Chapter Two
Review of Atmospheric Thermodynamics

Humidity Variables

This section contains a review of the humidity variables used by meteorologists.

⌡ **Vapor pressure, e**: The partial pressure of the water vapor in the atmosphere.

⌡ **Saturation vapor pressure, e_s**: The vapor pressure at which liquid water and vapor would be in equilibrium.

- Saturation vapor pressure is found from the *Clausius-Clapeyron* Equation,

$$e_s = e_o \exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \tag{2.1}$$

   where $T_o = 273.15\text{K}$, $e_{o} = 611$ Pa, L_v is the *latent heat* of vaporization, and R_v is the specific gas constant for water vapor.

- The Clausius-Clapeyron equation gives the saturation vapor pressure over a flat surface of pure liquid water.

- If the liquid contains impurities, or the interface between the liquid and vapor is curved, corrections for the *solute effect* and *curvature effect* must be applied.

⌡ **Relative Humidity, RH**: Relative humidity is defined as the ratio of vapor pressure to saturation vapor pressure, and is expressed as a percent.

$$RH = \frac{e}{e_s} \times 100\% \tag{2.2}$$

- Relative humidity is always defined in terms of a flat surface of pure liquid water.

- The World Meteorological Organization (WMO) uses an alternate definition of relative humidity, which is the ratio of mixing ratio to saturation mixing ratio,

$$RH = \frac{r}{r_s} \times 100\% \tag{2.3}$$

- The two definitions (2.2) and (2.3) are not identical, but are very close and are usually considered to be interchangeable.

) **Saturation Ratio, S**: The relative humidity expressed as a simple ratio rather than as a percent. For example, if $RH = 45\%$ then $S = 0.45$.

) **Absolute humidity, $_v$**: The mass of water vapor per volume of air. The relation between vapor pressure and absolute humidity is given by the ideal gas law for pure water vapor, (2.11).

) **Mixing ratio, r**: The mass of water vapor per mass of dry air. Mixing ratio is related to vapor pressure by

$$r \approx \frac{R_d}{R_v} \frac{e}{p - e} \approx \frac{e}{p - e} \tag{2.4}$$

where R_d and R_v are the specific gas constants for dry air and water vapor respectively, and p is the total air pressure.

) **Specific humidity, q**: The mass of water vapor per total mass of air.
- Mixing ratio and specific humidity are related via

$$q \approx \frac{r}{1 + r} \tag{2.5}$$

- Mixing ratio and specific humidity are very close in value, and are often used interchangeably.

) **Dewpoint, T_d**: The temperature to which air must be cooled at *constant pressure* and *specific humidity* in order to reach 100% relative humidity.

- When the temperature is equal to the dewpoint temperature, the vapor pressure is equal to the saturation vapor pressure. Thus, if dewpoint temperature is used in the Clausius-Clapeyron equation the result is the vapor pressure,

$$e \approx e_o \exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_o} - \frac{1}{T_d}\right)\right]$$

Ideal Gas Law

) The ideal gas law is

$$pV = nRT \tag{2.6}$$

where R is the *universal gas constant*, $8.3145 \text{ J mol}^{-1}\text{K}^{-1}$.

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⟩ Equation (2.6) is not the most convenient form for meteorology. Instead we use the form
$$p \, X\partial R \, \mathcal{T} \tag{2.7}$$

where R is the specific gas constant, a unique constant for each individual gas species.

- The specific gas constant is defined as
$$R \, \circledR X R \, / \, M \tag{2.8}$$

  where M is the molar mass of the gas.

⟩ The ideal gas law for dry air is
$$p \, X\partial R_d T \tag{2.9}$$

where R_d is the specific gas constant for dry air, 287.1 J kg^{-1} K^{-1}.

⟩ The ideal gas law can also be written in term of *specific volume*, $= 1/$,
$$p \Im \, X R_d T \tag{2.10}$$

⟩ For pure water vapor the ideal gas law is:
$$e \, X\partial_v R_v T \tag{2.11}$$
where R_v is the specific gas constant for water vapor, 461.5 J kg^{-1} K^{-1}, and $_v$ is the *absolute humidity*.

⟩ For moist air, which is a mixture of dry air and water vapor, the ideal gas law is:
$$p \, X\partial R_d T \, (1 \, \Gamma q \, Zq \, / \, \aleph \tag{2.12}$$

where q is the *specific humidity* and $= R_d/R_v$.

⟩ By defining the *virtual temperature* as:
$$T_v \, XT \, (1 \, Zq \, \Gamma q \, / \, \aleph \tag{2.13}$$
we can write (2.12) as
$$p \, X\partial R_d T_v \tag{2.14}$$

- Virtual temperature is simply a definition, allowing us to use the dry-air ideal gas law for moist air by simply using the virtual temperature in place of the actual temperature.

- Virtual temperature is not a measurable temperature. It must be calculated.

- Substituting for the value of   allows equation (2.13) to be written as:
$$T_v \, XT \, (1 \, \Gamma \, 0.61 q) \tag{2.15}$$

The First Law of Thermodynamics

⟩ The First Law of Thermodynamics states that there are two ways to change the internal energy, U of a system: 1) Add or remove heat, Q; 2) Via work, W, done on or by the system.

⟩ Mathematically it is stated as
$$dU = dQ + dW \tag{2.16}$$

⟩ The variables U, W, and Q are *extensive* variables, meaning that they depend on the mass of the system.

⟩ Dividing an extensive variable by mass results in an *intensive* variable that does not depend on mass. We usually (but not always) add the word specific to such variables. Dividing (2.16) by mass results in

$$du = dq + dw \tag{2.17}$$

where u is *internal energy per unit mass*, also called *specific internal energy*; q is *heat per unit mass*

⟩ For *quasistatic* processes the work can be expressed as $dw = -pd\alpha$, and the First Law becomes
$$du = dq - pd\alpha \tag{2.18}$$

- Note that for *isochoric* processes that the change in internal energy is synonymous with heat.

⟩ Using the product rule for differentiation, $d(p\alpha) = pd\alpha + \alpha dp$, and (2.18) can be rearranged as
$$dh = dq + \alpha dp \tag{2.19}$$

where $h = u + p\alpha$, and is the *specific enthalpy*.

- Note that for *isobaric* processes that the change in enthalpy is synonymous with heat.

⟩ For ideal gasses the specific internal energy is a function of temperature only, and can be expressed as $du = c_v dT$, where c_v is the *specific heat at constant volume*.

⟩ Also, for ideal gasses the specific enthalpy is a function of temperature only, and can be expressed as $dh = c_p dT$, where c_p is the *specific heat at constant pressure*.

⟩ Thus, for ideal gasses undergoing quasistatic processes the First Law of Thermodynamics can be written as either
$$c_v dT = dq - pd\alpha \tag{2.20}$$

or

$$c_p dT \ \text{X} dq \ \Gamma \Im dp \tag{2.21}$$

) In meteorology the First Law of Thermodynamics is also called the *thermodynamic energy equation*, and is one of the seven governing equations for the atmosphere.

Potential Temperature

) *Potential temperature,* , is defined as the temperature an air parcel would have if it were moved adiabatically to a reference pressure of $p_o = 1000$ mb.

- The equation for potential temperature is derived by starting with (2.21), setting $dq = 0$ and substituting for from the ideal gas law. The result is:

$$\frac{dT}{T} \ \text{X} \frac{R_d}{c_p} \frac{dp}{p} \tag{2.22}$$

Integrating (2.22) between temperatures T and , and between pressures p and p_o,

$$\int_T^\forall \frac{dT}{T} \ \text{X} \int_p^{p_o} \frac{R_d}{c_p} \frac{dp}{p}$$

yields the *Poisson relation*

$$\forall \text{X} T \ \left(\frac{p_o}{p} \right)^{R_d/c_p} \tag{2.23}$$

- Potential temperature is conserved in adiabatic motion. This means that the dry adiabats on a Skew-T diagram are also lines of constant potential temperature.

) *Equivalent potential temperature,* $_e$, is defined as the potential temperature the air parcel would have if it were lifted pseudo adiabatically until all of the water vapor were condensed, and the latent heat added to the parcel.

- Equivalent potential temperature is always greater than or equal to the potential temperature.
- Equivalent potential temperature is conserved in reversible moist-adiabatic motion.

Dry-adiabatic Lapse Rate

) Adiabatic processes are those in which no heat is transferred ($dq = 0$), and are of fundamental importance in atmospheric processes.

) As an air parcel rises adiabatically expands so that its pressure equilibrates to that of the surrounding environment.

- The parcel does work as it expands, and therefore loses internal energy and its temperature drops.

) The decrease in temperature with height can be found by starting with the first law of thermodynamics. For an air parcel undergoing an adiabatic process the first law of thermodynamics becomes

$$c_p\,dT' = \alpha'\,dp' \qquad (2.24)$$

where the primes indicate properties of the air parcel.

- Dividing (2.24) by dz results in

$$c_p\,\frac{dT'}{dz} = \alpha'\,\frac{dp'}{dz} \qquad (2.25)$$

- The pressure of the air parcel, p' is assumed to always be equal to the pressure of the its environment, p.

- If the environment is assumed to be in *hydrostatic balance*, then

$$\frac{dp'}{dz} = \frac{dp}{dz} = -\frac{g}{\alpha}$$

and (2.25) can be rearranged to

$$\frac{dT'}{dz} = -\frac{\alpha}{\alpha'}\frac{g}{c_p} \qquad (2.26)$$

) Equation (2.26) describes how the temperature change with altitude of an unsaturated air parcel lifted adiabatically. The ratio $\dfrac{\alpha}{\alpha'} \approx 1$, and is therefore ignored.

) Since *lapse rate* is defined as $-\dfrac{dT}{dz}$, *dry-adiabatic lapse rate* as

$$\Gamma_d = -\frac{dT}{dz} = \frac{g}{c_p} \qquad (2.27)$$

which has a numerical value of $\Gamma_d = 9.8\ \text{C km}^{-1}$.

- The specific heat actually depends in a very small way on the humidity content of the air. This correction is small enough that it is usually ignored and so c_p in (2.27) is that for dry air.

) Even though Γ_d is called the dry-adiabatic lapse rate, it is appropriate for a moist air parcel as long as the parcel remains unsaturated.

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Lapse Rate of a Saturated Parcel

⌡ If an air parcel is saturated, then as it rises and cools the relative humidity will exceed 100%.

  – Any excess vapor will condense and release latent heat back into the parcel.

  – The lapse rate in saturated ascent will be less than the dry-adiabatic lapse rate.

⌡ The value of the lapse rate in saturated ascent will depend on what assumptions are made as to:

  – whether or not the liquid water remains in the parcel for falls out immediately.

  – whether or not the correction to the specific heat, c_{pv}, for the water vapor is included or ignored.

⌡ The three different lapse rates for saturated ascent are:

  ⌡ ***Reversible moist-adiabatic lapse rate***: This assumes that any condensed liquid remains with the air parcel. The specific heats of the dry air, water vapor, and liquid water are all included.

  ⌡ ***Pseudoadiabatic lapse rate***: This assumes that any condensed liquid immediately leaves the parcel. The specific heat of water vapor is still explicitly included.

    ✓ Since the liquid water leaves the parcel, this process is *irreversible*.

  ⌡ ***Saturation-adiabatic lapse rate***: This is the same as the pseudoadiabatic lapse rate except is does not include the specific heat of the water vapor is ignored. This process is also irreversible.

⌡ The lapse rate for an ascending saturated air parcel is given by

$$\iota_s \, \text{X} \iota_d \; \frac{1\Gamma\dfrac{L_v r_s}{R_d T}}{1\Gamma\dfrac{\aleph L_v^2 r_s}{R_d c_p T^2}} \tag{2.28}$$

where L_v is the latent heat of vaporization, r_s is the saturation mixing ratio, and $= R_d/R_v$.

• At colder temperatures, such as those found in the upper troposphere, the moisture content of the air is very small, and there is little latent heating added to a rising air parcel. Thus, in the upper troposphere the moist adiabatic lapse rate approaches the dry adiabatic lapse rate.

Adiabatic Mixing of Air Parcels

⟩ If two air parcels are adiabatically mixed together, many thermodynamics properties of the mixture are a *mass-weighted mean* of their properties before mixing.

- A mass-weighted mean of some property s of two air parcels of masses m_1 and m_2 is given by the formula

$$\bar{s}_m = \frac{m_1}{m_1 + m_2}s_1 + \frac{m_2}{m_1 + m_2}s_2 \tag{2.29}$$

⟩ Formula (2.29) applies exactly if s is specific humidity q, and approximately for mixing ratio r and potential temperature .

⟩ If the air parcels being mixed are also at the same pressure (**isobaric mixing**), then temperature and vapor pressure also mix as mass-weighted means, and (2.29) also applies.

⟩ Adiabatic mixing of two initially unsaturated air parcels may actually result in a saturated air parcel

- This is why we can sometimes 'see our breath' on cold days.

⟩ The concept of mass-weighted mean can be applied to a continuous layer of air as follows:

- We imagine the layer consisting of a series of N very thin air parcels, each having a horizontal area A and thickness z_i.
- The mass-weighted mean is given by the sum

$$\bar{s}_m = \frac{\sum_i m_i s_i}{\sum_i m_i} \tag{2.30}$$

- Each parcel has a mass given by $\partial_i A\, z_i$, so that (2.30) becomes

$$\bar{s}_m = \frac{\sum_i \partial_i A \zeta z_i s_i}{\sum_i \partial_i A \zeta z_i} = \frac{\sum_i \partial_i \zeta z_i s_i}{\sum_i \partial_i \zeta z_i} \tag{2.31}$$

– In the limit as the thicknesses of the air parcels go to zero the summation turns into an integral, and the formula for the mass-weighted mean of a layer becomes

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$$\bar{s}_m \approx \frac{\int_{z_1}^{z_2} \partial s\, dz}{\int_{z_1}^{z_2} \partial dz} \tag{2.32}$$

∫ Formula (2.32) applies only to those parameters s that do not change as the air parcel moves up or down.

- Thus, it can be applied to specific humidity, mixing ratio, and potential temperature.
- Formula (2.32) _cannot_ be applied to temperature.

∫ Formula (2.32) can be written as a derivative with respect to pressure. The hydrostatic equation allows us to write $dz = -g\,dp$, so that (2.32) becomes

$$\bar{s}_m \approx \frac{\int_{p_2}^{p_1} g s\, dp}{\int_{p_2}^{p_1} g\, dp} \approx \frac{1}{\zeta p}\int_{p_2}^{p_1} s\, dp \tag{2.33}$$

where $p = p_1 - p_2$.

∫ During adiabatic mixing the specific humidity and potential temperature mix as mass-weighted means, and take on constant values in the mixed layer. The mixing ratio also mixes to a close approximation as a mass-weighted mean from (2.33) these values are

$$\bar{q}_m \approx \frac{1}{\zeta p}\int_{p_2}^{p_1} q\, dp \tag{2.34}$$

$$\bar{r}_m \approx \frac{1}{\zeta p}\int_{p_2}^{p_1} r\, dp \tag{2.35}$$

$$\bar{\forall}_m \approx \frac{1}{\zeta p}\int_{p_2}^{p_1} \forall\, dp \tag{2.36}$$

∫ On a diagram using a logarithmic pressure axis the averages for (2.34), (2.35), and (2.36) can be approximated graphically, by using the *method of equal areas*.

– The mass-weighted mean mixing ratio, r_m, is the isohume that splits the dewpoint profile into two equal areas, as shown in Figure 1.

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– The mass-weighted mean potential temperature, $_m$, is the adiabat that splits the temperature profile into two equal areas, as shown in Figure 1

) Adiabatic mixing is why surface temperatures on a windy night will be warmer than on a calm night.
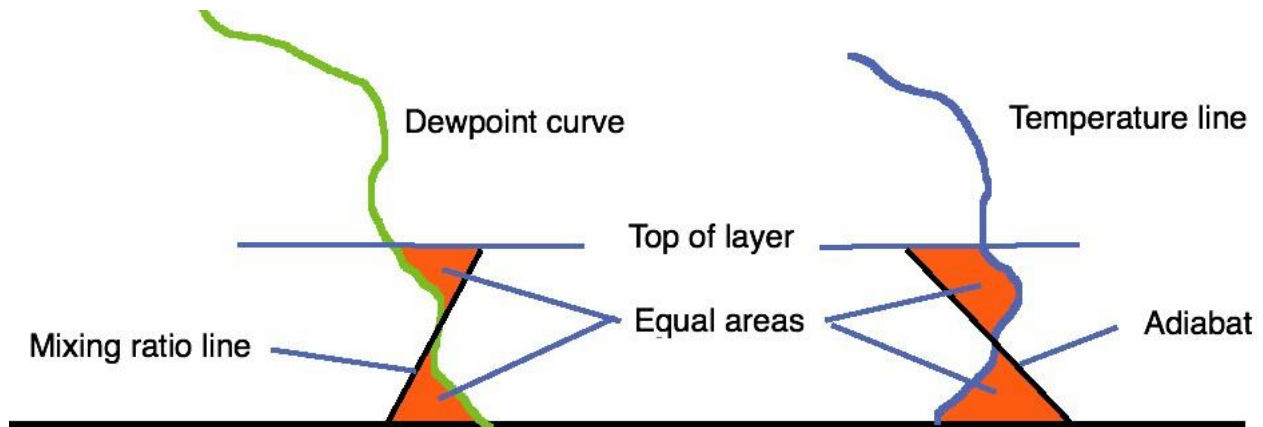

Figure 1: Equal-area method for determining mass-weighted mean of mixing ratio and potential temperature.

Convective Mixing and the CCL

) Another important mixing process for the atmosphere is *convective mixing*, which occurs when a layer of air is heated from below and the upward and downward over-turning of the layer mixes the air parcels.

) Convective mixing is *not adiabatic*.

– In a convectively mixed layer still takes on a constant value, but it is not given by (2.36).

– Instead, in a convectively mixed layer will be the value of the adiabatic through the surface temperature.

– Mixing ratio in a convectively mixed layer will still be given by (2.35).

) A morning sounding usually has a surface inversion

) The *convective temperature*, T_c, is the temperature that the surface must reach in order for an air parcel to ascend dry adiabatically to reach the CCL.

– The convective temperature is found by following a dry adiabatic downward from the CCL to the surface, and reading the temperature at that point.
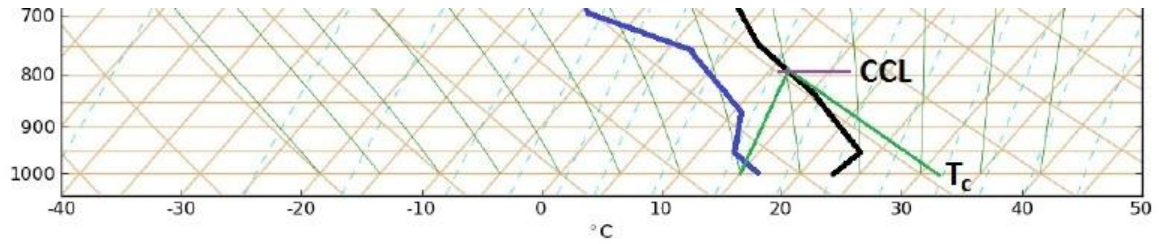– Figure 2 illustrates the determination of the convective temperature.

Figure 2: Example Skew-T showing how to find the convective temperature, T_c.