Atmospheric Thermodynamics

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The theory of thermodynamics is one of the cornerstones and crowning glories of classical physics. It has applications not only in physics, chemistry, and the Earth sciences, but in subjects as diverse as biology and economics. Thermodynamics plays an important role in our quantitative understanding of atmospheric phenomena ranging from the smallest cloud microphysical processes to the general circulation of the atmosphere. The purpose of this chapter is to introduce some fundamental ideas and relationships in thermodynamics and to apply them to a number of simple, but important, atmospheric situations. Further applications of the concepts developed in this chapter occur throughout this book.

The first section considers the *ideal gas equation* and its application to dry air, water vapor, and moist air. In Section 3.2 an important meteorological relationship, known as the *hydrostatic equation*, is derived and interpreted. The next section is concerned with the relationship between the mechanical work done by a system and the heat the system receives, as expressed in the *first law of thermodynamics*. There follow several sections concerned with applications of the foregoing to the atmosphere. Finally, in Section 3.7, the *second law of thermodynamics* and the concept of *entropy* are introduced and used to derive some important relationships for atmospheric science.

3.1 Gas Laws

Laboratory experiments show that the pressure, volume, and temperature of any material can be related by an *equation of state* over a wide range of conditions. All gases are found to follow approximately the same equation of state, which is referred to as the *ideal gas equation*. For most purposes we may assume that atmospheric gases, whether considered individually or as a mixture, obey the ideal gas equation exactly. This section considers various forms of the ideal gas equation and its application to dry and moist air.

The ideal gas equation may be written as

$$pV = mRT \tag{3.1}$$

where p, V, m, and T are the pressure (Pa), volume (m^3), mass (kg), and absolute temperature (in kelvin, K, where K = °C + 273.15) of the gas, respectively, and R is a constant (called the *gas constant*) for 1 kg of a gas. The value of R depends on the particular gas under consideration. Because $m/V = \rho$, where ρ is the density of the gas, the ideal gas equation may also be written in the form

$$p = \rho RT \tag{3.2}$$

For a unit mass (1 kg) of gas $m = 1$ and we may write (3.1) as

$$p\alpha = RT \tag{3.3}$$

where $\alpha = 1/\rho$ is the *specific volume* of the gas, i.e., the volume occupied by 1 kg of the gas at pressure p and temperature T.

If the temperature is constant (3.1) reduces to *Boyle's law*,[1] which states *if the temperature of a fixed mass of gas is held constant, the volume of the*

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[1] The Hon. **Sir Robert Boyle** (1627–1691) Fourteenth child of the first Earl of Cork. Physicist and chemist, often called the "father of modern chemistry." Discovered the law named after him in 1662. Responsible for the first sealed thermometer made in England. One of the founders of the Royal Society of London, Boyle declared: "The Royal Society values no knowledge but as it has a tendency to use it!"

gas is inversely proportional to its pressure. Changes in the physical state of a body that occur at constant temperature are termed *isothermal*. Also implicit in (3.1) are *Charles' two laws*.[2] The first of these laws states *for a fixed mass of gas at constant pressure, the volume of the gas is directly proportional to its absolute temperature*. The second of Charles' laws states *for a fixed mass of gas held within a fixed volume, the pressure of the gas is proportional to its absolute temperature*.

3.1 Gas Laws and the Kinetic Theory of Gases: Handball Anyone?

The kinetic theory of gases pictures a gas as an assemblage of numerous identical particles (atoms or molecules)[3] that move in random directions with a variety of speeds. The particles are assumed to be very small compared to their average separation and are perfectly elastic (i.e., if one of the particles hits another, or a fixed wall, it rebounds, on average, with the same speed that it possessed just prior to the collision). It is shown in the kinetic theory of gases that the mean kinetic energy of the particles is proportional to the temperature in degrees kelvin of the gas.

Imagine now a handball court in a zero-gravity world in which the molecules of a gas are both the balls and the players. A countless (but fixed) number of elastic balls, each of mass m and with mean velocity v, are moving randomly in all directions as they bounce back and forth between the walls.[7] The force exerted on a wall of the court by the bouncing of balls is equal to the momentum exchanged in a typical collision (which is proportional to mv) multiplied by the frequency with which the balls impact the wall. Consider the following thought experiments.

i. Let the volume of the court increase while holding v (and therefore the temperature of the gas) constant. The frequency of collisions will decrease in inverse proportion to the change in volume of the court, and the force (and therefore the pressure) on a wall will decrease similarly. This is Boyle's law.
ii. Let v increase while holding the volume of the court constant. Both the frequency of collisions with a wall and the momentum exchanged in each collision of a ball with a wall will increase in linear proportion to v. Therefore, the pressure on a wall will increase as mv^2, which is proportional to the mean kinetic energy of the molecules and therefore to their temperature in degrees kelvin. This is the second of Charles' laws. It is left as an exercise for the reader to prove Charles' first law, using the same analogy.

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[2] **Jacques A. C. Charles** (1746–1823) French physical chemist and inventor. Pioneer in the use of hydrogen in man-carrying balloons. When Benjamin Franklin's experiments with lightning became known, Charles repeated them with his own innovations. Franklin visited Charles and congratulated him on his work.

[3] The idea that a gas consists of atoms in random motion was first proposed by Lucretius.[4] This idea was revived by Bernouilli[5] in 1738 and was treated in mathematical detail by Maxwell.[6]

[4] **Titus Lucretius Carus** (*ca*. 94–51 B.C.) Latin poet and philosopher. Building on the speculations of the Greek philosophers Leucippus and Democritus, Lucretius, in his poem *On the Nature of Things*, propounds an atomic theory of matter. Lucretius' basic theorem is "nothing exists but atoms and voids." He assumed that the quantity of matter and motion in the world never changes, thereby anticipating by nearly 2000 years the statements of the conservation of mass and energy.

[5] **Daniel Bernouilli** (1700–1782) Member of a famous family of Swiss mathematicians and physicists. Professor of botany, anatomy, and natural philosophy (i.e., physics) at University of Basel. His most famous work, *Hydrodynamics* (1738), deals with the behavior of fluids.

[6] **James Clark Maxwell** (1831–1879) Scottish physicist. Made fundamental contributions to the theories of electricity and magnetism (showed that light is an electromagnetic wave), color vision (produced one of the first color photographs), and the kinetic theory of gases. First Cavendish Professor of Physics at Cambridge University; designed the Cavendish Laboratory.

[7] In the kinetic theory of gases, the appropriate velocity of the molecules is their root mean square velocity, which is a little less than the arithmetic mean of the molecular velocities.

We define now a *gram-molecular weight* or *a mole* (abbreviated to *mol*) of any substance as the molecular weight, M, of the substance expressed in grams.[8] For example, the molecular weight of water is 18.015; therefore, 1 mol of water is 18.015 g of water. The number of moles n in mass m (*in grams*) of a substance is given by

$$n = \frac{m}{M} \tag{3.4}$$

Because the masses contained in 1 mol of different substances bear the same ratios to each other as the molecular weights of the substances, 1 mol of any substance must contain the same number of molecules as 1 mol of any other substance. Therefore, the number of molecules in 1 mol of any substance is a universal constant, called *Avogadro's*[9] *number,* N_A. The value of N_A is 6.022×10^{23} per mole.

According to *Avogadro's hypothesis*, gases containing the same number of molecules occupy the same volumes at the same temperature and pressure. It follows from this hypothesis that provided we take the same number of molecules of any gas, the constant R in (3.1) will be the same. However, 1 mol of any gas contains the same number of molecules as 1 mol of any other gas. Therefore, the constant R in (3.1) for 1 mol is the same for all gases; it is called the *universal gas constant* (R^*). The magnitude of R^* is 8.3145 J K^{-1} mol^{-1}. The ideal gas equation for 1 mol of any gas can be written as

$$pV = R^*T \tag{3.5}$$

and for n moles of any gas as

$$pV = nR^*T \tag{3.6}$$

The gas constant for one molecule of any gas is also a universal constant, known as *Boltzmann's*[10] *constant,* k. Because the gas constant for N_A molecules is R^*, we have

$$k = \frac{R^*}{N_A} \tag{3.7}$$

Hence, for a gas containing n_0 molecules per unit volume, the ideal gas equation is

$$p = n_0 kT \tag{3.8}$$

If the pressure and specific volume of dry air (i.e., the mixture of gases in air, excluding water vapor) are p_d and α_d, respectively, the ideal gas equation in the form of (3.3) becomes

$$p_d\,\alpha_d = R_d T \tag{3.9}$$

where R_d is the gas constant for 1 kg of dry air. By analogy with (3.4), we can define the *apparent molecular weight* M_d of dry air as the total mass (in grams) of the constituent gases in dry air divided by the total number of moles of the constituent gases; that is,

$$M_d = \frac{\sum_i m_i}{\sum_i \frac{m_i}{M_i}} \tag{3.10}$$

where m_i and M_i represent the mass (in grams) and molecular weight, respectively, of the ith constituent in the mixture. The apparent molecular weight of dry air is 28.97. Because R^* is the gas constant for 1 mol of any substance, or for M_d (= 28.97) grams of dry air, the gas constant for 1 g of dry air is R^*/M_d, and for 1 kg of dry air it is

$$R_d = 1000\,\frac{R^*}{M_d} = 1000\,\frac{8.3145}{28.97} = 287.0 \text{ J K}^{-1}\text{kg}^{-1} \tag{3.11}$$

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[8] In the first edition of this book we defined a *kilogram*-molecular weight (or *kmole*), which is 1000 moles. Although the kmole is more consistent with the SI system of units than the mole, it has not become widely used. For example, the mole is used almost universally in chemistry. One consequence of the use of the mole, rather than kmole, is that a factor of 1000, which serves to convert kmoles to moles, appears in some relationships [e.g. (3.11) and (3.13) shown later].

[9] **Amedeo Avogadro, Count of Quaregna** (1776–1856) Practiced law before turning to science at age 23. Later in life became a professor of physics at the University of Turin. His famous hypothesis was published in 1811, but it was not generally accepted until a half century later. Introduced the term "molecule."

[10] **Ludwig Boltzmann** (1844–1906) Austrian physicist. Made fundamental contributions to the kinetic theory of gases. Adhered to the view that atoms and molecules are real at a time when these concepts were in dispute. Committed suicide.

The ideal gas equation may be applied to the individual gaseous components of air. For example, for water vapor (3.3) becomes

$$e\alpha_v = R_v T \qquad (3.12)$$

where e and α_v are, respectively, the pressure and specific volume of water vapor and R_v is the gas constant for 1 kg of water vapor. Because the molecular weight of water is M_w (= 18.016) and the gas constant for M_w grams of water vapor is R^*, we have

$$R_v = 1000\frac{R^*}{M_w} = 1000\frac{8.3145}{18.016} = 461.51 \text{ J K}^{-1}\text{kg}^{-1} \qquad (3.13)$$

From (3.11) and (3.13),

$$\frac{R_d}{R_v} = \frac{M_w}{M_d} \equiv \varepsilon = 0.622 \qquad (3.14)$$

Because air is a mixture of gases, it obeys *Dalton's*[11] *law of partial pressures*, which states *the total pressure exerted by a mixture of gases that do not interact chemically is equal to the sum of the partial pressures of the gases*. The *partial pressure* of a gas is the pressure it would exert at the same temperature as the mixture if it alone occupied all of the volume that the mixture occupies.

Exercise 3.1 If at 0 °C the density of dry air alone is 1.275 kg m^{-3} and the density of water vapor alone is 4.770×10^{-3} kg m^{-3}, what is the total pressure exerted by a mixture of the dry air and water vapor at 0 °C?

Solution: From Dalton's law of partial pressures, the total pressure exerted by the mixture of dry air and water vapor is equal to the sum of their partial pressures. The partial pressure exerted by the dry air is, from (3.9),

$$p_d = \frac{1}{\alpha_d} R_d T = \rho_d R_d T$$

where ρ_d is the density of the dry air (1.275 kg m^{-3} at 273 K), R_d is the gas constant for 1 kg of dry air (287.0 J K^{-1} kg^{-1}), and T is 273.2 K. Therefore,

$$p_d = 9.997 \times 10^4 \text{Pa} = 999.7 \text{ hPa}$$

Similarly, the partial pressure exerted by the water vapor is, from (3.12),

$$e = \frac{1}{\alpha_v} R_v T = \rho_v R_v T$$

where ρ_v is the density of the water vapor (4.770×10^{-3} kg m^{-3} at 273 K), R_v is the gas constant for 1 kg of water vapor (461.5 J K^{-1} kg^{-1}), and T is 273.2 K. Therefore,

$$e = 601.4\ Pa = 6.014 \text{ hPa}$$

Hence, the total pressure exerted by the mixture of dry air and water vapor is (999.7 + 6.014) hPa or 1006 hPa. ■

3.1.1 Virtual Temperature

Moist air has a smaller apparent molecular weight than dry air. Therefore, it follows from (3.11) that the gas constant for 1 kg of moist air is larger than that for 1 kg of dry air. However, rather than use a gas constant for moist air, the exact value of which would depend on the amount of water vapor in the air (which varies considerably), it is convenient to retain the gas constant for dry air and use a fictitious temperature (called the *virtual temperature*) in the ideal gas equation. We can derive an expression for the virtual temperature in the following way.

Consider a volume V of moist air at temperature T and total pressure p that contains mass m_d of dry air and mass m_v of water vapor. The density ρ of the moist air is given by

$$\rho = \frac{m_d + m_v}{V} = \rho'_d + \rho'_v$$

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[11] **John Dalton** (1766–1844) English chemist. Initiated modern atomic theory. In 1787 he commenced a meteorological diary that he continued all his life, recording 200,000 observations. Showed that the rain and dew deposited in England are equivalent to the quantity of water carried off by evaporation and by the rivers. This was an important contribution to the idea of a hydrological cycle. First to describe color blindness. He "never found time to marry!" His funeral in Manchester was attended by 40,000 mourners.

where ρ'_d is the density that the same mass of dry air would have if it alone occupied all of the volume V and ρ'_v is the density that the same mass of water vapor would have if it alone occupied all of the volume V. We may call these *partial densities*. Because $\rho = \rho'_d + \rho'_v$, it might appear that the density of moist air is greater than that of dry air. However, this is not the case because the partial density ρ'_v is less than the true density of dry air.[12] Applying the ideal gas equation in the form of (3.2) to the water vapor and dry air in turn, we have

$$e = \rho'_v R_v T$$

and

$$p'_d = \rho'_d R_d T$$

where e and p'_d are the partial pressures exerted by the water vapor and the dry air, respectively. Also, from Dalton's law of partial pressures,

$$p = p'_d + e$$

Combining the last four equations

$$\rho = \frac{p - e}{R_d T} + \frac{e}{R_v T}$$

or

$$\rho = \frac{p}{R_d T}\left[1 - \frac{e}{p}(1 - \varepsilon)\right]$$

where ε is defined by (3.14). The last equation may be written as

$$p = \rho R_d T_v \tag{3.15}$$

where

$$T_v \equiv \frac{T}{1 - \frac{e}{p}(1 - \varepsilon)} \tag{3.16}$$

T_v is called the *virtual temperature*. If this fictitious temperature, rather than the actual temperature, is used for moist air, the total pressure p and density ρ of the moist air are related by a form of the ideal gas equation [namely, (3.15)], but with the gas constant the same as that for a unit mass of *dry air* (R_d) and the actual temperature T replaced by the virtual temperature T_v. It follows that the virtual temperature is the temperature that dry air would need to attain in order to have the same density as the moist air at the same pressure. Because moist air is less dense than dry air at the same temperature and pressure, the virtual temperature is always greater than the actual temperature. However, even for very warm and moist air, the virtual temperature exceeds the actual temperature by only a few degrees (e.g., see Exercise 3.7 in Section 3.5).

3.2 The Hydrostatic Equation

Air pressure at any height in the atmosphere is due to the force per unit area exerted by the weight of all of the air lying above that height. Consequently, atmospheric pressure decreases with increasing height above the ground (in the same way that the pressure at any level in a stack of foam mattresses depends on how many mattresses lie above that level). The net upward force acting on a thin horizontal slab of air, due to the decrease in atmospheric pressure with height, is generally very closely in balance with the downward force due to gravitational attraction that acts on the slab. If the net upward force on the slab is equal to the downward force on the slab, the atmosphere is said to be in *hydrostatic balance*. We will now derive an important equation for the atmosphere in hydrostatic balance.

Consider a vertical column of air with unit horizontal cross-sectional area (Fig. 3.1). The mass of air between heights z and $z + \delta z$ in the column is $\rho \delta z$, where ρ is the density of the air at height z. The downward force acting on this slab of air due to the weight of the air is $g\rho\delta z$, where g is the acceleration due to gravity at height z. Now let us consider the net

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[12] The fact that moist air is less dense than dry air was first clearly stated by Sir Isaac Newton[13] in his "*Opticks*" (1717). However, the basis for this relationship was not generally understood until the latter half of the 18th century.

[13] **Sir Isaac Newton** (1642–1727) Renowned English mathematician, physicist, and astronomer. A posthumous, premature ("I could have been fitted into a quart mug at birth"), and only child. Discovered the laws of motion, the universal law of gravitation, calculus, the colored spectrum of white light, and constructed the first reflecting telescope. He said of himself: "I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the seashore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, while the great ocean of truth lay all undiscovered before me."

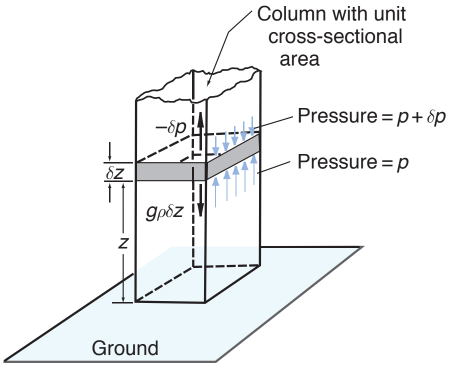

Fig. 3.1 Balance of vertical forces in an atmosphere in which there are no vertical accelerations (i.e., an atmosphere in hydrostatic balance). Small blue arrows indicate the downward force exerted on the air in the shaded slab due to the pressure of the air above the slab; longer blue arrows indicate the upward force exerted on the shaded slab due to the pressure of the air below the slab. Because the slab has a unit cross-sectional area, these two pressures have the same numerical values as forces. The net upward force due to these pressures ($-\delta p$) is indicated by the upward-pointing thick black arrow. Because the incremental pressure change δp is a negative quantity, $-\delta p$ is positive. The downward-pointing thick black arrow is the force acting on the shaded slab due to the mass of the air in this slab.

vertical force that acts on the slab of air between z and $z + \delta z$ due to the pressure of the surrounding air. Let the change in pressure in going from height z to height $z + \delta z$ be δp, as indicated in Fig. 3.1. Because we know that pressure decreases with height, δp must be a negative quantity, and the upward pressure on the lower face of the shaded block must be slightly greater than the downward pressure on the upper face of the block. Therefore, the net vertical force on the block due to the vertical gradient of pressure is upward and given by the positive quantity $-\delta p$, as indicated in Fig. 3.1. For an atmosphere in hydrostatic balance, the balance of forces in the vertical requires that

$$-\delta p = g\rho\delta z$$

or, in the limit as $\delta z \to 0$,

$$\frac{\partial p}{\partial z} = -g\rho \tag{3.17}$$

Equation (3.17) is the *hydrostatic equation*.[14] It should be noted that the negative sign in (3.17) ensures that the pressure decreases with increasing height. Because $\rho = 1/\alpha$ (3.17) can be rearranged to give

$$gdz = -\alpha dp \tag{3.18}$$

If the pressure at height z is $p(z)$, we have, from (3.17), above a fixed point on the Earth

$$-\int_{p(z)}^{p(\infty)} dp = \int_z^\infty g\rho dz$$

or, because $p(\infty) = 0$,

$$p(z) = \int_z^\infty g\rho dz \tag{3.19}$$

That is, the pressure at height z is equal to the weight of the air in the vertical column of unit cross-sectional area lying above that level. If the mass of the Earth's atmosphere were distributed uniformly over the globe, retaining the Earth's topography in its present form, the pressure at sea level would be 1.013×10^5 Pa, or 1013 hPa, which is referred to as *1 atmosphere* (or *1 atm*).

3.2.1 Geopotential

The *geopotential* Φ at any point in the Earth's atmosphere is defined as the work that must be done against the Earth's gravitational field to raise a mass of 1 kg from sea level to that point. In other words, Φ is the gravitational potential per unit mass. The units of geopotential are J kg^{-1} or m^2 s^{-2}. The force (in newtons) acting on 1 kg at height z above sea level is numerically equal to g. The work (in joules) in raising 1 kg from z to $z + dz$ is gdz; therefore

$$d\Phi \equiv gdz$$

or, using (3.18),

$$d\Phi \equiv gdz = -\alpha dp \tag{3.20}$$

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[14] In accordance with Eq. (1.3), the left-hand side of (3.17) is written in partial differential notation, i.e., $\partial p/\partial z$, because the variation of pressure with height is taken with other independent variables held constant.

The geopotential $\Phi(z)$ at height z is thus given by

$$\Phi(z) = \int_0^z g dz \tag{3.21}$$

where the geopotential $\Phi(0)$ at sea level ($z = 0$) has, by convention, been taken as zero. The geopotential at a particular point in the atmosphere depends only on the height of that point and not on the path through which the unit mass is taken in reaching that point. The work done in taking a mass of 1 kg from point A with geopotential Φ_A to point B with geopotential Φ_B is $\Phi_B - \Phi_A$.

We can also define a quantity called the *geopotential height* Z as

$$Z \equiv \frac{\Phi(z)}{g_0} = \frac{1}{g_0}\int_0^z g dz \tag{3.22}$$

where g_0 is the globally averaged acceleration due to gravity at the Earth's surface (taken as 9.81 m s^{-2}). Geopotential height is used as the vertical coordinate in most atmospheric applications in which energy plays an important role (e.g., in large-scale atmospheric motions). It can be seen from Table 3.1 that the values of z and Z are almost the same in the lower atmosphere where $g_0 \simeq g$.

In meteorological practice it is not convenient to deal with the density of a gas, ρ, the value of which is generally not measured. By making use of (3.2) or (3.15) to eliminate ρ in (3.17), we obtain

$$\frac{\partial p}{\partial z} = -\frac{pg}{RT} = -\frac{pg}{R_d T_v}$$

Rearranging the last expression and using (3.20) yields

$$d\Phi = g\,dz = -RT\frac{dp}{p} = -R_d T_v \frac{dp}{p} \tag{3.23}$$

Table 3.1 Values of geopotential height (Z) and acceleration due to gravity (g) at 40° latitude for geometric height (z)

z (km)	Z (km)	g (m s^{-2})
0	0	9.81
1	1.00	9.80
10	9.99	9.77
100	98.47	9.50
500	463.6	8.43

If we now integrate between pressure levels p_1 and p_2, with geopotentials Φ_1 and Φ_2, respectively,

$$\int_{\Phi_1}^{\Phi_2} d\Phi = -\int_{p_1}^{p_2} R_d T_v \frac{dp}{p}$$

or

$$\Phi_2 - \Phi_1 = -R_d \int_{p_1}^{p_2} T_v \frac{dp}{p}$$

Dividing both sides of the last equation by g_0 and reversing the limits of integration yields

$$Z_2 - Z_1 = \frac{R_d}{g_0}\int_{p_2}^{p_1} T_v \frac{dp}{p} \tag{3.24}$$

This difference $Z_2 - Z_1$ is referred to as the (geopotential) *thickness* of the layer between pressure levels p_1 and p_2.

3.2.2 Scale Height and the Hypsometric Equation

For an *isothermal* atmosphere (i.e., temperature constant with height), if the virtual temperature correction is neglected, (3.24) becomes

$$Z_2 - Z_1 = H \ln(p_1/p_2) \tag{3.25}$$

or

$$p_2 = p_1 \exp\left[-\frac{(Z_2 - Z_1)}{H}\right] \tag{3.26}$$

where

$$H \equiv \frac{RT}{g_0} = 29.3T \tag{3.27}$$

H is the scale height as discussed in Section 1.3.4.

Because the atmosphere is well mixed below the turbopause (about 105 km), the pressures and densities of the individual gases decrease with altitude at the same rate and with a scale height proportional to the gas constant R (and therefore inversely proportional to the apparent molecular weight of the mixture). If we take a value for T_v of 255 K (the approximate mean value for the troposphere and stratosphere), the scale height H for air in the atmosphere is found from (3.27) to be about 7.5 km.

Above the turbopause the vertical distribution of gases is largely controlled by molecular diffusion and a scale height may then be defined for each of the individual gases in air. Because for each gas the scale height is proportional to the gas constant for a unit mass of the gas, which varies inversely as the molecular weight of the gas [see, for example (3.13)], the pressures (and densities) of heavier gases fall off more rapidly with height above the turbopause than those of lighter gases.

Exercise 3.2 If the ratio of the number density of oxygen atoms to the number density of hydrogen atoms at a geopotential height of 200 km above the Earth's surface is 10^5, calculate the ratio of the number densities of these two constituents at a geopotential height of 1400 km. Assume an isothermal atmosphere between 200 and 1400 km with a temperature of 2000 K.

Solution: At these altitudes, the distribution of the individual gases is determined by diffusion and therefore by (3.26). Also, at constant temperature, the ratio of the number densities of two gases is equal to the ratio of their pressures. From (3.26)

$$\frac{(p_{1400\text{ km}})_{\text{oxy}}}{(p_{1400\text{ km}})_{\text{hyd}}} = \frac{(p_{200\text{ km}})_{\text{oxy}} \exp[-1200\text{ km}/H_{\text{oxy}}\text{ (km)}]}{(p_{200\text{ km}})_{\text{hyd}} \exp[-1200\text{ km}/H_{\text{hyd}}\text{ (km)}]}$$

$$= 10^5 \exp\left[-1200\text{ km}\left(\frac{1}{H_{\text{oxy}}} - \frac{1}{H_{\text{hyd}}}\right)\right]$$

From the definition of scale height (3.27) and analogous expressions to (3.11) for oxygen and hydrogen atoms and the fact that the atomic weights of oxygen and hydrogen are 16 and 1, respectively, we have at 2000 K

$$H_{\text{oxy}} = \frac{1000R^*}{16}\frac{2000}{9.81}\text{ m} = \frac{8.3145}{16}\frac{2\times 10^6}{9.81}\text{ m}$$
$$= 0.106 \times 10^6\text{ m}$$

and

$$H_{\text{hyd}} = \frac{1000R^*}{1}\frac{2000}{9.81}\text{ m} = 8.3145\frac{2\times 10^6}{9.81}\text{ m}$$
$$= 1.695 \times 10^6\text{ m}$$

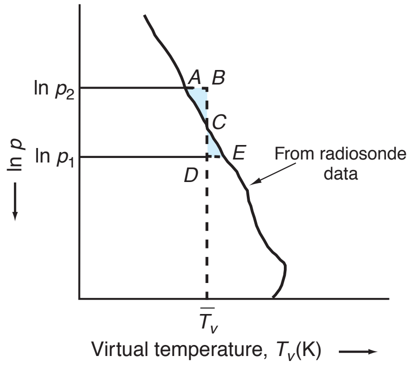

Fig. 3.2 Vertical profile, or sounding, of virtual temperature. If area ABC = area CDE, $\overline{T}_v$ is the mean virtual temperature with respect to ln p between the pressure levels p_1 and p_2.

Therefore,

$$\frac{1}{H_{\text{oxy}}} - \frac{1}{H_{\text{hyd}}} = 8.84 \times 10^{-6}\text{ m}^{-1}$$
$$= 8.84 \times 10^{-3}\text{ km}^{-1}$$

and

$$\frac{(p_{1400\text{ km}})_{\text{oxy}}}{(p_{1400\text{ km}})_{\text{hyd}}} = 10^5 \exp(-10.6) = 2.5$$

Hence, the ratio of the number densities of oxygen to hydrogen atoms at a geopotential height of 1400 km is 2.5. ■

The temperature of the atmosphere generally varies with height and the virtual temepratureg correction cannot always be neglected. In this more general case (3.24) may be integrated if we define a mean virtual temperature $\overline{T}_v$ with respect to p as shown in Fig. 3.2. That is,

$$\overline{T}_v \equiv \frac{\int_{p_2}^{p_1} T_v\, d(\ln p)}{\int_{p_2}^{p_1} d(\ln p)} = \frac{\int_{p_2}^{p_1} T_v \frac{dp}{p}}{\ln\left(\frac{p_1}{p_2}\right)} \tag{3.28}$$

Then, from (3.24) and (3.28),

$$Z_2 - Z_1 = \overline{H} \ln\left(\frac{p_1}{p_2}\right) = \frac{R_d \overline{T}_v}{g_0} \ln\left(\frac{p_1}{p_2}\right) \tag{3.29}$$

Equation (3.29) is called the *hypsometric equation*.

Exercise 3.3 Calculate the geopotential height of the 1000-hPa pressure surface when the pressure at sea level is 1014 hPa. The scale height of the atmosphere may be taken as 8 km.

Solution: From the hypsometric equation (3.29)

$$Z_{1000\text{ hPa}} - Z_{\text{sea level}} = \overline{H}\ln\left(\frac{p_0}{1000}\right)$$
$$= \overline{H}\ln\left(1+\frac{p_0-1000}{1000}\right) \simeq \overline{H}\left(\frac{p_0-1000}{1000}\right)$$

where p_0 is the sea-level pressure and the relationship $\ln(1+x)\simeq x$ for $x \ll 1$ has been used. Substituting $\overline{H}\simeq 8000$ into this expression, and recalling that $Z_{\text{sea level}} = 0$ (Table 3.1), gives

$$Z_{1000\text{ hPa}} \simeq 8\,(p_0 - 1000)$$

Therefore, with $p_0 = 1014$ hPa, the geopotential height $Z_{1000\text{ hPa}}$ of the 1000-hPa pressure surface is found to be 112 m above sea level. ■

3.2.3 Thickness and Heights of Constant Pressure Surfaces

Because pressure decreases monotonically with height, pressure surfaces (i.e., imaginary surfaces on which pressure is constant) never intersect. It can be seen from (3.29) that the thickness of the layer between any two pressure surfaces p_2 and p_1 is proportional to the mean virtual temperature of the layer, $\overline{T}_v$. We can visualize that as $\overline{T}_v$ increases, the air between the two pressure levels expands and the layer becomes thicker.

Exercise 3.4 Calculate the thickness of the layer between the 1000- and 500-hPa pressure surfaces (a) at a point in the tropics where the mean virtual temperature of the layer is 15 °C and (b) at a point in the polar regions where the corresponding mean virtual temperature is −40 °C.

Solution: From (3.29)

$$\Delta Z = Z_{500\text{ hPa}} - Z_{1000\text{ hPa}} = \frac{R_d\overline{T}_v}{g_0}\ln\left(\frac{1000}{500}\right) = 20.3\,\overline{T}_v\text{ m}$$

Therefore, for the tropics with $\overline{T}_v = 288$ K, $\Delta Z = 5846$ m. For polar regions with $\overline{T}_v = 233$ K, $\Delta Z = 4730$ m. In operational practice, thickness is rounded to the nearest 10 m and is expressed in decameters (dam). Hence, answers for this exercise would normally be expressed as 585 and 473 dam, respectively. ■

Before the advent of remote sensing of the atmosphere by satellite-borne radiometers, thickness was evaluated almost exclusively from radiosonde data, which provide measurements of the pressure, temperature, and humidity at various levels in the atmosphere. The virtual temperature T_v at each level was calculated and mean values for various layers were estimated using the graphical method illustrated in Fig. 3.2. Using soundings from a network of stations, it was possible to construct topographical maps of the distribution of geopotential height on selected pressure surfaces. These calculations, which were first performed by observers working on site, are now incorporated into sophisticated data assimilation protocols, as described in the Appendix of Chapter 8 on the book Web site.

In moving from a given pressure surface to another pressure surface located above or below it, the change in the geopotential height is related geometrically to the thickness of the intervening layer, which, in turn, is directly proportional to the mean virtual temperature of the layer. Therefore, if the three-dimensional distribution of virtual temperature is known, together with the distribution of geopotential height on one pressure surface, it is possible to infer the distribution of geopotential height of any other pressure surface. The same hypsometric relationship between the three-dimensional temperature field and the shape of pressure surface can be used in a qualitative way to gain some useful insights into the three-dimensional structure of atmospheric disturbances, as illustrated by the following examples.

i. The air near the center of a hurricane is warmer than its surroundings. Consequently, the intensity of the storm (as measured by the depression of the isobaric surfaces) must decrease with height (Fig. 3.3a). The winds in such *warm core lows*

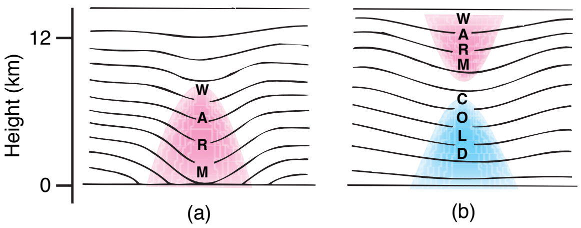

Fig. 3.3 Cross sections in the longitude–height plane. The solid lines indicate various constant pressure surfaces. The sections are drawn such that the thickness between adjacent pressure surfaces is smaller in the cold (blue) regions and larger in the warm (red) regions.

always exhibit their greatest intensity near the ground and diminish with increasing height above the ground.

ii. Some upper level lows do not extend downward to the ground, as indicated in Fig. 3.3b. It follows from the hypsometric equation that these lows must be *cold core* below the level at which they achieve their greatest intensity and *warm core* above that level, as shown in Fig. 3.3b.

3.2.4 Reduction of Pressure to Sea Level

In mountainous regions the difference in surface pressure from one observing station to another is largely due to differences in elevation. To isolate that part of the pressure field that is due to the passage of weather systems, it is necessary to reduce the pressures to a common reference level. For this purpose, sea level is normally used.

Let the subscripts g and 0 refer to conditions at the ground and at sea level ($Z = 0$), respectively. Then, for the layer between the Earth's surface and sea level, the hypsometric equation (3.29) assumes the form

$$Z_g = \overline{H} \ln \frac{p_0}{p_g} \tag{3.30}$$

which can be solved to obtain the sea-level pressure

$$p_0 = p_g \exp\left(\frac{Z_g}{\overline{H}}\right) = p_g \exp\left(\frac{g_0 Z_g}{R_d \overline{T}_v}\right) \tag{3.31}$$

If Z_g is small, the scale height $\overline{H}$ can be evaluated from the ground temperature. Also, if $Z_g / \overline{H} \ll 1$, the exponential in (3.31) can be approximated by $1 + Z_g / \overline{H}$, in which case (3.31) becomes

$$p_0 - p_g \simeq p_g \frac{Z_g}{\overline{H}} = p_g \left(\frac{g_0 Z_g}{R_d \overline{T}_v}\right) \tag{3.32}$$

Because $p_g \simeq 1000$ hpa and $\overline{H} \simeq 8000$ m, the pressure correction (in hPa) is roughly equal to Z_g (in meters) divided by 8. In other words, for altitudes up to a few hundred meters above (or below) sea level, the pressure decreases by about 1 hPa for every 8 m of vertical ascent.

3.3 The First Law of Thermodynamics[15]

In addition to the macroscopic kinetic and potential energy that a system as a whole may possess, it also contains *internal energy* due to the kinetic and potential energy of its molecules or atoms. Increases in internal kinetic energy in the form of molecular motions are manifested as increases in the temperature of the system, whereas changes in the potential energy of the molecules are caused by changes in their relative positions by virtue of any forces that act between the molecules.

Let us suppose that a closed system[16] of unit mass takes in a certain quantity of thermal energy q (measured in joules), which it can receive by thermal conduction and/or radiation. As a result the system may do a certain amount of *external work* w (also measured in joules). The excess of the energy supplied to the body over and above the external work done by the body is $q - w$. Therefore, if there is no change in the macroscopic kinetic and potential energy of the body, it follows from the principle of conservation of energy that the internal energy of the system must increase by $q - w$. That is,

$$q - w = u_2 - u_1 \tag{3.33}$$

where u_1 and u_2 are the internal energies of the system before and after the change. In differential form (3.33) becomes

$$dq - dw = du \tag{3.34}$$

where dq is the differential increment of heat added to the system, dw is the differential element

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[15] The first law of thermodynamics is a statement of the conservation of energy, taking into account the conversions between the various forms that it can assume and the exchanges of energy between a system and its environment that can take place through the transfer of heat and the performance of mechanical work. A general formulation of the first law of thermodynamics is beyond the scope of this text because it requires consideration of conservation laws, not only for energy, but also for momentum and mass. This section presents a simplified formulation that ignores the macroscopic kinetic and potential energy (i.e., the energy that air molecules possess by virtue of their height above sea level and their organized fluid motions). As it turns out, the expression for the first law of thermodynamics that emerges in this simplified treatment is identical to the one recovered from a more complete treatment of the conservation laws, as is done in J. R. Holton, *Introduction to Dynamic Meteorology*, 4th Edition, Academic Press, New York, 2004, pp. 146–149.

[16] A closed system is one in which the total amount of matter, which may be in the form of gas, liquid, solid or a mixture of these phases, is kept constant.

of work done by the system, and du is the differential increase in internal energy of the system. Equations (3.33) and (3.34) are statements of the *first law of thermodynamics*. In fact (3.34) provides a definition of du. The change in internal energy du depends only on the initial and final states of the system and is therefore independent of the manner by which the system is transferred between these two states. Such parameters are referred to as *functions of state*.[17]

To visualize the work term dw in (3.34) in a simple case, consider a substance, often called the *working substance*, contained in a cylinder of fixed cross-sectional area that is fitted with a movable, frictionless piston (Fig. 3.4). The volume of the substance is proportional to the distance from the base of the cylinder to the face of the piston and can be represented on the horizontal axis of the graph shown in Fig. 3.4. The pressure of the substance in the cylinder can be represented on the vertical axis of this graph. Therefore, every state of the substance, corresponding to a given position of the piston, is represented by a point on this pressure–volume (p–V) diagram. When the substance is in equilibrium at a state represented by point P on the graph, its pressure is p and its volume is V (Fig. 3.4). If the piston moves outward through an incremental distance dx while its pressure remains essentially constant at p, the work dW done by the substance in pushing the external force F through a distance dx is

$$dW = Fdx$$

or, because $F = pA$ where A is the cross-sectional area of the face of the piston,

$$dW = pA\,dx = pdV \tag{3.35}$$

In other words, the work done by the substance when its volume increases by a small increment dV is equal to the pressure of the substance multiplied by its increase in volume, which is equal to the blue-shaded area in the graph shown in Fig. 3.4; that is, it is equal to the area under the curve PQ. When the substance passes from state A with volume V_1 to state B with volume V_2 (Fig. 3.4), during which its pressure p changes, the work W done by the material is equal to the area under the curve AB. That is,

$$W = \int_{V_1}^{V_2} pdV \tag{3.36}$$

Equations (3.35) and (3.36) are quite general and represent work done by any substance (or system) due to a change in its volume. If $V_2 > V_1$, W is positive, indicating that the *substance does work on its environment*. If $V_2 < V_1$, W is negative, which indicates that the *environment does work on the substance*.

The $p-V$ diagram shown in Fig. 3.4 is an example of a *thermodynamic diagram* in which the physical state of a substance is represented by two thermodynamic variables. Such diagrams are very useful in meteorology; we will discuss other examples later in this chapter.

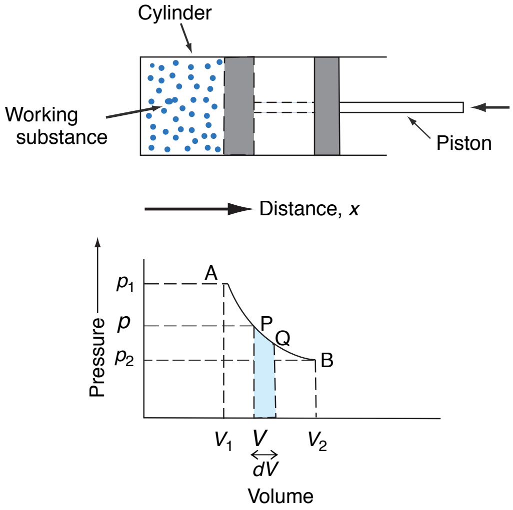

Fig. 3.4 Representation of the state of a working substance in a cylinder on a p–V diagram. The work done by the working substance in passing from P to Q is $p\,dV$, which is equal to the blue-shaded area. [Reprinted from *Atmospheric Science: An Introductory Survey*, 1st Edition, J. M. Wallace and P. V. Hobbs, p. 62, Copyright 1977, with permission from Elsevier.]

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[17] Neither the heat q nor the work w are functions of state, since their values depend on *how* a system is transformed from one state to another. For example, a system may or may not receive heat and it may or may not do external work as it undergoes transitions between different states.

If we are dealing with a unit mass of a substance, the volume V is replaced by the specific volume α. Therefore, the work dw that is done when the specific volume increases by $d\alpha$ is

$$dw = pd\alpha \tag{3.37}$$

Combination of (3.34) and (3.37) yields

$$dq = du + pd\alpha \tag{3.38}$$

which is an alternative statement of the first law of thermodynamics.[18]

3.3.1 Joule's Law

Following a series of laboratory experiments on air, Joule[19] concluded in 1848 that when a gas expands without doing external work, by expanding into a chamber that has been evacuated, and without taking in or giving out heat, the temperature of the gas does not change. This statement, which is known as *Joule's law*, is strictly true only for an ideal gas, but air (and many other gases) behaves very similarly to an ideal gas over a wide range of conditions.

Joule's law leads to an important conclusion concerning the internal energy of an ideal gas. If a gas neither does external work nor takes in or gives out heat, $dw = 0$ and $dq = 0$ in (3.38), so that $du = 0$. Also, according to Joule's law, under these conditions the temperature of the gas does not change, which implies that the kinetic energy of the molecules remains constant. Therefore, because the total internal energy of the gas is constant, that part of the internal energy due to the potential energy must also remain unchanged, even though the volume of the gas changes. In other words, the internal energy of an ideal gas is independent of its volume if the temperature is kept constant. This can be the case only if the molecules of an ideal gas do not exert forces on each other. In this case, the internal energy of an ideal gas will depend only on its temperature.[20]

3.2 More Handball?

Box 3.1. showed that the gas laws can be illustrated by picturing the molecules of a gas as elastic balls bouncing around randomly in a handball court. Suppose now that the walls of the court are permitted to move outward when subjected to a force. The force on the walls is supplied by the impact of the balls, and the work required to move the walls outward comes from a decrease in the kinetic energy of the balls that rebound from the walls with lower velocities than they struck them. This decrease in kinetic energy is in accordance with the first law of thermodynamics under adiabatic conditions. The work done by the system by pushing the walls outward is equal to the decrease in the internal energy of the system [see (3.38)]. Of course, if the outside of the walls of the court are bombarded by balls in a similar manner to the inside walls, there will be no net force on the walls and no work will be done.

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[18] We have assumed here that the only work done by or on a system is due to a change in the volume of the system. However, there are other ways in which a system may do work, e.g., by the creation of new surface area between two phases (such as between liquid and air when a soap film is formed). Unless stated otherwise, we will assume that the work done by or on a system is due entirely to changes in the volume of the system.

[19] **James Prescott Joule** (1818–1889) Son of a wealthy English brewer; one of the great experimentalists of the 19th century. He started his scientific work (carried out in laboratories in his home and at his own expense) at age 19. He measured the mechanical equivalent of heat, recognized the dynamical nature of heat, and developed the principle of conservation of energy.

[20] Subsequent experiments carried out by Lord Kelvin[21] revealed the existence of small forces between the molecules of a gas.

[21] **Lord Kelvin 1st Baron (William Thomson)** (1824–1907) Scottish mathematician and physicist. Entered Glasgow University at age 11. At 22 became Professor of Natural Philosophy at the same university. Carried out incomparable work in thermodynamics, electricity, and hydrodynamics.

3.3.2 Specific Heats

Suppose a small quantity of heat dq is given to a unit mass of a material and, as a consequence, the temperature of the material increases from T to $T + dT$ without any changes in phase occurring within the material. The ratio dq/dT is called the *specific heat* of the material. The specific heat defined in this way could have any number of values, depending on how the material changes as it receives the heat. If the volume of the material is kept constant, a *specific heat at constant volume* c_v is defined

$$c_v = \left(\frac{dq}{dT}\right)_{v\text{ const}} \tag{3.39}$$

However, if the volume of the material is constant (3.38) becomes $dq = du$. Therefore

$$c_v = \left(\frac{du}{dT}\right)_{v\text{ const}}$$

For an ideal gas, Joule's law applies and therefore u depends only on temperature. Therefore, regardless of whether the volume of a gas changes, we may write

$$c_v = \left(\frac{du}{dT}\right) \tag{3.40}$$

From (3.38) and (3.40), the first law of thermodynamics for an ideal gas can be written in the form[22]

$$dq = c_v dT + p d\alpha \tag{3.41}$$

Because u is a function of state, no matter how the material changes from state 1 to state 2, the change in its internal energy is, from (3.40),

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT$$

We can also define a specific heat at constant pressure c_p

$$c_p = \left(\frac{dq}{dT}\right)_{p\text{ const}} \tag{3.42}$$

where the material is allowed to expand as heat is added to it and its temperature rises, but its pressure remains constant. In this case, a certain amount of the heat added to the material will have to be expended to do work as the system expands against the constant pressure of its environment. Therefore, a larger quantity of heat must be added to the material to raise its temperature by a given amount than if the volume of the material were kept constant. For the case of an ideal gas, this inequality can be seen mathematically as follows. Equation (3.41) can be rewritten in the form

$$dq = c_v dT + d(p\alpha) - \alpha\, dp \tag{3.43}$$

From the ideal gas equation (3.3), $d(p\alpha) = RdT$. Therefore (3.43) becomes

$$dq = (c_v + R)dT - \alpha\, dp \tag{3.44}$$

At constant pressure, the last term in (3.44) vanishes; therefore, from (3.42) and (3.44),

$$c_p = c_v + R \tag{3.45}$$

The specific heats at constant volume and at constant pressure for dry air are 717 and 1004 J K^{-1} kg^{-1}, respectively, and the difference between them is 287 J K^{-1} kg^{-1}, which is the gas constant for dry air. It can be shown that for ideal monatomic gases $c_p{:}c_v{:}R = 5{:}3{:}2$, and for ideal diatomic gases $c_p{:}c_v{:}R = 7{:}5{:}2$.

By combining (3.44) and (3.45) we obtain an alternate form of the first law of thermodynamics:

$$dq = c_p dT - \alpha\, dp \tag{3.46}$$

3.3.3 Enthalpy

If heat is added to a material at constant pressure so that the specific volume of the material increases from α_1 to α_2, the work done by a unit mass of the material is $p(\alpha_2 - \alpha_1)$. Therefore, from (3.38), the finite quantity of heat Δq added to

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[22] The term dq is sometimes called the *diabatic* (or nonadiabatic) *heating* or *cooling*, where "diabatic" means involving the transfer of heat. The term "diabatic" would be redundant if "heating" and "cooling" were always taken to mean "the addition or removal of heat." However, "heating" and "cooling" are often used in the sense of "to raise or lower the temperature of," in which case it is meaningful to distinguish between that part of the temperature change dT due to diabatic effects (dq) and that part due to adiabatic effects ($p d\alpha$).

a unit mass of the material at constant pressure is given by

$$\Delta q = (u_2 - u_1) + p(\alpha_2 - \alpha_1)$$
$$= (u_2 + p\alpha_2) - (u_1 + p\alpha_1)$$

where u_1 and u_2 are, respectively, the initial and final internal energies for a unit mass of the material. Therefore, at constant pressure,

$$\Delta q = h_2 - h_1$$

where h is the *enthalpy* of a unit mass of the material, which is defined by

$$h \equiv u + p\alpha \qquad (3.47)$$

Because u, p, and α are functions of state, h is a function of state. Differentiating (3.47), we obtain

$$dh = du + d(p\alpha)$$

Substituting for du from (3.40) and combining with (3.43), we obtain

$$dq = dh - \alpha dp \qquad (3.48)$$

which is yet another form of the first law of thermodynamics.

By comparing (3.46) and (3.48) we see that

$$dh = c_p dT \qquad (3.49)$$

or, in integrated form,

$$h = c_p T \qquad (3.50)$$

where h is taken as zero when $T = 0$. In view of (3.50), h corresponds to the heat required to raise the temperature of a material from 0 to T K at constant pressure.

When a layer of air that is at rest and in hydrostatic balance is heated, for example, by radiative transfer, the weight of the overlying air pressing down on it remains constant. Hence, the heating is at constant pressure. The energy added to the air is realized in the form of an increase in enthalpy (or *sensible heat*, as atmospheric scientists commonly refer to it) and

$$dq = dh = c_p dT$$

The air within the layer expands as it warms, doing work on the overlying air by lifting it against the Earth's gravitational attraction. Of the energy per unit mass imparted to the air by the heating, we see from (3.40) and (3.41) that $du = c_v dT$ is reflected in an increase in internal energy and $pd\alpha = RdT$ is expended doing work on the overlying air. Because the Earth's atmosphere is made up mainly of the diatomic gases N_2 and O_2, the energy added by the heating dq is partitioned between the increase in internal energy du and the expansion work $pd\alpha$ in the ratio 5:2.

We can write a more general expression that is applicable to a moving air parcel, the pressure of which changes as it rises or sinks relative to the surrounding air. By combining (3.20), (3.48), and (3.50) we obtain

$$dq = d(h + \Phi) = d(c_p T + \Phi) \qquad (3.51)$$

Hence, if the material is a parcel of air with a fixed mass that is moving about in an hydrostatic atmosphere, the quantity $(h + \Phi)$, which is called the *dry static energy*, is constant provided the parcel neither gains nor loses heat (i.e., $dq = 0$).[23]

3.4 Adiabatic Processes

If a material undergoes a change in its physical state (e.g., its pressure, volume, or temperature) without any heat being added to it or withdrawn from it, the change is said to be *adiabatic*.

Suppose that the initial state of a material is represented by the point A on the p–V diagram in Fig. 3.5 and that when the material undergoes an isothermal transformation it moves along the line AB. If the same material underwent a similar change in volume but under adiabatic conditions, the transformation would

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[23] Strictly speaking, Eq. (3.51) holds only for an atmosphere in which there are no fluid motions. However, it is correct to within a few percent for the Earth's atmosphere where the kinetic energy of fluid motions represents only a very small fraction of the total energy. An exact relationship can be obtained by using Newton's second law of motion and the continuity equation in place of Eq. (3.20) in the derivation. See J. R. Holton, *An Introduction to Dynamic Meteorology*, 4th ed., Academic Press, pp. 46–49 (2004).

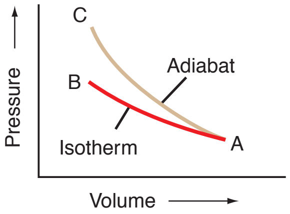

Fig. 3.5 An isotherm and an adiabat on a p–V diagram.

be represented by a curve such as AC, which is called an *adiabat*. The reason why the adiabat AC is steeper than the isotherm AB on a p–V diagram can be seen as follows. During adiabatic compression, the internal energy increases [because $dq = 0$ and $p d\alpha$ is negative in (3.38)] and therefore the temperature of the system rises. However, for isothermal compression, the temperature remains constant. Hence, $T_C > T_B$ and therefore $p_C > p_B$.

3.4.1 Concept of an Air Parcel

In many fluid mechanics problems, mixing is viewed as a result of the random motions of individual molecules. In the atmosphere, molecular mixing is important only within a centimeter of the Earth's surface and at levels above the turbopause (~105 km). At intermediate levels, virtually all mixing in the vertical is accomplished by the exchange of macroscale "air parcels" with horizontal dimensions ranging from millimeters to the scale of the Earth itself.

To gain some insights into the nature of vertical mixing in the atmosphere, it is useful to consider the behavior of an air parcel of infinitesimal dimensions that is assumed to be

i. thermally insulated from its environment so that its temperature changes adiabatically as it rises or sinks, always remaining at exactly the same pressure as the environmental air at the same level,[24] which is assumed to be in hydrostatic equilibrium; and
ii. moving slowly enough that the macroscopic kinetic energy of the air parcel is a negligible fraction of its total energy.

Although in the case of real air parcels one or more of these assumptions is nearly always violated to some extent, this simple, idealized model is helpful in understanding some of the physical processes that influence the distribution of vertical motions and vertical mixing in the atmosphere.

3.4.2 The Dry Adiabatic Lapse Rate

We will now derive an expression for the rate of change of temperature with height of a parcel of dry air that moves about in the Earth's atmosphere while always satisfying the conditions listed at the end of Section 3.4.1. Because the air parcel undergoes only adiabatic transformations ($dq = 0$) and the atmosphere is in hydrostatic equilibrium, for a unit mass of air in the parcel we have, from (3.51),

$$d(c_p T + \Phi) = 0 \tag{3.52}$$

Dividing through by dz and making use of (3.20) we obtain

$$-\left(\frac{dT}{dz}\right)_{\text{dry parcel}} = \frac{g}{c_p} \equiv \Gamma_d \tag{3.53}$$

where Γ_d is called the *dry adiabatic lapse rate*. Because an air parcel expands as it rises in the atmosphere, its temperature will decrease with height so that Γ_d defined by (3.53) is a positive quantity. Substituting $g = 9.81\ \text{m s}^{-2}$ and $c_p = 1004\ \text{J K}^{-1}\ \text{kg}^{-1}$ into (3.53) gives $\Gamma_d = 0.0098\ \text{K m}^{-1}$ or $9.8\ \text{K km}^{-1}$, which is the numerical value of the dry adiabatic lapse rate.

It should be emphasized again that Γ_d is the rate of change of temperature following a parcel of dry air that is being raised or lowered adiabatically in the atmosphere. The actual lapse rate of temperature in a column of air, which we will indicate by $\Gamma = \partial T/\partial z$, as measured, for example, by a radiosonde, averages 6–7 K km^{-1} in the troposphere, but it takes on a wide range of values at individual locations.

3.4.3 Potential Temperature

The *potential temperature* θ of an air parcel is defined as the temperature that the parcel of air would have if it were expanded or compressed adiabatically from its existing pressure and temperature to a standard pressure p_0 (generally taken as 1000 hPa).

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[24] Any pressure differences between the parcel and its environment give rise to sound waves that produce an almost instantaneous adjustment. Temperature differences, however, are eliminated by much slower processes.

We can derive an expression for the potential temperature of an air parcel in terms of its pressure p, temperature T, and the standard pressure p_0 as follows. For an adiabatic transformation ($dq = 0$) (3.46) becomes

$$c_p dT - \alpha dp = 0$$

Substituting α from (3.3) into this expression yields

$$\frac{c_p}{R}\frac{dT}{T} - \frac{dp}{p} = 0$$

Integrating upward from p_0 (where, by definition, $T = \theta$) to p, we obtain

$$\frac{c_p}{R}\int_{\theta}^{T}\frac{dT}{T} = \int_{p_0}^{p}\frac{dp}{p}$$

or

$$\frac{c_p}{R}\ln\frac{T}{\theta} = \ln\frac{p}{p_0}$$

Taking the antilog of both sides

$$\left(\frac{T}{\theta}\right)^{c_p/R} = \frac{p}{p_0}$$

or

$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p} \tag{3.54}$$

Equation (3.54) is called *Poisson's*[25] *equation*. It is usually assumed that $R \simeq R_d = 287\ \mathrm{J\,K^{-1}\,kg^{-1}}$ and $c_p \simeq c_{pd} = 1004\ \mathrm{J\,K^{-1}\,kg^{-1}}$; therefore, $R/c_p \simeq 0.286$.

Parameters that remain constant during certain transformations are said to be *conserved*. Potential temperature is a conserved quantity for an air parcel that moves around in the atmosphere under adiabatic conditions (see Exercise 3.36). Potential temperature is an extremely useful parameter in atmospheric thermodynamics, since atmospheric processes are often close to adiabatic, and therefore θ remains essentially constant, like density in an incompressible fluid.

3.4.4 Thermodynamic Diagrams

Poisson's equation may be conveniently solved in graphical form. If pressure is plotted on the ordinate on a distorted scale, in which the distance from the origin is proportional to p^{R_d/c_p}, or $p^{0.286}$ is used, regardless of whether air is dry or moist, and temperature (in K) is plotted on the abscissa, then (3.54) becomes

$$p^{0.286} = \left(\frac{p_0^{0.286}}{\theta}\right)T \tag{3.55}$$

For a constant value of θ, Eq. (3.55) is of the form $y \propto x$ where $y = p^{0.286}$, $x = T$, and the constant of proportionality is $p_0^{0.286}/\theta$. Each constant value of θ represents a dry adiabat, which is defined by a straight line with a particular slope that passes through the point $p = 0$, $T = 0$. If the pressure scale is inverted so that p increases downward, the relation takes the form shown in Fig. 3.6, which is the basis for the *pseudoadiabatic chart* that used to be widely used for meteorological computations. The region of the chart of greatest interest in the atmosphere is the portion shown within the dotted lines in Fig. 3.6, and this is generally the only portion of the chart that is printed.

In the pseudoadiabatic chart, isotherms are vertical and dry adiabats (constant θ) are oriented at an acute angle relative to isotherms (Fig. 3.6). Because changes in temperature with height in the atmosphere generally lie between isothermal and dry adiabatic, most temperature soundings lie within a narrow range of angles when plotted on a pseudoadiabatic chart. This restriction is overcome in the so-called *skew* $T - \ln p$ *chart*, in which the ordinate (y) is $-\ln p$ (the minus sign ensures that lower pressure levels are located above higher pressure levels on the chart) and the abscissa (x) is

$$x = T + (\text{constant})y = T - (\text{constant})\ln p \tag{3.56}$$

Since, from (3.56),

$$y = \frac{x - T}{(\text{constant})}$$

and for an isotherm T is constant, the relationship between y and x for an isotherm is of the form

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[25] **Simeon Denis Poisson** (1781–1840) French mathematician. Studied medicine but turned to applied mathematics and became the first professor of mechanics at the Sorbonne in Paris.

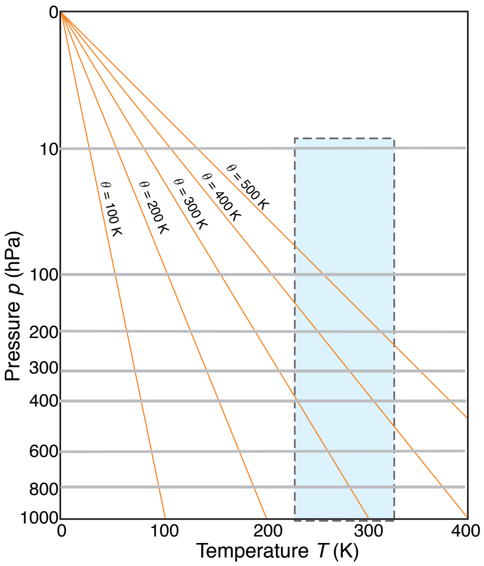


Fig. 3.6 The complete pseudoadiabatic chart. Note that p increases downward and is plotted on a distorted scale (representing $p^{0.286}$). Only the blue-shaded area is generally printed for use in meteorological computations. The sloping lines, each labeled with a value of the potential temperature θ, are dry adiabats. As required by the definition of θ, the actual temperature of the air (given on the abscissa) at 1000 hPa is equal to its potential temperature.

$y = mx + c$, where m is the same for all isotherms and c is a different constant for each isotherm. Therefore, on the skew $T - \ln p$ chart, isotherms are straight parallel lines that slope upward from left to right. The scale for the x axis is generally chosen to make the angle between the isotherms and the isobars about 45°, as depicted schematically in Fig. 3.7. Note that the isotherms on a skew $T - \ln p$ chart are intentionally "skewed" by about 45° from their vertical orientation in the pseudoadiabatic chart (hence the name *skew* $T - \ln p$ *chart*). From (3.55), the equation for a dry adiabat (θ constant) is

$$-\ln p = (\text{constant}) \ln T + \text{constant}$$

Hence, on a $-\ln p$ versus $\ln T$ chart, dry adiabats would be straight lines. Since $-\ln p$ is the ordinate on the skew $T - \ln p$ chart, but the abscissa is not $\ln T$, dry adiabats on this chart are slightly curved lines that run from the lower right to the upper left. The angle between the isotherms and the dry adiabats on a skew $T - \ln p$ chart is approximately 90° (Fig. 3.7). Therefore, when atmospheric temperature soundings are plotted on this chart, small differences in slope are more apparent than they are on the pseudoadiabatic chart.

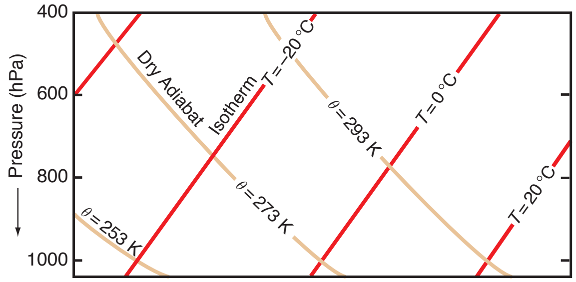


Fig. 3.7 Schematic of a portion of the skew $T - \ln p$ chart. (An accurate reproduction of a larger portion of the chart is available on the book web site that accompanies this book, from which it can be printed and used for solving exercises.)

Exercise 3.5 A parcel of air has a temperature of −51 °C at the 250-hPa level. What is its potential temperature? What temperature will the parcel have if it is brought into the cabin of a jet aircraft and compressed adiabatically to a cabin pressure of 850 hPa?

Solution: This exercise can be solved using the skew $T - \ln p$ chart. Locate the original state of the air parcel on the chart at pressure 250 hPa and temperature −51 °C. The label on the dry adiabat that passes through this point is 60 °C, which is therefore the potential temperature of the air.

The temperature acquired by the ambient air if it is compressed adiabatically to a pressure of 850 hPa can be found from the chart by following the dry adiabat that passes through the point located by 250 hPa and −51 °C down to a pressure of 850 hPa and reading off the temperature at that point. It is 44.5 °C. (Note that this suggests that ambient air brought into the cabin of a jet aircraft at cruise altitude has to be *cooled* by about 20 °C to provide a comfortable environment.) ■

3.5 Water Vapor in Air

So far we have indicated the presence of water vapor in the air through the vapor pressure e that it exerts, and we have quantified its effect on the density of air by introducing the concept of virtual temperature. However, the amount of water vapor present in a certain quantity of air may be expressed in many different ways, some of the more important of which are presented later. We must also discuss what happens when water vapor condenses in air.

3.5.1 Moisture Parameters

a. Mixing ratio and specific humidity

The amount of water vapor in a certain volume of air may be defined as the ratio of the mass m_v of water vapor to the mass of dry air; this is called the *mixing ratio* w. That is

$$w \equiv \frac{m_v}{m_d} \tag{3.57}$$

The mixing ratio is usually expressed in grams of water vapor per kilogram of dry air (but in solving numerical exercises w must be expressed as a dimensionless number, e.g., as kg of water vapor per kg of dry air). In the atmosphere, the magnitude of w typically ranges from a few grams per kilogram in middle latitudes to values of around 20 g kg^{-1} in the tropics. If neither condensation nor evaporation takes place, the mixing ratio of an air parcel is constant (i.e., it is a conserved quantity).

The mass of water vapor m_v in a unit mass of air (dry air plus water vapor) is called the *specific humidity* q, that is

$$q \equiv \frac{m_v}{m_v + m_d} = \frac{w}{1 + w}$$

Because the magnitude of w is only a few percent, it follows that the numerical values of w and q are nearly equivalent.

Exercise 3.6 If air contains water vapor with a mixing ratio of 5.5 g kg^{-1} and the total pressure is 1026.8 hPa, calculate the vapor pressure e.

Solution: The partial pressure exerted by any constituent in a mixture of gases is proportional to the number of moles of the constituent in the mixture. Therefore, the pressure e due to water vapor in air is given by

$$e = \frac{n_v}{n_d + n_v} p = \frac{\dfrac{m_v}{M_w}}{\dfrac{m_d}{M_d} + \dfrac{m_v}{M_w}} p \tag{3.58}$$

n_v and n_d are the number of moles of water vapor and dry air in the mixture, respectively, M_w is the molecular weight of water, M_d is the apparent molecular weight of dry air, and p is the total pressure of the moist air. From (3.57) and (3.58) we obtain

$$e = \frac{w}{w + \varepsilon} p \tag{3.59}$$

where $\varepsilon = 0.622$ is defined by (3.14). Substituting $p = 1026.8$ hPa and $w = 5.5 \times 10^{-3}$ kg kg^{-1} into (3.59), we obtain $e = 9.0$ hPa. ■

Exercise 3.7 Calculate the virtual temperature correction for moist air at 30 °C that has a mixing ratio of 20 g kg^{-1}.

Solution: Substituting e/p from (3.59) into (3.16) and simplifying

$$T_v = T \frac{w + \varepsilon}{\varepsilon (1 + w)}$$

Dividing the denominator into the numerator in this expression and neglecting terms in w^2 and higher orders of w, we obtain

$$T_v - T \simeq \frac{1 - \varepsilon}{\varepsilon} wT$$

or, substituting $\varepsilon = 0.622$ and rearranging,

$$T_v \simeq T(1 + 0.61w) \tag{3.60}$$

With $T = 303$ K and $w = 20 \times 10^{-3}$ kg kg^{-1}, Eq. (3.60) gives $T_v = 306.7$ K. Therefore, the virtual temperature correction is $T_v - T = 3.7$ degrees (K or °C). Note that (3.60) is a useful expression for obtaining T_v from T and the moisture parameter w. ■

b. Saturation vapor pressures

Consider a small closed box, the floor of which is covered with pure water at temperature T. Initially assume that the air is completely dry. Water will begin to evaporate and, as it does, the number of water molecules in the box, and therefore the water vapor pressure, will increase. As the water vapor pressure increases, so will the rate at which the water molecules condense from the vapor phase back to the liquid phase. If the rate of condensation is less than the rate of evaporation, the box is said to be *unsaturated* at temperature T (Fig. 3.8a). When the water vapor pressure in the box increases to the point that the rate of condensation is equal to the rate of evaporation (Fig. 3.8b), the air is said to be *saturated with respect*

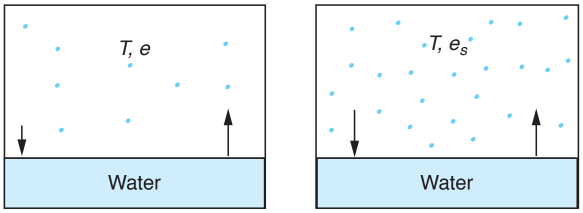
3.3 Can Air Be Saturated with Water Vapor?[26]

It is common to use phrases such as "the air is saturated with water vapor," "the air can hold no more water vapor," and "warm air can hold more water vapor than cold air." These phrases, which suggest that air absorbs water vapor, rather like a sponge, are misleading. We have seen that the total pressure exerted by a mixture of gases is equal to the sum of the pressures that each gas would exert if it alone occupied the total volume of the mixture of gases (Dalton's law of partial pressures). Hence, the exchange of water molecules between its liquid and vapor phases is (essentially) independent of the presence of air. Strictly speaking, the pressure exerted by water vapor that is in equilibrium with water at a given temperature is referred more appropriately to as *equilibrium vapor pressure* rather than saturation vapor pressure at that temperature. However, the latter term, and the terms "unsaturated air" and "saturated air," provide a convenient shorthand and are so deeply rooted that they will appear in this book.

to a plane surface of pure water at temperature T, and the pressure e_s that is then exerted by the water vapor is called the *saturation vapor pressure over a plane surface of pure water at temperature T*.

Similarly, if the water in Fig. 3.8 were replaced by a plane surface of pure ice at temperature T and the rate of condensation of water vapor were equal to the rate of evaporation of the ice, the pressure e_{si} exerted by the water vapor would be the saturation vapor pressure over a plane surface of pure ice at T. Because, at any given temperature, the rate of evaporation from ice is less than from water, $e_s(T) > e_{si}(T)$.

The rate at which water molecules evaporate from either water or ice increases with increasing temperature.[27] Consequently, both e_s and e_{si} increase with increasing temperature, and their magnitudes depend only on temperature. The variations with temperature of e_s and $e_s - e_{si}$ are shown in Fig. 3.9, where it can be seen that the magnitude of $e_s - e_{si}$ reaches a peak value at about −12 °C. It follows that if an ice particle is in water-saturated air it will grow due to the deposition of water vapor upon it. In Section 6.5.3 it is shown that this phenomenon



(a) Unsaturated (b) Saturated

Fig. 3.8 A box (a) unsaturated and (b) saturated with respect to a plane surface of pure water at temperature T. Dots represent water molecules. Lengths of the arrows represent the relative rates of evaporation and condensation. The saturated (i.e., equilibrium) vapor pressure over a plane surface of pure water at temperature T is e_s as indicated in (b).

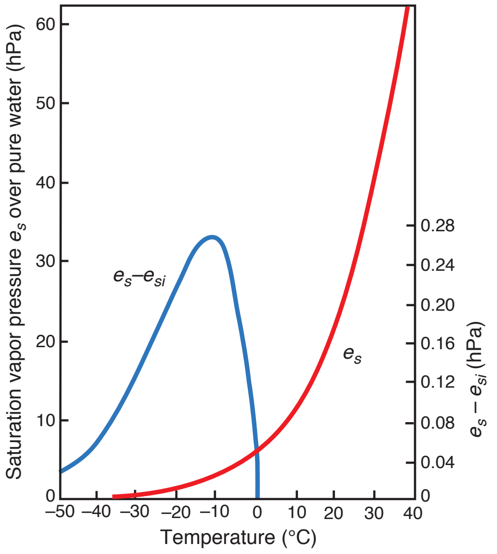


Fig. 3.9 Variations with temperature of the saturation (i.e., equilibrium) vapor pressure e_s over a plane surface of pure water (red line, scale at left) and the difference between e_s and the saturation vapor pressure over a plane surface of ice e_{si} (blue line, scale at right).

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[26] For further discussion of this and some other common misconceptions related to meteorology see C. F. Bohren's *Clouds in a Glass of Beer*, Wiley and Sons, New York, 1987.

[27] As a rough rule of thumb, it is useful to bear in mind that the saturation vapor pressure roughly doubles for a 10 °C increase in temperature.

plays a role in the initial growth of precipitable particles in some clouds.

c. Saturation mixing ratios

The *saturation mixing ratio* w_s with respect to water is defined as the ratio of the mass m_{vs} of water vapor in a given volume of air that is saturated with respect to a plane surface of pure water to the mass m_d of the dry air. That is

$$w_s \equiv \frac{m_{vs}}{m_d} \tag{3.61}$$

Because water vapor and dry air both obey the ideal gas equation

$$w_s = \frac{\rho'_{vs}}{\rho'_d} = \frac{e_s}{(R_v T)} \bigg/ \frac{(p - e_s)}{(R_d T)} \tag{3.62}$$

where ρ'_{vs} is the partial density of water vapor required to saturate air with respect to water at temperature T, ρ'_d is the partial density of the dry air (see Section 3.1.1), and p is the total pressure. Combining (3.62) with (3.14), we obtain

$$w_s = 0.622 \frac{e_s}{p - e_s}$$

For the range of temperatures observed in the Earth's atmosphere, $p \gg e_s$; therefore

$$w_s \simeq 0.622 \frac{e_s}{p} \tag{3.63}$$

Hence, at a given temperature, the saturation mixing ratio is inversely proportional to the total pressure.

Because e_s depends only on temperature, it follows from (3.63) that w_s is a function of temperature and pressure. Lines of constant saturation mixing ratio are printed as dashed green lines on the skew $T - \ln p$ chart and are labeled with the value of w_s in grams of water vapor per kilogram of dry air. It is apparent from the slope of these lines that at constant pressure w_s increases with increasing temperature, and at constant temperature w_s increases with decreasing pressure.

d. Relative humidity; dew point and frost point

The relative humidity (RH) with respect to water is the ratio (expressed as a percentage) of the actual mixing ratio w of the air to the saturation mixing ratio w_s with respect to a plane surface of pure water at the same temperature and pressure. That is

$$RH \equiv 100 \frac{w}{w_s} \simeq 100 \frac{e}{e_s} \tag{3.64}$$

The *dew point* T_d is the temperature to which air must be cooled at constant pressure for it to become saturated with respect to a plane surface of pure water. In other words, the dew point is the temperature at which the saturation mixing ratio w_s with respect to liquid water becomes equal to the actual mixing ratio w. It follows that the relative humidity at temperature T and pressure p is given by

$$RH = 100 \frac{w_s \text{ (at temperature } T_d \text{ and pressure } p)}{w_s \text{ (at temperature } T \text{ and pressure } p)} \tag{3.65}$$

A simple rule of thumb for converting RH to a dew point depression ($T - T_d$) for moist air ($RH > 50\%$) is that T_d decreases by ~1 °C for every 5% decrease in RH (starting at T_d = dry bulb temperature (T), where $RH = 100\%$). For example, if the RH is 85%, $T_d = T - \left(\frac{100 - 85}{5}\right)$ and the dew point depression is $T - T_d = 3\ °\text{C}$.

The *frost point* is defined as the temperature to which air must be cooled at constant pressure to saturate it with respect to a plane surface of pure ice. Saturation mixing ratios and relative humidities with respect to ice may be defined in analogous ways to their definitions with respect to liquid water. When the terms mixing ratio and relative humidity are used without qualification they are with respect to liquid water.

Exercise 3.8 Air at 1000 hPa and 18 °C has a mixing ratio of 6 g kg^{-1}. What are the relative humidity and dew point of the air?

Solution: This exercise may be solved using a skew $T - \ln p$ chart. The students should duplicate the following steps. First locate the point with pressure 1000 hPa and temperature 18 °C. We see from the chart that the saturation mixing ratio for this state is ~13 g kg^{-1}. Since the air specified in the problem has a mixing ratio of only 6 g kg^{-1}, it is unsaturated and its relative humidity is, from (3.64), $100 \times 6/13 = 46\%$. To find the dew point we move from right to left along the 1000-hPa ordinate until we intercept the saturation mixing ratio line of magnitude 6 g kg^{-1}; this occurs at a temperature of about 6.5 °C. Therefore, if the air is cooled at constant pressure, the water vapor it contains will just saturate the air with respect to water at a temperature of 6.5 °C. Therefore, by definition, the dew point of the air is 6.5 °C. ■

At the Earth's surface, the pressure typically varies by only a few percent from place to place and from time to time. Therefore, the dew point is a good indicator of the moisture content of the air. In warm, humid weather the dew point is also a convenient indicator of the level of human discomfort. For example, most people begin to feel uncomfortable when the dew point rises above 20 °C, and air with a dew point above about 22 °C is generally regarded as extremely humid or "sticky." Fortunately, dew points much above this temperature are rarely observed even in the tropics. In contrast to the dew point, relative humidity depends as much upon the temperature of the air as upon its moisture content. On a sunny day the relative humidity may drop by as much as 50% from morning to afternoon, just because of a rise in air temperature. Neither is relative humidity a good indicator of the level of human discomfort. For example, a relative humidity of 70% may feel quite comfortable at a temperature of 20 °C, but it would cause considerable discomfort to most people at a temperature of 30 °C.

The highest dew points occur over warm bodies of water or vegetated surfaces from which water is evaporating. In the absence of vertical mixing, the air just above these surfaces would become saturated with water vapor, at which point the dew point would be the same as the temperature of the underlying surface. Complete saturation is rarely achieved over hot surfaces, but dew points in excess of 25 °C are sometimes observed over the warmest regions of the oceans.

e. Lifting condensation level

The *lifting condensation level* (LCL) is defined as the level to which an unsaturated (but moist) parcel of air can be lifted adiabatically before it becomes saturated with respect to a plane surface of pure water. During lifting the mixing ratio w and potential temperature θ of the air parcel remain constant, but the saturation mixing ratio w_s decreases until it becomes equal to w at the LCL. Therefore, the LCL is located at the intersection of the potential temperature line passing through the temperature T and pressure p of the air parcel, and the w_s line that passes through the pressure p and dew point T_d of the parcel (Fig. 3.10). Since the dew point and LCL are related in the manner indicated in Fig. 3.10, knowledge of either one is sufficient to determine the other. Similarly, a knowledge of T, p, and any one moisture parameter is sufficient to determine all the other moisture parameters we have defined.

f. Wet-bulb temperature

The wet-bulb temperature is measured with a thermometer, the glass bulb of which is covered with a moist cloth over which ambient air is drawn. The heat required to evaporate water from the moist cloth to saturate the ambient air is supplied by the air as it comes into contact with the cloth. When the difference between the temperatures of the bulb and the ambient air is steady and sufficient to supply the heat needed to evaporate the water, the thermometer will read a steady temperature, which is called the *wet-bulb temperature*. If a raindrop falls through a layer of air that has a constant wet-bulb temperature, the raindrop will eventually reach a temperature equal to the wet-bulb temperature of the air.

The definition of wet-bulb temperature and dew point both involve cooling a hypothetical air parcel to saturation, but there is a distinct difference. If the unsaturated air approaching the wet bulb has a mixing ratio w, the dew point T_d is the temperature to which the air must be cooled at constant pressure

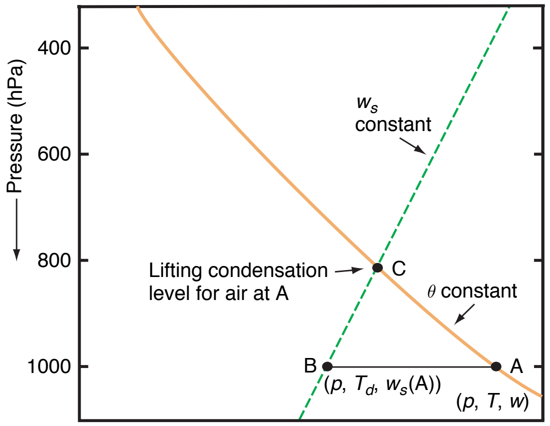

Fig. 3.10 The lifting condensation level of a parcel of air at A, with pressure p, temperature T, and dew point T_d, is at C on the skew $T - \ln p$ chart.

to become saturated. The air that leaves the wet bulb has a mixing ratio w' that saturates it at temperature T_w. If the air approaching the wet bulb is unsaturated, w' is greater than w; therefore, $T_d \leq T_w \leq T$, where the equality signs apply only to air saturated with respect to a plane surface of pure water. Usually T_w is close to the arithmetic mean of T and T_d.

3.5.2 Latent Heats

If heat is supplied to a system under certain conditions it may produce a change in phase rather than a change in temperature. In this case, the increase in internal energy is associated entirely with a change in molecular configurations in the presence of intermolecular forces rather than an increase in the kinetic energy of the molecules (and therefore the temperature of the system). For example, if heat is supplied to ice at 1 atm and 0 °C, the temperature remains constant until all of the ice has melted. The *latent heat of melting* (L_m) is defined as the heat that has to be given to a unit mass of a material to convert it from the solid to the liquid phase without a change in temperature. The temperature at which this phase change occurs is called the *melting point*. At 1 atm and 0 °C the latent heat of melting of the water substance is 3.34×10^5 J kg^{-1}. The *latent heat of freezing* has the same numerical value as the latent heat of melting, but heat is released as a result of the change in phase from liquid to solid.

Similarly, the *latent heat of vaporization* or *evaporation* (L_v) is the heat that has to be given to a unit mass of material to convert it from the liquid to the vapor phase without a change in temperature. For the water substance at 1 atm and 100 °C (the *boiling point* of water at 1 atm), the latent heat of vaporization is 2.25×10^6 J kg^{-1}. The *latent heat of condensation* has the same value as the latent heat of vaporization, but heat is released in the change in phase from vapor to liquid.[28]

As will be shown in Section 3.7.3, the melting point (and boiling point) of a material depends on pressure.

3.5.3 Saturated Adiabatic and Pseudoadiabatic Processes

When an air parcel rises in the atmosphere its temperature decreases with altitude at the dry adiabatic lapse rate (see Section 3.4.2) until it becomes saturated with water vapor. Further lifting results in the condensation of liquid water (or the deposition of ice), which releases latent heat. Consequently, the rate of decrease in the temperature of the rising parcel is reduced. If all of the condensation products remain in the rising parcel, the process may still be considered to be adiabatic (and reversible), even though latent heat is released in the system, provided that heat does not pass through the boundaries of the parcel. The air parcel is then said to undergo a *saturated adiabatic process*. However, if all of the condensation products immediately fall out of the air parcel, the process is irreversible, and not strictly adiabatic, because the condensation products carry some heat. The air parcel is then said to undergo a *pseudoadiabatic process*. As the reader is invited to verify in Exercise 3.44, the amount of heat carried by condensation products is small compared to that carried by the air itself. Therefore, the saturated-adiabatic and the pseudoadiabatic lapse rates are virtually identical.

3.5.4 The Saturated Adiabatic Lapse Rate

In contrast to the dry adiabatic lapse rate Γ_d, which is constant, the numerical value of the saturated adiabatic lapse rate Γ_s varies with pressure and temperature. (The reader is invited to derive an expression for Γ_s in Exercise 3.50; see the book Web site.) Because water vapor condenses when a saturated air parcel rises, it follows that $\Gamma_s < \Gamma_d$. Actual values of Γ_s range from about 4 K km^{-1} near the ground in warm, humid air masses to typical values of 6−7 K km^{-1} in the middle troposphere. For typical temperatures near the tropopause, Γ_s is only slightly less than Γ_d because the saturation vapor pressure of the air is so small that the effect of condensation is negligible.[29] Lines that show the rate of decrease in

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[28] Normally, when heat is given to a substance, the temperature of the substance increases. This is called *sensible heat*. However, when heat is given to a substance that is melting or boiling, the temperature of the substance does not change until all of the substance is melted or vaporized. In this case, the heat appears to be *latent* (i.e., hidden). Hence the terms *latent heat of melting* and *latent heat of vaporization*.

[29] **William Thomson** (later Lord Kelvin) was the first (in 1862) to derive quantitative estimates of the dry and saturated adiabatic lapse rates based on theoretical arguments. For an interesting account of the contributions of other 19th-century scientists to the realization of the importance of latent heat in the atmosphere, see W. E. K. Middleton, *A History of the Theories of Rain*, Franklin Watts, Inc., New York, 1965, Chapter 8.

temperature with height of a parcel of air that is rising or sinking in the atmosphere under saturated adiabatic (or pseudoadiabatic) conditions are called *saturated adiabats* (or *pseudoadiabats*). On the skew $T - \ln p$ chart these are the curved green lines that diverge upward and tend to become parallel to the dry adiabats.

Exercise 3.9 A parcel of air with an initial temperature of 15 °C and dew point 2 °C is lifted adiabatically from the 1000-hPa level. Determine its LCL and temperature at that level. If the air parcel is lifted a further 200 hPa above its LCL, what is its final temperature and how much liquid water is condensed during this rise?

Solution: The student should duplicate the following steps on the skew $T - \ln p$ chart (see the book Web site). First locate the initial state of the air on the chart at the intersection of the 15 °C isotherm with the 1000-hPa isobar. Because the dew point of the air is 2 °C, the magnitude of the saturation mixing ratio line that passes through the 1000-hPa pressure level at 2 °C is the actual mixing ratio of the air at 15 °C and 1000 hPa. From the chart this is found to be about 4.4 g kg^{-1}. Because the saturation mixing ratio at 1000 hPa and 15 °C is about 10.7 g kg^{-1}, the air is initially unsaturated. Therefore, when it is lifted it will follow a dry adiabat (i.e., a line of constant potential temperature) until it intercepts the saturation mixing ratio line of magnitude 4.4 g kg^{-1}. Following upward along the dry adiabat ($\theta = 288$ K) that passes through 1000 hPa and 15 °C isotherm, the saturation mixing ratio line of 4.4 g kg^{-1} is intercepted at about the 820-hPa level. This is the LCL of the air parcel. The temperature of the air at this point is about −0.7 °C. For lifting above this level the air parcel will follow a saturated adiabat. Following the saturated adiabat that passes through 820 hPa and −0.7 °C up to the 620-hPa level, the final temperature of the air is found to be about −15 °C. The saturation mixing ratio at 620 hPa and −15 °C is ~1.9 g kg^{-1}. Therefore, about ~4.4 − 1.9 = 2.5 g of water must have condensed out of each kilogram of air during the rise from 820 to 620 hPa. ■

3.5.5 Equivalent Potential Temperature and Wet-Bulb Potential Temperature

We will now derive an equation that describes how temperature varies with pressure under conditions of saturated adiabatic ascent or descent. Substituting (3.3) into (3.46) gives

$$\frac{dq}{T} = c_p \frac{dT}{T} - R\frac{dp}{p} \tag{3.66}$$

From (3.54) the potential temperature θ is given by

$$\ln\theta = \ln T - \frac{R}{c_p}\ln p + \text{constant}$$

or, differentiating,

$$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R\frac{dp}{p} \tag{3.67}$$

Combining (3.66) and (3.67) and substituting $dq = -L_v\, dw_s$, we obtain

$$-\frac{L_v}{c_pT} dw_s = \frac{d\theta}{\theta} \tag{3.68}$$

In Exercise 3.52 we show that

$$\frac{L_v}{c_pT}\, dw_s \simeq d\left(\frac{L_v w_s}{c_pT}\right) \tag{3.69}$$

From (3.68) and (3.69)

$$-d\left(\frac{L_v w_s}{c_pT}\right) \simeq \frac{d\theta}{\theta}$$

This last expression can be integrated to give

$$-\frac{L_v w_s}{c_pT} \simeq \ln\theta + \text{constant} \tag{3.70}$$

We will define the constant of integration in (3.70) by requiring that at low temperatures, as $w_s/T \rightarrow 0$, $\theta \rightarrow \theta_e$. Then

$$-\frac{L_v w_s}{c_pT} \simeq \ln\left(\frac{\theta}{\theta_e}\right)$$

or

$$\theta_e \simeq \theta \exp\left(\frac{L_v w_s}{c_pT}\right) \tag{3.71}$$

The quantity θ_e given by (3.71) is called the *equivalent potential temperature*. It can be seen that θ_e is the potential temperature θ of a parcel of air when all the water vapor has condensed so that its saturation mixing ratio w_s is zero. Hence, recalling the definition of θ, the equivalent potential temperature of an air parcel may be found as follows. The air is expanded (i.e., lifted) pseudoadiabatically until all the vapor has condensed, released its latent heat, and fallen out. The air is then compressed dry adiabatically to the standard pressure of 1000 hPa, at which point it will attain the temperature θ_e. (If the air is initially unsaturated, w_s and T are the saturation mixing ratio and temperature at the point where the air first becomes saturated after being lifted dry adiabatically.) We have seen in Section 3.4.3 that potential temperature is a conserved quantity for adiabatic transformations. The equivalent potential temperature is conserved during both dry and saturated adiabatic processes.

If the line of constant equivalent potential temperature (i.e., the pseudoadiabat) that passes through the wet-bulb temperature of a parcel of air is traced back on a skew $T - \ln p$ chart to the point where it intersects the 1000-hPa isobar, the temperature at this intersection is called the *wet-bulb potential temperature* θ_w of the air parcel. Like the equivalent potential temperature, the wet-bulb potential temperature is conserved during both dry and saturated adiabatic processes. On skew $T - \ln p$ charts, pseudoadiabats are labeled (along the 200-hPa isobar) with the wet-bulb potential temperature θ_w (in °C) and the equivalent potential temperature θ_e (in K) of air that rises or sinks along that pseudoadiabat. Both θ_w and θ_e provide equivalent information and are valuable as tracers of air parcels.

When height, rather than pressure, is used as the independent variable, the conserved quantity during adiabatic or pseudoadiabatic ascent or descent with water undergoing transitions between liquid and vapor phases is the *moist static energy* (MSE)[30]

$$MSE = c_p T + \Phi + L_v q \tag{3.72}$$

where T is the temperature of the air parcel, Φ is the geopotential, and q_v is the specific humidity (nearly the same as w). The first term on the right side of (3.72) is the enthalpy per unit mass of air. The second term is the potential energy, and the third term is the latent heat content. The first two terms, which also appear in (3.51), are the *dry static energy*. When air is lifted dry adiabatically, enthalpy is converted into potential energy and the latent heat content remains unchanged. In saturated adiabatic ascent, energy is exchanged among all three terms on the right side of (3.72): potential energy increases, while the enthalpy and latent heat content both decrease. However, the sum of the three terms remains constant.

3.5.6 Normand's Rule

Many of the relationships discussed in this section are embodied in the following theorem, known as *Normand's*[31] *rule*, which is extremely helpful in many computations involving the skew $T - \ln p$ chart. Normand's rule states that on a skew $T - \ln p$ chart the lifting condensation level of an air parcel is located at the intersection of the potential temperature line that passes through the point located by the temperature and pressure of the air parcel, the equivalent potential temperature line (i.e., the pseudoadiabat) that passes through the point located by the wet-bulb temperature and pressure of the air parcel, and the saturation mixing ratio line that passes through the point determined by the dew point and pressure of the air. This rule is illustrated in Fig. 3.11 for the case of an air parcel with temperature T, pressure p, dew point T_d, and wet-bulb temperature T_w. It can be seen that if T, p, and T_d are known, T_w may be readily determined using Normand's rule. Also, by extrapolating the θ_e line that passes through T_w to the 1000-hPa level, the wet-bulb potential temperature θ_w may be found (Fig. 3.11).

3.5.7 Net Effects of Ascent Followed by Descent

When a parcel of air is lifted above its LCL so that condensation occurs and if the products of the condensation fall out as precipitation, the latent heat gained by the air during this process will be retained by the air if the parcel returns to its original level.

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[30] The word *static* derives from the fact that the kinetic energy associated with macroscale fluid motions is not included. The reader is invited to show that the kinetic energy per unit mass is much smaller than the other terms on the right side of (3.72), provided that the wind speed is small in comparison to the speed of sound.

[31] **Sir Charles William Blyth Normand** (1889–1982) British meteorologist. Director-General of Indian Meteorological Service, 1927–1944. A founding member of the National Science Academy of India. Improved methods for measuring atmospheric ozone.

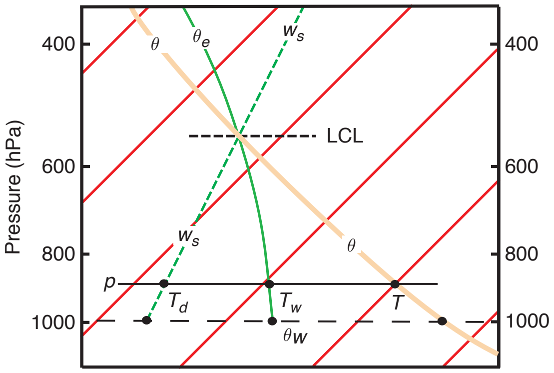

Fig. 3.11 Illustration of Normand's rule on the skew $T - \ln p$ chart. The orange lines are isotherms. The method for determining the wet-bulb temperature (T_w) and the wet-bulb potential temperature (θ_w) of an air parcel with temperature T and dew point T_d at pressure p is illustrated. LCL denotes the lifting condensation level of this air parcel.

The effects of the saturated ascent coupled with the adiabatic descent are:

i. net increases in the temperature and potential temperature of the parcel;
ii. a decrease in moisture content (as indicated by changes in the mixing ratio, relative humidity, dew point, or wet-bulb temperature); and,
iii. no change in the equivalent potential temperature or wet-bulb potential temperature, which are conserved quantities for air parcels undergoing both dry and saturated processes.

The following exercise illustrates these points.

Exercise 3.10 An air parcel at 950 hPa has a temperature of 14 °C and a mixing ratio of 8 g kg^{-1}. What is the wet-bulb potential temperature of the air? The air parcel is lifted to the 700-hPa level by passing over a mountain, and 70% of the water vapor that is condensed out by the ascent is removed by precipitation. Determine the temperature, potential temperature, mixing ratio, and wet-bulb potential temperature of the air parcel after it has descended to the 950-hPa level on the other side of the mountain.

Solution: On a skew $T - \ln p$ chart (see the book Web site), locate the initial state of the air at 950 hPa and 14 °C. The saturation mixing ratio for an air parcel with temperature and pressure is found from the chart to be 10.6 g kg^{-1}. Therefore, because the air has a mixing ratio of only 8 g kg^{-1}, it is unsaturated. The wet-bulb potential temperature (θ_w) can be determined using the method indicated schematically in Fig. 3.11, which is as follows. Trace the constant potential temperature line that passes through the initial state of the air parcel up to the point where it intersects the saturation mixing ratio line with value 8 g kg^{-1}. This occurs at a pressure of about 890 hPa, which is the LCL of the air parcel. Now follow the equivalent potential temperature line that passes through this point back down to the 1000-hPa level and read off the temperature on the abscissa—it is 14 °C. This is in the wet-bulb potential temperature of the air.

When the air is lifted over the mountain, its temperature and pressure up to the LCL at 890 hPa are given by points on the potential temperature line that passes through the point 950 hPa and 14 °C. With further ascent of the air parcel to the 700-hPa level, the air follows the saturated adiabat that passes through the LCL. This saturated adiabat intersects the 700-hPa level at a point where the saturation mixing ratio is 4.7 g kg^{-1}. Therefore, $8 - 4.7 = 3.3$ g kg^{-1} of water vapor has to condense out between the LCL and the 700-hPa level, and 70% of this, or 2.3 g kg^{-1}, is precipitated out. Therefore, at the 700-hPa level 1 g kg^{-1} of liquid water remains in the air. The air parcel descends on the other side of the mountain at the saturated adiabatic lapse rate until it evaporates all of its liquid water, at which point the saturation mixing ratio will have risen to $4.7 + 1 = 5.7$ g kg^{-1}. The air parcel is now at a pressure of 760 hPa and a temperature of 1.8 °C. Thereafter, the air parcel descends along a dry adiabat to the 950-hPa level, where its temperature is 20 °C and the mixing ratio is still 5.7 g kg^{-1}. If the method indicated in Fig. 3.11 is applied again, the wet-bulb potential temperature of the air parcel will be found to be unchanged at 14 °C. (The heating of air during its passage over a mountain, 6 °C in this example, is responsible for the remarkable warmth of *Föhn* or *Chinook* winds, which often blow downward along the lee side of mountain ranges.[32]) ■

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[32] The person who first explained the Föhn wind in this way appears to have been J. von Hann[33] in his classic book *Lehrbuch der Meteorologie*, Willibald Keller, Leipzig, 1901.

[33] **Julius F. von Hann** (1839–1921) Austrian meteorologist. Introduced thermodynamic principles into meteorology. Developed theories for mountain and valley winds. Published the first comprehensive treatise on climatology (1883).

3.6 Static Stability

3.6.1 Unsaturated Air

Consider a layer of the atmosphere in which the actual temperature lapse rate Γ (as measured, for example, by a radiosonde) is less than the dry adiabatic lapse rate Γ_d (Fig. 3.12a). If a parcel of unsaturated air originally located at level O is raised to the height defined by points A and B, its temperature will fall to T_A, which is lower than the ambient temperature T_B at this level. Because the parcel immediately adjusts to the pressure of the ambient air, it is clear from the ideal gas equation that the colder parcel of air must be denser than the warmer ambient air. Therefore, if left to itself, the parcel will tend to return to its original level. If the parcel is displaced downward from O it becomes warmer than the ambient air and, if left to itself, the parcel will tend to rise back to its original level. In both cases, the parcel of air encounters a restoring force after being displaced, which inhibits vertical mixing. Thus, the condition $\Gamma < \Gamma_d$ corresponds to a *stable stratification* (or positive static stability) for unsaturated air parcels. In general, the larger the difference $\Gamma_d - \Gamma$, the greater the restoring force for a given displacement and the greater the static stability.[34]

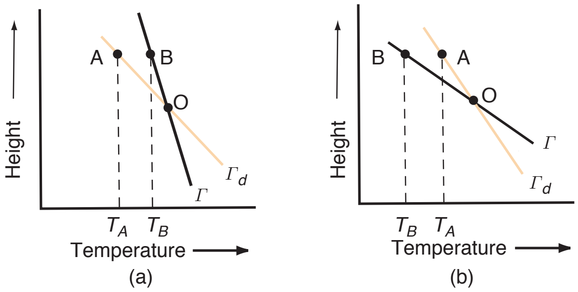

Fig. 3.12 Conditions for (a) positive static stability ($\Gamma < \Gamma_d$) and (b) negative static instability ($\Gamma > \Gamma_d$) for the displacement of unsaturated air parcels.

Exercise 3.11 An unsaturated parcel of air has density ρ' and temperature T', and the density and temperature of the ambient air are ρ and T. Derive an expression for the upward acceleration of the air parcel in terms of T, T', and g.

Solution: The situation is depicted in Fig. 3.13. If we consider a unit volume of the air parcel, its mass is ρ'. Therefore, the downward force acting on unit volume of the parcel is $\rho' g$. From the Archimedes[35] principle we know that the upward force acting on the parcel is equal in magnitude to the gravitational force that acts on the ambient air that is displaced by the air parcel. Because a unit volume of ambient air of density ρ is displaced by the air parcel, the magnitude of the upward force acting on the air parcel is ρg. Therefore, the net upward force (F) acting on a unit volume of the parcel is

$$F = (\rho - \rho')\, g$$

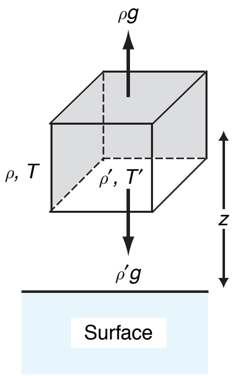

Fig. 3.13 The box represents an air parcel of unit volume with its center of mass at height z above the Earth's surface. The density and temperature of the air parcel are ρ' and T', respectively, and the density and temperature of the ambient air are ρ and T. The vertical forces acting on the air parcel are indicated by the thicker arrows.

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[34] A more general method for determing static stability is given in Section 9.3.4.

[35] **Archimedes** (287–212 B.C.) The greatest of Greek scientists. He invented engines of war and the water screw and he derived the principle of buoyancy named after him. When Syracuse was sacked by Rome, a soldier came upon the aged Archimedes absorbed in studying figures he had traced in the sand: "Do not disturb my circles" said Archimedes, but was killed instantly by the soldier. Unfortunately, right does not always conquer over might.

Because the mass of a unit volume of the air parcel is ρ', the upward acceleration of the parcel is

$$\frac{d^2z}{dt^2} = \frac{F}{\rho'} = \left(\frac{\rho - \rho'}{\rho'}\right) g$$

where z is the height of the air parcel. The pressure of the air parcel is the same as that of the ambient air, since they are at the same height in the atmosphere. Therefore, from the gas equation in the form of (3.2), the densities of the air parcel and the ambient air are inversely proportional to their temperatures. Hence,

$$\frac{d^2z}{dt^2} = \frac{\dfrac{1}{T} - \dfrac{1}{T'}}{\dfrac{1}{T'}} g$$

or

$$\frac{d^2z}{dt^2} = g\left(\frac{T' - T}{T}\right) \tag{3.73}$$

■

Strictly speaking, virtual temperature T_v should be used in place of T in all expressions relating to static stability. However, the virtual temperature correction is usually neglected except in certain calculations relating to the boundary layer.

Exercise 3.12 The air parcel in Fig. 3.12a is displaced upward from its equilibrium level at $z' = 0$ by a distance z' to a new level where the ambient temperature is T. The air parcel is then released. Derive an expression that describes the subsequent vertical displacement of the air parcel as a function of time in terms of T, the lapse rate of the ambient air (Γ), and the dry adiabatic lapse rate (Γ_d).

Solution: Let $z = z_0$ be the equilibrium level of the air parcel and $z' = z - z_0$ be the vertical dispalcement of the air parcel from its equilibrium level. Let T_0 be the environmental air temperature at $z = z_0$. If the air parcel is lifted dry adiabatically through a distance z' from its equilibrium level, its temperature will be

$$T' = T_0 - (\Gamma_d)\, z'$$

Therefore

$$T' - T = -(\Gamma_d - \Gamma)\, z'$$

Substituting this last expression into (3.73), we obtain

$$\frac{d^2z'}{dt^2} = -\frac{g}{T}(\Gamma_d - \Gamma)\, z'$$

which may be written in the form

$$\frac{d^2z'}{dt^2} + N^2 z' = 0 \tag{3.74}$$

where

$$N = \left[\frac{g}{T}(\Gamma_d - \Gamma)\right]^{1/2} \tag{3.75}$$

N is referred to as the *Brunt*[36]*–Väisälä*[37] *frequency*. Equation (3.74) is a second order ordinary differential equation. If the layer in question is stably stratified (that is to say, if $\Gamma_d > \Gamma$), then we can be assured that N is real, N^2 is positive, and the solution of (3.74) is

$$z' = A \cos Nt + B \sin Nt$$

Making use of the conditions at the point of maximum displacement at time $t = 0$, namely that $z' = z'(0)$ and $dz'/dt = 0$ at $t = 0$, it follows that

$$z'(t) = z'(0) \cos Nt$$

That is to say, the parcel executes a *buoyancy oscillation* about its equilibrium level z with amplitude equal to its initial displacement $z'(0)$, and frequency N (in units of radians per second). The Brunt–Väisälä frequency is thus a measure of the static stability: the higher the frequency, the greater the ambient stability. ■

Air parcels undergo buoyancy oscillations in association with *gravity waves*, a widespread phenomenon in planetary atmospheres, as illustrated in Fig. 3.14. Gravity waves may be excited by flow over

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[36] **Sir David Brunt** (1886–1995) English meteorologist. First full-time professor of meteorology at Imperial College (1934–1952). His textbook *Physical and Dynamical Meteorology*, published in the 1930s, was one of the first modern unifying accounts of meteorology.

[37] **Vilho Väisälä** (1899–1969) Finnish meteorologist. Developed a number of meteorological instruments, including a version of the radiosonde in which readings of temperature, pressure, and moisture are telemetered in terms of radio frequencies. The modern counterpart of this instrument is one of Finland's successful exports.

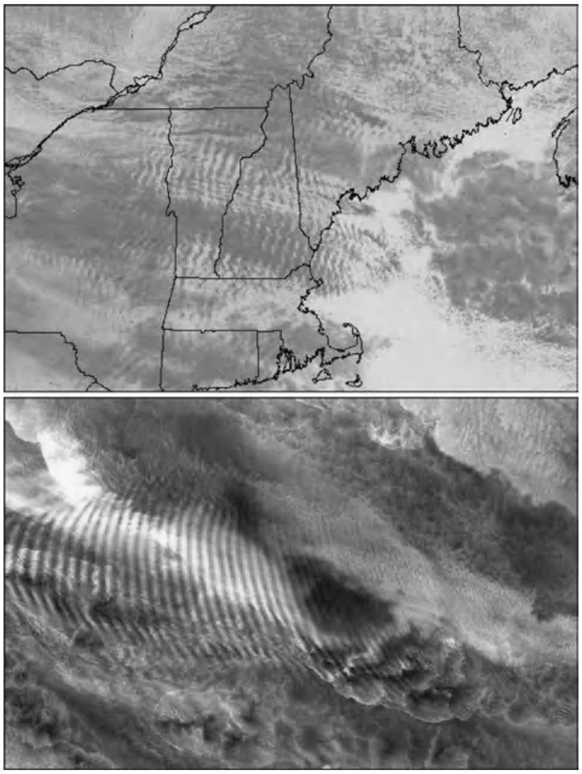

Fig. 3.14 Gravity waves, as revealed by cloud patterns. The upper photograph, based on NOAA GOES 8 visible satellite imagery, shows a wave pattern in west to east (right to left) airflow over the north–south-oriented mountain ranges of the Appalachians in the northeastern United States. The waves are transverse to the flow and their horizontal wavelength is ~20 km. The atmospheric wave pattern is more regular and widespread than the undulations in the terrain. The bottom photograph, based on imagery from NASA's multiangle imaging spectro-radiometer (MISR), shows an even more regular wave pattern in a thin layer of clouds over the Indian Ocean.

mountainous terrain, as shown in the top photograph in Fig. 3.14 or by an intense local disturbance, as shown in the bottom photograph. The following exercise illustrates how buoyancy oscillations can be excited by flow over a mountain range.

Exercise 3.13 A layer of unsaturated air flows over mountainous terrain in which the ridges are 10 km apart in the direction of the flow. The lapse rate is 5 °C km^{-1} and the temperature is 20 °C. For what value of the wind speed U will the period of the orographic (i.e., terrain-induced) forcing match the period of a buoyancy oscillation?

Solution: For the period τ of the orographic forcing to match the period of the buoyancy oscillation, it is required that

$$\tau = \frac{L}{U} = \frac{2\pi}{N}$$

where L is the spacing between the ridges. Hence, from this last expression and (3.75),

$$U = \frac{LN}{2\pi} = \frac{L}{2\pi}\left[\frac{g}{T}(\Gamma_d - \Gamma)\right]^{1/2}$$

or, in SI units,

$$U = \frac{10^4}{2\pi}\left[\frac{9.8}{293}\left((9.8 - 5.0) \times 10^{-3}\right)\right]^{1/2}$$
$$\simeq 20 \text{ m s}^{-1}$$ ■

Layers of air with negative lapse rates (i.e., temperatures increasing with height) are called *inversions*. It is clear from the aforementioned discussion that these layers are marked by very strong static stability. A low-level inversion can act as a "lid" that traps pollution-laden air beneath it (Fig. 3.15). The layered structure of the stratosphere derives from the fact that it represents an inversion in the vertical temperature profile.

If $\Gamma > \Gamma_d$ (Fig. 3.12b), a parcel of unsaturated air displaced upward from O will arrive at A with a temperature greater than that of its environment. Therefore, it will be less dense than the ambient air

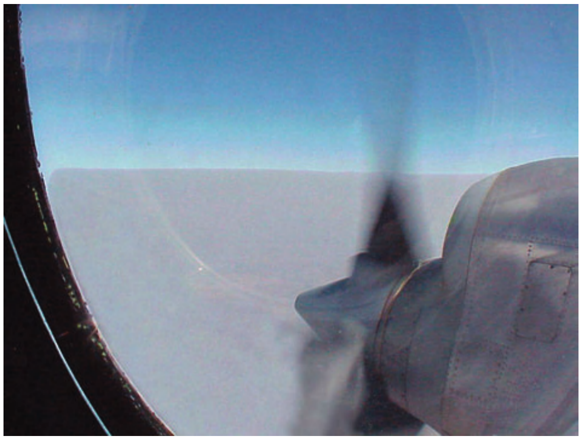

Fig. 3.15 Looking down onto widespread haze over southern Africa during the biomass-burning season. The haze is confined below a temperature inversion. Above the inversion, the air is remarkably clean and the visibility is excellent. (Photo: P. V. Hobbs.)

and, if left to itself, will continue to rise. Similarly, if the parcel is displaced downward it will be cooler than the ambient air, and it will continue to sink if left to itself. Such *unstable* situations generally do not persist in the free atmosphere, because the instability is eliminated by strong vertical mixing as fast as it forms. The only exception is in the layer just above the ground under conditions of very strong heating from below. ■

Exercise 3.14 Show that if the potential temperature θ increases with increasing altitude the atmosphere is stable with respect to the displacement of unsaturated air parcels.

Solution: Combining (3.1), (3.18), and (3.67), we obtain for a unit mass of air

$$c_p T \frac{d\theta}{\theta} = c_p\, dT + g dz$$

Letting $d\theta = (\partial\theta/\partial z)dz$ and $dT = (\partial T/\partial z)dz$ and dividing through by $c_p T dz$ yields

$$\frac{1}{\theta}\frac{\partial\theta}{\partial z} = \frac{1}{T}\left(\frac{\partial T}{\partial z} + \frac{g}{c_p}\right) \tag{3.76}$$

Noting that $-dT/dz$ is the actual lapse rate Γ of the air and the dry adiabatic lapse rate Γ_d is g/c_p (3.76) may be written as

$$\frac{1}{\theta}\frac{\partial\theta}{\partial z} = \frac{1}{T}(\Gamma_d - \Gamma) \tag{3.77}$$

However, it has been shown earlier that when $\Gamma < \Gamma_d$ the air is characterized by positive static stability. It follows that under these same conditions $\partial\theta/\partial z$ must be positive; that is, the potential temperature must increase with height. ■

3.6.2 Saturated Air

If a parcel of air is saturated, its temperature will decrease with height at the saturated adiabatic lapse rate Γ_s. It follows from arguments similar to those given in Section 3.6.1 that if Γ is the actual lapse rate of temperature in the atmosphere, saturated air parcels will be stable, neutral, or unstable with respect to vertical displacements, depending on whether $\Gamma < \Gamma_s$, $\Gamma = \Gamma_s$, or $\Gamma > \Gamma_s$, respectively. When an environmental temperature sounding is plotted on a skew $T - \ln p$ chart the distinctions between Γ, Γ_d, and Γ_s are clearly discernible (see Exercise 3.53).

3.6.3 Conditional and Convective Instability

If the actual lapse rate Γ of the atmosphere lies between the saturated adiabatic lapse rate Γ_s and the dry adiabatic lapse rate Γ_d, a parcel of air that is lifted sufficiently far above its equilibrium level will become warmer than the ambient air. This situation is illustrated in Fig. 3.16, where an air parcel lifted from its equilibrium level at O cools dry adiabatically until it reaches its lifting condensation level at A. At this level the air parcel is colder than the ambient air. Further lifting produces cooling at the moist adiabatic lapse rate so the temperature of the parcel of air follows the moist adiabat ABC. If the air parcel is sufficiently moist, the moist adiabat through A will cross the ambient temperature sounding; the point of intersection is shown as B in Fig. 3.16. Up to this point the parcel was colder and denser than the ambient air, and an expenditure of energy was required to lift it. If forced lifting had stopped prior to this point, the parcel would have returned to its equilibrium level at point O. However, once above point B, the parcel develops a positive buoyancy that carries it upward even in the absence of further forced lifting. For this reason, B is referred to as the *level of free convection* (LFC). The level of free convection depends on the amount of moisture in the rising parcel of air, as well as the magnitude of the lapse rate Γ.

From the aforementioned discussion it is clear that for a layer in which $\Gamma_s < \Gamma < \Gamma_d$, vigorous convective overturning will occur if forced vertical motions are

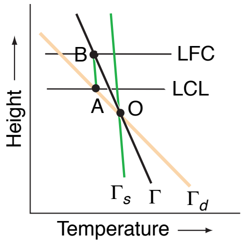

Fig. 3.16 Conditions for conditional instability ($\Gamma_s < \Gamma < \Gamma_d$). Γ_s and Γ_d are the saturated and dry adiabatic lapse rates, and Γ is the lapse rate of temperature of the ambient air. LCL and LFC denote the *lifting condensation level* and the *level of free convection*, respectively.

3.4 Analogs for Static Stability, Instability, Neutral Stability, and Conditional Instability

Sections 3.6.1 and 3.6.2 discussed the conditions for parcels of unsaturated air and saturated air to be stable, unstable, or neutral when displaced vertically in the atmosphere. Under stable conditions, if an air parcel is displaced either upward or downward and is then left to itself (i.e., the force causing the original displacement is removed), the parcel will return to its original position. An analogous situation is shown in Fig. 3.17a where a ball is originally located at the lowest point in a valley. If the ball is displaced in any direction and is then left to itself, it will return to its original location at the base of the valley.

Under unstable conditions in the atmosphere, an air parcel that is displaced either upward or downward, and then left to itself, will continue to move upward or downward, respectively. An analog is shown in Fig. 3.17b, where a ball is initially on top of a hill. If the ball is displaced in any direction, and is then left to itself, it will roll down the hill.

If an air parcel is displaced in a neutral atmosphere, and then left to itself, it will remain in the displaced location. An analog of this condition is a ball on a flat surface (Fig. 3.17c). If the ball is displaced, and then left to itself, it will not move.

If an air parcel is conditionally unstable, it can be lifted up to a certain height and, if left to itself, it will return to its original location. However, if the air parcel is lifted beyond a certain height (i.e., the level of free convection), and is then left to itself, it will continue rising (Section 3.6.3). An analog of this situation is shown in Fig. 3.17d, where a displacement of a ball to a point A, which lies to the left of the hillock, will result in the ball rolling back to its original position. However, if the displacement takes the ball to a point B on the other side of the hillock, the ball will not return to its original position but will roll down the right-hand side of the hillock.

It should be noted that in the analogs shown in Fig. 3.17 the only force acting on the ball after it is displaced is that due to gravity, which is always downward. In contrast, an air parcel is acted on by both a gravitational force and a buoyancy force. The gravitational force is always downward. The buoyancy force may be either upward or downward, depending on whether the air parcel is less dense or more dense than the ambient air.

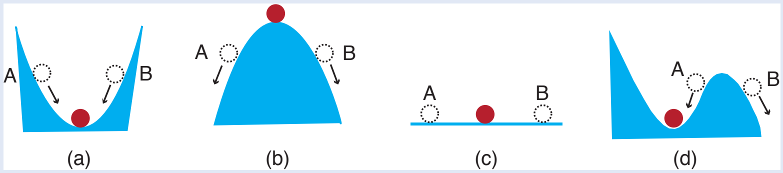

Fig. 3.17 Analogs for (a) stable, (b) unstable, (c) neutral, and (d) conditional instability. The red circle is the original position of the ball, and the white circles are displaced positions. Arrows indicate the direction the ball will move from a displaced position if the force that produced the displacement is removed.

large enough to lift air parcels beyond their level of free convection. Such an atmosphere is said to be *conditionally unstable* with respect to convection. If vertical motions are weak, this type of stratification can be maintained indefinitely.

The potential for instability of air parcels is also related to the vertical stratification of water vapor. In the profiles shown in Fig. 3.18, the dew point decreases rapidly with height within the inversion layer AB that marks the top of a moist layer. Now, suppose that this layer is lifted. An air parcel at A will reach its LCL quickly, and beyond that point it will cool moist adiabatically. In contrast, an air parcel starting at point B will cool dry adiabatically through a deep layer before it reaches its LCL. Therefore, as the inversion layer is lifted, the top part of it cools much more rapidly than the bottom part, and the lapse rate quickly becomes destabilized. Sufficient lifting may cause the layer to become conditionally unstable, even if the entire sounding is absolutely

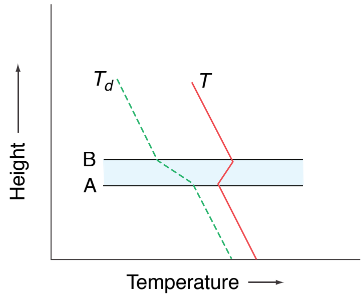

Fig. 3.18 Conditions for convective instability. T and T_d are the temperature and dew point of the air, respectively. The blue-shaded region is a dry inversion layer.

stable to begin with. It may be shown that the criterion for this so-called *convective (or potential) instability* is that $\partial\theta_e/\partial z$ be negative (i.e., θ_e decrease with increasing height) within the layer.

Throughout large areas of the tropics, θ_e decreases markedly with height from the mixed layer to the much drier air above. Yet deep convection breaks out only within a few percent of the area where there is sufficient lifting to release the instability.

3.7 The Second Law of Thermodynamics and Entropy

The first law of thermodynamics (Section 3.3) is a statement of the principle of conservation of energy. The *second law of thermodynamics*, which was deduced in various forms by Carnot,[38] Clausius,[39] and Lord Kelvin, is concerned with the maximum fraction of a quantity of heat that can be converted into work. The fact that for any given system there is a theoretical limit to this conversion was first clearly demonstrated by Carnot, who also introduced the important concepts of cyclic and reversible processes.

3.7.1 The Carnot Cycle

A *cyclic process* is a series of operations by which the state of a substance (called the *working substance*) changes but the substance is finally returned to its original state in all respects. If the volume of the working substance changes, the working substance may do external work, or work may be done on the working substance, during a cyclic process. Since the initial and final states of the working substance are the same in a cyclic process, and internal energy is a function of state, the internal energy of the working substance is unchanged in a cyclic process. Therefore, from (3.33), the *net* heat absorbed by the working substance is equal to the external work that it does in the cycle. A working substance is said to undergo a *reversible* transformation if each state of the system is in equilibrium so that a reversal in the direction of an infinitesimal change returns the working substance and the environment to their original states. A *heat engine* (or *engine* for short) is a device that does work through the agency of heat.

If during one cycle of an engine a quantity of heat Q_1 is absorbed and heat Q_2 is rejected, the amount of work done by the engine is $Q_1 - Q_2$ and its *efficiency* η is defined as

$$\eta = \frac{\text{Work done by the engine}}{\text{Heat absorbed by the working substance}} = \frac{Q_1 - Q_2}{Q_1} \tag{3.78}$$

Carnot was concerned with the important practical problem of the efficiency with which heat engines can do useful mechanical work. He envisaged an ideal heat engine (Fig. 3.19) consisting of a working substance contained in a cylinder (Y) with insulating walls and a conducting base (B) that is fitted with an insulated, frictionless piston (P) to which a variable force can be applied, a nonconducting stand (S) on which the cylinder may be placed to insulate its base, an infinite warm reservoir of heat (H) at constant temperature T_1, and an infinite cold reservoir for heat (C) at constant temperature T_2 (where $T_1 > T_2$). Heat can be supplied from the warm reservoir to the working substance contained in the cylinder, and heat can be extracted from the working substance by the cold reservoir. As the working substance expands (or contracts), the piston moves outward (or inward) and external work is done by (or on) the working substance.

---

[38] **Nicholas Leonard Sadi Carnot** (1796–1832) Born in Luxenbourg. Admitted to the École Polytechnique, Paris, at age 16. Became a captain in the Corps of Engineers. Founded the science of thermodynamics.

[39] **Rudolf Clausius** (1822–1888) German physicist. Contributed to the sciences of thermodynamics, optics, and electricity.

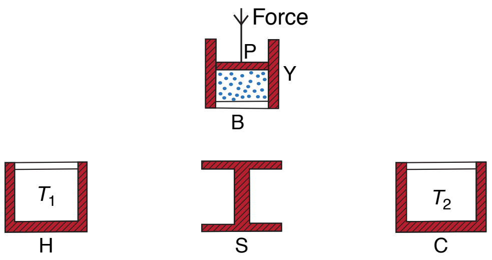

Fig. 3.19 The components of Carnot's ideal heat engine. Red-shaded areas indicate insulating material, and white areas represent thermally conducting material. The working substance is indicated by the blue dots inside the cylinder.

Carnot's cycle consists of taking the working substance in the cylinder through the following four operations that together constitute a reversible, cyclic transformation:

i. The substance starts with temperature T_2 at a condition represented by A on the p–V diagram in Fig. 3.20. The cylinder is placed on the stand S and the working substance is compressed by increasing the downward force applied to the piston. Because heat can neither enter nor leave the working substance in the cylinder when it is on the stand, the working substance undergoes an adiabatic compression to the state represented by B in Fig. 3.20 in which its temperature has risen to T_1.

ii. The cylinder is now placed on the warm reservoir H, from which it extracts a quantity of heat Q_1. During this process the working substance expands isothermally at temperature T_1 to point C in Fig. 3.20. During this process the working substance does work by expanding against the force applied to the piston.

iii. The cylinder is returned to the nonconducting stand and the working substance undergoes an adiabatic expansion along book web site in Fig. 3.20 until its temperature falls to T_2. Again the working substance does work against the force applied to the piston.

iv. Finally, the cylinder is placed on the cold reservoir and, by increasing the force applied to the piston, the working substance is compressed isothermally along DA back to its original state A. In this transformation the working substance gives up a quantity of heat Q_2 to the cold reservoir.

It follows from (3.36) that the net amount of work done by the working substance during the Carnot cycle is equal to the area contained within the figure ABCD in Fig. 3.20. Also, because the working substance is returned to its original state, the net work done is equal to $Q_1 - Q_2$ and the efficiency of the engine is given by (3.78). In this cyclic operation the engine has done work by transferring a certain quantity of heat from a warmer (H) to a cooler (C) body. One way of stating the second law of thermodynamics is "only by transferring heat from a warmer to a colder body can heat be converted into work in a cyclic process." In Exercise 3.56 we prove that *no engine can be more efficient than a reversible engine working between the same limits of temperature, and that all reversible engines working between the same temperature limits have the same efficiency*. The validity of these two statements, which are known as *Carnot's theorems*, depends on the truth of the second law of thermodynamics.

Exercise 3.15 Show that in a Carnot cycle the ratio of the heat Q_1 absorbed from the warm reservoir at temperature T_1 K to the heat Q_2 rejected to the cold reservoir at temperature T_2 K is equal to T_1/T_2.

Solution: To prove this important relationship we let the substance in the Carnot engine be 1 mol of an ideal gas and we take it through the Carnot cycle ABCD shown in Fig. 3.20.

For the adiabatic transformation of the ideal gas from A to B we have (using the adiabatic equation that the reader is invited to prove in Exercise 3.33)

$$p_{\rm A} V_{\rm A}^{\gamma} = p_{\rm B} V_B^{\gamma}$$

where γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume. For

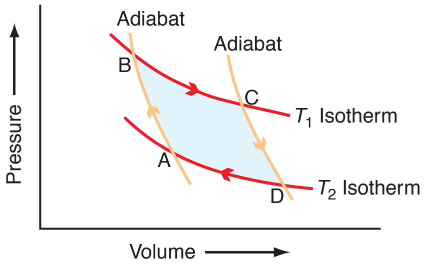

Fig. 3.20 Representations of a Carnot cycle on a p–V diagram. Red lines are isotherms, and orange lines are adiabats.

the isothermal transformation from B to C, we have from Boyle's law

$$p_B V_B = p_C V_C$$

The transformation from C to D is adiabatic. Therefore, from the adiabatic equation,

$$p_C V_C^\gamma = p_D V_D^\gamma$$

For the isothermal change from D to A

$$p_D V_D = p_A V_A$$

Combining the last four equations gives

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \tag{3.79}$$

Consider now the heats absorbed and rejected by the ideal gas. In passing from state B to C, heat Q_1 is absorbed from the warm reservoir. Since the internal energy of an ideal gas depends only on temperature, and the temperature of the gas does not change from B to C, it follows from (3.33) that the heat Q_1 given to the gas goes solely to do work. Therefore, from (3.36),

$$Q_1 = \int_{V_B}^{V_C} p\,dV$$

or, using (3.6) applied to 1 mol of an ideal gas,

$$Q_1 = \int_{V_B}^{V_C} \frac{R^* T_1}{V} dV = R^* T_1 \int_{V_B}^{V_C} \frac{dV}{V}$$

Therefore

$$Q_1 = R^* T_1 \ln\left(\frac{V_C}{V_B}\right) \tag{3.80}$$

Similarly, the heat Q_2 rejected to the cold reservoir in the isothermal transformation from D to A is given by

$$Q_2 = R^* T_2 \ln\left(\frac{V_D}{V_A}\right) \tag{3.81}$$

From (3.80) and (3.81)

$$\frac{Q_1}{Q_2} = \frac{T_1 \ln(V_C/V_B)}{T_2 \ln(V_D/V_A)} \tag{3.82}$$

Therefore, from (3.79) and (3.82),

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{3.83}$$ ■

Examples of real heat engines are the steam engine and a nuclear power plant. The warm and cold reservoirs for a steam engine are the boiler and the condenser, respectively. The warm and cold reservoirs for a nuclear power plant are the nuclear reactor and the cooling tower, respectively. In both cases, water (in liquid and vapor forms) is the working substance that expands when it absorbs heat and thereby does work by pushing a piston or turning a turbine blade. Section 7.4.2 discusses how differential heating within the Earth's atmosphere maintains the winds against frictional dissipation through the action of a global heat engine.

Carnot's cycle can be reversed in the following way. Starting from point A in Fig. 3.20, the material in the cylinder may be expanded at constant temperature until the state represented by point D is reached. During this process a quantity of heat Q_2 is *taken from* the cold reservoir. An adiabatic expansion takes the substance from state D to C. The substance is then compressed from state C to state B, during which a quantity of heat Q_1 is *given up* to the warm reservoir. Finally, the substance is expanded adiabatically from state B to state A.

In this reverse cycle, Carnot's ideal engine serves as a *refrigerator* or *air conditioner*, for a quantity of heat Q_2 is taken from a cold body (the cold reservoir) and heat Q_1 ($Q_1 > Q_2$) is given to a hot body (the warm reservoir). To accomplish this transfer of heat, a quantity of mechanical work equivalent to $Q_1 - Q_2$ must be expended by some outside agency (e.g., an electric motor) to drive the refrigerator. This leads to another statement of the second law of thermodynamics, namely "heat cannot of itself (i.e., without the performance of work by some external agency) pass from a colder to a warmer body in a cyclic process."

3.7.2 Entropy

We have seen that isotherms are distinguished from each other by differences in temperature and that dry adiabats can be distinguished by their potential temperature. Here we describe another way of characterizing the differences between adiabats. Consider the three adiabats labeled by their potential temperatures θ_1, θ_2, and θ_3 on the p–V diagram shown in Fig. 3.21.

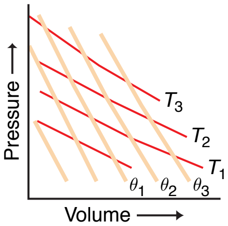

Fig. 3.21 Isotherms (red curves labeled by temperature T) and adiabats (tan curves labeled by potential temperature θ) on a p–V diagram.

In passing reversibly from one adiabat to another along an isotherm (e.g., in one operation of a Carnot cycle) heat is absorbed or rejected, where the amount of heat Q_{rev} (the subscript "rev" indicates that the heat is exchanged reversibly) depends on the temperature T of the isotherm. Moreover, it follows from (3.83) that the ratio Q_{rev}/T is the same no matter which isotherm is chosen in passing from one adiabat to another. Therefore, the ratio Q_{rev}/T could be used as a measure of the difference between the two adiabats; Q_{rev}/T is called the *difference in entropy (S)* between the two adiabats. More precisely, we may define the increase in the entropy dS of a system as

$$dS \equiv \frac{dQ_{\text{rev}}}{T} \tag{3.84}$$

where dQ_{rev} is the quantity of heat that is added reversibly to the system at temperature T. For a unit mass of the substance

$$ds \equiv \frac{dq_{\text{rev}}}{T} \tag{3.85}$$

Entropy is a function of the state of a system and not the path by which the system is brought to that state. We see from (3.38) and (3.85) that the first law of thermodynamics for a reversible transformation may be written as

$$Tds = du + pd\alpha \tag{3.86}$$

In this form the first law contains functions of state only.

When a system passes from state 1 to state 2, the change in entropy of a unit mass of the system is

$$s_2 - s_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} \tag{3.87}$$

Combining (3.66) and (3.67) we obtain

$$\frac{dq}{T} = c_p \frac{d\theta}{\theta} \tag{3.88}$$

Therefore, because the processes leading to (3.66) and (3.67) are reversible, we have from (3.85) and (3.88)

$$ds = c_p \frac{d\theta}{\theta} \tag{3.89}$$

Integrating (3.89) we obtain the relationship between entropy and potential temperature

$$s = c_p \ln \theta + \text{constant} \tag{3.90}$$

Transformations in which entropy (and therefore potential temperature) is constant are called *isentropic*. Therefore, *adiabats* are often referred to as *isentropies* in atmospheric science. We see from (3.90) that the potential temperature can be used as a surrogate for entropy, as is generally done in atmospheric science.

Let us consider now the change in entropy in the Carnot cycle shown in Fig. 3.20. The transformations from A to B and from C to D are both adiabatic and reversible; therefore, in these two transformations there can be no changes in entropy. In passing from state B to state C, the working substance takes in a quantity of heat Q_1 reversibly from the source at temperature T_1; therefore, the entropy of the *source* decreases by an amount Q_1/T_1. In passing from state D to state A, a quantity of heat Q_2 is rejected reversibly from the working substance to the sink at temperature T_2; therefore, the entropy of the *sink* increases by Q_2/T_2. Since the working substance itself is taken in a cycle, and is therefore returned to its original state, it does not undergo any net change in entropy. Therefore, the net increase in entropy in the complete Carnot cycle is $Q_2/T_2 - Q_1/T_1$. However, we have shown in Exercise 3.15 that $Q_1/T_1 = Q_2/T_2$. Hence, there is no change in entropy in a Carnot cycle.

It is interesting to note that if, in a graph (called a *temperature–entropy* diagram[40]), temperature (in kelvin) is taken as the ordinate and entropy as the abscissa, the Carnot cycle assumes a rectangular shape, as shown in Fig. 3.22 where the letters A, B, C, and D correspond to the state points in the previous discussion. Adiabatic processes (AB and CD) are represented by vertical lines (i.e., lines of constant entropy) and isothermal processes (BC and DA) by horizontal lines. From (3.84) it is evident that in a cyclic transformation ABCDA, the heat Q_1 taken in reversibly by the working substance from the warm reservoir is given by the area XBCY, and the heat Q_2 rejected by the working substance to the cold reservoir is given by the area XADY. Therefore, the work $Q_1 - Q_2$ done in the cycle is given by the difference between the two areas, which is equivalent to the shaded area ABCD in Fig. 3.22. Any reversible heat engine can be represented by a closed loop on a temperature–entropy diagram, and the area of the loop is proportional to the net work done by or on (depending on whether the loop is traversed clockwise or counterclockwise, respectively) the engine in one cycle.

Thermodynamic charts on which equal areas represent equal net work done by or on the working substance are particularly useful. The skew $T - \ln p$ chart has this property.

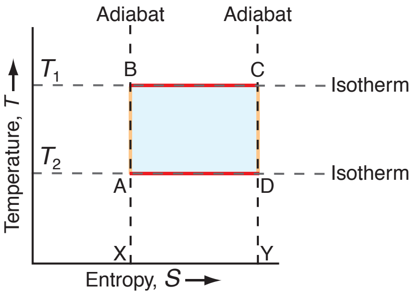

Fig. 3.22 Representation of the Carnot cycle on a temperature (T)–entropy (S) diagram. AB and CD are adiabats, and BC and DA are isotherms.

3.7.3 The Clausius–Clapeyron Equation

We will now utilize the Carnot cycle to derive an important relationship, known as the *Clausius–Clapeyron*[42] *equation* (sometimes referred to by physicists as the *first latent heat equation*). The Clausius–Clapeyron equation describes how the saturated vapor pressure above a liquid changes with temperature and also how the melting point of a solid changes with pressure.

Let the working substance in the cylinder of a Carnot ideal heat engine be a liquid in equilibrium with its saturated vapor and let the initial state of the substance be represented by point A in Fig. 3.23 in which the saturated vapor pressure is $e_s - de_s$ at temperature $T - dT$. The adiabatic compression from state A to state B, where the saturated vapor pressure is e_s at temperature T, is achieved by placing the cylinder on the nonconducting stand and compressing the piston infinitesimally (Fig. 3.24a). Now let the cylinder be placed on the source of heat at temperature T and let the substance expand isothermally until a unit mass of the liquid evaporates (Fig. 3.24b).

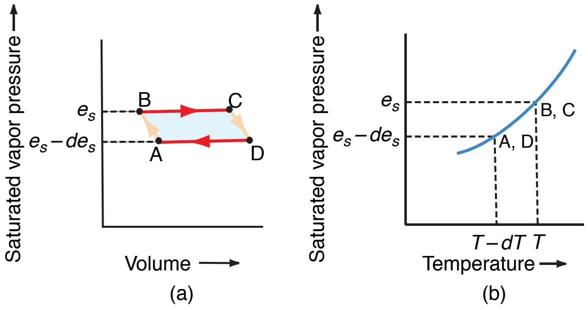

Fig. 3.23 Representation on (a) a saturated vapor pressure versus volume diagram and on (b) a saturated vapor pressure versus temperature diagram of the states of a mixture of a liquid and its saturated vapor taken through a Carnot cycle. Because the saturated vapor pressure is constant if temperature is constant, the isothermal transformations BC and DA are horizontal lines.

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[40] The temperature–entropy diagram was introduced into meteorology by Shaw.[41] Because entropy is sometimes represented by the symbol ϕ (rather than S), the temperature–entropy diagram is sometimes referred to as a *tephigram*.

[41] **Sir (William) Napier Shaw** (1854–1945) English meteorologist. Lecturer in Experimental Physics, Cambridge University, 1877–1899. Director of the British Meteorological Office, 1905–1920. Professor of Meteorology, Imperial College, University of London, 1920–1924. Shaw did much to establish the scientific basis of meteorology. His interests ranged from the atmospheric general circulation and forecasting to air pollution.

[42] **Benoit Paul Emile Clapeyron** (1799–1864) French engineer and scientist. Carnot's theory of heat engines was virtually unknown until Clapeyron expressed it in analytical terms. This brought Carnot's ideas to the attention of William Thomson (Lord Kelvin) and Clausius, who utilized them in formulating the second law of thermodynamics.

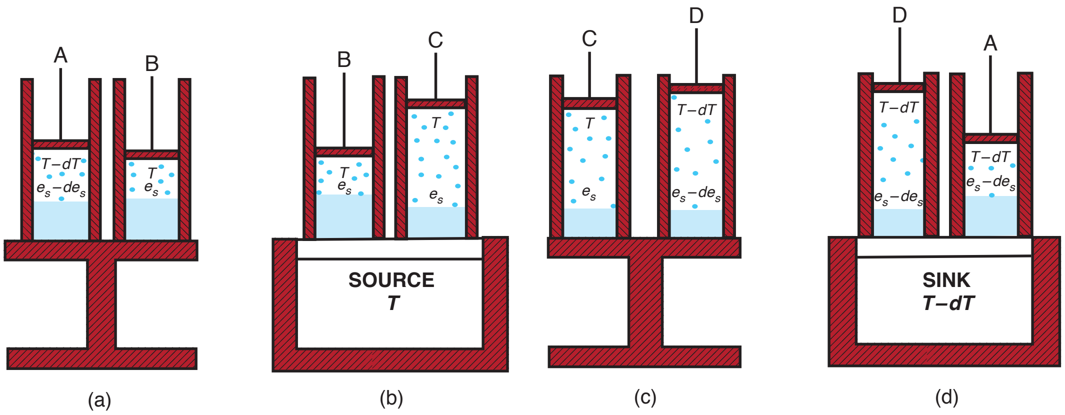

Fig. 3.24 Transformations of a liquid (solid blue) and its saturated vapor (blue dots) in a Carnot cycle. The letters A, B, C, D indicate the states of the mixture shown in Fig. 3.23. Red-shaded areas are thermally insulating materials.

In this transformation the pressure remains constant at e_s and the substance passes from state B to state C (Fig. 3.24b). If the specific volumes of liquid and vapor at temperature T are α_1 and α_2, respectively, the increase in the volume of the system in passing from state B to C is $(\alpha_2 - \alpha_1)$. Also the heat absorbed from the source is L_v where L_v is the latent heat of vaporization. The cylinder is now placed again on the nonconducting stand and a small adiabatic expansion is carried out from state C to state D in which the temperature falls from T to $T - dT$ and the pressure from e_s to $e_s - de_s$ (Fig. 3.24c). Finally, the cylinder is placed on the heat sink at temperature $T - dT$ and an isothermal and isobaric compression is carried out from state D to state A during which vapor is condensed (Fig. 3.24d). All of the aforementioned transformations are reversible.

From (3.83)

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2} \tag{3.91}$$

where $Q_1 - Q_2$ is the net heat absorbed by the working substance in the cylinder during one cycle, which is also equal to the work done by the working substance in the cycle. However, as shown in Section 3.3, the work done during a cycle is equal to the area of the enclosed loop on a p–V diagram. Therefore, from Fig. 3.23, $Q_1 - Q_2 = BC \times de_s = (\alpha_2 - \alpha_1)de_s$. Also, $Q_1 = L_v$, $T_1 = T$, and $T_1 - T_2 = dT$. Therefore, substituting into (3.91),

$$\frac{L_v}{T} = \frac{(\alpha_2 - \alpha_1)de_s}{dT}$$

or

$$\frac{de_s}{dT} = \frac{L_v}{T(\alpha_2 - \alpha_1)} \tag{3.92}$$

which is the *Clausius–Clapeyron equation* for the variation of the equilibrium vapor pressure e_s with temperature T.

Since the volume of a unit mass of vapor is very much greater than the volume of a unit mass of liquid ($\alpha_2 \gg \alpha_1$), Eq. (3.92) can be written to close approximation as

$$\frac{de_s}{dT} \simeq \frac{L_v}{T\alpha_2} \tag{3.93}$$

Because α_2 is the specific volume of water vapor that is in equilibrium with liquid water at temperature T, the pressure it exerts at T is e_s. Therefore, from the ideal gas equation for water vapor,

$$e_s\,\alpha_2 = R_v T \tag{3.94}$$

combining (3.93) and (3.94), and then substituting $R_v = 1000\,R^*/M_w$ from (3.13), we get

$$\frac{1}{e_s}\frac{de_s}{dT} \simeq \frac{L_v}{R_v T^2} = \frac{L_v M_w}{1000\,R^* T^2} \tag{3.95}$$

which is a convenient form of the Clausius–Clapeyron equation. Over the relatively small range of temperatures of interest in the atmosphere, to good approximation (3.95) can be applied in incremental form, that is

$$\frac{1}{e_s}\frac{\Delta e_s}{\Delta T} \simeq \frac{L_v M_w}{1000\,R^* T^2} \tag{3.96}$$

Applying (3.95) to the water substance, and integrating from 273 K to T K,

$$\int_{e_s\,(273\ \mathrm{K})}^{e_s\,(T\,\mathrm{K})} \frac{de_s}{e_s} = \frac{L_v M_w}{1000\ R^*} \int_{273}^{T} \frac{dT}{T^2}$$

Alternatively, because e_s at 273 K = 6.11 hPa (Fig. 3.9), $L_v = 2.500 \times 10^6\ \mathrm{J\ kg^{-1}}$, the molecular weight of water (M_w) is 18.016, and $R^* = 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}$, the saturated vapor pressure of water e_s (in hPa) at temperature T K is given by

$$\ln \frac{e_s\,(\text{in hPa})}{6.11} = \frac{L_v M_w}{1000\ R^*}\left(\frac{1}{273} - \frac{1}{T}\right)$$
$$\simeq 5.42 \times 10^3 \left(\frac{1}{273} - \frac{1}{T}\right) \qquad (3.97)$$

3.5 Effect of Ambient Pressure on the Boiling Point of a Liquid

A liquid is said to boil when it is heated to a temperature that is sufficient to produce copious small bubbles within the liquid. Why do bubbles form at a certain temperature (the *boiling point*) for each liquid? The key to the answer to this question is to realize that if a bubble forms in a liquid, the interior of the bubble contains only the vapor of the liquid. Therefore, the pressure inside the bubble is the saturation vapor pressure at the temperature of the liquid. If the saturation vapor pressure is less than the ambient pressure that acts on the liquid (and therefore on a bubble just below the surface of a liquid), bubbles cannot form. As the temperature increases, the saturation vapor pressure increases (see Fig. 3.9) and, when the saturation vapor pressure is equal to the ambient pressure, bubbles can form at the surface of the liquid and the liquid boils (Fig. 3.25).

Water boils at a temperature T_B such that the saturation vapor pressure at T_B is equal to the atmospheric (or ambient) pressure (p_{atmos})[43]

$$e_s(T_B) = p_{\mathrm{atmos}} \qquad (3.98)$$

From (3.92) expressed in incremental form, and (3.98)

$$\frac{\Delta p_{\mathrm{atmos}}}{\Delta T_B} = \frac{L_v}{T_B\,(\alpha_2 - \alpha_1)}$$

or

$$\frac{\Delta T_B}{\Delta p_{\mathrm{atmos}}} = \frac{T_B\,(\alpha_2 - \alpha_1)}{L_v} \qquad (3.99)$$

Equation (3.99) gives the change in the boiling point of water with atmospheric pressure (or ambient pressure in general). Because $\alpha_2 > \alpha_1$, T_B increases with increasing p_{atmos}. If the atmospheric pressure is significantly lower than 1 atm, the boiling point of water will be significantly lower than 100 °C. This is why it is difficult to brew a good cup of hot tea on top of a high mountain (see Exercise 3.64)!

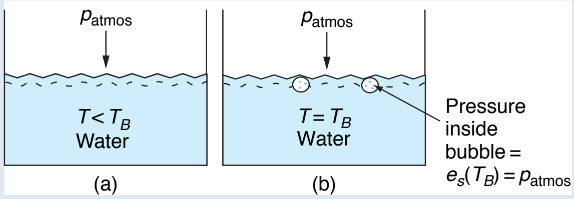

Fig. 3.25 (a) Water below its boiling point (T_B): bubbles cannot form because $e_s(T) < p_{\mathrm{atmos}}$. (b) Water at its boiling point: bubbles can form because the pressure inside them, $e_s(T_B)$, is equal to the atmospheric pressure (p_{atmos}) acting on them.

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[43] If, as is generally the case, the water is in a vessel that is heated from below, the pressure where the bubbles originate is slightly greater than atmospheric pressure due to the extra pressure exerted by the water above the bubble. Therefore, when the water is boiling steadily, the temperature at the bottom of the vessel will be slightly in excess of T_B. When water is heated in a transparent vessel, the first visible sign of bubbling occurs well below T_B as trains of small bubbles of *dissolved air* rise to the surface. (Note: the solubility of a gas in a liquid decreases with increasing temperature.) The "singing" that precedes boiling is due to the collapse of bubbles of water vapor in the upper part of the vessel. Those vapor bubbles probably form around air bubbles that act as nuclei, which originate in the slightly hotter water nearer the source of the heat. Nuclei of some sort appear to be necessary for continuous steady boiling at T_B. Without nuclei the water will not begin to boil until it is superheated with respect to the boiling point and "bumping" (i.e., delayed boiling) occurs. When bubbles finally form, the vapor pressure in the bubbles is much greater than the ambient pressure, and the bubbles expand explosively as they rise. Chapter 6 discusses the formation of water drops from the vapor phase, and ice particles from the vapor and liquid phases both of which require nucleation.

3.7.4 Generalized Statement of the Second Law of Thermodynamics

So far we have discussed the second law of thermodynamics and entropy in a fairly informal manner, and only with respect to ideal reversible transformations. The second law of thermodynamics states (in part) that *for a reversible transformation there is no change in the entropy of the universe* (where "universe" refers to a system and its surroundings). In other words, if a system receives heat reversibly, the increase in its entropy is exactly equal in magnitude to the decrease in the entropy of its surroundings.

The concept of reversibility is an abstraction. A reversible transformation moves a system through a series of equilibrium states so that the direction of the transformation can be reversed at any point by making an infinitesimal change in the surroundings. All natural transformations are irreversible to some extent. In an *irreversible* (sometimes called a *spontaneous*) *transformation*, a system undergoes finite transformations at finite rates, and these transformations cannot be reversed simply by changing the surroundings of the system by infinitesimal amounts. Examples of irreversible transformations are the flow of heat from a warmer to a colder body, and the mixing of two gases.

If a system receives heat dq_{irrev} at temperature T during an irreversible transformation, the change in the entropy of the system is *not* equal to dq_{irrev}/T. In fact, for an irreversible transformation there is no simple relationship between the change in the entropy of the system and the change in the entropy of its surroundings. However, the remaining part of the second law of thermodynamics states that *the entropy of the universe increases as a result of irreversible transformations*.

The two parts of the second law of thermodynamics stated earlier can be summarized as follows

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \tag{3.100a}$$

$$\Delta S_{\text{universe}} = 0 \text{ for reversible (equilibrium) transformations} \tag{3.100b}$$

$$\Delta S_{\text{universe}} > 0 \text{ for irreversible (spontaneous) transformations} \tag{3.100c}$$

The second law of thermodynamics cannot be proved. It is believed to be valid because it leads to deductions that are in accord with observations and experience. The following exercise provides an example of such a deduction.

Exercise 3.16 Assuming the truth of the second law of thermodynamics, prove that an isolated ideal gas can expand spontaneously (e.g., into a vacuum) but it cannot contract spontaneously.

Solution: Consider a unit mass of the gas. If the gas is isolated it has no contact with its surroundings, hence $\Delta S_{\text{surroundings}} = 0$. Therefore, from (3.100a)

$$\Delta S_{\text{universe}} = \Delta S_{\text{gas}} \tag{3.101}$$

Because entropy is a function of state, we can obtain an expression for ΔS_{gas} by taking any reversible and isothermal path from state 1 to state 2 and evaluating the integral

$$\Delta S_{\text{gas}} = \int_1^2 \frac{dq_{\text{rev}}}{T}$$

Combining (3.46) with (3.3), we have for a reversible transformation of a unit mass of an ideal gas

$$\frac{dq_{\text{rev}}}{T} = c_p \frac{dT}{T} - R\frac{dp}{p}$$

Therefore

$$\Delta S_{\text{gas}} = c_p \int_{T_1}^{T_2} \frac{dT}{T} - R\int_{p_1}^{p_2} \frac{dp}{p}$$

or

$$\Delta S_{\text{gas}} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$$

Because the gas is isolated, $\Delta q = \Delta w = 0$; therefore, from (3.34), $\Delta u = 0$. If $\Delta u = 0$, it follows from Joule's law for an ideal gas that $\Delta T = 0$. Hence, the gas must pass from its initial state (1) to its final state (2) isothermally.

For an isothermal process, the ideal gas equation reduces to Boyle's law, which can be written as $p_1\alpha_1 = p_2\alpha_2$, where the α's are specific volumes. Therefore, the last expression becomes

$$\begin{aligned}\Delta S_{\text{gas}} &= c_p \ln 1 - R \ln \frac{p_2}{p_1} \\ &= -R \ln \frac{\alpha_1}{\alpha_2} = R \ln \frac{\alpha_2}{\alpha_1}\end{aligned} \tag{3.102}$$

From (3.101) and (3.102)

$$\Delta S_{\text{universe}} = R \ln \frac{\alpha_2}{\alpha_1} \tag{3.103}$$

Hence, if the second law of thermodynamics is valid, it follows from (3.100c) and (3.103) that

$$R \ln \frac{\alpha_2}{\alpha_1} > 0$$

or

$$\alpha_2 > \alpha_1$$

That is, the gas expands spontaneously. However, if the gas contracted spontaneously, $\alpha_2 < \alpha_1$ and $\Delta S_{\text{universe}} < 0$, which would violate the second law of thermodynamics.

When a gas expands, the disorder of its molecules increases and, as shown in this exercise, the entropy of the gas increases. This illustrates what is, in fact, a general result, namely that entropy is a measure of the degree of disorder (or randomness) of a system. ■

Section 3.7.2 showed that there is no change in entropy in a Carnot cycle. Because *any* reversible cycle can be divided up into an infinite number of adiabatic and isothermal transformations, and therefore into an infinite number of Carnot cycles, it follows that in any reversible cycle the total change in entropy is zero. This result is yet another way of stating the second law of thermodynamics.

In the real world (as opposed to the world of reversible cycles), systems left to themselves tend to become more disordered with time, and therefore their entropy increases. Consequently, a parallel way of stating the two laws of thermodynamics is (1) "the energy of the universe is constant" and (2) "the entropy of the universe tends to a maximum."

Exercise 3.17 One kilogram of ice at 0 °C is placed in an isolated container with 1 kg of water at 10 °C and 1 atm. (a) How much of the ice melts? (b) What change is there in the entropy of the universe due to the melting of the ice?

Solution: (a) The ice will melt until the ice-water system reaches a temperature of 0 °C. Let mass m kg of ice melt to bring the temperature of the ice-water system to 0 °C. Then, the latent heat required to melt m kg of ice is equal to the heat released when the temperature of 1 kg of water decreases from 10 to 0 °C. Therefore,

$$mL_M = c\Delta T$$

where L_M is the latent heat of melting of ice (3.34×10^5 J kg^{-1}), c is the specific heat of water (4218 J K^{-1} kg^{-1}), and ΔT is 10 K. Hence, the mass of ice that melts (m) is 0.126 kg. (Note: Because $m < 1$ kg, it follows that when the system reaches thermal equilibrium some ice remains in the water, and therefore the final temperature of the ice-water system must be 0 °C.)

(b) Because the container is isolated, there is no change in the entropy of its surroundings. Therefore, (3.100a) becomes

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}}$$

Because the ice-water system undergoes an irreversible transformation, it follows from (3.100c) that its entropy increases. (We could also have deduced that the entropy of the ice-water system increases when some of the ice melts, because melting increases the disorder of the system.)

There are two contributions to ΔS_{system}: the melting of 0.126 kg of ice (ΔS_{ice}) and the cooling of 1 kg of water from 10 to 0 °C (ΔS_{water}). The change in entropy when 0.126 kg of ice is melted at 0 °C is $\Delta S_{\text{ice}} = \Delta Q/T = mL_M/T = (0.126)(3.34 \times 10^5)/273 = 154$ J K^{-1}. The change in entropy associated with cooling the 1 kg of water from 10 to 0 °C is

$$\Delta S_{\text{water}} = \int_{283\,K}^{273\,K} \frac{dQ}{T} = \int_{283\,K}^{273\,K} \frac{c\,dT}{T}$$
$$= c\int_{283\,K}^{273\,K} \frac{dT}{T} = c \ln \frac{273}{283}$$

Because $c = 4218$ J K^{-1} kg^{-1}

$$\begin{aligned}\Delta S_{\text{water}} &= 4218 \ln \frac{273}{283} \\ &= 4218\,(-0.036) \\ &= -152 \text{ J K}^{-1}.\end{aligned}$$

Hence

$$\begin{aligned}\Delta S_{\text{universe}} = \Delta S_{\text{system}} &= \Delta S_{\text{ice}} + \Delta S_{\text{water}} \\ &= 154 - 152 \\ &= 2 \text{ J K}^{-1}\end{aligned}$$

Exercises

3.18 Answer or explain the following in light of the principles discussed in this chapter.

(a) To carry a given payload, a hot air balloon cruising at a high altitude needs to be bigger or hotter than a balloon cruising at a lower altitude.

(b) More fuel is required to lift a hot air balloon through an inversion than to lift it through a layer of the same depth that exhibits a steep temperature lapse rate. Other conditions being the same, more fuel is required to operate a hot air balloon on a hot day than on a cold day.

(c) Runways are longer at high altitude airports such as Denver and stricter weight limits are imposed on aircraft taking off on hot summer days.

(d) The gas constant for moist air is greater than that for dry air.

(e) Pressure in the atmosphere increases approximately exponentially with depth, whereas the pressure in the ocean increases approximately linearly with depth.

(f) Describe a procedure for converting station pressure to sea-level pressure.

(g) Under what condition(s) does the hypsometric equation predict an exponential decrease of pressure with height?

(h) If a low pressure system is colder than its surroundings, the amplitude of the depression in the geopotential height field increases with height.

(i) On some occasions low surface temperatures are recorded when the 1000- to 500-hPa thickness is well above normal. Explain this apparent paradox.

(j) Air released from a tire is cooler than its surroundings.

(k) Under what conditions can an ideal gas undergo a change of state without doing external work?

(l) A parcel of air cools when it is lifted. Dry parcels cool more rapidly than moist parcels.

(m) If a layer of the atmosphere is well mixed in the vertical, how would you expect the potential temperature within it to change with height?

(n) In cold climates the air indoors tends to be extremely dry.

(o) Summertime dew points tend to be higher over eastern Asia and the eastern United States than over Europe and the western United States.

(p) If someone claims to have experienced hot, humid weather with a temperature in excess of 90 °F and a relative humidity of 90%, it is likely that he/she is exaggerating or inadvertently juxtaposing an afternoon temperature with an early morning relative humidity.

(q) Hot weather causes more human discomfort when the air is humid than when it is dry.

(r) Which of the following pairs of quantities are conserved when unsaturated air is lifted: potential temperature and mixing ratio, potential temperature and saturation mixing ratio, equivalent potential temperature and saturation mixing ratio?

(s) Which of the following quantities are conserved during the lifting of saturated air: potential temperature, equivalent potential temperature, mixing ratio, saturation mixing ratio?

(t) The frost point temperature is higher than the dew point temperature.

(u) You are climbing in the mountains and come across a very cold spring of water. If you had a glass tumbler and a thermometer, how might you determine the dew point of the air?

(v) Leaving the door of a refrigerator open warms the kitchen. (How would the refrigerator need to be reconfigured to make it have the reverse effect?)

(w) A liquid boils when its saturation vapor pressure is equal to the atmospheric pressure.

3.19 Determine the apparent molecular weight of the Venusian atmosphere, assuming that it consists of 95% of CO_2 and 5% N_2 by volume. What is the gas constant for 1 kg of such an atmosphere? (Atomic weights of C, O, and N are 12, 16, and 14, respectively.)

3.20 If water vapor comprises 1% of the volume of the air (i.e., if it accounts for 1% of the molecules in air), what is the virtual temperature correction?

3.21 Archimedes' buoyancy principle asserts that an object placed in a fluid (liquid or gas) will be lighter by an amount equal to the weight of the fluid it displaces. Provide a proof of this principle. [**Hint**: Consider the vertical forces that act on a stationary element of fluid prior to the element being displaced by an object.]

3.22 Typical hot air balloons used on sightseeing flights attain volumes of 3000 m^3. A typical gross weight (balloon, basket, fuel and passengers, but not the air in the balloon) on such a balloon flight is 600 kg. If the ground temperature is 20 °C, the lapse rate is zero, and the balloon is in hydrostatic equilibrium at a cruising altitude of 900 hPa, determine the temperature of the air inside the balloon.

3.23 The gross weight (balloon, basket, fuel and passengers but not the gas in the balloon) of two balloons is the same. The two balloons are cruising together at the same altitude, where the temperature is 0 °C and the ambient air is dry. One balloon is filled with helium and the other balloon with hot air. The volume of the helium balloon is 1000 m^3. If the temperature of the hot air balloon is 90 °C, what is the volume of the hot air balloon?

3.24 Using Eq. (3.29) show that pressure decreases with increasing height at about 1 hPa per 15 m at the 500-hPa level.

3.25 A cheap aneroid barometer aboard a radiosonde is calibrated to the correct surface air pressure when the balloon leaves the ground, but it experiences a systematic drift toward erroneously low pressure readings. By the time the radiosonde reaches the 500-hPa level, the reading is low by the 5-hPa level (i.e., it reads 495 hPa when it should read 500 hPa). Estimate the resulting error in the 500-hPa height. Assume a surface temperature of 10 °C and an average temperature lapse rate of 7 °C km^{-1}. Assume the radiosonde is released from sea level and that the error in the pressure reading is proportional to the height of the radiosonde above sea level (which, from Eq. (3.29), makes it nearly proportional to ln p). Also, assume that the average decrease of pressure with height is 1 hPa per 11 m of rise between sea level and 500 hPa.

3.26 A hurricane with a central pressure of 940 hPa is surrounded by a region with a pressure of 1010 hPa. The storm is located over an ocean region. At 200 hPa the depression in the pressure field vanishes (i.e., the 200-hPa surface is perfectly flat). Estimate the average temperature difference between the center of the hurricane and its surroundings in the layer between the surface and 200 hPa. Assume that the mean temperature of this layer outside the hurricane is −3 °C and ignore the virtual temperature correction.

3.27 A meteorological station is located 50 m below sea level. If the surface pressure at this station is 1020 hPa, the virtual temperature at the surface is 15 °C, and the mean virtual temperature for the 1000- to 500-hPa layer is 0 °C, compute the height of the 500-hPa pressure level above sea level at this station.

3.28 The 1000- to 500-hPa layer is subjected to a heat source having a magnitude of 5.0×10^6 J m^{-2}. Assuming that the atmosphere is at rest (apart from the slight vertical motions associated with the expansion of the layer) calculate the resulting increase in the mean temperature and in the thickness of the layer. [**Hint**: Remember that pressure is force per unit area.]

3.29 The 1000- to 500-hPa thickness is predicted to increase from 5280 to 5460 m at a given station. Assuming that the lapse rate remains constant, what change in surface temperature would you predict?

3.30 Derive a relationship for the height of a given pressure surface (p) in terms of the pressure p_0 and temperature T_0 at sea level assuming that the temperature decreases uniformly with height at a rate Γ K km^{-1}.

Solution: Let the height of the pressure surface be z; then its temperature T is given by

$$T = T_0 - \Gamma_z \qquad (3.104)$$

combining the hydrostatic equation (3.17) with the ideal gas equation (3.2) yields

$$\frac{dp}{p} = -\frac{g}{RT}dz \qquad (3.105)$$

From (3.104) and (3.105)

$$\frac{dp}{p} = -\frac{g}{R(T_0 - \Gamma_z)}dz$$

Integrating this equation beween pressure levels p_0 and p and corresponding heights 0 and z and neglecting the variation of g with z, we obtain

$$\int_{p_0}^{p} \frac{dp}{p} = -\frac{g}{R}\int_{0}^{z} \frac{dz}{(T_0 - \Gamma_z)}$$

or

$$\ln \frac{p}{p_0} = \frac{g}{R\Gamma} \ln \left(\frac{T_0 - \Gamma_z}{T_0}\right)$$

Therefore,

$$z = \frac{T_0}{\Gamma}\left[1 - \left(\frac{p}{p_0}\right)^{RT/g}\right] \qquad (3.106)$$

This equation forms the basis for the calibration of aircraft altimeters. An altimeter is simply an aneroid barometer that measure ambient air pressure p. However, the scale of the altimeter is expressed at the height z of the aircraft, where z is related to p by (3.106) with values of T_0, p_0 and Γ appropriate to the U.S. Standard Atmosphere, namely, $T_0 = 288$ K, $p_0 = 1013.25$ hPa, and $\Gamma = 6.50$ K km^{-1}. ■

3.31 A hiker sets his pressure altimeter to the correct reading at the beginning of a hike during which he climbs from near sea level to an altitude of 1 km in 3 h. During this same time interval the sea-level pressure drops by 8 hPa due to the approach of a storm. Estimate the altimeter reading at the end of the hike.

3.32 Calculate the work done in compressing isothermally 2 kg of dry air to one-tenth of its volume at 15 °C.

3.33 (a) Prove that when an ideal gas undergoes an adiabatic transformation $pV^{\gamma} =$ constant, where γ is the ratio of the specific heat at constant pressure (c_p) to the specific heat at constant volume (c_v). [**Hint**: By combining (3.3) and (3.41) show that for an adiabatic transformation of a unit mass of gas $c_v(pd\alpha + \alpha dp) + Rpd\alpha = 0$. Then combine this last expression with (3.45) and proceed to answer.] (b) 7.50 cm^3 of air at 17 °C and 1000 hPa is compressed isothermally to 2.50 cm^3. The air is then allowed to expand adiabatically to its original volume. Calculate the final temperature and final pressure of the gas.

3.34 If the balloon in Exercise 3.22 is filled with air at the ambient temperature of 20 °C at ground level where the pressure is 1013 hPa, estimate how much fuel will need to be burned to lift the balloon to its cruising altitude of 900 hPa. Assume that the balloon is perfectly insulated and that the fuel releases energy at a rate of 5×10^7 J kg^{-1}.

3.35 Calculate the change in enthalpy when 3 kg of ice at 0 °C is heated to liquid water at 40 °C. [The specific heat at constant pressure of liquid water (in J K^{-1} kg^{-1}) at T K is given by $c_{pw} = 4183.9 + 0.1250\ T$.]

3.36 Prove that the potential temperature of an air parcel does not change when the parcel moves around under adiabatic and reversible conditions in the atmosphere. [**Hint**: Use Eq. (3.1) and the adiabatic equation $pV^{\gamma} =$ constant (see Exercise 3.33) to show that $T\,(p_0/p)^{R/cp} =$ constant, and hence from Eq. (3.54) that $\theta =$ constant.]

3.37 The pressure and temperature at the levels at which jet aircraft normally cruise are typically 200 hPa and −60 °C. Use a skew $T - \ln p$ chart to estimate the temperature of this air if it were compressed adiabatically to 1000 hPa. Compare your answer with an accurate computation.

3.38 Consider a parcel of dry air moving with the speed of sound (c_s), where

$$c_s = (\gamma R_d T)^{\frac{1}{2}}$$

$\gamma = c_p/c_v = 1.40$, R_d is the gas constant for a unit mass of dry air, and T is the temperature of the air in degrees kelvin.

(a) Derive a relationship between the macroscopic kinetic energy of the air parcel K_m and its enthalpy H.

(b) Derive an expression for the fractional change in the speed of sound per degree kelvin change in temperature in terms of c_v, R_d, and T.

3.39 A person perspires. How much liquid water (as a percentage of the mass of the person) must evaporate to lower the temperature of the person by 5 °C? (Assume that the latent heat of evaporation of water is 2.5×10^6 J kg^{-1}, and the specific heat of the human body is 4.2×10^3 J K^{-1} kg^{-1}.)

3.40 Twenty liters of air at 20 °C and a relative humidity of 60% are compressed isothermally to a volume of 4 liters. Calculate the mass of water condensed. The saturation vapor pressure of water at 20 °C is 23 hPa. (Density of air at 0 °C and 1000 hPa is 1.28 kg m^{-3}.)

3.41 If the specific humidity of a sample of air is 0.0196 at 30 °C, find its virtual temperature. If the total pressure of the moist air is 1014 hPa, what is its density?

3.42 A parcel of moist air has a total pressure of 975 hPa and a temperature of 15 °C. If the mixing ratio is 1.80 g kg^{-1}, what are the water vapor pressure and the virtual temperature?

3.43 An isolated raindrop that is evaporating into air at a temperature of 18 °C has a temperature of 12 °C. Calculate the mixing ratio of the air. (Saturation mixing ratio of air at 12 °C is 8.7 g kg^{-1}. Take the latent heat of evaporation of water to be 2.25×10^6 J kg^{-1}.)

3.44 Four grams of liquid water condense out of 1 kg of air during a moist-adiabatic expansion. Show that the internal energy associated with this amount of liquid water is only 2.4% of the internal energy of the air.

3.45 The current mean air temperature at 1000 hPa in the tropics is about 25 °C and the lapse rate is close to saturated adiabatic. Assuming that the lapse rate remains close to saturated adiabatic, by how much would the temperature change at 250 hPa if the temperature in the tropics at 1000 hPa were to increase by 1 °C. [**Hint**: Use a skew $T - \ln p$ chart.]

3.46 An air parcel at 1000 hPa has an initial temperature of 15 °C and a dew point of 4 °C. Using a skew $T - \ln p$ chart,

(a) Find the mixing ratio, relative humidity, wet-bulb temperature, potential temperature, and wet-bulb potential temperature of the air.

(b) Determine the magnitudes of the parameters in (a) if the parcel rises to 900 hPa.

(c) Determine the magnitudes of the parameters in (a) if the parcel rises to 800 hPa.

(d) Where is the lifting condensation level?

3.47 Air at 1000 hPa and 25 °C has a wet-bulb temperature of 20 °C.

(a) Find the dew point.

(b) If this air were expanded until all the moisture condensed and fell out and it were then compressed to 1000 hPa, what would be the resulting temperature?

(c) What is this temperature called?

3.48 Air at a temperature of 20 °C and a mixing ratio of 10 g kg^{-1} is lifted from 1000 to 700 hPa by moving over a mountain. What is the initial dew point of the air? Determine the temperature of the air after it has descended to 900 hPa on the other side of the mountain if 80% of the condensed water vapor is removed by precipitation during the ascent. (**Hint**: Use the skew $T - \ln p$ chart.)

3.49 (a) Show that when a parcel of dry air at temperature T' moves adiabatically in ambient air with temperature T, the temperature lapse rate following the parcel is given by

$$-\frac{dT'}{dz} = \frac{T'}{T}\frac{g}{c_p}$$

(b) Explain why the lapse rate of the air parcel in this case differs from the dry adiabatic lapse rate (g/c_p). [**Hint**: Start with Eq. (3.54) with $T = T'$. Take the natural logarithm of both sides of this equation and then differentiate with respect to height z.]

Solution:

(a) From (3.54) with $T = T'$ we have for the air parcel

$$\theta = T'\left(\frac{p_0}{p}\right)^{R/c_p}$$

Therefore,

$$\ln\theta = \ln T' + \frac{R}{c_p}(\ln p_0 - \ln p)$$

Differentiating this last expression with respect to height z

$$\frac{1}{\theta}\frac{d\theta}{dz} = \frac{1}{T'}\frac{dT'}{dz} - \frac{R}{c_p}\frac{1}{p}\frac{dp}{dz} \tag{3.110}$$[44]

However, for the ambient air we have, from the hydrostatic equation,

$$\frac{dp}{dz} = -g\rho \tag{3.111}$$

From (3.110) and (3.111):

$$\frac{1}{\theta}\frac{d\theta}{dz} = \frac{1}{T'}\frac{dT'}{dz} - \frac{R}{c_p}\frac{1}{p}(-g\rho)$$

For an adiabatic process θ is conserved (i.e., $\frac{d\theta}{dz} = 0$. Therefore,

$$0 = \frac{1}{T'}\frac{dT'}{dz} + \frac{Rg\rho}{pc_p}$$

or

$$\frac{dT'}{dz} = -\frac{R\rho T' g}{pc_p} \tag{3.112}$$

However, the ideal gas equation for the ambient air is

$$p = R\rho T \tag{3.113}$$

From (3.112) and (3.113),

$$\frac{dT'}{dz} = -\frac{T'}{T}\frac{g}{c_p} \tag{3.114}$$

(b) The derivation of an expression for the dry adiabatic lapse rate, namely $\Gamma_d \equiv -\left(\frac{dT}{dz}\right)_{\text{dry parcel}} = \frac{g}{c_p}$, was based on the assumption that the macroscopic kinetic energy of the air parcel was negligible compared to its total energy (see Sections 3.4.1 and 3.4.2). However, in the present exercise the temperature of the air parcel (T') differs from the temperature of the ambient air (T). Therefore, the air parcel is acted upon by a buoyancy force, which accelerates the air parcel in the vertical and gives it macroscopic kinetic energy. Note that if $T' = T$, Eq. (3.114) reduces to

$$-\frac{dT}{dz} = \frac{g}{c_p} = \Gamma_d$$ ■

3.50 Derive an expression for the rate of change in temperature with height (Γ_s) of a parcel of air undergoing a saturated adiabatic process. Assume that $\rho L_v\left(\frac{dw_s}{dp}\right)_T$ is small compared to 1.

Solution: Substituting (3.20) into (3.51) yields

$$dq = c_p dT + g dz \tag{3.115}$$

If the saturation ratio of the air with respect to water is w_s, the quantity of heat dq released into (or absorbed from) a unit mass of dry air due to condensation (or evaporation) of liquid water is $-L_v\, dw_s$, when L_v is the latent heat of condensation. Therefore,

$$-L_v dw_s = c_p dT + g dz \tag{3.116}$$

If we neglect the small amounts of water vapor associated with a unit mass of dry air, which are also warmed (or cooled) by the release (or absorption) of the latent heat, then c_p in (3.116) is the specific heat at constant pressure of dry air. Dividing both sides of (3.116) by $c_p\, dz$ and rearranging terms, we obtain

$$\begin{aligned}\frac{dT}{dz} &= -\frac{L_v}{c_p}\frac{dw_s}{dz} - \frac{g}{c_p} \\ &= -\frac{L_v}{c_p dz}\left[\left(\frac{dw_s}{dp}\right)_T dp + \left(\frac{dw_s}{dT}\right)_p dT\right] - \frac{g}{c_p}\end{aligned}$$

Therefore,

$$\frac{dT}{dz}\left[1 + \frac{L_v}{c_p}\left(\frac{dw_s}{dT}\right)_p\right] = -\frac{g}{c_p}\left[1 + \frac{L_v}{g}\left(\frac{dw_s}{dp}\right)_T \frac{dp}{dz}\right] \tag{3.117}$$

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[44] Eqs. (3.107)–(3.110) appear in Exercise solutions provided on the book web site.

Alternatively, using the hydrostatic equation on the last term on the right side of (3.117)

$$\Gamma_s \equiv -\frac{dT}{dz} = \frac{\dfrac{g}{c_p}\left[1 - \rho L_v\left(\dfrac{dw_s}{dp}\right)_T\right]}{1 + \dfrac{L}{c_p}\left(\dfrac{dw_s}{dT}\right)_p}$$

or

$$\Gamma_s \equiv -\frac{dT}{dz} = \Gamma_d\frac{\left[1 - \rho L_v\left(\dfrac{dw_s}{dp}\right)_T\right]}{\left[1 + \dfrac{L_v}{c_p}\left(\dfrac{dw_s}{dT}\right)_p\right]} \tag{3.118}$$

In Exercise (3.51) we show that

$$-\rho L_v\left(\frac{dw_s}{dp}\right)_T \simeq 0.12$$

If we neglect this small term in (3.118) we obtain

$$\Gamma_s \equiv -\frac{dT}{dz} \simeq \frac{\Gamma_d}{1 + \dfrac{L_v}{c_p}\left(\dfrac{dw_s}{dT}\right)_p}$$

■

3.51 In deriving the expression for the saturated adiabatic lapse rate in the previous exercise, it is assumed that $\rho L_v\,(dw_s/dp)_T$ is small compared to 1. Estimate the magnitude of $\rho L_v\,(dw_s/dp)_T$. Show that this last expression is dimensionless. [**Hint**: Use the skew $T - \ln p$ chart given in the book web site enclosed with this book to estimate the magnitude of $(dw_s/dp)_T$ for a pressure change of, say, 1000 to 950 hPa at 0 °C.]

Solution: Estimation of magnitude of

$$\rho L_v\left(\frac{dw_s}{dp}\right)_T$$

Take $\rho \simeq 1.275$ kg m^{-3} and $L_v = 2.5 \times 10^6$ J kg^{-1}. Suppose pressure changes from 1000 to 950 hPa so that $dp = -50$ hPa $= -5000$ Pa. Then, from the skew $T - \ln p$ chart, we find that

$$\begin{aligned} dw_s &\simeq (4 - 3.75) = 0.25 \text{ g/kg} \\ &\simeq 0.25 \times 10^{-3} \text{ kg/kg} \end{aligned}$$

Hence,

$$\rho L_v\left(\frac{dw_s}{dp}\right)_T \simeq (1.275 \text{ kg m}^{-3})(2.5 \times 10^6 \text{ J kg}^{-1})\left(\frac{0.25 \times 10^{-3} \text{ kg kg}^{-1}}{-5000 \text{ Pa}}\right) \simeq -0.12$$

The units of $\rho L_v\left(\dfrac{dw_s}{dp}\right)_T$ are

$$(\text{kg m}^{-3})\ (\text{J kg}^{-1})(\text{kg kg}^{-1})\left(\frac{1}{\text{Pa}}\right)$$

which is dimensionless. ■

3.52 In deriving Eq. (3.71) for equivalent potential temperature it was assumed that

$$\frac{L_v}{c_p T}\,dw_s \simeq d\left(\frac{L_v w_s}{c_p T}\right) \tag{3.119}$$

Justify this assumption. [**Hint**: Differentiate the right-hand side of the aforementioned expression and, assuming L_v/c_p is independent of temperature, show that the aforementioned approximation holds provided

$$\frac{dT}{T} \ll \frac{dw_s}{w_s}$$

Verify this inequality by noting the relative changes in T and w_s for small incremental displacements along saturated adiabats on a skew $T - \ln p$ chart.]

Solution: Differentiating the right side of (3.119) and assuming L_v/c_p is a constant,

$$\begin{aligned} \frac{L_v}{c_p}\left[\frac{1}{T}\,dw_s - w_s\frac{dT}{T^2}\right] &= \frac{L_v}{Tc_p}\left[dw_s - w_s\frac{dT}{T}\right] \\ &= \frac{L_v\,dT}{Tc_p}\left[\frac{dw_s}{dT} - \frac{w_s}{T}\right] \end{aligned} \tag{3.120}$$

If $\dfrac{dT}{T} \ll \dfrac{dw_s}{w_s}$ (which can be verified from skew $T - \ln p$ chart) then

$$\frac{dw_s}{dT} \gg \frac{w_s}{T} \tag{3.121}$$

Therefore, from (3.120) and (3.121):

Right side of (3.119) $= \dfrac{L_v}{Tc_p} dw_s =$ Left side of (3.119) ■

3.53 Plot the following sounding on a skew $T - \ln p$ chart:

	Pressure level (hPa)	Air temperature (°C)	Dew point (°C)
A	1000	30.0	21.5
B	970	25.0	21.0
C	900	18.5	18.5
D	850	16.5	16.5
E	800	20.0	5.0
F	700	11.0	−4.0
G	500	−13.0	−20.0

(a) Are layers AB, BC, CD, etc. in stable, unstable, or neutral equilibrium?

(b) Which layers are convectively unstable?[45]

3.54 *Potential density D* is defined as the density that dry air would attain if it were transformed reversibly and adiabatically from its existing conditions to a standard pressure p_0 (usually 1000 hPa).

(a) If the density and pressure of a parcel of the air are ρ and p, respectively, show that

$$D = \rho \left(\frac{p_0}{p}\right)^{c_v/c_p}$$

where c_p and c_v are the specific heats of air at constant pressure and constant volume, respectively.

(b) Calculate the potential density of a quantity of air at a pressure of 600 hPa and a temperature of −15 °C.

(c) Show that

$$\frac{1}{D}\frac{dD}{dz} = -\frac{1}{T}(\Gamma_d - \Gamma)$$

where Γ_d is the dry adiabatic lapse rate, Γ the actual lapse rate of the atmosphere, and T the temperature at height z. [**Hint**: Take the natural logarithms of both sides of the expression given in (a) and then differentiate with respect to height z.]

(d) Show that the criteria for stable, neutral, and unstable conditions in the atmosphere are that the potential density decreases with increasing height, is constant with height, and increases with increasing height, respectively. [**Hint**: Use the expression given in (c).]

(e) Compare the criteria given in (d) with those for stable, neutral, and unstable conditions for a liquid.

3.55 A necessary condition for the formation of a mirage is that the density of the air increases with increasing height. Show that this condition is realized if the decrease of atmospheric temperature with height exceeds 3.5 Γ_d, where Γ_d is the dry adiabatic lapse rate. [**Hint**: Take the natural logarithm of both sides of the expression for D given in Exercise 3.54a and then differentiate with respect to height z. Follow the same two steps for the gas equation in the form $p = \rho R_d T$. Combine the two expressions so derived with the hydrostatic equation to show that $\frac{1}{\rho}\frac{d\rho}{dt} = -\frac{1}{T}(dT/dz + g/R_d)$. Hence, proceed to the solution.]

3.56 Assuming the truth of the second law of thermodynamics, prove the following two statements (known as *Carnot's theorems*):

(a) No engine can be more efficient than a reversible engine working between the same limits of temperature. [**Hint**: The efficiency of any engine is given by Eq. (3.78); the distinction between a reversible (**R**) and an irreversible (**I**) engine is that **R** can be driven backward but **I** cannot. Consider a reversible and an irreversible engine working between the same limits of

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[45] For a more realistic treatment of the stability of a layer, see Chapter 9.3.5.

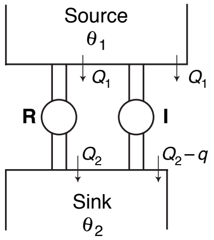

Fig. 3.26

temperature. Suppose initially that **I** is more efficient than **R** and use **I** to drive **R** backward. Show that this leads to a violation of the second law of thermodynamics, and hence prove that **I** cannot be more efficient than **R**.]

(b) All reversible engines working between the same limits of temperature have the same efficiency. [**Hint**: Proof is similar to that for part (a).]

Solution:

(a) To prove that no engine can be more efficient than a reversible engine working between the same limits of temperature, consider a reversible (**R**) and irreversible (**I**) engine working between θ_1 and θ_2. Assume **I** is more efficient than **R** and that **R** takes heat Q_1 from source and yields heat Q_2 to sink (Fig. 3.26). Therefore, if **I** takes Q_1 from source it must yield heat $Q_2 - q$ (q positive) to sink. Now let us use **I** to drive **R** backward. This will require **I** to do work $Q_1 - Q_2$ on **R**. However, in one cycle, **I** develops work $Q_1 - (Q_2 - q) = (Q_1 - Q_2) + q$. Hence, even when **I** is drawing **R** backward, mechanical work q is still available. However, in one cycle of the combined system, heat $Q_2 - (Q_2 - q) = q$ is taken from a colder body. Because this violates the second law of thermodynamics, **I** cannot be more efficient than **R**.

(b) Take two reversible engines operating between θ_1 and θ_2 and assume one engine is more efficient than the other. Then, following same procedure as in (a), it can be shown that if one reversible engine is more efficient than another the second law is violated. ■

3.57 Lord Kelvin introduced the concept of *available energy*, which he defined as the maximum amount of heat that can be converted into work by using the coldest available body in a system as the sink for an ideal heat engine. By considering an ideal heat engine that uses the coldest available body as a sink, show that the available energy of the universe is tending to zero and that

loss of available energy = T_0 (increase in entropy)

where T_0 is the temperature of the coldest available body.

Solution: For an ideal reversible engine

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$\text{Work done in 1 cycle} = Q_1 - Q_2 = \frac{T_1 - T_2}{T_1} Q_1.$$

If an engine operates with sink at T_0 ($= T_2$):

$$\text{Available energy} = \frac{T_1 - T_0}{T_1} Q_1$$

Let Q pass from T_1 to T_2 ($T_1 > T_2$) by, say, conduction or radiation. Then,

Loss of available energy

$$= \left(\frac{T_1 - T_0}{T_1}\right) Q - \left(\frac{T_2 - T_0}{T_2}\right) Q$$

$$= Q T_0 \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Because $T_1 > T_2$, there is a loss of available energy for natural processes

Loss of available energy

$$= T_0 \left(\frac{Q}{T_2} - \frac{Q}{T_1}\right)$$

$$= T_0 \text{ (increase in entropy)}$$ ■

3.58 An ideal reversible engine has a source and sink at temperatures of 100 and 0 °C, respectively. If the engine receives 20 J of heat from the source in every cycle, calculate the work done by the engine in 10 cycles. How much heat does the engine reject to the sink in 10 cycles?

3.59 A refrigerator has an internal temperature of 0 °C and is situated in a room with a steady temperature of 17 °C. If the refrigerator is driven by an electric motor 1 kW in power, calculate the time required to freeze 20 kg of water already cooled to 0 °C when the water is placed in the refrigerator. The refrigerator may be considered to act as an ideal heat engine in reverse.

3.60 A Carnot engine operating in reverse (i.e., as an air conditioner) is used to cool a house. The indoor temperature of the house is maintained at T_i and the outdoor temperature is T_o ($T_o > T_i$). Because the walls of the house are not perfectly insulating, heat is transferred into the house at a constant rate given by

$$\left(\frac{dq}{dt}\right)_{\text{leakage}} = K(T_o - T_i)$$

where K (>0) is a constant.

(a) Derive an expression for the power (i.e., energy used per second) required to drive the Carnot engine in reverse in terms of T_o, T_i, and K.

(b) During the afternoon, the outdoor temperature increases from 27 to 30 °C. What percentage increase in power is required to drive the Carnot engine in reverse to maintain the interior temperature of the house at 21 °C?

3.61 Calculate the change in entropy of 2 g of ice initially at −10 °C that is converted to steam at 100 °C due to heating.

3.62 Calculate the change in entropy when 1 mol of an ideal diatomic gas initially at 13 °C and 1 atm changes to a temperature of 100 °C and a pressure of 2 atm.

3.63 Show that the expression numbered (3.118) in the solution to Exercise 3.50 can be written as

$$\Gamma_s = \Gamma_d \frac{(1 + w_s L_v / R_d T)}{(1 + w_s L_v^2 / c_p R_v T^2)}$$

3.64 The pressure at the top of Mt. Rainier is about 600 hPa. Estimate the temperature at which water will boil at this pressure. Take the specific volumes of water vapor and liquid water to be 1.66 and 1.00×10^{-3} m^3 kg^{-1}, respectively.

3.65 Calculate the change in the melting point of ice if the pressure is increased from 1 to 2 atm. (The specific volumes of ice and water at 0 °C are 1.0908×10^{-3} and 1.0010×10^{-3} m^3 kg^{-1}, respectively.) [**Hint**: Use (3.112).]

3.66 By differentiating the enthalpy function, defined by Eq. (3.47), show that

$$\left(\frac{dp}{dT}\right)_s = \left(\frac{ds}{d\alpha}\right)_p$$

where s is entropy. Show that this relation is equivalent to the Clausius–Clapeyron equation.

Solution: From Eq. (3.47) in the text,

$$h = u + p\alpha$$

Therefore,

$$dh = du + pd\alpha + \alpha dp$$

or, using Eq. (3.38) in the text,

$$dh = (dq - pd\alpha) + pd\alpha + \alpha dp$$

$$= dq + \alpha dp$$

Using Eq. (3.85) in the text,

$$dh = Tds + \alpha dp \qquad (3.151)$$

We see from (3.151) that h is a function of two variables, namely s and p. Hence, we can write

$$dh = \left(\frac{dh}{ds}\right)_p ds + \left(\frac{dh}{dp}\right)_s dp = \alpha \qquad (3.152)$$

From (3.151) and (3.152),

$$\left(\frac{dh}{ds}\right)_p = T \text{ and } \left(\frac{dh}{dp}\right)_s = \alpha \qquad (3.153)$$

Because the order of differentiating does not matter,

$$\frac{\partial}{\partial p}\left(\frac{dh}{ds}\right)_p = \frac{\partial}{\partial s}\left(\frac{dh}{dp}\right)_s \qquad (3.154)$$

From (3.153) and (3.154),

$$\left(\frac{dT}{dp}\right)_s = \left(\frac{d\alpha}{ds}\right)_p$$

or

$$\left(\frac{dp}{dT}\right)_s = \left(\frac{ds}{d\alpha}\right)_p \qquad (3.155)$$

Because, from Eq. (3.85) in the text,

$$ds = \frac{dq}{T}$$

for a phase change from liquid to vapor at temperature T

$$ds = \frac{L_v}{T} \qquad (3.156)$$

where L_v is the latent heat of evaporation. If the vapor is saturated so that $p = e_s$ and $d\alpha = \alpha_2 - \alpha_1$, where α_2 and α_1 are the specific volume of the vapor and liquid, respectively, we have from (3.155) and (3.156),

$$\left(\frac{de_s}{dT}\right)_s = \frac{L_v}{T(\alpha_2 - \alpha_1)}$$

which is the Clausius–Clapeyron equation [see Eq. (3.92) in the text]. Equation (3.155) is one of **Maxwell's four thermodynamic equations**. The others are

$$\left(\frac{ds}{d\alpha}\right)_T = \left(\frac{dp}{dT}\right)_\alpha \qquad (3.157)$$

$$\left(\frac{d\alpha}{dT}\right)_p = -\left(\frac{ds}{dp}\right)_T \qquad (3.158)$$

and

$$\left(\frac{dT}{d\alpha}\right)_s = -\left(\frac{dp}{ds}\right)_\alpha \qquad (3.159)$$

Equations (3.157)–(3.159) can be proven in analogous ways to the proof of (3.155) given earlier but, in place of (3.151), starting instead with the state functions $f = u - Ts$, $g = u - Ts + p\alpha$, and $du = Tds - pd\alpha$, respectively. The state functions f and g are called *Helmholtz free energy* and *Gibbs function*, respectively. ■