll, 1970) so liquid water is unlikely to persist (Hecht, 2002). One caveat is that water that is very salty can have a lower vapor pressure and would be more stable against evaporation on Mars. In addition, certain salts can depress the freezing point far below 0°C (see Table 12.9).