Chapter 2

Entropy, Water Vapor, and Precipitation

2.1 Basic equations

We assume the ideal gas law

$$\frac{p}{\rho} = \frac{RT}{m} \tag{2.1}$$

where p is the pressure, ρ is the density, T is the absolute temperature, m is the molecular weight of the gas, and R is the universal gas constant. We also assume that the specific entropy s, or entropy per unit mass, of an ideal gas is

$$s = C_p \ln(T/T_R) - (R/m)\ln(p/p_R) + s_R \tag{2.2}$$

where C_p is the specific heat at constant pressure, T_R and p_R are constant reference temperature and pressure, and where s_R is a constant reference entropy. These results come from basic thermodynamics and are demonstrated in basic texts on thermodynamics.

For a mixture of ideal gases which don't interact, the total pressure equals the sum of the partial pressures of the individual components p_i, with a similar relation holding for the partial densities ρ_i:

$$p = \sum p_i \tag{2.3}$$

$$\rho = \sum \rho_i. \tag{2.4}$$

Solving equation (2.1) for the pressure and adding the pressures of all the partial components together gives us the ideal gas law for a mixture

$$p = \frac{RT\rho}{\overline{m}} \tag{2.5}$$

where the mean molecular weight is defined

$$\frac{1}{\overline{m}} = \frac{1}{\rho}\sum \frac{\rho_i}{m_i}. \tag{2.6}$$

Mixing ratios are ratios of densities of various water phases in the atmosphere to the density of dry air. Thus, the water vapor mixing ratio is

$$r_v = \rho_v/\rho_d \tag{2.7}$$

where ρ_v and ρ_d are the densities of water vapor and dry air, and the liquid mixing ratio is

$$r_l = \rho_l/\rho_d \tag{2.8}$$

where ρ_l is the density of condensed water. Mixing ratios are conserved in parcel expansions and contractions as long as no phase changes or liquid sedimentation (i. e., precipitation) occur.

2.2 Rain

Normally condensation of water vapor in the atmosphere yields many small particles with a typical diameter of $\approx 10^{-5}$ m. These *cloud droplets* tend to be carried along with the air. The total water mixing ratio thus is conserved by parcels under these circumstances. Expansion and cooling converts vapor to cloud droplets, whereas compression and warming simply reverses this process.

Under the right conditions cloud droplets coalesce into larger *drizzle* and *rain* drops, which fall relative to the air. The total water mixing ratio in a parcel therefore decreases when cloud droplets convert to drizzle and rain and falls out. The reverse process can happen as well. If rain falls through air which is unsaturated, evaporation occurs and the total water mixing ratio of this air increases.

2.3 Entropy of moist air

The entropy is a useful variable in atmospheric dynamics because processes in the atmosphere are generally slow in a thermodynamic sense. Entropy is therefore nearly conserved in parcel expansions and compressions, even those in which evaporation, condensation, and precipitation take place. Entropy increases primarily in irreversible mixing processes. For a dry atmosphere, the entropy as defined by equation (2.2) is satisfactory. However, when moisture is present, especially in condensed form, the entropy becomes somewhat more complex. In this section we derive a formula for the entropy in the presence of both water vapor and liquid water and then define an approximate form useful in the study of atmospheric dynamics. For complete fidelity to the atmosphere, one must also introduce frozen condensate. However that analysis is beyond the scope of this course. This treatment is based on that of Emanuel (1994).

In the earth's atmosphere the specific entropy of the mixture of air, water vapor, and condensed water is generally defined as the total entropy *per unit mass of dry air*. The specific entropies of these three parts are

$$\begin{aligned}
s_d &= C_{pd}\ln(T/T_R) - R_d\ln(p_d/p_R) + s_{Rd} \\
s_v &= C_{pv}\ln(T/T_R) - R_v\ln(p_v/p_R) + s_{Rv} \\
s_l &= C_l\ln(T/T_R) + s_{Rl}
\end{aligned} \tag{2.9}$$

where as above the subscripted d, v, and l indicate dry air, water vapor, and liquid water, and where $R_d = R/m_d$ and $R_v = R/m_v$. In terms of the mixing ratios for vapor and liquid, the total entropy per unit mass of dry air is

$$\begin{aligned} s &= s_d + r_v s_v + r_l s_l \\ &= (C_{pd} + r_v C_{pv} + r_l C_l)\ln(T/T_R) - R_d \ln(p_d/p_R) - r_v R_v \ln(p_v/p_R) \\ &\quad + s_{Rd} + r_v s_{Rv} + r_l s_{Rl} \end{aligned} \tag{2.10}$$

Defining the total water mixing ratio $r_t = r_v + r_l$ we can eliminate r_l from this equation. The vapor and liquid water mixing ratios vary as an air parcel undergoes condensation, but the total water mixing ratio stays constant as long as no precipitation is formed or evaporated. We can also rewrite $p_v/p_R = He_s/p_R$ where e_s is the saturation vapor pressure for water vapor and $H \equiv p_v/e_s$ is the relative humidity. Equation (2.10) thus becomes

$$\begin{aligned} s &= (C_{pd} + r_t C_l)\ln(T/T_R) - R_d \ln(p_d/p_R) - r_v R_v \ln(H) \\ &\quad - r_v[(C_l - C_{pv})\ln(T/T_R) + R_v \ln(e_s/p_R) - (s_{Rv} - s_{Rl})] \\ &\quad + s_{Rd} + r_t s_{Rl}, \end{aligned} \tag{2.11}$$

where $C_{pd} = 1005$ J K^{-1} kg^{-1}, $C_{pv} = 1850$ J K^{-1} kg^{-1}, $C_l = 4218$ J K^{-1} kg^{-1}, $R_d = 287$ J K^{-1} kg^{-1}, and $R_v = 461$ J K^{-1} kg^{-1}.

The saturation vapor pressure of water vapor over a flat surface of pure water is to an excellent approximation a function only of temperature:

$$e_S(T) = e_{SF}\left(\frac{T_F}{T}\right)^{(C_l - C_{pv})/R_v} \exp\left[\frac{L_0}{R_v}\left(\frac{1}{T_F} - \frac{1}{T}\right)\right], \tag{2.12}$$

where $T_F = 273.15$ K is the freezing point of water, $e_{SF} = 6.11$ hPa is the saturation vapor pressure at freezing, and $L_0 = 3.14 \times 10^6$ J kg^{-1} is the latent heat of condensation extrapolated to 0 K without regard to changes in phase or the dependence of specific heats on temperature. The latent heat of condensation L is not constant, but takes the form

$$L = L_F - (C_l - C_{pv})(T - T_F) \tag{2.13}$$

where $L_F = 2.501 \times 10^6$ J kg^{-1} is a constant. Thus, $L_0 = L_F + (C_l - C_{pv})T_F$. The specific entropy for a moist atmosphere thus becomes

$$s = (C_{pd} + r_t C_l)\ln(T/T_R) - R_d \ln(p_d/p_R) - r_v R_v \ln(H) + L r_v/T, \tag{2.14}$$

where we have substituted equation (2.12) into equation (2.11) and have also taken the liberty of setting s_{Rd} and s_{Rl} to zero. (See Emanuel, 1994.)

Equation (2.14) is too complex for our purposes. We simplify it by setting all mixing ratios (which are small compared to unity in the earth's atmosphere) to zero except in the latent heat term. This is justified because the latent heat term is two orders of magnitude larger than the other water vapor terms. In order to make this approximation consistent, we also set $T = T_F$ in the latent heat term. This is necessary in order to make the total entropy, the dry entropy, and the water vapor mixing ratio all constant in unsaturated parcel expansions and contractions. We thus define the approximate total entropy as

$$s \approx s_d + L_F r_v/T_F \tag{2.15}$$

where

$$s_d = C_{pd} \ln(T/T_R) - R_d \ln(p/p_R). \tag{2.16}$$

Note that in this approximation we have also replaced p_d by p.

A useful additional variable is the *saturated entropy*, obtained by replacing r_v with its saturated value r_s and setting $r_l = 0$:

$$s_s = (C_{pd} + r_s C_l) \ln(T/T_R) - R_d \ln(p_d/p_R) + L r_s/T. \tag{2.17}$$

An approximate formula for the saturated entropy is obtained by making the same approximations made above with respect to the moist entropy:

$$s_s \approx s_d + L_F r_s/T_F. \tag{2.18}$$

Notice that whereas the total entropy is a function of temperature, pressure, vapor mixing ratio, and in its exact form, liquid water mixing ratio, the saturated total entropy is a function of just temperature and pressure. This is because

$$r_s = \frac{\rho_{vs}}{\rho_d} = \frac{m_v e_s(T)}{m_d p_d} \approx \frac{\epsilon e_s(T)}{p} \tag{2.19}$$

where $\epsilon \equiv m_v/m_a$, i. e., r_s itself is a function only of temperature and pressure.

2.4 Potential temperatures

Meteorologists typically use potential temperatures more than entropies. A potential temperature is the temperature a parcel would attain if it were compressed or expanded at constant entropy (i. e., isentropically) to a standard pressure, which we take here as the reference pressure p_R. The usual choice for a standard pressure is 1000 hPa.

For the potential temperature θ the dry entropy is held constant, and θ is defined

$$\theta = T_R \exp(s_d/C_{pd}) = T(p_R/p)^{R_d/C_{pd}}. \tag{2.20}$$

For an ideal diatomic gas (which closely approximates the actual properties of dry air), $\gamma \equiv C_{pd}/C_{vd} = 1.4$, and since $C_{pd} - C_{vd} = R_d$, $R_d/C_{pd} = (\gamma - 1)/\gamma = 0.286$.

The equivalent potential temperature θ_e for our purposes can be taken as being analogous to the potential temperature, but with the total entropy held constant:

$$\theta_e = T_R \exp(s/C_{pd}) \approx \theta \exp[L_F r_v/(C_{pd} T_F)]. \tag{2.21}$$

The last expression in the above equation is the approximate form obtained from substituting equation (2.15) for the entropy. A word of warning: There are many different ways to define equivalent potential temperature, involving many different and incompatable approximations. See Emanuel (1994) for further information.

The saturated equivalent potential temperature is obtained analogously from the saturated entropy:

$$\theta_{es} = T_R \exp(s_s/C_{pd}) \approx \theta \exp[L_F r_s/(C_{pd} T_F)]. \tag{2.22}$$

2.5 References

Emanuel, K. A., 1994: *Atmospheric Convection.* Oxford University Press, New York, 580 pp.

2.6 Problems

1. Differentiate the logrithm of equation (2.12) with respect to T to obtain a formula for $e_s^{-1} de_s/dT$. Note how this may be simplified by writing it in terms of the temperature-dependent latent heat of condensation L.

2. Determine how the temperature varies with pressure in the case of isentropic expansion or compression in which there is water vapor but no condensation in the atmosphere. In particular, if the temperature is T_0 at the reference pressure, what is the temperature for arbitrary pressure, assuming that entropy is conserved and no condensation occurs? Hint: Eliminate p_v in favor of r_v, which is conserved in this case, in equation (2.10).

3. Derive an equation for the density of a mixture of dry air and water vapor as a function of temperature T, pressure p, water vapor mixing ratio r_v, and the constants R_d and $\epsilon = m_v/m_d$.

   (a) Compare to the corresponding expression for the density to that of the density for dry air alone.

   (b) Define a "virtual temperature" T_v, which makes the expression for the density of a mixture of dry air and water vapor look like the density expression for dry air alone when the the actual temperature is replaced by the virtual temperature.