Thermodynamic Equations Review

- Cloud processes depend strongly on thermodynamic principles
  - Phase changes impact latent heating
  - Static stability determines cloud lifting and vertical extent
  - Stability is influenced by water (vapor, phase changes)
  - Availability of moisture affects the rate at which cloud particles can grow by vapor deposition

Much of the seemingly complex thermodynamics in atmospheric sciences derives from several basic equations that are reviewed here:

IDEAL GAS LAW

$$pV = nR_*T \tag{1}$$

where p is pressure, V is the volume of gas containing n moles, R_* is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature. This law almost perfectly describes gases in the Earth's atmosphere.

However, the form of [1] is not the most common form used in the atmospheric sciences. Usually, we are dealing with air, so we introduce a specific gas constant appropriate for dry air, using $R = R_*/m_{\text{air}}$ where m_{air} is the molar mass of dry air (≈0.029 kg mol^{-1}), such that R=287.04 J K^{-1} kg^{-1}. Then, noting that $nm_{\text{air}} = m$ = mass of air, and defining density $\rho = m/V$ from [1] we can rewrite [1] in its more common form:

$$p = \rho RT \tag{2}$$

If the composition of air were constant, then R would be a fixed number. However, moisture can vary in the atmosphere from 0 to 4% by mass, and since R_{vapor} = 461 J K^{-1} kg^{-1}, the value of R appropriate for a mixture of dry air and water vapor depends upon the vapor content. The conventional approach is to continue to use the gas constant for dry air, but to incorporate its moisture dependency into a new temperature measure called the **virtual temperature** T_v (see Lamb and Verlinde 1st edition, P221, or Wallace and Hobbs section 3.1.1).

HYDROSTATIC EQUATION

$$\frac{dp}{dz} = -\rho g \tag{3}$$

Balance of vertical pressure gradient force with gravity. Combining with the ideal gas law [2], we obtain this form:

$$\frac{dp}{dz} = -\frac{pg}{RT} \tag{4}$$

Whose consequence is the atmospheric scale height $H = RT/g$ (~7.5 km).

FIRST LAW OF THERMODYNAMICS

Expresses conservation of energy for a system in which external energy (heat) input dq can change the internal energy u and/or do work dw,

$$dq = du + dw \tag{5}$$

For the atmosphere, [5] is rarely used directly. Instead, we normalize by the mass of air, substitute $dw = pd\alpha$, where α is the specific volume (volume per mass, i.e. ρ^{-1}), substitute $du = c_v dT$, where c_v is the heat capacity at constant volume, to give

$$dq = c_v dT + \ pd\alpha \tag{6}$$

With the product rule trick, $d(p\alpha) = pd\alpha + \alpha dp$, and noting that $p\alpha = RT$ from the ideal gas law (R being the gas constant for air) we can substitute into [1] to obtain

$$dq = c_v dT + RdT - \alpha dp = c_p dT - \alpha dp \tag{7}$$

Combining [7] with the hydrostatic equation [3], we arrive at a useful form of the first law:

$$dq = d(c_p T + gz) \tag{8}$$

This form is useful for instantly understanding how temperature changes with height under adiabatic lifting (dq=0), i.e. $\frac{dT}{dz} = -\frac{g}{c_p} = -\Gamma_d$, which defines the dry adiabatic lapse rate Γ_d (≈10 K km^{-1}). If one defines **potential temperature** as

$$c_p d\theta = d(c_p T + gz) \tag{9}$$

i.e. a variable with units of temperature whose changes are defined to be zero under adiabatic changes, then one can integrate [7] with $dq = c_p d\theta = 0$, so that $c_p dT - \alpha dp$=0. Integrating this from a reference pressure p_0 where we define $T = \theta$, to pressure p, we obtain the **Poisson equation for the potential temperature**:

$$\theta = T\left(\frac{p_0}{p}\right)^{R/c_p} \tag{10}$$

CLAUSIUS-CLAPEYRON EQUATION

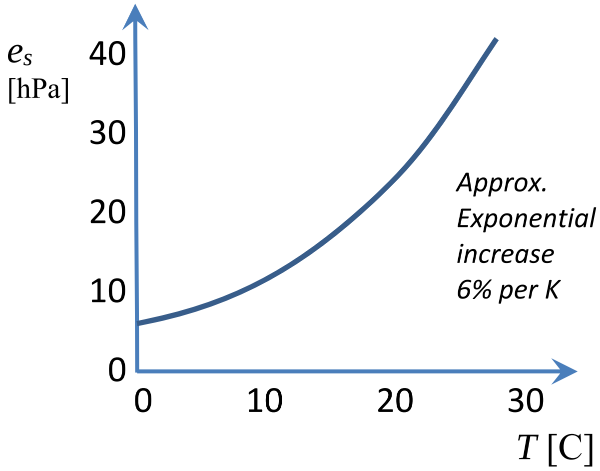
We will spend a little more time later in the class discussing the physical basis for the Clausius-Clapeyron equation (see notes on Equilibria and Phase). Here, we will simply present it. The equation describes how the **equilibrium (saturation) vapor pressure** of water (e_s) changes with temperature T. The most common form of it in the atmospheric sciences is:

$$\frac{de_s}{dT} \approx \frac{L_v e_s}{R_v T^2} \tag{11}$$

where L_v is the latent heat of condensation and R_v is the gas constant for water vapor.

Note: Although [11] is technically an approximation it differs from the true expression by only 1 part in 1240 (ratio of the molar volume of liquid water to the molar volume of air).

Integration of [11] gives the quasi-exponential curve shown in the figure (right):



The saturation vapor pressure represents the maximum vapor pressure of water before air becomes saturated. One consequence of the strong temperature dependence of e_s is that modest amounts of lifting (adiabatic cooling) easily lead to saturation given most typical moisture levels.

Relative humidity (*RH*) is defined as the ratio of the actual water vapor pressure to the saturation vapor pressure, i.e. $RH = e/e_s$.

Water vapor mixing ratio (usually given the symbol q or q_v) is a common way to represent the water vapor content of the air, and is the mass of water vapor per mass of dry air. The vapor pressure e can be converted to a mixing ratio using:

$$q = \frac{\varepsilon e}{p - e} \qquad [12]$$

Where p is the air pressure and ε (=0.622) is the ratio of molar masses of water M_w and dry air M_a. An approximate form of equation [12] is often used because e is small compared with p:

$$q \approx \frac{\varepsilon e}{p} \qquad [13]$$

Saturation water vapor mixing ratio is calculated by applying [12] to the saturation vapor pressure e_s:

$$q_s = \frac{\varepsilon e_s}{p - e} \qquad [14]$$

The homework – Thermodynamics and Cloud Vertical Structure – explores some of the consequences for cloud formation and structure of the thermodynamic equations presented here.