

# Climate Physics Chapter 2: Thermodynamics

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How can we use thermodynamics to understand the structure of our atmosphere?

From weather balloon data, we know that pressure in the atmosphere decreases monotonically with height. We use pressure as a fundamental vertical coordinate because it is easily measurable, and it is a fundamental thermodynamic variable that tells us about the state of gases in the atmosphere. Because height is linearly related to the log of pressure, we also often use  $-\ln \frac{p}{p_o}$ , where  $p_o$  is the largest relevant pressure, as a height-like coordinate that increases with height.

Temperature decreases with height until a critical height, called the tropopause, above which it increases with height. The atmosphere below the tropopause is called the troposphere, and the portion immediately above is the stratosphere. This is a typical pattern that we observe in many planetary atmospheres.

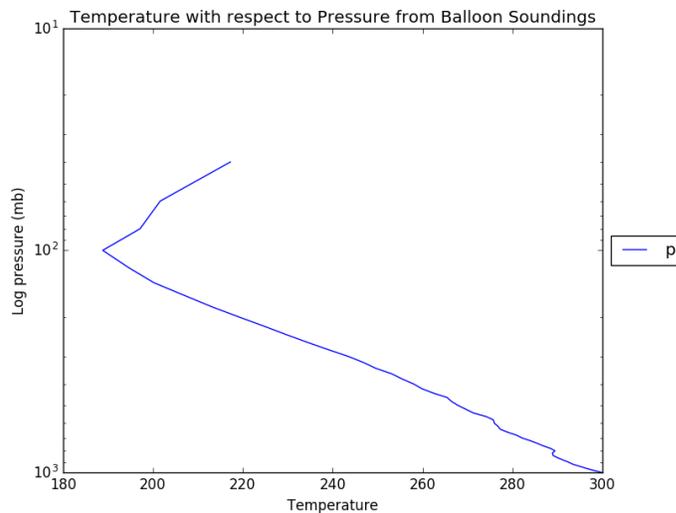


Figure 1: Balloon Sounding of the atmosphere over the tropical Pacific, taken during the CEPEX field campaign on March 12, 1993.

## 1 Dry Thermodynamics of an Ideal Gas

### 1.1 The Ideal Gas Equation

In thermodynamics, we are concerned with three main variables:

Temperature ( $T$ ): Proportional to the average kinetic energy per molecule. We say two objects have the same temperature when they are in thermodynamic equilibrium, where heat flows from hotter areas to cooler

areas no longer occur.

Pressure( $p$ ): Force per unit area exerted on a surface in a direction perpendicular to the surface.

Density( $\rho$ ): mass divided by volume.

The ideal gas law relates these three variables:

$$p = k_B n T = R \rho T \quad (1)$$

In the first equality,  $k_B$  is Boltzmann's constant, with a value of  $1.3806 \text{ kg } \left(\frac{\text{m}}{\text{s}}\right)^2 \text{ K}^{-1}$ , and  $n$  is the number of molecules per unit volume. In the second equality, we instead write the equation in terms of mass density  $\rho$  and  $R$ , the gas constant, defined as  $R = \frac{R^*}{M}$ , where the universal gas constant  $R^* = 8314.5 \left(\frac{\text{m}}{\text{s}}\right)^2 \text{ K}^{-1}$  and the molecular weight  $M$  is an integer telling the number of protons and neutrons in a molecule.

### 1.1.1 Example Problem: The Ideal Gas Law

A bicycle tire with mass 0.1 kg when empty and a volume of 3 liters is pumped up with Earth air to a pressure of 4 bars. Its temperature remains at the ambient air temperature of 290 K. What is the mass of the tire after it has been pumped up?

We have  $R_{dryair} = 287 \frac{\text{m}^2/\text{s}^2}{\text{K}}$ .

$$m = \frac{pV}{RT} = \frac{4 \cdot 10^5 \text{ Pa} \cdot 0.003 \text{ m}^3}{287 \frac{\text{m}^2/\text{s}^2}{\text{K}} \cdot 290 \text{ K}} = 0.015 \text{ kg} \quad (2)$$

## 1.2 Partial Pressures

In a mixture of gases in a given volume, each component gas behaves as if it occupies the volume alone. The pressure due to a single component is the partial pressure of that component. The ratio of partial pressures in a gas describes the composition of that gas.

If we look at a mixture of 2 gases A and B, with partial pressures:

$$p_A = k_B n_A T \text{ and } p_B = k_B n_B T \quad (3)$$

Then the molar mixing ratio  $\xi_A$  of A to B is:

$$\xi_A = \frac{p_A}{p_B} = \frac{n_A}{n_B} \quad (4)$$

This relates to the molar concentration of A  $\eta_A$ :

$$\eta_A = \frac{\xi_A}{(1 + \xi_A)} = \frac{n_A}{(n_A + n_B)} \quad (5)$$

If the gas is very diffuse, and  $\xi \ll 1$ ,  $\xi$  and  $\eta$  will be nearly the same.

We can also describe composition by mass. The mass mixing ratio  $r$  is the ratio of masses of the substances in a given parcel of gas:

$$r_A = \frac{\rho_A}{\rho_B} = \frac{M_A p_A}{M_B p_B} \quad (6)$$

Similarly we define the mass specific concentration  $q$ :

$$q_A = \frac{\rho_A}{\rho_{total}} = \frac{M_A}{\bar{M}} \frac{p_A}{p_{total}} = \frac{M_A}{\bar{M}} \eta_A, \quad (7)$$

where  $\bar{M}$  is the mean molecular weight of the mixture according to the molar concentrations. We use these ratios because they remain unchanged if the gas contracts or expands, and because unless gases are quickly being created or destroyed, most mixtures of gases will be well-mixed, meaning these ratios will be uniform throughout.

### 1.3 Specific Heat and Conservation of Energy

When a gas expands or contracts, the work done over a volume change  $dV$  is  $pdV$ . Dividing by mass, we can write this as  $pd(\rho^{-1})$ . When a gas changes temperature at a fixed volume the energy stored changes by  $c_v dT$ , where  $c_v$  is the gas's specific heat at constant volume. We can then write, by conservation of energy:

$$\delta Q = c_v dT + pd(\rho^{-1}) \quad (8)$$

Using the chain rule and the ideal gas law, we can rewrite this as:

$$\delta Q = (c_v + R)dT - \rho^{-1}dp \quad (9)$$

This allows us to define the specific heat at constant pressure  $c_p \equiv c_v + R$ .

### 1.4 Entropy and Potential Temperature

We define entropy:

$$S = c_p \ln(Tp^{-R/c_p}) \quad (10)$$

The second law of thermodynamics tells us that entropy never decreases for a closed system. A process which has constant entropy is therefore reversible. For an adiabatic process, where  $\delta Q = 0$ , entropy will stay constant provided the system stays in thermodynamic equilibrium at all times.

We can use entropy to determine how temperature changes with changing pressure. For an adiabatic expansion or compression from some initial state at  $T_o$  and  $p_o$ , the second law tells us we have:

$$Tp^{-R/c_p} = T_o p_o^{-R/c_p} \quad (11)$$

Based on this equation, we define potential temperature:

$$\theta = T \left( \frac{p}{p_o} \right)^{-R/c_p} \quad (12)$$

The potential temperature is the temperature the air would have if it was all brought to some reference pressure  $p_o$ . It is conserved in adiabatic processes.

The atmosphere tends towards constant  $\theta$  in its vertical composition. This yields the temperature profile of the dry adiabat:

$$T(p) = \theta \left( \frac{p}{p_o} \right)^{R/c_p}, \quad (13)$$

where  $\theta = T(p_o)$  is the temperature at the reference pressure  $p_o$ .

The dry adiabat gives us a basic model for the temperature profile of an atmosphere. The slope of the dry adiabat  $\frac{d \ln T}{d \ln p} = \frac{R}{c_p}$ , which determines how sharply the temperature decreases with height.

#### 1.4.1 Example Problem: Dry Adiabat

The aforementioned bicycle tire with a volume of 3 liters is pumped up with Earth air to a pressure of 4 bars. If is pumped up rapidly enough that it does not lose any heat to its surroundings. If the ambient air is at 290 K, what is the temperature in the tire immediately after it has been pumped up?

We use the potential temperature, which tells us the temperature at some reference pressure  $p_o = 4$  bar.

$$\theta = T \left( \frac{p}{p_o} \right)^{-R/c_p} = 290 \text{ K} \left( \frac{1 \text{ bar}}{4 \text{ bar}} \right)^{-2/7} = 430 \text{ K} \quad (14)$$

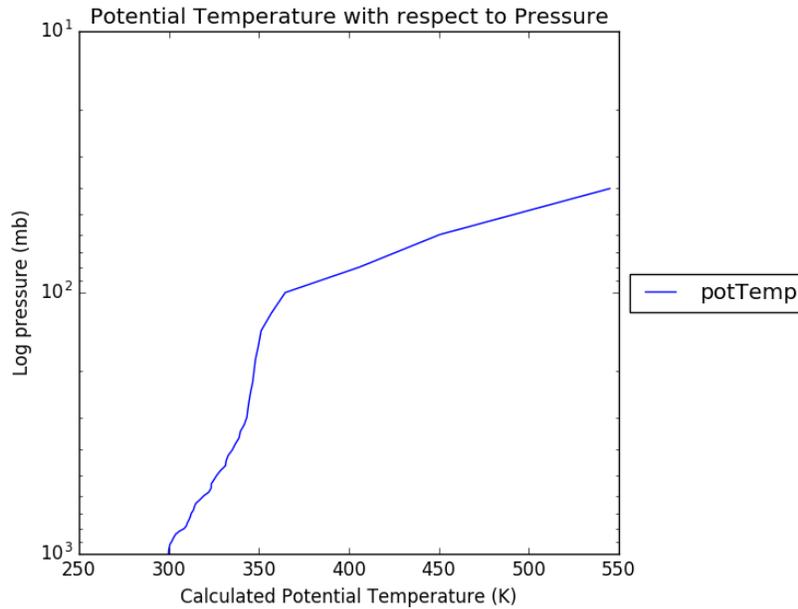


Figure 2: Potential temperature with respect to pressure from the CEPEX sounding. In the stratosphere, air is highly stratified. If you were to move a piece of atmosphere to a lower altitude, it would heat up enough to make it rise back up to its spot. In the troposphere, the gradient of  $\theta$  is lower so it is less stratified. The atmosphere is compressible so it tends towards constant  $\theta$  as opposed to constant  $T$ . This is because  $\theta$  is conserved for adiabatic processes such as those caused by rapid vertical displacements. However, this means that  $T$  decreases with height. There is something that prevents  $\theta$  from being completely well mixed, but what determines this gradient is still largely unsettled. The code from the previous sounding plot can also be used to generate this plot.

What is the pressure after the tire has had time to cool to the ambient temperature?  
 First, we find the density of the gas when it is still hot:

$$\rho = \frac{p_i}{RT_i} = \frac{4 \cdot 10^5 \text{ Pa}}{287 \frac{\text{m/s}^2}{\text{K}} \cdot 430 \text{ K}} = 3.24 \text{ kg/m}^3 \quad (15)$$

The density when hot is the same as the density when it is cold, because the quantity of gas is confined to a constant volume. So we can now solve for the new cooled pressure.

$$p = R\rho T = 287 \frac{\text{m/s}^2}{\text{K}} \cdot 3.24 \text{ kg/m}^3 \cdot 290 \text{ K} = 2.7 \text{ bar} \quad (16)$$

## 2 Static Stability of Inhomogeneous Mixtures

An atmosphere is statically unstable if air displaced from its original position tends to continue rising or sinking instead of returning to its original position. A statically unstable state tends to mix until it becomes stable.

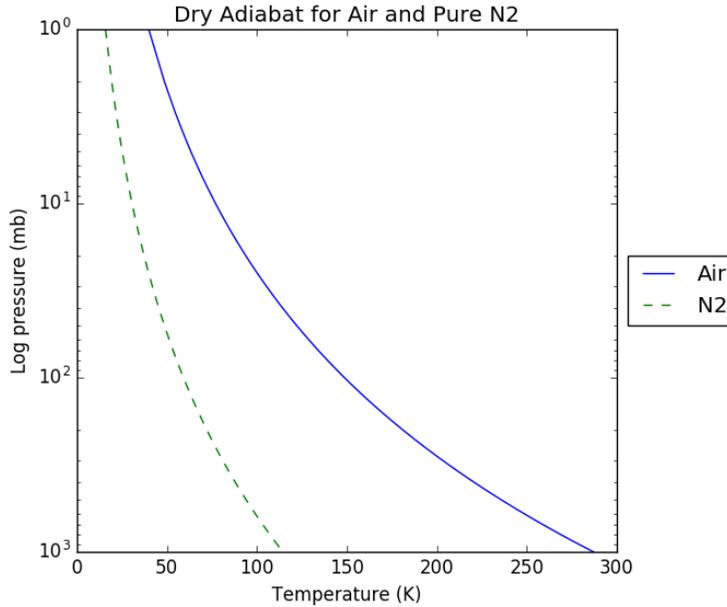


Figure 3: This graph compares the dry adiabat profiles for air, which is 20% oxygen and 80% nitrogen by mole, and for pure nitrogen, which was the composition of the pre-biotic atmosphere on earth.

In a well mixed atmosphere, air with potential temperature  $\theta_o$ , when moved to altitude  $p_1$  has density

$$\rho_o = \frac{p_1}{RT} = p_1 \left( R\theta_o \left( \frac{p_1}{p_o} \right)^{R/c_p} \right)^{-1}. \quad (17)$$

If the air was raised up to  $p_1$ , it will return to its position at  $p_o$  only if  $\rho_o > \rho_1$ . This is the case if and only if  $\theta_o < \theta_1$ . So if the potential temperature increases with height, the atmosphere will be statically stable.

In an inhomogeneous atmosphere, however, this is not the case because the gas constant  $R$  may vary from place to place. At constant  $\theta$ , changing  $R$  can cause unstable density jumps between areas, so the substances will tend to mix.

We define a potential density as the density an air parcel would have if compressed or expanded adiabatically to a standard reference pressure  $p_o$ .

$$\rho(p) = \frac{p_o}{R\theta} = \frac{p_o}{RT} \left( \frac{p}{p_o} \right)^{R/c_p} = \rho(p) \left( \frac{p}{p_o} \right)^{R/c_p-1} \quad (18)$$

This tells us about the stability of the system. If  $\rho(p)$  increases with  $p$ , the system is stable because air pushed down to  $p_o > p$  will have a lower density than the surrounding air and will then rise back towards its original spot, and similarly if the air is displaced upwards.

For a homogeneous atmosphere, it is easy to tell from a single plot of potential density where the atmosphere is stable. For an inhomogeneous atmosphere, one must reduce the parcels of the different gases to a common pressure each according to their own values of  $R/c_p$ , and compare the densities there.

### 3 Hydrostatic Relation

This equation relates atmospheric pressure to altitude. This relation is what allows us to work in pressure coordinates, instead of altitude.

We consider a column of air with pressure  $p$ , height  $z$ , and cross-sectional area  $A$ . By looking at the force on a small horizontal slice of the column, assuming the acceleration due to gravity,  $g$ , remains relatively constant throughout the column, we can say:

$$dm = -\frac{dp}{g} \quad (19)$$

$$\frac{dp}{dz} = -\rho g \quad (20)$$

An important consequence is that this allows us to find the mass per unit of planet surface area of an atmosphere.

$$m = \frac{p_s}{g} \quad (21)$$

Where  $p_s$  is the surface pressure. To find the mass of a specific substance A, multiply by the mass specific concentration  $q_a$ . To find the mass from a partial pressure  $p_A$  in a well mixed mixture of gasses, replace  $p_s$  with  $p_A \frac{M_A}{\bar{M}}$ , where  $M_A$  is the molecular weight of A and  $\bar{M}$  is the mean molecular weight of the mixture.

### 3.0.1 Example Problem: Finding mass of atmosphere

Venus has a surface pressure of 92 bar, and a surface gravity of 8.87 m/s<sup>2</sup>. 3.5 percent of the atmosphere by mole fraction consists of  $N_2$ . Compute the mass of  $N_2$  per unit surface area of Venus.

Mass per square meter =  $m q_a = q_a \frac{p_s}{g} = 3.6 \cdot 10^4$  kg

We can also use integrate the hydrostatic relation to get the pressure as a function of altitude.

$$p(z) = p_s \exp\left(-\frac{g}{R\bar{T}}z\right) \quad (22)$$

$\bar{T}$  is the harmonic mean temperature, and since it is measured relative to absolute zero it is relatively constant.

We can also use the hydrostatic relation to rewrite our thermodynamic heat budget, yielding (assuming  $c_p$  is constant):

$$\delta Q = d(c_p T + gz) \quad (23)$$

The quantity  $c_p T + gz$  is the dry static energy, which tells us the energy per unit mass of atmosphere.

### 3.0.2 Example Problem: Dry Static Energy

Show that  $\frac{dT}{dz} = -\frac{g}{c_p}$ , assuming dry static energy is independent of height. By assumption:

$$c = c_p T + gz$$

Differentiating with respect to  $z$ :

$$0 = \frac{dT}{dz} c_p + g$$

$$\frac{dT}{dz} = -\frac{g}{c_p}$$

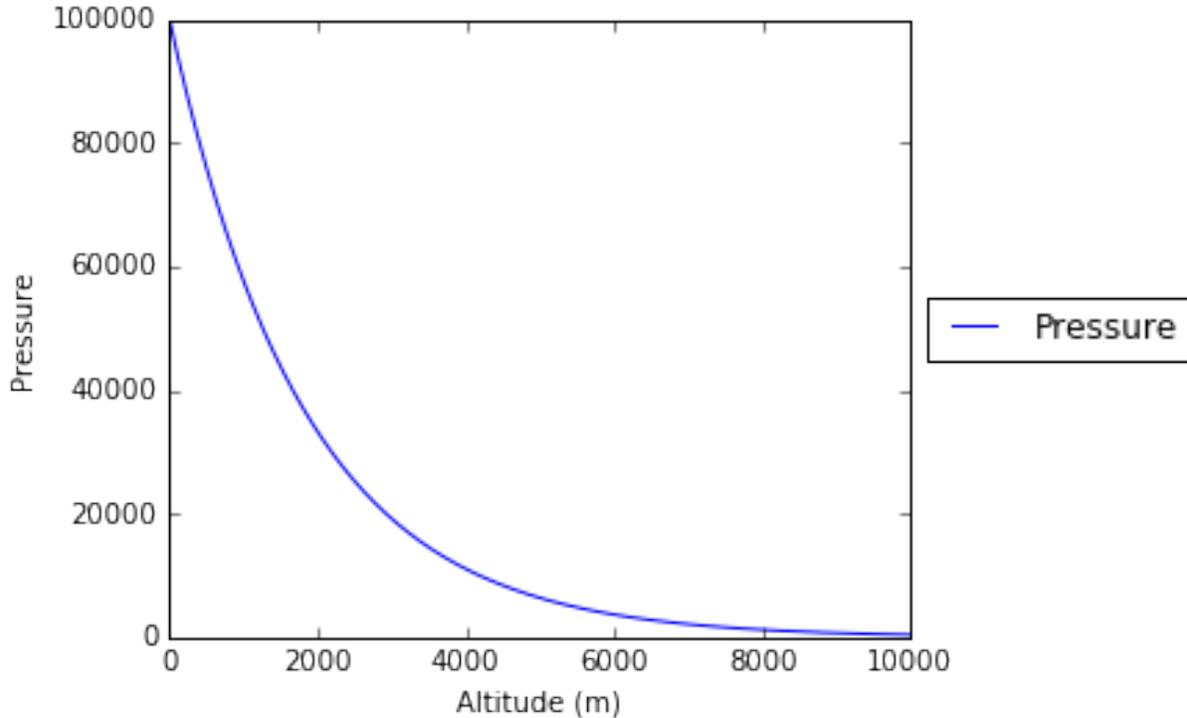


Figure 4: A graph of the altitude versus pressure of the atmosphere as calculated by the integrated hydrostatic relation. As expected, we see pressure decrease as we go to higher altitudes.

## 4 Phase Change, Latent Heat, and Clausius Clapyron

### 4.1 Latent Heat

Latent heat ( $L$ ) is the energy released/absorbed when a unit mass of a substance goes through a phase change. It varies a little with temperature, but for the most part we treat it as constant. Atmospheres can transport energy through phase change by evaporating a liquid into an air parcel, which increases the mixing ratio by  $\delta r$ , moving it, and recondensing the liquid. This moves  $L\delta r$  heat per unit mass of incompressible air. The saturation vapor pressure ( $p_{sat}$ ) of a gas tells us the ability of a gas to condense. If partial pressure of gas is below  $p_{sat}$ , we can add more of the gas without condensation. When  $p_{sat}$  is reached, the gas is saturated, and adding more of it will cause gas to condense out until it once again reached  $p_{sat}$ .

#### 4.1.1 Example Problem: Latent Heat

Consider a glacier of water ice that is 1km thick and covers an area of  $10^8 \text{ km}^2$ . The ice absorbs  $50 \text{ W/m}^2$  of solar radiation, and all of this is used to either sublimate or melt the ice. How long does it take for the glacier to disappear? Ice has a density of  $930 \text{ kg/m}^3$

The amount of energy the glacier absorbs per second is equal to the absorption rate times the area, and for the ice to disappear, it has to absorb an amount of energy equal to the latent heat of the phase change times the mass of the ice. Setting these equal to each other:

$$\text{Absorption} * SA * t = L * m = L * \rho * V$$

If all the ice melts, we use the latent heat of ice melting:  $L = 3.34 \cdot 10^5 \text{ J/kg}$ . Solving for  $t$  and plugging in values yields:

$$t = \frac{L\rho V}{\text{Absorption SA}} = \frac{3.34 \cdot 10^5 \text{ J/kg} \cdot 930 \text{ kg/m}^3 \cdot 10^{17} \text{ m}^3}{50 \text{ W/m}^2 \cdot 10^{19} \text{ m}^2} = 6e9 \text{ s} \approx 200 \text{ yr}$$

Similarly, if the ice sublimates, we can use the latent heat of ice sublimating:  $L = 28.4 \cdot 10^5$ . In this case, since it requires more energy to convert the ice into a vapor, the process will take around 1700 years. Which will occur will depend on if we are above or below the triple point temperature and pressure of water.

## 4.2 Clausius Clapyron

The Clausius Clapyron equation tells us the temperature dependence of saturation vapor pressure of a substance. We can use this equation to tell us if a substance at some temperature is likely to change phase.

$$\frac{dp_{sat}}{dT} = \left(\frac{1}{T}\right) \left(\frac{L}{\rho_v^{-1} - \rho_c^{-1}}\right) \quad (24)$$

Where  $L$  is the latent heat of the phase transition,  $\rho_v$  is the density of the less condensed phase, and  $\rho_c$  is the density of the more-condensed phase.

For vapor transitions,  $\rho_c \gg \rho_v$ , so we can ignore the second term in the denominator. Using the gas law to substitute for the density, we get a simplified form:

$$\frac{dp_{sat}}{dT} = \frac{L}{R_A T^2} p_{sat} \quad (25)$$

where  $R_A$  is the gas constant of the substance. If we assume  $L$  is constant, we can solve in terms of some reference temperature  $T_0$  to get:

$$p_{sat}(T) = p_{sat}(T_0) \exp\left(-\frac{L}{R_A} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (26)$$

However, at high  $T$ , this assumption breaks down and  $L$  goes to 0.

### 4.2.1 Example Problem: Clausius Clapyron on Titan

Titan has a surface temp of 95 K. Suppose there is a lake of liquid methane on the surface, and that the air just above is saturated with respect to methane. What is the partial pressure of methane near the surface? Since the air is saturated, the partial pressure of methane is equal to the saturation pressure, which we can use Clausius Clapyron to find. As a reference point, we can use the triple point of methane, which occurs at  $T_0 = 90.67 \text{ K}$  and  $p_{sat} = 0.117e5 \text{ Pa}$ . We also need some properties of methane:  $L = 5.36e5 \text{ J/kg}$ , and  $R_A = 8314.5/16 \text{ (m/s)}^2/\text{K}$ . We can plug these values into the equation:

$$p_{sat}(T) = p_{sat}(T_0) \exp\left(-\frac{L}{R_A} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

$$p_{sat} = 0.117 \cdot 10^5 \text{ Pa} \exp\left(-\frac{5.36 \cdot 10^5 \text{ J/kg}}{8314.5/16 \text{ (m/s)}^2/\text{K}} \left(\frac{1}{95 \text{ K}} - \frac{1}{90.67 \text{ K}}\right)\right) = 0.197 \cdot 10^5 \text{ Pa}$$

## 5 The Moist Adiat

If a component of the atmosphere condenses, this releases energy, causing it to be warmer than the dry adiabat predicts. If the system stays at saturation, we can describe it using the moist adiabat. We look at 2 different cases: a single component condensing atmosphere, and an atmosphere that is a mixture of a condensable substance with a substance that won't condense in the given conditions.

## 5.1 Single Component

Since we only have 1 component, the partial pressure of the component is the total pressure. So if the atmosphere is saturated,  $p = p_{sat}$ , which is given by the Clausius Clapyron relation. Solving that for T, we get the saturated moist adiabat:

$$T(p) = \frac{T_0}{1 - \frac{RT_0}{L} \ln\left(\frac{p}{p(T_0)}\right)} \quad (27)$$

This tells us the temperature at which the substance will condense for a given pressure. A convenient point to use for our reference point  $p(T_0)$  is the surface temperature and pressure. As pressure decreases, temperature increases, which is what we would expect for an increase in altitude.

## 5.2 Mixture of condensable and non-condensable gas

The condensable gas is denoted with the subscript c, and the non-condensable gas is denoted with the subscript a. We assume the gas is initially saturated, and that when condensation occurs, the condensate is removed. By looking at the heat budget of the system, we can derive a differential equation for  $\ln T$  as a function of  $\ln p_a$ :

$$\frac{d \ln T}{d \ln p_a} = \frac{R_a}{c_{pa}} \frac{1 + \frac{L}{R_a T} r_{sat}}{1 + \left( \frac{c_{pc}}{c_{pa}} + \left( \frac{L}{R_c T} - 1 \right) \frac{L}{c_{pa} T} \right) r_{sat}} \quad (28)$$

Where  $r_{sat} = \epsilon \frac{p_{c,sat}(T)}{p_a}$  where  $p_{c,sat}$  is determined from Clausius Clapyron and  $\epsilon$  is the ration of the molecular weights  $\frac{M_c}{M_a}$ .

If the atmosphere isn't fully saturated, for example, if the surface temperature is high enough that the surface pressure is less than  $p_{sat}$ , the air will follow the dry adiabat until it reaches an altitude at which it becomes saturated, whereupon it will begin following the moist adiabat. This altitude is called the lifted condensation level.

How do we know if condensation happens upon ascent or descent through the atmosphere? If the moist adiabat slope  $\frac{d \ln T}{d \ln p}$  is smaller than the dry adiabatic slope  $\frac{R}{c_p}$ , then adiabatically lifting a parcel of air creates enough cooling to condense the gas. If the moist adiabatic slope is larger than the dry adiabatic slope, then condensation will happen on descent. In practice, we usually find ourselves in the situation where condensation occurs on ascent.