

# 1 Thermodynamics: some Preliminaries

Before we begin to consider the transfer of radiation through an atmosphere, let's consider the structure of an atmosphere with a little thermodynamics. This material hopefully is a review for you. It is also perfect stuff for an orals exam, something to note if you haven't had the pleasure yet. So the questions that we address here are following. What is the relationship between the macroscopic variables that define an atmosphere and that are treated in thermodynamics, i.e. pressure ( $P$ ), temperature ( $T$ ), gravity ( $g$ ), density ( $\rho$ ) and, where applicable, altitude ( $z$ ).

## 1.1 Hydrostatic Equilibrium

The pressure of an atmosphere varies with height, because gas is easily compressed by the weight of the overlying atmosphere. Consider a parcel of gas extended over an altitude  $z$  to  $z + \Delta z$  and a horizontal area  $A$ . The parcel is not moving; the sum of all forces is zero:

$$[P(z + dz) - P(z)]A + \rho g A \Delta z = 0,$$

where the first term is the force due to pressure on the parcel and the second the weight of the parcel. Note that  $g$  is the acceleration of gravity (and can be adjusted to include centripetal acceleration and the non-spherical nature of rotating planets). In the limit as the height of this parcel becomes infinitesimally small:

$$\frac{[P(z + dz) - P(z)]}{\Delta z} = \frac{dP}{dz} = -\rho g,$$

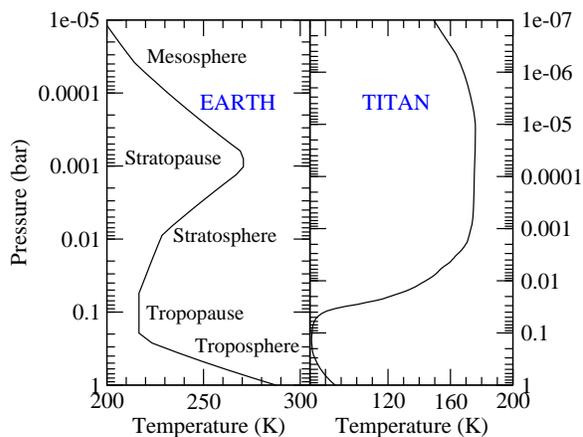


Figure 1: **US Standard atmosphere for Earth, used for aircraft simulations. Titan's profile as measured by Voyager.**

which is the equation of hydrostatic equilibrium.

Consider the ideal gas law,

$$PV = nRT = NkT,$$

where  $R = 8.3145$  J/mol K is the universal gas constant, and the Boltzmann constant is  $k = 1.38066 \times 10^{-23}$  m<sup>2</sup> kg s<sup>-2</sup> K<sup>-1</sup> =  $R/N_A$ . Here  $N_A = 6.022141 \times 10^{23}$  molecules, is the number of molecules in a *mole*. Finally  $N$  is number of molecules and  $n = N/N_A$  is

the number of moles. The mass density is then the number of moles per unit volume times the mass of a mole:

$$\rho = \frac{Pm}{RT}.$$

Here  $m$  is oddly called the mean molecular mass, but in fact it is the mass of a mole of molecules. Integrate this expression:

$$\int_{P_0}^P \frac{dP}{P} = - \int_{z_0}^z \frac{gm}{RT} dz \quad (2)$$

That is:

$$P = P_0 \exp\left[- \int_{z_0}^z \frac{gm}{RT} dz\right] = P_0 \exp\left[- \int_{z_0}^z \frac{dz}{H}\right].$$

Here we have introduced the pressure scale height,  $H$ :

$$H = \frac{RT}{mg} \quad (3)$$

Note that for an isothermal atmosphere (over little change in  $g$ ),  $H$  is constant and is the e-folding distance for changes in  $\rho$  and  $P$ . That is:

$$P = P_0 \exp[-z/H].$$

This is a simple method for estimating the pressure of an atmosphere at a given height. For a more exact derivation of the pressure, we integrate the hydrostatic equation, taking into account the correct equation of state (which is important for Titan) and the altitude variation in the temperature and gravity (which is important for Jupiter, extrasolar planets and brown dwarfs).

## 1.2 Define Column Abundance

Now that we have a simple method for deriving the pressure change with height, you might then need to calculate the total number of molecules of gas, per unit area, that are contained in a slab of atmosphere defined by two pressure levels. After all, to calculate the absorption properties of gases, we need to know how many molecules we're dealing with.

The integrated number of moles per unit area of an atmosphere above an altitude  $z$  is called the column number density:

$$U = \int_z^\infty N dz,$$

which, assuming hydrostatic equilibrium, can be written as

$$U = \int_z^\infty \frac{N}{-\rho g} dP.$$

Noting that  $\rho/N$  is the average mass of a molecule in the atmosphere, i.e.  $m/N_A$ , we get:

$$U = - \int_P^0 \frac{N_A dP}{mg} = \frac{PN_A}{mg}. \quad (4)$$

Now I introduce a very obscure unit of density that pervades planetary astronomy, the amagat. An amagat is the number density of air at standard temperature and pressure:

$$N_{amag} = P_0/RT_0 = 44.615 \text{ moles/m}^3,$$

or

$$N_{amag} = 44.615 N_A = 2.6868 \times 10^{25} \text{ m}^{-3}.$$

Here  $P_0$  and  $T_0$  are the pressures and temperatures at STP. The density of air at a pressure,  $P$ , and temperature,  $T$  is then in units of amagats equal to:

$$N = \frac{N(\text{moles/ m}^3)}{P_0/RT_0} \text{ amagats.}$$

Often column abundances are discussed in terms of meter amagats:

$$U = \frac{P}{mg} \frac{RT_0}{P_0}$$

or

$$U = \frac{P}{P_0} \frac{RT_0}{mg} = P(\text{atm}) \frac{RT_0}{mg}$$

It's interesting to consider the atmospheres of brown dwarfs at this point. The cool ones ( $T_{eff} < 1000$  K) have compositions very similar to those of Jupiter and Saturn. So why study such an atmosphere if we've got some close by? One reason is that they provide a view down to the deep atmospheres of giant planets where the pressures and temperatures are higher than those that we can see in the solar system. A brown dwarf that is 50 times the mass of Jupiter has the same overlying column abundance of gas at 50 bars as Jupiter has at 1 bar, assuming the same radius and temperature!

Another interesting thing to ponder is the general composition and size of the bodies in the Solar System with the largest atmospheres. In the calculations of the table below, I've assumed values of  $c_p$  of 1.0, 0.85, 0.83, 1.04 J/gm/K for Earth, Venus, Mars, & Titan, respectively. Note that we have two CO<sub>2</sub> rich atmospheres, the smallest and

largest, and two N<sub>2</sub> atmospheres, the middle guys, Titan and Earth. Titan is also resembles Earth in that it has a methane cycle, which similar to the hydrological cycle, sports clouds, rain and seas. Titan might resemble conditions on early, possibly methane rich, Earth.

## 2 Temperature

The temperatures of planetary atmospheres are obviously set to some extent by the total integrated insulation entering an atmosphere, because at the top of the atmosphere the energy per second entering in an atmosphere must equal that emitted by the atmosphere, assuming no internal source of energy, which is important particularly for Jupiter. The emission rate of a planetary atmosphere depends its temperature, which therefore must depend on the distance of the planet to the Sun, as we would expect.

To estimate a planet's temperature we can start by simplifying assumption that the atmosphere and surface have the same constant temperature. Then it emits energy at the rate of a black body, that is with a power per unit area of

$$P_{Sun} = \sigma T_{eff}^4$$

where  $\sigma = 5.67 \times 10^{-8}$  kg m<sup>2</sup> s<sup>-3</sup> K<sup>-4</sup> is the Stefan-Boltzmann constant. This temperature is called the effective temperature of the planet. The Sun emits a total power (luminosity) of  $L = 3.839 \times 10^{26}$  Watts, which at Earth's distance from the Sun,  $D =$

| Planet | $P_S$<br>bar | $T_S$<br>K | $g$<br>m/s <sup>2</sup> | $U$<br>km am | $H$<br>km | $\Gamma$<br>K/km | Composition                                 |
|--------|--------------|------------|-------------------------|--------------|-----------|------------------|---|
| Earth  | 1.01         | 288        | 9.8                     | 8.1          | 8.5       | 9.8              | 78% N <sub>2</sub> , 21% O <sub>2</sub>     |
| Venus  | 92           | 755        | 8.9                     | 540          | 15.9      | 10.5             | 96.5% CO <sub>2</sub> , 3.5% N <sub>2</sub> |
| Mars   | 0.008        | 210        | 3.7                     | 0.1          | 11.1      | 4.5              | 95.3% CO <sub>2</sub> , 2.7% N <sub>2</sub> |
| Titan  | 1.45         | 94.5       | 1.35                    | 87           | 20        | 1.3              | 95% N <sub>2</sub> , 3% CH <sub>4</sub>     |

$1.496 \times 10^{11}$  m, is a flux of

$$F_{Planet} = \frac{L}{4\pi D^2}.$$

Earth receives this radiation over its projected area,  $\pi R^2$  where  $R$  is the radius of the Earth. Only a fraction equal to  $1-A$ , where  $A$  is the bond albedo is absorbed. Equating the power of radiation absorbed by Earth is to that emitted:

$$\pi R^2 (1 - A) \frac{L}{4\pi D^2} = \sigma T_{eff}^4 4\pi R^2$$

A simple derivation of an atmosphere's temperature profile is more involved because it manifests the partitioning of solar and reradiated infrared radiation from Earth. On Earth most of the solar radiation reaches the surface ( 57%). The atmosphere is on average warmest at the surface. It cools radiatively, and secondarily through convection, in the lower 15 km of the atmosphere, the troposphere. At roughly 15 km altitude there is a temperature minimum, the tropopause, above which temperatures rise, as first discovered by balloon experiments in 1902. The temperature minimum is correlated with changes in composition. The partial pressure of water is constrained to lie

below its saturation pressure of  $1.3 \times 10^{-5}$  at the tropopause (assuming  $T=216$  K,  $P=0.2$  bar), much lower than the surface value of 0.017 bar (at  $T=288$  K,  $P=1$ bar). The ozone concentration, increasing by an order of magnitude within the first couple of kilometers above the tropopause, is formed from the photodissociation of O<sub>2</sub>. Ozone absorbs radiation shortward of 320 nm, thereby heating the atmosphere to temperatures of  $\sim 270$  K at 50 km altitude, the stratopause. Above this level, in the mesosphere, temperatures fall to a minimum of  $\sim 180$  K at  $\sim 90$  km altitude, as a result of cooling by CO<sub>2</sub> emission. Temperatures rise above roughly 90 km altitude, as the atmosphere absorbs extreme ultraviolet solar radiation, to temperatures as high as  $\sim 2000$  K. This region of the atmosphere is called the thermosphere, or upper atmosphere.

Titan shows a similar atmospheric structure, however the radiative forcing is caused by different species. Similarly, Titan's troposphere cools mainly radiatively, giving rise to a decreasing temperature profile up to the tropopause at 40 km altitude. Between  $\sim 40$  and 200 km, the atmosphere warms as a result of the absorption of sunlight by haze and methane. At 200 km, radiative cooling to

space competes with radiative warming, giving rise to a nearly isothermal temperature profile of  $\sim 176$  K up to roughly 350 km altitude. Titans atmosphere cools above 350 km from emission by  $C_2H_6$  and other hydrocarbons to form a mesopause at  $\sim 550$  km.

### 3 Convective tropopause.

As mentioned above atmospheres are largely in radiative equilibrium. We will be deriving the thermal profiles of various atmospheres later on in the course, however not now because we haven't learned how to calculate the optical depth of gases that result from transitions between different quantum mechanical states. In addition, we haven't constructed even a simple model of an atmosphere. But we'll get to these points early in the course. For now let's consider a thermal profile that is established by convection rather than radiative equilibrium. This is much easier, and characterizes the temperature profile right above the surface. Why would that be?

For the Earth, Venus, Mars and Titan, the tropospheric temperature, on average, decreases with altitude above the surface. The surface is warmer than the overlying atmosphere because it absorbs more radiation than does the atmosphere. The atmosphere is cooled by either convecting the heat to higher levels and/or by radiating away the heat. Convection occurs when the temperature (that would result only from radiative cooling) decreases fast enough with height that the air parcels below a given level are

less dense than those above it. In this case the lower air parcels rise to the altitude at which they have the same density as the ambient atmosphere. The atmosphere is cooled by the actual motion of air, that is by convection.

So what vertical temperature gradient, or *lapse rate*, is needed to cause convection? This is an interesting question because convection causes cloud formation if humid air is involved, and is associated with some of the big weather events on Earth, e.g. thunderstorms and hurricanes. Cloud formation occurs when the parcel rises, expands (as it meets lower pressures), and thus cools to temperatures below that of saturation.

Convection occurs quickly enough that one can assume to first order that no heat is exchanged between the rising parcels and their environment. Let us therefore consider the adiabatic, vertical rise of a parcel of an ideal gas. Assume that the parcel has a temperature,  $T$ , pressure,  $P$ , mass density,  $\rho$ , and specific volume,  $\alpha=1/\rho$ . We will assume hydrostatic equilibrium.

Assume an ideal gas,

$$P\alpha = (R/m)T,$$

and differentiate the equation of state:

$$Pd\alpha + \alpha dP = (R/m)dT.$$

Note that

$$c_p = c_v + R/m,$$

where  $c_p$  and  $c_v$  are the specific heat capacities,  $(\frac{dq}{dT})_{p,v}$ , at constant pressure and volume, respectively. Thus,

$$Pd\alpha + \alpha dP = (c_p - c_v)dT. \quad (4)$$

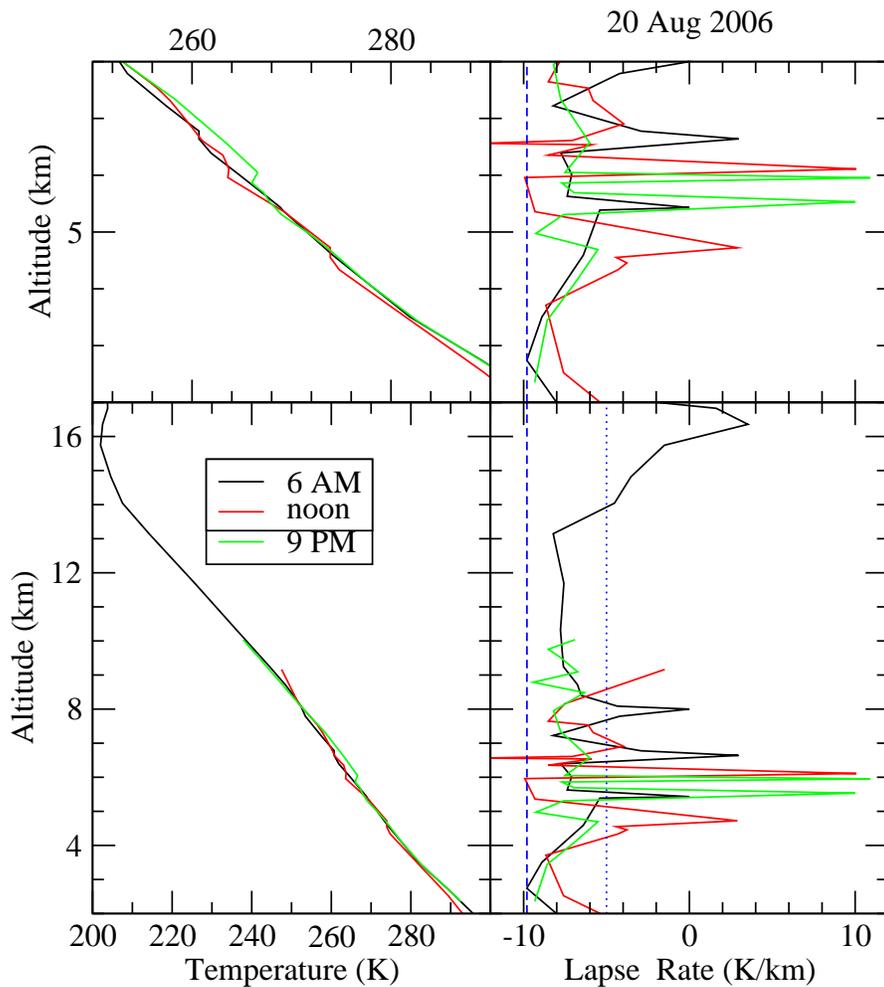


Figure 2: The temperature profiles of Tucson's atmosphere, above the airport, at 6 AM, noon, and 9 PM on 20 August 2006. Tucson's hourly temperature profiles (along with other great stuff) can be obtained at the website: [http : //weather.unisys.com/upper<sub>a</sub>ir/skew/skew<sub>K</sub>TUS.html](http://weather.unisys.com/upper_air/skew/skew_KTUS.html).

The first law of thermodynamics,

$$dq = c_v dT + P d\alpha,$$

for adiabatic motion, i.e. where no energy,  $q$ , leaves or enters the parcel, reduces to:

$$c_v dT = -P d\alpha,$$

where  $c_v$  is the specific heat at a constant volume (erg/g K). Do review your understanding of this law if you're a little rusty. Substituting this expression into equation 4:

$$c_p dT = \alpha dP. \quad (5)$$

Considering hydrostatic equilibrium expressed in terms of  $\alpha=1/\rho$ ,

$$\alpha dP = -g dz,$$

we find that

$$\Gamma = \frac{dT}{dz} = \frac{-g}{c_p}. \quad (6)$$

This is the change in temperature that a parcel experiences if it is adiabatically nudged upward or downward from its present state. Thus  $\Gamma$  is the gradient in an atmosphere that transfers energy only through adiabatic motions, that is convectively.

For saturated air, the latent heat released by water condensing must be considered. Therefore we add a term  $Ldw$  to the energy equation:

$$c_v dT = -P d\alpha - Ldw.$$

Here  $w$  is the mass of saturated water per mass of air and  $L$  is the latent heat of vaporization. The saturated adiabatic lapse rate is then

$$\frac{dT}{dz} = \frac{-g}{c_p} * \frac{1}{1 + (L/c_p)(dw/dT)}. \quad (7)$$

Let's consider a hypothetical atmosphere that is warmed by the sun and has a temperature profile in steady state, according to its opacity structure, and the absorption and emission of radiation at each atmospheric level. Let's suppose that a gust of wind lifted a parcel of air from the ground and introduced this parcel to a higher level. These motions occur generally quick enough that there is no heat exchanged with the environment. The parcel will then have a temperature that follows the adiabatic lapse rate. If the parcel is warmer than the environment then the parcel is buoyant and rises to higher levels. If the converse is true the parcel is not buoyant and returns to its starting place. In the former case, we say that the atmosphere is unstable to convection. In this case the radiative lapse rate must be replaced by the adiabatic lapse rate, because convection is then the main mechanism for transferring energy. The convective lapse rate then rises from the surface to the level at which the flux is conserved across the radiative and convective boundary.

In figure 2, we can see two temperature profiles measured at the Tucson airport. On the day of this measurement, there were no typical summer thunderstorms, and yet temperatures are seen to vary a couple of Kelvin at 6 km altitude. Note that much of the troposphere is conditionally unstable, that is its temperature lies between the wet and dry lapse rates.

A good indication that an atmosphere is convective is a vertical temperature profile that follows the dry or wet lapse rate (depending on the humidity). We find on Earth that the temperature profile varies hourly, occasionally reaching the dry or wet adiabat. The terrestrial wet lapse rate is 5 K/km, while the dry lapse rate is roughly 9.8 K/km. The average lapse rate is actually in between at 6.5 K/km. Note in the table above, how small the dry lapse rate,  $\Gamma$ , is for Titan. This is a result of its small gravity, which facilitates convection.

In 1981, Voyager measured two temperature profiles for Titan. These pertain to two different places (at opposite sides of the globe), both near the equator, one at sunset and one at sunrise. The profiles were found to perfectly match each other within 0.7 K. Years later, in 2005, the Huygens probe measured Titan's temperature profile as it descended through the atmosphere. This profile, now measured over different terrain also near the equator, during a different season from those measured by Voyager, and a different time of day, also matched the Voyager profiles. Unlike Earth, it appears that Titan's temperature profile changes little across the tropics, and responds only subtly to daily and seasonal variations in insolation. Why is Titan, in this way, so different from Earth?