

Atmospheric Thermodynamics

3

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

$$pV = mRT \quad (3.1)$$

where p , V , m , and T are the pressure (Pa), volume (m^3), mass (kg), and absolute temperature (in kelvin, K, where $\text{K} = ^\circ\text{C} + 273.15$) 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

$$p = \rho RT \quad (3.2)$$

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

$$p\alpha = RT \quad (3.3)$$

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*

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!”

64 Atmospheric Thermodynamics

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.

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 Bernoulli⁵ 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 Bernoulli** (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

$$n = \frac{m}{M} \quad (3.4)$$

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 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 $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$. The ideal gas equation for 1 mol of any gas can be written as

$$pV = R^*T \quad (3.5)$$

and for n moles of any gas as

$$pV = nR^*T \quad (3.6)$$

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

$$k = \frac{R^*}{N_A} \quad (3.7)$$

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

$$p = n_0kT \quad (3.8)$$

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

$$p_d \alpha_d = R_d T \quad (3.9)$$

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,

$$M_d = \frac{\sum_i m_i}{\sum_i \frac{m_i}{M_i}} \quad (3.10)$$

where m_i and M_i represent the mass (in grams) and molecular weight, respectively, of the i th 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

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

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.

66 Atmospheric Thermodynamics

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

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

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

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

From (3.11) and (3.13),

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

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 $4.770 \times 10^{-3} \text{ kg m}^{-3}$, 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 ($287.0 \text{ J K}^{-1} \text{ kg}^{-1}$), 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 ($4.770 \times 10^{-3} \text{ kg m}^{-3}$ at 273 K), R_v is the gas constant for 1 kg of water vapor ($461.5 \text{ J K}^{-1} \text{ kg}^{-1}$), and T is 273.2 K . Therefore,

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

Hence, the total pressure exerted by the mixture of dry air and water vapor is $(999.7 + 6.014) \text{ hPa}$ 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

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

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

$$p = \rho R_d T_v \quad (3.15)$$

where

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

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

¹² The fact that moist air is less dense than dry air was first clearly stated by Sir Isaac Newton¹³ 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."