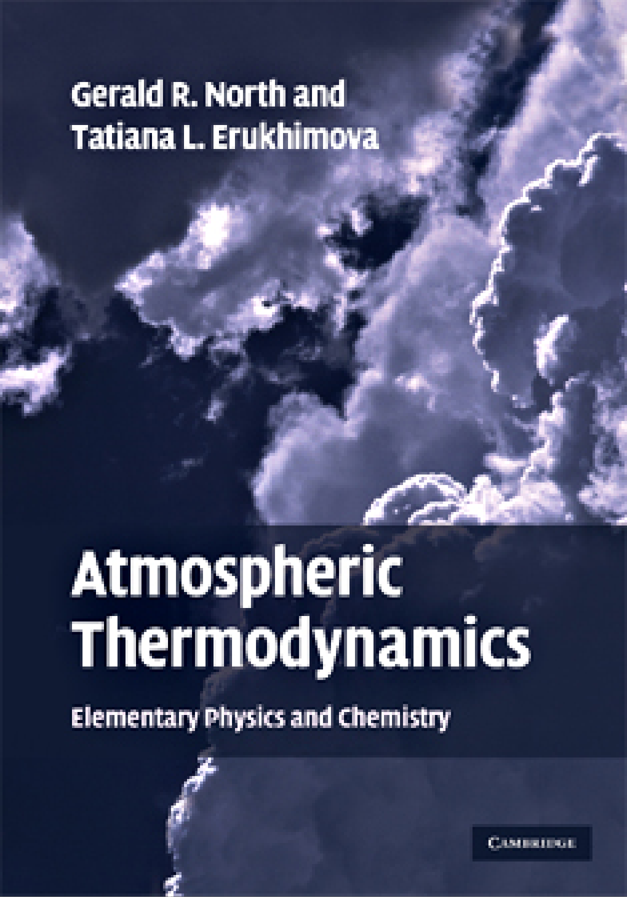

Gerald R. North and
Tatiana L. Erukhimova

# Atmospheric Thermodynamics

## Elementary Physics and Chemistry

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# ATMOSPHERIC THERMODYNAMICS

## Elementary Physics and Chemistry

This textbook presents a uniquely integrated approach in linking both physics and chemistry to the study of atmospheric thermodynamics.

The book begins by explaining the classical laws of thermodynamics, and discusses Gibbs energy and the elementary kinetic theory of gases with special applications to the atmosphere. Individual chapters focus on various fluid systems, including vapor pressure over flat and curved surfaces of pure liquids and solutions, and examine the vertical dependence of temperature and pressure for environmental sounding and moving air parcels. Recognizing the increasing importance of chemistry in the meteorological and climate sciences, a chapter is devoted to chemical thermodynamics and contains an overview of photochemistry.

Although students are expected to have some background knowledge of calculus, general chemistry and classical physics, the book provides set-aside refresher boxes as useful reminders. It contains over 100 diagrams and graphs to supplement the discussions. It also contains a similar number of worked examples and exercises, with solutions included at the end of the book. It is ideal for a single-semester advanced course on atmospheric thermodynamics, and will prepare students for higher-level synoptic and dynamics courses.

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# ATMOSPHERIC THERMODYNAMICS

## Elementary Physics and Chemistry

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We both wish to dedicate this book to our families, who have
kindly endured our long preoccupation with the project.

# Contents

# Preface

This book is intended as a text for undergraduates in the atmospheric sciences. The students are expected to have some calculus, general chemistry and classical physics background although we provide a number of refreshers for those who might have less experience or need reminders. Our students have also had a survey of the atmospheric sciences in a qualitative course at freshman level. The primary aim of the book is to prepare the student for the synoptic and dynamics courses that follow. We intend that the student gain some understanding of thermodynamics as it applies to the elementary systems of interest in the atmospheric sciences. A major goal is for the students to gain some facility in making straightforward calculations. We have taught the material in a semester course, but in a shorter course some material can be omitted without regrets later in the book. The book ends with two chapters that are independent of one another: Chapter 8 on thermochemistry and Chapter 9 on the thermodynamic equation.

This book is the result of teaching an introductory atmospheric thermodynamics course to sophomores and juniors at Texas A&M University. Several colleagues have taught the course using earlier versions of the notes and we gratefully acknowledge Professors R. L. Panetta, Ping Yang, and Don Collins as well as the students for their many helpful comments. In addition, we have received useful comments on the chemistry chapter from Professors Sarah Brooks, Gunnar Schade, and Renyi Zhang. We also thank Professor Kenneth Bowman for many fruitful discussions. We are grateful for financial support provided by the Harold J. Haynes Endowed Chair in Geosciences.

# 1

# Introductory concepts

The atmosphere is a compressible fluid, and the description of such a form of matter is usually unfamiliar to students who are just completing calculus and classical mechanics as part of a standard university physics course. To complicate matters the atmosphere is composed of not just a single ingredient, but several ingredients, including different (mostly nonreactive) gases and particles in suspension (aerosols). Some of the ingredients change phase (primarily water) and there is an accompanying exchange of energy with the environment. The atmosphere also interacts with its lower boundary which acts as a source (and sink) of friction, thermal energy, water vapor, and various chemical species. Electromagnetic radiation enters and leaves the atmosphere and in so doing it warms and cools layers of air, interacting selectively with different constituents in different wavelength bands.

Meteorology is concerned with describing the present state of the atmosphere (temperature, pressure, winds, humidity, precipitation, cloud cover, etc.) and in predicting the evolution of these primary variables over time intervals of a few days. The broader field of atmospheric science is concerned with additional themes such as climate (statistical summaries of weather), air chemistry (its present, future, and history), atmospheric electricity, atmospheric optics (across all wavelengths), aerosols and cloud physics. Both the present state of the bulk atmosphere and its evolution are determined by Newton's laws of mechanics as they apply to such a compressible fluid. *Dynamics* is concerned primarily with the motion of the atmosphere under the influence of various natural forces. But before one can undertake the study of atmospheric dynamics, one must be able to *describe* the atmosphere in terms of its primary variables. An essential tool needed in this description is thermodynamics, which helps relate the fundamental quantities of pressure, temperature and density as atmospheric parcels move from place to place. Such parcels contract and expand, their temperatures rise and fall; water changes phase, back and forth from vapor to liquid to ice; chemical constituents react, etc. The key to understanding these changes lies in applications of the laws of thermodynamics which relate these changes to fluxes of energy and other less familiar functions which will be introduced as needed.

## 1.1 Units

The units used in atmospheric science are the *Standard International* (SI) units. These are essentially the MKS units familiar from introductory physics and chemistry courses. The unit of length is the *meter*, abbreviated m; that for mass is the *kilogram*, abbreviated kg; and for time the unit is the *second*, abbreviated s. The units for velocity then are $\mathrm{m\,s^{-1}}$. The unit of force is the *newton* ($1\,\mathrm{kg\,m\,s^{-2}}$, abbreviated N). Tables 1.1–1.2 show the SI units for some basic physical quantities commonly used in atmospheric science.

The unit of pressure, the *pascal* ($1\ \mathrm{N\,m^{-2}} = 1\,\mathrm{Pa}$), is of special importance in meteorology. In particular, atmospheric scientists like the *millibar* (abbreviated mb), but in keeping with SI units more and more meteorologists use the *hectopascal* (abbreviated hPa, 100 Pa = 1 mb). The *kilopascal* (1 kPa = 10 hPa) is the formal SI unit and some authors prefer it. *One atmosphere* (abbreviated 1 atm) of pressure is

$$\begin{aligned} 1\,\mathrm{atm} &= 1.013\,\mathrm{bar} \\ &= 1013.25\,\mathrm{mb} \\ &= 1013.25\,\mathrm{hPa} \\ &= 101.325\,\mathrm{kPa} \\ &= 101325\,\mathrm{Pa} \\ &= 1.01325\times10^{5}\,\mathrm{Pa} \end{aligned} \tag{1.1}$$

and 1 mb = 1 hectopascal = 100 Pa. In some operational contexts and often in the popular media one still encounters pressure in inches of mercury (in Hg) or millimeters of mercury (mm Hg); 1 atm = 760.000 mm Hg = 29.9213 in Hg.

The *dimensions* of a quantity such as density, $\rho$, can be constructed from the fundamental dimensions of length, mass, time and temperature, denoted by $\mathbf{L}, \mathbf{M}, \mathbf{T}, \mathbf{Temp}$ respectively. The dimensions of density, indicated with square brackets $[\rho]$, are $\mathbf{M\,L}^{-3}$. In the SI system the *units* are $\mathrm{kg\,m^{-3}}$. Many quantities are pure numbers and have no dimension; examples include arguments of functions such as sine or log. The radian is a ratio of lengths and is considered here to be dimensionless.

Temperature in SI units is expressed in degrees Celsius, e.g. 20 °C; or Kelvin, e.g. 285 K. We say "285 kelvins" and omit writing the superscript "∘" when

Table 1.1 *Useful numerical values*

| | |
|---|---|
| **Universal** | |
| gravitational constant | $6.673\times10^{-11}$ N m$^2$ kg$^{-2}$ |
| universal gas constant ($R^*$) | 8.3145 J K$^{-1}$ mol$^{-1}$ |
| Avogadro's number ($N_A$) [gram mole] | $6.022\times10^{23}$ molecules mol$^{-1}$ |
| Boltzmann's constant ($k_B$) | $1.381\times10^{-23}$ J K$^{-1}$molecule$^{-1}$ |
| proton rest mass | $1.673\times10^{-27}$ kg |
| electron rest mass | $9.109\times10^{-31}$ kg |
| Planck's constant | $6.626\times10^{-34}$ J s |
| speed of light in vacuum | $3.00\times10^{8}$ m s$^{-1}$ |
| **Planet Earth** | |
| equatorial radius | 6378 km |
| polar radius | 6357 km |
| mass of Earth | $5.983\times10^{24}$ kg |
| rotation period (24 h) | $8.640\times10^{4}$ s |
| acceleration of gravity (at about 45°N) | 9.8067 m s$^{-2}$ |
| solar constant | 1370 W m$^{-2}$ |
| **Dry air** | |
| gas constant ($R_d$) | 287.0 J K$^{-1}$kg$^{-1}$ |
| molecular weight ($M_d$) | 28.97 g mol$^{-1}$ |
| speed of sound at 0 °C, 1000 hPa | 331.3 m s$^{-1}$ |
| density at 0 °C and 1000 hPa | 1.276 kg m$^{-3}$ |
| specific heat at constant pressure ($c_p$) | 1004 J K$^{-1}$ kg$^{-1}$ |
| specific heat at constant volume ($c_v$) | 717 J K$^{-1}$ kg$^{-1}$ |
| **Water substance** | |
| molecular weight ($M_w$) | 18.015 g mol$^{-1}$ |
| gas constant for water vapor ($R_w$) | 461.5 J K$^{-1}$kg$^{-1}$ |
| density of liquid water at 0 °C | $1.000\times10^{3}$ kg m$^{-3}$ |
| standard enthalpy of vaporization at 0 °C | $2.500\times10^{6}$ J kg$^{-1}$ |
| standard enthalpy of fusion at 0 °C | 332.7 kJ kg$^{-1}$ |
| specific heat of liquid water | 4179 kJ kg$^{-1}$ K$^{-1}$ |
| **STP** | $T = 273.16$ K, $p = 1013.25$ hPa |

using degrees kelvin. In operational meteorology we sometimes find temperature expressed in degrees Fahrenheit, e.g. 70 °F.

Each side of an equation must have the same dimensions. This principle can often be used to find errors in a problem solution. The argument of functions such as the exponential has to be dimensionless.

## 1.2 Earth, weight and mass

The Earth is an oblate spheroid, with slightly larger diameter in the equatorial plane than in a meridional (pole-to-pole) plane. The distance from the center to the poles

Table 1.2 *Selected physical quantities and their units*

| Quantity | Unit | Abbreviation |
|---|---|---|
| mass | kilogram | kg |
| length | meter | m |
| time | second | s |
| force | newton | N |
| pressure | pascal | $\mathrm{Pa} = \mathrm{N\,m^{-2}} = 0.01\,\mathrm{hPa}$ |
| energy | joule | J |
| temperature | degree Celsius | °C |
| temperature | degree Kelvin | K |
| speed | | $\mathrm{m\,s^{-1}}$ |
| density | | $\mathrm{kg\,m^{-3}}$ |
| specific heat | | $\mathrm{J\,kg^{-1}\,K^{-1}}$ |

Table 1.3 *Greek prefixes applied to SI units*

| Prefix | Numerical meaning | Example | Abbreviation |
|---|---|---|---|
| nano | $10^{-9}$ | nanometer | nm |
| micro | $10^{-6}$ | micrometer | μm |
| milli | $10^{-3}$ | millimeter | mm |
| centi | $10^{-2}$ | centimeter | cm |
| hecto | $10^{2}$ | hectopascal | hPa |
| kilo | $10^{3}$ | kilogram | kg |
| mega | $10^{6}$ | megawatt | MW |
| giga | $10^{9}$ | gigawatt | GW |
| tera | $10^{12}$ | terawatt | tW |

Table 1.4 *Selected conversions to SI units*

| Quantity | Conversion |
|---|---|
| energy | $4.186\,\mathrm{J} = 1\,\mathrm{cal}$ |
| | $1\,\mathrm{kWh} = 3.6\times10^{6}\,\mathrm{J}$ |
| pressure | $1\ \mathrm{atm} = 760\,\mathrm{mm\ Hg}$ |
| | $1\,\mathrm{atm} = 29.9213\,\mathrm{in\ Hg}$ |
| distance | $1\,\mathrm{m} = 3.281\,\mathrm{ft}$ |
| temperature | $T(\mathrm{K}) = T(^\circ\mathrm{C}) + 273.16$ |
| | $T(^\circ\mathrm{F}) = \frac{9}{5}T(^\circ\mathrm{C}) + 32$ |
| | $T(^\circ\mathrm{C}) = \frac{5}{9}(T(^\circ\mathrm{F}) - 32)$ |

Table 1.5 *Some relationships between SI units*

| Quantity | Equivalent |
|---|---|
| 1 N | $1\,\mathrm{kg\,m\,s^{-2}}$ |
| 1 J | $1\,\mathrm{kg\,m^2\,s^{-2}}$ |
| 1 Pa | $1\,\mathrm{N\,m^{-2}}$ |

is 6356.91 km and the radius in the equatorial plane is 6378.39 km. About two thirds of the Earth's atmosphere lies below 10 km above the surface, hence the atmosphere and the oceans (depth averaging 4–5 km) only form a very thin skin of about 1/60 the radius of the sphere.

The *weight* of a mass is the force applied to that mass by the force of gravity. It may be expressed as the mass in kilograms times the acceleration due to gravity, $g = 9.81\,\mathrm{m\,s^{-2}}$:

$$\boxed{\mathcal{W} = \mathcal{M}g} \quad \text{[weight and mass].} \tag{1.2}$$

Weight is expressed in *newtons*, abbreviated N; $\mathrm{N} = \mathrm{kg\,m\,s^{-2}}$. The acceleration due to gravity varies slightly with altitude above sea level

$$g_z = g_0(1 - 3.14 \times 10^{-7}z)\ z \text{ in meters.} \tag{1.3}$$

There is also a slight variation ($< 0.3\%$) with latitude due to the ellipsoidal shape of the Earth (due to both centrifugal force and the equatorial bulge). In most meteorological applications these variations are negligible. However, in calculations of satellite orbits such variations are extremely important.

*Example 1.1* The density of water in old fashioned units (cgs) is

$$\rho_{\text{water}} = \frac{1\ \text{gram}}{\text{cm}^3}.$$

To express this in SI units, we can multiply by

$$1 = \frac{1\ \text{kg}}{10^3\ \text{gram}} = \text{unity (no dimension).}$$

We obtain:

$$\rho_{\text{water}} = 1\frac{\text{kg}}{10^3\ \text{cm}^3} = 1\frac{\text{kg}}{\text{liter}}.$$

This gives us an intuitive measure of the kilogram. Now we can multiply by

$$1 = \left(\frac{10^2\,\text{cm}}{1\,\text{m}}\right)^3.$$

The final result is

$$\rho_{\text{water}} = 10^3\,\text{kg}\,\text{m}^{-3}. \qquad \square$$

*Physics refresher: vertical motion of a particle* The acceleration due to gravity is $g = 9.81\,\text{m}\,\text{s}^{-2}$. A particle falling from a height $z_0$ with no initial velocity, has a velocity $-gt$ after time $t$. After the same time interval it will have fallen $\frac{1}{2}gt^2$ meters. These are both obtained by simple integration:

$$v_z(t) = \int_0^t -g\,\mathrm{d}t = -g\int_0^t \mathrm{d}t = -gt, \quad \text{since } g = \text{constant} \tag{1.4}$$

and

$$z(t) - z(0) = \int_0^t v_z(t)\,\mathrm{d}t = \int_0^t -gt\,\mathrm{d}t = -\frac{1}{2}gt^2. \tag{1.5}$$

*More vertical motion mechanics* The minimum *work* necessary to lift a particle a vertical distance $z$ against the force of gravity is force × distance $= \mathcal{M}gz$ ($\mathcal{M}g$ is the weight or vertical force necessary to lift the mass without accelerating it). This work done in lifting the particle is equal to the change in its *potential energy* $\mathcal{M}gz$. If the particle is released, work will be done by the gravitational force applied to the particle. The *kinetic energy* of the particle during its fall is $\frac{1}{2}\mathcal{M}v^2$. The conservation of mechanical energy says the sum of these two forms of energy is conserved: $E = \text{PE} + \text{KE} = \text{constant}$, or more explicitly

$$\boxed{\frac{1}{2}\mathcal{M}v_0^2 + \mathcal{M}gz_0 = \frac{1}{2}\mathcal{M}v_t^2 + \mathcal{M}gz_t} \tag{1.6}$$

where the subscript 0 denotes the initial time and the subscript $t$ denotes evaluation at a later time.

The conservation law is derived by first writing Newton's Second Law:

$$\mathcal{M}\frac{\mathrm{d}v_z}{\mathrm{d}t} = F_z = -\mathcal{M}g. \tag{1.7}$$

Now multiply through by $v\,\mathrm{d}t$ and integrate with respect to $t$. The left-hand side becomes

$$\int_0^t v\mathcal{M}\frac{\mathrm{d}v}{\mathrm{d}t}\,\mathrm{d}t = \frac{1}{2}\mathcal{M}v_t^2 - \frac{1}{2}\mathcal{M}v_0^2. \tag{1.8}$$

On the other side of Newton's equation we have

$$\int_0^t -v\mathcal{M}g\,\mathrm{d}t = \int_{z_0}^{z_t} -\mathcal{M}g\,\mathrm{d}z = -\mathcal{M}g(z_t - z_0). \tag{1.9}$$

Equating these expressions gives our answer (1.6).

## 1.3 Systems and equilibrium

Thermodynamics is the study of *macroscopic* or *bulk* systems of masses and their interrelations under conditions of steady state (no dependence on time). By macroscopic we mean the system contains large numbers of individual molecules (within a few orders of magnitude of a *mole*[1] which contains $6.02\times10^{23}$ molecules). We call these states *equilibrium states* if they are not only time independent but also stable under small perturbations. Thermodynamic states are describable by a set of dimensional quantities which we refer to as *coordinates*. Thermodynamics is concerned with the changes in energy-related quantities (certain of the coordinates) when the system undergoes a transition from one state to another. A *thermodynamic system* is a region of space containing matter with certain *internally uniform properties* such as pressure and temperature. We will be concerned with the interior of the system and the variables (coordinates) that characterize it. For example, a mass of pure gas (only one chemical species) contained in a vessel may be characterized by the pressure it exerts on the walls of the vessel, the volume of the vessel and the temperature $(p, V, T)$. These comprise the complete set of *thermodynamic coordinates* for this particular system. For more general situations such as mixtures of species or phases, the coordinates necessary to describe the state have to be determined experimentally. It is important to note that an individual thermodynamic system is uniform in its interior. There are no gradients of pressure or temperature, for example, inside the system.[2]

---

[1] The mole is an SI unit defined as the number of carbon atoms in a mass of 0.012 kg of pure carbon. The number of moles of a substance is the number of multiples of this number (known as Avogadro's number: $N_\mathrm{A} = 6.02 \times 10^{23}$). In formulas the unit is designated as "mol."

[2] Note that a column of air in the atmosphere is not a simple thermodynamic system because its pressure and temperature vary with altitude. However, it is convenient to consider the column as composed of thin slabs, each of which contains substance with approximately uniform temperature, pressure and composition. Then each individual slab may be considered as a simple thermodynamic system for many purposes.

### 1.3.1 Examples of thermodynamic systems

*Gas in a vessel* Suppose a container holds a gas of uniform chemical composition. Let the walls of the container be thermally insulating and let the volume be fixed. In a very short time after fixing these conditions the gas will come to values of temperature and pressure that are uniform throughout and independent of the shape of the container. This is the simplest thermodynamic system in a state of equilibrium.

A second case is where the container's walls are held at a fixed temperature and the pressure is allowed to vary. Equilibrium will be established such that the temperature of the gas becomes equal to that of the surrounding walls, the volume is given and the pressure comes to some value that we can estimate.

A third case is where the container has a frictionless movable piston that is pushed upon externally by a fixed pressure (such as the atmospheric pressure). This means that the pressure in the vessel is held fixed along with that of the temperature. The piston will shift in such a way to make the pressure inside equal to that outside, and the volume will change until all these conditions are met.

Our gas might not be homogeneous, but instead it might be composed of a mixture of chemically noninteracting gases, such as those in our atmosphere: nitrogen, oxygen and argon. We still have a thermodynamic system as long as the composition does not vary from location to location or from time to time. In each of the above cases let two of the following be fixed: volume, temperature, or pressure. Then the remaining variable is allowed to find its equilibrium value. Note that once in equilibrium, the variables or coordinates are uniform throughout the vessel.

*Two-phase system* Suppose we have a liquid of uniform chemical composition such as water in our vessel and vacuum above the liquid surface. Let the temperature and volume be fixed. After a sufficient adjustment time some liquid will have evaporated into the volume above its surface and an equilibrium will be established (the flux of water molecules leaving the surface becomes equal to the flux entering and sticking to the surface). There will be a gas pressure exerted on the walls by the vapor that evaporated from the liquid surface. This is a two-phase system with liquid and gaseous phases, but only one *component* (water) which depicts the number of distinct chemical species. The pressure throughout will be uniform (ignore the pressure increase as a function of depth due to gravity in the liquid). The temperature will also be uniform throughout both phases of the system. This two-phase configuration is also a thermodynamic system. The system can be made to pass through changes in volume, temperature, etc., to establish new thermodynamic states of equilibrium. Note that the temperature and pressure are uniform throughout but the density varies from one phase to the other. As we shall see in a later chapter there is another quantity that is also uniform in the two-phase system called the specific Gibbs energy (chemical potential in the chemical literature when expressed as molar Gibbs energy). It acts as an intensive variable (see Section 1.5) in such multicomponent systems similarly to pressure or temperature.

*Aqueous solutions* Imagine a vessel filled with water (at a fixed temperature and pressure) and some salt is placed in the liquid. If we continue to put more salt into the water eventually some salt will remain in crystal form sinking to the bottom (but ignore gravity otherwise). We will have established an equilibrium between the *saturated* saline solution and the precipitated crystalline salt. A change in temperature will result in a new equilibrium state with a different concentration of salt in solution (concentration of a species in solution is another thermodynamic coordinate). This is an example of a thermodynamic system. Variations on this include allowing the water vapor above the liquid to be in equilibrium with the saline solution. The presence of salt in solution will alter the vapor pressure over the liquid surface (as well as the freezing temperature). As the temperature changes the vapor pressure will change, etc.

*Chemical equilibrium* Imagine a gaseous mixture in our vessel at fixed temperature and pressure composed of O and $O_2$. There will be a reaction

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M}, \tag{1.10}$$

where M is a background molecule used to carry away momentum (e.g., $O_2$, $N_2$ or Ar in the atmosphere).[3] Some ozone will decay and after a while there will be an equilibrium established and the reaction can be written:

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \leftrightharpoons \mathrm{O_3} + \mathrm{M}. \tag{1.11}$$

The amount of *reactants* (the left-hand side) may be more than the amount of *products* (right-hand side) for a given temperature. But as the temperature is changed the balance may shift. This is a thermodynamic system. The ratio of $O_2$ to $O_3$ is now a thermodynamic coordinate along with $T, p, V, \mathcal{M}_{\text{total}}$.

Of course, there are many other types of thermodynamic systems, and we will encounter several of them in due course.

Everything outside the system which may affect the system's behavior is called the *surroundings*. In atmospheric science, we can often approximate an infinitesimal volume of gas embedded in the natural atmosphere as having uniform interior properties. When appropriate, such an infinitesimal volume element can be considered as a thermodynamic system. In many cases the "infinitesimal volume element" might be as big as a classroom or sometimes as small as a cubic centimeter depending on the application.

A thermodynamic system composed of a very large mass is called a *reservoir* and is characterized by a temperature, $T_R$. If a finite system is brought into contact with the reservoir through a *diathermal* membrane (one which allows the passage

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[3] Energy and momentum cannot be conserved simultaneously when two bodies go to one with a release of energy. A third body in the collision can provide the means of conserving both.

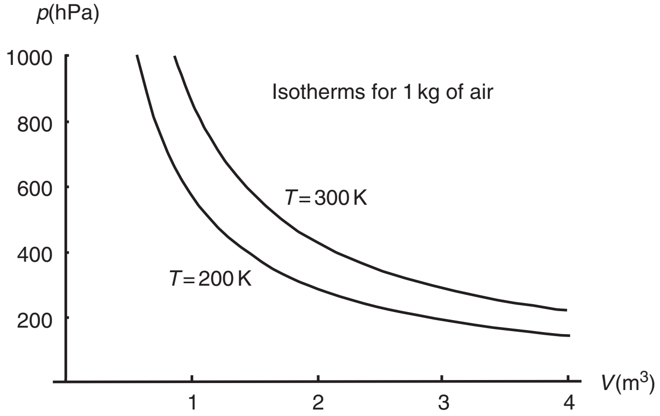

Figure 1.1 Isotherms for 1 kg of dry air taken as an ideal gas. The vertical coordinate is pressure in hPa, the abscissa is volume in $m^3$. Upper curve, 300 K; lower curve, 200 K.

of thermal energy,[4] but not mass), the smaller system will adjust the values of its coordinates (for a gas, $p$, $V, T$) to new values, while the reservoir does not change its state appreciably (this actually defines how massive the reservoir has to be). The system is said to come into thermal equilibrium with the reservoir (its temperature approaches that of the reservoir). In the case of a gaseous system, experiments have shown that there is a locus of pairs of values $(V, p)$ for which the system is in equilibrium with a given reservoir – in other words, a curve $p = p_T(V)$ in the $V$–$p$ plane. To put it another way, if our system has a certain fixed volume, then when it is brought into contact with the reservoir of temperature $T$, the pressure will always come to the same value, $p = p_T(V)$. As we do the experiment with different control volumes we can sweep out the locus of points in the $V$–$p$ plane. This curve is called the *isotherm* of the system for that reservoir temperature (Figure 1.1). The isotherm represents a series of equilibrium states that can occur while the system is in contact with the reservoir (of fixed temperature). For example, the volume might be forced to alter by a change in the wall dimension (e.g., a piston can have different positions in a cylinder which contains the system in question). In this case the pressure will change as a function of volume along the isotherm. While we could invent an algorithm based upon a series of reservoirs of different temperatures to build a temperature scale, it will suffice for our present purposes simply to use the familiar thermometer.

---

[4] Thermal energy refers to the microscopic motion of molecules in the system. When in diathermal contact, the thermal energy of molecules from one system can pass from the system to its neighbor through collisions. In time the thermal energies of the two systems will equalize. More on this in later chapters. The transfer of thermal energy is loosely referred to as *heat transfer*.

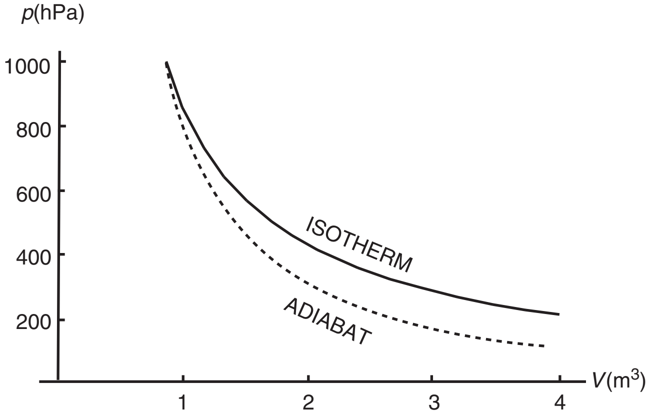

Figure 1.2 Isotherm and adiabat for 1 kg of dry air taken as an ideal gas. The upper curve (solid line) is the 300 K isotherm and the dashed curve is the adiabat passing through the 300 K isotherm at $V = 1\ \text{m}^3$. The vertical coordinate is pressure in hPa, the abscissa is volume in $\text{m}^3$.

A system can also be in equilibrium when isolated (no mass or thermal energy flows into or out of the system) from other systems. We call this an *isolated system*. It can have coordinates just as in the case of a system in contact with a reservoir. We call the locus of values of pressure in the isolated system for different volumes of the system *adiabats* (Figure 1.2). We could find the temperature of the isolated system at fixed values of $p$ and $V$ by bringing it into contact with different reservoirs until we find one which does not cause the coordinates of the system to change. The system has the same temperature as this reservoir. In this way we could map out the locus of points defining the isotherm which crosses the adiabat at the point in question. As a simpler alternative, we could insert a thermometer, whose mass is so small that it will come to equilibrium with the system (which now acts as a reservoir with respect to the tiny thermometer) without disturbing the state of the system appreciably.

States of thermodynamic equilibrium must not involve time. They are steady and only require a knowledge of the thermodynamic coordinates such as temperature, pressure and volume. When the “states” traversed by a system involve the time we cannot use thermodynamic equilibrium states to describe them. Conventional thermodynamics cannot be used to describe what goes on in states that are not in equilibrium.

Certain changes of a system can be made to occur through a sequence of infinitesimally nearby equilibrium states. For example, we might bring the system into contact one at a time with a series of reservoirs of infinitesimally differing temperatures, and at each step we wait for equilibrium to be established. We call this a *quasi-static process*. Such quasi-static processes can be approximated in the laboratory. From a molecular point of view the gas in the interior of the system has to have time during each infinitesimal shift of the constraints to adjust to a new equilibrium with its surroundings. In a gas this is roughly the time for a typical molecule to make a few hundred collisions, but over a finite sized volume it might be more appropriate to use the time for sound waves to traverse the volume several hundred times. This multiple pass traversal time works for pressure, but other properties might take considerably longer. For example, temperature and species concentrations smooth out much more slowly because these differences are smoothed out by diffusive processes such as thermal conduction. Stirring due to turbulence can speed up the homogenization but even then the adjustment is slower than for pressure differences. At each infinitesimal step (waiting for these adjustments) along such a system path, we could reverse direction and retrace the same steps. This is a *reversible process*.

Note that a system may go from one thermodynamic state to another by a path which does not involve such a sequence of thermodynamic states. We call this an *irreversible* change in state. An example of an irreversible process is the case of a system which goes from state A to state B spontaneously, but not from B to A. A concrete example is if two bricks, one hot and one cold, are brought into contact, the result is two warm bricks. This is an irreversible process. Note that it never happens that when we bring two warm bricks into contact we end up with a warm brick and a cold brick (even though energy is conserved).

Reversible processes do not actually occur in nature. So why study them? The reasons are pretty simple. First of all, irreversible processes are nearly impossible to treat theoretically. Secondly, experience has shown that approximating the nearly quasi-static processes that do occur in nature works reasonably well in many cases when we treat them as exactly quasi-static. We proceed then to adopt the philosophy used by practitioners for many years: we will freely approximate many processes in the real atmosphere by idealized reversible analogies in order to obtain numerical results that can be used in practical situations.

## 1.4 Constraints

An important concept in the study of thermodynamic systems is that of constraints. This notion is best illustrated by example. Consider the gas in a cylinder whose volume is determined by the position of a piston as in Figure 1.3. Several constraints are operative in this case. Most obvious is the position of the piston. It constrains the volume to have a certain value. If the piston is removed by a small amount the constraint is said to be relaxed. Note that a force must be applied

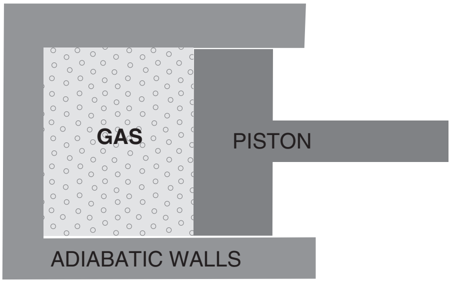

Figure 1.3 Schematic diagram of a gas filled cylinder with adiabatic walls and a movable piston.

(actually relaxed, then gradually reapplied) externally to implement this change in the constraint. If the piston is removed by a small amount, some agent must perform *work* to restore it to its original position. Similarly, the walls that are impervious to the transfer of thermal energy form a constraint. If a leak of thermal energy were to occur, such as on bringing the system into contact with a temperature reservoir at a slightly different temperature, this constraint would be said to have been relaxed and the thermodynamic coordinates of the system will have to be changed to restore the original temperature. Thermodynamic systems are always subject to certain constraints and their nature and number are essential ingredients in the description of the system and its state.

Consider two thermally isolated chambers adjacent to one another separated by a partition. On one side is gas A and on the other is gas B. Let the chambers have the same temperature and pressure. The partition forms a constraint restricting the two gases from mixing. If the partition is removed, the constraint is relaxed and the two systems will pass through nonequilibrium states to their final well-mixed equilibrium state. The irreversible process following removal of the constraint represents one which for ideal gases involves no changes in pressure or temperature, but external work must be performed to restore the original conditions.

## 1.5 Intensive and extensive quantities

Consider a thermodynamic system. The interior properties of the system are uniform. Now, imagine subdividing the system into two equal parts (say, two warm bricks in contact). If a variable is the same for the two individual parts (e.g., pressure, temperature, chemical composition, density, etc.), the variable is an *intensive variable*. On the other hand, if the thermodynamic variable for each subsystem is proportional to the mass of the constituents in that subsystem (e.g., volume, mass), we call it an *extensive variable*.

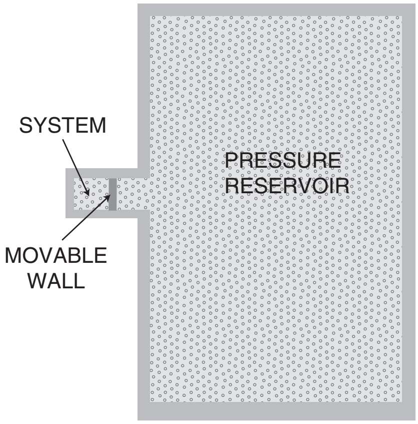

Figure 1.4 Schematic diagram of a gaseous pressure reservoir in contact with a small system. The membrane between the system and the pressure reservoir is movable so that the two systems can adjust their volumes in such a way that the pressures equalize.

*Example 1.2* An example of an isolated system is a 1 kg mass of gaseous $O_2$, confined in a box with thermally insulating walls. Suppose the volume is 1 $\text{m}^3$. This means the density of the gas is 1 kg $\text{m}^{-3}$. If the temperature of the gas is given, say 300 K, then the pressure will be determined (this is an experimental fact). The thermodynamic coordinates of this (pure) system are: $V$, the volume; $\mathcal{M}$, the mass; $T$, the temperature; and $p$, the pressure. □

*Example 1.3* A thermodynamic system might be in thermal equilibrium with a reservoir. In the case of the mass of $O_2$ gas in a fixed volume of 1 $\text{m}^3$, take the gas to be in thermal contact with a reservoir at 350 K. The pressure will be quite different from the last example. □

*Example 1.4* We might have a pressure reservoir. Consider the box of gas to be in contact with a reservoir with a slidable interface, such that the pressures can equalize between the two systems. Let the system otherwise be insulated thermally from the reservoir and the rest of the universe. If the gas has a given temperature initially, it will expand or contract until its pressure equals that of the reservoir (please let it happen gradually). The volume and temperature of the gas may change in order to establish equilibrium with the pressure reservoir (see Figure 1.4). □

## 1.6 System boundaries

Before setting up a problem in thermodynamics it is extremely important to choose the part of the universe you want to call your system. It might be a mass of matter or it might be a certain volume in space. As in the atmospheric examples the mass or volume might be in motion. If we are considering a mass in space with no additional matter allowed to enter or leave this fixed mass we say it is a *closed system*. In the fixed volume case mass might enter or leave. We call this an open system.

*Calculus refresher: the exponential function* The function $y(x)$ whose derivative is itself is called the exponential function:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = y. \tag{1.12}$$

Suppose we try $y = a^x$. Then

$$\frac{\Delta y}{\Delta x} = \frac{a^{x+\Delta x} - a^x}{\Delta x} = a^x \frac{a^{\Delta x} - 1}{\Delta x}. \tag{1.13}$$

The factor on the right must tend to unity as $\Delta x \to 0$. It will be more easily seen if we let $\Delta x = 1/N$ where $N$ is an integer. A little rearrangement yields

$$a_\infty = \lim_{N\to\infty}\left(1 + \frac{1}{N}\right)^N \tag{1.14}$$

and the number $a_\infty$ is given the symbol e whose numerical value turns out to be 2.718281.... To see how the limit comes about call the approximate value of $a_\infty = e_N$. Simple computation gives, $e_5 = 2.48832, e_{10} = 2.59374, e_{100} = 2.70481, e_{1000} = 2.71692$, and $e_{10000} = 2.71815\ldots$.

Note that $\mathrm{e}^0 = 1$, $\mathrm{e}^{-1} = 0.367879\ldots$, and $\mathrm{e}^x$ is called the exponential function. We can easily derive a few properties of $y = \mathrm{e}^x$. From its definition, $\mathrm{d}\mathrm{e}^x/\mathrm{d}x = \mathrm{e}^x$, and we can use the chain rule to show that $\mathrm{d}\mathrm{e}^{\alpha x}/\mathrm{d}x = \alpha \mathrm{e}^{\alpha x}$.

The function $\mathrm{e}^{-\alpha x}$ decreases *exponentially* from a value of unity at $x = 0$ to a value

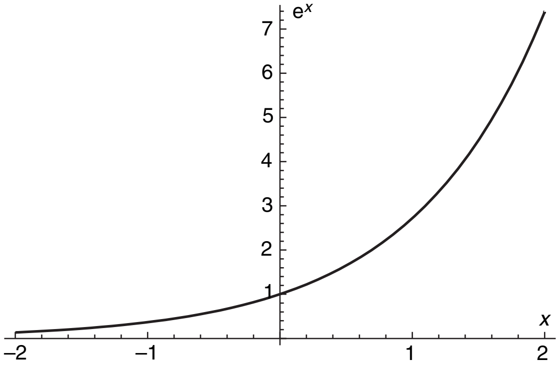

Figure 1.5 The exponential function $\mathrm{e}^x$ as a function of $x$.