2

Atmospheric structure, composition, and thermodynamics

The atmosphere contains a few highly concentrated gases, such as nitrogen, oxygen, and argon, and many trace gases, among them water vapor, carbon dioxide, methane, and ozone. All such gases are constituents of air. Important characteristics of air are its pressure, density, and temperature. These parameters vary with altitude, latitude, longitude, and season and are related to each other by the equation of state. Two other fundamental equations applicable to the atmosphere are the Clausius–Clapeyron equation and the first law of thermodynamics. The Clausius–Clapeyron equation relates temperature to the quantity of water vapor over a surface at saturation. The first law of thermodynamics relates the temperature change of a gas to energy transfer and the change in work. In this chapter, atmospheric variables and gases are discussed, and basic equations describing atmospheric physics and thermodynamics are introduced.

2.1 PRESSURE, DENSITY, AND COMPOSITION

In the Earth's atmosphere, air density, pressure, and temperature change with altitude. **Air density** is the mass of air per unit volume of air, where the mass of air is summed over all gases, aerosol particles, and hydrometeor particles. Since the mass concentration of gas in the air is 500 times that of hydrometeor particles in the thickest cloud and ten million times that of aerosol particles in polluted air (Table 13.1), air density is accurately determined from the mass of gas only. Air density decreases exponentially with altitude, as shown in Fig. 2.1(a). Air density is the greatest near the surface since atmospheric mass is concentrated near the surface.

Air pressure is ideally the weight (force) of air above a horizontal plane, divided by the area of the plane. This type of air pressure is called **hydrostatic air pressure**, which is the pressure due solely to the weight of air in a column above a given altitude. The term **hydrostatic** means "fluid at rest." Air pressure is hydrostatic only if air is not accelerating vertically, which occurs either if it is at rest or if it has a constant vertical speed. The assumption that air pressure is hydrostatic is reasonable when air pressure is averaged over a large horizontal area (>2–3 km in diameter) and outside of a storm system, since vertical accelerations in such cases are generally small. Over small areas (<2–3 km in diameter) and in individual clouds, vertical accelerations can be large. When air accelerates vertically, air pressure is nonhydrostatic. **Nonhydrostatic air pressure** is discussed in Section 5.1.3.

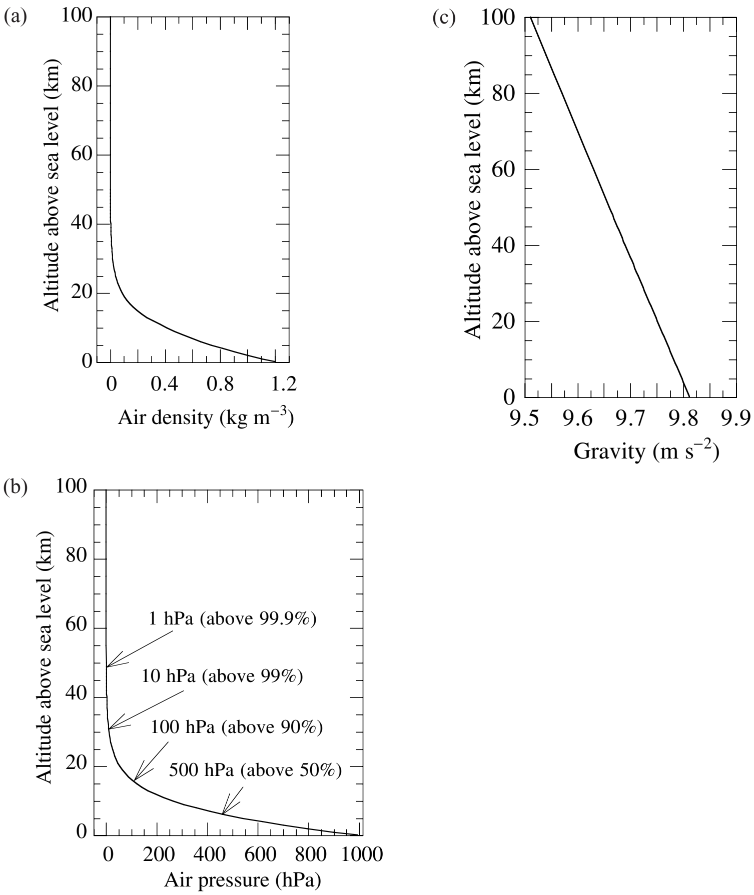

Figure 2.1 Variation of (a) air density, (b) air pressure, and (c) gravitational acceleration versus altitude in the Earth's lower atmosphere. The pressure diagram shows that 99.9 percent of the atmosphere lies below an altitude of about 48 km (1 hPa), and 50 percent lies below about 5.5 km (500 hPa).

Hydrostatic air pressure at any altitude z (m) above sea level is found by integrating the product of air density and gravity from the top of the atmosphere to altitude z with

$$p_a(z) = \int_z^\infty \rho_a(z) g(z) \mathrm{d}z \tag{2.1}$$

where $p_a(z)$ is air pressure as a function of altitude (pascal, where 1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2} = 0.01 hPa = 0.01 millibar or mb), $\rho_a(z)$ is air density as a function of altitude (kg m^{-3}) from Fig. 2.1(a), and $g(z)$ is gravitational acceleration (m s^{-2}). Alternative units for air pressure are given in Appendix Table A.6. Figures 2.1(b) and (c) show variations in pressure and gravitational acceleration, respectively, with altitude in the atmosphere. Tabulated values of these variables are given in Appendix Table B.1.

Table 2.1 Average composition of the lowest 100 km in the Earth's atmosphere

	Volume mixing ratio	
Gas	**(percent)**	**(ppmv)**
Fixed gases		
Nitrogen (N_2)	78.08	780 000
Oxygen (O_2)	20.95	209 500
Argon (Ar)	0.93	9 300
Neon (Ne)	0.0015	15
Helium (He)	0.0005	5
Krypton (Kr)	0.0001	1
Xenon (Xe)	0.000005	0.05
Variable gases		
Water vapor (H_2O)	0.00001–4.0	0.1–40 000
Carbon dioxide (CO_2)	0.0375	375
Methane (CH_4)	0.00017	1.8
Ozone (O_3)	0.000003–0.001	0.03–10

Figure 2.1(b) shows that, as altitude (z) increases, air pressure decreases exponentially. Air pressure decreases with increasing altitude because less air lies above a higher altitude than a lower altitude. Air pressure decreases exponentially with increasing altitude because density, used to derive pressure, decreases exponentially with increasing altitude (Fig. 2.1(a)).

Figure 2.1(b) also shows that 50 percent of atmospheric mass lies between sea level and 5.5 km. About 99.9 percent of mass lies below about 48 km. The Earth's radius is approximately 6370 km. Thus, almost all of Earth's atmosphere lies in a layer thinner than 1 percent of the radius of the Earth.

Standard sea-level surface pressure is 1013 hPa (or 1013 mb or 760 mm Hg). The sea-level pressure at a given location and time typically varies by +10 to −20 hPa from standard sea-level pressure. In a strong low-pressure system, such as at the center of a hurricane, the actual sea-level pressure may be more than 50 hPa lower than standard sea-level pressure. At the surface of the Earth, which averages 231.4 m above sea level globally, gravitational acceleration is 9.8060 $\text{m}\,\text{s}^{-2}$. Gravitational acceleration is discussed further in Section 4.2.3.

2.1.1 Fixed gases

Table 2.1 gives the basic composition of the bottom 100 km of the Earth's atmosphere, called the **homosphere**. In this region, the primary gases are molecular nitrogen (N_2) and molecular oxygen (O_2), which together make up over 99 percent of all air molecules. Argon (Ar), a chemically inert gas, makes up most of the remaining 1 percent. Nitrogen, oxygen, and argon are **fixed gases** in that their **volume mixing ratios** (number of molecules of each gas divided by the total number of molecules of dry air) do not change substantially in time or space. Fixed gases are well mixed in the homosphere. At any given altitude, oxygen makes up about

20.95 percent and nitrogen makes up about 78.08 percent of all non-water gas molecules by volume (23.17 and 75.55 percent, respectively, by mass).

2.1.1.1 *Molecular nitrogen*

Gas-phase molecular nitrogen (N_2) is produced biologically in soils by **denitrification**, a two-step process carried out by denitrifying bacteria in **anaerobic** (oxygen-depleted) soils. In the first step, the bacteria reduce the nitrate ion (NO_3^-) to the nitrite ion (NO_2^-). In the second, they reduce the nitrite ion to molecular nitrogen and some nitrous oxide gas (N_2O).

Molecular nitrogen is removed from the air by **nitrogen fixation**. This process is carried out by bacteria, such as *Rhizobium*, *Azotobacter*, and *Beijerinckia*, in **aerobic** (oxygen-rich) environments, and produces the ammonium ion (NH_4^+). Ammonium in soils is also produced by the bacterial decomposition of organic matter during **ammonification**. Fertilizer application also adds ammonium to soils.

The ammonium ion regenerates the nitrate ion in soils during **nitrification**, which is a two-step aerobic process. In the first step, nitrosofying (nitrite-forming) bacteria produce nitrite from ammonium. In the second step, nitrifying (nitrate-forming) bacteria produce nitrate from nitrite.

Because N_2 does not react significantly in the atmosphere and because its removal by nitrogen fixation is slower than its production by denitrification, its atmospheric concentration has built up over time.

2.1.1.2 *Molecular oxygen*

Gas-phase molecular oxygen is produced by **green-plant photosynthesis**, which occurs when carbon dioxide gas (CO_2) reacts with water (H_2O) in the presence of sunlight and green-pigmented **chlorophylls**. Chlorophylls exist in plants, trees, blue-green algae, and certain bacteria. They appear green because they absorb red and blue wavelengths of visible light and reflect green wavelengths. Products of photosynthesis reactions are carbohydrates and molecular oxygen gas. One photosynthetic reaction is

$$6CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2 \tag{2.2}$$

where $h\nu$ is a photon of radiation, and $C_6H_{12}O_6$ is glucose. Some bacteria that live in anaerobic environments photosynthesize carbon dioxide with hydrogen sulfide (H_2S) instead of with water to produce organic material and elemental sulfur (S). This type of photosynthesis is **anoxygenic photosynthesis** and predates the onset of green-plant photosynthesis.

2.1.1.3 *Argon and others*

Argon is a noble gas that is colorless and odorless. Like other noble gases, argon is inert and does not react chemically. It forms from the radioactive decay of potassium. Other fixed but inert gases present in trace concentrations are neon (Ne), helium (He), krypton (Kr), and xenon (Xe). The source of helium, krypton, and xenon is radioactive decay of elements in the Earth's crust, and the source of neon is volcanic outgassing. The mixing ratios of these gases are given in Table 2.1.

2.1.2 Variable gases

Gases in the atmosphere whose volume mixing ratios change significantly in time and space are **variable gases**. Thousands of variable gases are present in the atmosphere. Several dozen are very important. Four of these, water vapor, carbon dioxide, methane (CH_4), and ozone (O_3), are discussed below.

2.1.2.1 *Water vapor*

Major sources of **water vapor** to the air are evaporation from soils, lakes, streams, rivers, and oceans, sublimation from glaciers, sea ice, and snow packs, and **transpiration** from plant leaves. Water vapor is also produced during fuel combustion and many gas-phase chemical reactions. Approximately 85 percent of water in the atmosphere originates from ocean surface evaporation. Sinks of water vapor are condensation to the liquid phase, ice deposition to the solid phase, transfer to the ocean and other surfaces, and gas-phase chemical reaction. The mixing ratio of water vapor varies with location. When temperatures are low, water vapor readily condenses as a liquid or deposits as ice, so its gas-phase mixing ratio is low. Over the North and South Poles, water vapor mixing ratios are almost zero. When temperatures are high, liquid water readily evaporates and ice readily sublimates to the gas phase, so water vapor mixing ratios are high. Over equatorial waters, where temperatures are high and evaporation from ocean surfaces occurs readily, the atmosphere contains up to 4 percent or more water vapor by volume. Water vapor is not only a **greenhouse gas** (a gas that readily absorbs thermal-infrared radiation), but also a chemical reactant and carrier of latent heat.

2.1.2.2 *Carbon dioxide*

Carbon dioxide gas is produced by cellular respiration in plants and trees, biological decomposition of dead organic matter, evaporation from the oceans, volcanic outgassing, and fossil-fuel combustion. **Cellular respiration** occurs when oxygen reacts with carbohydrates in the presence of enzymes in living cells to produce CO_2, H_2O, and energy. The reverse of (2.2) is a cellular respiration reaction. **Biological decomposition** occurs when bacteria and other organisms convert dead organic matter to CO_2 and H_2O.

Like water vapor, CO_2 is a greenhouse gas. Unlike water vapor, CO_2 does not react chemically in the atmosphere. Its lifetime against chemical destruction is approximately 100–200 years. CO_2 is removed more readily by green-plant

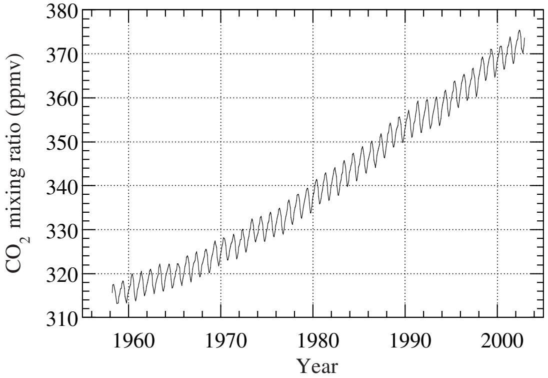

Figure 2.2 Yearly and seasonal fluctuations in CO_2 mixing ratio since 1958. Data from C. D. Keeling at the Mauna Loa Observatory, Hawaii.

photosynthesis and dissolution into ocean water and raindrops. These processes reduce its overall lifetime in the air to 30–95 years.

Average global CO_2 mixing ratios have increased from approximately 275 parts per million by volume (ppmv) in the mid 1700s to approximately 375 ppmv in 2004. Figure 2.2 shows how observed CO_2 mixing ratios have increased steadily since 1958. The yearly increases are due to increased rates of CO_2 emission from fossil-fuel combustion. The seasonal fluctuation in CO_2 mixing ratio is due to photosynthesis and biological decomposition. When annual plants grow in the spring and summer, they remove CO_2 from air by photosynthesis. When they die in the fall and winter, they return CO_2 by biological decomposition.

2.1.2.3 *Methane*

Methane, the main component of natural gas, is a variable gas. It is produced in anaerobic environments, where methane-producing bacteria (methanogens) consume organic material and excrete methane. Ripe anaerobic environments include rice paddies, landfills, wetlands, and the digestive tracts of cattle, sheep, and termites. Methane is also produced in the ground from the decomposition of fossilized carbon. This methane often leaks to the atmosphere or is harnessed and used as a source of energy. Additional methane is produced from biomass burning and as a by-product of atmospheric chemical reaction. Sinks of methane include slow chemical reaction and dry deposition. Methane's mixing ratio in the lower atmosphere is near 1.8 ppmv, which is an increase from about 0.7 ppmv in the mid 1700s. Its mixing ratio has increased steadily due to increased farming and landfill usage. Methane is important because it is a greenhouse gas that absorbs infrared radiation emitted by the Earth 21 times more efficiently, molecule for molecule, than does carbon dioxide. Mixing ratios of carbon dioxide, however, are much larger than are those of methane.

2.1.2.4 *Ozone*

Ozone is a trace gas formed by photochemical reaction and is not emitted into the atmosphere. In the stratosphere, it is produced following photolysis of molecular oxygen. Near the surface of Earth, it is produced following photolysis of nitrogen dioxide (NO_2). Photolysis of molecular oxygen does not occur near the surface, since the wavelengths of radiation required to break apart oxygen are absorbed by molecular oxygen and ozone in the upper atmosphere. In urban regions, ozone production is enhanced by organic gases. Typical ozone mixing ratios in urban air, rural surface air, and stratospheric air are 0.1, 0.04, and 10 ppmv, respectively. Thus, ozone's mixing ratios are the highest in the **stratosphere**, the location of which is shown in Fig. 2.4 (Section 2.2.2.1).

2.2 TEMPERATURE STRUCTURE

Temperature is a measure of the kinetic energy of an air molecule. At a given temperature, the speeds at which air molecules travel are distributed statistically about a Maxwellian distribution. From this distribution, one can define an **average thermal speed** ($\bar{v}_a$), a **root-mean-square speed** (v_{rms}), and a **most probable speed** (v_p) of an air molecule (m s^{-1}). These speeds are related to absolute temperature (T, K) by

$$\boxed{\bar{v}_a = \sqrt{\frac{8k_B T}{\pi \bar{M}}} \qquad v_{rms} = \sqrt{\frac{3k_B T}{\bar{M}}} \qquad v_p = \sqrt{\frac{2k_B T}{\bar{M}}} \qquad (2.3)}$$

respectively, where k_B is **Boltzmann's constant** (1.380658×10^{-23} kg m^2 s^{-2} K^{-1} molec.$^{-1}$; alternative units are given in Appendix A) and $\bar{M}$ is the average mass of one air molecule (4.8096×10^{-26} kg molec.$^{-1}$). Equation (2.3) can be rewritten as

$$\frac{4}{\pi}k_B T = \frac{1}{2}\bar{M}\bar{v}_a^2 \qquad \frac{3}{2}k_B T = \frac{1}{2}\bar{M}v_{rms}^2 \qquad k_B T = \frac{1}{2}\bar{M}v_p^2 \qquad (2.4)$$

The right side of each equation in (2.4) is kinetic energy. When defined in terms of $\bar{v}_a$, temperature is proportional to the kinetic energy of an air molecule traveling at its average speed. When defined in terms of v_{rms}, temperature is proportional to the average kinetic energy among all air molecules since v_{rms}^2 is determined by summing the squares of all individual speeds then dividing by the total number of speeds. When defined in terms of v_p, temperature is proportional to the kinetic energy of an air molecule traveling at its most probable speed. In this text, temperature is defined in terms of $\bar{v}_a$.

Example 2.1

What is the average thermal speed, the root-mean-square speed, and the most probable speed of an air molecule when $T = 300$ K? What about at 200 K? Although these speeds are faster than those of an airplane, why do air molecules hardly move relative to airplanes over the same time increment?

SOLUTION

At 300 K, $\bar{v}_a = 468.3\ \text{m s}^{-1}$ ($1685\ \text{km hr}^{-1}$), $v_{\text{rms}} = 508.3\ \text{m s}^{-1}$, and $v_p = 415.0\ \text{m s}^{-1}$. At 200 K, $\bar{v}_a = 382.4\ \text{m s}^{-1}$ ($1376\ \text{km hr}^{-1}$), $v_{\text{rms}} = 415.0\ \text{m s}^{-1}$, and $v_p = 338.9\ \text{m s}^{-1}$. Although air molecules move quickly, they continuously collide with and are redirected by other air molecules, so their net migration rate is slow, particularly in the lower atmosphere. Airplanes, on the other hand are not redirected when they collide with air molecules.

The bottom 100 km of Earth's atmosphere, the **homosphere**, is the lower atmosphere and is divided into four major regions in which temperature changes with altitude. These are, from bottom to top, the **troposphere**, **stratosphere**, **mesosphere**, and **thermosphere**. The troposphere is divided into the **boundary layer**, which is the region from the surface to about 500–3000-m altitude, and the **free troposphere**, which is the rest of the troposphere.

2.2.1 Boundary layer

The **boundary layer** is the portion of the troposphere influenced by the Earth's surface and that responds to surface forcing with a time scale of about an hour or less (Stull 1988). The free troposphere is influenced by the boundary layer, but on a longer time scale. Temperature varies significantly in the boundary layer during the day and between day and night. Variations are weaker in the free troposphere. Temperatures in the boundary are affected by the specific heats of soil and air and by energy transfer processes, such as conduction, radiation, mechanical turbulence, thermal turbulence, and advection. These factors are described below.

2.2.1.1 *Specific heat*

Specific heat capacity (specific heat, for short) is the energy required to increase the temperature of 1 gram of a substance 1 degree Celsius (°C). Soil has a lower specific heat than has liquid water. During the day, the addition of a fixed amount of sunlight increases soil temperature more than it increases water temperature. At night, emission of a fixed amount of infrared radiation decreases soil temperature more than it decreases water temperature. Thus, between day and night, soil temperature varies more than does water temperature.

Table 2.2 Specific heats and thermal conductivities of four media

Substance	**Specific heat ($\mathrm{J\ kg^{-1}\ K^{-1}}$)**	**Thermal conductivity at 298 K ($\mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}}$)**
Dry air at constant pressure	1004.67	0.0256
Liquid water	4185.5	0.6
Clay	1360	0.920
Dry sand	827	0.298

Specific heat varies not only between land and water, but also among soil types. Table 2.2 shows that the specific heat of clay is greater than is that of sand, and the specific heat of liquid water is greater than is that of clay or sand. If all else is the same, sandy soil heats to a higher temperature than does clay soil, and dry soil heats to a higher temperature than does wet soil during the day. Dry, sandy soils cool to a greater extent than do wet, clayey soils at night.

2.2.1.2 *Conduction*

Specific heat is a property of a material that affects its temperature change. Temperature is also affected by processes that transfer energy within or between materials. One such process is conduction. **Conduction** is the passage of energy from one molecule to the next in a medium (the conductor). The medium, as a whole, experiences no molecular movement. Conduction occurs through soil, air, and particles. Conduction affects ground temperature by transferring energy between the soil surface and bottom molecular layers of the atmosphere, and between the soil surface and molecules of soil just below the surface. The rate of a material's conduction is determined by its **thermal conductivity**, which quantifies the rate of flow of thermal energy through a material in the presence of a temperature gradient. Empirical expressions for the **thermal conductivities of dry air and water vapor** ($\mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}}$) are

$$\kappa_\mathrm{d} \approx 0.023807 + 7.1128 \times 10^{-5}(T - 273.15) \tag{2.5}$$

$$\kappa_\mathrm{v} \approx 0.015606 + 8.3680 \times 10^{-5}(T - 273.15) \tag{2.6}$$

respectively, which are used in an interpolation equation to give the **thermal conductivity of moist air** (dry air plus water vapor)

$$\boxed{\kappa_\mathrm{a} \approx \kappa_\mathrm{d}\left[1 - \left(1.17 - 1.02\frac{\kappa_\mathrm{v}}{\kappa_\mathrm{d}}\right)\frac{n_\mathrm{v}}{n_\mathrm{v} + n_\mathrm{d}}\right]} \tag{2.7}$$

(Pruppacher and Klett 1997). Here, n_v and n_d are the number of moles of water vapor and dry air, respectively, and T is temperature (K). Under atmospheric conditions, the thermal conductivity of moist air is not much different from that of dry air. Table 2.2 shows that liquid water, clay, and dry sand are more conductive than is dry air. Clay is more conductive and dry sand is less conductive than is liquid water.

The flux of energy through the atmosphere due to conduction can be estimated with the **conductive heat flux equation**,

$$H_c = -\kappa_a \frac{\Delta T}{\Delta z} \tag{2.8}$$

(W m^{-2}), where ΔT (K) is the change in temperature over an incremental height Δz (m). Adjacent to the ground, molecules of soil, water, and other surface elements transfer energy by conduction to molecules of air overlying the surface. Since the temperature gradient ($\Delta T/\Delta z$) between the surface and a thin (e.g., 1 mm) layer of air just above the surface is large, the conductive heat flux at the ground is large. Above the ground, temperature gradients are small, and the conductive heat flux is much smaller than at the ground.

Example 2.2

Find the conductive heat flux through a 1-mm thin layer of air touching the surface if $T = 298$ K, $\Delta T = -12$ K, and assuming the air is dry. Do a similar calculation for the free troposphere, where $T = 273$ K and $\Delta T/\Delta z = -6.5$ K km^{-1}.

SOLUTION

Near the surface, $\kappa_a \approx \kappa_d = 0.0256$ J m^{-1} s^{-1} K^{-1}, giving a conductive heat flux of $H_c = 307$ W m^{-2}. In the free troposphere, $\kappa_a \approx \kappa_d = 0.0238$ J m^{-1} s^{-1} K^{-1}, giving $H_c = 1.5 \times 10^{-4}$ W m^{-2}. Thus, heat conduction through the air is important only at the ground.

2.2.1.3 *Radiation*

Radiation is the transfer of energy by electromagnetic waves, which do not require a medium, such as air, for their transmission. **Solar radiation** is relatively short-wavelength radiation emitted by the Sun. **Thermal-infrared radiation** is relatively long-wavelength radiation emitted by the Earth, atmosphere, and clouds. The Earth's surface receives solar radiation during the day only, but its surface and atmosphere emit thermal-infrared radiation during day and night. Radiation is an important energy transfer process and is discussed in Chapter 9.

2.2.1.4 *Mechanical turbulence and forced convection*

Convection is a predominantly vertical motion that results in the transport and mixing of atmospheric properties. **Forced convection** is vertical motion produced by mechanical means, such as mechanical turbulence. **Mechanical turbulence** arises when winds travel over objects protruding from a surface, producing swirling motions of air, or eddies. **Turbulence** is the effect of groups of eddies of different size. Turbulence mixes energy and other variables vertically and horizontally. Strong winds produce strong eddies and turbulence. Turbulence from wind-generated eddies is mechanical turbulence.

When mechanical turbulence is the dominant process of vertical motion in the boundary layer, the boundary layer is in a state of forced convection. Mechanical turbulence is only one type of forced convection; forced convection also occurs when air rises along a topographical barrier or weather front, or when horizontal winds converge and rise.

2.2.1.5 *Thermal turbulence and free convection*

Free convection is a predominantly vertical motion produced by buoyancy. The boundary layer is in a state of free convection when thermal turbulence is the dominant process of vertical motion. **Thermal turbulence** occurs when the Sun heats the ground differentially, creating thermals. Differential heating occurs because clouds or hills block the sun in some areas but not in others or because different surfaces lie at different angles. **Thermals** are parcels of air that rise buoyantly, generally over land during the day. When the Sun heats the ground, conduction transfers energy from the ground to molecules of air adjacent to the ground. The warmed air above the ground rises buoyantly and expands. Cooler air from nearby is drawn in near the surface to replace the rising air. The cooler air heats by conduction and rises.

Free convection differs from conduction in that free convection is the mass movement of air molecules containing energy due to density difference, and conduction is the transfer of energy from molecule to molecule. Free convection occurs most readily over land when the sky is cloud-free and winds are light.

2.2.1.6 *Advection and other factors*

Advection is the horizontal propagation of the mean wind. Horizontal winds advect energy spatially just as they advect gases and particles. Advection is responsible for transferring energy on small and large scales. Other processes that affect temperature in the boundary layer are emissivity, albedo, pressure systems, and length of day.

Emissivity is the ratio of the radiation emitted by an object to the radiation emitted by a perfect emitter. Sand has an emissivity of 0.84–0.91, and clay has an emissivity of 0.9–0.98. The higher its emissivity, the faster a surface, such as soil, cools at night. **Albedo** (or reflectivity) is the ratio of reflected radiation to incident radiation. For dry sand, the albedo varies from 20 to 40 percent. For clay, it varies from 5 to 20 percent. Thus, sand reflects more solar radiation during the day and emits less infrared radiation at night than does clay, counteracting some of the effects of the low specific heat and thermal conductivity of sand.

Large-scale pressure systems also affect temperatures in the boundary layer. Within a large-scale **high-pressure system**, air descends and warms, often on top of cooler surface air, creating an **inversion**, which is an increase in temperature with

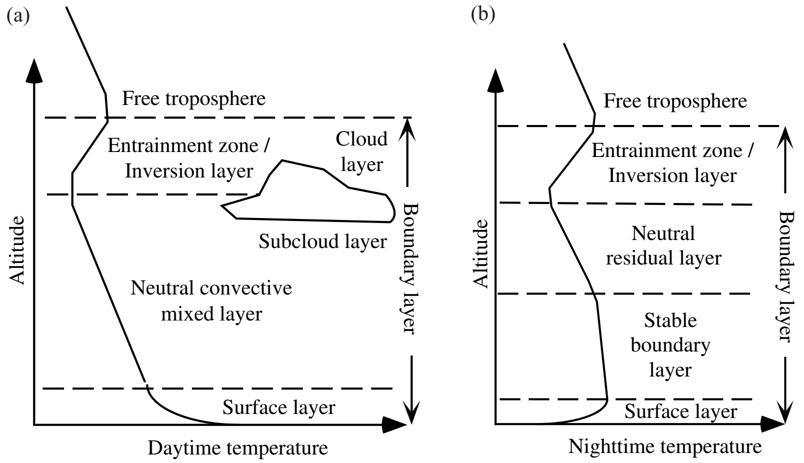

Figure 2.3 Variation of temperature with height during the (a) day and (b) night in the atmospheric boundary layer over land under a high-pressure system. Adapted from Stull (1988).

increasing height. An inversion associated with a large-scale pressure system is a **large-scale subsidence inversion**. As air warms when it sinks in a subsidence inversion, it evaporates clouds, increasing the sunlight reaching the ground, increasing ground temperature. Within a large-scale **low-pressure system**, air rises and cools, often creating clouds and decreasing sunlight reaching the surface.

Temperature is also affected by length of day. Longer days produce longer periods of surface heating by sunlight, and longer nights produce longer periods of cooling due to lack of sunlight and continuous thermal-infrared emission.

2.2.1.7 *Boundary-layer characteristics*

Figures 2.3(a) and (b) show idealized temperature variations in the boundary layer over land during the day and night, respectively, under a high-pressure system. During the day, the boundary layer consists of a surface layer, a convective mixed layer, and an entrainment zone. The **surface layer** is a region of strong wind shear that comprises the bottom 10 percent of the boundary layer. Since the boundary-layer depth ranges from 500 to 3000 m, the surface layer is about 50–300 m thick.

Over land during the day, temperature decreases rapidly with increasing altitude in the surface layer but less so in the mixed layer. In the surface layer, the strong temperature gradient is caused by rapid solar heating of the ground. The temperature gradient is usually so strong that air adjacent to the ground buoyantly rises and accelerates into the mixed layer. The atmosphere is called **unstably stratified** when it exhibits the strong decrease in temperature with increasing height required for air parcels to rise and accelerate buoyantly.

In the mixed layer, the temperature gradient is not strong enough to allow unrestrained convection but not weak enough to prevent some convection. Under such a condition, the atmosphere is **neutrally stratified**, and parcels of air can mix up or down but do not accelerate in either direction.

When a high-pressure system is present, a large-scale subsidence inversion resides above the mixed layer. Environments in which temperatures increase with increasing height (an inversion) or slightly decrease with increasing height are **stably stratified**. Thermals originating in the surface layer or mixed layer cannot easily penetrate buoyantly through an inversion. Some mixing (entrainment) between an inversion layer and mixed layer always occurs; thus, the inversion layer is also called an **entrainment zone**.

Other features of the daytime boundary layer are the cloud layer and subcloud layer. A region in which clouds appear in the boundary layer is the **cloud layer**, and the region underneath is the **subcloud layer**. A cloud forms if rising air in a thermal cools sufficiently. An inversion may prevent a cloud from rising past the mixed layer.

During the night, the surface cools radiatively, causing temperature to increase with increasing height from the ground, creating a surface inversion. Eventual cooling at the top of the surface layer cools the bottom of the mixed layer, increasing the stability of the mixed layer at its base. The portion of the daytime mixed layer that is stable at night is the **stable (nocturnal) boundary layer**. The remaining portion of the mixed layer, which stays neutrally stratified, is the **residual layer**. Because thermals do not form at night, the residual layer does not undergo significant change, except at its base. At night, the nocturnal boundary layer grows, eroding the base of the residual layer. The top of the residual layer is not affected by this growth.

Over the ocean, the boundary layer is influenced more by large-scale pressure systems than by thermal or mechanical turbulence. Since water temperature does not change significantly during the day, thermal turbulence over the ocean is not so important as over land. Since the ocean surface is relatively smooth, mechanical turbulence is also weaker than over land. Large-scale high-pressure systems still cause subsidence inversions to form over the ocean.

2.2.2 Free atmosphere

2.2.2.1 *Troposphere*

The free troposphere lies above the boundary layer. Figure 2.4 shows a standard profile of the temperature structure of the lower atmosphere, ignoring the boundary layer. The **troposphere**, which is the bottom layer of the lower atmosphere, is the region extending from the surface in which the temperature, on average, decreases with increasing altitude. The average rate of temperature decrease in the free troposphere (above the boundary layer) is about 6.5 K km^{-1}.

The temperature decreases with increasing altitude in the free troposphere for the following simplified reason: Earth's surface receives energy from the Sun daily, heating the ground. Simultaneously, the top of the troposphere continuously radiates energy upward, cooling the upper troposphere. The troposphere, itself, has relatively little capacity to absorb solar energy; thus, it relies on radiative, turbulent,

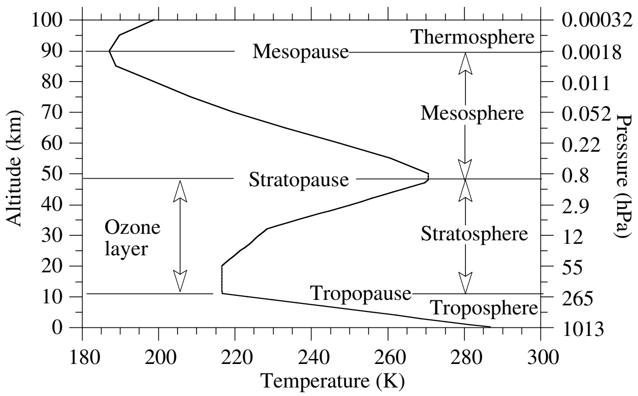

Figure 2.4 Temperature structure of the Earth's lower atmosphere, ignoring the boundary layer.

and conductive energy transfer from the ground to maintain its temperature. The most important of these transfer processes is (thermal-infrared) radiation transfer, followed by turbulence, then conduction. The last two processes transfer energy to the boundary layer only. Thermal-infrared radiation emitted by the ground is absorbed by selective gases in the air, including water vapor and carbon dioxide. These and other gases are most concentrated near the surface, thus they have the first opportunity to absorb the radiation. Once they absorb the radiation, they reemit half of it upward and the other half downward, but their emission is at a lower temperature than is the emission of the radiation they absorbed. The lower the temperature of radiant emission, the less intense the emission. Thus, not only does less thermal-infrared radiation penetrate to higher than to lower altitudes, but the radiation that does penetrate is less intense than at lower altitudes. Because less radiation is available for absorption with increasing altitude, temperatures decrease with increasing altitude in the troposphere.

Figures 2.5(a) and (b) show global latitude–altitude contour plots of zonally averaged temperatures for a generic January and July, respectively. A **zonally averaged** temperature is found from a set of temperatures, averaged over all longitudes at a given latitude and altitude. The figures indicate that near-surface tropospheric temperatures decrease from the Equator to high latitudes, which is expected, since the Earth receives the greatest quantity of incident solar radiation near the Equator.

The **tropopause** is the upper boundary of the troposphere. It is defined by the World Meteorological Organization (WMO) as the lowest altitude at which the lapse rate (rate of decrease of temperature with increasing height) decreases to 2 K km^{-1} or less, and at which the lapse rate, averaged between this altitude and any altitude within the next 2 km, does not exceed 2 K km^{-1}. Above the tropopause base, the temperature is relatively constant with increasing altitude (**isothermal**) before it increases with increasing height in the stratosphere.

Figures 2.5(a) and (b) indicate that the tropopause height decreases from 15–18 km near the Equator to 8 km near the poles. Because temperature decreases with increasing height in the troposphere, and because tropopause height is higher

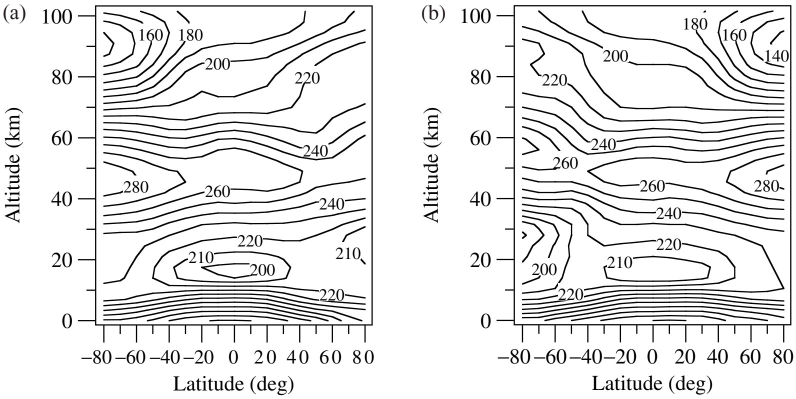

Figure 2.5 Zonally and monthly averaged temperatures for (a) January and (b) July. Data for the plots were compiled by Fleming *et al.* (1988).

over the Equator than over the poles, temperature decreases to a lower value over the Equator than over the poles. As a result, minimum tropopause temperatures occur over equatorial regions, as shown in Figs. 2.5(a) and (b). Tropopause heights are the highest over the Equator because strong vertical motions over the Equator raise the base of the ozone layer and force ozone to spread horizontally to higher latitudes. Since ozone is responsible for warming above the tropopause, pushing ozone to a greater height increases the altitude at which warming begins. Near the poles, downward motion pushes ozone downward. The resulting latitudinal gradient of the ozone-layer base decreases the tropopause height from the Equator to the poles.

Tropopause temperature is also affected by water vapor. Water vapor absorbs the Earth's thermal-infrared radiation, preventing some of it from reaching the tropopause. Water-vapor mixing ratios are much higher over the Equator than over the poles. The high mixing ratios near the surface over the Equator enhance cooling of the tropopause above.

2.2.2.2 *Stratosphere*

The stratosphere is a region of the atmosphere above the troposphere that contains 90 percent of the Earth's ozone and in which temperature increases with increasing height. The temperature profile in the stratosphere is caused by ozone interactions with radiation, discussed below.

Ozone is produced when molecular oxygen absorbs ultraviolet radiation and photodissociates by the reactions,

$$\mathrm{O_2} + h\nu \rightarrow \dot{\mathrm{O}}\cdot(^1D) + \dot{\mathrm{O}}\cdot \qquad \lambda < 175\,\mathrm{nm} \tag{2.9}$$

$$\mathrm{O_2} + h\nu \rightarrow \dot{\mathrm{O}}\cdot + \dot{\mathrm{O}}\cdot \qquad 175 < \lambda < 245\,\mathrm{nm} \tag{2.10}$$

where $h\nu$ is a photon of radiation, $\mathrm{O}(^1D)$ is excited atomic oxygen, O [$=\mathrm{O}(^3P)$] is ground state atomic oxygen, the dots identify the valence of an atom (Chapter 10), and λ is a wavelength of radiation affecting the reaction. $O(^1D)$ produced from (2.9) rapidly converts to O via

$$\cdot\dot{O}(^1D) + M \rightarrow \cdot\dot{O} + M \tag{2.11}$$

where M provides collisional energy for the reaction, but is not created or destroyed by it. Because N_2 and O_2 are the most abundant gases in the air, M is most likely N_2 or O_2, although it can be another gas. The most important reaction creating ozone is

$$\dot{O}\cdot + O_2 + M \rightarrow O_3 + M \tag{2.12}$$

where M, in this case, carries away energy released by the reaction.

Ozone in the stratosphere is destroyed naturally by the photolysis reactions,

$$O_3 + h\nu \rightarrow O_2 + \cdot\dot{O}(^1D) \qquad \lambda < 310\,\text{nm} \tag{2.13}$$

$$O_3 + h\nu \rightarrow O_2 + \dot{O}\cdot \qquad \lambda > 310\,\text{nm} \tag{2.14}$$

and the two-body reaction

$$\dot{O}\cdot + O_3 \rightarrow 2O_2 \tag{2.15}$$

Chapman (1930) postulated that the reactions (2.10), (2.12), (2.14), and (2.15), together with

$$\dot{O}\cdot + \dot{O}\cdot + M \rightarrow O_2 + M \tag{2.16}$$

describe the natural formation and destruction of ozone in the stratosphere. These reactions make up the **Chapman cycle**, and they simulate the process fairly well. Some Chapman reactions are more important than others. The reactions (2.10), (2.12), and (2.14) affect ozone most significantly. The non-Chapman reaction, (2.13), is also important.

The peak ozone density in the atmosphere occurs at about 25–32 km (Chapter 11, Fig. 11.3). The reason is that ozone forms most readily when sufficient oxygen and ultraviolet radiation are present to produce atomic oxygen through reactions (2.9) and (2.10). Since oxygen density, like air density, decreases exponentially with increasing altitude, and since ultraviolet radiation intensity increases with increasing altitude (because radiation attenuates as it passes through the atmosphere), an altitude exists at which the quantities of radiation and oxygen are optimal for producing an ozone maximum. This altitude is between 25 and 32 km. At higher altitudes, the oxygen density is too low to produce peak ozone, and at lower altitudes, the radiation is not intense enough to photodissociate enough oxygen to produce peak ozone.

Peak stratospheric temperatures occur at the top of the stratosphere, because this is the altitude at which ozone absorbs the shortest ultraviolet wavelengths reaching the stratosphere (about 0.175 μm). Although the concentration of ozone at the top of the stratosphere is small, each molecule there can absorb short wavelengths, increasing the average kinetic energy and temperature of all molecules. In the lower stratosphere, short wavelengths do not penetrate, and temperatures are lower than in the upper stratosphere.

2.2.2.3 *Mesosphere*

In the **mesosphere**, ozone densities are too low for ozone to absorb radiation and affect temperatures. As such, temperatures decrease with increasing altitude in a manner similar to in the upper troposphere.

2.2.2.4 *Thermosphere*

In the **thermosphere**, temperatures increase with increasing altitude because molecular oxygen and nitrogen there absorb very short wavelengths of solar radiation. Air in the thermosphere does not *feel* hot to the skin, because the thermosphere contains so few gas molecules. But each gas molecule in the thermosphere is highly energized, so the average temperature is high. Direct sunlight in the thermosphere is more intense and damaging than at the surface. Because oxygen and nitrogen absorb the shortest wavelengths of radiation in the thermosphere, such wavelengths do not penetrate to the mesopause.

2.3 EQUATION OF STATE

The **equation of state** describes the relationship among pressure, volume, and absolute temperature of a real gas. The **ideal gas law** describes this relationship for an ideal gas. An ideal gas is a gas for which the product of the pressure and volume is proportional to the absolute temperature. A real gas is ideal only to the extent that intermolecular forces are small, which occurs when pressures are low enough or temperatures are high enough for the gas to be sufficiently dilute. Under typical atmospheric temperature and pressure conditions, the ideal gas law gives an error of less than 0.2 percent for dry air and water vapor in comparison with an expanded equation of state (Pruppacher and Klett 1997). Thus, the ideal gas law can reasonably approximate the equation of state.

The **ideal gas law** is expressed as a combination of Boyle's law, Charles' law, and Avogadro's law. In 1661, Robert Boyle (1627–1691) found that doubling the pressure exerted on a gas at constant temperature reduced the volume of the gas by one-half. This relationship is embodied in **Boyle's law**,

$$p \propto \frac{1}{V} \quad \text{atconstant temperature} \tag{2.17}$$

where p is the pressure exerted on the gas (hPa), and V is the volume enclosed by the gas (m^3 or cm^3). Boyle's law describes the compressibility of a gas. When high pressure is exerted on a gas, as in the lower atmosphere, the gas compresses (its volume decreases) until it exerts an equal pressure on its surroundings. When low pressure is exerted on a gas, as in the upper atmosphere, the gas expands until it exerts an equal pressure on its surroundings.

In 1787, Jacques Charles (1746–1823) found that increasing the absolute temperature of a gas at constant pressure increased the volume of the gas. This relationship is embodied in **Charles' law**,

$$V \propto T \quad \text{at constant pressure} \tag{2.18}$$

where T is the temperature of the gas (K). Charles' law states that, at constant pressure, the volume of a gas must decrease when its temperature decreases. Since gases change phase to liquids or solids before 0 K, Charles' law cannot be extrapolated to 0 K.

Amedeo Avogadro (1776–1856) hypothesized that equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules. In other words, the volume of a gas is proportional to the number of molecules of gas present and independent of the type of gas. This relationship is embodied in **Avogadro's law**,

$$V \propto n \quad \text{at constant pressure and temperature} \tag{2.19}$$

where n is the number of gas moles. The number of molecules in a mole is constant for all gases and given by **Avogadro's number**, $A = 6.0221367 \times 10^{23}$ molec. mol^{-1}.

Combining Boyle's law, Charles' law, and Avogadro's law gives the **ideal gas law** or **simplified equation of state** as

$$\boxed{p = \frac{nR^*T}{V} = \frac{nA}{V}\left(\frac{R^*}{A}\right)T = Nk_B T} \tag{2.20}$$

where R^* is the **universal gas constant** (0.0831451 m^3 hPa mol^{-1} K^{-1} or 8.31451×10^4 cm^3 hPa mol^{-1} K^{-1}), $N = nA/V$ is the number concentration of gas molecules (molecules of gas per cubic meter or cubic centimeter of air), and $k_B = R^*/A$ is **Boltzmann's constant** in units of 1.380658×10^{-25} m^3 hPa K^{-1} molec.$^{-1}$ or 1.380658×10^{-19} cm^3 hPa K^{-1} molec.$^{-1}$. Appendix A contains alternative units for R^* and k_B.

Example 2.3

Calculate the number concentration of air molecules in the atmosphere at standard sea-level pressure and temperature and at a pressure of 1 hPa.

SOLUTION

At standard sea level, $p = 1013$ hPa and $T = 288$ K. Thus, from (2.20), $N = 2.55 \times 10^{19}$ molec. cm^{-3}. From Fig. 2.1(b), $p = 1$ hPa occurs at 48 km. At this altitude and pressure, $T = 270$ K, as shown in Fig. 2.4. Under such conditions, $N = 2.68 \times 10^{16}$ molec. cm^{-3}.

Equation (2.20) can be used to relate the partial pressure exerted by a gas to its number concentration. In 1803, John Dalton (1766–1844) stated that total atmospheric pressure equals the sum of the partial pressures of the individual gases in a mixture. This is **Dalton's law of partial pressure**. The **partial pressure** exerted by a gas in a mixture is the pressure the gas exerts if it alone occupies the same volume as the mixture. Mathematically, the partial pressure of gas q is

$$p_q = N_q k_\mathrm{B} T \tag{2.21}$$

where N_q is the number concentration of the gas (molec. cm^{-3}). Total atmospheric pressure is

$$p_\mathrm{a} = \sum_q p_q = k_\mathrm{B} T \sum_q N_q = N_\mathrm{a} k_\mathrm{B} T \tag{2.22}$$

where N_a is the number concentration of the air, determined as the sum of the number concentrations of individual gases.

Total atmospheric pressure can also be written as $p_\mathrm{a} = p_\mathrm{d} + p_\mathrm{v}$, where p_d is the partial pressure exerted by dry air, and p_v is the partial pressure exerted by water vapor. Similarly, the number concentration of air molecules can be written as $N_\mathrm{a} = N_\mathrm{d} + N_\mathrm{v}$, where N_d is the number concentration of dry air, and N_v is the number concentration of water vapor.

Dry air consists of all gases in the atmosphere, except water vapor. Table 2.1 shows that together, N_2, O_2, Ar, and CO_2 constitute 99.996 percent of dry air by volume. The concentrations of all gases aside from these four can be ignored, without much loss in accuracy, when dry-air pressure is calculated. This assumption is convenient in that the concentrations of most trace gases vary in time and space.

Partial pressure is related to the mass density and number concentration of dry air through the **equation of state for dry air,**

$$\boxed{p_\mathrm{d} = \frac{n_\mathrm{d} R^* T}{V} = \frac{n_\mathrm{d} m_\mathrm{d}}{V}\left(\frac{R^*}{m_\mathrm{d}}\right)T = \rho_\mathrm{d} R' T = \frac{n_\mathrm{d} A}{V}\left(\frac{R^*}{A}\right)T = N_\mathrm{d} k_\mathrm{B} T \qquad (2.23)}$$

where p_d is dry-air partial pressure (hPa), n_d is the number of moles of dry air, m_d is the molecular weight of dry air, ρ_d is the mass density of dry air (kg m^{-3} or g cm^{-3}), and R' is the gas constant for dry air. The **molecular weight of dry air** is a volume-weighted average of the molecular weights of N_2, O_2, Ar, and CO_2. The standard value of m_d is 28.966 g mol^{-1}. The dry-air mass density, number concentration, and gas constant are, respectively,

$$\rho_\mathrm{d} = \frac{n_\mathrm{d} m_\mathrm{d}}{V} \qquad N_\mathrm{d} = \frac{n_\mathrm{d} A}{V} \qquad R' = \frac{R^*}{m_\mathrm{d}} \tag{2.24}$$

where R' has a value of 2.8704 m^3 hPa kg^{-1} K^{-1} or 2870.3 cm^3 hPa g^{-1} K^{-1}. Alternative units for R' are given in Appendix A.

Example 2.4

When $p_d = 1013$ hPa and $T = 288$ K, the density of dry air from (2.23) is $\rho_d = 1.23$ kg m^{-3}.

The **equation of state for water vapor** is

$$\boxed{p_v = \frac{n_v R^* T}{V} = \frac{n_v m_v}{V}\left(\frac{R^*}{m_v}\right)T = \rho_v R_v T = \frac{n_v A}{V}\left(\frac{R^*}{A}\right)T = N_v k_B T \quad (2.25)}$$

where p_v is the partial pressure exerted by water vapor (hPa), n_v is the number of moles of water vapor, m_v is the molecular weight of water vapor, ρ_v is the mass density of water vapor (kg m^{-3} or g cm^{-3}), and R_v is the gas constant for water vapor (4.6140 m^3 hPa kg^{-1} K^{-1} or 4614.0 cm ^{3} hPa g^{-1} K^{-1}). Alternative units for R_v are given in Appendix A. The water-vapor mass density, number concentration, and gas constant are, respectively,

$$\rho_v = \frac{n_v m_v}{V} \qquad N_v = \frac{n_v A}{V} \qquad R_v = \frac{R^*}{m_v} \tag{2.26}$$

Example 2.5

When $p_v = 10$ hPa and $T = 298$ K, water vapor density from (2.21) is $\rho_v = 7.27 \times 10^{-3}$ kg m^{-3}.

The equation of state for water vapor can be rewritten in terms of the dry-air gas constant as

$$p_v = \rho_v R_v T = \rho_v\left(\frac{R_v}{R'}\right)R'T = \frac{\rho_v R'T}{\varepsilon} \tag{2.27}$$

where

$$\varepsilon = \frac{R'}{R_v} = \frac{R^*}{m_d}\left(\frac{m_v}{R^*}\right) = \frac{m_v}{m_d} = 0.622 \tag{2.28}$$

The number concentration of a gas (molecules per unit volume of air) is an absolute quantity. The abundance of a gas may also be expressed in terms of a relative quantity, **volume mixing ratio**, defined as the number of gas molecules per molecule of dry air, and expressed for gas q as

$$\chi_q = \frac{N_q}{N_d} = \frac{p_q}{p_d} = \frac{n_q}{n_d} \tag{2.29}$$

where N_q, p_q, and n_q are the number concentration, partial pressure, and number of moles of gas q, respectively. Another relative quantity, mass mixing ratio, is the mass of gas per mass of dry air. The **mass mixing ratio** of gas q (kilograms of gas per kilogram of dry air) is

$$\omega_q = \frac{\rho_q}{\rho_d} = \frac{m_q N_q}{m_d N_d} = \frac{m_q p_q}{m_d p_d} = \frac{m_q n_q}{m_d n_d} = \frac{m_q}{m_d}\chi_q \tag{2.30}$$

where ρ_q is the mass density (kg m^{-3}) and m_q is the molecular weight of gas q (g mol^{-1}). Volume and mass mixing ratios may be multiplied by 10^6 and expressed in **parts per million by volume** (ppmv) or **parts per million by mass** (ppmm), respectively.

Example 2.6

Find the mass mixing ratio, number concentration, and partial pressure of ozone if its volume mixing ratio in an urban air parcel is $\chi_q = 0.10$ ppmv. Assume $T = 288$ K and $p_d = 1013$ hPa.

SOLUTION

The molecular weight of ozone is $m_q = 48.0$ g mol^{-1}, and the molecular weight of dry air is $m_d = 28.966$ g mol^{-1}. From (2.30), the mass mixing ratio of ozone is $\omega_q = 48.0$ g mol^{-1} × 0.10 ppmv/28.966 g mol^{-1} = 0.17 ppmm. From Example 2.3, $N_d = 2.55 \times 10^{19}$ molec. cm^{-3}. Thus, from (2.29), the number concentration of ozone is $N_q = 0.10$ ppmv $\times 10^{-6} \times 2.55 \times 10^{19}$ molec. cm^{-3} $= 2.55 \times 10^{12}$ molec. cm^{-3}. From (2.21), the partial pressure exerted by ozone is $p_q = 0.000101$ hPa.

Combining (2.28) and (2.30) gives the **mass mixing ratio of water vapor** (kilograms of water vapor per kilogram of dry air) as

$$\omega_v = \frac{\rho_v}{\rho_d} = \frac{m_v p_v}{m_d p_d} = \varepsilon\frac{p_v}{p_d} = \frac{\varepsilon p_v}{p_a - p_v} = \varepsilon\chi_v \tag{2.31}$$

Example 2.7

If the partial pressure exerted by water vapor is $p_v = 10$ hPa, and the total air pressure is $p_a = 1010$ hPa, the mass mixing ratio of water vapor from (2.31) is $\omega_v = 0.00622$ kg kg^{-1}.

Water vapor can also be expressed in terms of relative humidity, discussed in Section 2.5, or **specific humidity**. The mass of any substance per unit mass of moist air (dry air plus water vapor) is the **moist-air mass mixing ratio** (q). Specific humidity is the moist-air mass mixing ratio of water vapor (mass of water vapor per unit mass of moist air). An expression for specific humidity (kilograms of water vapor per kilogram of moist air) is

$$\mathrm{q_v} = \frac{\rho_\mathrm{v}}{\rho_\mathrm{a}} = \frac{\rho_\mathrm{v}}{\rho_\mathrm{d} + \rho_\mathrm{v}} = \frac{\dfrac{p_\mathrm{v}}{R_\mathrm{v}T}}{\dfrac{p_\mathrm{d}}{R'T} + \dfrac{p_\mathrm{v}}{R_\mathrm{v}T}} = \frac{\dfrac{R'}{R_\mathrm{v}}p_\mathrm{v}}{p_\mathrm{d} + \dfrac{R'}{R_\mathrm{v}}p_\mathrm{v}} = \frac{\varepsilon p_\mathrm{v}}{p_\mathrm{d} + \varepsilon p_\mathrm{v}} \tag{2.32}$$

where $\rho_\mathrm{a} = \rho_\mathrm{d} + \rho_\mathrm{v}$ is the **mass density of moist air.** Specific humidity is related to the mass mixing ratio of water vapor by

$$\mathrm{q_v} = \omega_\mathrm{v}\frac{\rho_\mathrm{d}}{\rho_\mathrm{a}} = \frac{\omega_\mathrm{v}}{1 + \omega_\mathrm{v}} \tag{2.33}$$

Example 2.8

If $p_\mathrm{v} = 10$ hPa and $p_\mathrm{a} = 1010$ hPa, $p_\mathrm{a} = p_\mathrm{d} + p_\mathrm{v}$ gives $p_\mathrm{d} = 1000$ hPa. Under such conditions, (2.32) gives the specific humidity as $\mathrm{q_v} = 0.00618\ \mathrm{kg\ kg^{-1}}$.

The **equation of state for moist air** is the sum of the equations of state for dry air and water vapor. Thus,

$$p_\mathrm{a} = p_\mathrm{d} + p_\mathrm{v} = \rho_\mathrm{d}R'T + \rho_\mathrm{v}R_\mathrm{v}T = \rho_\mathrm{a}R'T\frac{\rho_\mathrm{d} + \rho_\mathrm{v}R_\mathrm{v}/R'}{\rho_\mathrm{a}} \tag{2.34}$$

Substituting $\varepsilon = R'/R_\mathrm{v}$, $\rho_\mathrm{a} = \rho_\mathrm{d} + \rho_\mathrm{v}$, and $\omega_\mathrm{v} = \rho_\mathrm{v}/\rho_\mathrm{d}$ into (2.34) yields the equation of state for moist air as

$$p_\mathrm{a} = \rho_\mathrm{a}R'T\frac{\rho_\mathrm{d} + \rho_\mathrm{v}/\varepsilon}{\rho_\mathrm{d} + \rho_\mathrm{v}} = \rho_\mathrm{a}R'T\frac{1 + \rho_\mathrm{v}/(\rho_\mathrm{d}\varepsilon)}{1 + \rho_\mathrm{v}/\rho_\mathrm{d}} = \rho_\mathrm{a}R'T\frac{1 + \omega_\mathrm{v}/\varepsilon}{1 + \omega_\mathrm{v}} \tag{2.35}$$

This equation can be simplified to

$$\boxed{p_\mathrm{a} = \rho_\mathrm{a}R_\mathrm{m}T = \rho_\mathrm{a}R'T_\mathrm{v}} \tag{2.36}$$

where

$$R_\mathrm{m} = R'\frac{1 + \omega_\mathrm{v}/\varepsilon}{1 + \omega_\mathrm{v}} = R'\left(1 + \frac{1 - \varepsilon}{\varepsilon}\mathrm{q_v}\right) = R'(1 + 0.608\mathrm{q_v}) \tag{2.37}$$

is the **gas constant for moist air** and

$$T_\mathrm{v} = T\frac{R_\mathrm{m}}{R'} = T\frac{1 + \omega_\mathrm{v}\varepsilon}{1 + \omega_\mathrm{v}} = T\left(1 + \frac{1 - \varepsilon}{\varepsilon}\mathrm{q_v}\right) = T(1 + 0.608\mathrm{q_v}) \tag{2.38}$$

is **virtual temperature.** This quantity is the temperature of a sample of dry air at the same density and pressure as a sample of moist air. Since the gas constant for moist air is larger than that for dry air, moist air has a lower density than does dry air at the same temperature and pressure. For the dry-air density to equal the moist-air density at the same pressure, the temperature of the dry air must be higher than that of the moist air by the factor R_m/R'. The resulting temperature is the virtual temperature, which is always larger than the actual temperature. In (2.38), the liquid water content is assumed to equal zero.

Equating $R_m = R^*/m_a$ with R_m from (2.37) and noting that $R' = R^*/m_d$ give the **molecular weight of moist air** (g mol^{-1}) as

$$m_a = \frac{m_d}{1 + 0.608q_v} \tag{2.39}$$

The molecular weight of moist air is less than that of dry air.

Example 2.9

If $p_d = 1013$ hPa, $p_v = 10$ hPa, and $T = 298$ K, calculate q_v, m_a, R_m, T_v, and ρ_a.

SOLUTION

From (2.32), $q_v = 0.622 \times 10/(1013 + 0.622 \times 10) = 0.0061$ kg kg^{-1}.
From (2.39), $m_a = 28.966/(1 + 0.608 \times 0.0061) = 28.86$ g mol^{-1}.
From (2.37), $R_m = 2.8704 \times (1 + 0.608 \times 0.0061) = 2.8811$ m^3 hPa kg^{-1} K^{-1}.
From (2.38), $T_v = 298 \times (1 + 0.608 \times 0.0061) = 299.1$ K.
From (2.36), $\rho_a = p_a/(R_m T) = 1023/(2.8811 \times 298) = 1.19$ kg m^{-3}.

2.4 CHANGES OF PRESSURE WITH ALTITUDE

The variation of pressure with altitude in the atmosphere can be estimated several ways. The first is by considering the equation for hydrostatic air pressure given in (2.1). The differential form of the equation, called the **hydrostatic equation**, is

$$\boxed{\mathrm{d}p_a = -\rho_a g\, \mathrm{d}z} \tag{2.40}$$

where air pressure, air density and gravity are functions of altitude (z), but parentheses have been removed. The negative sign arises because pressure decreases with increasing altitude. The hydrostatic equation assumes that the downward force of gravity per unit volume of air ($-\rho_a g$) exactly balances an upward pressure gradient force per unit volume ($\partial p_a/\partial z$). Figure 2.1(b) shows that pressure decreases exponentially with increasing altitude, giving rise to an upward pressure gradient force (a force that moves air from high to low pressure – Section 4.2.4). If gravity did not exist, the upward pressure gradient would accelerate air to space.

Pressure at a given altitude can be estimated from the hydrostatic equation with

$$p_{a,k} \approx p_{a,k+1} - \rho_{a,k+1} g_{k+1}(z_k - z_{k+1}) \tag{2.41}$$

where $p_{a,k}$ is the pressure at any upper altitude z_k, and $p_{a,k+1}$, $\rho_{a,k+1}$, and g_{k+1} are pressure, density, and gravity, respectively, at any lower altitude, z_{k+1}. If the pressure is known at the surface, and a vertical density and gravity profile are known, (2.41) can be used to estimate the pressure at each altitude above the surface, as illustrated in Example 2.10. Appendix Table B.1 gives vertical profiles of density and gravity in the atmosphere.

Example 2.10

If pressure, density, and gravity at sea level are $p_{\mathrm{a},k+1} = 1013.25$ hPa, $\rho_{\mathrm{a},k+1} = 1.225$ kg m^{-3}, and $g_{k+1} = 9.8072$ m s^{-2}, respectively, estimate the pressure at 100-m altitude.

SOLUTION

From (2.41), $p_{\mathrm{a},100\,\mathrm{m}} = 1013.25\,\mathrm{hPa} - 1.225\,\frac{\mathrm{kg}}{\mathrm{m}^3}\left(9.8072\,\frac{\mathrm{m}}{\mathrm{s}^2}\right)(100 - 0\,\mathrm{m})\,\frac{\mathrm{hPa\,m\,s}^2}{100\,\mathrm{kg}} =$ 1001.24 hPa, which compares well with the standard atmosphere pressure at 100 m given in Appendix Table B.1. This result also suggests that, near the surface, pressure decreases approximately 1 hPa for every 10 m increase in altitude.

Altitude versus pressure can also be determined from a pressure altimeter, which measures the pressure at an unknown altitude with an **aneroid barometer** (Section 1.1). From the barometric pressure, altitude is calculated under **standard atmospheric conditions**. Under such conditions, sea-level air pressure, sea-level air temperature, and the environmental lapse rate (average negative change in air temperature with altitude in the free troposphere) are $p_{\mathrm{a,s}} = 1013.25$ hPa, $T_{\mathrm{a,s}} = 288$ K, and $\Gamma_{\mathrm{s}} = -\partial T/\partial z = +6.5$ K km^{-1}, respectively (List 1984).

The equation for altitude in a standard atmosphere is derived by substituting $p_{\mathrm{a}} = \rho_{\mathrm{a}} R_{\mathrm{m}} T$ into the hydrostatic equation from (2.40). The result is

$$\frac{\partial p_{\mathrm{a}}}{\partial z} = -\frac{p_{\mathrm{a}}}{R_{\mathrm{m}} T} g \tag{2.42}$$

Substituting $T = T_{\mathrm{a,s}} - \Gamma_{\mathrm{s}} z$, where $z = 0$ km corresponds to sea level, into (2.42), rearranging, then integrating from $p_{\mathrm{a,s}}$ to p_{a} and 0 to z yields

$$\ln\left(\frac{p_{\mathrm{a}}}{p_{\mathrm{a,s}}}\right) = \frac{g}{\Gamma_{\mathrm{s}} R_{\mathrm{m}}} \ln\left(\frac{T_{\mathrm{a,s}} - \Gamma_{\mathrm{s}} z}{T_{\mathrm{a,s}}}\right) \tag{2.43}$$

Rearranging again gives altitude as a function of pressure in a standard troposphere as

$$z = \frac{T_{\mathrm{a,s}}}{\Gamma_{\mathrm{s}}}\left[1 - \left(\frac{p_{\mathrm{a}}}{p_{\mathrm{a,s}}}\right)^{\frac{\Gamma_{\mathrm{s}} R_{\mathrm{m}}}{g}}\right] \tag{2.44}$$

Temperature variations with altitude and sea-level pressure in the real atmosphere usually differ from those in the standard atmosphere. Empirical and tabulated expressions correcting for the differences are available (List 1984). Since the corrections are not always accurate, airplanes rarely use pressure altimeters to measure altitude. Instead, they use radar altimeters, which measure altitude with radio waves.

Example 2.11

If a pressure altimeter reads $p_a = 850$ hPa and the air is dry, find the standard-atmosphere altitude.

SOLUTION

Because the air is dry, $R_m = R' = 287.04\ \mathrm{m^2\ s^{-2}\ K^{-1}}$. Thus, $\Gamma_s R_m/g = 0.1902$, and from (2.44), $z = 1.45$ km.

A third way to estimate pressure versus altitude is with the **scale-height equation**. From the equation of state for moist air, air density is

$$\rho_a = \frac{p_a}{R' T_v} = \frac{m_d}{R^*}\frac{p_a}{T_v} = \frac{p_a}{T_v}\left(\frac{A}{R^*}\right)\frac{m_d}{A} \approx \frac{p_a}{T_v}\left(\frac{1}{k_B}\right)\bar{M} = \frac{p_a \bar{M}}{k_B T_v} \tag{2.45}$$

where $\bar{M} \approx m_d/A$ was previously defined as the **average mass of one air molecule**. Equation (2.45) can be combined with the hydrostatic equation to give

$$\frac{\mathrm{d}p_a}{p_a} = -\frac{\bar{M}g}{k_B T_v}\mathrm{d}z = -\frac{\mathrm{d}z}{H} \tag{2.46}$$

where

$$H = \frac{k_B T_v}{\bar{M}g} \tag{2.47}$$

is the **scale height** of the atmosphere at a given virtual temperature. The scale height is the height above a reference height at which pressure decreases to 1/e of its value at the reference height. Since temperature varies with altitude in the atmosphere, scale height also varies with altitude.

Example 2.12

Determine the scale height at $T_v = 298$ K and $p_a = 1013.25$ hPa. Assume dry air.

SOLUTION

From Appendix A and Appendix Table B.1, $\bar{M} = 4.8096 \times 10^{-26}$ kg, $g = 9.8072\ \mathrm{m\,s^{-2}}$, and $k_B = 1.380658 \times 10^{-23}\ \mathrm{kg\ m^2\ s^{-2}\ K^{-1}\ molec.^{-1}}$ at the given pressure. Thus, from (2.47), the scale height is $H = 8.72$ km.

Integrating (2.46) at constant temperature gives pressure as a function of altitude as

$$p_a = p_{a,\mathrm{ref}} e^{-(z - z_{\mathrm{ref}})/H} \tag{2.48}$$

where $p_{a,\mathrm{ref}}$ is pressure at a reference level, $z = z_{\mathrm{ref}}$. In a model with several vertically stacked layers, each with a known average temperature, pressure at the top of each layer can be calculated from (2.48) assuming that the reference pressure at the base of the layer is the pressure calculated for the top of the next-lowest layer. At the ground, the pressure is the surface pressure, which must be known.

2.5 WATER IN THE ATMOSPHERE

Water appears in three states – gas, liquid, and solid. Sources and sinks of water vapor in the atmosphere were discussed in Section 2.1.2.1. Sources of liquid water include sea spray emission, volcanos, combustion, condensation of water vapor, and melting of ice crystals. Sinks of liquid water include evaporation, freezing, and sedimentation to the surface of aerosol particles, fog drops, drizzle, and raindrops. Ice in the atmosphere forms from freezing of liquid water and solid deposition of water vapor. Losses of ice occur by sublimation to the gas phase, melting to the liquid phase, and sedimentation to the surface.

2.5.1 Types of energy

When water changes state, it releases or absorbs energy. **Energy** is the capacity of a physical system to do work on matter. **Matter** is mass that exists as a solid, liquid, or gas. Energy takes many forms.

Kinetic energy is the energy within a body due to its motion and equals one-half the mass of the body multiplied by its speed squared. The faster a body moves, the greater its kinetic energy. To change the speed and kinetic energy of a body in motion, mechanical work must be done.

Potential energy is the energy of matter that arises due to its position, rather than its motion. Potential energy represents the amount of work that a body can do. A coiled spring, charged battery, and chemical reactant have potential energy. When an object is raised vertically, it possesses gravitational potential energy because it can potentially do work by sinking.

Internal energy is the kinetic and/or potential energy of molecules within an object, but does not include the kinetic and/or potential energy of the object as a whole.

Work is the energy added to a body by the application of a force that moves the body in the direction of the force.

Electromagnetic (radiant) energy is the energy transferred by electromagnetic waves that originate from bodies with temperatures above 0 K.

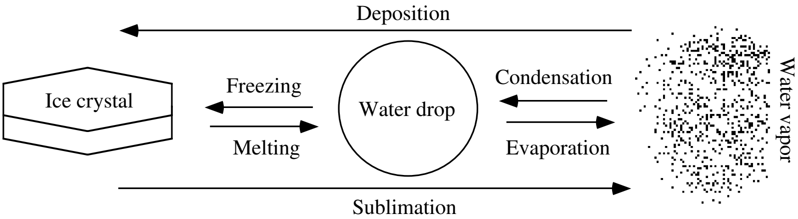

Figure 2.6 Phase changes of water. Freezing (melting) at 0 °C releases (absorbs) 333.5 J g^{-1}, deposition (sublimation) at 0 °C releases (absorbs) 2835 J g^{-1}, and condensation (evaporation) releases (absorbs) 2510 J g^{-1} at 0 °C and 2259 J g^{-1} at 100 °C.

Heat, itself, is not a form of energy. However, **heat transfer** is a term used to describe the energy transfer between two bodies that occurs, for example, when their internal energies (or temperatures) differ. **Heat capacity** (e.g., specific heat capacity) is the energy required to change the temperature of a given quantity of a substance 1 °C. Finally, **heat release** (**absorption**) occurs when a substance releases (absorbs) energy to (from) the surrounding environment upon a change of state. Below, heat release/absorption is discussed.

2.5.2 Latent heat

During condensation, freezing, and solid deposition of a substance, energy is released. During evaporation, melting, and sublimation, energy is absorbed. The stored energy released or the energy absorbed during such processes is called **latent heat**. Latent heat absorbed (released) during evaporation (condensation) is **latent heat of evaporation**. It varies with temperature as

$$\boxed{\frac{\mathrm{d}L_\mathrm{e}}{\mathrm{d}T} = c_{p,\mathrm{V}} - c_\mathrm{W} \qquad (2.49)}$$

where $c_{p,\mathrm{V}}$ is the specific heat of water vapor at constant pressure, and c_W is the specific heat of liquid water. The latent heat absorbed (released) during sublimation (deposition) is the **latent heat of sublimation**. The latent heat absorbed (released) during melting (freezing) is the **latent heat of melting**. The latent heats of sublimation and melting vary with temperature according to

$$\frac{\mathrm{d}L_\mathrm{s}}{\mathrm{d}T} = c_{p,\mathrm{V}} - c_\mathrm{I} \qquad \frac{\mathrm{d}L_\mathrm{m}}{\mathrm{d}T} = c_\mathrm{W} - c_\mathrm{I} \qquad (2.50)$$

respectively, where c_I is the specific heat of ice. Figure 2.6 gives the quantity of energy absorbed or released during phase changes of water.

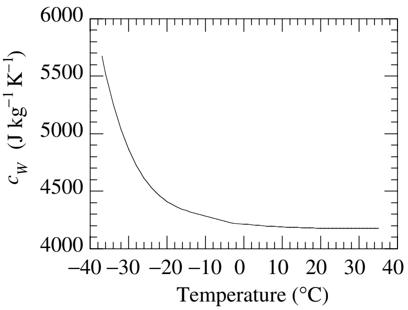

Figure 2.7 Variation of specific heat of liquid water with temperature, from (2.51).

The specific heats of liquid water, ice, and water vapor vary with temperature. Polynomial expressions for the specific heat of liquid water (J kg^{-1} K^{-1}) are

$$c_{\mathrm{W}} = \begin{cases} 4187.9 - 11.319T_{\mathrm{c}} - 0.097215T_{\mathrm{c}}^2 + 0.018317T_{\mathrm{c}}^3 + 0.0011354T_{\mathrm{c}}^4 & -37 \le T_{\mathrm{c}} < 0 \\ 4175.2 + 0.01297\,(T_{\mathrm{c}} - 35)^2 + 1.5899 \times 10^{-5}(T_{\mathrm{c}} - 35)^4 & 0 \le T_{\mathrm{c}} < 35 \end{cases} \tag{2.51}$$

(Osborne *et al.* 1939; Angell *et al.* 1982; Pruppacher and Klett 1997), where T_{c} is temperature in degrees Celsius. Figure 2.7 shows c_{W} versus temperature from (2.51). The variation of c_{W} below 0 °C is large, but that above 0 °C is small. An expression for the specific heat of ice is

$$c_{\mathrm{I}} = 2104.6 + 7.322T_{\mathrm{c}} \qquad -40 \le T_{\mathrm{c}} < 0\,^{\circ}\mathrm{C} \tag{2.52}$$

(Giauque and Stout 1936; Flubacher *et al.* 1960; Pruppacher and Klett 1997). The specific heat of water vapor at constant pressure also varies slightly with temperature. At 298.15 K, $c_{p,V} \approx 1865.1$ (Lide 1993). At 303.15 K, it is 2 percent larger than at 243.15 K (Rogers and Yau 1989).

Because changes in c_{W} and $c_{p,V}$ are small for temperatures above 0 °C, these parameters may be held constant when the variation of the latent heat of evaporation with temperature is calculated. Integrating (2.49) with constant specific heat gives

$$L_{\mathrm{e}} = L_{\mathrm{e},0} - (c_{\mathrm{W}} - c_{p,V})\,(T - T_0) \tag{2.53}$$

where $L_{\mathrm{e},0}$ is the latent heat of evaporation at temperature T_0 (K). An empirical expression for the latent heat of evaporation (J kg^{-1}) is (Bolton 1980; List 1984)

$$L_{\mathrm{e}} \approx 2.501 \times 10^6 - 2370T_{\mathrm{c}} \tag{2.54}$$

Example 2.13

Equation (2.54) predicts that, at 0 °C, 2501 J (about 600 cal) is required to evaporate 1 g of liquid water. At 100 °C, 2264 J (about 540 cal) is required to evaporate 1 g of liquid water.

An empirical expression for the latent heat of melting ($\mathrm{J\,kg^{-1}}$), valid for temperatures below 0 °C, is

$$L_\mathrm{m} \approx 3.3358 \times 10^5 + T_\mathrm{c}(2030 - 10.46T_\mathrm{c}) \tag{2.55}$$

(List 1984). While pure water at standard pressure always melts at temperatures above 0 °C, it may or may not freeze at temperatures below 0 °C. Water that remains liquid below 0 °C is **supercooled liquid water**.

Example 2.14

Equation (2.55) predicts that, when 1 g of liquid water freezes, 333.5 J (about 80 cal) is released at 0 °C and 312.2 J (74.6 cal) is released at −10 °C.

The latent heat of sublimation ($\mathrm{J\,kg^{-1}}$) is the sum of the latent heats of evaporation and melting. Thus,

$$L_\mathrm{s} = L_\mathrm{e} + L_\mathrm{m} \approx 2.83458 \times 10^6 - T_\mathrm{c}(340 + 10.46T_\mathrm{c}) \tag{2.56}$$

2.5.3 Clausius–Clapeyron equation

The rates of formation and growth of liquid water drops and ice crystals depend on several factors, described in Chapters 16 and 18. One important parameter, derived here, is the **saturation vapor pressure** (SVP, also called the equilibrium vapor pressure or surface vapor pressure). This parameter is the partial pressure of a gas over a particle surface at a specific temperature when the gas is in equilibrium with its liquid or solid phase on the surface.

A simplistic way of looking as SVP is to view it as the maximum amount of vapor the air can sustain without the vapor condensing as a liquid or depositing as ice on a surface. When the air is cold, SVPs are lower than when the air is warm. At low temperatures, liquid-water molecules on a particle surface have little kinetic energy and cannot easily break free (evaporate) from the surface. Thus, in equilibrium, air just above a surface contains few vapor molecules and exerts a low SVP. When the air is warm, liquid-water molecules have higher kinetic energies, are more agitated, and break loose more readily from a surface. The resulting evaporation increases the vapor content of the air, and thus the SVP over the particle surface.

The temperature variation of the saturation vapor pressure of water over a liquid surface ($p_{\mathrm{v,s}}$, hPa) is approximated with the **Clausius–Clapeyron equation,**

$$\boxed{\frac{\mathrm{d}p_{\mathrm{v,s}}}{\mathrm{d}T} = \frac{\rho_{\mathrm{v,s}}}{T} L_{\mathrm{e}} \qquad (2.57)}$$

where L_{e} is the latent heat of evaporation of water (J kg^{-1}), and $\rho_{\mathrm{v,s}}$ is the **saturation mass density of water vapor** (kg m^{-3}). Combining $\rho_{\mathrm{v,s}} = p_{\mathrm{v,s}}/R_{\mathrm{v}}T$ from (2.25) with (2.57) gives

$$\frac{\mathrm{d}p_{\mathrm{v,s}}}{\mathrm{d}T} = \frac{L_{\mathrm{e}} p_{\mathrm{v,s}}}{R_{\mathrm{v}} T^2} \tag{2.58}$$

Substituting L_{e} from (2.54) into (2.58) and rearranging give

$$\frac{\mathrm{d}p_{\mathrm{v,s}}}{p_{\mathrm{v,s}}} = \frac{1}{R_{\mathrm{v}}}\left(\frac{A_{\mathrm{h}}}{T^2} - \frac{B_{\mathrm{h}}}{T}\right)\mathrm{d}T \tag{2.59}$$

where $A_{\mathrm{h}} = 3.14839 \times 10^6$ J kg^{-1} and $B_{\mathrm{h}} = 2370$ J kg^{-1} K^{-1}. Integrating (2.59) from $p_{\mathrm{v,s,0}}$ to $p_{\mathrm{v,s}}$ and T_0 to T, where $p_{\mathrm{v,s,0}}$ is a known saturation vapor pressure at T_0, gives the **saturation vapor pressure of water over a liquid surface** as

$$p_{\mathrm{v,s}} = p_{\mathrm{v,s,0}} \exp\left[\frac{A_{\mathrm{h}}}{R_{\mathrm{v}}}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{B_{\mathrm{h}}}{R_{\mathrm{v}}} \ln\left(\frac{T_0}{T}\right)\right] \tag{2.60}$$

At $T = T_0 = 273.15$ K, $p_{\mathrm{v,s,0}} = 6.112$ hPa. Substituting these values, $R_{\mathrm{v}} = 461.91$ J kg^{-1} K^{-1}, A_{h}, and B_{h} into (2.60) gives

$$p_{\mathrm{v,s}} = 6.112 \exp\left[6816\left(\frac{1}{273.15} - \frac{1}{T}\right) + 5.1309 \ln\left(\frac{273.15}{T}\right)\right] \tag{2.61}$$

where T is in kelvin and $p_{\mathrm{v,s}}$ is in hPa.

Example 2.15

From (2.60), $p_{\mathrm{v,s}} = 1.26$ hPa at $T = 253.15$ K (-20 °C) and $p_{\mathrm{v,s}} = 31.60$ hPa at $T = 298.15$ K (25 °C).

An empirical parameterization of the saturation vapor pressure of water over a liquid surface is

$$p_{\mathrm{v,s}} = 6.112 \exp\left(\frac{17.67 T_{\mathrm{c}}}{T_{\mathrm{c}} + 243.5}\right) \tag{2.62}$$

(Bolton 1980), where T_{c} is in degrees Celsius and $p_{\mathrm{v,s}}$ is in hPa. The fit is valid for $-35 < T_{\mathrm{c}} < 35$ °C. Equations (2.61) and (2.62) are saturation vapor pressures over flat, dilute liquid surfaces. Saturation vapor pressures are affected by surface

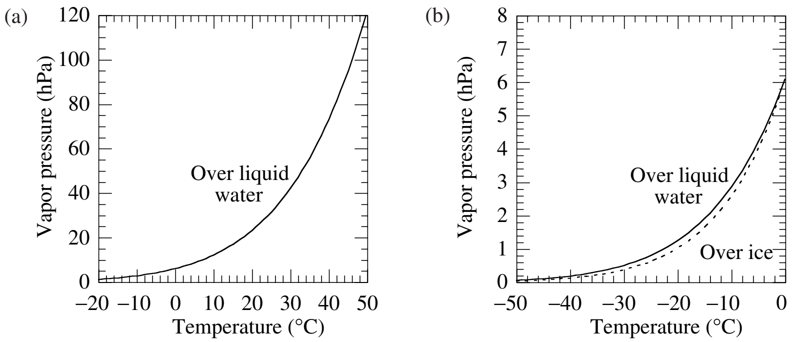

Figure 2.8 Saturation vapor pressure over (a) liquid water and (b) liquid water and ice, versus temperature.

curvature, the presence of solutes in water, and the rate of drop heating or cooling. These effects are discussed in Chapter 16.

Example 2.16

At $T = 253.15$ K (-20 °C), the saturation vapor pressure from (2.62) is $p_{v,s} = 1.26$ hPa. At $T = 298.15$ K (25 °C), $p_{v,s} = 31.67$ hPa. A comparison of these results with those from the previous examples shows that (2.61) and (2.62) give almost identical estimates for $p_{v,s}$.

Figure 2.8(a) shows saturation vapor pressure of water over a liquid surface versus temperature, obtained from (2.62). The figure indicates that saturation vapor pressure increases with increasing temperature. At 0 °C, $p_{v,s} = 6.1$ hPa, which is equivalent to 0.6 percent of the total sea-level air pressure (1013 hPa). At 30 °C, $p_{v,s} = 42.5$ hPa (4.2 percent of the total sea-level air pressure). Since the partial pressure of water vapor can rarely exceed its saturation vapor pressure, the maximum partial pressure of air varies from <1 percent to ≈4 percent of total atmospheric air pressure. Near the poles, where temperatures are low, saturation vapor pressures and partial pressures approach zero. Near the Equator, where temperatures are high, saturation vapor pressures and partial pressures can increase to 4 percent or more of the total air pressure.

The saturation vapor pressure of water over an ice surface is lower than that over a liquid surface at the same subfreezing temperature because ice molecules require more energy to sublimate than liquid molecules require to evaporate at the same temperature. The Clausius–Clapeyron equation for the saturation vapor pressure of water over ice ($p_{v,I}$, hPa) is rewritten from (2.58) as

$$\frac{\mathrm{d}p_{v,I}}{\mathrm{d}T} = \frac{L_s p_{v,I}}{R_v T^2} \qquad (2.63)$$

Substituting the latent heat of sublimation from (2.56) into (2.63) and integrating give the **saturation vapor pressure of water over ice** as

$$p_{v,I} = 6.112\ \exp\left[4648\left(\frac{1}{273.15} - \frac{1}{T}\right) - 11.64 \ln\left(\frac{273.15}{T}\right) + 0.02265(273.15 - T)\right] \tag{2.64}$$

where $T \leq 273.15$ K is in kelvin and $p_{v,I}$ is in hPa. At $T = 273.15$ K, the saturation vapor pressure over ice equals that over liquid water ($p_{v,I,0} = 6.112$ hPa). Figure 2.8(b) shows that, at subfreezing temperatures, $p_{v,I} < p_{v,s}$. Above 273.15 K (0 °C), ice surfaces do not exist. An alternative parameterization, valid from 223.15 K to 273.15 K is

$$p_{v,I} = 6.1064 \exp\left[\frac{21.88\,(T - 273.15)}{T - 7.65}\right] \tag{2.65}$$

(Pruppacher and Klett 1997), where $T \leq 273.15$ K is in kelvin and $p_{v,I}$ is in hPa.

Example 2.17

At $T = 253.15$ K (−20 °C), (2.64) gives $p_{v,I} = 1.034$ hPa, which is less than $p_{v,s} = 1.26$ hPa at the same temperature. Thus, the saturation vapor pressure of water over liquid is greater than that over ice.

2.5.4 Condensation and deposition

Saturation vapor pressures are critical for determining the extent of liquid drop and ice crystal formation. When the air temperature is above the freezing temperature of water (273.15 K) and the partial pressure of water vapor is greater than the saturation vapor pressure of water over a liquid surface ($p_v > p_{v,s}$), water vapor generally condenses as a liquid. Liquid water evaporates when $p_v < p_{v,s}$. Figures 2.9(a) and (b) illustrate growth and evaporation.

If the air temperature falls below freezing and $p_v > p_{v,I}$, water vapor deposits as ice. When $p_v < p_{v,I}$, ice sublimates to water vapor. If liquid water and ice coexist in the same parcel of air and $p_{v,I} < p_{v,s} < p_v$, deposition onto ice particles is favored over condensation onto liquid water drops because growth is driven by the difference between partial pressure and saturation vapor pressure, and $p_v - p_{v,I} > p_v - p_{v,s}$.

When $p_{v,I} < p_v < p_{v,s}$, water evaporates from liquid surfaces and deposits onto ice surfaces, as shown in Fig. 2.10. This is the central assumption behind the **Wegener–Bergeron–Findeisen (Bergeron) process** of ice crystal growth in cold clouds. In such clouds, supercooled liquid water cloud droplets coexist with ice crystals. When the ratio of liquid cloud drops to ice crystals is less than 100 000:1, each ice crystal receives water that evaporates from less than 100 000 cloud drops, and ice crystals do not grow large or heavy enough to fall from their cloud. When the ratio is greater than 1 000 000:1, the relatively few ice crystals present grow

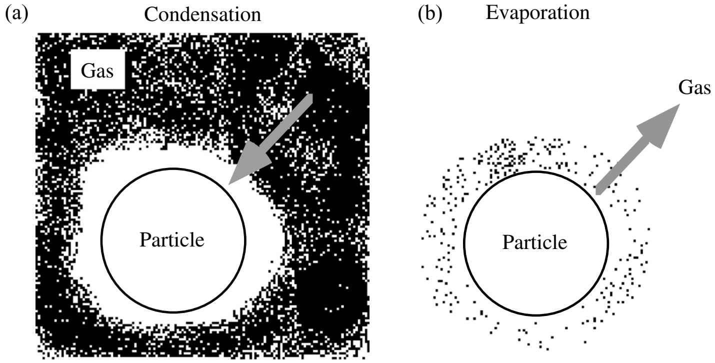

Figure 2.9 (a) Condensation occurs when the partial pressure of a gas exceeds its saturation vapor pressure over a particle surface. (b) Evaporation occurs when the saturation vapor pressure exceeds the partial pressure of the gas. The schematics are not to scale.

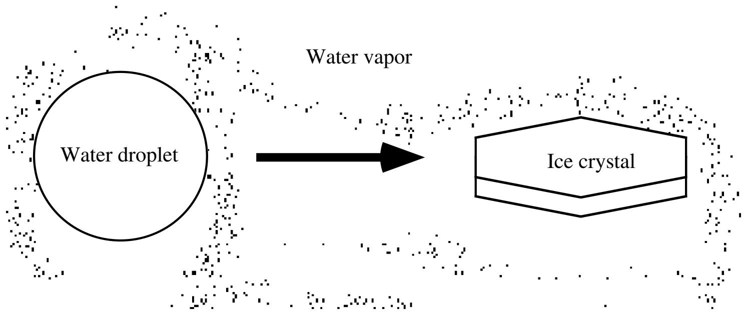

Figure 2.10 Bergeron process. When $p_{\mathrm{v,I}} < p_{\mathrm{v}} < p_{\mathrm{v,s}}$ at a subfreezing temperature, liquid evaporates, and the resulting gas diffuses to and deposits onto ice crystals.

large and fall quickly from their cloud before much liquid water evaporates, leaving the cloud with lots of liquid drops too small to fall from the cloud. When the ratio is between 100 000:1 and 1 000 000:1, each ice crystal receives the liquid water from 100 000 to 1 000 000 droplets. These ice crystals fall from the cloud, maximizing precipitation.

Figure 2.8(b) shows that the greatest difference between the saturation vapor pressures over liquid water and ice occurs at $T_{\mathrm{c}} = -15\ ^{\circ}\mathrm{C}$. This is the temperature at which ice crystals grow the fastest. Dendrites, which are snowflake-shaped crystals, form most favorably at this temperature.

The ratio of the water vapor partial pressure to its saturation vapor pressure over a liquid surface determines whether the vapor condenses. This ratio is embodied in the **relative humidity**, defined as

$$f_{\mathrm{r}} = 100\% \times \frac{\omega_{\mathrm{v}}}{\omega_{\mathrm{v,s}}} = 100\% \times \frac{p_{\mathrm{v}}(p_{\mathrm{a}} - p_{\mathrm{v,s}})}{p_{\mathrm{v,s}}(p_{\mathrm{a}} - p_{\mathrm{v}})} \approx 100\% \times \frac{p_{\mathrm{v}}}{p_{\mathrm{v,s}}} \qquad (2.66)$$

by the World Meteorological Organization (WMO), where ω_v is the mass mixing ratio of water vapor in the air from (2.31), and

$$\omega_{v,s} = \frac{\varepsilon p_{v,s}}{p_a - p_{v,s}} \approx \frac{\varepsilon p_{v,s}}{p_d} \tag{2.67}$$

is the **saturation mass mixing ratio of water vapor** over a liquid surface, found by substituting $p_{v,s}$ for p_v and $\omega_{v,s}$ for ω_v in (2.31). The saturation mass mixing ratio in the equation for the relative humidity is always taken with respect to liquid water, even if $T \leq 273.15$ K (List 1984). Prior to the WMO definition, the relative humidity was defined exactly as $f_r = 100\% \times p_v/p_{v,s}$.

Example 2.18

If $T = 288$ K and $p_v = 12$ hPa, what is the relative humidity?

SOLUTION

From (2.62), $p_{v,s} = 17.04$ hPa. From (2.66), $f_r = 100$ percent × 12 hPa / 17.04 hPa = 70.4 percent.

Equation (2.66) implies that, if the relative humidity exceeds 100 percent and $T > 273.15$ K, water vapor condenses. If the relative humidity exceeds 100 percent and $T \leq 273.15$ K, water vapor may condense as a liquid or deposit as ice.

Another parameter used to predict when bulk condensation occurs is the **dew point** (T_D), which is the temperature to which air must be cooled, at constant water vapor partial pressure and air pressure, to reach saturation with respect to liquid water. Similarly, the **frost point** is the temperature to which air must be cooled, at constant water vapor partial pressure and air pressure, to reach saturation with respect to ice. If the air temperature drops below the dew point, the relative humidity increases above 100 percent and condensation occurs. If the dew point is known, the partial pressure of water can be obtained from Fig. 2.8. If the ambient temperature is known, the saturation vapor pressure can be obtained from the same figure.

Example 2.19

If $T_D = 20\,^\circ$C and $T = 30\,^\circ$C, estimate the partial pressure of water, the saturation vapor pressure of water, and the relative humidity from Fig. 2.8.

SOLUTION

From the figure, $p_v \approx 23.4$ hPa and $p_{v,s} \approx 42.5$ hPa. Thus, $f_r \approx 55$ percent.

An equation for the dew point can be derived from any equation for saturation vapor pressure by substituting p_v for $p_{v,s}$ and solving for the temperature. Applying

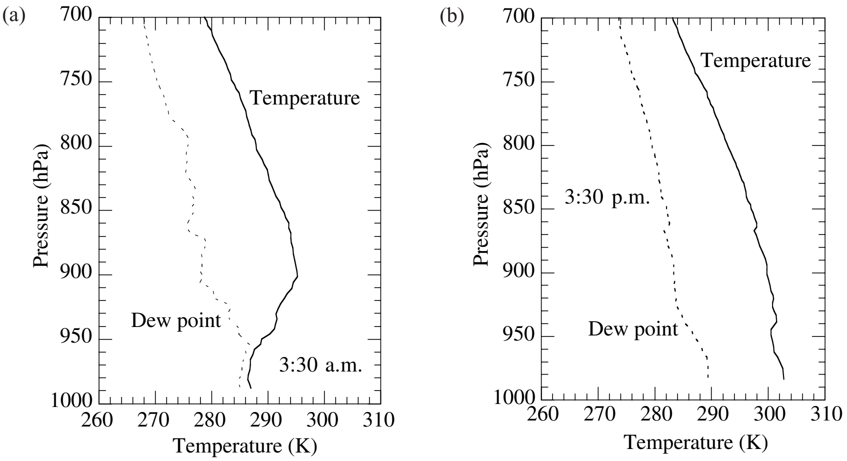

Figure 2.11 Observed vertical profiles of temperature and dew point at (a) 3:30 a.m. and (b) 3:30 p.m. on August 27, 1987 at Riverside, California. The air was nearly saturated near the surface in the morning.

this technique to (2.62) and converting the result to absolute temperature give the dew point as

$$T_D = \frac{4880.357 - 29.66 \ln p_v}{19.48 - \ln p_v} = \frac{4880.357 - 29.66 \ln(\omega_v p_d/\varepsilon)}{19.48 - \ln(\omega_v p_d/\varepsilon)} \qquad (2.68)$$

where $\omega_v = \varepsilon p_v / p_d$ from (2.31), T is in kelvin, and p_v is in hPa.

Example 2.20

Calculate the dew point when $p_v = 12$ hPa.

SOLUTION

From (2.68), $T_D = 282.8$ K. Thus, if unsaturated air at 288 K cools to 282.8 K when $p_v = 12$ hPa, condensation occurs.

When the ambient temperature is close to the dew point ($T \approx T_D$), the relative humidity is high. When the ambient temperature and dew point are far apart, the relative humidity is low. Figures 2.11(a) and (b) show observed vertical profiles of temperature and dew point at Riverside, California, in the morning and afternoon, respectively, of August 27, 1987. In the morning, near the ground, the dew point and air temperature were close to each other, indicating the air was nearly saturated, the relative humidity was high, and a fog was almost present. Above 950 hPa (about 500 m above sea level) in the morning, the dew point and air temperature were far apart, indicating the relative humidity was low and the air was unsaturated. In the afternoon, when air near the surface was warm, the dew point and air temperature were also far apart, and the relative humidity was low.

2.6 FIRST LAW OF THERMODYNAMICS

As applied to the atmosphere, the first law of thermodynamics relates the change in temperature of a parcel of air to energy transfer between the parcel and its environment and work done by or on the parcel. The first law is used to derive the **thermodynamic energy equation**, which gives the time-rate-of-change of temperature in the atmosphere due to energy transfer and work. The first law is also used to derive analytical expressions for atmospheric stability.

The **first law of thermodynamics** as applied to the atmosphere is

$$\mathrm{dQ}^* = \mathrm{dU}^* + \mathrm{dW}^* \tag{2.69}$$

where dQ^* is called the **diabatic heating term**, which is the **energy** (J) transferred between an air parcel and its environment, dU^* is the change in **internal energy** (J) of the parcel, and dW^* is the **work** (J) done by or on the parcel. When $\mathrm{dQ}^* > 0$, energy is transferred to the parcel from the environment, and the process is **endothermic**. When $\mathrm{dQ}^* < 0$, energy is transferred to the environment from the parcel, and the process is **exothermic**. When $\mathrm{dW}^* > 0$, work is done by the parcel. When $\mathrm{dW}^* < 0$, work is done on the parcel. Equation (2.69) states that if energy is added to an air parcel, some of it is used to change the internal energy (and temperature) of the parcel, and the rest is used by the parcel to do work. The equation also states that changes in the internal energy (temperature) of a parcel result from energy transfer or work. Internal energy changes resulting from energy transfer are **diabatic** while those resulting from work are **adiabatic**. Diabatic sources or sinks of energy include conduction, radiative cooling/heating, and latent heat release/absorption. Substituting

$$\mathrm{dQ} = \frac{\mathrm{dQ}^*}{M_\mathrm{a}} \qquad \mathrm{dU} = \frac{\mathrm{dU}^*}{M_\mathrm{a}} \qquad \mathrm{dW} = \frac{\mathrm{dW}^*}{M_\mathrm{a}} \tag{2.70}$$

where $M_\mathrm{a} = M_\mathrm{d} + M_\mathrm{v}$ is the mass of a parcel of air (kg) consisting of dry air mass M_d and water vapor mass M_v, into (2.69) gives the first law in terms of energy per unit mass of air (J kg^{-1}) as

$$\mathrm{dQ} = \mathrm{dU} + \mathrm{dW} \tag{2.71}$$

Terms in this equation are discussed below.

When a gas expands, work is done by the gas. When air expands, work done by the air is $\mathrm{dW}^* = p_\mathrm{a}\,\mathrm{d}V$, and work done per unit mass of air is

$$\mathrm{dW} = \frac{\mathrm{dW}^*}{M_\mathrm{a}} = \frac{p_\mathrm{a}\,\mathrm{d}V}{M_\mathrm{a}} = p_\mathrm{a}\,\mathrm{d}\alpha_\mathrm{a} \tag{2.72}$$

In this equation, $\mathrm{d}V$ is the change in volume of the air, and

$$\alpha_\mathrm{a} = \frac{V}{M_\mathrm{a}} = \frac{1}{\rho_\mathrm{a}} \tag{2.73}$$

is the **specific volume of air**. Air expands when it rises to lower pressure. In such cases, work is done by the air, and $\mathrm{d}V > 0$. When a parcel of air sinks to higher pressure, the parcel compresses, work is done on the air in the parcel, and $\mathrm{d}V < 0$.

Energy transfer between a parcel and its environment occurs when $\mathrm{dQ} \neq 0$. In the atmosphere, major sources (sinks) of external energy are radiative heating (cooling), condensation (evaporation), deposition (sublimation), and freezing (melting).

The change in **internal energy** of the air is its change in temperature multiplied by the energy required to change its temperature one degree Celsius (1 K) without affecting the volume or work done by or on the air. In other words,

$$\mathrm{dU} = \left(\frac{\partial \mathrm{Q}}{\partial T}\right)_{\alpha_\mathrm{a}} \mathrm{d}T = c_{v,\mathrm{m}}\,\mathrm{d}T \tag{2.74}$$

where $c_{v,\mathrm{m}} = (\partial \mathrm{Q}/\partial T)_{\alpha_\mathrm{a}}$ is the **specific heat of moist air at constant volume.** It is the energy required to raise the temperature of 1 g of air 1 K at constant volume and varies with water-vapor mass mixing ratio. An expression for $c_{v,\mathrm{m}}$ can be derived by noting that, at constant volume,

$$(M_\mathrm{d} + M_\mathrm{v})\mathrm{dQ} = (M_\mathrm{d} c_{v,\mathrm{d}} + M_\mathrm{v} c_{v,\mathrm{V}})\mathrm{d}T \tag{2.75}$$

where $c_{v,\mathrm{d}} = 717.63\ \mathrm{J\ kg^{-1}\ K^{-1}}$ at 298 K is the **specific heat of dry air at constant volume** and $c_{v,\mathrm{V}} = 1403.2\ \mathrm{J\ kg^{-1}\ K^{-1}}$ is the **specific heat of water vapor at constant volume.** The specific heat of dry air at constant volume decreases by less than 0.2 percent down to 200 K. Dividing (2.75) through by $(M_\mathrm{d} + M_\mathrm{v})\,\mathrm{d}T$ gives

$$c_{v,\mathrm{m}} = \left(\frac{\partial \mathrm{Q}}{\partial T}\right)_{\alpha_\mathrm{a}} = \frac{M_\mathrm{d} c_{v,\mathrm{d}} + M_\mathrm{v} c_{v,\mathrm{V}}}{M_\mathrm{d} + M_\mathrm{v}} = \frac{c_{v,\mathrm{d}} + c_{v,\mathrm{V}}\omega_\mathrm{v}}{1 + \omega_\mathrm{v}} = c_{v,\mathrm{d}}(1 + 0.955\mathrm{q_v}) \tag{2.76}$$

where $\mathrm{q_v} = \omega_\mathrm{v}/(1 + \omega_\mathrm{v})$ from (2.33) and $c_{v,\mathrm{V}}/c_{v,\mathrm{d}} - 1 = 0.955$.

Substituting (2.74) and (2.72) into (2.71) gives the **first law of thermodynamics for the atmosphere** as

$$\boxed{\mathrm{dQ} = c_{v,\mathrm{m}}\,\mathrm{d}T + p_\mathrm{a}\,\mathrm{d}\alpha_\mathrm{a}} \tag{2.77}$$

Combining the equation of state, $p_\mathrm{a} = \rho_\mathrm{a} R_\mathrm{m} T$, with $\alpha_\mathrm{a} = 1/\rho_\mathrm{a}$ gives $p_\mathrm{a}\alpha_\mathrm{a} = R_\mathrm{m} T$, which can be differentiated to give

$$p_\mathrm{a}\,\mathrm{d}\alpha_\mathrm{a} + \alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a} = R_\mathrm{m}\,\mathrm{d}T \tag{2.78}$$

Combining (2.78) with (2.77) yields another form of the first law as

$$\boxed{\mathrm{dQ} = c_{p,\mathrm{m}}\,\mathrm{d}T - \alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a}} \tag{2.79}$$

where

$$\begin{aligned} c_{p,\mathrm{m}} = \left(\frac{\mathrm{dQ}}{\mathrm{d}T}\right)_{p_\mathrm{a}} &= \frac{M_\mathrm{d} c_{p,\mathrm{d}} + M_\mathrm{v} c_{p,\mathrm{V}}}{M_\mathrm{d} + M_\mathrm{v}} = \frac{c_{p,\mathrm{d}} + c_{p,\mathrm{V}}\omega_\mathrm{v}}{1 + \omega_\mathrm{v}} \\ &= c_{p,\mathrm{d}}(1 + 0.856\mathrm{q_v}) \\ &\approx c_{p,\mathrm{d}}(1 + 0.859\omega_\mathrm{v}) \end{aligned} \tag{2.80}$$

is the **specific heat of moist air at constant pressure**. In this equation, $c_{p,\mathrm{V}}/c_{p,\mathrm{d}} - 1 = 0.856$, where $c_{p,\mathrm{d}} = 1004.67\ \mathrm{J\ kg^{-1}\ K^{-1}}$ at 298 K is the specific heat of dry air at constant pressure, and $c_{p,\mathrm{V}} = 1865.1\ \mathrm{J\ kg^{-1}\ K^{-1}}$ is the **specific heat of water vapor at constant pressure**. Like $c_{v,\mathrm{d}}$, $c_{p,\mathrm{d}}$ and $c_{p,\mathrm{V}}$ vary slightly with temperature. The specific heat of moist air at constant pressure is the energy required to increase the temperature of 1 g of air 1 K without affecting air pressure.

Differentiating (2.77) at constant pressure gives another expression for $c_{p,\mathrm{m}}$ as

$$c_{p,\mathrm{m}} = \left(\frac{\mathrm{dQ}}{\mathrm{d}T}\right)_{p_\mathrm{a}} = c_{v,\mathrm{m}} + p_\mathrm{a}\left(\frac{\mathrm{d}\alpha_\mathrm{a}}{\mathrm{d}T}\right)_{p_\mathrm{a}} = c_{v,\mathrm{m}} + p_\mathrm{a}\left(\frac{\mathrm{d}}{\mathrm{d}T}\frac{R_\mathrm{m}T}{p_\mathrm{a}}\right)_{p_\mathrm{a}} = c_{v,\mathrm{m}} + R_\mathrm{m} \tag{2.81}$$

When the air is dry, this expression simplifies to $c_{p,\mathrm{d}} = c_{v,\mathrm{d}} + R'$. Substituting $c_{v,\mathrm{m}} = c_{v,\mathrm{d}}(1 + 0.955\mathrm{q_v})$ from (2.76) and $R_\mathrm{m} = R'(1 + 0.608\mathrm{q_v})$ from (2.37) into (2.81) gives the empirical expressions in (2.80).

The first law of thermodynamics can be approximated in terms of virtual temperature instead of temperature with

$$\boxed{\mathrm{dQ} = \frac{1 + 0.856\mathrm{q_v}}{1 + 0.608\mathrm{q_v}} c_{p,\mathrm{d}}\,\mathrm{d}T_\mathrm{v} - \alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a} \approx c_{p,\mathrm{d}}\,\mathrm{d}T_\mathrm{v} - \alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a}} \tag{2.82}$$

which was derived by substituting $c_{p,\mathrm{m}} = c_{p,\mathrm{d}}(1 + 0.856\mathrm{q_v})$ from (2.80) and $T = T_\mathrm{v}/(1 + 0.608\mathrm{q_v})$ from (2.38) into (2.79). An advantage of (2.82) is that the specific heat is in terms of dry instead of moist air. The maximum energy error in (2.82) due to neglecting the empirical water vapor terms is 1 percent. The average error is 0.2 percent.

2.6.1 Applications of the first law of thermodynamics

Here, the first law of thermodynamics is modified for four special cases. First, for an **isobaric process** ($\mathrm{d}p_\mathrm{a} = 0$), the first law simplifies from (2.79) to

$$\mathrm{dQ} = c_{p,\mathrm{m}}\,\mathrm{d}T = \frac{c_{p,\mathrm{m}}}{c_{v,\mathrm{m}}}\mathrm{dU} \tag{2.83}$$

Second, for an **isothermal process** ($\mathrm{d}T = 0$), (2.79) becomes

$$\mathrm{dQ} = -\alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a} = p_\mathrm{a}\,\mathrm{d}\alpha_\mathrm{a} = \mathrm{dW} \tag{2.84}$$

Third, for an **isochoric process** ($\mathrm{d}\alpha_\mathrm{a} = 0$), the first law simplifies from (2.77) to

$$\mathrm{dQ} = c_{v,\mathrm{m}}\,\mathrm{d}T = \mathrm{dU} \tag{2.85}$$

A fourth case is for an **adiabatic process**. Under adiabatic conditions, no energy is transferred to or from a parcel of air ($\mathrm{dQ} = 0$). Instead, a parcel's temperature changes only when the parcel expands or contracts as it ascends or descends, respectively. When a parcel rises, it encounters lower pressure and expands. As it expands, the kinetic energy of the air molecules within the parcel is converted to work used to expand the air. Since temperature decreases proportionally to kinetic energy from (2.4), a rising, expanding parcel of air cools under adiabatic conditions. The expansion of an air parcel in the absence of diabatic sources or sinks of energy is called an **adiabatic expansion**.

When a parcel sinks, it compresses and warms. When no energy transfer is considered, the compression is called an **adiabatic compression**. Under adiabatic conditions, the first law can be rewritten from (2.77), (2.79), and (2.82), respectively, to

$$c_{v,\mathrm{m}}\,\mathrm{d}T = -p_\mathrm{a}\,\mathrm{d}\alpha_\mathrm{a} \tag{2.86}$$

$$c_{p,\mathrm{m}}\,\mathrm{d}T = \alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a} \tag{2.87}$$

$$c_{p,\mathrm{d}}\,\mathrm{d}T_v \approx \alpha_\mathrm{a}\,\mathrm{d}p_\mathrm{a} \tag{2.88}$$

2.6.1.1 *Dry adiabatic lapse rate*

When an air parcel rises and cools, and no condensation occurs, the parcel's rate of cooling with height is approximately 9.8 K km^{-1}, which is the **dry (unsaturated) adiabatic lapse rate**. A lapse rate is the negative change in temperature with height. A positive lapse rate indicates that temperature decreases with increasing height.

The dry adiabatic lapse rate can be derived from the hydrostatic equation and the adiabatic form of the first law of thermodynamics. Taking the negative differential of (2.88) with respect to altitude, substituting the hydrostatic equation from (2.40), and substituting $\alpha_\mathrm{a} = 1/\rho_\mathrm{a}$ give the **dry adiabatic lapse rate in terms of virtual temperature** as

$$\Gamma_\mathrm{d} = -\left(\frac{\partial T_\mathrm{v}}{\partial z}\right)_\mathrm{d} \approx -\left(\frac{\alpha_\mathrm{a}}{c_{p,\mathrm{d}}}\right)\frac{\partial p_\mathrm{a}}{\partial z} = \left(\frac{\alpha_\mathrm{a}}{c_{p,\mathrm{d}}}\right)\rho_\mathrm{a} g = \frac{g}{c_{p,\mathrm{d}}} = +9.8\ \mathrm{K\ km^{-1}} \tag{2.89}$$

where the subscript d indicates that the change is dry (unsaturated) adiabatic. Equation (2.89) states that the virtual temperature of an unsaturated air parcel cools 9.8 K for every kilometer it ascends in the atmosphere under dry adiabatic conditions. From (2.87), the **dry adiabatic lapse rate in terms of actual temperature** can be written as

$$\Gamma_\mathrm{d,m} = -\left(\frac{\partial T}{\partial z}\right)_\mathrm{d} = \frac{g}{c_{p,\mathrm{m}}} = \frac{g}{c_{p,\mathrm{d}}}\left(\frac{1+\omega_\mathrm{v}}{1+c_{p,\mathrm{V}}\omega_\mathrm{v}/c_{p,\mathrm{d}}}\right) \tag{2.90}$$

where $c_{p,\mathrm{m}}$, obtained from (2.80), varies with water vapor content. The advantage of (2.89) is that the right side of the equation does not depend on water vapor content.

2.6.1.2 *Potential temperature*

A parameter used regularly in atmospheric analysis and modeling is potential temperature. **Potential temperature** is the temperature an unsaturated air parcel attains if it is brought adiabatically from its altitude down to a pressure of 1000 hPa.

Potential temperature is derived by first substituting $\alpha_\mathrm{a} = R_\mathrm{m}T/p_\mathrm{a}$ into (2.87), giving

$$\frac{\mathrm{d}T}{T} = \left(\frac{R_\mathrm{m}}{c_{p,\mathrm{m}}}\right)\frac{\mathrm{d}p_\mathrm{a}}{p_\mathrm{a}} \tag{2.91}$$

Integrating (2.91) from T_0 to T and $p_{a,0}$ to p_a yields **Poisson's equation,**

$$T = T_0\left(\frac{p_a}{p_{a,0}}\right)^{\frac{R_m}{c_{p,m}}} = T_0\left(\frac{p_a}{p_{a,0}}\right)^{\frac{R'(1+0.608q_v)}{c_{p,d}(1+0.856q_v)}} \approx T_0\left(\frac{p_a}{p_{a,0}}\right)^{\kappa(1-0.251q_v)} \qquad (2.92)$$

where

$$\kappa = \frac{R'}{c_{p,d}} = \frac{c_{p,d} - c_{v,d}}{c_{p,d}} = 0.286 \qquad (2.93)$$

When $p_{a,0} = 1000$ hPa, T_0 is called the **potential temperature of moist air** ($\theta_{p,m}$), and (2.92) becomes

$$\theta_{p,m} = T\left(\frac{1000\text{ hPa}}{p_a}\right)^{\kappa(1-0.251q_v)} \qquad (2.94)$$

In the absence of water vapor, $q_v = 0$ and $p_a = p_d$. In such a case, (2.94) simplifies to

$$\theta_p = T\left(\frac{1000\,\text{hPa}}{p_d}\right)^{\kappa} \qquad (2.95)$$

where θ_p is the **potential temperature of dry air.** Since q_v is usually smaller than 0.03 kg kg^{-1}, neglecting q_v in (2.94) causes an error in κ of less than 0.75 percent. Thus, for simplicity, (2.95) is usually used instead of (2.94) for defining potential temperature, even when water vapor is present. Potential temperature is conserved (stays constant) if an unsaturated air parcel is displaced adiabatically.

Figure 2.12 shows vertical profiles of potential temperature in the morning and afternoon at Riverside, California on August 27, 1987.

Example 2.21

If the temperature of a dry air parcel at $p_d = 800$ hPa is $T = 270$ K, then $\theta_p = 287.8$ K from (2.95).

A parameter related to potential temperature is **potential virtual temperature** (θ_v), which is found by converting all the moisture in a parcel to dry air, then bringing the parcel to a pressure of 1000 hPa and determining its temperature. θ_v is the potential temperature of a sample of moist air as if it were dry and at the same density and pressure as the moist air. It is derived by substituting $\alpha_a = R'T_v/p_a$ into (2.88), then integrating from $T_0 = \theta_v$ to T and $p_{a,0} = 1000$ hPa to p_a. The result is

$$\theta_v = T(1 + 0.608q_v)\left(\frac{1000\text{ hPa}}{p_a}\right)^{\kappa} = T_v\left(\frac{1000\text{ hPa}}{p_a}\right)^{\kappa} \qquad (2.96)$$

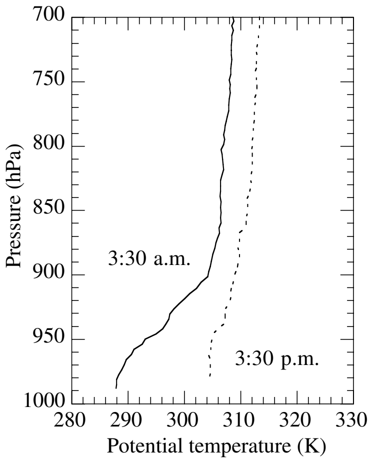

Figure 2.12 Observed vertical profiles of potential temperature at 3:30 a.m. and 3:30 p.m. on August 27, 1987 at Riverside, California. Potential temperatures correspond to actual temperatures shown in Fig. 2.11(a) and (b), respectively.

The change in **entropy** of an air parcel per unit mass (J kg^{-1} K^{-1}) due to energy transfer between the parcel and its environment is $\text{dS} = \text{dQ}/T$. During adiabatic expansion and compression, $\text{dQ} = 0$ and no change in entropy occurs. Since $\text{dQ} = 0$ along surfaces of constant potential virtual temperature, $\text{dS} = 0$ along such surfaces as well, and the surfaces are called **isentropic**. Figure 2.13 illustrates that potential virtual temperatures increase monotonically with height in the Northern-Hemisphere troposphere, causing isentropic surfaces to slant toward the North Pole.

A parameter related to potential virtual temperature is **virtual potential temperature**, which is found by bringing a moist parcel to a pressure of 1000 hPa, then converting all moisture in the parcel to dry air and determining the parcel's temperature. It is the virtual temperature of air that has been brought adiabatically to 1000 hPa. It is obtained by applying the virtual temperature correction from (2.38) to the potential temperature of moist air. The result is

$$\theta_{\text{p,v}} = \theta_{\text{p,m}}\,(1 + 0.608\text{q}_\text{v}) = T_\text{v}\left(\frac{1000\,\text{hPa}}{p_\text{a}}\right)^{\kappa(1-0.251\text{q}_\text{v})} \tag{2.97}$$

The difference between potential virtual temperature and virtual potential temperature is relatively small (Brutsaert 1991).

The **Exner function**, which is used in future chapters, is defined as $c_{\text{p,d}}P$, where

$$P = \left(\frac{p_\text{a}}{1000\,\text{hPa}}\right)^{\kappa} \tag{2.98}$$

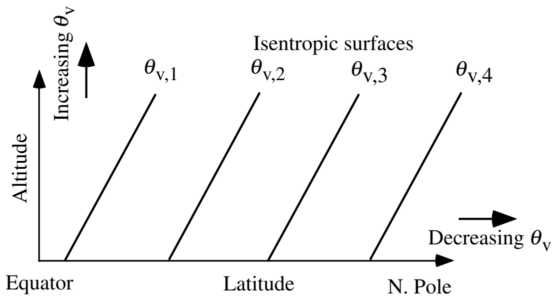

Figure 2.13 Isentropic surfaces (surfaces of constant potential virtual temperature) between the Equator and the North Pole. Sea-level temperature and, therefore, θ_v decrease from the Equator to the pole. Since the free troposphere is stably stratified with respect to unsaturated air, θ_v increases with altitude, and lines of constant θ_v slant toward the poles in the vertical.

Substituting P into (2.95) and (2.96) gives

$$T_v = \theta_v P \tag{2.99}$$

2.6.2 Stability criteria for unsaturated air

The concepts derived above from the first law of thermodynamics are useful for analyzing atmospheric stability. The atmosphere is stable (stably stratified) when a parcel of air, displaced vertically, decelerates and returns to its original position. The atmosphere is unstable when a displaced parcel accelerates in the direction in which it is displaced. The atmosphere is neutral when a parcel does not accelerate or decelerate after being displaced.

When the atmosphere is stable near the surface, pollution builds up, since air parcels cannot accelerate out of the stable layer to disperse the pollution. Stability also inhibits clouds of vertical development from forming. When the atmosphere is unstable, emitted pollutants accelerate vertically, decreasing their concentration near the surface. Clouds of vertical development can form in unstable air.

2.6.2.1 *Determining stability from the dry adiabatic lapse rate*

When the air is unsaturated with water vapor (i.e., the relative humidity is less than 100 percent), stability can be determined by comparing the environmental lapse rate with the dry adiabatic lapse rate ($\Gamma_{d,m}$ from (2.90)). The **environmental lapse rate,** $\Gamma_e = -\partial T/\partial z$, is the negative change of actual temperature with altitude. When temperature decreases with increasing altitude, $\Gamma_e > 0$. In terms of Γ_e and $\Gamma_{d,m}$, the stability criteria for unsaturated air are

$$\Gamma_e \begin{cases} > \Gamma_{d,m} & \text{unsaturated unstable} \\ = \Gamma_{d,m} & \text{unsaturated neutral} \\ < \Gamma_{d,m} & \text{unsaturated stable} \end{cases} \tag{2.100}$$

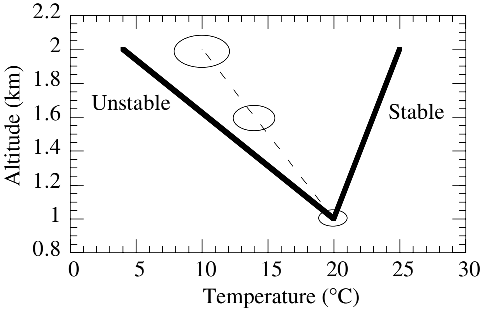

Figure 2.14 Demonstration of stability and instability in unsaturated air. When a parcel is displaced vertically, it rises and cools adiabatically (along the dashed line). If the environmental temperature profile is stable (right thick line), the rising parcel is cooler than the environment, decelerates, then sinks to its original position. If the environmental temperature profile is unstable (left thick line), the rising parcel is warmer than the air around it and continues to rise. The parcel stops rising only when it encounters air with the same temperature as itself. This occurs when the parcel reaches a layer with a new environmental temperature profile.

Figure 2.14 demonstrates how stability can be determined graphically.

Example 2.22

If the observed change in temperature with altitude is $\partial T/\partial z = -15$ K km^{-1} and the air contains no water vapor, what is the stability class of the atmosphere?

SOLUTION

The environmental lapse rate in this case is $\Gamma_e = +15$ K km^{-1}, which is greater than $\Gamma_{d,m} = +9.8$ K km^{-1}; thus, the atmosphere is unstable with respect to unsaturated air.

Equation (2.100) indicates that temperature can increase or decrease with increasing altitude in stable air but must decrease with increasing altitude in unstable air. A **temperature inversion** is an increase in temperature with increasing altitude. An inversion occurs only in stable air, but the presence of stable air does not necessarily mean that an inversion is present, as illustrated in Example 2.23.

Example 2.23

When temperature decreases slightly with increasing altitude (e.g., $\Gamma_e = +2.0\,\mathrm{K\,km^{-1}}$), the atmosphere is stable but an inversion is not present. An inversion occurs when temperature increases with altitude, as demonstrated by the line marked **stable** in Fig. 2.14.

Stability is enhanced by any process that warms air at higher altitudes relative to air at lower altitudes. At night, surface air becomes stable because the ground cools radiatively. During the day, stability is enhanced over land near the sea when cool marine air travels inland and displaces warm land-air vertically (creating warm air over cold air). Stability also increases when warm air blows over a cold surface or when air in a high-pressure system sinks, compresses, and warms on top of cool marine air below. Instability occurs when the land heats rapidly during the day or when a cold wind blows over a warm surface.

2.6.2.2 *Determining stability from potential virtual temperature*

Stability can also be determined from potential virtual temperature. Differentiating (2.96) gives

$$\mathrm{d}\theta_\mathrm{v} = \mathrm{d}T_\mathrm{v}\left(\frac{1000}{p_\mathrm{a}}\right)^{\kappa} + T_\mathrm{v}\kappa\left(\frac{1000}{p_\mathrm{a}}\right)^{\kappa-1}\left(-\frac{1000}{p_\mathrm{a}^2}\right)\mathrm{d}p_\mathrm{a} = \frac{\theta_\mathrm{v}}{T_\mathrm{v}}\,\mathrm{d}T_\mathrm{v} - \kappa\frac{\theta_\mathrm{v}}{p_\mathrm{a}}\,\mathrm{d}p_\mathrm{a} \tag{2.101}$$

Taking the partial derivative of (2.101) with respect to height and substituting $\partial p_\mathrm{a}/\partial z = -\rho_\mathrm{a} g$ and the **virtual temperature lapse rate,** $\Gamma_\mathrm{v} = -\partial T_\mathrm{v}/\partial z$, into the result give

$$\frac{\partial\theta_\mathrm{v}}{\partial z} = \frac{\theta_\mathrm{v}}{T_\mathrm{v}}\frac{\partial T_\mathrm{v}}{\partial z} - \kappa\frac{\theta_\mathrm{v}}{p_\mathrm{a}}\frac{\partial p_\mathrm{a}}{\partial z} = -\frac{\theta_\mathrm{v}}{T_\mathrm{v}}\Gamma_\mathrm{v} + \frac{R'}{c_{p,\mathrm{d}}}\frac{\theta_\mathrm{v}}{p_\mathrm{a}}\rho_\mathrm{a} g \tag{2.102}$$

Substituting $T_\mathrm{v} = p_\mathrm{a}/\rho_\mathrm{a} R'$ and $\Gamma_\mathrm{d} = g/c_{p,\mathrm{d}}$ from (2.89) into (2.102) results in

$$\boxed{\frac{\partial\theta_\mathrm{v}}{\partial z} = -\frac{\theta_\mathrm{v}}{T_\mathrm{v}}\Gamma_\mathrm{v} + \frac{\theta_\mathrm{v} g}{T_\mathrm{v} c_{p,\mathrm{d}}} = \frac{\theta_\mathrm{v}}{T_\mathrm{v}}\left(\Gamma_\mathrm{d} - \Gamma_\mathrm{v}\right)} \tag{2.103}$$

Equation (2.100) indicates that the air is stable when $\Gamma_\mathrm{d} > \Gamma_\mathrm{v}$, suggesting that $\partial\theta_\mathrm{v}/\partial z > 0$ also indicates that the air is stable. Thus, the stability criteria in terms of potential virtual temperature are

$$\frac{\partial\theta_\mathrm{v}}{\partial z}\begin{cases} < 0 & \text{unsaturated unstable} \\ = 0 & \text{unsaturated neutral} \\ > 0 & \text{unsaturated stable} \end{cases} \tag{2.104}$$

Figure 2.15 demonstrates how stability can be determined from a graph of potential virtual temperature versus altitude.

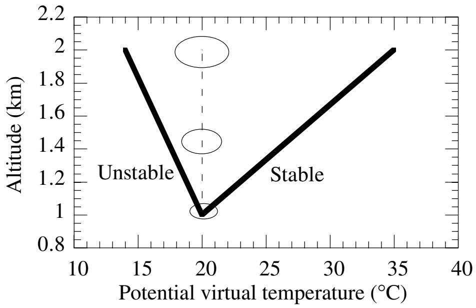

Figure 2.15 Demonstration of stability and instability from potential virtual temperature. When an unsaturated parcel is displaced vertically, it rises and cools adiabatically (along the dashed line). If the ambient potential-virtual-temperature profile slopes positively, a rising parcel is always cooler than the environment, the atmosphere is stable, and the parcel sinks back to its original position. If the ambient potential-virtual-temperature profile slopes negatively, a rising parcel is always warmer than the environment, the atmosphere is unstable, and the parcel continues rising.

The advantage of deriving stability from θ_v instead of from potential temperature of dry air is that the latter parameter does not account for water vapor whereas the former does. The advantage of deriving stability from θ_v instead of from the potential temperature of moist air or from virtual potential temperature is that, although the latter parameters include water vapor more accurately than does θ_v, their differentiation requires several additional terms of little consequence not required in the differentiation of θ_v.

Example 2.24

Given $\Gamma_v = +7\ \text{K km}^{-1}$, $p_a = 925$ hPa, and $T_v = 290$ K, find $\partial\theta_v/\partial z$.

SOLUTION

From (2.96), $\theta_v = 296.5$ K. Thus, from (2.103), $\partial\theta_v/\partial z = 2.86\ \text{K km}^{-1}$, and the atmosphere is stable with respect to unsaturated air.

2.6.2.3 *Determining stability from the Brunt–Väisälä frequency*

Another way to write equation (2.103) is

$$\frac{\partial \ln \theta_v}{\partial z} = \frac{1}{T_v}\left(\Gamma_d - \Gamma_v\right) \tag{2.105}$$

Multiplying by gravitational acceleration, g, gives

$$\boxed{N_{\mathrm{bv}}^2 = g\frac{\partial \ln \theta_{\mathrm{v}}}{\partial z} = \frac{g}{T_{\mathrm{v}}}\left(\Gamma_{\mathrm{d}} - \Gamma_{\mathrm{v}}\right)} \qquad (2.106)$$

where N_{bv} is the **Brunt–Väisälä frequency** (or buoyancy frequency).

The Brunt–Väisälä frequency measures the static stability of the atmosphere. If θ_{v} increases with increasing height ($\Gamma_{\mathrm{d}} > \Gamma_{\mathrm{v}}$), then $N_{\mathrm{bv}}^2 > 0$, and the atmosphere is stable. In such a case, buoyancy acts as a restoring force, causing a perturbed parcel of air to oscillate about its initial altitude with a period $\tau_{\mathrm{bv}} = 2\pi / N_{\mathrm{bv}}$. During the oscillation, kinetic energy is exchanged with potential energy. The oscillations arising from buoyancy restoration are **gravity waves**, discussed in Chapter 4.

If θ_{v} is constant with increasing altitude ($N_{\mathrm{bv}}^2 = 0$), the atmosphere is **neutral**, and displacements occur without resistance from a restoring buoyancy force. If θ_{v} decreases with increasing altitude ($N_{\mathrm{bv}}^2 < 0$), the atmosphere is **unstable**, and a parcel's displacement increases exponentially with time. In sum, the stability criteria from the Brunt–Väisälä frequency are

$$N_{\mathrm{bv}}^2 \begin{cases} < 0 & \text{unsaturated unstable} \\ = 0 & \text{unsaturated neutral} \\ > 0 & \text{unsaturated stable} \end{cases} \qquad (2.107)$$

Example 2.25

Given $\Gamma_{\mathrm{v}} = +6.5\ \mathrm{K\,km^{-1}}$ and $T_{\mathrm{v}} = 288$ K, estimate the Brunt–Väisälä frequency and the period of oscillation of a perturbed parcel of air.

SOLUTION

Since $\Gamma_{\mathrm{d}} = +9.8\ \mathrm{K\,km^{-1}}$ and $g = 9.81\ \mathrm{m\,s^{-2}}$, we have $N_{\mathrm{bv}} = 0.0106\ \mathrm{s^{-1}}$ from (2.106), and $\tau_{\mathrm{bv}} = 593$ s. The atmosphere is statically stable with respect to unsaturated air in this case.

2.7 SUMMARY

In this chapter, the structure and composition of the atmosphere were discussed. The bottom 100 km of the atmosphere consists of four primary regions of temperature variation: the troposphere, stratosphere, mesosphere, and thermosphere. The troposphere consists of the boundary layer and the free troposphere. Three important variables describing the atmosphere, temperature, pressure, and density, are related by the equation of state. Other variables discussed include the relative humidity and potential virtual temperature. Some equations derived included the hydrostatic equation, Clausius–Clapeyron equation, and first law of thermodynamics. The equation of state and hydrostatic equation were combined to give expressions for altitude as a function of air pressure and vice versa. The Clausius–Clapeyron equation was combined with empirical relationships for latent heat to derive expressions for the saturation vapor pressure of water over liquid and ice. The first law of thermodynamics was used to derive atmospheric stability criteria. In the next chapter, the continuity and thermodynamic energy equations are discussed.

2.8 PROBLEMS

2.1 If $T = 295$ K at 1 mm above the ground and the conductive heat flux is $H_c = 250$ W m^{-2}, estimate the temperature at the ground. Assume the air is dry.

2.2 If $N_q = 1.5 \times 10^{12}$ molec. cm^{-3} for O_3 gas, $T = 285$ K, and $p_d = 980$ hPa, find the volume mixing ratio, dry-air mass mixing ratio, and partial pressure of ozone.

2.3 If $\omega_q = 1.3$ ppmm for carbon monoxide gas, $T = 285$ K, and $p_d = 980$ hPa, find the volume mixing ratio, number concentration, and partial pressure of carbon monoxide.

2.4 If $T = 268$ K and $p_d = 700$ hPa, respectively, find $p_{v,s}$ in hPa, and find the corresponding mixing ratio of water vapor in percent, ppmm, and ppmv.

2.5 Find the mass density of moist air (ρ_a) if $T = 283$ K, $f_r = 78$ percent, and $p_d = 850$ hPa.

2.6 Find the pressure exerted by moist air if $T = 288$ K, $f_r = 82$ percent, and $p_d = 925$ hPa.

2.7 Find the virtual temperature when $N_a = 2.1\times 10^{19}$ molec. cm^{-3}, $T = 295$ K, and $f_r = 92$ percent.

2.8 Find the partial pressure of water vapor if $q_v = 3$ g kg^{-1}, $T = 278$ K, and $\rho_d = 0.5$ kg m^{-3}.

2.9 If $T_v = 281$ K, $p_v = 3$ hPa, and $p_a = 972$ hPa, find the air temperature.

2.10 If the total air pressure, temperature, and relative humidity are $p_a = 945$ hPa, $T = 276$ K, and $f_r = 46$ percent, find ω_v, m_a, R_m, T_v, and ρ_a.

2.11 If dry-air pressure, temperature, and water-vapor–dry-air mass mixing ratio are $p_d = 927$ hPa, $T = 281$ K, and $\omega_v = 0.005$ kg kg^{-1}, find f_r, m_a, R_m, T_v, and ρ_a.

2.12 If the total air pressure, water-vapor volume mixing ratio, and temperature are $p_a = 966$ hPa, $\chi_v = 3000$ ppmv, and $T = 284$ K, find p_v, m_a, R_m, T_v, and ρ_a.

2.13 Find the altitude in a standard atmosphere that a pressure altimeter gives if the pressure measured by the altimeter is $p_a = 770$ hPa and the air is dry.

2.14 Estimate the scale height of the atmosphere (H) and resulting pressure at $z = 200$ m altitude if the air is dry, the pressure at $z = 100$ m is $p_d = 990$ hPa, and the average temperature between $z = 100$ m and $z = 200$ m is $T = 284$ K.

2.15 If the air is dry, $z = 10$ km, $p_d = 250$ hPa, and $T = 218$ K (base of the tropopause), estimate the scale height at $z = 10$ km and pressure at $z = 10.5$ km.

2.16 Calculate the saturation vapor pressure of water over liquid and ice if $T_c = -15$ °C. Find ω_v and p_v at this temperature if $f_r = 3$ percent and $p_d = 230$ hPa.

2.17 Calculate the dew point if $f_r = 54$ percent and $T = 263$ K.

2.18 Derive the expression for the water-vapor mass mixing ratio as a function of dew point and pressure from (2.68). If $T_D = 284$ K and $p_d = 1000$ hPa, find ω_v.

2.19 If $T_D = 279$ K, $T = 281$ K, and $p_d = 930$ hPa, calculate f_r, p_v, ω_v, and $\omega_{v,s}$.

2.20 **(a)** Estimate the diabatic energy (dQ) that needs to be added to or removed from a parcel of air to increase its virtual temperature $dT_v = +2$ K when $\rho_a = 1.2$ kg m^{-3} and when the pressure change in the parcel due to adiabatic expansion is $dp_a = -10$ hPa.

(b) If dQ is removed from part (a) and other conditions stay the same, what is the parcel virtual-temperature change? What type of process is this?

(c) If the parcel in part (a) does not rise or expand ($dp_a = 0$), but dQ calculated from part (a) remains, what is the virtual-temperature change of the parcel? What is the name of this type of process?

(d) If the parcel in part (a) does not change virtual temperature ($dT_v = 0$), but $dp_a = -10$ hPa, what is the new value of dQ? What is the name of this process?

2.21 Calculate the potential virtual temperature of dry air when (a) $p_a = 900$ hPa and $T = 280$ K; (b) $p_a = 850$ hPa and $T = 278$ K. Is the air parcel between 900 and 850 hPa stable, unstable, or neutral with respect to unsaturated air?

2.22 If $\theta_p = 303$ K at $p_d = 825$ hPa, find the air temperature at this pressure.

2.23 Calculate the change in potential virtual temperature with altitude ($\partial\theta_v/\partial z$) when the ambient virtual-temperature lapse rate is $\Gamma_v = +6.2$ K km^{-1}, the air pressure is $p_a = 875$ hPa, and $T_v = 283$ K. Is this air stable, unstable, or neutral with respect to unsaturated air?

2.24 If the air is dry and the potential virtual temperature increases at the rate $\partial\theta_v/\partial z = 1$ K km^{-1}, calculate the ambient virtual-temperature lapse rate when $p_a = 925$ hPa and $T = 288$ K. Is this air stable, unstable, or neutral with respect to unsaturated air?

2.25 If the potential virtual temperature increases at the rate $\partial\theta_v/\partial z = 2$ K km^{-1} in dry air at an altitude where $p_a = 945$ hPa and $T = 287$ K, estimate T at 100 m above this altitude.

2.26 Would liquid water and/or ice particles grow when (a) $p_v = 1$ hPa, $T = -30$ K; (b) $p_v = 1.2$ hPa, $T = -20$ K; or (c) $p_v = 1$ hPa, $T = -16$ K? Use Fig. 2.8(b).

2.27 Does potential virtual temperature at sea level increase, decrease, or stay constant (on average) between the Equator and North Pole? Why? Does potential virtual temperature increase, decrease, or stay constant with altitude if $\Gamma_v = +6.5$ K km^{-1}? Why?

2.28 What might Figs. 2.3(a) and (b) look like under a low-pressure system, if all other conditions were the same?

2.9 COMPUTER PROGRAMMING PRACTICE

2.29 Write a computer script to calculate air pressure (p_a) as a function of altitude from (2.41). Assume $p_a = 1013$ hPa and $T = 288$ K at the surface, the temperature decreases at the rate of 6.5 K km^{-1}, and the air is dry. Use the program to estimate the pressure from $z = 0$ to 10 km in increments of 100 m. Calculate the density ρ_a with the equation of state at the base of each layer before each pressure calculation for the next layer. Plot the results.

2.30 Write a computer script to calculate p_a as a function of altitude from (2.44). Assume $T = 298$ K and $p_a = 1013$ hPa at the surface and the air is dry. Use the program to estimate the pressure from $z = 0$ to 10 km in increments of 100 m. Plot the results.

2.31 Write a computer script to calculate p_a as a function of altitude from (2.48). Assume $T = 298$ K and $p_a = 1013$ hPa at the surface, the air is dry, and the temperature decreases from the surface at 6.5 K km^{-1}. Use the program to estimate the pressure from $z = 0$ to 10 km in increments of 100 m, calculating the scale height for each layer. Plot the results.

2.32 Write a computer script to calculate the saturation vapor pressure of water over liquid and ice from (2.61) and (2.64), respectively. Use the program to estimate $p_{v,s}$ between -50 °C and +50 °C and $p_{v,I}$ between -50 °C and 0 °C, in increments of 1 °C. Plot the results.

2.33 Write a computer script to calculate $p_{v,s}$, $p_{v,I}$, and T_D versus altitude. Assume T is 298 K at $z = 0$ km and decreases 6.5 K km^{-1}. Assume also that $f_r = 90$ percent at all altitudes. Use the program to estimate parameters from $z = 0$ to 10 km in increments of 100 m. Plot the results.