Chapter 2

Approximate Thermodynamics

2.1 Atmosphere

Various texts (Byers 1965, Wallace and Hobbs 2006) provide elementary treatments of atmospheric thermodynamics, while Iribarne and Godson (1981) and Emanuel (1994) present more advanced treatments. We provide only an approximate treatment which is acceptable for idealized calculations, but must be replaced by a more accurate representation if quantitative comparisons with the real world are desired.

2.1.1 Dry entropy

In an atmosphere without moisture the ideal gas law for dry air is

$$\frac{p}{\rho} = R_d T \tag{2.1}$$

where p is the pressure, ρ is the air density, T is the absolute temperature, and $R_d = R/m_d$, R being the universal gas constant and m_d the molecular weight of dry air. If moisture is present there are minor modifications to this equation, which we ignore here. The dry entropy per unit mass of air is

$$s_d = C_p \ln(T/T_R) - R_d \ln(p/p_R)$$
(2.2)

where C_p is the mass (not molar) specific heat of dry air at constant pressure, T_R is a constant reference temperature (say 300 K), and p_R is a constant reference pressure (say 1000 hPa). Recall that the specific heats at constant pressure and volume (C_v) are related to the gas constant by

$$C_p - C_v = R_d. \tag{2.3}$$

A variable related to the dry entropy is the potential temperature θ , which is defined

$$\theta = T_R \exp(s_d/C_p) = T(p_R/p)^{R_d/C_p}.$$
(2.4)

The potential temperature is the temperature air would have if it were compressed or expanded (without condensation of water) in a reversible adiabatic fashion to the reference pressure p_R .

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Constant	Value	Meaning
R	8.314 J K^{-1}	Universal gas constant
m_d	$28.9 \times 10^{-3} \text{ kg mol}^{-1}$	Molecular weight of dry air
m_v	$18.0 \times 10^{-3} \text{ kg mol}^{-1}$	Molecular weight of water
R_d	$287 \text{ J K}^{-1} \text{ kg}^{-1}$	Gas constant for dry air
R_v	$461 \text{ J K}^{-1} \text{ kg}^{-1}$	Gas constant for water vapor
C_p	$1005 \text{ J K}^{-1} \text{ kg}^{-1}$	Specific heat of dry air at const pres
C_v	$718 \text{ J K}^{-1} \text{ kg}^{-1}$	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
L	$2.50 \times 10^{6} \text{ J kg}^{-1}$	Latent heat of condensation at freezing
μ_B	$3.15 \times 10^6 \text{ J kg}^{-1}$	Binding energy for liquid water
e_{SF}	611 Pa	Saturation vapor pressure at freezing
T_F	273.15 K	Freezing point
p_R	10^5 Pa	Reference pressure
T_R	300 K	Reference temperature

Table 2.1: Thermodynamic constants.

We ignore heat conduction and the irreversible production of entropy, which means that latent heat release and radiation (solar and thermal) are the only sources of entropy. The governing equation for dry entropy is therefore

$$\frac{ds_d}{dt} = \frac{Q}{T_R},\tag{2.5}$$

where $Q = Q_l + Q_r$ is the heating rate per unit mass and is composed of latent and radiative heating parts. Strictly speaking the denominator on the right side should contain the actual temperature, but we have replaced it by the constant reference temperature for the sake of a consistent approximation. The latent heating at this level of approximation is

$$Q_l = -L\frac{dr_v}{dt} \tag{2.6}$$

where L is the latent heat of condensation, assumed constant here, and r_v is the mixing ratio of water vapor. The mixing ratio of a quantity is the mass of that quantity in an air parcel divided by the mass of air in the parcel.

Equation (2.5) implies that the dry entropy of a parcel is conserved if there is no heating of the parcel. Of course, entropy can always increase by irreversible processes even in the absence of heating. However, this effect is typically small in the atmosphere and the approximations made here exclude this possibility. The potential temperature is also conserved in the absence of heating, since it is a unique function of the dry entropy.

2.1.2 Moist entropy

The moist entropy per unit mass is defined at our level of approximation as

$$s = s_d + \frac{Lr_v}{T_R} \tag{2.7}$$

and the governing equation is

$$\frac{ds}{dt} = \frac{Q_r}{T_R}.$$
(2.8)

The radiative heating per unit volume ρQ_r is generally supplied by atmospheric radiation models. A variable related to the moist entropy is the equivalent potential temperature, defined

$$\theta_e = T_R \exp(s/C_p). \tag{2.9}$$

Replacing the actual water vapor mixing ratio in equation (2.7) with the saturation mixing ratio results in a variable called the saturated moist entropy:

$$s_s = s_d + \frac{Lr_s}{T_R}.$$
(2.10)

Note that since $r_s = r_s(T, p)$, the saturated moist entropy is also a function of only temperature and pressure. This is in contrast to the actual moist entropy, which is a function also of the water vapor mixing ratio, which for the unsaturated case is independent of pressure and temperature. The saturated equivalent potential temperature is given by

$$\theta_{es} = T_R \exp(s_s/C_p). \tag{2.11}$$

The moist entropy and the equivalent potential temperature are conserved not only in processes without heating, but also in processes in which heating and cooling by condensation and evaporation of liquid water occur. Under these conditions the mixing ratio remains close to the saturation mixing ratio. Because of this, the saturated moist entropy and the saturated equivalent potential temperature are conserved in a saturated parcel undergoing moist adiabatic expansion or compression. However, the saturated moist entropy is not conserved in dry adiabatic processes – it changes in a manner that keeps the dry entropy (or potential temperature) constant under these conditions.

2.1.3 Entropy-pressure chart

Figure 2.1 shows an alternate way of plotting a thermodynamic sounding which is useful in the case of moist convection. Total entropy and saturated entropy are plotted against pressure, with auxiliary lines showing contours of potential temperature (or dry entropy) as a function of pressure and saturated entropy. Parcel trajectories of entropy in all cases and saturated entropy in the saturated case follow vertical lines, while trajectories of saturated entropy in the unsaturated case follow lines of constant potential temperature.

The main advantages of this type of chart are that moist ascending parcels follow a simple trajectory and that temperature and moisture effects on parcel instability are presented on commensurate scales. One disadvantage is that the buoyancy of a parcel is harder to determine quantitatively than in a skew T-log p chart. However, the potential temperature contour lines help in this regard.



Figure 2.1: Entropy-pressure chart of mean tropical east Pacific sounding. The left curve shows the total entropy while the right curve shows the saturated entropy. The dashed lines show contours at 5 K intervals of potential temperature as a function of the pressure and the saturated moist entropy.

2.1.4 Water

If condensation is occurring, the water vapor mixing ratio r_v is generally quite close to the saturation mixing ratio r_s . The saturation mixing ratio may be written in terms of the ratio of the saturation vapor pressure $e_s(T)$ of water divided by the partial pressure of dry air, approximated as the total pressure:

$$r_s = \frac{m_v}{m_d} \frac{e_s(T)}{p} \tag{2.12}$$

where m_w is the molecular weight of water vapor.

The saturation vapor pressure is given quite accurately by the equation

$$e_S(T) = e_{SF} \left(\frac{T_F}{T}\right)^{(C_l - C_{pv})/R_v} \exp\left[\frac{\mu_B}{R_v} \left(\frac{1}{T_F} - \frac{1}{T}\right)\right]$$
(2.13)

where T_F is the freezing point of water, C_l is the specific heat of liquid water, C_{pv} is the specific heat of water vapor at constant pressure, $R_v = R/m_v$ is the gas constant for water vapor, and μ_B and e_{SF} are constants.

Condensation results in the production of tiny water droplets typically of order 10^{-5} m in diameter. These droplets are small enough to be carried along with the flow. If these cloud droplets are not converted into precipitation, the sum of the water vapor mixing ratio and the cloud droplet mixing ratio r_c is conserved in parcels. This quantity $r_t = r_v + r_c$ is called the *total cloud water mixing ratio*. Conversion into precipitation is the coalescence of cloud droplets into larger drops which fall relative to the air. Precipitation can also be converted into water vapor if it evaporates in sub-saturated air. If P is the net conversion rate per unit mass of total cloud water into precipitation (with negative values corresponding to evaporation of precipitation), then the time rate of change of total cloud water in a parcel of air obeys the equation

$$\frac{dr_t}{dt} = -P. \tag{2.14}$$

Thus, the total cloud water mixing ratio is conserved by parcels as long as there is no formation or evaporation of precipitation. the water vapor mixing ratio is conserved only when there is no condensation or evaporation of any form of condensed water, including cloud droplets.

It is often useful to use the moist entropy and the total cloud water mixing ratio as dependent variables in numerical models. A problem with this approach is that one must also infer the dry entropy and the water vapor mixing ratio from these variables. This is not possible to do analytically when the air is saturated. In this case an iterative approach using a numerical technique such as Newton's method is needed.

2.1.5 Atmospheric density

For atmospheric calculations the density must be expressed in terms of the above atmospheric thermodynamic variables. We now see in particular how the density can be written in terms of the dry entropy or the potential temperature and the pressure. Given the ideal gas law and the definitions of dry entropy and potential temperature, we easily derive

$$\rho = \rho_R (p/p_R)^{C_v/C_p} \exp(-s_d/C_p) = \frac{p_R (p/p_R)^{C_v/C_p}}{R_d \theta}$$
(2.15)

where the reference density is defined using the ideal gas law: $\rho_R = p_R/(R_dT_R)$.

2.2 Ocean

We make the approximation that ocean water is incompressible. Under this condition the temperature of a parcel of ocean water only changes when heating occurs, resulting in the governing equation

$$C_l \frac{dT}{dt} = Q, \qquad (2.16)$$

where Q is the heating rate per unit mass in the ocean and C_l is the mass-specific heat of ocean water. In the interior of the ocean the only contributor to this is solar radiation. At the surface evaporation can cool the ocean, but as this is a surface phenomenon, it requires special treatment.

To the extent that surface changes in salinity are ignored, the salinity (which is essentially a mixing ratio or mass concentration for salt) obeys a very simple equation:

$$\frac{dS}{dt} = 0. (2.17)$$

The density of ocean water is in general a complex function of temperature, salinity, and pressure. For our simplified calculations we ignore the dependence of this density on pressure, thus allowing ocean water to be treated as an incompressible fluid:

$$\rho = \rho(T, S) \tag{2.18}$$

2.3 References

- **Byers,** H. R., 1965: *Elements of cloud physics*. University of Chicago Press, Chicago, 191 pp.
- **Emanuel,** K. A., 1994: Atmospheric convection. Oxford University Press, New York, 580 pp.
- Gill, A. E., 1982: Atmosphere-ocean dynamics. Academic Press, New York, 662 pp.
- Iribarne, J. V., and W. L. Godson, 1981: Atmospheric thermodynamics, 2nd Ed. D. Reidel, Dordrecht, 259 pp.
- Wallace, J. M., and P. V. Hobbs, 2006: Atmospheric science, 2nd Ed. Elsevier, Amsterdam, 483 pp.

2.4 Problems

- 1. Given equations (2.5) and (2.6), verify equation (2.8).
- 2. Answer the following questions using the sounding presented on the entropy-pressure chart (figure 2.1):
 - (a) Determine the lifting condensation level of parcels lifted from 1000 hPa.
 - (b) Determine the initial level of neutral buoyancy for a parcel lifted from 1000 hPa.
 - (c) Determine the highest level which exhibits positive parcel buoyancy upon lifting.
 - (d) Determine the level of free convection (i. e., the first level at which the buoyancy becomes positive) for parcels originating at 950 hPa.
 - (e) Determine by how much the potential temperature of a parcel lifted from the surface exceeds the potential temperature of the environment at 600 hPa.
 - (f) A parcel starting at 700 hPa is cooled by 10 K in potential temperature by evaporation of precipitation. What is its new level of neutral buoyancy?
- 3. Derive dT/dp for a non-condensing parcel under the condition that it is expanding or contracting dry adiabatically. Hint: Hold the dry entropy constant.
- 4. Derive dT/dp for a saturated parcel under the condition that it is expanding or contracting moist adiabatically. Hint: Hold the saturated moist entropy constant. (There is no need to evaluate $de_S(T)/dT$.)

¹Actually, potential density, which is the density of ocean water raised adiabatically to sea level.

- 5. Derive equation (2.15) and calculate the reference density in terms of the reference pressure and temperature given in table 2.1.
- 6. If a parcel of ocean water is cooled by evaporation, the salinity is increased because the evaporated water leaves behind its salt content. Compute the ratio of final to initial salinity of a parcel of ocean water cooled by evaporation from 30° C to 0° C.
- 7. Suppose the ocean salinity field has the form $S = S_0 + \Gamma(x v_x t)$ where S_0 and Γ are positive constants. The velocity field is given by $\mathbf{v} = (v_x, 0, 0)$, where v_x is a positive constant.
 - (a) Verify that dS/dt = 0, where the total time derivative is the time rate of change of salinity in a moving parcel.
 - (b) Compute $\partial S/\partial x$ and use this to discuss the spatial structure of salinity.
 - (c) Compute $\partial S/\partial t$ and explain physically why this is not equal to dS/dt.