Atmospheric Thermodynamics

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1 Molecular Thermodynamics

Perhaps the most basic equation in atmospheric thermodynamics is the ideal gas law

\[ p = \rho RT \]

where \( p \) is pressure, \( \rho \) is the air density, \( T \) is temperature, and \( R \) is the gas constant for dry air. While the derivation of this equation takes some effort, it is very much worth it because it gives us a deep understanding of what pressure and temperature really are.

Any work the atmosphere can do to move around air is derived from the internal energy of its component gases. How much of this energy does a unit volume of gas have? Consider the following diagram:

\[ \text{Figure 1.1: A piston} \]

Say you are pushing on a piston filled with a gas. The pressure is simply

\[ p = \frac{F}{A} \]  \hspace{1cm} (1.1)\n
and the amount of work you would have to do to compress the gas is

\[ dW = F(-dx) \]  \hspace{1cm} (1.2)\n
but

\[ F = pA \]  \hspace{1cm} (1.3)\n
so from (1.2) and (1.3)

\[ dW = -pAdx = -pdV \]  \hspace{1cm} (1.4)\n
where \( dV = Adx \) since you are pushing an area through a differential length to get a differential volume.

Alternatively, we could switch the sign to get not the amount of work done \textit{on} the gas but the amount of work done \textit{by} the gas

\[ dW = pdV \]  \hspace{1cm} (1.5)\n
Where does the pressure come from? The pressure arises from the motion of the molecules of gas inside the piston banging against the piston wall. Each time they bang against the piston wall, the piston acts like a perfect reflector. If the piston does not move due to this constant banging, then there must be a force balancing the momentum \( p \) associated with the banging of the molecules (note bold font to distinguish from pressure – momentum is a vector), that is imparted to the piston wall with every collision. This force is

\[
F = \frac{dp}{dt} \tag{1.6}
\]

We are assuming here that every molecule that hits the piston leaves with the same energy, i.e. the same average speed \( v \) and mass \( m \), and therefore the same momentum. The piston is a perfect reflector. But momentum is a vector! Therefore, the momentum imparted to the piston by a single molecule is the change in momentum associated with coming in and bouncing out:

\[
\Delta p_x = mv_x - (-mv_x) = 2mv_x \tag{1.7}
\]

What is \( \Delta t \) though? Suppose we have \( N \) molecules in volume \( V \), or \( n = N/V \) as the concentration

1. Only molecules within distance \( v_x \Delta t \) hit the piston
2. The volume occupied by these molecules is \( \Delta V = v_x A \Delta t \)
3. The number of molecules that hit the piston is \( \Delta N = n \Delta V = nv_x A \Delta t \), where \( n = \Delta N/\Delta V \) is the molecular number concentration
4. The number of molecules that hit per unit time is \( \Delta N/\Delta t = n \Delta V/\Delta t = nv_x A \)

Therefore, for all molecules, we combine number 4 and (1.7) to get

\[
F_x = \Delta N \times \frac{\Delta p_x}{\Delta t} = \frac{\Delta N}{\Delta t} \Delta p_x
\]

So

\[
F_x = nv_x A \cdot 2mv_x
\]

Now, taking (1.1), this leads to the expression for pressure exerted by all molecules in the \( x \)-direction

\[
p = \frac{F_x}{A} = 2nmv_x^2
\]

But if we only want the one half of the \( x \)-direction that is in the direction of the piston. Since we are only interested in the average velocity squared, we need to divide by two to get the pressure on the piston alone

\[
p = \frac{F_x}{A} = nmv_x^2 \tag{1.8}
\]

We could also multiply and divide by two to write

\[
p = 2nmv_x^2/2 \tag{1.9}
\]
The term in brackets is obviously merely the average kinetic translational energy of each gas molecule in the x-direction

$$\dot{u}_{\text{trans},x} = \frac{mv_x^2}{2} \quad (1.10)$$

(the dot refers to “per molecule”). Since it will come up later, we will also note that, at equilibrium, the kinetic energy equals the potential energy of the molecule. We now have

$$p = 2n\dot{u}_{\text{trans},x} \quad (1.11)$$

We also note the gaseous motion is obviously three-dimensional, and there is kinetic energy in each of these directions. Assuming (through the equipartition principle) that the energy is shared equally among each degree of freedom:

$$m\frac{v_x^2}{2} = m\frac{v_y^2}{2} = m\frac{v_z^2}{2}$$

or, since all degrees should share the energy equally, each gets a third of the total

$$v_x^2 = \frac{v^2}{3}$$

so, the total internal energy is given by

$$\dot{u}_{\text{trans}} = f\dot{u}_{\text{trans},x} = 3\dot{u}_{\text{trans},x} = m\frac{v^2}{2}$$

so

$$p = \frac{2}{3}n\dot{u}_{\text{trans}} \quad (1.12)$$

This equation should start to be looking vaguely familiar. We should really be calling $\dot{u}_{\text{trans}}$ the temperature of the gas molecule. However, hindsight is 20/20, and due to some historical missteps we have defined a temperature $T$ that is related to $\dot{u}_{\text{trans}}$ by a constant factor

$$\dot{u}_{\text{trans}} = \frac{f}{2}kT = \frac{3}{2}kT \quad (1.13)$$

where, $k = 1.38 \times 10^{-23}$ J/K/molecule is Boltzmann’s constant and $3kT/2 = mv^2/2$. The average kinetic (or potential) energy per degree of freedom $f$ is $kT/2$.

Therefore, substituting Eq. 1.13 into Eq. 1.12

$$p = nkT \quad (1.14)$$

It is revealing here to consider that pressure $p$ has units of $J/m^3$, and therefore it is an expression of energy density – the number density of molecules $n$ times $kT$. What does $kT$ represent? It is not the internal energy density per molecule, which for translational energy alone is $\dot{u}_{\text{trans}} = \frac{3}{2}kT > kT$, and there is vibrational and rotational energy too, which makes the internal energy even bigger. Perhaps the best way to think about $kT$ is that it is the total energy (kinetic plus potential) carried along the direction normal to a surface. Note $k.e. = \frac{1}{2}kT$ and $p.e. = \frac{1}{2}kT$. Thus $kT$ is the total
average energy per molecule that is available to do \( pdV \) work. \( p = nkT \) is then the density of this available energy.

There are several ways to express the ideal gas law, which relates pressure, temperature, and density in the atmosphere (among other places). The most common formulations are

\[
pV = NR^*T
\]

where \( N \) is the number of kilomoles.

In the atmospheric sciences, we typically make some simplifications. We replace \( R^* \) by \( R = R^*/M \), where \( M \) is the molecular weight of the gas in kg/kmol. In this case

\[
p = \rho RT
\]

Alternatively, we can replace \( \rho \) by the specific volume \( \alpha = 1/\rho \):

\[
p\alpha = RT
\]

**Main points**

- Pressure is a force over an area where the force is due to the change in momentum associated with molecules bouncing off their surroundings
- Pressure has units of energy density
- Temperature has units of energy. The amount of energy \( kT/2 \) is the amount of translational (or potential) energy per degree of freedom per molecule.
- There are three degrees of translational freedom so internal translational energy is \( 3kT/2 \).
- Pressure has in effect two degrees of freedom due the molecular bounce
- The amount of energy \( kT \) is the energy per molecule available to do \( pdV \) work.
- Pressure is the density of energy available to do \( pdV \) work on the surroundings

**Question**

What if the volume of gas is an air parcel in a surrounding atmosphere? Do the equations above need to change in any way if the box is removed and there is no piston?

**1.1 Atmospheric application: water vapor and dry air**

The pressure exerted by a mixture of chemically inert gases is equal to the sum of partial pressures of the gases. The partial pressure is proportional to the molecular density. As we showed in Eqs. 1.14 and 1.15, in total

\[
p = nkT = \rho RT
\]
But what if there is a mixture of gases, as in the atmosphere? Dalton’s Law states that we can treat the gases as if they are independent from one another, making the good assumption that all the molecules have the same temperature (or translational kinetic energy). In other words, we can just add up the molecular densities $n_i$, or energy densities $p_i$, so that

$$p = kT\sum n_i = T\sum \rho_i R_i = \Sigma_i p_i$$  \hspace{1cm} (1.17)$$

So it is convenient to separate gases into their major constituents, which in the case of the atmosphere, is mostly dry air and moist air.

For dry air (which is mostly nitrogen and oxygen)

$$p_d = \rho_d R_d T$$  \hspace{1cm} (1.18)

For water vapor we use the symbol $e$ for pressure and

$$e = \rho_v R_v T$$  \hspace{1cm} (1.19)

The mean molar weight for dry air is $M_d = 28.97$ kg/kmol so $R_d = R^*/M_d = 287$ J deg$^{-1}$ kg$^{-1}$, and for moist air $M_v = 18.0$ kg/kmol so $R_v = R^*/M_v = 461$ J deg$^{-1}$ kg$^{-1}$.

Thus the total pressure is

$$p = p_d + e = (\rho_d R_d + \rho_v R_v) T$$

Note again, that we are saying that the water vapor molecules have the same temperature (kinetic energy) as the dry air molecules. We’ll introduce an important parameter here

$$\varepsilon = \frac{R_d}{R_v} = \frac{M_v}{M_d} = 0.622$$  \hspace{1cm} (1.20)$$

We define the mixing ratio (i.e. the ratio water vapor mass to dry air) in the atmosphere as

$$w = \frac{m_v}{m_d}$$  \hspace{1cm} (1.21)

Substitute the ideal gas law (1.18) and (1.19), we get

$$w = \frac{\rho_v}{\rho_d} = \frac{e/R_v T}{(p-e)/R_d T}$$

$$= \varepsilon \frac{e}{p-e}$$

$$w \simeq \varepsilon \frac{e}{p}$$  \hspace{1cm} (1.22)$$

An important adjustment that can be made to the ideal gas equation is to adjust for the added buoyancy that is associated with water vapor being lighter than dry air so that within a given volume, the density of air is given by

$$\rho = \frac{m_d + m_v}{V} = \rho_d + \rho_v = \frac{p-e}{R_d T} + \frac{e}{R_v T}$$
or, with some algebra

\[ \rho = \frac{p}{R_d T} \left[ 1 - \frac{e}{p} (1 - e) \right] = \frac{p}{R_d T} \left[ 1 - \frac{(1 - e)}{e} w \right] \]

Rearranging

\[ p = \frac{\rho R_d T}{1 - \frac{(1 - e)}{e} w} = \rho R_d T_v \]

where \( T_v \) is defined this way, is the “virtual temperature”. It works out that to a good approximation

\[ T_v \approx T \left( 1 + \frac{1 - e}{e} w \right) = T (1 + 0.61w) \]

(1.23)

Figure 1.2: Moist versus dry air

\[ \rho_{\text{dry}} > \rho_{\text{moist}} \]

If \( T_{\text{dry}} = T_{\text{moist}} \) then \( T_{v,\text{dry}} < T_{v,\text{moist}} \)

This is a very useful quantity to know since the density of moist air is given by:

\[ \rho = \frac{p}{R_d T_v} = \frac{p}{R_d T (1 + 0.61w)} \]

At constant pressure, air that is either moist or hot will be less dense than air that isn’t, and be more inclined to rise (Fig. 1.2).

**Question**

Dalton’s law states that partial densities and pressures are additive. Can you provide a compelling reason why temperatures are not additive as well? Why is there not a partial temperature?
2 Intensive and extensive variables

When considering physical systems, it is often very useful to stay aware of whether the property being considered is intensive or extensive. An intensive variable is one that does not depend on the volume of the system, and an extensive variable is one that does. Intensive variables are sometimes called the bulk properties of the system. For example, consider the following expression of the ideal gas law

\[ p = \rho RT \]  

(2.1)

Say we had a box with each of the properties \( p, \rho \) and \( T \), and we subdivided the box, it would not change the values of these properties, so each of these properties is intensive. However,

\[ \rho = m/V \]  

(2.2)

Subdividing the box, into small boxes with smaller \( V \) would lead to a corresponding reduction in the mass in each subdivided box \( m \). Thus, \( m \) and \( V \) are extensive variables.

The distinction is important, because often we want to know how much we have of a particular thing. The nature of the thing is defined by one or two of the intensive variables \( p, \rho, \) and \( T \) (note that from 2.1, we only need two to define the third). The amount we have is defined by the mass \( m \).

In atmospheric sciences, when we consider the ideal gas equation

\[ p = \rho RT \]

where \( \rho \) is an intensive variable and mass \( m = \rho V \) is the extensive variable, where \( m \) normally refers to either the mass of dry air or the mass of water vapor. The convention used in Wallace and Hobbs, one that is commonly employed is to use the lower case for intensive quantities and the upper case for extensive quantities. Thus, for example, the internal energy per unit mass is given the symbol \( u \) and the internal energy is given the symbol \( U \). In atmospheric sciences, we very often
thing about intensive quantities, because we reference them to a parcel of air in which the mass of the air (but not the volume) does not change with time. Thus

\[ u = \frac{U}{m} \]

In the notes here, I will express intensive variables that are referenced with respect to volume in bold lower case, i.e. the internal energy per unit volume is \( u \). Where the intensive variable is per molecule it is expressed, e.g., as \( \dot{u} \).

**Main points**

- Intensive variables are independent of how much matter there is.
- Extensive variables depend on how much matter there is.

**Question**

This distinction between extensive variables and intensive variables is particularly important whenever we talk about flows, of air, radiation, or whatever. Why?
3 Heat, Work and the First Law of Thermodynamics

We can express Eq. 1.12 for the ideal gas equation in terms of per unit mass rather than per molecule:

\[ p = \frac{2}{3} \rho u_{\text{trans}} \]  
(3.1)

where

\[ u_{\text{trans}} = \frac{3}{2} RT \]  
(3.2)

is the translational energy per kilogram due to molecules whizzing around in three dimensions. There are other types of internal energy we can consider (and will later), but suffice to say we can talk about a total internal energy per kilogram \( u \). Note that, like \( T \), \( u \) is an intensive variable, so the extensive property is

\[ U = mu \]

where \( m \) is the mass of air. We call \( U \), the total internal energy.

Our question is how do we change the total internal energy?

- Some outside agency adds energy to the system (e.g. condensation, absorption of sunlight or terrestrial radiation), through flows of some foreign material that does not define \( U \). We call this energy “heat”

- The system changes its energy through flows of whatever material does define \( U \) (e.g. through expansion \( pdV \) or lifting \( mgdz \)). We call this “work”.

Whatever happens, there must be conservation of energy. We express this as the First Law of Thermodynamics

\[ \Delta U = \Delta Q - \Delta W \]  
(3.3)

where, \( \Delta Q \) is the heat added to the system, and \( \Delta W \) is the work done by the system. Both heat and work can be either positive or negative, so what is the difference between the two? What is most important to recognize is that “heat” and “work” are just names for energy. Our goal is foremost to keep an accurate account of the amount of energy that flows into and out of a system.

That said, there are different types of energy. The best way to distinguish heat from work is that heat is associated with with flows of a different type of matter than is associated with internal energy \( U \). So if \( U = mu \), where \( m \) is the mass of the material we are interested in (say the air in a parcel of air), there is also an external energy associated with a different type of material that we call heat (say photons associated with warming sunlight). For example, radiative heating is associated with photons. Radiative heating can heat a parcel of air composed of molecules. Heating does not directly change the extensive variable of the air parcel \( m \).

In the atmosphere, we think about gases. For a gas, an easy way of visualizing work is to examine a piston

Imagine there being a chemical explosion in the piston that releases external energy \( \Delta Q \) to the gas. The external material flow here is due to a redistribution of electrons in a chemical reaction. This flow of external energy or “heating” adds to the internal energy of the gas. An increase in the
internal energy of the gas is an increase in the amount of energy it has that is available to do work. As a consequence, the differential rate of doing work by the gas on the piston is

\[
\frac{dW}{dt} = pA \frac{dx}{dt} = p \frac{dV}{dt}
\]

but \( pV = mRT \) so

\[
\frac{dW}{dt} = mRT \frac{dV}{V} \frac{dt}{dt}
\]

and noting that \( x^{-1} \frac{dx}{dt} = d \ln x / dt \)

\[
\frac{dW}{dt} = p \frac{dV}{dt} = mRT \frac{d\ln V}{dt}
\]

The amount of work that is done by the gas in the piston is the amount of area under the curve.

\[
\Delta W = \int_{V_1}^{V_2} pdV
\]

or, at constant temperature

\[
\Delta W = mRT \int_{t_0}^{t'} \frac{d\ln V}{dt'} dt'
\]

A similar derivative can be applied to the heating

\[
\Delta Q = \int_{0}^{t'} \frac{dQ}{dt} dt'
\]
Thus, the change in internal energy is

$$\Delta U = \int_0^t \frac{dQ}{dt'} dt' - mRT \int_0^t \frac{d\ln V}{dt'} dt'$$  \hspace{1cm} (3.4)$$

Since, in the atmospheric science we do things per unit mass, i.e

$$\alpha = \frac{V}{m}$$

$$dw = pd\alpha$$

Thus,

$$\frac{du}{dt} = \frac{dq}{dt} - \frac{dw}{dt} = \frac{dq}{dt} - p \frac{d\alpha}{dt}$$  \hspace{1cm} (3.5)$$

and

$$\Delta u = \Delta q - \Delta w = \int_0^t \frac{dq}{dt'} dt' - RT \int_0^t \frac{d\ln \alpha}{dt'} dt'$$  \hspace{1cm} (3.6)$$

Heating adds to internal energy so that it can do work through expansion, which allows the internal energy to relax. An important point to be aware of is that the total amount of internal energy we have $\Delta U$ (or $\Delta u$) is a consequence of a time integral of heating and doing work. The present is linked to the changes in the past.

Main points

- Total energy is conserved, meaning it can only be shifted from one form to another
- When energy flows into a system, two things can happen. One is that the internal energy can go up. The other is that the system can do work on something else.
- Work, heating, and changes to internal energy happen over time. Current states evolve from past states.

Question

- When a system does work on something else, where does that energy go? Is one system’s work another systems heat?

3.1 Atmospheric Application: the general circulation

Within the context of Figure 3.2 and Eq. 3.4, we can think about why the atmosphere is able to do work. Due to an imbalance between incoming shortwave radiation and outgoing longwave radiation, there is net heating at the equator and there is a net cooling at the poles. Presumably these two things balance in total, so that the internal energy of the atmosphere as a whole does not change, so $\Delta u = 0$ and from Eq. 3.6

$$\Delta q = RT \int_0^t \frac{d\ln \alpha}{dt'} dt'$$  \hspace{1cm} (3.7)$$
Figure 3.2: Balance between incoming shortwave radiation and outgoing longwave radiation at the top of the atmosphere

This equation pretty much sums up climate! Radiative heating $\Delta q$ permits work to be done through the expansive processes of convection and winds $\int_0^t \frac{dV}{dt} dt$. Cooling at the poles leads to work done on the poles through a shrinking. Meanwhile, the globally-averaged atmospheric temperature $T$ stays constant. Energy that is available to do work takes the form of meridional motions that we call the wind. Energy will not be created or destroyed, but it will be transported from the equators to the poles because a high energy density is maintained by the imbalance at the equator and a low energy density is maintained at the poles. The one thing that is missing in this discussion is that air does not leave the poles once it gets there, so there must be a return circulation.
4 Internal energy in an ideal gas

What if the internal energy is not constant when a gas is heated? In terms of mass, Eq. 1.13 can be expressed as

\[ u_{\text{trans}} = \frac{3}{2}RT \]

where the number three represents the number of degrees of freedom associated with the kinetic energy in the x, y, and z directions. By extension, the total internal energy per kilogram is

\[ u = \frac{f}{2}RT \]  \hspace{1cm} (4.1)

where \( f \) is the number of degrees of freedom for a molecule. The total internal energy is not just the energy derived from the translational motions of the individual gas molecules, but also from internal motions by the molecules.

Now this is central to atmospheric sciences because it allows us to express how the temperature of gas is linked to how much we heat it (through, for example, radiative absorption), i.e. the specific heat. Remember, heating doesn’t change extensive quantities associated with how much of a particular thing we have (e.g. mass or number of molecules). What it does change is the intensive property of the amount of internal energy per unit stuff, or equivalently, the temperature. But, by how much? From the First Law of thermodynamics (Eq. 3.5),

\[ \frac{du}{dt} = \frac{dq}{dt} - \frac{dw}{dt} \]

Rearranging

\[ \frac{dq}{dt} = \frac{du}{dt} + \frac{dw}{dt} = \frac{du}{dt} + RT \frac{d \ln \alpha}{dt} \]

If a substance that is defined by the intensive property \( u \) is heated at constant specific volume \( \alpha \) (e.g., we add heat to a box filled with air, then \( d \ln \alpha / dt = 0 \), and the internal energy change is equal to

\[ \left( \frac{du}{dt} \right)_{\alpha} = \left( \frac{dq}{dt} \right)_{\alpha} \]

We would expect the temperature to go up in the box at some rate \( dT / dt \). Dividing both sides by \( dT / dt \), we get

\[ \left( \frac{du}{dT} \right)_{\alpha} = \left( \frac{dq}{dT} \right)_{\alpha} = c_v \]

where \( c_v \) is what we call the “specific heat at constant volume” (or, equivalently, constant \( \alpha \)). Note that it is much more intuitive to think of it in inverse

\[ \left( \frac{dT}{dq} \right)_{\alpha} = \frac{1}{c_v} \]

Framed this way, \( c_v \) tells us how much the temperature will rise for a given amount of heating.

Now, we can substitute for \( u \), our expression from Eq. 4.1, leading to

\[ c_v = \left( \frac{\partial q}{\partial T} \right)_{\alpha} = \left( \frac{du}{dT} \right)_{\alpha} = \frac{f}{2}R \]  \hspace{1cm} (4.2)
$\alpha = \text{const.}$ \hspace{1cm} $\left( \frac{dq}{dt} \right)_{\alpha} = \left( \frac{du}{dt} \right)_{\alpha} = c_v \left( \frac{dT}{dt} \right)_{\alpha}$

![Diagram](image)

Figure 4.1: Heating at constant volume leads to a temperature and internal energy rise

Just by inspection, we can see that, if we add energy to a volume through heating, and the volume doesn’t change, then the temperature will rise. But it will not rise by as much as might be expected because there are other degrees of freedom in the substance that get a share of the energy. $f$ is at least three due to the translational modes of the molecules. If $f$ is more then temperature must rise even less. If you were a French engineer in the 19th century, this would be rather important to know because increasing temperature is what is going to drive the piston, and you would want to know what the increase in temperature is for a given release of energy from burning coal. Since the engineers needed to figure out how much temperature (or internal energy rises), this led them to the concept of the “specific heat at constant volume” $c_v$.

From an atmospheric science standpoint, radiative heating drives temperature perturbations, although it is not quite the same because the perturbations are not normally considered at constant volume (unless we are considering the planet as a whole), but rather at constant pressure (see the section on enthalpy). Still there is a fundamental problem, as will be shown below, which is that there is basic disagreement between what classical physics would predict the value of $f$ to be and the value of $c_v$ that is actually measured experimentally. In fact, this was a key point that led 19th century physicists to be concerned that the wonderful successes of the kinetic theory of gases weren’t all that. In commenting on this problem in 1869 Maxwell said in a lecture “I have now put before you what I consider to be the greatest difficulty yet encountered by the molecular theory,” a conundrum that paved the way for the quantum theory of matter.

1. Monotomic Molecule (example Ar)
   3 translational degrees of freedom $f = 3$, $U_{tot} = \frac{3}{2} R^* T$. Value of $f$ for Ar implied by observations at atmospheric temperatures $f = 3$.

2. Diatomic molecule (examples: $N_2$ and $O_2$)
3 translational degrees of freedom
2 rotational degrees of freedom (whole body)
2 vibrational degrees of freedom (P.E. plus K.E. \(kT/2\) each) associated with change in bond length

7 degrees of freedom \(f = 7\), \(U_{tot} = 7R^*T\). Value of \(f\) for \(N_2\) and \(O_2\) implied by observations at atmospheric temperatures \(f = 5\).

There is a big discrepancy here! The classical theory works great for Argon but terrible for nitrogen and oxygen. Air is mostly a diatomic gas \((N_2, O_2)\), so for per kilogram of gas

\[
\begin{align*}
u &= \frac{5}{2}RT = c_vT
\end{align*}
\] (4.3)

where we would expect \(u = 7RT/2\) based on the kinetic theory of gases. A curious thing happens though which is that if the temperature of the gas goes up a lot, say to several thousand degrees, then \(f\) does indeed approach a value of 7 as initially predicted. How can \(f\) be a function of temperature? Nitrogen is nitrogen is nitrogen, no matter the temperature. Right? Off hand, it makes no sense.

One of the first successes of the quantum theory was to resolve this problem. The value \(kT/2\) (like \(RT/2\)) is a fine representation of the kinetic energy per independent mode provided that \(kT\) is not much less than the smallest possible energy, the quantum energy \(h\nu\), where \(\nu\) is the oscillation frequency for that mode! Here, \(h\) is the Planck constant. Vibrational modes are higher energy than rotational or translational modes. What happens is that if the natural frequency of a vibrational mode \(\nu\) is sufficiently high that \(kT \lesssim h\nu\) then these modes simply will not respond to an addition of energy to the gas. Effectively these vibrational modes are “frozen” because the bonds are too stiff. If the temperature gets sufficiently high, then these modes can be activated again. Otherwise, these degrees of freedom are unavailable at normal atmospheric temperatures. Our atmosphere is composed primarily of nitrogen and oxygen, both of which have stiff bonds with high natural vibration frequencies. These vibrational modes are simply too high potential energy to interact with the translational modes we sense as temperature. They are way up in the hills while the translational modes live in the valley.

In any case, from Eq. 4.3, we can now rewrite our expression for the first law to be

\[
\frac{dq}{dt} = c_v \left( \frac{\partial T}{\partial t} \right)_\alpha + p \left( \frac{\partial \alpha}{\partial t} \right)_T
\] (4.4)

Heating leads to some combination of a temperature rise at constant volume and an expansion at constant temperature

**Main points**

- Heating doesn’t all go into expansion work. Some goes into raising the temperature
- Energy is shared among all available degrees of freedom. The more degrees of freedom the less temperature rises.
- Air has 5 degrees of freedom, three translational and two rotational.
Question

Eq. 4.4 is not actually used very often in the atmospheric sciences to examine temperature changes in an air parcel. What is a limitation for applying the equation to the atmosphere that wouldn’t have been a concern of most 19th century engineers and physicists?
5 Total energy or the Enthalpy

So now we can think of there being two types of energy associated with the volume of a gas. There is the internal energy per unit mass \( u \) that is due to the rotational and translational motions of the molecules. There is also energy per unit mass associated with the pressure of the molecules on their surroundings \( \alpha p \). The total energy is normally called the enthalpy

\[
\begin{align*}
\mathbf{h} &= u + \alpha p \\
\mathbf{(5.1)}
\end{align*}
\]

For an ideal gas, since \( p\alpha = RT \)
\[
\mathbf{h} = c_v T + RT
\]
or
\[
\begin{align*}
\mathbf{h} &= (c_v + R) T = \frac{f + 2}{2} RT \\
\mathbf{(5.2)}
\end{align*}
\]

where \( f \) is the number of degrees of freedom for the molecules, or

\[
\begin{align*}
\frac{dh}{dT} &= c_v + R \\
\mathbf{(5.3)}
\end{align*}
\]

For air \( f = 5 \), so
\[
\begin{align*}
\frac{dh}{dt} &= \frac{7}{2} \frac{R}{dt} \\
\mathbf{(5.4)}
\end{align*}
\]

To see why we have introduced the enthalpy, let’s go back to the first law again (Eq. 3.6)
\[
dq = du + dw = du + RT d\ln \alpha
\]

Now, previously we evaluate \( (\partial q/\partial T)_\alpha \) to obtain the specific heat at constant volume \( c_v \) (Eq. 4.2). What about the specific heat at constant pressure? From Eq. 5.5, taking the derivative with respect to temperature:
\[
\begin{align*}
\left( \frac{\partial q}{\partial T} \right)_p &= \left( \frac{\partial u}{\partial T} \right)_p + RT \left( \frac{\partial \ln \alpha}{\partial T} \right)_p \\
\mathbf{(5.5)}
\end{align*}
\]

but, since \( \alpha = RT/p \) then \( (d \ln \alpha)_p = (d \ln T)_p \), so
\[
\begin{align*}
\left( \frac{\partial q}{\partial T} \right)_p &= \left( \frac{\partial u}{\partial T} \right)_p + RT \left( \frac{\partial \ln T}{\partial T} \right)_p \\
\mathbf{(5.6)}
\end{align*}
\]

Recognizing that \( u = c_v T \) and \( RT d\ln T = RdT \), we get

\[
\left( \frac{\partial q}{\partial T} \right)_p = c_v + R
\]

This is the same expression derived in Eq. 5.3! Thus
\[
\frac{dh}{dt} = \left( \frac{\partial q}{\partial t} \right)_p
\]

\[
\mathbf{(5.7)}
\]
The reason we have introduced enthalpy as well as heating, even if they change at the same rate, is because enthalpy is a property of the system (or a state variable) where as heat is not. You cannot point to the heat of a substance but you can point to its enthalpy. Enthalpy is one of the most important variables in atmospheric sciences, because we cannot control for the volume of an air parcel, but we can control for its pressure. When there is is radiative heating of an air parcel at constant pressure, the temperature rises.

But by how much? The relationship between the enthalpy rise and the temperature rise is given by the specific heat at constant pressure:

\[
c_p = \frac{dh}{dT} = \left( \frac{\partial q}{\partial T} \right)_p
\]  

(5.8)

where

\[
h = (c_v + R)T = c_p T
\]  

(5.9)

Therefore, it is easy to see that, since \( c_v = 5R/2 \), then \( c_p = 7R/2 \). For dry air, \( R = 287J/\text{deg/kg} \), \( c_v = 717J/\text{deg/kg} \), so \( c_p = 1004J/\text{deg/kg} \). For water vapor \( R = 461J/\text{deg/kg}, c_v = 1463J/\text{deg/kg}, \) so \( c_p = 1952J/\text{deg/kg} \). For air, the internal energy has five degrees of freedom and pressure two (due to the bounce). Thus \( c_p : c_v : R \approx 7 : 5 : 2 \). This very important, because what it means that if we add energy to air, five parts of seven go into increasing the internal energy density, and two parts in seven go into increasing the pressure.

Combining Eq. 5.9 with Eq. 3.5, and noting that \( d(p\alpha) = pd\alpha + \alpha dp \) gives an alternative expression of the First Law

\[
\frac{dq}{dt} = c_p \left( \frac{\partial T}{\partial t} \right)_p - \alpha \left( \frac{\partial p}{\partial t} \right)_T
\]  

(5.10)

If there is heating the temperature rises and the pressure drops.

**Main points**

- The enthalpy is the internal energy plus the energy the system exerts on its surroundings
- The energy exerted on the surroundings is a pressure volume energy
- The specific heat is related to the number of degrees of freedom associated with the internal energy plus the number of degrees of freedom associated with the pressure
- The total number of degrees of freedom is \( 3 + 2 + 2 = 7 \). Therefore \( c_p : c_v : R = 7:5:2 \) for air.

**Questions**

Why are we generally more interested in the enthalpy of an air parcel than its internal energy?
5.1 Atmospheric Application: the dry and moist static energy

In the atmosphere, we need to consider that there are other forms of internal energy that a parcel of air can have, other than just those associated with translational, vibrational and translational motions of a gas. A second form of internal energy is gravitational energy. In our atmosphere, air can move up and down. Thus, add to the total internal energy the gravitational potential per unit mass

\[ u = c_v T + gz \]

Adding \( p\alpha = RT \) to this we get a revised enthalpy called the “dry static energy”

\[ h_d = gz + c_v T + RT = gz + c_p T \]

so heating at constant pressure yields

\[ \left( \frac{\partial q}{\partial t} \right)_p = \frac{dh_d}{dt} = c_p \frac{dT}{dt} + g \frac{dz}{dt} \]

A second form of internal energy is that associated with the thermodynamic phase of a substance. The latent heat per unit mass associated with a change in phase from liquid to vapor is \( L_v = 2.5 \times 10^6 \text{ J/kg} \) at 0 degrees C. Thus the energy associated with some fraction of dry air being in the vapor phase is \( L_v w \) where \( w = m_v / m_d \) (Eq. 1.21). Thus, adding the latent heat to the total internal energy, we get

\[ u = c_v T + gz + L_v w \]

which leads us to the moist static energy (MSE in Wallace and Hobbs)

\[ h_m = c_p T + gz + L_v w \]

so

\[ \left( \frac{\partial q}{\partial t} \right)_p = \frac{dh_m}{dt} = c_p \frac{dT}{dt} + g \frac{dz}{dt} + L_v \frac{dw}{dt} \]

Of course, we could keep going and specify any number of things depending on the question we were interested.

As shown in Fig. 3.2, heating can be related to the radiative flux divergence through

\[ \frac{1}{\rho} \left( \frac{\partial F_{\text{net}}}{\partial z} \right)_p = \left( \frac{\partial q}{\partial t} \right)_p \]

So the energy that is available to create changes in \( T, z \) and \( w \) comes from the absorption and emission of radiation. The conversion of radiative flux divergence to a change in \( h_m \) is the starting point for radiative and climate processes.
6 Equilibrium solutions

Very often we want to consider situations that are *adiabatic*, which strictly means that the internal energy and enthalpy do not change because there is no heating. But this is a bit boring, and in fact it is never possible (as will be shown). All objects radiate for example. What we look at far more frequently is equilibrium conditions where energetic flows are in balance. Most of the textbook equations in atmospheric sciences are derived from this principle.

The starting point is three expressions of the first law (Eq. 3.7), all basically equivalent. The first expression is

\[
\frac{du}{dt} = \frac{\Delta q}{\Delta t} - \frac{dw}{dt}
\]

or, if the work is done by an ideal gas,

\[
\frac{du}{dt} = \frac{\Delta q}{\Delta t} - p \frac{d\alpha}{dt}
\]

And from Eq. 5.10

\[
\frac{dh}{dt} = \frac{\Delta q}{\Delta t} + \alpha \frac{dp}{dt}
\]

So again, as in Eq. 5.7, if energy is added to a parcel of air at constant pressure, it’s enthalpy will go up by the same amount.

6.1 Case 1: Equilibrium solution for a closed system or parcel

As will be shown, constant entropy \( s \) is a short hand for no net heating of the system, i.e. is is adiabatic and \( \Delta q = 0 \), but work is being done on or by the system. In this case, from Eq. 6.1, we obtain

\[
\left( \frac{\partial u}{\partial t} \right)_s = - \left( \frac{\partial w}{\partial t} \right)_s
\]

Main points

- For a materially closed system, the adiabatic or equilibrium condition is that work done on a system raises its internal or potential energy. Work done by the system lowers it.
- Alternatively, a rise in the potential energy can be balanced by an ability to do work on something else. Potential energy is an ability to do work.

6.1.1 Atmospheric application: the geopotential

What is the potential energy of the atmosphere? There are many possible forms of potential energy but here we look at the gravitational potential. Remember from Eq. 1.2 that work is required to move a system a distance through a force field. Here, the force field is \( F_g = mg \), and the distance might be \( \delta z \). Thus, the work done on the system to increase its height, per unit mass is \( g\delta z \). At
constant temperature, from Eq. 5.11, \( du = gdz \). Thus, we can term a potential energy that is the amount of energy required to lift a mass \( m \) through a gravitation acceleration \( g \) through a distance \( \delta z \). The intensive variable is the geopotential, which has units of energy per mass

\[
\Phi(z) = \int_0^z g(z) \, dz
\]

Basically, the geopotential is the potential energy per unit mass that comes from lifting through a variable gravitational field at constant temperature (see Table 3.1 in Wallace and Hobbs). For most purposes, we can assume gravity is a constant, so that

\[
\Phi(z) = g \int_0^z dz
\]

or equivalently, we can take the derivative to get

\[
d\Phi(T) = gdz \tag{6.5}
\]

### 6.2 Case 2: Equilibrium solution for a materially closed system at constant pressure

![Figure 6.1: An abstract illustration of where heating of a system is balanced by an equivalent rate of dissipation or cooling, so that all primary system state variables stay fixed.](image-url)
Figure 6.2: Heating at constant pressure leads to an enthalpy or total energy rise

Now we can consider a second system in which net heating of the system at constant pressure is zero. Energy may be entering the system through heating, and leaving the system through dissipation or cooling, but there is no net flux convergence or divergence. In other words, from Eq. 6.3:

\[
\frac{dh}{dt} = \left( \frac{\partial q}{\partial t} \right)_p = 0
\]

Transformations can still occur however, but they must obey the “adiabatic” condition above. Adiabatic here doesn’t mean no heating, but rather no net heating.

Main points

- For a materially closed system at constant pressure, the adiabatic or equilibrium condition is that energetic flows in must be balanced by energetic flows out, such that total energy per unit mass \( h \) (in whatever form) does not change.

- The different components of total energy can still vary, but there must be a balance between so that gains in one are offset by loss of another

6.2.1 Atmospheric application: the dry adiabatic lapse rate

For example, if the air is dry, and we consider the dry static energy, a change in \( h_d \) at equilibrium is given by (Eq. 5.13)

\[
\frac{d h_d}{d t} = c_p \frac{dT}{dt} + g \frac{dz}{d t} = 0
\]
A parcel that rises or falls without exchanging energy with its surroundings at a given pressure will have $dh/dt = 0$ and will change its temperature at rate

$$c_p \left( \frac{\partial T}{\partial t} \right)_p = -g \left( \frac{\partial z}{\partial t} \right)_p$$

or

$$\left( \frac{\partial T}{\partial z} \right)_p = -\frac{g}{c_p}$$

(6.7)

This is the “dry adiabatic lapse rate” of about $\Gamma_d = -g/c_p = 9.8 \text{ K/km}$. Of course we could do something similar for the moist static energy, but the derivation is more complicated (and outlined in Wallace and Hobbs problem 3.50). Note that $c_p$ is not a function of pressure, and $g$ is only a very very weak function of pressure (the atmosphere largely disappears by the time we care), so to a very close approximation:

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

6.3 Case 3: Equilibrium in a materially closed system at constant temperature

Figure 6.3: An abstract illustration of where heating of a system leads to working by a system while the internal energy or enthalpy stay fixed

The final condition is constant temperature. A system doesn’t have to be adiabatic to be in equilibrium. Alternatively, the system might be heated, but it sufficiently fast that the temperature, or energy per degree of freedom, stays constant. In this way heating balances working. From Eq. 6.1
Figure 6.4: Heating at constant temperature leads to an equivalent amount of working

\[
\left( \frac{\partial q}{\partial t} \right)_T = \left( \frac{\partial w}{\partial t} \right)_T = RT \left( \frac{\partial \ln \alpha}{\partial t} \right)_T
\]

(6.8)

Substituting the ideal gas law

\[
\left( \frac{\partial q}{\partial t} \right)_T = \left( \frac{\partial w}{\partial t} \right)_T = \left( \frac{\partial \ln \alpha}{\partial t} \right)_T = \frac{RT}{\alpha} \left( \frac{\partial p}{\partial t} \right)_T = \frac{a}{\alpha} \left( \frac{\partial \rho}{\partial t} \right)_T
\]

(6.9)

Main points

- For a materially closed system at constant temperature, the adiabatic or equilibrium condition is that energetic flows in must be balanced by expansion work, such that total energy per unit mass \(h \) or \(u\) (in whatever form) does not change.

- If temperature does not change, then net heating leads to an increase in volume or a drop of pressure.

6.3.1 Atmospheric application: the hydrostatic equation

Since the total internal energy is given by \(u = c_p T + gz\) (Eq. 5.12), at constant temperature \(du = gdz\). Thus, from Eq. 6.9

\[gdz|_\alpha = \alpha dp|_\alpha\]
since $\alpha = 1/\rho$, we obtain the equation

$$\left( \frac{\partial p}{\partial z} \right)_T = \rho g$$

which suggests that pressure would increase with height. But, the atmosphere doesn’t fall down. There must be a balancing pressure pushing upwards as shown in Fig. 6.5. No vertical motions requires that the total vertical pressure gradient at any location is zero. By changing sign we obtain the **hydrostatic equation**

$$\left( \frac{\partial p}{\partial z} \right)_T = -\rho g \quad \text{(6.10)}$$

Since density is always positive, the air pressure must decrease with height.

### 6.3.2 Atmospheric application: atmospheric thickness

We can now substitute the ideal gas law. Assuming that the atmospheric layer is isothermal (i.e. constant temperature), then the density is (Eq. 1.23)

$$\rho = \frac{p(z)}{RT} = \frac{p(z)}{R_d T_v}$$
Thus, substituting we get

\[
\frac{\partial p}{\partial z} \bigg|_T = -\frac{p(z)g}{R_d T_v} \tag{6.11}
\]

Suppose we want to get the amount of potential energy per unit mass found between two layers, we are looking for a geopotential difference \( \Phi_2 - \Phi_1 \). This is useful, because air flows from high to low potential energy, so we can use this difference in two locations to figure out where the air will go. How do we find out this quantity? Re-arranging

\[
dp{p}{p} = \frac{-g dz}{R_d T_v}
\]

Since at constant temperature \( d\Phi = gdz \) (Eq. 6.5) and \( dp/p = d\ln p \)

\[
R_d T_v d\ln p = -gdz \tag{6.12}
\]

Integrating between two levels

\[
\int_{z_1}^{z_2} gdz = \int_{\Phi_1}^{\Phi_2} d\Phi = -R_d T_v \int_{p_1}^{p_2} d\ln p = R_d T_v \int_{p_2}^{p_1} d\ln p
\]

Giving us

\[
\Delta \Phi = \Phi_2 - \Phi_1 = R_d T_v \ln \frac{p_1}{p_2} \tag{6.13}
\]

This is really important because differences in \( \Delta \Phi \) gives us the amount of energy per unity mass that is available to do thermodynamic work through atmospheric flows. It is one possible form of the potential \( g \) we described earlier. Note that if we integrate Eq. 6.9 and change sign to account for the hydrostatic equation we can also obtain Eq. 6.13

\[
\Delta \Phi = g\Delta z = R_d T_v \ln \frac{p_1}{p_2} \tag{6.14}
\]

Hurricanes are driven by a net heating of an atmospheric column, through a flux of energy from the ocean and a radiative cooling to space. The heating permits work to be done by way of an expansion of the column and a pressure drop.

An expression that is related to Eq. 6.13 is to talk about the thickness of an atmospheric layer between two pressure surfaces. To get this we just divide Eq. 6.13 by gravity to get the hypsometric equation:

\[
\Delta Z = Z_2 - Z_1 = \frac{R_d T_v}{g} \ln \frac{p_1}{p_2} \tag{6.15}
\]

It is easy to see from this equation a very intuitive result. A warm air column with higher \( T_v \) will be thicker than a cold air column, provided that the column is defined as lying between two pressure surfaces \( p_1 \) and \( p_2 \). Warm air is less dense as illustrated in Fig. 6.6.
The virtual temperature is the temperature of the layer between the 1000- and 500-hPa pressure surfaces. Recall that the thickness of the layer between any two pressure surfaces (i.e., imaginary surfaces on which pressure is constant) never intersect. It can be seen from (3.29) that the thickness of the layer, pressure surfaces, is proportional to the mean virtual temperature of the layer:

\[ \text{thickness} \propto \text{mean virtual temperature} \]

Assuming equilibrium, we were able to derive, for example the dry adiabatic lapse rate \((\partial T / \partial z)_p = -g/c_p\).

The second sense is that there is heating at constant temperature is balanced by working through a change in pressure at constant temperature. This leads to the following key result:

\[ \left( \frac{\partial q}{\partial t} \right)_T = \left( \frac{\partial w}{\partial t} \right)_T = RT \left( \frac{\partial \ln \alpha}{\partial t} \right)_T = -RT \left( \frac{\partial \ln p}{\partial t} \right)_T = p \left( \frac{\partial \alpha}{\partial t} \right)_T = -\alpha \left( \frac{\partial p}{\partial t} \right)_T \]  

From which we were able to show that heating increases the atmospheric thickness.

Now we ask “what will happen to the relationship between heating and enthalpy if the pressure is changed a little bit for the constant pressure condition (Eq. 7.2)” or “what will happen to the relationship between heating and working if the temperature is changed a little bit for the constant temperature condition (Eq. 7.2)”.

Effectively, we are asking what is the sensitivity of these equilibrium conditions to small changes. We are still looking for an equilibrium condition. However, we now want to know how the equilibrium solution is different at different temperatures. Effectively what we are seeking is an expression for “quasi-equilibrium transitions”. Conditions are changing slowly enough that something very close to equilibrium is always maintained.

### 7.1 Case 1: An ideal gas

Suppose for example, there is no heating at constant pressure, then, from Eq. 7.1 and Eq. 5.10,

\[ c_p dT|_p - \alpha dp|_T = 0 \]
But if pressure is constant then we only get the trivial solution that temperature is constant too. Not very interesting.

But, let’s integrate to see how a very small change in pressure would relate to a very small change in temperature at equilibrium:

\[ c_p (T - T_0) = \alpha (p - p_0) \]

Now, we keep pressure \( p_0 \) constant as we promised, and \( T_0 \) too, but now we take the derivative of a small change with respect to temperature

\[ c_p \frac{d(T - T_0)}{dT} = \alpha \frac{d(p - p_0)}{dT} \]

We end up with the expression

\[ c_p = \alpha \frac{d|T_p}{dT} \] (7.3)

that could have obtained easily before, but how we got there matters as will become more clear below. Since \( \alpha = RT/p \)

\[ \frac{d \ln p}{dT} \bigg|_p = c_p \]

(7.4)
or more generally from Eq. 5.8

\[
\frac{d \ln p |_T}{d \ln T |_p} = \left( \frac{\partial q}{\partial T} \right) _p = \frac{dh}{d \left( p \alpha \right)}
\]  

(7.5)

Both the numerator and the denominator on the RHS are related to the number of degrees of freedom in the system. Eq. 7.5 is a bit of a “master equation” that we can take to almost any situation. It’s really useful.

### 7.2 Case 2: Phase changes

But what about phase changes where changes are more abrupt? What we have discussed thus far is the internal energy associated with “sensible heat”, i.e. the energy that can be associated with \( m < v^2/2 > \) temperature \( T \). A second form of internal energy is that associated with the thermodynamic phase of a substance. It plays an extremely important role in the atmosphere because water is found in the liquid, ice and vapor phase, and rapidly changes between all three, releasing or absorbing vast amounts of energy.

From Eq. 7.2, the equilibrium solution is that the change in volume for a given heating is equal to inverse of the current pressure

\[
\left( \frac{\partial \alpha}{\partial q} \right) _T = \frac{1}{p}
\]

When we look at phase changes, we are concerned with the amount of heat that must be applied to a liquid to cause it go from a dense liquid phase to a gas that occupies much more space per molecules. Because we are looking at a “jump”, since this is a phase change and the difference between a gas and a liquid is very large, we are interested in \( \Delta \) differences. Thus, the relationship is no longer a differential, but rather

\[
\left( \frac{\Delta \alpha}{\Delta q} \right) _T = \frac{1}{p}
\]

The amount of heat that must be applied to enable a phase change is the latent heat of vaporization

\[ \Delta q = L_v \]

At equilibrium, the pressure in the gas and liquid phase are equal. Taking the pressure in the vapor phase, \( p, \alpha_v = R_v T \), so

\[ \Delta \alpha |_T = \frac{L_v \alpha_v}{R_v T} \]

How does this equilibrium expression for constant temperature change if the temperature changes a small amount? Taking the derivative with respect to temperature and keeping the pressure fixed

\[ \left( \frac{d \Delta \alpha |_T}{dT} \right) |_p = \frac{L \alpha_v}{R_v T^2} \]
Here, we make a simplification. For specific volume, the difference between vapor and liquid is

\[ \Delta \alpha = \alpha_v - \alpha_l = \frac{1}{\rho_v} - \frac{1}{\rho_l} \]

But the density of vapor is typically tiny compared to that of liquid, by about a factor of 1000, so

\[ \Delta \alpha \approx \frac{1}{\rho_v} = \alpha_v \]

Thus, the expression for the quasi-equilibrium transition to another temperature becomes

\[ \frac{d\alpha_v}{dT} = -L_v \alpha_v \left( \frac{1}{R_v T^2} \right) \]

or

\[ \frac{d\ln \alpha_v}{d\ln T} = - \frac{L_v}{R_v T} \] \hspace{1cm} (7.6)

Normally, this is expressed a little differently. Recognizing that \( d\ln \alpha_v = -d\ln p \), we get

\[ \frac{d\ln p}{d\ln T} = - \frac{L_v}{R_v T^2} \] \hspace{1cm} (7.7)

which again is similar to Eq. 7.5, except

\[ \frac{d\ln p}{d\ln T} = \frac{\Delta h}{p \alpha_v} \] \hspace{1cm} (7.8)

where \( \Delta h = L_v \) and \( p \alpha_v = R_v T \).

**Main points**

- We are often not only interested in the equilibrium solution at constant pressure or temperature, but how the equilibrium solution changes as pressure or temperature change.
- The “quasi-equilibrium” solution for an ideal gas is related to the ratio of the gas constant to the specific heat at constant pressure
- The quasi-equilibrium solution for a phase change is related to the ratio of the gas constant times the temperature to the latent heat
- Either expression is dimensionless

**Question**

What are the similarities between Eq. 7.5 and Eq. 7.7? Can you get to Eq. 7.7 directly from Eq. 7.5?
7.3 Atmospheric application: potential temperature

Integrating Eq. 7.4 from initial state $i$ to final state $f$ gives us

$$T_f = T_i \left( \frac{p_f}{p_i} \right)^{R/c_p}$$

We can use the above equation to derive an expression for the potential temperature $\theta$, which represents the temperature a parcel would have if it were brought adiabatically from from $(p, T)$ to standard pressure $p_0$, which is typically set to 1000 mb. In this case

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

The potential temperature is an important concept as it represents a line of thermodynamic equilibrium for dry air in which there is no net exchange of energy with the environment through radiative absorption or emission, or through turbulent mixing, such that $dh_d = 0$. In quasi-equilibrium transitions an air parcel may rise or sink, or move around horizontally, simultaneously changing both its temperature and pressure. But if there is no energy exchange, $\theta$ is constant. Effectively, all parcels lying along a constant theta surface are in local thermodynamic equilibrium (Fig. 7.3).

For example, suppose an air parcel rises from the surface at 1000 mb to 700 mb without mixing with its surroundings. If it’s surface temperature is 25 C, what is its final temperature?

$$T_f = T_i \left( \frac{p_f}{p_i} \right)^{R/c_p} = 269 K$$

Actually this equation can be related to the dry adiabat on a Skew T log p plot, if we consider from above that

$$\ln T = \frac{R}{c_p} \ln p + const$$

On the Skew T log p plot $\ln p$ is the ordinate. Since $T$ not $\ln T$ is the abscissa, adiabats are not straight but slightly curved from the lower right to upper left of the diagram Dry adiabats on a Skew-T are the same as lines of constant $\theta$.

It is interesting to look at potential climatologically too since air motions tend to follow surfaces of constant potential temperature. This is often used in air quality modeling to see where air is going or coming from (look up HYSPLIT for example).

At least, the potential temperature is very useful for being a tracer of air motions in systems that are not changing rapidly. What do we mean by rapidly? Well, consider the following important timescales in the atmosphere.

- Free troposphere with no condensational processes – 1 to 2 weeks is the timescale for radiative cooling to have an influence
- Synoptic disturbances: timescale – 1 to 2 weeks – the same as the above, which is not a coincidence since radiative cooling and heating drive atmospheric motions
- Moist convection: timescales – minutes to hours

The implication is that an assumption of thermodynamic equilibrium, and motion along constant $\theta$ surfaces is a useful guide over shorter time scales of perhaps a few days, provide there is no moist convection. Where would this work? Not the tropics!
7.4 Atmospheric application: saturation vapor pressure of water

The famous Clausius Clapeyron equation gives the sensitivity of the saturation (equilibrium) vapor pressure over a plane surface of pure water $e_S(T)$. From Eq. 7.7, we have

$$\frac{d \ln e_S}{d \ln T} = \frac{L_v}{R_v T}$$  \hspace{1cm} (7.9)

One would be tempted to derive a solution for this equation as

$$e_S(T) = e_{S0}(T) \exp \left( \frac{L_v}{R_v} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right)$$  \hspace{1cm} (7.10)

At freezing the latent heat is $2.5 \times 10^6$ J kg$^{-1}$ and $R_v = 461$ J/K/kg. This is fine, but only if the difference between $T$ and $T_0$ is small. The expression $d \ln p/d \ln T$ is extraordinarily powerful, but it must not be solved without care, because it is a sensitivity and other things that we have assumed to be constant might be changing with temperature also. The latent heat $L_v$ does vary somewhat by a few percent over the normal range of atmospheric temperatures, and this does bad things to the accuracy of our nice exponential solution for $e(T)$. A more accurate solution takes into account a solution for $L_v(T)$.

$$e_s(T) = 611.2 \exp \left( \frac{17.67 T}{T + 243.5} \right)$$
where, T is in C. The reason for the slightly different form of the equation is that $L_v$ itself is a weak function of temperature.

Often you will hear the expression that at warm temperatures the air can hold more water vapor. Certainly from the C-C equation this seems to be correct, but semantically it is misleading. Nowhere in our discussion of the derivation have we needed to mention air at all. Rather, the C-C equation would hold even in the absence of dry air. That said, in our atmosphere at least, having air present is what enables the temperature to be as high as it is, since it is molecular collisions that enable radiative absorption to show up as a measurable temperature.
Figure 7.4: Fig 3.9 from Wallace and Hobbs. Saturation vapor pressure over liquid $e_s$ and the difference of saturation vapor pressures between liquid and ice $e_s - e_{si}$.

8 Conservation of matter and energy

From Eq. 6.6, we stated that the enthalpy (or total energy) of an adiabatic parcel does not change with time. We also alluded to the fact that the system is “materially closed”, requiring that the amount of matter in the system is also constant.

8.1 Atmospheric application: Adiabatic liquid water content of a cloud

The basic physics we need to consider for understanding the formation of cloud in a parcel that rises and falls adiabatically is that heat and energy in the parcel are conserved

- $Q = \chi + w = \text{const}$. (Conservation of mass)
- $h_m = c_p T + g z + L_v w = \text{const}$. (Conservation of energy)
where $w$ is the water vapor mixing ratio and $\chi$ is the liquid water mixing ratio. $Q$ is the total water content, the quantity that is conserved if the parcel does not gain or lose mass. In a pseudo-adiabatic process, as the air expands, conservation of mass requires that the saturated mixing ratio decreases by an amount $dw_s$ as vapor is converted to condensed liquid. If the air remains saturated

$$Q = \chi + w_s \quad (8.1)$$

$$dQ = 0 = d\chi + dw_s \quad (8.2)$$

$$d\chi = -dw_s \quad (8.3)$$

The liquid water content has units of $g/m^3$, so

$$LWC = \rho \chi \quad (8.4)$$

where $\rho$ is the air density. Typical values range from $0.05 \, g/m^3$ in thin stratus to in excess of $1 \, g/m^3$ in cumulus towers.

In a saturated adiabatic process

$$dh_m = 0 = c_p dT + gdz + L_v dw_s \quad (8.5)$$

Therefore

$$-L_v dw_s = c_p dT + gdz$$

$$\frac{dw_s}{dz} = \frac{c_p}{L_v} \left[ \frac{dT}{dz} + \frac{g}{c_p} \right]$$

$$\frac{dw_s}{dz} = -\frac{c_p}{L_v} (\Gamma_d - \Gamma_s) \simeq \text{const.} \quad (8.6)$$

or, from Eq. 8.3 and 8.4

$$\frac{dLWC}{dz} = \frac{\rho c_p}{L_v} (\Gamma_d - \Gamma_s) \simeq \text{const.} \quad (8.7)$$

So we have just shown that $LWC$ increases approximately linearly with height. Lets try some typical values for stratocumulus

$$\Gamma_s \simeq 6 \times 10^{-3}$$

$$\Gamma_d = 9.8 \times 10^{-3}$$

$$\rho \simeq 1$$

$$c_p = 1004$$

$$L_v = 2.5 \times 10^6$$

which gives us

$$\frac{dLWC}{dz} \simeq 1.5 \times 10^{-3} \, g/m^3/\text{km}$$

which is about right. A 200 m thick stratus cloud typically has a cloud top value of $LWC$ of 0.3 g/kg.
8.2 Atmospheric application: Saturated adiabatic lapse rate and the equivalent potential temperature

But what is the moist adiabatic lapse rate $\Gamma_s$?

Again, in a moist adiabatic process where mass is also conserved

$$ dh_m = c_p dT + gdz + L_s dw_s = 0 $$

We can use this to derive the saturated adiabatic lapse rate,

$$ \Gamma_s = -\frac{dT}{dz} = \frac{g}{c_p} + \frac{L_s}{c_p} \frac{dw_s}{dz} $$

but $w_s$ is a function of temperature and pressure since $w_s \simeq e_s(T)/p$, where $e_s(T)$ is given by the Clausius Clapeyron equation (Eq. 7.9)

$$ \frac{de_s}{dT} = \frac{L_s e_s}{R_v T^2} $$

Thus

$$ dw_s = \left( \frac{\partial w_s}{\partial p} \right)_T dp + \left( \frac{\partial w_s}{\partial T} \right)_p dT $$

$$ \frac{dw_s}{dz} = \left( \frac{\partial w_s}{\partial p} \right)_T \frac{dp}{dz} + \left( \frac{\partial w_s}{\partial T} \right)_p \frac{dT}{dz} $$

But the hydrostatic equation tells us that $dp/dz = -\rho g$. Also $\Gamma_s = -dT/dz$

$$ \frac{dw_s}{dz} = - \left( \frac{\partial w_s}{\partial p} \right)_T \rho g - \left( \frac{\partial w_s}{\partial T} \right)_p \Gamma_s $$

Equating this with Eq. 8.6, and solving for $\Gamma_s$, we get

$$ \Gamma_s = \frac{g}{c_p} \frac{1 - \rho L_v \left( \frac{\partial w_s}{\partial p} \right)_T}{1 + \frac{L_s}{c_p} \left( \frac{\partial w_s}{\partial T} \right)_p} $$

And recognizing $w_s \simeq e_s(T)/p$, and the C-C equation for $e_s(T)$ we get

$$ \Gamma_s = \frac{g}{c_p} \frac{1 + \frac{L_v w_s}{R_v T}}{1 + \frac{\varepsilon L_v w_s}{c_p R_v T^2}} $$

It is often useful to refer to a thermodynamic chart for a first guess. The point of learning them is to see how the essential ingredients of cloud physics can be combined: conservation of energy and mass, the hydrostatic equation, and the Clausius-Clapeyron equation for the saturation vapor pressure over a liquid surface.

Another expression, that is useful, one that is derived in Wallace and Hobbs, is the Equivalent Potential Temperature, which is conserved along moist adiabats. As before when we said that it is equivalent to say
\[
\frac{dh_d}{dt} = 0, \quad \frac{d\theta}{dt} = 0
\]

Here

\[
\theta_e = T \left( \frac{p_0}{\rho} \right)^{R/c_p} \exp \left[ \frac{w_s L_v}{c_p T} \right]
\]

\[
\theta_e = \theta \exp \left[ \frac{w_s L_v}{c_p T} \right]
\]

and

\[
\frac{dh_m}{dt} = 0, \quad \frac{d\theta_e}{dt} = 0
\]

On the Skew-T plot shown in Fig. 7.2, moist adiabats are the purple lines. Note that they do not cool with height as rapidly as the orange dry adiabats. Note too that in the region around 600 mb where the dewpoint and the temperature are almost the same, the temperature nearly parallels the nearest moist adiabat line. This suggests a well-mixed cloud layer, perhaps altocumulus.

### 8.3 Atmospheric application: Stability

We are going to try to address the problem of how a parcel of air rises within its environment when there is no exchange of energy or matter. The basic conceptual idea is that a parcel starts somewhere in the atmosphere with some updraft velocity, perhaps due to orographic lifting or localized convergence of some sort. As the parcel rises its further acceleration or deceleration is due to its temperature relative to its environment. If the parcel is warmer than its environment, a buoyancy force will accelerate the parcel upwards towards regions of similar low environmental density aloft. However, as the parcel rises, it cools. In an idealized model in which the parcel does not mix with its surroundings, it cools with height at the dry adiabatic lapse rate. Since the environment is cooling at slower rate with height, eventually the parcel is colder and less buoyant than its surroundings, and it begins to sink.

What we will show is that an unstable dry atmosphere is characterized by \(-dT/dz = \Gamma > \Gamma_d\) or \(d\theta/dz < 0\). A stable dry atmosphere is characterized by \(\Gamma < \Gamma_d\) or \(d\theta/dz > 0\).

The physics is as follows:

Within both the parcel and the environmental air, from the hydrostatic equation (Eq. 6.10)

\[
\frac{dp}{dz} = -\rho g
\]
Figure 8.1: Fig 3.13 from Wallace and Hobbs. Vertical forces acting on an air parcel due to a density and temperature difference between an air parcel (primes) and its environment.

But the density $\rho$ is different between the parcel and the environmental air. If $\rho'$ and $T'$, and $\rho$
and \( T \) are the density and temperature of the parcel and the environment respectively 8.1, then the upward positive force experienced by the parcel is

\[
-\left( \rho' - \rho \right) g
\]

per unit volume, or

\[
-\left( \rho' - \rho \right) \frac{g}{\rho}
\]

per unit mass. In other words, a parcel denser than its environment will accelerate downwards. Substituting the ideal gas equation, and assuming that the environmental temperature is close to the parcel temperature, we get

\[
a_b = \frac{(T' - T)}{T} g
\]

for the upward buoyancy force per mass (or acceleration).

![Figure 8.2: The period of the oscillations resulting from an initial perturbation is \( 2\pi/N \)](image)

Actually, we should really be taking into account the fact that humidity also contributes to the buoyancy of the parcel, and use the virtual temperature \( T_v \) instead of the temperature \( T \) (Eq. 1.23)

\[
T_v \approx T \left(1 + 0.61w\right)
\]

where \( w \) is the mixing ratio. So the buoyancy acceleration is then

\[
a_b = \frac{(T'_v - T_v)}{T_v} g
\]

This leads us to Eq. 3.73 in Wallace and Hobbs, since acceleration is the second time derivative of position

\[
\frac{d^2 z}{dt^2} = \frac{(T'_v(z) - T_v(z))}{T_v(z)} g
\] (8.11)
We can improve on this expression by noting that as the parcel goes up or down, its going to cool or warm at the dry adiabatic lapse rate $\Gamma_d$. Thus

$$T_v' = T_{v0} - \Gamma_d z'$$

where $z' = z - z_0$ is the displacement from the equilibrium position. Similarly, the environmental temperature at the same level is given by

$$T_v = T_{v0} - \Gamma z'$$

This leads to

$$\frac{(T_v' - T_v)}{T_v} = \frac{(T_{v0} - \Gamma_d z') - (T_{v0} - \Gamma z')}{T_{v0} - \Gamma z'} = -\frac{(\Gamma_d - \Gamma) z'}{T_{v0}}$$

Provided that the vertical temperature perturbation is small compared to the actual temperature we get

$$\frac{(T_v' - T_v)}{T_v} = -\frac{(\Gamma_d - \Gamma) z'}{T_{v0} - \Gamma z'} \approx -\frac{(\Gamma_d - \Gamma) z'}{T_{v0}}$$

Substituting now into Eq. 8.11, we get

$$\frac{d^2 z'}{dt^2} = -\frac{(\Gamma_d - \Gamma)}{T_{v0}} g$$

(8.12)

![Diagram](image)

Figure 8.3: Fig 3.12 from Wallace and Hobbs. Conditions for (a) positive static stability and (b) negative static stability

So notice here that if the displacement $z'$ is positive and the parcel is above its equilibrium point, and $\Gamma < \Gamma_d$ (which is the normal case), then the RHS is negative because the air parcel is colder than its surroundings (Fig. 8.3). The parcel has inertia, of course, but eventually the negative acceleration or buoyancy pushes the parcel back towards its equilibrium point. Again because it has inertia, it will overshoot the equilibrium, and the displacement will be negative, making the
parcel positively buoyant, which accelerates the parcel upwards. And so on. If this sounds like an oscillation, this is true. We can rewrite Eq. 8.12 in the form of the wave equation

$$\frac{d^2 z'}{dt^2} + N^2 z' = 0$$  (8.13)

where

$$N^2 = \frac{g}{T_v} (\Gamma_d - \Gamma)$$  (8.14)

is the square of the Brunt-Vaisala frequency. This is a hugely important number in atmospheric sciences, as it is like the second hand in the atmospheric clock. Rule of thumb is that $N = 0.01 \text{ radians s}^{-1}$.

$$N = \sqrt{\frac{9.8}{255} (9.8 - 6) \times 10^{-3}} = 0.012$$

So if a full cycle is $2\pi$ radians then an oscillation period is

$$\tau = \frac{2\pi}{N} \approx 600 \text{ s}$$

or about 10 minutes. Clouds are the easiest place to see this. They rise and decay roughly over this time scale, as they go through a full buoyancy oscillation.

The solution to Eq. 8.13 is, of course, sinusoidal. If the amplitude of the wave is $z_0'$, and the parcel is at peak positive displacement at $t = 0$, then in complex notation

$$z'(t) = z_0' e^{-iNt} = z_0' (\cos Nt - i\sin Nt)$$

Looking just at the real component

$$z'(t) = z_0' \cos Nt$$

The advantage of using the complex solution, is that something becomes very apparent for the special case that the atmosphere is absolutely unstable, in which case $\Gamma > \Gamma_d$. From Eq. 8.14

$$N = \sqrt{\frac{g}{T_v} (\Gamma_d - \Gamma)} = \sqrt{(-1) \frac{g}{T_v} (\Gamma - \Gamma_d)} = i \sqrt{\frac{g}{T_v} (\Gamma - \Gamma_d)}$$

where $i = \sqrt{-1}$ is the imaginary number. Since $i^2 = -1$, this then implies that

$$z'(t) = z_0' e^{-iNt} = z_0' \exp \left[ -i^2 \sqrt{\frac{g}{T_v} (\Gamma - \Gamma_d)} t \right] = z_0' \exp \left[ \sqrt{\frac{g}{T_v} (\Gamma - \Gamma_d)} t \right]$$

Since the expression in the brackets is positive, any initial displacement upwards results in the parcel continuing to rise exponentially. There is no restoring force to bring the parcel back towards equilibrium.
In terms of potential temperature

Earlier, in an assignment, we derived the expression relating the dry static energy to the potential temperature

$$\frac{dh_d}{dt} = c_p T \frac{d \ln \theta}{dt}$$

This can also be expressed in terms of a gradient with respect to height

$$\frac{dh_d}{dz} = c_p T \frac{d \ln \theta}{dz}$$

Since $h_d = c_p T + g z$, it follows that

$$c_p \frac{dT}{dz} + g = c_p T \frac{d \ln \theta}{dz}$$

Dividing by $c_p T$ and substituting expressions for $\Gamma$ and $\Gamma_d$

$$\frac{d \ln \theta}{dz} = \frac{1}{T} \left( \frac{dT}{dz} + \frac{g}{c_p} \right) = \frac{1}{T} \left( \Gamma_d - \Gamma \right)$$

So

$$\frac{d \theta}{dz} = \frac{\theta}{T} \left( \Gamma_d - \Gamma \right)$$

This is very useful since we know that if $\Gamma < \Gamma_d$ then the atmosphere is stable and meaning that $d \theta / dz > 0$. So we can look at a sounding on a Skew-T plot and compare the temperature profile to the lines of constant potential temperature. If the temperature sounding is going to higher values of potential temperature $\theta$ as it goes up with height, then the atmosphere is stable. Of course, if $d \theta / dz < 0$ then the atmosphere is unstable, and a storm is sure to happen because air must rise to restore stability, taking high $\theta$ air up with it, and restoring the stable situation of $d \theta / dz$.

Because the atmosphere is moist, the more general expression for moist static stability is

$$\frac{d \theta_e}{dz} = \frac{\theta_e}{T} \left( \Gamma_s - \Gamma \right) > 0$$

It’s actually very rare to see situations where $d \theta / dz < 0$ which are called absolutely unstable, since they cannot last long at all. However, we can see situations quite frequently when $d \theta_e / dz < 0$. These are easily identified on an atmospheric sounding on a Skew-T plot by comparing the temperature sounding to the moist-adiabatic. We call such situations convectively unstable, because they lead to cloud formation.
9 Second Law of Thermodynamics and Entropy

Reversibility and the Second Law

We start with a definition. Imagine a closed system. The system is not isolated, but rather exists in within a universe, or perhaps to keep things on a more manageable scale, a bigger system. Let’s say through a transfer of heat to the system, we change its state from (defined by its state variables) from \( S_i \) to \( S_f \) (\( S \) just being some arbitrary symbol defining the state). If by taking an equivalent amount of heat away from the system the system returns exactly to its original state \( S_i \), then the system is said to be reversible. Any process that cannot satisfy these requirements is said to be irreversible.

An example of a reversible process might be an purely cyclical process like the buoyancy oscillation described by the wave equation (Eq. 8.13). However, the second law of thermodynamics states that all natural processes are irreversible. Ultimately, any wave is damped. It loses energy through friction or radiative cooling, and its amplitude must be restored through some other external forcing like orographic forcing or radiative heating.

A corollary of the Second Law of Thermodynamics (which we shall not prove) is

\[
\Delta S_{sys} = -\frac{\Delta Q}{T_{sys}} \\
\Delta S_{env} = \frac{\Delta Q}{T_{env}}
\]

if \( T_{sys} > T_{env} \) then \( \Sigma \Delta S > 0 \)

Figure 9.1: Transfer of heat from the system to its environment is spontaneous if entropy production is positive, requiring that the system has a higher temperature.

Another:

\[
In\ a\ reversible\ transformation,\ heat\ can\ only\ be\ converted\ to\ work\ by\ moving\ heat\ from\ a\ warmer\ to\ a\ colder\ body
\]
In the absence of external work done on a body, heat can only move from warm to cold.

For example, absorbing heat \( Q_2 \) from a cold reservoir and releasing \( Q_1 \) to a hot reservoir gives us a refrigerator, which requires an amount of work \( Q_1 - Q_2 \) to have been done by some outside agency.

We can term the change in entropy \( \Delta S \) of the system during a transformation.

\[
\Delta S = \frac{\Delta Q_{\text{rev}}}{T} \quad (9.1)
\]

or per unit mass

\[
\Delta s = \frac{\Delta q_{\text{rev}}}{T} \quad (9.2)
\]

In a complete reversible process, the system is returned to its original state, so the entropy does not change and there is no change in the entropy of the surrounding universe (i.e. \( \Delta S = 0 \)).

Since all natural processes are irreversible, the total entropy of the universe always increases.

\[ \Sigma \Delta S > 0 \]

The zero in this case is simply a recognition that the net change of energy in the universe as a whole is always zero. The reason for the inequality is predicated on conservation of energy and the condition of an amount of energy \( \Delta Q \) moving from a high potential, high temperature system to a low potential, low temperature environment.

\[ \Sigma \Delta S = -\frac{\Delta Q}{T_{\text{sys}}} + \frac{\Delta Q}{T_{\text{env}}} \geq 0 \]

The inequality holds provided \( T_{\text{sys}} > T_{\text{env}} \). The inequality is zero under assumed reversible conditions of local thermodynamic equilibrium for which \( T_{\text{sys}} = T_{\text{env}} \).

Note that in the above example that it is possible for the entropy of the system to go down even while the entropy of the universe and the environment to go up. In general, the change in entropy (per unit mass) is

\[ ds = dq/T \]

Under this assumption, the first law can be written

\[ Tds = dh - \alpha dp = c_p dT - \alpha dp \quad (9.3) \]

or

\[ ds = c_p d\ln T - Rd\ln p \quad (9.4) \]

but we can show that from the equation for the potential temperature that

\[ d\ln \theta = d\ln T - \frac{R}{c_p} d\ln p \]

from which we can see that

\[ ds = c_p d\ln \theta \quad (9.5) \]
Note, that in the presence of condensation it is better to use $\theta_e$

$$ds = c_p d \ln \theta_e$$  \hspace{1cm} (9.6)

If we are assuming adiabatic motions (which is sometimes a fair assumption in synoptic meteorology, particularly at high altitudes where phase changes don’t affect entropy as much) then $dq/T = ds = 0$ and $d\theta = 0$. That is why when we say air moves along an isentropic surface (isentropic = constant entropy), it is equivalent to saying it is moving along lines of constant $\theta$. For dry air in the absence or balance of diabatic heating (from the sun for example) and cooling (due to radiation of heat to outer space), this is a decent approximation.

### 9.1 Examples of changes in entropy

1. Increase the sensible heat of an object at constant pressure

   $$T ds = c_p dT - \alpha dp$$

   $$\left( \frac{\partial s}{\partial t} \right)_p = c_p \left( \frac{\partial \ln T}{\partial t} \right)_p$$  \hspace{1cm} (9.7)

   or, another way this could be expressed, from Eq. 6.6 is

   $$\left( \frac{\partial s}{\partial t} \right)_p = \frac{1}{T} \left( \frac{\partial h}{\partial t} \right)_p = \frac{1}{T} \left( \frac{\partial q}{\partial t} \right)_p$$  \hspace{1cm} (9.8)

   Heating at constant pressure increases the entropy of the system.

2. Decrease in the pressure at constant temperature

   $$T ds = c_p dT - \alpha dp$$

   $$\left( \frac{\partial s}{\partial t} \right)_T = -R \left( \frac{\partial \ln p}{\partial t} \right)_p$$  \hspace{1cm} (9.9)

   This is very important because it means we can interpret the second law intuitively as a requirement that, absent some external force, the pressure must decrease with time. Remember that maintaining constant temperature requires that heating equals working, i.e. from Eq. 6.8

   $$\left( \frac{\partial q}{\partial t} \right)_T = \left( \frac{\partial w}{\partial t} \right)_T$$

   We showed previously in Eq. 6.9 that work is done when, at constant temperature, the volume goes up or the pressure goes down

   $$\left( \frac{\partial w}{\partial t} \right)_T = -RT \frac{d \ln p}{dt} = RT \frac{d \ln \alpha}{dt}$$

   So you can see now that entropy goes up when heating enables work to be done so that the pressure goes down.

   $$\left( \frac{\partial s}{\partial t} \right)_T = \frac{1}{T} \left( \frac{\partial q}{\partial t} \right)_T = \frac{1}{T} \left( \frac{\partial w}{\partial t} \right)_T = -R \left( \frac{\partial \ln p}{\partial t} \right)_T$$  \hspace{1cm} (9.10)
9.2 Atmospheric Application: Entropy production in the atmosphere

The two possibilities for entropy production described above can show up in many different ways in the atmosphere. Obvious examples are as follows. Along a constant pressure surface, the atmosphere responds to radiative heating by increasing molecular motions to give a rise in temperature. Along a constant temperature surface, hot air expands so that the pressure decreases. Another possibility is that entropy is produced through cloud production, since latent heat is released through condensation.

10 Heat engines

Nineteenth century engineers like Carnot and Watt were very interested in designing engines that efficiently burned coal in order to do work. These “heat engines” were the basis of the European and later the American Industrial evolution. Carnot imagined an idealized form of the “heat engine” called the Carnot Cycle. In the atmospheric sciences, this cycle is particularly useful to help us imagine how the atmosphere behaves as a heat engine.

![Carnot Cycle Diagram](image)

Figure 10.1: Carnot cycle: heating does positive expansion work at constant temperature; cooling does negative contraction work; in between there is adiabatic expansion and compression.

Fig. 10.1 shows an illustration of the Carnot cycle. There are four steps in the cycle.
1. From point A to B, there is some *adiabatic* process that raises the temperature by way of compression and an increase in pressure, without any increase in entropy. From Eq. 9.3

\[ c_p \Delta T = \alpha \Delta p \]

or, more generally

\[ \Delta h = \alpha \Delta p \]

2. Then, from point B to C, there is diabatic heating at a constant *high* temperature. Energy flows into the engine. From Eq. 6.9 we know this leads to *positive* work being done by way of expansion and a drop in pressure.

\[ \Delta q|_T = \Delta w = -\alpha \Delta p|_T \]

The remaining steps deal with the return phases of the cycle. The same expressions apply, but there is a negative sign.

3. In step C to D, the heating stops, but there is continued expansion through a decrease in pressure so the temperature adjusts by falling to a lower value.

4. Finally, in step D to A, there is diabatic cooling at a constant *low* temperature. Energy flows out of the engine. *Negative* work is done by the heat engine.

**Main points**

There are some key messages to remember here:

- In a complete cycle, the temperature does not change. The internal energy might change in any given leg of the cycle, but averaged over the course of a complete cycle, there is no change in internal energy.

- Work done by the system in step B to C is offset by work done on the system in step D to A. Since the work is driven by heating at constant temperature, and there is no change in internal energy the total amount of work done by the system is

\[ \Delta w = \sum \Delta w = \sum \Delta q = \Delta q_{in} - \Delta q_{out} \]

Note that conservation applies: \( \Delta q_{in} = \Delta q_{out} + \Delta w \). Only a portion of the energy that flows into the system is available to do work. This implies that we can express an engine efficiency

\[ \eta = \frac{\Delta w}{\Delta q_{in}} = \frac{\Delta q_{in} - \Delta q_{out}}{\Delta q_{in}} \]  

(10.1)

The Second Law prescribes that the overall entropy of the universe must increase for any process:

\[ T ds \text{(universe)} > du \text{(system)} + \Delta w \text{(system)} \]

Therefore, if the state of the system doesn’t change (\( \Delta u = 0 \)), the second law says you must always put more heat \( \Delta q_{in} = T \Delta s \) into a system than the amount of work \( \Delta w \) you get out of it - the efficiency of any process must be less than 100%.

\[ \eta < 1 \]  

(10.2)
• A Carnot Cycle ends up exactly where it started, as if nothing had happened. Entropy is created in the universe because there is a flow of heat from high to low temperature. The total increase in entropy is

\[ \Delta s = \frac{\Delta q_{\text{out}}}{T_2} - \frac{\Delta q_{\text{in}}}{T_1} \]

But, within the engine, there is no change in entropy at all. Thus, the Carnot Cycle is an idealization, albeit a very useful one.

• Work is only the type of energy that we are interested in – it is your choice! There is only ever energy in and energy out, and these flows are always in balance. There is no objective definition of what counts as work. It may seem silly, but the exhaust of a car does work by forcing away surrounding air. From this perspective, any energy that is wasted in propelling the vehicle forward would be termed waste heat.

![Figure 10.2: The Carnot Cycle in S-T space, from Wallace and Hobbs.](image)

![Figure 10.3: Illustration of the Carnot cycle](image)

Figures 10.2 and 10.3 show the Carnot Cycle graphically, arguably from a cleaner perspective. The goal of these figures is to set up two orthogonal co-ordinates, something we should always try to do when setting up a problem. In Figure 10.2, the cycle axes are set up in a space of entropy and temperature. The legs of the Carnot Cycle carve out a rectangle whose area is the work done. To see how, consider that the area of the rectangle is

\[ \text{Area} = (T_1 - T_2)(\Delta s) \]
\[ = T_1 \Delta s - T_2 \Delta s \]
\[ = \Delta q_{\text{in}} - \Delta q_{\text{out}} \]
\[ = \Delta w \]

From this perspective, because a rectangle is carved out, the following axiom is clear

*A Carnot Cycle represents the maximum amount of work that can be done in a cycle that returns the system to its initial state.*
Figure 10.3 gives the Carnot Cycle a more 3D perspective in which the legs of the Carnot Cycle are not explicitly resolved, but instead are represented by circulations along isentropes. The circulations are sustained by energetic flows in and out of the system. Some fraction of the incoming flow goes to work.

10.1 Atmospheric Application: A hurricane

In the atmosphere, we can easily think of the sun heating the Earth. This lowers the air’s density, and then the heated airmass does work by expanding upwards or outwards. Meanwhile it radiatively cools to space, and then it contracts. Circulations are along isentropic surfaces. Cross-isentropic flows are due to diabatic heating, as derived in an assignment question.

Figure 10.4: The Carnot Cycle in a Hurricane. Note that point D above corresponds to point A in Figs. 10.1 and 10.2.

A good example of this is a hurricane as shown in Fig. 10.4. The ocean heats the air at a high constant temperature, following which there is ascent along isentropes within the hurricane eye-wall. Ascent in the eye-wall really is nearly isentropic. There is cooling as the air expands. Then the hurricane cools efficiently to space through thermal radiation. Finally the cooled air mass sinks slowly and compresses quasi-isentropically. It is through this cycle of heating and cooling that the hurricane is able to perform thermodynamic work in the form of horizontal and vertical motions.

10.2 Atmospheric Application: The general circulation

You eat food to do work, and the rest of the energy gets lost as heat. The Earth gets heated by the sun, and it uses this $\Delta q_{in}$ energy to do work in the form of atmospheric motions, with the remainder
of the energy $\Delta q_{\text{out}}$ getting lost to space through thermal radiation at the top of the atmosphere. The efficiency in this case is only about 1 to 2% if work is defined in terms of a capacity to create atmospheric motions.