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1

Basic Concepts and Terminology

1.1. What Is Thermodynamics?

Thermodynamics is the study of energy and its transformations. Several books on this subject begin with that line, or something very much like it, and I can't think of a better way to start this one. In my experiences as a student, teacher, and user of thermodynamics, I've read several of these books, each one directed to a slightly different audience. The purpose of *this* book is to provide undergraduate meteorology students with a solid theoretical (physical and mathematical) basis for understanding "energy and its transformations" in the Earth's atmosphere, and an appreciation for both the *limitations* and the *practical usefulness* of the thermodynamic models we use to describe the atmosphere. If, at the end of this book, you know where these ideas came from, what their weaknesses are, and how to apply them to your job as a working meteorologist, then you have learned what I hoped you would learn.

It's worth saying a little more about the word *model*. Meteorologists are physical scientists, and as such we like to use equations (models) to describe what's happening in the Earth system. This is pragmatic, because it makes it possible to do quantitative research and make weather forecasts. But some scientists forget about the differences between their models and the real objects they're studying, and this is a mistake. A model (i.e., the physics we use) gives us a glimpse at an underlying reality, but the real atmosphere is much more complex. For example, there are no real "isolated parcels," that is, there are no little packets of air that do not exchange mass or heat with their surrounding environment. This idea is just an approximation that makes it possible for us to solve the equations and make weather forecasts. Over some short period of time, it isn't a *bad* approximation, but it's still only a simplified picture of the real atmosphere. Remember that when you're using these equations.

Thermodynamics evolved into a well-integrated science from several separate threads over the last three centuries. Scholars from many different parts of the world, and highly varied scientific disciplines, have contributed to its evolution. In addition

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to this text, I'd like to recommend that you read von Baeyer's fun and interesting *Warmth Disperses and Time Passes*,[1] which describes this history very well. One of the points that von Baeyer mentions early in his book is the mistaken belief, once widely held, that heat is some kind of fluid that "flows" through matter. This fluid – called *caloric* – was thought to come from the spaces between the atoms of a substance, and could be "squeezed out" under the right circumstances. We now know this is wrong, but you'll find that many of the ideas we use to describe heat are the same ideas we use to describe fluid flow. We still use the idea of heat as a fluid, although we know it's only an analogy, because it works very well under *some* circumstances.

1.2. Systems

The fundamental model underlying practical atmospheric thermodynamics breaks the atmosphere up into components. The first component, called a *system*, is an object, such as a quantity of matter consisting of many particles, which take up a volume of space (see Figure 1.1). It is separated from its *surroundings* by a *boundary*, which is an imaginary barrier that may or may not allow mixing between the system and the surroundings. In meteorology, we use the word *parcel* as a substitute for "system," and *environment* or *ambient* (or *background*) *air* as a substitute for "surroundings." This model assumes that changes can occur to a system completely independent of its surroundings, or as a result of some forcing *by* the surroundings, but that these internal changes have no important effect *on* the surroundings.

The parcel may be *open*, *closed*, or *isolated*.

- In an open parcel, the boundary permits the exchange of both energy and matter between the parcel and its environment.[2]
- In a closed parcel, the boundary permits the exchange of energy but prevents the exchange of matter.
- In an isolated parcel, the boundary prevents the exchange of both matter and energy with the environment.

Open parcels (exchanging both matter and energy with the environment) can often be treated as closed parcels (exchanging energy only) by considering the surface-to-volume ratios of small and large spheres. Recall that the surface area (A) of a sphere is given by:

$$A = 4\pi r^2 \tag{1.1}$$

where r is the radius of the sphere. The volume (V) of a sphere is given by:

$$V = \frac{4}{3}\pi r^3 \tag{1.2}$$

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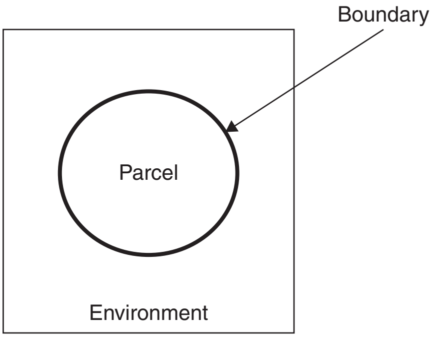

Figure 1.1. Parcel, environment, and boundary.

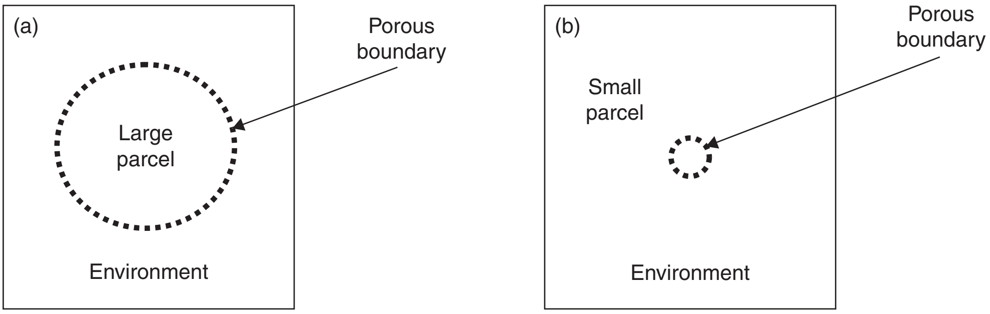

Figure 1.2. (a) Large and (b) small parcels with porous boundaries. Changes to the internal volume of the large parcel occur slowly, because of the relatively small surface area enclosing it. Changes to the internal volume of the small parcel are assumed to have already occurred.

The surface-to-volume ratio is therefore:

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \tag{1.3}$$

which gets smaller as the radius of the sphere increases. As the volume increases (scaled to r^3), the surface area (scaled to r^2) enclosing it doesn't increase as quickly. Because exchanges between a parcel and its environment occur through the boundary, (1.3) implies that there is a diminishing effect on the internal volume of a parcel as its radius increases.

We can treat open parcels as closed parcels by making the following simplifying assumptions (see Figure 1.2):

- For *small* parcels, the surface-to-volume ratio is *large*, and we can assume that any changes to the internal volume of the parcel that are going to occur *have already done so*.

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- For *large* parcels, the surface-to-volume ratio is *small*, and we can assume that the rate of change in the internal volume of the parcel is so small that it can be ignored for short periods of time.

Two questions ought to immediately pop into your mind. The first is "what about middle-sized parcels?" The answer to this one is not very satisfying, but we'll use it anyway: there are no "middle-size" parcels in our model atmosphere. The second question is "who cares?" *Why is this important?* To answer that question, we have to talk about energy and equilibrium.

1.3. Energy and Equilibrium

Energy is an abstract idea for something that appears in nature in many different forms. In practical terms, it is often described as the ability to do *work*, and so energy and work share the same physical units (*Joules*, in the *Système International d'Unités* or SI system). Energy can be divided into categories such as *external* and *internal*. In thermodynamic terms, "external energy" is the energy some object has in relation to its surroundings, such as the energy of position (known as *potential energy*), or the energy of motion (*kinetic energy*). "Internal energy" is determined using information about the internal *state* of the system. The "state" is the collection of physical properties describing the system, such as its temperature.

The internal state of a system may undergo changes, such as phase changes between solids, liquids, or gases, but, if left undisturbed, eventually all of these changes will cease, and the system reaches *internal equilibrium*. A system in internal equilibrium has a fixed set of properties that can be measured with a high degree of precision. Any small perturbations to a system in internal equilibrium won't result in any large changes to its state; once the perturbation ends, the system will return to equilibrium. An open or closed system can also be in *external equilibrium*, which means that any exchanges between the system and the environment are exactly balanced by exchanges in the opposite direction.

One example of external equilibrium is the classic bowling ball at the bottom of a valley (Figure 1.3). A small nudge to the bowling ball to either the left or right may get it moving back and forth a little, but eventually it will settle back at the lowest point in the valley. This is equivalent to stating that the bowling ball is in a minimum potential energy state. As long as the kinetic energy of the nudge is less than the energy necessary to push the bowling ball all the way up the hill, it will never escape,[3] and over time, will return to its equilibrium position at the bottom of the valley. Another example of external equilibrium involves temperature: When you bring two objects together that begin at different temperatures, over time the temperature difference between them will disappear, and reach an equilibrium point that's somewhere between the two starting temperatures. We'll return to this example again in Chapter 3.

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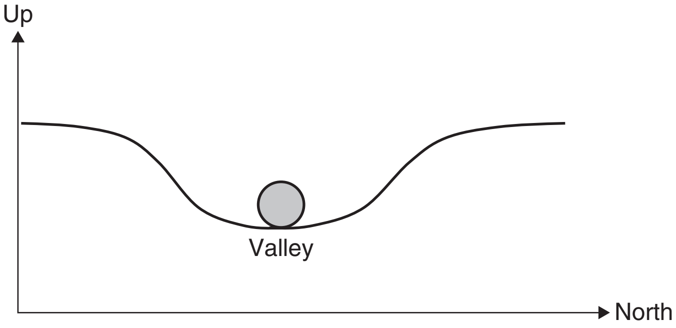

Figure 1.3. A state of external equilibrium: Bowling ball at the bottom of a valley. In classical physics, the only way to get the bowling ball out of this potential energy well is to impart enough kinetic energy to push it up the hill on either side.

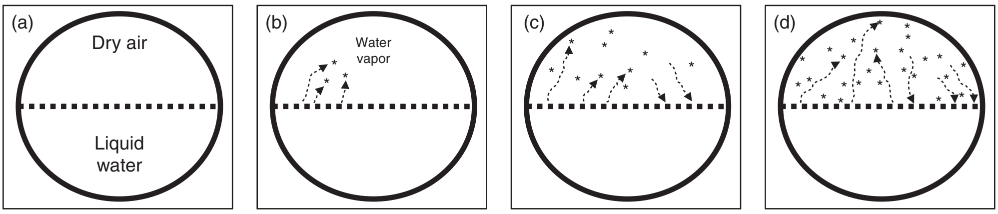

Figure 1.4. Saturation – a compound system in equilibrium. Initially (a) the system consists of dry air above and liquid water below. In (b) evaporation begins, adding water vapor to the air. The vapor molecules float around in the air above the liquid water. In (c), condensation begins, and some of the vapor molecules stick back onto the surface of the liquid water. At first the evaporation rate is much greater than the condensation rate, but as the amount of water vapor in the air increases, the condensation rate increases too. Eventually (d) the evaporation and condensation rates are the same – that is, reach an equilibrium state – and the air is saturated.

An example of internal equilibrium is a compound system consisting of a subsystem of water vapor plus dry air, and another subsystem of liquid water (Figure 1.4). The two subsystems are open to each other (but isolated from the external environment), meaning that both mass and energy can move back and forth between them (but nothing can leave or enter from outside). Water vapor molecules will escape from the surface of the liquid water (evaporate), causing it to lose mass. At the same time, vapor molecules will also stick back to the surface of the liquid water (condense), causing the liquid to gain mass. If the two phase changes are occurring at the same rate, the system is in equilibrium. Evaporation and condensation are still occurring, but the two exactly cancel each other. Once equilibrium is reached, there will be no noticeable change in the masses of the liquid water or the water vapor over time. This kind of equilibrium is called *saturation*.

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1.4. Extensive and Intensive Properties; State Variables

Extensive properties are dependent on the mass of the parcel. One example of an extensive property is the *total heat capacity* (C), which can be used to describe the transfer of heat when two objects with different temperatures are brought into direct contact. In Table 1.4, volume (V) is an extensive property. *Intensive properties* are independent of mass, that is, the mass of the parcel is divided out of the property. These are also referred to *specific properties*. In Table 1.4, specific volume (α) is an intensive property, and has units of m^3/kg. As we begin to discuss work and heat and the *Ideal Gas Law*, specific volume will be used quite a bit.

A parcel is called *homogeneous* if its intensive properties are the same at every point. If a parcel is composed of an *ideal gas*,[4] and is homogeneous and in equilibrium, the Ideal Gas Law can be used to describe the relationship between its state variables. For this reason, the Ideal Gas Law belongs to a class of mathematical models known as *equations of state*. There are additional equations of state that can be invoked if a gas is not "ideal."

For a parcel composed of an ideal gas, the Ideal Gas Law describes the relationship between its *state variables* – that is, its pressure (p), volume (V), mass (m), and temperature (T). If mass is held constant, or the behavior of the parcel is described in terms of intensive (specific) properties, mass can be eliminated, leaving a total of only three state variables in the relationship. Knowledge of any two state variables provides information about the third, through an equation of state. There are additional state variables, such as chemical composition, internal energy (u), and enthalpy (h). The latter two will be discussed later.

Now, to answer the question posed in the preceding text: we want a "large" or "small" parcel (but not a "medium-size" parcel), so that we can, in turn, assume it reaches equilibrium, making an equation of state (such as the Ideal Gas Law) a valid way to describe the relationship between its state variables. Without this, we can't write an equation relating pressure, volume, and temperature to each other, which, you'll see in later chapters, would leave us unable to model most of the atmosphere.

1.5. Fundamental Quantities and Units

In classical physics (i.e., the physics before relativity and quantum mechanics intruded in the twentieth century), there were seven *fundamental* quantities. By fundamental, we mean quantities that are not dependent on one another and cannot be reduced to functions of other quantities. These are:

- Length,
- Mass,
- Time,
- Temperature,

Table 1.1. *Fundamental quantities and SI units.*

Quantity	Quantity abbreviation	SI Unit	Unit abbreviation
Length	l	Meter	m
Time	t	Second	s
Mass	m	Kilogram	kg
Temperature	T	Kelvin	K
Electric charge	q	Coulomb	C
Luminous intensity	I	Candela	cd
Amount of substance	n	Mole	mol

- Electric charge,
- Luminous intensity, and
- Amount of substance.

Each of these is associated with a distinct class of unit that is totally unlike those associated with the other fundamental quantities. Over time, several different systems of units accumulated, resulting in more than one way, for example, to express *length*. One example is the *English* system; another is the *British Imperial* system. This necessitated the creation of conversion factors to convert a length expressed in one system to the same length expressed in another.

In Earth sciences there are currently two dominant systems, both of which are based on the metric system: CGS and MKS. CGS stands for centimeter-gram-second, and is still the system preferred by some scientists. MKS stands for meter-kilogram-second, and is the system used by most physical scientists. In 1960, the MKS system was expanded into the *Système International d'Unités* (SI). The SI units for the quantities listed in the preceding text are shown in Table 1.1.

In this text, we'll stick with SI-MKS as much as possible. This simplifies the calculations and, through careful unit analysis, also provides a convenient method to check the results of the calculations.

The quantity of length is a *scalar* quantity, meaning that it has a magnitude, but no direction. The equivalent *vector* quantity, *position*, has both a magnitude and a direction. In this text, scalars will be shown in plain text (e.g., L), and vectors will be shown with an arrow (e.g., $\vec{L}$). Units will usually be specified using square brackets (e.g., [m]).

The SI temperature scale is known as the *absolute* scale, which has units of *Kelvins* (not "*degrees Kelvin*"). *Absolute zero* is defined as the temperature at which all random molecular motion stops, and is therefore the coldest temperature possible, but it doesn't actually occur anywhere in nature. There is no parallel maximum possible temperature in classical physics.

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Table 1.2. *Temperature scale conversions.*

To compute	From	Use
Absolute	Celsius	$T_K = T_C + 273.16$
Absolute	Fahrenheit	$T_K = \frac{5}{9}T_F - 255.38$
Celsius	Absolute	$T_C = T_K - 273.16$
Celsius	Fahrenheit	$T_C = \frac{5}{9}(T_F - 32)$
Fahrenheit	Absolute	$T_F = \frac{9}{5}T_K - 459.67$
Fahrenheit	Celsius	$T_F = \frac{9}{5}T_C + 32$

Two additional temperature scales, probably more familiar to the reader, are the *Celsius*[5] (or "*centigrade*") scale, and the older *Fahrenheit* scale.[6] The former is still widely used in science, but must be converted to the absolute scale before performing any physical calculations. There are one or two uses of Celsius temperatures in this text. Until the 1960s, the Fahrenheit scale was the primary temperature scale used in English-speaking countries, but by the 2010s, it had almost passed completed out of use. Only the United States, the U.S. Virgin Islands, Puerto Rico (a U.S. territory), and a few smaller countries still use this scale. The rest of the world now uses the Celsius scale for everyday purposes, such as weather forecasting. The units of both scales are called *degrees*, but one degree of temperature change on the Celsius scale is larger than a degree on the Fahrenheit scale. In fact, one Celsius degree is exactly 1.8 Fahrenheit degrees. One Celsius degree *does* represent, however, the same change in temperature as one Kelvin on the absolute scale. Conversions between the absolute, Celsius, and Fahrenheit scales are shown in Table 1.2. Some common temperature reference points are shown on all three scales in Table 1.3.

1.6. Derived Quantities and Units

All physical quantities not listed in Table 1.1 are derived by combining one or more fundamental quantities. One example of this is *pressure*, which is *force* per unit *area*. Force, in turn, is reducible to mass (a fundamental quantity) and *acceleration*; acceleration to the time rate of change of *velocity*; and velocity to the time-rate-of-change of *position* (length). Area is reducible to length. Table 1.4 summarizes the derived quantities used in this text, and their associated units.

Table 1.3. *Common temperature reference points.*

All values are rounded to the nearest whole unit.

Description	Celsius scale [°C]	Fahrenheit scale [°F]	Absolute scale [K]
Water boils at sea level	100	212	373
Highest temperature ever recorded at a surface station (Libya)[i]	58	136	331
	50	122	323
	40	104	313
	30	86	303
	20	68	293
	10	50	283
Water freezes/melts at sea level	0	32	273
	–10	14	263
	–20	–4	253
	–30	–22	243
Coldest temperature at which supercooled water droplets can exist	–40	–40	233
Lowest temperature ever recorded at a surface station (Antarctica)[ii]	–89	–129	184
Absolute zero	–273	–460	0

[i,ii] Wikipedia (2012).

The unit of force is obviously named for Isaac Newton, who defined it as the product of mass and acceleration. The unit of pressure is named for Blaise Pascal, a French mathematician and physicist, and the unit of energy, the *Joule* (J), is named after James Prescott Joule, an English brewer (and scientist) who took pride in his ability to make remarkably precise measurements of temperature with an ordinary thermometer. In addition to the definition of the J shown in Table 1.4, one J is also equal to the energy required to lift one pound of water[7] nine inches, increase its speed by seven ft/s (walking speed), or heat it up by 0.001 °F.[8]

There are several other pressure units used in meteorology. The *Pascal* (*Pa*) must be used when performing most physical calculations, but it is too small a unit for practical use in weather forecasting. For this reason the *hecto-Pascal* (100 Pa, or 1 *hPa*) is now in common use. In addition to this, there are several older units in the scientific literature, such as *inches of mercury* (*in.Hg*), which are still used in some applications, such as aviation. The older unit *millibar* (one 1000th of a bar) is

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Table 1.4. *Derived quantities and SI units.*

Quantity	Quantity abbreviation	Definition	SI Unit
Velocity, speed	$\vec{v}$, v	$\frac{d\vec{L}}{dt}$	$\frac{m}{s}$
Acceleration	$\vec{a}$	$\frac{d\vec{v}}{dt}$	$\frac{m}{s^2}$
Area	A	$L \times L$	m^2
Volume	V	$L \times L \times L$	m^3
Specific volume	α	$\frac{V}{m}$	$\frac{m^3}{kg}$
Density	ρ	$\frac{m}{V} = \frac{1}{\alpha}$	$\frac{kg}{m^3}$
Force	$\vec{F}$	$m\vec{a}$	$Newton(N) \equiv kg\frac{m}{s^2}$
Pressure	p	$\frac{F}{A}$	$Pascal(Pa) \equiv \frac{N}{m^2} = \frac{kg}{ms^2}$
Energy, work	E, W	mv^2	$Joule(J) \equiv kg\frac{m^2}{s^2}$
Power	P	$\frac{E}{t}$	$Watt(W) \equiv \frac{J}{s} = kg\frac{m^2}{s^3}$

equivalent to one hPa, so these two units are frequently used interchangeably. The hPa is preferred in recent literature. The equations in the following text summarize some factors for converting between the various pressure units.

$$1 \text{ bar} = 10^3 \text{ millibar (mb)} \tag{1.4a}$$

$$1 \text{ mb} = 10^2 \text{ Pa} \tag{1.4b}$$

$$1 \text{ hPa} = 10^2 \text{ Pa} \tag{1.4c}$$

$$1 \text{ atm} = 1.01325 \text{ bar} \tag{1.4d}$$

$$1 \text{ atm} = 1013.25 \text{ hPa} \tag{1.4e}$$

$$1 \text{ in.Hg} = 33.86 \text{ hPa} \tag{1.4f}$$