1.7 Equation of State for Air

Except when water vapor is near condensation, air is observed to obey the ideal gas law. The ideal gas law (1.9) is written in extensive form, since the volume V, and number of moles n, are extensive variables. When applying the ideal gas law to the atmosphere, it is convenient to write the equation in terms of intensive variables. This is accomplished by dividing both sides of (1.9) by mass, m, yielding

$$p\frac{V}{m} = \frac{n}{m}R^*T \tag{1.10}$$

Using the definition of *molecular weight*, $M = m/n$, and the definition of specific volume, (1.10) can be written as

$$pv = \frac{R^*}{M}T \tag{1.11}$$

A *specific gas constant*, R, may be defined as $R = R^*/M$, so that (1.11) becomes

$$pv = RT \tag{1.12}$$

Strictly speaking, air does not have a molecular weight, since it is a mixture of gases and there is no such thing as an "air molecule." However, it is possible to assign an apparent molecular weight to air, since air as a mixture is observed to behave like an ideal gas. To apply the ideal gas law to the mixture of atmospheric gases, consider first the mixture of "dry-air" gases, excluding for now the variable constituent water vapor. To understand the behavior of a mixture of gases, we employ *Dalton's law of partial pressures*. Dalton's law states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures that would be exerted by each constituent alone if it filled the entire volume at the temperature of the mixture. That is,

$$p = \sum_j p_j \tag{1.13}$$

where p is the total pressure and the p_j are the partial pressures.

Dalton's law implies that each gas individually obeys the ideal gas law and that the ideal gas law (1.12) for a mixture of gases can be written using (1.13) as

$$V\sum_j p_j = T\sum_j m_j R_j$$

where we have used $v = V/m$. We can now define a mean specific gas constant as

$$\overline{R} = \frac{\sum_j m_j R_j}{m} \tag{1.14}$$

The equation of state for the mixture of dry-air gases can therefore be written in intensive form as

$$pv = R_d T \tag{1.15}$$

where R_d is the specific gas constant for dry air. Using Table 1.1 and (1.14), a value for R_d is determined to be 287.104 J K^{-1} kg^{-1}. The mean molecular weight of the mixture is

$$\overline{M} = \frac{\sum_i n_i M_i}{n} = \frac{m}{n} \tag{1.16}$$

The mean molecular weight for dry-air gases, M_d, is determined to be 28.96 g $mole^{-1}$.

The equation of state for air is complicated by the presence of water vapor, which has a variable amount in the atmosphere (Table 1.1). Assuming that the water vapor is not near condensation, the ideal gas law may be used and we have

$$e = \rho_v R_v T \tag{1.17}$$

where the notation e is commonly used to denote the partial pressure of water vapor and the subscript v denotes the vapor. The specific gas constant for water vapor is $R_v = R^*/M_v = 461.51$ J K^{-1} kg^{-1}. In a mixture of dry air and water vapor (*moist air*), the equation of state is

$$p = p_d + e = \left(\rho_d R_d + \rho_v R_v\right)T \tag{1.18}$$

The subscript d denotes the dry-air value, and the absence of a subscript denotes the value for the mixture of dry air plus water vapor.

The specific gas constant for moist air is determined from (1.14) to be

$$R = \frac{m_d R_d + m_v R_v}{m_d + m_v} \tag{1.19}$$

where m_d and m_v are the mass of dry air and water vapor, respectively, and $m = m_d + m_v$.

An intensive variable, the *specific humidity*, q_v, is defined as

$$q_v = \frac{m_v}{m_v + m_d} \tag{1.20}$$

so that the specific gas constant for moist air can be written as

$$R = (1 - q_v) R_d + q_v R_v \tag{1.21}$$

Using the definition of the specific gas constant, the specific gas constant for water vapor, R_v, may be written in terms of R_d

$$R_v = \frac{M_d}{M_v} R_d = \varepsilon^{-1} R_d \tag{1.22}$$

where $\varepsilon = M_v/M_d = 18/29 = 0.622$. The specific gas constant for moist air may then be written as

$$R = R_d\left[1 + q_v\left(\tfrac{1}{\varepsilon} - 1\right)\right] = R_d\left(1 + 0.608\, q_v\right) \tag{1.23}$$

Incorporating (1.23) into (1.18), the equation of state for moist air becomes

$$pv = R_d\left(1 + 0.608\, q_v\right) T \tag{1.24}$$

It is awkward to have a variable gas constant, so it is the convention among meteorologists to make the humidity adjustment to the temperature rather than to the gas constant. Thus we define a *virtual temperature*, T_v

$$T_v = \left(1 + 0.608\, q_v\right) T \tag{1.25}$$

so that the ideal gas law for moist air becomes

$$pv = R_d T_v \tag{1.26}$$

The virtual temperature may be interpreted as the temperature of dry air having the same values of p and v as the moist air under consideration. Since q_v seldom exceeds 0.02, the virtual temperature correction rarely exceeds more than 2 or 3°C; however, it is shown in Chapter 7 that the small virtual temperature correction has an important effect on buoyancy and hence vertical motions in the atmosphere.

1.8 Equation of State for Seawater

For a one-component fluid such as pure water, density is a function only of temperature and pressure. Since seawater is a multi-component fluid owing to its dissolved salts, its density is a function of temperature, pressure, and salinity: $\rho = \rho(T,p,s)$. Seawater density is observed to increase with increasing pressure and salinity, but decrease with increasing temperature.

An accepted theory for the density of pure water, analogous to the kinetic theory of ideal gases, does not exist. Therefore, an empirically-determined equation of state is used for seawater. An internationally agreed-upon equation of state (UNESCO, 1981) fits the available ocean density measurements to high accuracy. This equation has the form

$$\rho = \rho(T,p,s) = \frac{\rho(T,0,s)}{1 - K_T(T,s,p)} \tag{1.27}$$

where $K_T(T,s,p)$ is the *mean bulk modulus,* which is inversely proportional to the compressibility (see Section 1.9). Each quantity on the right-hand side of (1.27), except pressure, is expressed as a polynomial series in s and T, expanded about values for zero salinity and a pressure of 1 bar. The density at the surface pressure ($p = 0$) is given by the polynomial form

$$\rho(T,0,s) = A + Bs + Cs^{3/2} + Ds^2 \tag{1.28}$$

The mean bulk modulus is given by

$$K_T(T,s,p) = E + Fs + Gs^{3/2} + \left(H + Is + Js^{3/2}\right)p + \left(M + Ns\right)p^2 \tag{1.29}$$

The coefficients A, B, ... N in (1.28) and (1.29) are polynomials up to fifth degree in temperature (Table 1.3). In Table 1.3 and (1.27)–(1.29), the temperature is specified in °C, the pressure in bars, the salinityin psu, and density is $m^3\,kg^{-1}$. This equation of state is accurate to within a standard error of approximately 0.009 $kg\ m^{-3}$ over the entire oceanic pressure range.

For seawater at standard atmospheric pressure, a contour plot of ρ is given in Figure 1.10 as a function of temperature and salinity. Values of constant density are called *isopycnals*. Near the freezing point, the density of seawater is relatively insensitive to temperature variations and small salinity differences can play a major role in density variations.

An expression for the temperature of maximum density of seawater, T_ρ, can be obtained by differentiating with respect to temperature the equation of state for seawater.

c) On February 3, 1989, sea-level pressure reached a North American record of 1078 hPa. Surface temperature reached a minimum value of 217 K. The vertical temperature profile in the lower atmosphere was nearly isothermal. For an aircraft flying at a pressure of 850 mb above a surface that is at sea level, estimate the error in the altimeter reading that would be made under these conditions. (Note: The U.S. Federal Aviation Administration banned night and instrument flights in Fairbanks, AK, because altimeters could not be accurately calibrated to give altitude readings.)

Chapter 2

The First and Second Laws of Thermodynamics

The classical physics principle of the conservation of mechanical energy states that while energy may manifest itself in a variety of forms (e.g., kinetic energy, gravitational potential energy), the sum of all different forms of energy in any particular system is fixed. Energy can be transformed from one type to another, but total energy can be neither created nor destroyed. Thermodynamics extends the principle of conservation of energy to include heat.

The *first law of thermodynamics* arose from a series of experiments first carried out in the 19th century. These experiments demonstrated that work can be converted into heat and that the expenditure of a fixed amount of work always produces the same amount of heat. The first law of thermodynamics places no limitations on the transformation between heat and work. As long as energy is conserved, these transformation processes do not violate the first law of thermodynamics.

The *second law of thermodynamics* limits both the amount and the direction of heat transfer. According to the second law, 1) a given amount of heat cannot be totally converted into work, thus limiting the amount of heat transfer; and 2) the spontaneous flow of heat must be from a body with a higher temperature to one with a lower temperature, thus stipulating the direction of heat transfer.

2.1 Work

When a force of magnitude $\mathcal{F}$ is applied to a mass which consequently moves through a distance dx, the mechanical work done is

$$dW = -\mathcal{F} \cos\theta \, dx \tag{2.1}$$

where θ is the angle between the displacement dx and the applied force. Only the component of the displacement along the force enters the computation of work. There is no universal sign convention for work, so we adopt the following convention: work done *on* a system is positive; work done *by* a system is negative. It makes no difference which convention is adopted as long as it is used consistently.

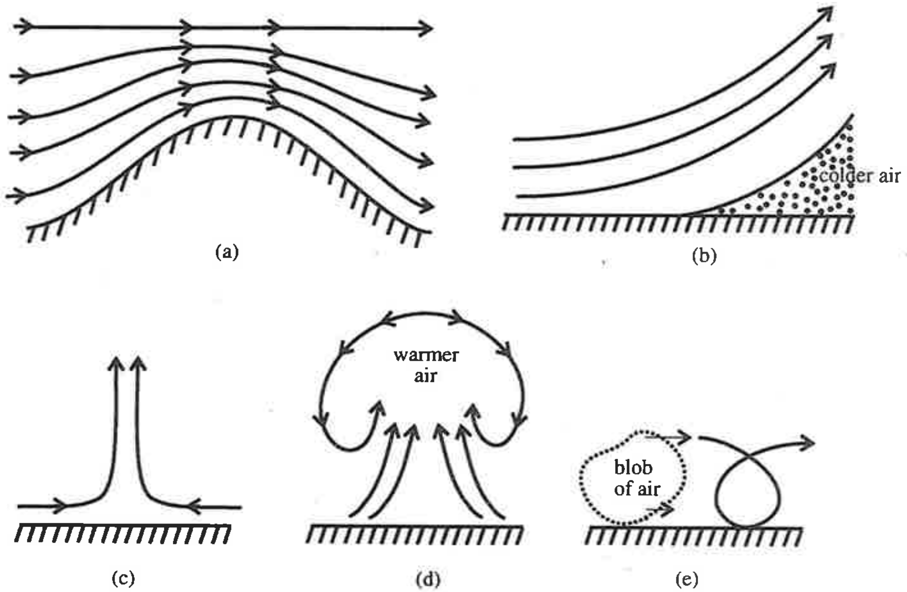
An important kind of work in thermodynamics is the work systems do when they expand or contract against an opposing pressure. *Expansion work* is defined as

$$dW = -\mathcal{F}dx = -pA\,dx = -p\,dV$$

where $Adx = dV$ is the differential volume change associated with the work done against the external pressure, p. The specific work, $w = W/m$, is an intensive variable, independent of mass, and thus

$$dw = -p\,dv \tag{2.2}$$

There are numerous examples of expansion work in the atmosphere (Figure 2.1), wherein a parcel of air rises in the atmosphere and its pressure decreases and volume increases. Some processes that cause air to rise are:
a) orographic lifting;
b) frontal lifting;
c) low-level convergence;
d) buoyant rising of warm air; and
e) mechanical mixing.
Analogous processes occur in the ocean. Work of expansion also occurs in the change of phase of water from liquid to gas and from liquid to ice.



(a) (b)

(c) (d) (e)

Figure 2.1 Rising motion occurs in the atmosphere due to (a) orographic lifting, (b) frontal lifting, (c) low-level convergence, (d) buoyant rising of warm air, and (e) mechanical mixing. Expansion work is done by an air parcel when it rises.

For a finite expansion or compression from v_1 to v_2, work is determined by integrating (2.2):

$$w = -\int_{v_1}^{v_2} p\,dv \tag{2.3}$$

The expansion from v_1 to v_2 is illustrated in Figure 2.2a by the top curve (A to B). The work done in this expansion is represented geometrically by the area under the curve. The area, and thus the work done, depends on the specific path followed during the expansion. For example, the temperature may remain constant or may vary during the expansion, resulting in different expansion paths. In fact, there is an infinite number of curves connecting the initial state v_1 to the final state v_2. If the system is compressed back to v_1 via a different process, net work will be done even though the system has returned to its initial state, as indicated by the shaded area between the two curves in Figure 2.2b.

Cyclical processes have the same initial and final states. A *cycle*, therefore, is a transformation that brings the system back to its initial state. The total work done in a cyclical process depends on the path, and is not necessarily zero. The work done by

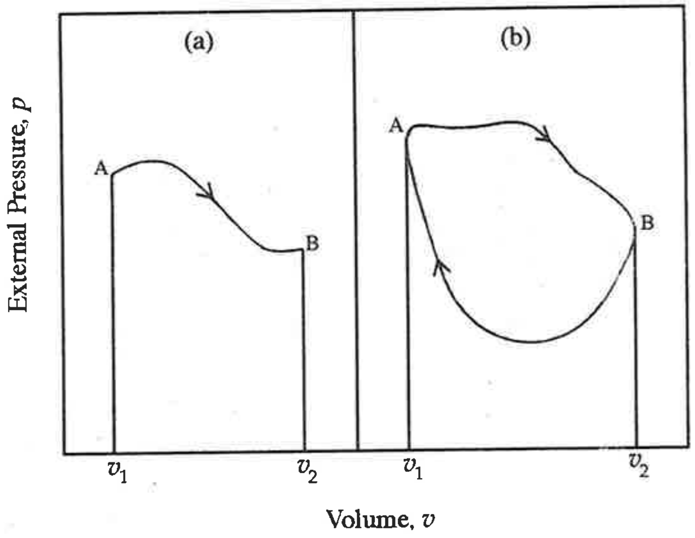


Figure 2.2 (a) The amount of work done in the expansion from v_1 to v_2 is equal to the area under the curve. In (b), the system is compressed back to v_1 via a different process. Even though the system has returned to its initial state, net work has been done, as indicated by the shaded area between the two curves.

a system in going from one state to another is a function of the path between the states. Therefore, generally

$$\oint dw \neq 0$$

To evaluate (2.3), the path of the expansion must be specified. Therefore, work is not an *exact differential* since *dw* cannot be obtained by differentiating a function of the state of the system alone, knowing only the initial and final states.

2.2 Heat

Heat is an extensive measure of the energy transferred between a system and its surroundings when there is a temperature difference between them. When two systems are placed in thermal contact, energy flows spontaneously from one system to the other. This energy flow can occur by various mechanisms, such as the transfer of vibrational energy between one solid and another whose surfaces are in contact, or the exchange of electromagnetic radiation. Such a spontaneous movement of energy is called a *heat flow*. It can be shown experimentally that if equal masses of water, one at 100°F and the other at 150°F, are mixed, then the resulting temperature is midway between the two extremes, or 125°F. If the same mass of warm mercury is used in place of the warm mass of water, however, the resulting final temperature is not midway between the two extremes, but rather 115°F, indicating that water has a greater "capacity" for heating than does mercury. That is, it takes more heat to raise the temperature of a given mass of water by one unit than it does to raise the temperature of the same mass of mercury by the same amount.

When two bodies with different temperatures, T_1 and T_2, are brought into contact with each other, the temperature difference eventually disappears, and the final temperature, T' is intermediate between the two initial temperatures. Experiments show that this heat transfer is governed by the following formula:

$$c_2 m_2 (T' - T_2) + c_1 m_1 (T' - T_1) = 0$$

where *c* is the *specific heat capacity,* which depends on the physical state and chemical composition of the substance. The amount of heat ΔQ lost by the warmer body is equal in magnitude to the amount of heat gained by the cooler body, so that

$$\Delta Q = c_1 m_1 (T_1 - T') = c_2 m_2 (T' - T_2) \tag{2.4}$$

The final equilibrium temperature is thus

$$T' = \frac{c_2 m_2 T_2 + c_1 m_1 T_1}{c_2 m_2 + c_1 m_1}$$

In differential form, the equation for heat (2.4) is

$$dQ = mc\, dT \tag{2.5}$$

The differential *dQ* is not exact since

$$\oint dQ \neq 0$$

To integrate *dQ*, one must know how the pressure and volume change during the transformation and if any phase changes occur during the transformation (e.g., gas to liquid).

Experiments have shown that the specific heat capacity is itself a function of temperature and is defined in terms of the differential heat flow and temperature change as

$$c = \frac{dq}{dT} \tag{2.6}$$

where $q = Q/m$ is the intensive heat.

Heat transfer processes in the atmosphere and ocean include radiation, molecular conduction, and the release of latent heat in phase changes (see Chapter 3).

2.3 First Law

The first law of thermodynamics is an extension of the principle of conservation of mechanical energy. We can use the conservation principle to define a function *U* called the *internal energy*. When an increment of heat *dQ* is added to a system, the energy may be used either to increase the speed of the molecules (i.e., to increase the temperature of the system), to create motion internal to each molecule (e.g., rotation and vibration), or to overcome the forces of attraction between the molecules (e.g., change of state from liquid to vapor), all of which contribute to the internal energy of the system. The internal energy of a system can increase when heat enters the system from the surroundings, and/or when work is done on the system by the surroundings.

If we take dU to denote an increment of internal energy, then

$$dU = dQ + dW \tag{2.7}$$

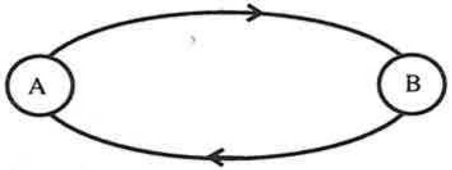
This statement is the differential form of the first law of thermodynamics. The intensive differential form of the first law of thermodynamics is written as

$$du = dq + dw \tag{2.8}$$

From the law of conservation of energy, the total energy of the system plus its environment must be constant. That is, the total energy change in the system plus its environment is zero:

$$0 = \Delta U_{syst} + \Delta U_{env}$$

What happens in a cyclical process?



In a cyclical process, $\Delta U_{syst}(A \rightarrow B \rightarrow A) = 0$, since otherwise we would be creating energy. Therefore,

$$0 = \Delta U_{syst}(A \rightarrow B \rightarrow A) = \oint dU$$

and ΔU depends only on the initial and final states but not on the path followed between them. The first law thus states that although dQ and dW are not exact differentials, their sum $dU = dQ + dW$ is an exact differential and thus a thermodynamic state variable.

An exact differential $d\xi$ has the following properties:

1. The integral of $d\xi$ about a closed path is equal to zero ($\oint d\xi = 0$).
2. For $\xi(x,y)$, we have $d\xi = (\partial\xi/\partial x)\,dx + (\partial\xi/\partial y)\,dy$ where x and y are *independent variables* of the system and the subscripts x and y on the partial derivatives indicate which variable is held constant in the differentiation.

3. If the exact differential is written as $d\xi = M dx + N dy$, we obtain *Euler's relation:*[1]

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \tag{2.9}$$

If an experiment is conducted under conditions of constant volume, the first law of thermodynamics (2.7) becomes

$$dU = dQ \tag{2.10}$$

since we are allowing only for the possibility of expansion work ($dW = -p\,dV$) and no other type of work, and since no expansion work is done during a process carried out at constant volume ($dV = 0$). The change in heat at constant volume gives us an experimental measure of ΔU for any process involving the same initial and final states.

What happens when we do an experiment at constant pressure, and no work is done except expansion work? Consider the changes accompanying a process at constant pressure:

$$\Delta U = U_2 - U_1 = Q_p + W = Q_p - \int_{V_1}^{V_2} p\,dV = Q_p - p(V_2 - V_1) \tag{2.11}$$

where Q_p denotes heating at constant pressure, and no work other than expansion work is done. We can rearrange (2.11) to obtain

$$(U_2 + pV_2) - (U_1 + pV_1) = Q_p$$

It is convenient to define a new function called the *enthalpy*, H, by

$$H = U + pV \tag{2.12}$$

so that

$$\Delta H = H_2 - H_1 = (U_2 + p_2 V_2) - (U_1 + p_1 V_1) = Q_p$$

---

[1] We depart here from the tradition in thermodynamics where it is customary to enclose partial derivatives in parentheses and append subscripts to denote the variable(s) held constant in the differentiation, e.g., $\partial M/\partial y \equiv (\partial M/\partial y)_x$. The subscripts on the partial differential are usually not required mathematically, and their use serves to make the equations unneccessarily cumbersome. In those cases where omitting subscripts and parentheses may cause confusion, they are retained.

Since $H = H(U, p, V)$ and U, p, and V are all state functions, H is also a state function; this is another way of saying that dH is an exact differential. In differential form,

$$dH = dU + p\,dV + V\,dp = dQ + V\,dp \tag{2.13}$$

and in intensive form

$$dh = dq + v\,dp \tag{2.14}$$

where $h = H/m$. From (2.14), it is clear that when we allow an expansion at constant pressure ($dp = 0$), we obtain an experimental measure of a state property, enthalpy. Equations (2.13) and (2.14) are equivalent forms of the first law of thermodynamics to (2.7) and (2.8). The enthalpy form of the first law is advantageous when considering constant-pressure processes.

Since u and h are state functions, we can write

$$u = u(p,v,T) = u(v,T)$$
$$h = h(p,v,T) = h(p,T)$$

Although u and h are functions of three variables (p, v, T), an equation of state allows us to eliminate one of the three variables. Since u and h are exact differentials, we can expand du and dh as follows:

$$du = \left(\frac{\partial u}{\partial T}\right) dT + \left(\frac{\partial u}{\partial v}\right) dv$$

$$dh = \left(\frac{\partial h}{\partial T}\right) dT + \left(\frac{\partial h}{\partial p}\right) dp$$

At constant volume $dv = 0$ and $du = dq_v$, which leads to

$$du = \left(\frac{\partial u}{\partial T}\right) dT = dq_v$$

In a constant-pressure process, $dp = 0$, and

$$dh = \left(\frac{\partial h}{\partial T}\right) dT = dq_p$$

where q_v and q_p refer to constant-volume and constant-pressure heating, respectively. From the definition of specific heat (2.6), we can write

$$c_v = \frac{dq_v}{dT} = \frac{\partial u}{\partial T} \tag{2.15a}$$

and

$$c_p = \frac{dq_p}{dT} = \frac{\partial h}{\partial T} \tag{2.15b}$$

where c_v and c_p are defined, respectively, as the *specific heat at constant volume* and the *specific heat at constant pressure*. We may thus write

$$du = c_v\,dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$dh = c_p\,dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

For an ideal gas, it has been shown experimentally that $(\partial u/\partial v)_T = 0$, so that internal energy is a function only of temperature for an ideal gas, i.e., $u = u(T)$. It can also be shown that $(\partial h/\partial p)_T = 0$ and $h = h(T)$. This implies that for ideal gases

$$\begin{aligned} du &= c_v\,dT \\ dh &= c_p\,dT \end{aligned} \tag{2.16}$$

How does c_v differ from c_p quantitatively? In a constant-pressure process, some of the added heat must be expended in doing work on the surroundings, while in a constant-volume process, all of the heat is devoted to raising the temperature of the substance. Therefore it takes more heat per unit temperature rise at constant pressure than at constant volume, and $c_p > c_v$. The difference between c_p and c_v can be evaluated from

$$c_p - c_v = \left(\frac{\partial h}{\partial T}\right)_p - \left(\frac{\partial u}{\partial T}\right)_v$$

Using the definition of enthalpy, $h = u + pv$, we can write

$$c_p - c_v = \left(\frac{\partial u}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial u}{\partial T}\right)_v \tag{2.17a}$$

Expanding the differential $du(v,T)$ as

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

and dividing by dT while requiring constant pressure, we obtain

$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{\partial u}{\partial T}\right)_v + \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

We can now write (2.17a) as

$$c_p - c_v = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p \tag{2.17b}$$

For an ideal gas, $(\partial u/\partial v) = 0$ and $p(\partial v/\partial T)_p = R$, so (2.17b) can be evaluated to be

$$c_p - c_v = R \tag{2.17c}$$

where R is the specific gas constant. Hence for an ideal gas, the magnitude of the difference between the two specific heat capacities is simply the specific gas constant.

2.4 Applications of the First Law to Ideal Gases

We now apply the first law of thermodynamics to ideal gases, which is useful in the interpretation of thermodynamic processes in the atmosphere. The thermodynamic characteristics of an ideal gas have been shown to be:

1. The equation of state is $pv = RT$.
2. The internal energy is a function of its temperature alone ($du = c_v\,dT$; $dh = c_p\,dT$).
3. The specific heats are related by $c_p - c_v = R$.

The first law of thermodynamics for an ideal gas is thus written as

$$c_v\,dT = dq - p\,dv \tag{2.18a}$$

$$c_p\,dT = dq + v\,dp \tag{2.18b}$$

in internal energy (2.18a) and enthalpy (2.18b) forms.

Consider the isothermal ($dT = 0$) expansion of an ideal gas. Because internal energy is a function only of temperature, the internal energy of the gas is unchanged in an isothermal expansion. The first law of thermodynamics (2.18a) for an isothermal expansion may therefore be written as

$$dq = p\,dv$$

assuming that the only work done is expansion work. In the isothermal expansion of an ideal gas, the system does work, and the energy from this work comes from the environment and enters the system as heat. Since work is not an exact differential, we cannot integrate the right-hand side of the equation until we specify a path. As seen from Figure 2.2b, an infinite number of paths can be specified. Here we consider the path of an isothermal reversible expansion. A reversible path is one connecting intermediate states, all of which are equilibrium states. Exact conditions for reversible processes and how they differ from irreversible processes are described in Section 2.5. For now, we consider a reversible path where the equation of state is exactly satisfied during all stages of the expansion. Therefore, p may be evaluated using the ideal gas law, and the equation becomes

$$dq = RT\frac{dv}{v}$$

Integrating from v_1 to v_2 yields

$$\Delta q = RT\ln\left(\frac{v_2}{v_1}\right) = RT\ln\left(\frac{p_1}{p_2}\right)$$

The solution states, for example, that the amount of heat required to expand a gas from 10^6 Pa to 10^5 Pa is the same as that required to expand from 10^5 Pa to 10^4 Pa.

For a constant-volume process ($dv = 0$), the first law (2.18a) may be written as

$$du = dq$$

From the definition of internal energy for an ideal gas, $du = c_v dT$, the amount of heat required to raise the temperature of the gas from T_1 to T_2 at constant volume is

$$\Delta q = c_v\,(T_2 - T_1)$$

For a constant-pressure process ($dp = 0$), it is advantageous to use the first law in enthalpy form (2.18b), so that the first law for a constant-pressure process becomes

$$dh = dq$$

From the definition of enthalpy for an ideal gas, $dh = c_p dT$, the amount of heat required to raise the temperature of the gas from T_1 to T_2 at constant pressure is

$$\Delta q = c_p \left(T_2 - T_1 \right)$$

The constant-volume and constant-pressure results may be anticipated from the definitions of specific heat in Section 2.3.

An *adiabatic* process is one in which no heat is exchanged between the system and its environment, so that $dq = 0$. The first law for a reversible adiabatic process may thus be written as

$$du = dw$$

An adiabatic compression increases the internal energy of the system. The first law (2.18a,b) for an adiabatic expansion of an ideal gas is thus written

$$c_v \, dT = - p \, dv \tag{2.19a}$$

$$c_p \, dT = v \, dp \tag{2.19b}$$

Considering a reversible adiabatic expansion for an ideal gas, we have from (2.19a) and the equation of state (1.12)

$$c_v \frac{dT}{T} = - R \frac{dv}{v}$$

which may be integrated between an initial and final state (assuming that c_v is constant) to give

$$c_v \ln\left(\frac{T_2}{T_1} \right) = - R \ln\left(\frac{v_2}{v_1} \right)$$

so that

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{R/c_v} \tag{2.20}$$

During an adiabatic expansion of a gas, the temperature decreases. In the reverse

process (adiabatic compression), work is done on the gas and the temperature increases. Using the ideal gas law and the relationship $c_p - c_v = R$, we may write (2.20) in the following equivalent forms:

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2} \right)^{c_p/c_v} \tag{2.21}$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{R/c_p} \tag{2.22}$$

Equations (2.20), (2.21), and (2.22) are commonly referred to as *Poisson's equations*. It is noted here that (2.22) may also be derived directly by starting from the enthalpy form of the first law (2.19b).

Figure 2.3 compares an isothermal expansion with a reversible adiabatic expansion on a p, V diagram. It is seen that a given pressure decrease produces a smaller volume increase in the adiabatic case relative to the isothermal case, because the temperature also decreases during the adiabatic expansion.

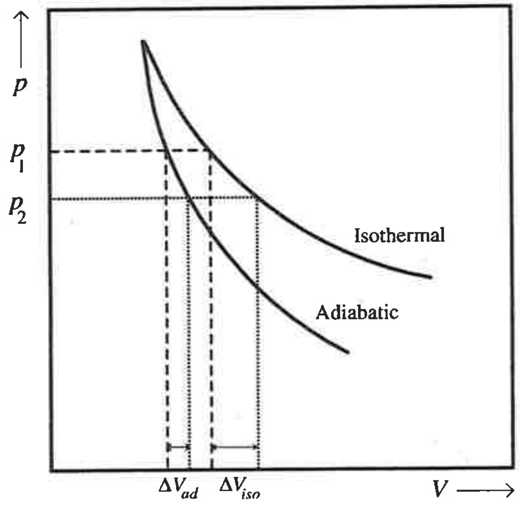


Figure 2.3 Isothermal expansion compared with a reversible adiabatic expansion. For a given drop in pressure, $\Delta V_{iso} > \Delta V_{ad}$, since during the adiabatic expansion, the temperature also decreases.

2.5 Entropy

Before discussing entropy, we first consider the difference between reversible and irreversible processes. In all thermodynamic processes, the changes that occur in the environment must be considered in conjunction with the changes that occur in the thermodynamic system. A *reversible process* is one in which the system is in an equilibrium state throughout the process. Thus the system passes at an infinitesimal rate through a continuous succession of balanced states that are infinitesimally different from each other. In such a scenario, the process can be reversed, and the system and its environment will return to the initial state. *Irreversible processes* proceed at finite rates: if the system is restored to its initial state, the environment will have changed from its initial state. The term "irreversible" does not mean that a system cannot return to its original state, but that the system plus its environment cannot be thus restored.

A comparison between reversible and irreversible atmospheric processes is illustrated in Figure 2.4. If a mass of moist air rises adiabatically and then descends adiabatically to the initial pressure level, the final temperature and mixing ratio of the air will be equal to the initial values and the process is thus reversible. However, if clouds form during the ascent and some of the cloud water rains out, then the air mass when brought down to the initial pressure will have a higher temperature and lower specific humidity than the initial values. Precipitation is an example of an irreversible process. If the rain falls to the ground and does not evaporate in the sub-cloud layer, then the total water content of the atmosphere decreases irreversibly and the temperature of the atmosphere increases irreversibly.

Consider the first law of thermodynamics in enthalpy form (2.18b) for a reversible process:

$$dq = c_p\,dT - v\,dp$$

Reversible heating is an abstract concept, whereby heating of a system occurs infinitesimally slowly through contact with an infinite heat reservoir. For the reversible expansion of an ideal gas, we may substitute for the specific volume from the equation of state and divide by temperature

$$\frac{dq}{T} = c_p\frac{dT}{T} - R\frac{dp}{p} = c_p\,d(\ln T) - R\,d(\ln p) \tag{2.23}$$

The two terms on the right-hand side of (2.23) are by definition exact differentials, and their sum must also be an exact differential. Therefore dq/T is an exact differential, i.e.,

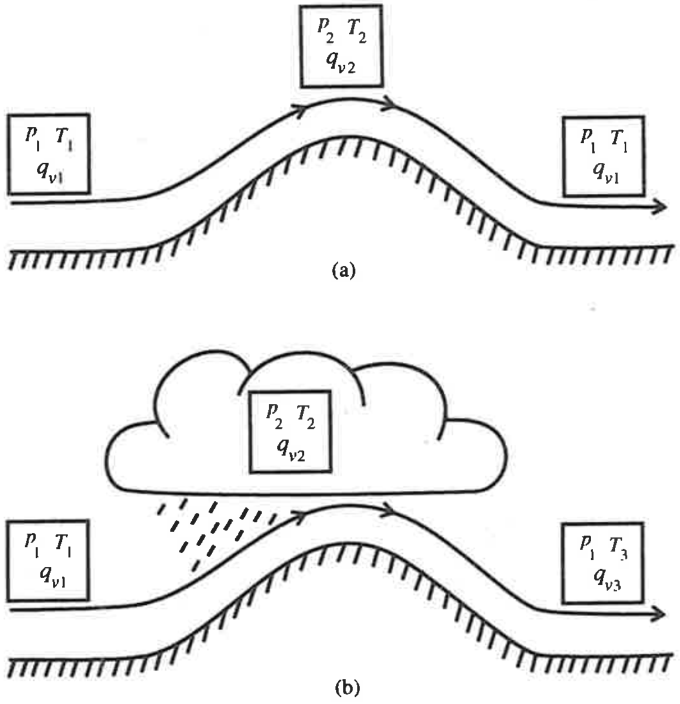


Figure 2.4 Comparison of a reversible and an irreversible process in the atmosphere. In (a), moist air initially at pressure p_1, and having temperature T_1 and specific humidity q_{v1}, rises adiabatically to the top of a mountain. It then descends adiabatically on the other side to the initial pressure. Because the process of passing over the mountain was done reversibly and adiabatically, the temperature and specific humidity are restored to their inital values, and the process is thus reversible. In (b), clouds form as the mass of moist air rises, and some of the cloud water rains out. When the mass of air descends on the other side to its initial pressure, its specific humidity is lower and its temperature is higher than the original values, and the process is thus irreversible: the total water content of the atmosphere decreases irreversibly and the atmosphere is warmed irreversibly.

$$\oint\left(\frac{dq}{T}\right)_{rev} = 0 \tag{2.24}$$

where the subscript *rev* emphasizes that this relationship holds only for a reversible process. Dividing heat by temperature converts the inexact differential dq into an exact differential. We can now define a new thermodynamic state function, the *entropy*, η, with units J K^{-1} kg^{-1}, to be

$$d\eta = \left(\frac{dq}{T} \right)_{rev} \tag{2.25a}$$

It is important to remember that entropy is defined so that the change in entropy from one state to another is associated with a reversible process connecting the two states.

When a change in entropy between two given states occurs via an irreversible process, the change in entropy is exactly the same as for a reversible process: this is because entropy is a state variable and $d\eta$ is an exact differential, which means that integration of $d\eta$ does not depend on the path of integration. Although the change in entropy is exactly the same for reversible and irreversible processes that have the same initial and final states, the integral of dq/T is not the same for reversible and irreversible processes. In fact,

$$\Delta\eta > \int \left(\frac{dq}{T} \right)_{irrev} \tag{2.25b}$$

where the subscript *irrev* indicates an irreversible process. This suggests that to accomplish a given change in entropy (or state) by an irreversible process, more heat is required than when a reversible process is involved. This implies that reversible processes are more efficient than irreversible processes.

Entropy changes for an ideal gas in a reversible process can be determined from (2.18a) and (2.25a):

$$d\eta = c_v\, d(\ln T) + R\, d(\ln v) \tag{2.26a}$$

or alternatively from (2.18b) and (2.25a):

$$d\eta = c_p\, d(\ln T) - R\, d(\ln p) \tag{2.26b}$$

The entropy change for isobaric heating is thus

$$\Delta\eta = c_p \ln\left(\frac{T_2}{T_1} \right)$$

and for isothermal processes

$$\Delta\eta = R \ln\left(\frac{v_2}{v_1} \right) = R \ln\left(\frac{p_1}{p_2} \right)$$

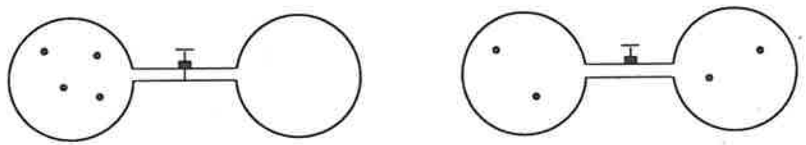


Figure 2.5 Expansion of an ideal gas illustrating the relationship between entropy and probability. Initially, four molecules of the gas are placed in the left bulb, and the right bulb is empty. When the stopcock is opened, the volume doubles, and the molecules are distributed between the left bulb and the right bulb. In this process, the number of possible configurations of molecules, and hence the entropy of the system, has increased.

As introduced above, entropy has arisen from purely mathematical considerations. Entropy can be interpreted physically in the context of statistical mechanics. The relationship between entropy and probabilities is illustrated using a simple example. Consider the ideal gas expansion shown in Figure 2.5. Two isolated bulbs, each of volume V, are connected by a stopcock. Initially, four molecules of the gas are placed in the left bulb, and the right bulb is empty. The stopcock is opened and the volume doubles (this is an example of an irreversible adiabatic expansion). The change in entropy from the intial (*init*) to final (*fin*) state is

$$\Delta\eta = Nk \ln\left(\frac{V_{fin}}{V_{init}} \right)$$

where N is the number of molecules and k is the Boltzmann constant (gas constant per molecule). Since $N = 4$ and $(V_{fin}/V_{init}) = 2$, we may write

$$\Delta\eta = 4k \ln 2 = k \ln 2^4$$

The entropy change is thus proportional to $\ln 2^4 = \ln 16$.

In the final state, the molecules are distributed between the left bulb and the right bulb. Table 2.1 lists the numbers and probabilities of the possible configurations of the final distribution of molecules. There are 16 ways of arranging the four molecules between the two bulbs in the final state. There is only one configuration for the initial state: all four molecules in the left bulb. The ratio of the final to the initial probability, P_{fin}/P_{init} and the final to the initial number of possible configurations, C_{fin}/C_{init} are

$$\frac{P_{fin}}{P_{init}} = \frac{C_{fin}}{C_{init}} = 16 = 2^4$$

Table 2.1 Ways of arranging four molecules in two bulbs of equal volume.

# in left bulb	# in right bulb		# of ways to achieve configuration, C	Probability of the configuration, P
0	4		1	1/16
1	3		4	4/16
2	2		6	6/16
3	1		4	4/16
4	0		1	1/16
		Total:	16	1

This suggests that we can associate entropies with probabilities, or numbers of possible configurations.

The equilibrium state of the four molecules distributed in two bulbs is more random than four molecules in one bulb, since we are less definite about the location of the molecules in the more random (or disordered) state. More rigorous developments of this relationship can be done in the context of quantum mechanics. However, the present example suffices to associate entropy with randomness. The natural path of all processes is from order to randomness. Entropy in an isolated system will tend to increase as the probability spreads out over the possible states and the system approaches equilibrium.

2.6 Second Law

The second law of thermodynamics forbids certain processes, even some in which energy is conserved. The second law of thermodynamics may be stated in several different ways, which appear to be different in content but can be shown to be logically equivalent.

The entropy statement of the second law is:

> *There exists an additive function of state known as the equilibrium entropy, which can never decrease in a thermally isolated system.*

In other words, a thermally isolated system cannot spontaneously regain order which has been lost. The second law may be applied to a system and its surroundings to determine the total entropy change $\Delta\eta_{tot}$

$$\Delta\eta_{tot} \geq 0$$

which is known as *Clausius' inequality*. For a reversible process we cannot have $\Delta\eta_{tot} > 0$, since we would have $\Delta\eta_{tot} < 0$ upon reversing the process, which would violate Clausius' inequality. Therefore, $\Delta\eta_{tot} = 0$ for all reversible changes. For the special case of a reversible adiabatic process, the entropy change is zero in the system, $\Delta\eta_{syst} = 0$. Reversible adiabatic processes are therefore *isentropic*. Using the definition of entropy in (2.25), we may write Clausius' inequality as

$$\oint \frac{dq}{T} \leq 0 \tag{2.27}$$

where the equal sign holds for a completely reversible process.

The temperature or Clausius statement of the second law is:

> *No process exists in which heat is transferred from a colder body to a less cold body while the constraints on the bodies and the state of the rest of the world are unchanged.*

A quantitative statement of this principle in terms of entropy can be made as follows. Consider a process that transfers heat between two bodies A and B, leaving the surroundings and the constraints on the bodies unchanged. After a small heat transfer,

$$d\eta_{tot} = d\eta_A + d\eta_B$$

This can be expanded for a constant-volume process as

$$d\eta_{tot} = \left(\frac{\partial\eta_A}{\partial u_A}\right)du_A + \left(\frac{\partial\eta_B}{\partial u_B}\right)du_B$$

If the heat transfer is denoted by $dq_A = du_A = -du_B$ we have

$$\eta_{tot} = \left(\frac{\partial\eta_A}{\partial u_A} - \frac{\partial\eta_B}{\partial u_B}\right)dq_A \geq 0 \tag{2.28}$$

We now define a quantity, T, the *absolute thermodynamic temperature*, as

$$\frac{1}{T} = \frac{\partial\eta}{\partial u}$$

We may therefore write (2.28) in terms of T as

$$\left(\frac{1}{T_A}-\frac{1}{T_B}\right) dq_A \geq 0 \tag{2.29}$$

This equation shows that dq_A cannot be positive if $1/T_B > 1/T_A$. It follows that the thermodynamic temperature alone determines the direction of heat transfer between bodies and that the heat transfer proceeds from warm to cold. The absolute thermodynamic temperature can be shown to be proportional to the gas scale temperature (Section 1.5) by evaluating the entropy change of an ideal gas over a cyclic process. Equality between these two temperatures is achieved by choosing the value 273.15 K for the reference state (the Kelvin scale).

The third statement of the second law is the heat engine or Kelvin statement. This statement derives its name from the problem that originally stimulated the formulation of the second law: the efficiency of a heat engine, a device that turns heat abstracted from a heat source into work. The heat engine statement of the second law is:

> *No process exists in which heat is extracted from a source at a single temperature and converted entirely into useful work, leaving the rest of the world unchanged.*

This statement tells us that a heat engine cannot have an efficiency of 100%. Part of the heat absorbed must be rejected to a heat sink. The second law implies a certain degree of unavailability of heat for the production of work. If all of the heat were converted into work, the total entropy would decrease, which is not physically possible.

The simplest possible heat engine is a device which works in a cycle, and in one cycle takes heat q_1 from a source at a high temperature T_1, converts part of the heat into useful work, w, and rejects waste heat q_2 to a heat sink at a lower temperature T_2. Such a system is the *Carnot engine* illustrated in Figure 2.6. From the conservation of energy, $w = q_1 - q_2$. The total entropy change is

$$\Delta\eta_{tot} = \Delta\eta_1 + \Delta\eta_2 = -\frac{q_1}{T_1} + \frac{q_2}{T_2} \geq 0$$

This equation may be written as a condition on waste heat q_2:

$$q_2 \geq \frac{T_2}{T_1} q_1$$

The efficiency $\mathscr{E}$ of the heat engine is defined as the ratio between the useful work of the engine compared to the heat input. That is,

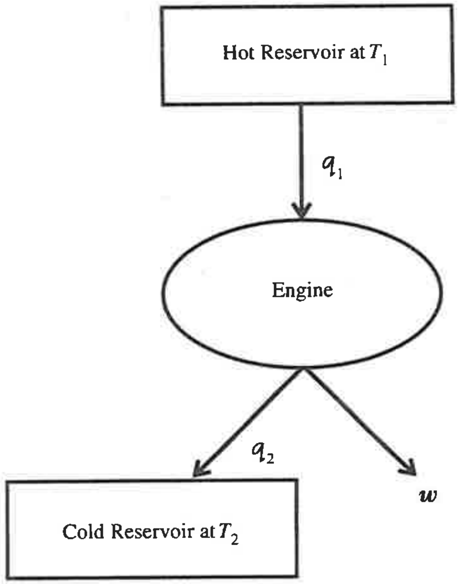


Figure 2.6 Carnot heat engine. Heat q_1 is brought from the hot reservoir to the engine. The engine does work w and rejects heat q_2 into the cold reservoir.

$$\mathscr{E} = \frac{w}{q_1} = 1 - \frac{q_2}{q_1} \tag{2.30a}$$

The engine is at its highest efficiency when q_2 is as small as possible, which is whenever the cycle is reversible. For a reversible Carnot engine, we have

$$\frac{q_2}{q_1} = \frac{T_2}{T_1}, \qquad \Delta\eta_{tot} = 0, \qquad \text{and} \qquad \mathscr{E} = 1 - \frac{T_2}{T_1} \tag{2.30b}$$

Thus, the efficiency of a reversible Carnot heat engine depends only on the source and sink temperatures.

2.7 Equilibrium and the Combined First and Second Laws

By using the first and second laws of thermodynamics in combination, we can derive some important results that apply to energy and entropy in the atmosphere and ocean. For any reversible process with expansion work only, we can write the first law as

$$du = dq_{rev} - p\,dv$$

Since $dq_{rev} = Td\eta$ from (2.25a), this becomes

$$du = T\,d\eta - p\,dv \tag{2.31}$$

The natural independent variables for internal energy are entropy and volume. If the enthalpy form of the first law is used, (2.14), we have

$$dh = T\,d\eta + v\,dp \tag{2.32}$$

The natural independent variables for enthalpy are entropy and pressure.

For many applications in the atmosphere and ocean, it is useful to define a new state function whose natural independent variables are temperature and pressure. The *Gibbs energy*, g, is defined as

$$g \;=\; u - T\eta + pv \;=\; h - T\eta \tag{2.33}$$

or in extensive form

$$G = H - T\mathcal{N}$$

where $\mathcal{N} = m\eta$ is used to denote extensive entropy and $G = mg$ is the extensive Gibbs energy. In differential form we have

$$dg = -\,\eta\,dT + v\,dp \tag{2.34}$$

The natural independent variables of the Gibbs energy are temperature and pressure.

The final basic thermodynamic relationship we consider here is the *Helmholtz energy*, a, defined as

$$a = u - T\eta \tag{2.35}$$

and in differential form

$$da = -\,\eta\,dT - p\,dv \tag{2.36}$$

The extensive form of the Helmholtz energy is $\mathcal{A} = ma$. The natural independent variables of the Helmholtz energy are temperature and volume.

Equations (2.31), (2.32), (2.34) and (2.36) are all equivalent forms of the combined first and second laws. The particular form one uses is guided by the specific application.

Consider the following statement of the combined first and second laws (2.31):

$$du = T\,d\eta - p\,dv$$

Equilibrium is a state of balance between a system and its environment, in which small variations in the system will not lead to a general change in its properties, and the system remains constant with time. In a process that occurs at constant entropy and constant volume, the change in internal energy will be zero. In such a process, the equilibrium state is thus specified for that state for which $du = 0$. It can be shown that under conditions of constant η and v that $d^2u > 0$, which says that internal energy is a minimum at equilibrium. Under conditions of constant internal energy and volume, the same version of the first and second laws combined shows that equilibrium is reached when $d\eta = 0$. It can also be shown that under conditions of constant u and v that $d^2\eta < 0$, which states that entropy is a maximum at equilibrium. The drive of thermodynamic systems toward equilibrium is thus a result of two factors. One is the tendency toward minimum energy. The other is the tendency towards maximum entropy. Only if u is held constant can η achieve its maximum; only if η is held constant can u achieve its minimum.

Since processes are rarely studied under conditions of constant entropy or constant energy, it is desirable to obtain criteria for thermodynamic equilibrium under practical conditions such as constant pressure. The four alternative statements of the combined first and second laws: (2.31), (2.32), (2.34), and (2.36), can be used to establish equilibrium criteria under different conditions. Under conditions of constant h and p, equilibrium is reached for $dh = 0$. Under conditions of constant T and p, equilibrium is specified for the condition $dg = 0$. The thermodynamic equilibrium conditions are thus summarized as

$$\begin{array}{llll}
\text{At constant } \eta,\ v: & du = 0, & d^2u > 0 \\
\text{At constant } \eta,\ p: & dh = 0, & d^2h > 0 \\
\text{At constant } T,\ v: & da = 0, & d^2a > 0 \\
\text{At constant } T,\ p: & dg = 0, & d^2g > 0
\end{array}$$

2.8 Calculation of Thermodynamic Relations

By manipulating the basic thermodynamic equations, we can derive relationships among the thermodynamic variables and thus avoid many difficult laboratory experiments by reducing the body of thermodynamic data to relations in terms of readily measurable functions. The convenience of these relationships will also become apparent through the simplicity introduced into many derivations.

Consider the basic thermodynamic relations (2.31), (2.32), (2.34), and (2.36):

$$\begin{aligned} du &= T d\eta - p dv \\ dh &= T d\eta + v dp \\ da &= -\eta dT - p dv \\ dg &= -\eta dT + v dp \end{aligned}$$

If we set the left-hand sides of these equations equal to zero, we obtain

$$\left(\frac{\partial \eta}{\partial v}\right)_u = \frac{p}{T} \tag{2.37}$$

$$\left(\frac{\partial \eta}{\partial p}\right)_h = -\frac{v}{T} \tag{2.38}$$

$$\left(\frac{\partial v}{\partial T}\right)_a = -\frac{\eta}{p} \tag{2.39}$$

$$\left(\frac{\partial p}{\partial T}\right)_g = -\frac{\eta}{v} \tag{2.40}$$

We can write expressions for the four functions in functional form as

$$\begin{aligned} u &= u(\eta, v) \\ h &= h(\eta, p) \\ a &= a(T, v) \\ g &= g(T, p) \end{aligned}$$

In differential form the functions can also be written as

$$du = \left(\frac{\partial u}{\partial v}\right)_\eta dv + \left(\frac{\partial u}{\partial \eta}\right)_v d\eta \tag{2.41}$$

$$dh = \left(\frac{\partial h}{\partial p}\right)_\eta dp + \left(\frac{\partial h}{\partial \eta}\right)_p d\eta \tag{2.42}$$

$$da = \left(\frac{\partial a}{\partial v}\right)_T dv + \left(\frac{\partial a}{\partial T}\right)_v dT \tag{2.43}$$

$$dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT \tag{2.44}$$

If we compare (2.41)–(2.44) with (2.31), (2.32), (2.34), and (2.36) and equate coefficients, we obtain

$$\left(\frac{\partial u}{\partial v}\right)_\eta = -p \qquad \left(\frac{\partial u}{\partial \eta}\right)_v = T \tag{2.45}$$

$$\left(\frac{\partial h}{\partial p}\right)_\eta = v \qquad \left(\frac{\partial h}{\partial \eta}\right)_p = T \tag{2.46}$$

$$\left(\frac{\partial a}{\partial v}\right)_T = -p \qquad \left(\frac{\partial a}{\partial T}\right)_v = -\eta \tag{2.47}$$

$$\left(\frac{\partial g}{\partial p}\right)_T = v \qquad \left(\frac{\partial g}{\partial T}\right)_p = -\eta \tag{2.48}$$

Since du, dh, da, and dg are exact differentials, they obey the Euler condition (2.9). Therefore from (2.31), (2.32), (2.34) and (2.36) we obtain the following set of useful relations called *Maxwell's equations*:

$$\left(\frac{\partial T}{\partial v}\right)_\eta = -\left(\frac{\partial p}{\partial \eta}\right)_v \tag{2.49}$$

$$\left(\frac{\partial T}{\partial p}\right)_\eta = \left(\frac{\partial v}{\partial \eta}\right)_p \tag{2.50}$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial \eta}{\partial v}\right)_T \tag{2.51}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial \eta}{\partial p}\right)_T \tag{2.52}$$

2.9 Heat Capacity

In this section we determine values of the specific heats for air and seawater. The heat capacities of ideal gases and crystalline solids can be determined theoretically by applications of statistical thermodynamics; however, there is not a generally accepted theory for the specific heat of liquids. Here we investigate theoretically the specific heat of ideal gases and describe empirically the specific heat of seawater.

Values of c_p and c_v can be determined for an ideal gas by considering the mechanical degrees of freedom and the equipartition of energy. A *mechanical degree of freedom* refers to an independent mode of motion (a translation, rotation, or vibration) of the molecule in one of three mutually independent directions in space. The total number of degrees of freedom of a mechanical system is equal to the number of variables required to specify the motion of the system. For example, a mass point (e.g., a monatomic molecule) has three degrees of freedom, for motion in each of the x, y, and z directions. For a mechanical system with more than one mass point (e.g., a diatomic or triatomic molecule), additional degrees of freedom arise from rotational and vibrational motions (Figure 2.7). An N-atomic molecule has 3N degrees of freedom:

	Nonlinear molecule	Linear molecule
Translation	3	3
Rotation	3	2
Vibration	3N – 6	3N – 5

Recall from elementary kinetic theory (Section 1.6) that the average molecular kinetic energy of an ideal gas is given by

$$\mathcal{E}_k = \frac{3}{2} nR^*T$$

This suggests that for one mole of a monatomic gas, we can associate $(1/2)R^*T$ thermal energy per mole with each translational degree of freedom. In the case of a more complex molecule, the energy is shared by rotational and vibrational degrees of freedom, rotational modes associated with $(1/2)R^*T$ per mole, and vibrational modes associated with R^*T per mole. Thus the total energy is equally divided among the translational, rotational, and vibrational degrees of freedom. This is called the *equipartition of energy*. The heat capacity of an ideal gas can in principle be determined by summing the contributions to the thermal energy for each of the mechanical degrees of freedom.

The specific heat capacity at constant volume for ideal gases can be determined from the equipartition of energy law to be

$$\begin{aligned} c_v &= (3/2)R \textit{ for a monatomic gas} \\ c_v &= (7/2)R \textit{ for a diatomic gas} \\ c_v &= 6R \textit{ for a nonlinear triatomic gas} \end{aligned}$$

where R is the specific gas constant. The equipartition of energy predicts a heat capacity that is independent of temperature. Real diatomic and polyatomic molecules have temperature-dependent heat capacities; further, at low temperatures all heat capacities (except for helium) are much lower than the value predicted above. This discrepancy was resolved by the development of quantum mechanics. The contribution of both the rotational and vibrational degrees of freedom to the heat capacity depends on the extent to which the excited vibrational and rotational states are populated for a particular gas, which depends on temperature. The rotationally excited states of the gases in the Earth's atmosphere are fully populated at Earth temperatures, while

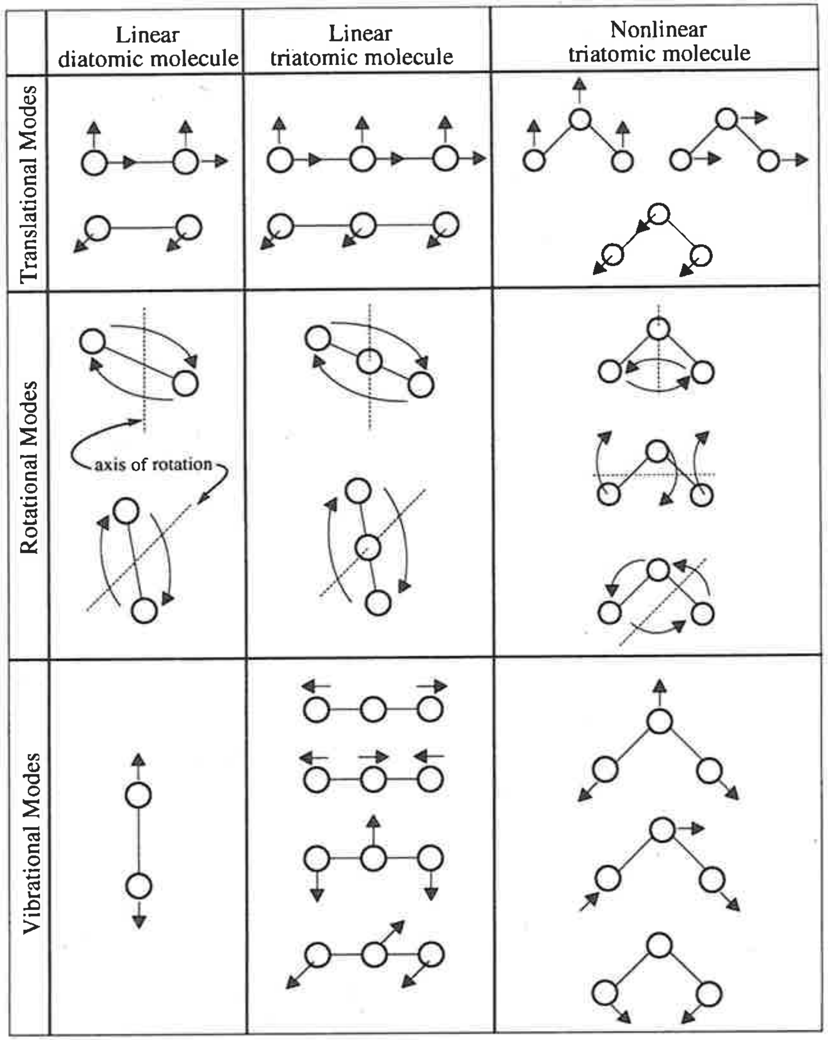


Figure 2.7 Illustration of molecular translational, rotational, and vibrational motions.

the Earth is too cold for the vibrationally excited states to be significantly populated. Thus the heat capacity of the major gases in the Earth's atmosphere do not have a contribution from the vibrational modes and are essentially invariant with temperature. The heat capacity of water vapor shows a weak temperature dependence, associated with weak population of excited vibrational states.

For the major atmospheric gases at typical Earth temperatures, the specific heat capacities at constant volume have been determined to be

$$c_v = (3/2)R \textit{ for a monatomic gas}$$
$$c_v = (5/2)R \textit{ for a diatomic gas}$$
$$c_v = 3R \textit{ for a nonlinear triatomic gas}$$

Since $c_p = c_v + R$, we also have

$$c_p = (5/2)R \textit{ for a monatomic gas}$$
$$c_p = (7/2)R \textit{ for a diatomic gas}$$
$$c_p = 4R \textit{ for nonlinear triatomic gas}$$

Air is composed of 98.6% diatomic gases, and thus the values of c_v and c_p for air can be estimated to be 717.76 J K^{-1} kg^{-1} and 1004.86 J K^{-1} kg^{-1}, respectively.

Specific heat capacities of liquids and solids depend on temperature, and are frequently expressed by a polynomial expression with empirically determined coefficients. Heat capacities of liquids are generally greater than those of solids and gases. The specific heat of pure water at surface pressure has been determined empirically to be (Millero *et al.*, 1973)

$$\begin{aligned} c_p(0,T,0) &= 4217.4 - 3.72083\,T + 0.1412855\,T^2 \\ &\quad - 2.654387\times 10^{-3}\,T^3 + 2.093236\times 10^{-5}\,T^4 \end{aligned} \tag{2.53}$$

where c_p is in J kg^{-1} K^{-1}, T is in °C, and $p = 0$. The influence of salinity is accounted for by

$$\begin{aligned} c_p(s,T,0) &= c_p(0,T,0) + s\,(-7.644 + 0.107276\,T - 1.3839\times 10^{-3}\,T^2) \\ &\quad + s^{3/2}\,(0.17709 - 4.0772\times 10^{-3}\,T + 5.3539\times 10^{-5}\,T^2) \end{aligned} \tag{2.54}$$

where s is in psu and $p = 0$. Applications of the formula can be checked against $c_p(40, 40, 0) = 3981.050$ J kg^{-1} K^{-1}. For pure water, the specific heat decreases with increasing temperature. The same effect is observed in seawater with low salinities and low temperatures (Figure 2.8). If the salinity exceeds 25 psu, the temperature effect is reversed and c_p increases with increasing temperature. This reversal in sign occurs at lower temperatures for increases in salinity. The specific heat decreases with increasing salinity.

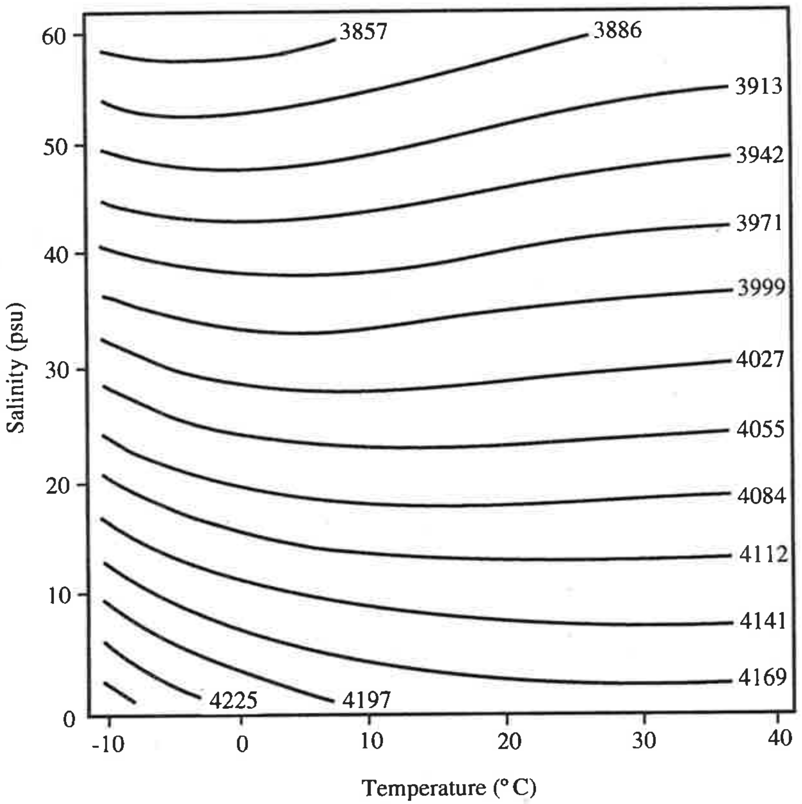


Figure 2.8 Relationship between specific heat, temperature, and salinity for $p = 0$. At high salinities, the specific heat increases with increasing temperature.

The variation of specific heat with pressure can be derived as follows. We begin with the definition of specific heat (2.15b):

$$c_p = \frac{\partial h}{\partial T} = T\left(\frac{\partial \eta}{\partial T}\right) \tag{2.55}$$

Substituting (2.31) into (2.55), we have

$$c_p = \frac{\partial u}{\partial T} + p\left(\frac{\partial v}{\partial T}\right) \tag{2.56}$$

Taking the derivative of (2.31) with respect to pressure gives

$$T\left(\frac{\partial \eta}{\partial p}\right) = \frac{\partial u}{\partial p} + p\left(\frac{\partial v}{\partial p}\right) \tag{2.57}$$

Subtracting the pressure derivative of (2.56) from the temperature derivative of (2.57) and using Maxwell's relation (2.52) gives the desired result

$$\frac{\partial c_p}{\partial p} = -T\left(\frac{\partial^2 v}{\partial T^2}\right) \tag{2.58}$$

which is determined easily from observations of temperature and specific volume.

The difference $c_p - c_v$ for seawater can be evaluated in the following way. Since entropy is an exact differential, we may write

$$T d\eta = T\left(\frac{\partial \eta}{\partial T}\right)_v dT + T\left(\frac{\partial \eta}{\partial v}\right)_T dv$$

Dividing by dT while holding p constant, we find that

$$T\left(\frac{\partial \eta}{\partial T}\right)_p = T\left(\frac{\partial \eta}{\partial T}\right)_v + T\left(\frac{\partial \eta}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p \tag{2.59}$$

From (2.55), we see that $c_p = T(\partial\eta/\partial T)_p$. Since $c_v = T(\partial\eta/\partial T)_v$, we have from (2.59)

$$c_p = c_v + T\left(\frac{\partial \eta}{\partial v}\right)\left(\frac{\partial v}{\partial T}\right)$$

Using (2.51) we can write

$$c_p = c_v + T\left(\frac{\partial p}{\partial T}\right)\left(\frac{\partial v}{\partial T}\right)$$

Using the chain rule for differentiation, we can write $(\partial p/\partial T) = -(\partial p/\partial v) \times (\partial v/\partial T)$ and thus

$$c_p - c_v = -T\left(\frac{\partial p}{\partial v}\right)\left(\frac{\partial v}{\partial T}\right)^2 \tag{2.60}$$

Hence the value of $c_p - c_v$ is easily obtained from (2.60) by measuring the compressibility (1.31b) and the thermal expansion coefficient (1.31a). Because of the near incompressibility of water, there is very little difference in the values of c_p and c_v. It can be shown from (2.60) that the ratio c_p/c_v for seawater at a salinity of 34.85 psu varies between 1.004 at 0°C and 1.0207 at 30°C. Thus, a distinction is commonly not made between the specific heats at constant pressure and volume for seawater.

2.10 Dry Adiabatic Processes in the Atmosphere

In Section 2.4, the following relationship between pressure and temperature was derived for a reversible adiabatic process for an ideal gas:

$$\frac{T_0}{T} = \left(\frac{p_0}{p}\right)^{R/c_p} \tag{2.61}$$

The lifting of air parcels by processes such as orographic lifting, frontal lifting, low-level convergence, and vertical mixing causes pressure to decrease, with a corresponding temperature decrease that is specified by (2.61). The lifting of air parcels can be considered a dry adiabatic process as long as condensation does not occur.

If we choose $p_0 = 1000$ mb to correspond to a temperature θ, (2.61) becomes

$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p} \tag{2.62}$$

where R/c_p for dry air is evaluated to be

$$\frac{R}{c_p} = \frac{R}{c_v + R} = \frac{R}{\frac{5}{2}R + R} = \frac{2}{7} = 0.286$$

The temperature θ is called the *potential temperature*. It is the temperature a sample of gas would have if it were compressed (or expanded) in an adiabatic reversible process from a given state, p and T, to a pressure of 1000 mb. Since θ is a function of two variables of state (p and T), it is itself a variable of state. θ is thus a characteristic of the gas sample and is invariant during a reversible adiabatic process. Such a quantity is called a *conservative quantity*. Because it is conserved for reversible adiabatic processes in the atmosphere, θ is a useful parameter in atmospheric thermodynamics. Potential temperature and other conserved variables will be used throughout the text to simplify the thermodynamic equations and in the context describing air and water mass characteristics.

Consider an atmospheric temperature profile with a lapse rate $\Gamma = 6°\mathrm{C\ km^{-1}}$. For atmospheric pressures less than 1000 mb, the potential temperature of a sample of air is greater than the physical temperature since adiabatic compression must be done to lower the parcel to 1000 mb. Conversely, the potential temperature of a sample of air with pressure greater than 1000 mb will be less than the physical temperature. At a pressure level of 1000 mb, $\theta = T$.

A relationship between entropy and potential temperature for the atmosphere is derived by logarithmically differentiating (2.62):

$$d(\ln\theta) = d(\ln T) - \frac{R}{c_p}\, d(\ln p) \tag{2.63}$$

Comparing (2.63) with (2.23) shows that

$$d\eta = c_p\, d(\ln\theta) \tag{2.64}$$

This means that for reversible processes in an ideal gas, potential temperature may be considered an alternative variable for entropy.

Equation (2.62) does not account for water vapor. The specific heat of moist air is

$$c_p = (1 - q_v)c_{pd} + q_v c_{pv} \approx c_{pd}(1 + 0.87q_v) \tag{2.65}$$

where the subscripts d and v refer to dry air and water vapor, respectively. The ratio R/c_p for moist air can then be determined using (1.23) to be

$$\frac{R}{c_p} = \frac{R_d}{c_{pd}}\left(\frac{1 + 0.608q_v}{1 + 0.87q_v}\right) \approx \frac{R_d}{c_{pd}}(1 - 0.26q_v) \tag{2.66}$$

The potential temperature of moist air then becomes

$$\theta = T\left(\frac{p_0}{p}\right)^{R_d(1-0.26q_v)/c_{pd}} \tag{2.67a}$$

The difference between the dry-air and moist-air values of θ is generally less than 0.1°C, so that adiabatic expansion or compression of moist air can be treated as if it were dry air. Note that θ is not conserved if a phase change of water occurs (see Section 6.7). We can also define a *virtual potential temperature*, θ_v, by neglecting the water vapor dependence of the exponent of (2.67a) and replacing the temperature by the virtual temperature

$$\theta_v = T_v\left(\frac{p_0}{p}\right)^{R_d/c_{pd}} \tag{2.67b}$$

If we consider the adiabatic ascent of a parcel of air in the atmosphere, the temperature of the parcel will decrease and the potential temperature will remain the same. The rate of decrease of temperature with height in an adiabatic ascent can be determined by considering the first law in enthalpy form for an adiabatic process (2.19b):

$$c_p\, dT = v\, dp$$

If we assume that the ascent of the parcel does not involve any large vertical accelerations and the hydrostatic relation applies, we can substitute the hydrostatic relation into (2.19b) to give

$$c_p\, dT = -g\, dz$$

Recalling that the definition of lapse rate is $\Gamma = -dT/dz$, we can write an expression for the *dry adiabatic lapse rate*, Γ_d, as

$$\Gamma_d = \frac{g}{c_{pd}} \tag{2.68}$$

which has a value of approximately $9.8°\mathrm{C\ km^{-1}}$. Both (2.62) and (2.68) describe the temperature evolution of a parcel of air in dry adiabatic ascent, but (2.68) is slightly more restrictive than (2.62) in that it applies only to a hydrostatic process. The adiabatic lapse rate for moist air differs only slightly from (2.68) and can be expressed as

$$\Gamma = \frac{g}{c_{pd}(1 + 0.87q_v)}$$

Outside of clouds, diabatic processes such as radiative heating operate on much longer timescales than the characteristic time scale of vertical displacement of the air parcel. Therefore, the lifting of air parcels by processes such as orographic lifting, frontal lifting, low-level convergence, and vertical mixing can be considered dry adiabatic processes as long as condensation does not occur.