

Chapter 3

Moist thermodynamics

In order to understand atmospheric convection, we need a deep understanding of the thermodynamics of mixtures of gases and of phase transitions. We begin with a review of some of the fundamental ideas of statistical mechanics as it applies to the atmosphere. We then derive the entropy and chemical potential of an ideal gas and a condensate. We use these results to calculate the saturation vapor pressure as a function of temperature. Next we derive a consistent expression for the entropy of a mixture of dry air, water vapor, and either liquid water or ice. The equation of state of a moist atmosphere is then considered, resulting in an expression for the density as a function of temperature and pressure. Finally the governing thermodynamic equations are derived and various alternative simplifications of the thermodynamic variables are presented.

3.1 Review of fundamentals

In statistical mechanics, the entropy of a system is proportional to the logarithm of the number of available states:

$$S(E, M) = k_B \ln(\delta\mathcal{N}), \quad (3.1)$$

where $\delta\mathcal{N}$ is the number of states available in the internal energy range $[E, E + \delta E]$. The quantity $M = mN/N_A$ is the mass of the system, which we relate to the number of molecules in the system N , the molecular weight of these molecules m , and Avogadro's number N_A . The quantity k_B is Boltzmann's constant.

Consider two systems in thermal contact, so that they can exchange energy. The total energy of the system $E = E_1 + E_2$ is fixed, so that if the energy of system 1 increases, the energy of system 2 decreases correspondingly. Likewise, the total entropy of the system is the sum of the entropies of each part, $S = S_1 + S_2$. In equilibrium, the total entropy will be at a maximum, which means that the partial derivative of entropy with respect to E_1 will be zero. Furthermore, since $dE_1 = -dE_2$, we have at thermal equilibrium

$$\frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0, \quad (3.2)$$

which tells us that $\partial S_1/\partial E_1 = \partial S_2/\partial E_2$. The thermodynamic definition of *temperature* T is given by

$$\frac{1}{T} = \frac{\partial S}{\partial E}, \quad (3.3)$$

so at thermal equilibrium we have $T_1 = T_2$.

If the two systems are also in diffusive equilibrium, with as many molecules going from system 1 to system 2 as vice versa, then we have in analogy to equation (3.2)

$$\frac{\partial S}{\partial M_1} = \frac{\partial S_1}{\partial M_1} + \frac{\partial S_2}{\partial M_1} = \frac{\partial S_1}{\partial M_1} - \frac{\partial S_2}{\partial M_2} = 0, \quad (3.4)$$

where the total mass $M = M_1 + M_2$ is constant so that the change in the mass of one system is minus the change in mass of the other system $dM_2 = -dM_1$. Thus, the condition for diffusive equilibrium is $\partial S_1/\partial M_1 = \partial S_2/\partial M_2$. The *chemical potential* μ is defined by

$$\frac{\mu}{T} = -\frac{\partial S}{\partial M}, \quad (3.5)$$

so the condition for diffusive equilibrium (but not necessarily thermal equilibrium) is $\mu_1/T_1 = \mu_2/T_2$. If thermal equilibrium also exists, then this simplifies to $\mu_1 = \mu_2$.

In most physical systems the entropy is also a function of one or more external parameters as well as of the internal energy and mass of the system. For instance, the entropy of an ideal gas is also a function of the volume V in which the gas is contained. Taking the differential of the entropy $S = S(E, M, V)$, we find

$$dS = \frac{\partial S}{\partial E}dE + \frac{\partial S}{\partial M}dM + \frac{\partial S}{\partial V}dV = \frac{1}{T}dE - \frac{\mu}{T}dM + \frac{\partial S}{\partial V}dV. \quad (3.6)$$

| Constant | Value | Meaning |
|------------|---|--|
| k_B | $1.38 \times 10^{-23} \text{ J K}^{-1}$ | Boltzmann's constant |
| N_A | 6.02×10^{23} | Avogadro's number |
| R | 8.314 J K^{-1} | Universal gas constant |
| m_D | 28.9 g mol^{-1} | Molecular weight of dry air |
| m_V | 18.0 g mol^{-1} | Molecular weight of water |
| ϵ | 0.623 | m_V/m_D |
| R_D | $287 \text{ J K}^{-1} \text{ kg}^{-1}$ | Gas constant for dry air R/m_D |
| R_V | $461 \text{ J K}^{-1} \text{ kg}^{-1}$ | Gas constant for water vapor R/m_V |
| C_{PD} | $1005 \text{ J K}^{-1} \text{ kg}^{-1}$ | Specific heat of dry air at const pres |
| C_{VD} | $718 \text{ J K}^{-1} \text{ kg}^{-1}$ | Specific heat of dry air at const vol |
| C_{PV} | $1850 \text{ J K}^{-1} \text{ kg}^{-1}$ | Specific heat of water vapor at const pres |
| C_{VV} | $1390 \text{ J K}^{-1} \text{ kg}^{-1}$ | Specific heat of water vapor at const vol |
| C_L | $4218 \text{ J K}^{-1} \text{ kg}^{-1}$ | Specific heat of liquid water |
| C_I | $1959 \text{ J K}^{-1} \text{ kg}^{-1}$ | Specific heat of ice (-20° C) |
| μ_{BL} | $3.15 \times 10^6 \text{ J kg}^{-1}$ | Binding energy for liquid water |
| μ_{BI} | $2.86 \times 10^6 \text{ J kg}^{-1}$ | Binding energy for ice |
| e_{SF} | 611 Pa | Saturation vapor pressure at freezing |
| T_F | 273.15 K | Freezing point |
| p_R | 10^5 Pa | Reference pressure |

Table 3.1: Thermodynamic constants.

Solving for dE results in a familiar equation:

$$dE = TdS - T \frac{\partial S}{\partial V} dV + \mu dM. \quad (3.7)$$

The second term on the right side of the above equation is the mechanical work done by the system on the outside world. Thus the coefficient of dV must be the pressure if the system under consideration is a gas:

$$T \frac{\partial S}{\partial V} = p. \quad (3.8)$$

The physical meaning of the chemical potential is now clear; $-\mu/T$ is the entropy per unit mass added to the system by inward mass transfer at constant energy and volume.

3.2 Ideal gas again

The entropy of a diatomic ideal gas is given by

$$S = \left(\frac{MR}{m}\right) \left[\frac{5}{2} \ln\left(\frac{E}{M}\right) + \ln\left(\frac{V}{M}\right) + D \right] \quad (3.9)$$

where $R = N_A k_B$ is the universal gas constant, N_A being Avogadro's number. The constant D can be taken as arbitrary for our purposes. The factor of $5/2$ changes to $3/2$ for a monatomic gas and 3 for non-linear triatomic molecules such as water.

The temperature may be obtained from equation (3.3), from which we find that

$$E = \frac{5MRT}{2m} = MC_V T, \quad (3.10)$$

where $C_V = 5RT/(2m)$ is the *specific heat at constant volume*. The specific energy, or the energy per unit mass, is given by

$$e = C_V T. \quad (3.11)$$

The pressure comes from equation (3.8) with the ideal gas law as a result:

$$p = \frac{MRT}{mV} = \frac{RT\rho}{m}. \quad (3.12)$$

The density is defined $\rho = M/V$. The chemical potential, as defined by equation (3.5), is

$$\mu = C_P T - sT \quad (3.13)$$

where $C_P = C_V + R/m = 7R/(2m)$ is the *specific heat at constant pressure* and $s = S/M$ is the *specific entropy*, or the entropy per unit mass. Finally, the specific enthalpy is defined as

$$h = e + p/\rho = C_P T. \quad (3.14)$$

The specific entropy, which is the preferred form of entropy for atmospheric thermodynamics, may be recast in terms of the temperature and density, temperature and pressure, or pressure and density, using the ideal gas law:

$$\begin{aligned} s &= C_V \ln(T/T_R) - (R/m) \ln(\rho/\rho_R) + s_R \\ &= C_P \ln(T/T_R) - (R/m) \ln(p/p_R) + s_R \\ &= C_V \ln(p/p_R) - C_p \ln(\rho/\rho_R) + s_R. \end{aligned} \quad (3.15)$$

The constant reference values T_R , p_R , and ρ_R are those values related by the ideal gas law which yield a specific entropy equal to s_R .

3.3 Equation of state for air

Air effectively consists of a mixture of gases in constant proportions plus water vapor in variable proportions plus any condensate content. Treating the gaseous components of air as ideal gases, we first consider all gas components with the exception of water vapor. The partial pressure of this dry gaseous component is the sum of the partial pressures of the constituent gases:

$$p_D = \sum p_i = RT \sum (\rho_i/m_i) = RT\rho_D/m_D = R_D T \rho_D, \quad (3.16)$$

where $R_D = R/m_D$ is the gas constant for dry air and the total density of dry air is the sum of the component densities

$$\rho_D = \sum \rho_i. \quad (3.17)$$

The mean molecular weight of the dry air is defined by

$$\frac{1}{m_D} = \frac{1}{\rho} \sum \left(\frac{\rho_i}{m_i} \right). \quad (3.18)$$

Dry air as a whole thus satisfies the ideal gas law with a molecular weight m_D . A similar equation exists for the vapor pressure of water:

$$p_V = R_V T \rho_V \quad (3.19)$$

where $R_V = R/m_V$ is the gas constant for water vapor.

The total pressure is the sum of the partial pressures of dry air and water vapor. Applying the ideal gas law to each of these components results in

$$p = p_D + p_V = RT \left(\frac{\rho_D}{m_D} + \frac{\rho_V}{m_V} \right) = \frac{RT\rho}{m_D} \left[1 + \frac{\rho_V}{\rho} \left(\frac{m_D}{m_V} - 1 \right) \right]. \quad (3.20)$$

The ratio $\rho_V/\rho = \rho_V/(\rho_D + \rho_V) = r_V/(1 + r_V) \approx r_V$ where $r_V = \rho_V/\rho_D$ is the mixing ratio of water vapor. Furthermore $m_D/m_V - 1 \approx 0.61$, so to a good approximation in the Earth's atmosphere,

$$p = R_D T \rho (1 + 0.61 r_V) \quad (3.21)$$

where $R_D = R/m_D$ is the gas constant for dry air. The quantity

$$T_V = T(1 + 0.61r_V) \quad (3.22)$$

is called the virtual temperature. It allows the dependence of the equation of state for air on moisture to be swept under the rug, resulting in the simple form

$$p = R_D T_V \rho. \quad (3.23)$$

3.4 Condensed matter

From elementary quantum statistical mechanics, the entropy of a collection of N identical harmonic oscillators with classical resonance frequency $\omega = E_0/\hbar$ and total energy E is

$$S = Nk_B \left[\ln \left(\frac{E - U}{NE_0} \right) + \text{const} \right] \quad (3.24)$$

where U is the potential energy of the oscillators exclusive of the oscillator potential energy. This potential energy could arise, for instance, if the entire set of oscillators exists in a potential well.

We can approximate the entropy of a blob of condensed matter at room temperature by this equation if we assume that each molecule is associated with three oscillators, one for each dimension. We first rewrite this equation in terms of the mass M of the blob rather than the number of oscillators, realizing that $Nk_B = 3nR = 3MR/m \equiv MC_C$, where k_B is Boltzmann's constant, n is the number of moles, m is the molecular weight of the condensate, and C_C is the specific heat:

$$S = MC_C \left[\ln \left(\frac{E - U}{M} \right) + D \right]. \quad (3.25)$$

The quantity D is an arbitrary constant.

To apply this equation to a real condensate we have to take into account the fact that the oscillators exist in a potential well with binding energy per unit mass μ_B . We also have to take into account the fact that the condensate is an elastic medium on the macroscopic scale, so that compressing it adds internal energy and therefore decreases binding energy. To the extent that the compression remains small and elastic, the potential energy is

$U = -M\mu_B + Mk(V/M - 1/\rho_C)^2/2$ where V is the compressed volume of the condensate and ρ_C is its uncompressed density. When there is no compression $V/M = 1/\rho_C$, and the last term vanishes. The constant k is related to the compressibility of the condensate. The result is

$$S = MC_C\{\ln[E/M + \mu_B - k(V/M - 1/\rho_C)^2/2] + D\}. \quad (3.26)$$

Applying equations (3.3) and (3.5), we find the temperature T

$$C_C T = E/M + \mu_B - k(V/M - 1/\rho_C)^2/2 \quad (3.27)$$

and chemical potential μ :

$$\mu = -sT + E/M - (kV/M)(V/M - 1/\rho_C), \quad (3.28)$$

where $s = S/M$ is the specific entropy. Using equations (3.8) and (3.27) we find an expression for the pressure:

$$p = -k(V/M - 1/\rho_C). \quad (3.29)$$

Using equations (3.27) and (3.29), we can rewrite the specific entropy in terms of just the temperature

$$s = C_C \ln(T/T_R) + s_{RC}, \quad (3.30)$$

where s_{RC} is the entropy of the condensate at the reference temperature T_R , and the chemical potential in terms of temperature, volume, mass, and pressure

$$\mu = -sT + C_C T - \mu_B + pV/M + p^2/(2k). \quad (3.31)$$

The term quadratic in pressure $p^2/(2k) = k(V/M - 1/\rho_C)^2/2$ can be omitted from the chemical potential under ordinary conditions since it is typically much less than μ_B . Furthermore, since the density of a condensate changes little under ordinary pressures, we can set $V/M = 1/\rho_C$ in this equation:

$$\mu = -sT + C_C T - \mu_B + p/\rho_C. \quad (3.32)$$

Finally, we use equation (3.27) to obtain an expression for the specific energy $e = E/M$:

$$e = C_C T - \mu_B. \quad (3.33)$$

The specific enthalpy is

$$h = e + pV/M = C_C T - \mu_B + p/\rho_C. \quad (3.34)$$

Terms involving $p^2/(2k)$ have been dropped in the specific energy and enthalpy equations as was done in the chemical potential equation.

3.5 Vapor and condensate in equilibrium

In equilibrium the vapor pressure of water equals its saturation vapor pressure. Since diffusive as well as thermal equilibrium exists between the phases, the temperatures and chemical potentials of the two phases must be equal. From equations (3.13) and (3.15) we find that the chemical potential of the vapor phase of water is

$$\mu_V = C_{PV}T[1 - \ln(T/T_R)] + (R_V T) \ln(p_V/p_R) - s_{RV}T \quad (3.35)$$

where C_{PV} is the specific heat of water vapor at constant pressure, T_R is a constant reference temperature, $R_V = R/m_V$ is the gas constant for water vapor, p_V is the partial pressure of water vapor, p_R is a constant reference pressure, and s_{RV} is the specific entropy of water vapor when T and p_V equal their reference values. Similarly, the chemical potential for condensed water is obtained from equations (3.30) and (3.32):

$$\mu_C = C_C T[1 - \ln(T/T_R)] - \mu_B + p_C/\rho_w - s_{RC}T \quad (3.36)$$

where C_C is the specific heat of the condensate, μ_B is its specific binding energy, p_C is the pressure in the condensate, ρ_w is the condensate density, and s_{RC} is the specific entropy of the condensate at temperature $T = T_R$.

Equating these two chemical potentials and solving for the vapor pressure of water p_V , which in equilibrium equals the saturation vapor pressure e_S yields

$$e_S = p_R \left(\frac{T_R}{T} \right)^{(C_C - C_{PV})/R_V} \exp \left(\frac{s_{RV} - s_{RC} + C_C - C_{PV}}{R_V} - \frac{\mu_B - p_C/\rho_w}{R_V T} \right). \quad (3.37)$$

A simple way to write this is

$$e_S = e_{SF} \left(\frac{T_F}{T} \right)^{(C_C - C_{PV})/R_V} \exp \left[\frac{\mu_B}{R_V} \left(\frac{1}{T_F} - \frac{1}{T} \right) \right] \exp \left(\frac{p_C}{R_V T \rho_w} \right), \quad (3.38)$$

where all of the left over constants have been absorbed into the constant e_{SF} . We have taken the freezing point $T_F = T_R$ as a convenient reference temperature. In practice e_{SF} is the saturation vapor pressure at $T = T_F$ and $p_C = 0$, and is determined by experiment, as is μ_B .

The condensate pressure in the last factor in equation (3.38) is conventionally approximated by zero, since this normally introduces a fractional

error of only about 0.001 in most atmospheric problems. However, there are applications in cloud physics for which this term is very important, as we shall see later.

3.6 Moist entropy

We now have the tools to compute the specific entropy of air containing water vapor and possibly condensate in the form of small water or ice particles which move with the airflow.

The entropy per unit mass of dry air under these conditions is

$$s = s_D + r_V s_V + r_C s_C, \quad (3.39)$$

where

$$s_D = C_{PD} \ln(T/T_R) - R_D \ln(p_D/p_R) + s_{RD} \quad (3.40)$$

is the specific entropy of dry air, C_{PD} is the specific heat of dry air at constant pressure, $R_D = R/m_D$ where m_D is the molecular weight of dry air, p_D is the partial pressure of dry air, s_{RD} is the constant reference entropy for dry air,

$$s_V = C_{PV} \ln(T/T_R) - R_V \ln(p_V/p_R) + s_{RV} \quad (3.41)$$

is the specific entropy of water vapor, C_{PV} is the specific heat of water vapor at constant pressure, $R_V = R/m_V$ where m_V is the molecular weight of water vapor, p_V is the partial pressure of water vapor, s_{RV} is the constant reference entropy for water vapor, and

$$s_C = C_C \ln(T/T_R) + s_{RC} \quad (3.42)$$

is the specific entropy of condensate (either liquid water or ice), C_C is its specific heat, and s_{RC} is the constant reference entropy for the condensate. The mixing ratio of water vapor is defined as the ratio of the densities of vapor and dry air, $r_V = \rho_V/\rho_D$, with a similar definition for the condensate mixing ratio in terms of the densities of condensate and dry air, $r_C = \rho_C/\rho_D$.

Substituting these expressions into equation (3.39) and rearranging, we get

$$s = (C_{PD} + r_V C_{PV} + r_C C_C) \ln(T/T_R) - R_D \ln(p_D/p_R) - r_V R_V \ln(p_V/p_R) + s_{RD} + r_V s_{RV} + r_C s_{RC}. \quad (3.43)$$

For many purposes this is a perfectly adequate form for the moist entropy. However, an alternate form is more commonly used, which takes advantage of the fact that $p_V/p_R = (p_V/e_S)(e_S/p_R) = \mathcal{H}(e_S/p_R)$, where \mathcal{H} is the relative humidity. The ratio e_S/p_R may be obtained from equation (3.37), resulting in the form

$$s = (C_{PD} + r_T C_C) \ln(T/T_R) - R_D \ln(p_D/p_R) + \frac{L_C r_V}{T} - r_V R_V \ln \mathcal{H} + s_{RD} + r_T s_{RC}, \quad (3.44)$$

where the *total cloud water mixing ratio* $r_T = r_V + r_C$ appears, and where the temperature-dependent *latent heat* is defined

$$L_C = \mu_B - (C_C - C_{PV})T. \quad (3.45)$$

We have ignored the term containing the pressure in the condensate p_C , as this is normally small as long as the condensate occurs in sufficiently large particles (see the chapter on cloud physics).

The final bit of physics needed is the fact that liquid and ice co-exist in diffusive equilibrium at the freezing temperature T_F . (The freezing point does not vary with pressure with the approximations used here for the entropy of the condensate, so the triple point has the same temperature as the freezing point in our treatment.) Setting the chemical potentials of ice and liquid to each other at the freezing point and taking this temperature as our reference temperature, we find

$$(C_L - s_{RL})T_F - \mu_{BL} = (C_I - s_{RI})T_F - \mu_{BI}, \quad (3.46)$$

where a subscripted L indicates liquid and a subscripted I indicates ice. This can be rearranged to yield

$$s_{RI} - s_{RL} = \frac{L_L(T_F) - L_I(T_F)}{T_F} \quad (3.47)$$

where the latent heats of condensation and fusion are defined

$$L_L(T) = \mu_{BL} - (C_L - C_{PV})T \quad (3.48)$$

and

$$L_I(T) = \mu_{BI} - (C_I - C_{PV})T. \quad (3.49)$$

We finally arrive at consistent equations for the entropy of moist air for temperatures warmer

$$s = (C_{PD} + r_T C_L) \ln(T/T_F) - R_D \ln(p_D/p_R) + \frac{L_L r_V}{T} - r_V R_V \ln \mathcal{H}, \quad T > T_F, \quad (3.50)$$

and colder

$$s = (C_{PD} + r_T C_I) \ln(T/T_F) - R_D \ln(p_D/p_R) + \frac{L_I r_V}{T} - r_V R_V \ln \mathcal{H} - \frac{[L_I(T_F) - L_L(T_F)] r_T}{T_F}, \quad T < T_F \quad (3.51)$$

than freezing. In these equations we have set $s_{RD} = s_{RL} = 0$, which leaves us with

$$s_{RI} = \frac{L_L(T_F) - L_I(T_F)}{T_F} \quad (3.52)$$

according to equation (3.47). Setting $T_R = T = T_F$ in equation (3.37), substituting condensate constants appropriate to liquid water, and using equation (3.48) we find that

$$s_{RV} = \frac{L_L(T_F)}{T_F} + R_V \ln(e_{SF}/p_R). \quad (3.53)$$

Using the above choices for entropy constants and reference temperature, we finally rewrite equation (3.43) into a form which is valid both above and below freezing:

$$s = (C_{PD} + r_V C_{PV} + r_L C_L + r_I C_I) \ln(T/T_F) - R_D \ln(p_D/p_R) - r_V R_V \ln(p_V/e_{SF}) + \frac{L_L(T_F) r_V + [L_L(T_F) - L_I(T_F)] r_I}{T_F}. \quad (3.54)$$

In deriving this equation we assume that $r_L = 0$ for $T < T_F$ and $r_I = 0$ for $T > T_F$. We can write the vapor pressure of water p_V in terms of the mixing ratio r_V using the ideal gas law for each of these components:

$$\frac{p_V}{p_D} = \frac{R_V T \rho_V}{R_D T \rho_D} = \frac{r_V}{\epsilon} \quad (3.55)$$

where $\epsilon = m_V/m_D = 0.623$.

So far we have not specified the reference pressure for dry air, p_R . It is convenient to set this to $p_R = 10^5$ Pa, which is near sea level pressure.

3.7 Thermodynamic governing equations

Equation (3.6) tells us that the entropy change in an open parcel of ideal gas takes the form

$$dS = \frac{dE}{T} + \frac{pdV}{T} - \frac{\mu dM}{T}. \quad (3.56)$$

The parcel is open because mass is allowed to flow in and out of it. If $dM = 0$, then the parcel is closed and $dS \equiv dS_{closed} = dE/T + (p/T)dV$, allowing us to rewrite equation (3.56) as

$$dS = dS_{closed} - \frac{\mu dM}{T}. \quad (3.57)$$

The entropy of a closed parcel of gas may be altered by heating or cooling it or by compressing or expanding it abruptly. The latter process is unimportant for atmospheric parcels in normal meteorological events, so we consider only the effects of heating. The entropy change due to the addition of heat dQ is dQ/T , so considering both this and the addition of mass, the entropy change of an open atmospheric parcel is

$$dS = \frac{dQ}{T} - \frac{\mu dM}{T}. \quad (3.58)$$

This equation is also valid for the change in the entropy of a condensate, since the same considerations apply.

We now limit the flow of matter in and out of our parcel to water substance, and insist that the mass of dry air remain fixed. We get the total change in entropy of our parcel by summing the entropy changes for the three components, dry air, water vapor, and advected condensate, i. e., liquid drops or ice particles small enough to be advected with the flow of dry air:

$$\begin{aligned} dS &= dS_D + dS_V + dS_C \\ &= \frac{dQ}{T} - \frac{\mu_V dM_V}{T} - \frac{\mu_C dM_C}{T}. \end{aligned} \quad (3.59)$$

The heating of all three components is combined into a single dQ and the mass change for the dry air component is omitted because this is zero by hypothesis. Dividing this equation by M_D converts it into an equation for

the change due to heating and mass exchange of the specific entropy derived in the previous section:

$$ds = \frac{dq}{T} - \frac{\mu_V dr_V}{T} - \frac{\mu_C dr_C}{T}, \quad (3.60)$$

where dq is the heat added per unit mass. If conversion of vapor to condensate and vice versa occurs in a reversible fashion, then $\mu_C = \mu_V$ whenever there is condensate present. This simplifies the above equation to

$$ds = \frac{dq}{T} - \frac{\mu_V dr_T}{T}, \quad (3.61)$$

where $r_T = r_V + r_C$ is the total cloud water mixing ratio as before and the chemical potential for water vapor has been substituted in the last term on the right. This is valid even when no condensate is present, as r_T just reduces to r_V in that case. Furthermore, since s is a state variable, it is valid even if intermediate processes are non-reversible.

With the reference entropy values we have chosen, equations (3.41) and (3.53) show that

$$\frac{\mu_V}{T} = C_{PV} - s_V = -\frac{L_L(T_F)}{T_F} + C_{PV} \left[1 - \ln \left(\frac{T}{T_F} \right) \right] + R_V \ln \left(\frac{p_V}{e_{SF}} \right) \quad (3.62)$$

where e_{SF} is the saturation vapor pressure of water at freezing. The first term on the right in equation (3.62) is typically at least 10 times as big as the other terms, so $C_{PV} - s_V$ varies only slightly from the constant value $-L_L(T_F)/T_F$. Thus, the coefficient of dr_T is nearly constant for typical ranges of atmospheric temperature and water vapor mixing ratio. However, the variations in this coefficient play an important role in the irreversible generation of entropy.

We have excluded from r_T condensate particles which are large enough to fall relative to the air, i. e., precipitation particles. Our governing equation for r_T must take this into account. It must also take include the effects of the eddy flux of moisture relative to the dry air parcel:

$$\frac{dr_T}{dt} = \nabla \cdot (K \nabla r_T) + E - P, \quad (3.63)$$

where K is the eddy mixing coefficient, E is the evaporation rate of precipitation and P is its formation rate per unit mass of dry air. Putting all this

together, we arrive at a governing equation for the entropy valid in mixed phase conditions

$$\frac{ds}{dt} = \frac{H}{T} - \frac{\mu_V}{T} \frac{dr_T}{dt} \quad (3.64)$$

where $H = dq/dt$ is the heating rate per unit mass from the emission and absorption of solar and thermal radiation, molecular heat conduction, and viscous dissipation.

3.8 Other thermodynamic variables

A variety of approximately conserved thermodynamic variables besides entropy are used in studies of convection. Here we mention a few and discuss their characteristics.

A simplified form of the entropy is

$$s = C_{PD} \ln(T/T_F) - R_D \ln(p/p_R) + \frac{Lr_V}{T_F}, \quad (3.65)$$

where L is the latent heat of condensation at freezing. This approximation comes from neglecting r_L and r_I in equation (3.54) and neglecting r_V everywhere except where multiplied by L . This also leads to the approximation $p_D = p$. It is sometimes used in numerical models where maximal simplification is desired. A common variation of this formula replaces the constant reference temperature T_F in the latent heat term by the actual temperature. This is actually a serious mistake, since it means that the dry entropy (given by the first two terms on the right side of equation (3.65)), the moist entropy s , and the water vapor mixing ratio r_V are not all simultaneously conserved in transformations which change the temperature but remain non-condensing. Use of this variation should be avoided.

Meteorologists use a variable called the *equivalent potential temperature*, which can be approximated roughly as

$$\theta_e = T_R \exp(s/C_P) = T(p_R/p)^{R_D/C_{PD}} \exp[Lr_V/(C_{PD}T_R)], \quad (3.66)$$

where the simplified entropy given by equation (3.65) has been substituted. The equivalent potential temperature is defined by the meteorologists as the temperature of a parcel carried moist adiabatically to very low pressure so as to condense out all the water, and then compressed dry adiabatically to the reference pressure.

The *pseudo-adiabatic* equivalent potential temperature is the version of equivalent potential temperature which is constant under adiabatic expansion with all condensed water removed as it is formed.

The *reversible* equivalent potential temperature is related to the entropy as defined by equation (3.50)

$$\theta_e = T_F \exp[s/(C_{PD} + r_T C_L)]. \quad (3.67)$$

The extra term $r_T C_L$ is included to make the equivalent potential temperature proportional to the temperature when the entropy is substituted. However, it has the unfortunate side effect of giving the entropy and the equivalent potential temperature different conservation properties when r_T varies, perhaps as a result of the fallout of precipitation.

The final variable we consider is the *moist static energy*. From the first law of thermodynamics for a closed parcel, we have for a parcel of unit mass

$$C_{PD}dT = dq + \frac{dp}{\rho} \quad (3.68)$$

where q is the heat added per unit mass. We thus ignore the contribution of vapor and condensate to the energetics of the system except by virtue of the effect of latent heat release: $dq = -Ldr_V$, where a constant latent heat of condensation L is assumed. The crucial assumption is that the pressure change is given by the hydrostatic equation $dp = -g\rho dz$, which allows us to write

$$d(C_{PD}T + Lr_V + gz) = d\sigma = 0, \quad (3.69)$$

where σ is the moist static energy.

The conservation properties of the moist static energy are problematic, not only from the point of view of the approximate thermodynamic treatment (a problem which can be fixed) but also from the assumption of hydrostatic equilibrium in pressure changes. Rearranging equation (3.68) results in $\rho^{-1}\nabla p = \nabla(C_{PD}T + Lr_V)$ which may be substituted in the momentum equation. Using the identity $\mathbf{v} \cdot \nabla \mathbf{v} = \nabla(v^2/2) - \mathbf{v} \times \zeta$ and dotting the momentum equation with \mathbf{v} , we get

$$\frac{\partial v^2/2}{\partial t} + \mathbf{v} \cdot \nabla(v^2/2 + C_{PD}T + Lr_V + gz) = 0. \quad (3.70)$$

In the steady state where $\partial(v^2/2)/\partial t = 0$, we infer that $v^2/2 + \sigma$ is conserved along streamlines. Thus, σ by itself is not conserved. The error is

often small, but can be significant in extreme cases. In non-steady situations, the conservation properties of σ are undefined, though non-conservation is probably of order $v^2/2$ here as well. However, there seems to be no obvious way to bound the error in the non-steady situation.

3.9 References

Bohren, C. F., and B. A. Albrecht, 1998: *Atmospheric Thermodynamics*. Oxford University Press, 402 pp. An interesting alternative to standard treatments of atmospheric thermodynamics.

Emanuel, K. A., 1994: *Atmospheric Convection*. Oxford University Press, 580 pp. This is a popular text on convection and has extensive coverage of atmospheric thermodynamics.

Groot, S. R. de, and P. Mazur, 1962: *Non-equilibrium thermodynamics*. North-Holland, Amsterdam, 510 pp. This is the place to go for a derivation of the irreversible entropy source.

López Carrillo, C., and D. J. Raymond, 2005: Moisture tendency equations in a tropical atmosphere. *J. Atmos. Sci.*, **62**, 1601-1613. This presents the latest work on moist entropy and moist static energy, and includes a derivation of the moist entropy with ice.

Pauluis, O., and I. M. Held, 2002: Entropy budget of an atmosphere in radiative-convective equilibrium. Part I: Maximum work and frictional dissipation. *J. Atmos. Sci.*, **59**, 125-139.

Pauluis, O., and I. M. Held, 2002: Entropy budget of an atmosphere in radiative-convective equilibrium. Part II: Latent heat transport and moist processes. *J. Atmos. Sci.*, **59**, 140-149. This and the previous reference explore the role of precipitation, evaporation, and diffusion of water vapor on the irreversible production of entropy in the atmosphere.

3.10 Problems

1. Given that the mean radiative brightness temperature of the atmosphere is about 259 K i. e., the earth radiates energy at the same rate

as a black body at this temperature, compute the outflow of energy from the earth per unit area per unit time.

2. Assuming that the surface latent heat flux exceeds the surface sensible heat flux by an order of magnitude (true over oceans), estimate the rainfall rate in radiative-convective equilibrium, converting the units to millimeters of rain per day. You will need the answer to the previous problem plus the assumption that all solar radiation is absorbed by the surface and that thermal radiation is emitted from the middle to upper troposphere. Moist convection is responsible for transporting this energy upwards.
3. Given the above-quoted brightness temperature of the earth, that the mean surface temperature of the earth in the tropics is near 300 K, and that most solar radiation is absorbed by the surface before being transferred to the atmosphere, estimate the irreversible entropy production per unit area per unit time in the earth's tropical regions. Hint: Recall that $dS = dQ/T$.
4. Given the rainfall rate in radiative-convective equilibrium and assuming that rainfall is formed on the average at an elevation of 5 km, estimate the work done on the atmosphere by the frictional force of falling raindrops. From this, estimate the irreversible entropy production per area per time due to this frictional heating.
5. Consider a box of volume V with air in it at temperature T and total pressure p . Initially the air in the left half of the box has partial pressure of water vapor equal to $p_V = 0$ whereas the air in the right half of it is $p_V = p_0 > 0$ (non-condensing). Compute the total entropy of the air in the box before moisture diffusion starts and after diffusion has homogenized the vapor pressure in the box. What is the change in the total entropy in the box, and what is the sign of the change? Hint: Take the total entropy in each half of the box as the sum of the entropies of the air and the water vapor. Note that the entropy of a mass M of ideal gas can be written $S = M[C_P \ln(T/T_R) - (R/m) \ln(p/p_R)]$. Also note that the mass of each component in each half of the box is proportional to its partial pressure in that half, since the temperature remains constant throughout the mixing process.

6. Given the velocity field $\mathbf{v}(x, y, z)$ and the kinematic viscosity ν , compute the viscous contribution to the heat source per unit mass H in equation (3.64). Hint: The rate of viscous heat production per unit mass is equal to the rate per unit mass at which mechanical energy is destroyed. Compute the entropy generation rate per unit mass for eddies with a typical outer scale of 10^3 m and a typical velocity at this scale of 10 m s⁻¹. For this problem exclude the precipitation-generated part of the dissipation.
7. Consider a steady flow in which parcels are accelerated from zero velocity to 100 m s⁻¹, such as might occur on being drawn into a jet stream. Compute the change in static energy under these conditions and express the change as an equivalent temperature change by dividing by C_{PD} .