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:

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

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

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

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

$$\frac{1}{T} = \frac{\partial S}{\partial E}, \tag{3.3}$$

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)

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

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

$$\frac{\mu}{T} = -\frac{\partial S}{\partial M}, \tag{3.5}$$

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

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

Solving for dE results in a familiar equation:

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

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:

$$T\frac{\partial S}{\partial V} = p. \tag{3.8}$$

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. The enthalpy of an ideal gas is defined $H = E + pV$. Combining this with equations (3.6) and (3.8) results in

$$dS = \frac{1}{T}dH - \frac{V}{T}dp - \frac{\mu}{T}dM. \tag{3.9}$$

3.2 Ideal gas again

The entropy of a diatomic ideal gas is given by

$$S = \left(\frac{MR}{m}\right)\left[\frac{5}{2}\ln\left(\frac{E}{M}\right) + \ln\left(\frac{V}{M}\right) + D\right] \tag{3.10}$$

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

$$E = \frac{5MRT}{2m} = MC_V T, \tag{3.11}$$

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

$$e = C_V T. \tag{3.12}$$

Constant	Value	Meaning
k_B	1.38×10^{-23} 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 J K^{-1} kg^{-1}	Gas constant for dry air R/m_D
R_V	461 J K^{-1} kg^{-1}	Gas constant for water vapor R/m_V
C_{PD}	1005 J K^{-1} kg^{-1}	Specific heat of dry air at const pres
C_{VD}	718 J K^{-1} kg^{-1}	Specific heat of dry air at const vol
C_{PV}	1850 J K^{-1} kg^{-1}	Specific heat of water vapor at const pres
C_{VV}	1390 J K^{-1} kg^{-1}	Specific heat of water vapor at const vol
C_L	4218 J K^{-1} kg^{-1}	Specific heat of liquid water
C_I	1959 J K^{-1} kg^{-1}	Specific heat of ice ($-20°$ C)
μ_{BL}	3.15×10^6 J kg^{-1}	Binding energy for liquid water
μ_{BI}	2.86×10^6 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.

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

$$p = \frac{MRT}{mV} = \frac{RT\rho}{m}. \tag{3.13}$$

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

$$\mu = C_P T - sT \tag{3.14}$$

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

$$h = e + p/\rho = C_P T. \tag{3.15}$$

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:

$$\begin{aligned} s &= C_V \ln(T/T_R) - (R/m)\ln(\rho/\rho_R) + s_R \\ &= C_P \ln(T/T_R) - (R/m)\ln(p/p_R) + s_R \\ &= C_V \ln(p/p_R) - C_p \ln(\rho/\rho_R) + s_R. \end{aligned} \tag{3.16}$$

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:

$$p_D = \sum p_i = RT \sum (\rho_i/m_i) = RT\rho_D/m_D = R_D T\rho_D, \tag{3.17}$$

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

$$\rho_D = \sum \rho_i. \tag{3.18}$$

The mean molecular weight of the dry air is defined by

$$\frac{1}{m_D} = \frac{1}{\rho_D} \sum \left(\frac{\rho_i}{m_i} \right). \tag{3.19}$$

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:

$$p_V = R_V T \rho_V \tag{3.20}$$

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

$$p = p_D + p_V = RT \left(\frac{\rho_D}{m_D} + \frac{\rho_V}{m_V} \right) = \frac{RT\rho}{m_D} \left[1 + \frac{\rho_V}{\rho} \left(\frac{m_D}{m_V} - 1 \right) \right]. \tag{3.21}$$

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,

$$p = R_D T \rho (1 + 0.61 r_V) \tag{3.22}$$

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

$$T_V = T(1 + 0.61 r_V) \tag{3.23}$$

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

$$p = R_D T_V \rho. \tag{3.24}$$

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

$$S = N k_B \left[\ln \left(\frac{E - U}{N E_0} \right) + \text{const} \right] \tag{3.25}$$

where U is the external potential energy of the oscillators exclusive of the internal oscillator 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 $C_C = 3R/m$ is the specific heat:

$$S = MC_C \left[\ln \left(\frac{E - U}{M} \right) + D \right]. \tag{3.26}$$

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

$$S = MC_C\{\ln[E/M + \mu_B - k(V/M - 1/\rho_C)^2/2] + D\}. \tag{3.27}$$

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

$$C_C T = E/M + \mu_B - k(V/M - 1/\rho_C)^2/2 \tag{3.28}$$

and chemical potential μ:

$$\mu = -sT + e - (kV/M)(V/M - 1/\rho_C), \tag{3.29}$$

where $s = S/M$ is the specific entropy and $e = E/M$ is the specific energy. Using equations (3.8) and (3.28) we find an expression for the pressure:

$$p = -k(V/M - 1/\rho_C). \tag{3.30}$$

Using equations (3.28) and (3.30), we can rewrite the specific entropy in terms of just the temperature

$$s = C_C \ln(T/T_R) + s_{RC}, \qquad (3.31)$$

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

$$\mu = -sT + C_C T - \mu_B + pV/M + p^2/(2k). \qquad (3.32)$$

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 $pV/M = p/\rho$, where ρ is the actual density of the condensate under pressure p. This is easily demonstrated:

$$\frac{p^2/(2k)}{pV/M} = \frac{p\rho}{2k} = -\frac{k(1/\rho - 1/\rho_C)\rho}{2k} = (\rho/\rho_C - 1)/2, \qquad (3.33)$$

which is much less than unity as long as the condensate's density doesn't increase much under compression. Given this near-incompressibility, we can also set $V/M = 1/\rho_C$ in equation (3.32), so that the chemical potential simplifies to

$$\mu = -sT + C_C T - \mu_B + p/\rho_C. \qquad (3.34)$$

Finally, we use equation (3.28) to obtain an expression for the specific energy $e = E/M$:

$$e = C_C T - \mu_B. \qquad (3.35)$$

The specific enthalpy is

$$h = e + pV/M = C_C T - \mu_B + p/\rho_C. \qquad (3.36)$$

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 (3.14) and (3.16) we find that the chemical potential of the vapor phase of water is

$$\mu_V = C_{PV}T[1 - \ln(T/T_R)] + R_V T \ln(p_V/e_{SF}) - s_{RV}T \tag{3.37}$$

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, e_{SF} is a constant reference pressure taken to equal the saturation vapor for freezing, 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 (3.31) and (3.34):

$$\mu_C = C_C T[1 - \ln(T/T_R)] - \mu_B + p_C/\rho_w - s_{RC}T \tag{3.38}$$

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

$$e_S = e_{SF} \left(\frac{T_R}{T}\right)^{(C_C - C_{PV})/R_V} \exp\left(\frac{s_{RV} - s_{RC} + C_C - C_{PV}}{R_V} - \frac{\mu_B - p_C/\rho_w}{R_V T}\right). \tag{3.39}$$

A simple way to write this is

$$e_S = e_{SF} \left(\frac{T_F}{T}\right)^{(C_C - C_{PV})/R_V} \exp\left(\frac{L_C(T_F)}{R_V T_F} - \frac{L_C(T)}{R_V T}\right) \exp\left(\frac{p_C}{R_V T \rho_w}\right), \tag{3.40}$$

where

$$L_C(T) = \mu_B - (C_C - C_{PV})T \tag{3.41}$$

is called the latent heat and where we must satisfy the constraint

$$s_{RV} - s_{RC} = \frac{L_C(T_F)}{T_F}. \tag{3.42}$$

We have taken the freezing point $T_F = T_R$ as a convenient reference temperature. In practice e_{SF} is determined by experiment, as is $L_C(T_F)$, and hence μ_B.

The condensate pressure in the last factor in the exponential in equation (3.40) is conventionally approximated by zero, since this term 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, condensate, either in the form of small water or ice particles that move with the airflow or precipitation that falls relative to the flow.

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

$$s = s_D + r_V s_V + r_C s_C, \tag{3.43}$$

where

$$s_D = C_{PD} \ln(T/T_R) - R_D \ln(p_D/p_R) + s_{RD} \tag{3.44}$$

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, and the reference pressure is unconstrained, but typically chosen to be $p_R = 1000$ hPa.

$$s_V = C_{PV} \ln(T/T_R) - R_V \ln(p_V/e_{SF}) + s_{RV} \tag{3.45}$$

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

$$s_C = C_C \ln(T/T_R) + s_{RC} \tag{3.46}$$

is the specific entropy of both advected condensate (s_C) and precipitation (s_R), 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 advected condensate mixing ratio in terms of the densities of the respective condensate components and dry air $r_C = \rho_C/\rho_D$.

Substituting these expressions into equation (3.43) and rearranging, we get

$$
\begin{aligned}
s &= (C_{PD} + r_V C_{PV} + r_C C_C) \ln(T/T_R) - R_D \ln(p_D/p_R) \\
&\quad - r_V R_V \ln(p_V/e_{SF}) + s_{RD} + r_V s_{RV} + r_C s_{RC}.
\end{aligned} \tag{3.47}
$$

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 $p_V/e_{SF} = \mathcal{H} e_S/e_{SF}$, where $\mathcal{H}$ is the relative humidity. The ratio e_S/e_{SF} may be obtained from equation (3.39), resulting in the form

$$
\begin{aligned}
s &= (C_{PD} + r_T C_C) \ln(T/T_R) - R_D \ln(p_D/p_R) \\
&\quad + \frac{L_C r_V}{T} - r_V R_V \ln \mathcal{H} + s_{RD} + r_T s_{RC},
\end{aligned} \tag{3.48}
$$

where the total cloud water mixing ratio $r_T = r_V + r_C$ appears. 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

$$
(C_L - s_{RL})T_F - \mu_{BL} = (C_I - s_{RI})T_F - \mu_{BI}, \tag{3.49}
$$

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

$$
s_{RI} - s_{RL} = \frac{L_L(T_F) - L_I(T_F)}{T_F} = \frac{L_F(T_F)}{T_F} \tag{3.50}
$$

where the latent heats of condensation and fusion are defined

$$
L_L(T) = \mu_{BL} - (C_L - C_{PV})T \tag{3.51}
$$

and

$$
L_I(T) = \mu_{BI} - (C_I - C_{PV})T. \tag{3.52}
$$

We also define the latent heat of freezing as the difference between the latent heats of fusion and condensation:

$$L_F(T) = L_I(T) - L_L(T) = \mu_{BI} - \mu_{BL} + (C_L - C_I)\,T. \tag{3.53}$$

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

$$
\begin{aligned}
s = {}& (C_{PD} + r_T C_L)\ln(T/T_F) - R_D \ln(p_D/p_R) \\
& + \frac{L_L r_V}{T} - r_V R_V \ln\mathcal{H}, \quad T > T_F,
\end{aligned} \tag{3.54}
$$

and colder

$$
\begin{aligned}
s = {}& (C_{PD} + r_T C_I)\ln(T/T_F) - R_D \ln(p_D/p_R) \\
& + \frac{L_I r_V}{T} - r_V R_V \ln\mathcal{H} \\
& - \frac{L_F(T_F) r_T}{T_F}, \quad T < T_F
\end{aligned} \tag{3.55}
$$

than freezing. We have made the assumption that condensate is ice below freezing and liquid water above freezing. In these equations we have set $s_{RD} = s_{RL} = 0$, which leaves us with

$$s_{RI} = -\frac{L_F(T_F)}{T_F} \tag{3.56}$$

according to equation (3.42). Setting $T_R = T = T_F$ in equation (3.39), substituting condensate constants appropriate to liquid water, and using equation (3.51) we find that

$$s_{RV} = \frac{L_L(T_F)}{T_F}. \tag{3.57}$$

Using the above choices for entropy constants and reference temperature, we finally rewrite equation (3.47) into a form which is valid both above and below freezing,

$$
\begin{aligned}
s = {}& (C_{PD} + r_V C_{PV} + r_L C_L + r_I C_I)\ln(T/T_F) \\
& - R_D \ln(p_D/p_R) - r_V R_V \ln(p_V/e_{SF}) \\
& + \frac{L_L(T_F) r_V - L_F(T_F) r_I}{T_F}.
\end{aligned} \tag{3.58}
$$

In deriving this equation we make the equilibrium assumption 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:

$$\frac{p_V}{p_D} = \frac{R_V T \rho_V}{R_D T \rho_D} = \frac{r_V}{\epsilon} \tag{3.59}$$

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

3.7 Wet-bulb temperature

The wet-bulb temperature T_W is the temperature at which a parcel reaches saturation as condensate is evaporated into it at constant pressure. Since moist entropy is (approximately) conserved in this evaporation process, the wet-bulb temperature may be obtained by inverting the entropy equation (3.58) for temperature, using the actual values of entropy and pressure with the actual vapor pressure and mixing ratio replaced by their saturation values at the wet-bulb temperature. Since these latter values are not known in advance, the calculation is necessarily iterative.

3.8 Governing equations

In this section we consider the governing equations for mass, water substance, and moist entropy in a real atmosphere.

3.8.1 Mass continuity

The fact that water substance can be added to and subtracted from a parcel of air complicates the mass continuity equation. Since the mass of the dry air component is conserved, we define the mass continuity equation in terms of the dry air component only, resulting in

$$\frac{\partial \rho_D}{\partial t} + \nabla \cdot (\rho_D \boldsymbol{v}) = 0 \tag{3.60}$$

where ρ_D is the density of dry air and $\boldsymbol{v}$ is the air velocity. Note in this case that the velocity must be defined as that of the dry air component in order for this equation to be correct.

3.8.2 Water substance

The total water substance divides naturally into three components in the atmosphere, with the total water substance mixing ratio equal to the sum of the vapor mixing ratio r_V, the advected condensate mixing ratio r_C, and the precipitation mixing ratio r_P. It is helpful to consider the vapor and advected condensate together, which gives us the total cloud water mixing ratio $r_T = r_V + r_C$. The cloud water mixing ratio obeys the equation

$$\frac{\partial \rho_D r_T}{\partial t} + \nabla \cdot (\rho_D r_T \boldsymbol{v} - K \nabla r_T) = \rho_D \left(\mathcal{E} - \mathcal{P} \right) - \frac{\partial F_V}{\partial z} \qquad (3.61)$$

where ρ_D is the density of dry air, $\mathcal{E}$ is the evaporation rate of precipitation per unit mass of dry air, $\mathcal{P}$ is the corresponding production rate of precipitation, K is the dynamic eddy mixing coefficient (i.e., it includes the density factor ρ_d), and $F_V(z)$ is the upward diffusive flux of water vapor from the surface into the lowest layers of the atmosphere. Note that eddy mixing tends to homogenize mixing ratios, which explains the form of the eddy mixing term in equation (3.61). The bulk flow velocity $\boldsymbol{v}$ is defined as the velocity of the dry air component.

The precipitation mixing ratio obeys a similar equation

$$\frac{\partial \rho_D r_R}{\partial t} + \nabla \cdot [\rho_D r_R (\boldsymbol{v} - w_T \boldsymbol{k}) - K \nabla r_R] = -\rho_D \left(\mathcal{E} - \mathcal{P} \right) \qquad (3.62)$$

with the exception that the precipitation terminal velocity $-w_T \boldsymbol{k}$ is included and the signs of the precipitation source and sink terms are reversed.

3.8.3 Entropy

The change of entropy of a parcel of air with volume V and fixed dry air mass M_D consists of three parts, the change due to added heat, the change due to added mass, and the change due to phase transformations and other chemistry:

$$dS = dS_{heat} + dS_{mass} + dS_{chem}. \qquad (3.63)$$

The heating part is simply

$$dS_{heat} = \frac{M_D Q dt}{T} \qquad (3.64)$$

where T is the temperature and Q is the heat added per unit mass of dry air per unit time.

We divide the change in mass of component i of the parcel as

$$dO_i = dM_i + dN_i \tag{3.65}$$

where dM_i is the net transfer of the mass of the ith component into the parcel and dN_i is the change in the mass of this component via phase change or chemical reaction. Given that the two components with variable mass are water vapor and advected condensate, the mass part can be written

$$dS_{mass} = s_V dM_V + s_C dM_C \tag{3.66}$$

where dM_V and dM_C represent the changes in the masses of water vapor and advected condensate in the parcel due to diffusion through the sides of the parcel as well as addition and removal of mass through precipitation formation and evaporation. (Precipitation is not considered to be part of the system.) We assume implicitly that mass enters and leaves the parcel with the specific entropies characteristic of the parcel.

The chemical part of the change in entropy is assumed to take place at constant volume, $dV = 0$, and zero mass flux in and out of the parcel, $dM_V = dM_C = 0$. In the case of phase transitions between water vapor and condensate it can be written

$$dS_{chem} = -\frac{\mu_V}{T} dN_V - \frac{\mu_C}{T} dN_C = -\frac{\mu_V - \mu_C}{T} dN_V \tag{3.67}$$

where dN_V and dN_C are the masses added to water vapor and advected condensate by evaporation and condensation respectively and where μ_V and μ_C are the chemical potentials of vapor and condensate. This equation arises from the fact that

$$\frac{\mu_i}{T} = -\left(\frac{\partial S}{\partial O_i}\right) = -\left(\frac{\partial S}{\partial N_i}\right) \tag{3.68}$$

where the last step is justified since dM_i is assumed to be zero for this part of the change in entropy. Since loss of water vapor by condensation results in an equal gain in condensate in this case, we have $dN_C = -dN_V$. The temperature of the advected condensate is assumed to equal the temperature of the air parcel as a whole. This is justified because equilibration between the small advected condensate particles and vapor occurs rapidly. Thus, to a good approximation the condensate will be in phase equilibrium with the vapor, resulting in $\mu_V = \mu_C$. In this case $dS_{chem} = 0$.

The specific entropy of water vapor is given by equations (3.45) and (3.57),

$$s_V = C_{PV} \ln(T/T_F) - R_V \ln(p_V/e_{SF}) + L_L(T_F)/T_F, \qquad (3.69)$$

while that for condensate is

$$s_C = \begin{cases} C_I \ln(T/T_F) - L_F(T_F)/T_F, & T < T_F \\ C_L \ln(T/T_F), & T > T_F \end{cases} \qquad (3.70)$$

from equations (3.46) and (3.56). For the dry air component,

$$s_D = C_{PD} \ln(T/T_F) - R_V \ln(p_D/p_R). \qquad (3.71)$$

The chemical potentials of vapor and condensate divided by temperature are similarly

$$\mu_V/T = -C_{PV} \ln(T/T_F) + R_V \ln(p_V/e_{SF}) + C_L - \mu_{BL}/T_F \qquad (3.72)$$

and

$$\mu_C/T = \begin{cases} C_I[1 - \ln(T/T_F)] - \mu_{BI}/T + L_F(T_F)/T_F, & T < T_F \\ C_L[1 - \ln(T/T_F)] - \mu_{BL}/T, & T > T_F \end{cases} . \qquad (3.73)$$

Recognizing $s = S/M_D = s_D + r_V s_V + r_C s_C$ as the specific entropy of air, dividing equation (3.63) by $M_D dt$, and substituting equations (3.64) and (3.66) results in the governing equation for entropy,

$$\frac{ds}{dt} = \frac{Q}{T} + s_V \left(\frac{dr_V}{dt} \right)_d + s_C \left[\left(\frac{dr_C}{dt} \right)_d + \left(\frac{dr_C}{dt} \right)_p \right] + s_C^* \left(\frac{dr_C}{dt} \right)_e, \qquad (3.74)$$

where $dr_V = dM_V/M_D$ and $dr_C = dM_C/M_D$ are the changes in mixing ratios of vapor and advected condensate. The subscripted d refers to mass addition by a diffusive process, the subscripted p refers to conversion of advected condensate to precipitation, and the subscripted e refers to conversion of precipitation to advected condensate. The quantity s_C^* is the condensate entropy at the wet-bulb temperature T_W, which is the temperature toward which precipitation tends as it falls through unsaturated air.

Multiplication by the density of dry air ρ_D and use of the mass continuity equation (3.60) allows conversion to flux form:

$$\frac{\partial \rho_D s}{\partial t} + \nabla \cdot (\rho_D s \boldsymbol{v}) = \frac{\rho_D Q}{T} + \rho_D s_V \left(\frac{dr_V}{dt} \right)_d +$$

$$\rho_D s_C \left[\left(\frac{dr_C}{dt} \right)_d + \left(\frac{dr_C}{dt} \right)_p \right] + \rho_D s_C^* \left(\frac{dr_C}{dt} \right)_e. \qquad (3.75)$$

The water vapor diffusion term can be written

$$\rho_D s_V \left(\frac{dr_V}{dt}\right)_d = -s_V \nabla \cdot \boldsymbol{J}_V = -\nabla \cdot (s_V \boldsymbol{J}_V) + \boldsymbol{J}_V \cdot \nabla s_V \qquad (3.76)$$

where $\boldsymbol{J}_V$ is the molecular flux of water vapor. This is proportional to minus the gradient of the chemical potential of water vapor, but this will not enter the analysis directly due to its small magnitude in atmospheric applications. In particular, the first term on the right side of equation (3.76) is completely negligible compared to the divergence of the bulk entropy flux on the left side of equation (3.75). However, the second term enters indirectly when there is turbulence. Turbulence transforms variance on large scales down to tiny scales at which molecular processes can act. We account for this by imposing implicit smoothing (a Reynolds separation) and replace the molecular flux of water vapor by the turbulent flux, so that $\boldsymbol{J}_V \rightarrow -K\nabla r_V$ where K is the eddy mixing coefficient. Assumed here is that turbulent mixing homogenizes mixing ratio, in contrast to molecular diffusion, which homogenizes chemical potential divided by temperature. Though both occur, the former dominates the latter. Applying a similar treatment to the advected cloud water diffusion term results in our final governing equation for entropy,

$$\frac{\partial \rho_D s}{\partial t} + \nabla \cdot (\rho_D s \boldsymbol{v} - K\nabla s) = \frac{\rho_D Q}{T} - K\nabla r_V \cdot \nabla s_V - K\nabla r_C \cdot \nabla s_C$$
$$- \rho_D s_C \mathcal{P} + \rho_D s_C^* \mathcal{E}, \qquad (3.77)$$

where the time tendencies of condensate mixing ratio due to formation and evaporation of precipitation have been replaced by $-\mathcal{P}$ and $\mathcal{E}$ respectively. A turbulent eddy flux term for the entropy has been added to the left side of the governing equation as well.

The heating term has contributions from radiation, heat conduction, turbulent dissipation of the flow, turbulent dissipation associated with falling precipitation, and heat transfer between precipitation and air:

$$\frac{Q}{T} = \frac{Q_{RAD} + Q_{COND} + Q_{DISS} + Q_{PDISS} + Q_{PTRANS}}{T}. \qquad (3.78)$$

The radiative heating per unit volume $\rho_D Q_{RAD}$ is specified externally. The contribution of heat conduction $\rho_D Q_{COND}$ was found to be very small by Pauluis and Held (2002a).

The dissipation term is given by

$$\rho_D Q_{DISS} = 2K|\boldsymbol{D}|^2 \tag{3.79}$$

Where $\boldsymbol{D}$ is the rate of strain tensor. As shown by Pauluis, Balaji, and Held (2000), the precipitation-induced dissipation term is

$$\rho_D Q_{PDISS} = g\rho_D r_P w_T \tag{3.80}$$

where r_P is the mixing ratio of precipitation and w_T is the precipitation terminal fall velocity.

The heating term due to sensible heat transfer from the falling precipitation to the air as it warms is approximately

$$\rho_D Q_{PTRANS} \approx \rho_D r_P (v_z - w_T) \left[-C_C \frac{dT_W}{dz} + L_F(T_F)\delta(z - z_F) \right]. \tag{3.81}$$

In this approximation, the temperature of precipitation is assumed to be the wet-bulb temperature T_W of the atmosphere. The second term on the right side represents melting or freezing, assumed to occur instantly at the freezing level z_F, of ascending or descending precipitation. (Technically, this is the level at which $T_W = T_F$.) The specific heat of condensate, C_C, is assumed to be that for liquid, C_L below the freezing level and that for ice, C_I, above the freezing level. Except for the freezing/melting term in Q_{PTRANS}, the terms Q_{PDISS} and Q_{PTRANS} are typically similar in magnitude and opposite in sign.

3.8.4   Classical entropy governing equation

The classical treatment for the generation of entropy by diffusion is given by de Groot (1951, pp 97-98), Landau and Lifshitz (1959, p 221), de Groot and Mazur (1962, pp 19-24), Yourgrau, van der Merwe, and Raw (1966, pp 13-14), etc. The arguments of these authors are all variations on a common theme that starts for our case with the Gibbs relation (with $dM_D = 0$),

$$TdS = dE + pdV - \mu_V dO_V - \mu_C dO_C \tag{3.82}$$

where the terminology is as before. The first law of thermodynamics is then applied, which we write for consistency with the above work as

$$dE = Qdt - pdV, \tag{3.83}$$

where Q is the heating rate per unit mass. The result is

$$dS = \frac{Qdt}{T} - \frac{\mu_V dO_V + \mu_C O_C}{T}.$$ (3.84)

The rest of the development follows along lines similar to those given above, where $dr_V = dO_V/M_D$, etc., with the result that

$$\frac{ds}{dt} = \frac{Q}{T} - \frac{\mu_V}{T}\left(\frac{dr_V}{dt}\right) - \frac{\mu_C}{T}\left(\frac{dr_C}{dt}\right)$$ (3.85)

in place of equation (3.74).

I believe this derivation to be incorrect for the following reasons: (1) The closed system first law is applied to an open system. (2) The work done by the system dW is incorrectly equated to pdV in the case in which only part of dV is associated with work-producing expansion.

Can the above derivation be rescued? Let us generalize equation (3.83) to use the actual work done by expansion dW and to include the import and export of energy via mass exchange,

$$dE = Qdt - dW + e_V dM_V + e_C dM_C,$$ (3.86)

where quantities e_V and e_C are the specific energies of water vapor and advected condensate. Note that this equation is derived from energy conservation and is therefore a true expression of the first law of thermodynamics. It differs from the expression for dE obtained by simply inverting the Gibbs equation (3.82) in that the heat added Qdt is not equated to the entropy term TdS, the work done dW is not set equal to pdV, and the specific energies replace the chemical potentials of water vapor and condensate.

The change in volume of the system actually consists of two parts, the change due to expansion and compression, dV_X, and the change due to the addition and removal of mass, dV_M. The total change in volume is thus $dV = dV_X + dV_M$. The work done by expansion is $dW = pdV_X$. On the other hand, the change in volume due to a change in mass alone holding pressure and temperature constant is

$$pdV_M = d(pV_M) = d(M_V R_V T + M_C R_C T) = R_V TdM_V + R_C TdM_C.$$ (3.87)

where we have used the ideal gas law. (The condensate can be considered as an ideal gas with very massive molecules, and hence a very small value of R_C.)

Combining equations (3.82), (3.86), and (3.87) and identifying $e_i + R_i T = h_i$ as the specific enthalpy of the ith component results in

$$TdS = Qdt + (h_V - \mu_V)dM_V - \mu_V dN_V + (h_C - \mu_C)dM_C - \mu_C dN_C \quad (3.88)$$

where we have used $dO_V = dM_V + dN_V$, etc. Dividing by T and recognizing the specific entropy of the ith component as $s_i = (h_i - \mu_i)/T$ brings us to our original equation (3.63):

$$\begin{aligned} dS &= \frac{Qdt}{T} + s_V dM_V + s_C dM_C - \frac{\mu_V - \mu_C}{T}dN_V \\ &= dS_{heat} + dS_{mass} + dS_{chem}. \end{aligned} \quad (3.89)$$

Thus, the Gibbs equation approach is consistent with our original result with phase equilibrium between vapor and advected condensate, provided that the proper version of the first law of thermodynamics is used.

3.8.5   Momentum

In order to derive the momentum equation, consider a parcel that moves with the dry air component and is closed with respect to that component, i.e., the mass of dry air in the parcel M_D is conserved. Newton's second law generalized for open systems takes the form

$$\frac{d}{dt}\left[(M_D + M_T)\,\boldsymbol{v}\right] = V\boldsymbol{F} + \boldsymbol{v}\frac{dM_T}{dt} \quad (3.90)$$

where M_T is the mass of the total cloud water, i.e., vapor plus advected condensate. The term on the left is the time rate of change of momentum of the dry air plus the total cloud water. Precipitation is not considered to be part of the system. The first term on the right is the product of the volume V of the parcel and the external force per unit volume,

$$\boldsymbol{F} = \nabla \cdot \boldsymbol{T} - g\rho_D\left(1 + r_T + r_R\right)\boldsymbol{k}, \quad (3.91)$$

where $\boldsymbol{T} = -p\boldsymbol{I} + 2K\boldsymbol{D}$ is the stress tensor with p being the pressure, K the eddy mixing coefficient, and $\boldsymbol{D}$ the strain rate of the fluid. The second part of equation (3.91) is just the weight of all material in the parcel, incorporating the mass densities of the dry air component ρ_D, the total cloud water $\rho_T = \rho_D r_T$ and the precipitation $\rho_P = \rho_D r_P$. The third term on the

right side of equation (3.90) represents the rate at which cloud water mass is added to the parcel, which we assume to enter with the parcel's velocity.

Expanding the derivative on the left side of equation (3.90), dividing by V, and simplifying results in

$$\rho_D(1 + r_T)\frac{d\boldsymbol{v}}{dt} = -\nabla p + \nabla \cdot (2K\boldsymbol{D}) - g\rho_D \left(1 + r_T + r_R\right)\boldsymbol{k}. \qquad (3.92)$$

Finally, dividing by $1 + r_T$ and converting the left side to flux form using equation (3.60) results in

$$\frac{\partial \rho_D \boldsymbol{v}}{\partial t} + \nabla \cdot (\rho_D \boldsymbol{vv}) = \frac{-\nabla p + \nabla \cdot (2K\boldsymbol{D})}{1 + r_T} - g\rho_D \left(1 + r_R\right)\boldsymbol{k}. \qquad (3.93)$$

We have made the minor approximation that $1 + r_R/(1 + r_T) \approx 1 + r_R$, which is valid because $r_R, r_T \ll 1$.

3.9 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

$$s = C_{PD} \ln(T/T_F) - R_D \ln(p/p_R) + \frac{Lr_V}{T_F}, \qquad (3.94)$$

where L is the latent heat of condensation at freezing. This approximation comes from neglecting r_L and r_I in equation (3.58) 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 (3.94)), 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

$$\theta_e = T_R \exp(s/C_P) = T(p_R/p)^{R_D/C_{PD}} \exp[Lr_V/(C_{PD}T_R)], \qquad (3.95)$$

where the simplified entropy given by equation (3.94) 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 (3.54)

$$\theta_e = T_F \exp[s/(C_{PD} + r_T C_L)]. \qquad (3.96)$$

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

$$C_{PD}dT = dq + \frac{dp}{\rho} \qquad (3.97)$$

where 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

$$d(C_{PD}T + Lr_V + gz) = d\sigma = 0, \qquad (3.98)$$

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 (3.97) 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

$$\frac{\partial v^2/2}{\partial t} + \mathbf{v} \cdot \nabla(v^2/2 + C_{PD}T + Lr_V + gz) = 0. \qquad (3.99)$$

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 signficant 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.

3.10   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.

de Groot, S. R., 1951: *Thermodynamics of irreversible processes.* North-Holland Publishing, 242 pp.

de Groot, S. R. and P. Mazur, 1962: *Non-equilibrium thermodynamics.* North-Holland, Amsterdam, 510 pp.

Landau, L. D., and E. M. Lifshitz (1959): *Fluid mechanics.* Pergamon Press, 536 pp.

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., V. Balaji, and I. M. Held, 2000: Frictional dissipation in a precipitating atmosphere. j*J. Atmos. Sci.*, **57**, 989-994.

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.

Yourgrau, W., A. van der Merwe, and G. Raw, 1982: *Treatise on irreversible and statistical thermophysics.* Dover Publications, 268 pp (reprinted from the original work published in 1966 by Macmillan).

3.11   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 rain-drops. 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. 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 due to mechanical dissipation 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}.