## 3.  THE FIRST LAW OF THERMODYNAMICS AND RELATED DEFINITIONS

### 3.1  General statement of the law

Simply stated, the First Law states that the energy of the universe is constant.  This is an empirical conservation principle (conservation of energy) and defines the term "energy."  We will also see that "internal energy" is defined by the First Law.  [As is always the case in atmospheric science, we will ignore the Einstein mass-energy equivalence relation.]  Thus, the First Law states the following:

1.  Heat is a form of energy.
2.  Energy is conserved.

The ways in which energy is transformed is of interest to us.  The First Law is the second fundamental principle in (atmospheric) thermodynamics, and is used extensively.  (The first was the equation of state.)  One form of the First Law defines the relationship among work, internal energy, and heat input.  In this chapter (and in subsequent chapters), we will explore many applications derived from the First Law and Equation of State.

### 3.2     Work of expansion

If a system (parcel) is not in mechanical (pressure) equilibrium with its surroundings, it will expand or contract.  Consider the example of a piston/cylinder system, in which the cylinder is filled with a gas.  The cylinder undergoes an expansion or compression as shown below.  Also shown in Fig. 3.1 is a p-V thermodynamic diagram, in which the physical state of the gas is represented by two thermodynamic variables: p,V in this case.  [We will consider this and other types of thermodynamic diagrams in more detail later.  Such diagrams will be used extensively in this course.]  For the example below, every state of the substance is represented by a point on the graph.  When the gas is in equilibrium at a state labeled P, its pressure is p and volume is V.  If the piston of cross-sectional area A moves outward a distance dx while the pressure remains constant at p, the work dW (work is defined by the differential $dw \equiv \mathbf{f} \cdot d\mathbf{s}$) is

$$dW = pAdx = pdV \quad \text{(shaded region of the graph).} \tag{3.1}$$

The total work is found by integrating this differential over the initial and final volumes $V_1$ and $V_2$:

$$W = \int_{V_1}^{V_2} pdV$$

On the p-V diagram, the work is equivalent to the area under the curve, as shown in Fig. 3.1.
In terms of specific volume (volume per unit mass), the incremental work (specific work, w = W/kg) is

$$dw = pd\alpha.$$

*Example 3.1:*

Calculate the work done in compressing (isothermally) 2 kg of dry air to one-tenth its initial volume at 15 ⁰C.

From the definition of work, $W = \int p dV$.

From the equation of state, $p = \rho_d R_d T = (m/V) R_d T$.

Then $W = m R_d T \int d\ln V = m R_d T \ln(V_2/V_1)$    (remember the process is isothermal)

$= (287 \text{ J K}^{-1} \text{ kg}^{-1})(288.15 \text{ K})(2 \text{ kg})(\ln 0.1)$

$= -3.81 \times 10^5 \text{ J}$.

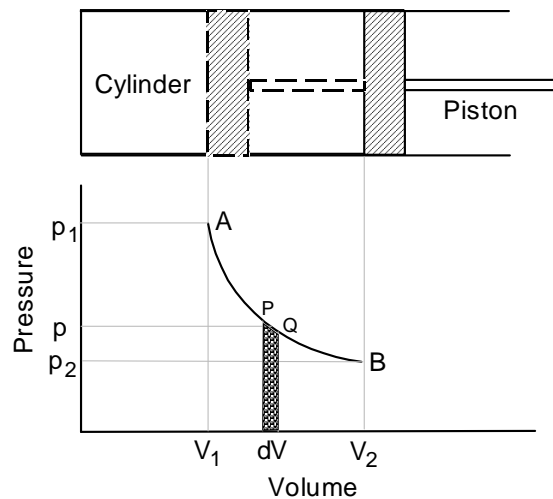The negative sign signifies that work is done on the volume (parcel) by the surroundings.



*Figure 3.1.  Representation of the state of a substance in a cylinder on a p-V diagram.  Adapted from Wallace and Hobbs (1977).*

The quantity of work done depends on the path taken; therefore, work is not an exact differential.  If it was, work would depend only on the beginning and end points (or initial and final conditions.  Let us reconsider Eq. (3.1) above, rewriting it as follows (noting that the displacement dx = vdt, where v is the magnitude of the velocity vector):

dW = pAdx = pAvdt

Since p = F/A (or F = pA), the above equation becomes

dW = Fvdt or dW/dt = Fv

Now from Newton's Law, F = ma = mdv/dt.  Substituting this in the above yields

$$\frac{dW}{dt} = mv\frac{dv}{dt} = \frac{d}{dt}\left(\frac{1}{2}mv^2\right)$$

or

$$\frac{dW}{dt} = \frac{dK}{dt}$$

where the kinetic energy $K = \frac{1}{2}mv^2$. Being an *inexact* differential, dW is sometimes denoted as δW (Tsonis) or DW (notes below).

*Example 3.2 (from problem 3.7, p. 22, in Tsonis): An ideal gas of p,V,T undergoes the following successive changes: (a) It is warmed under constant pressure until its volume doubles. (b) It is warmed under constant volume until its pressure doubles. (c) It expands isothermally until its pressure returns to its original pressure p. Calculate in each case the values of p, V, T, and plot the three processes on a (p,V) diagram.*

The three processes are shown in the graph below. In the first process, the work is

$$W_a = \int_{v}^{2V} pdV = p(2V - V) = pV$$

In the second process, the work is zero since volume does not change. In the third process, the value of work is similar (i.e., the same relation) to that done in Example 3.1. As this process proceeds through steps a-c, the temperature increases such that $T_b > T_a > T$.
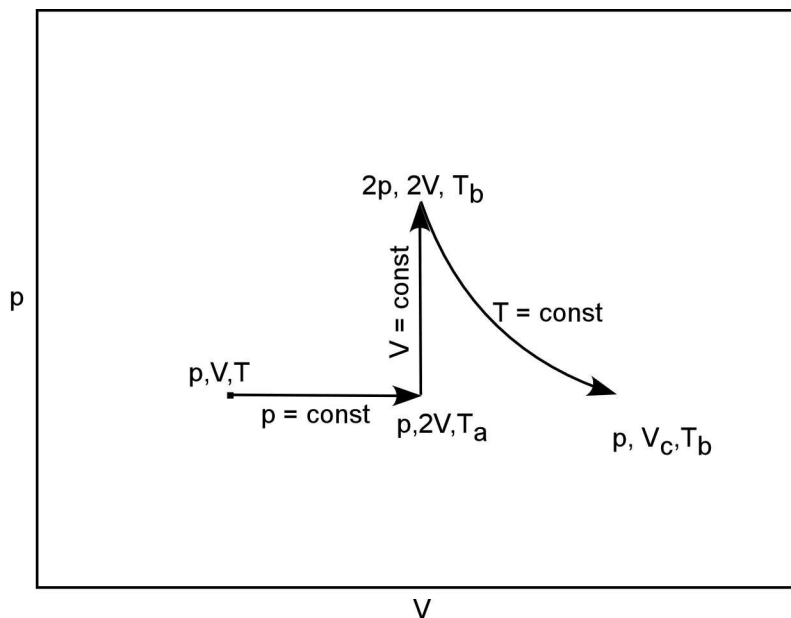


More on thermodynamic work:
http://en.wikipedia.org/wiki/Work_(thermodynamics)

### 3.3  Internal energy and mathematical statement of First Law

Consider now a system which undergoes a change from some heat input q per unit mass (q=Q/m), e.g., a temperature increase from an electrical wire or a paddle system to stir a fluid.  The system responds through the work of expansion, which we will call *w* (work per unit mass).  The excess energy beyond the work done by the system is *q-w*.  If there is no change in macroscopic or bulk kinetic and potential energy of the system, then it follows from conservation of energy that the internal energy (Δ*u* - per unit mass) of the system must increase, i.e.,

$$q - w = \Delta u. \qquad \text{(simple expression of the First Law)} \qquad (3.2)$$

Although the First Law defines the internal energy, it is (sometimes – as we will later see) convenient to write it in a more general form in terms of the various energy terms.  Here, we will sum the various forms of energy which have passed through the system-surroundings boundary and set this new sum equal to the change in the system internal energy, similar to what we did in the previous equation. This expression differentiates thermal and non-thermal forms of energy:

$$\Delta u = q + \Sigma e_i, \quad \text{(a more general form of the First Law)} \qquad (3.3)$$

where q is again the net thermal energy (per unit mass) passing into the system from the surroundings. [Thermal energy can be defined as the potential and kinetic energies that change as a consequence of a temperature change.]  Note that this last expression deals with the classification of energy passing through the system boundary -- it does not deal with a classification of energy within the system.

At this point, it is instructive to define thermal energy.  In the atmosphere, thermal energy can include heating/cooling by radiation and latent heating (associated with water phase changes).

http://en.wikipedia.org/wiki/First_law_of_thermodynamics

According to a series of experiments conducted by Joule in 1843, *u depends only on T* , a relationship known as *Joule's Law*.   It can also be shown (e.g., this was used in the derivation of the equation of state using statistical mechanics, Ch. 2 notes) that for an ideal monatomic gas, the kinetic energy of translations is given by

$$pV = (1/3)N_0mu^2 = (2/3)E_{kin} = RT,$$

where $N_0$ is Avogadro's number ($6.023 \times 10^{23}$).   Thus,

$$E_{kin} = (3/2)RT.$$

Since at constant temperature there are no energy changes in electronic energy, rotational energy, etc., the internal energy of an ideal gas is only a function of T.  This is also true for polyatomic ideal gases such as $CO_2$ (and air).

For an atmospheric system, the most general form of the First Law can be expressed in the differential form as

$$Dq = du + Dw = du + pD\alpha. \qquad (3.4)$$

[What has happened to the $\Sigma e_i$ term?]

The operator "d" refers to an exact differential and "D" to inexact.  One property of the inexact differential (e.g., Dw) is that the closed integral is in general nonzero, i.e.,

$$\oint \text{Dw} \neq 0.$$          (see also information below)
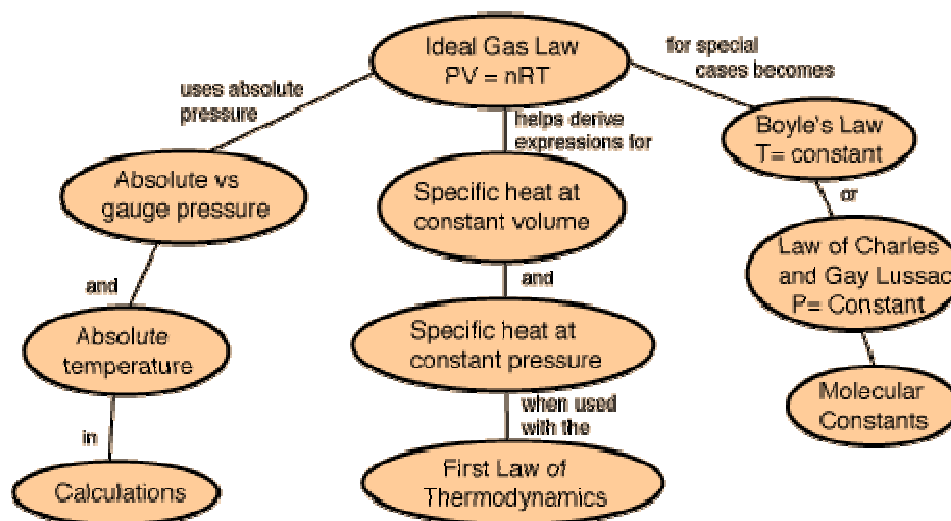
[see http://en.wikipedia.org/wiki/Inexact_differentials]

The first law demands that du be an exact differential -- one whose value depends only on the initial and final states, and not on the specific path.  However, from here on, we will ignore this formal distinction between exact and inexact differentials.

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Aside:  An exact differential can also be expressed as, for a function U = U(x,y) (Tsonis, Section 2.1)

$$dU = \frac{\partial U}{\partial x}\,dx + \frac{\partial U}{\partial y}\,dy$$

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Review:  http://sol.sci.uop.edu/~jfalward/thermodynamics/thermodynamics.html



Applicatiuoins of the equation of state, and connection with the First Law.  From http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/idgcon.html#c1

### 3.4  Specific heats

Consider the case where an incremental amount of heat $dq$ is added to a system.  The heat added will increase the temperature of the system by an incremental amount $dT$, assuming that a change of phase does not occur.  [We will see later that when a change of phase in water occurs, $T$ may remain constant upon an addition of $dq$.]   The ratio $dq/dT$ (or $\Delta q/\Delta T$) is defined as the specific heat, whose value is dependent on how the system changes as heat is input.  For atmosphere applications, there are two

such specific heats, one for a constant specific volume (or an isochoric process, $\alpha$ = const), and one for a constant pressure (or isobaric process, p = const).

Thus,

$$c_v \equiv (dq/dT)_{\alpha=const}$$

Since specific volume is constant, no work is done. According to the First Law, Eq. (3.1), dq = du and

$$c_V = (du/dT)_{\alpha=const} \qquad (\text{now } du=c_v dT) \qquad\qquad (3.5)$$

This expression can now be used to rewrite (3.4) as

$$dq = c_V dT + pd\alpha. \qquad\qquad (3.6)*$$

For the isobaric process, the specific heat is

$$c_p \equiv (dq/dT)_{p=const} \qquad\qquad (3.7)$$

In this case, some of the heat added is used in the work of expansion as the system expands against the constant external pressure of the environment. The value of $c_p$ must therefore be greater than that of $c_v$. To show this, we can write (3.6) as

$$dq = c_V dT + d(p\alpha) - \alpha dp = dh - \alpha dp,$$

where h, the _enthapy_ is defined as h $\equiv$ u + p$\alpha$. (Enthalpy is discussed further in the following section.)

Since p$\alpha$ = RT from the equation of state (for dry air), the previous equation can be rewritten as

$$dq = (c_V+R)dT - \alpha dp = c_p dT - \alpha dp. \qquad\qquad (3.8)*$$

If pressure is constant then dp=0 and, using (3.6), we note that $c_p$ exceeds $c_v$ by the amout R, the gas constant:

$$c_p = c_V + R. \qquad\qquad (3.9)*$$

For dry air, the values are:

$$c_V = 717 \text{ J K}^{-1} \text{ kg}^{-1}$$
$$c_p = 1005.7 \text{ J K}^{-1} \text{ kg}^{-1} \quad [\, = f(T,p); \text{ Bolton, 1980}]$$

For ideal monatomic and diatomic (air) gases, it can be shown from statistical mechanics theory that the ratios $c_p:c_v:R$ are 5:3:2 and 7:5:2, respectively. (See Tsonis, p. 32.) The variation of $c_p$ with T and p is presented in Table 3.1.

*Table 3.1.  Dependence of $c_{pd}$ (J K$^{-1}$ kg$^{-1}$) on T and p.  From Iribarne and Godson (1973).*

| p (mb) | T (°C) | | | |
|--------|--------|--------|--------|--------|
|        | -80    | -40    | 0      | 40     |
| 0      | 1003.3 | 1003.7 | 1004.0 | 1005.7 |
| 300    | 1004.4 | 1004.0 | 1004.4 | 1006.1 |
| 700    | 1006.5 | 1005.3 | 1005.3 | 1006.5 |
| 1000   | 1009.0 | 1006.5 | 1006.1 | 1007.4 |

Why is $c_p$ not constant?  See attached tables on $c_p$ of air and other materials.

### 3.5  Enthalpy

Many idealized and natural processes of interest in atmospheric science occur at constant pressure.  An example is evaporation of rain.  If heat is added isobarically to a system such that both the internal energy u and specific volume $\alpha$ change, then the First Law can be expressed as

$$\Delta q = (u_2-u_1) + p(\alpha_2- \alpha_1) = (u_2+p\alpha_2) - (u_1+p\alpha_1)$$
$$= h_2 - h_1,$$

where we have defined the enthalpy h as

$$h = u + p\alpha. \tag{3.10}$$

Upon differentiation, we obtain

$$dh = du + pd\alpha + \alpha dp,$$

or, using the First Law [Eq. (3.6)] we can obtain

$$dq = dh - \alpha dp.$$

Comparing this with (3.8) we can redefine dh as

$$dh = c_p dT. \tag{3.11}$$

This can be integrated to give (assuming h=0 when T=0 K)

$$h = c_p T.$$

Yet another form of the First Law is thus

$$dq = dh - \alpha dp = c_p dT - \alpha dp. \tag{3.12}*$$

We have now developed three useful forms of the first law: (3.6), (3.8) and (3.12).

### 3.6  Example: an isothermal process and reversibility

Consider a fixed mass (m=const) of ideal gas confined in a cylinder with a movable piston of variable weight.  The piston weight and its cross-sectional area determine the internal pressure.  Assume that the entire assembly is maintained at T=const (an isothermal process).  Let the initial pressure be 10 atm and the initial volume $V_i$ be 1 liter ($\ell$).  Consider the following three processes:
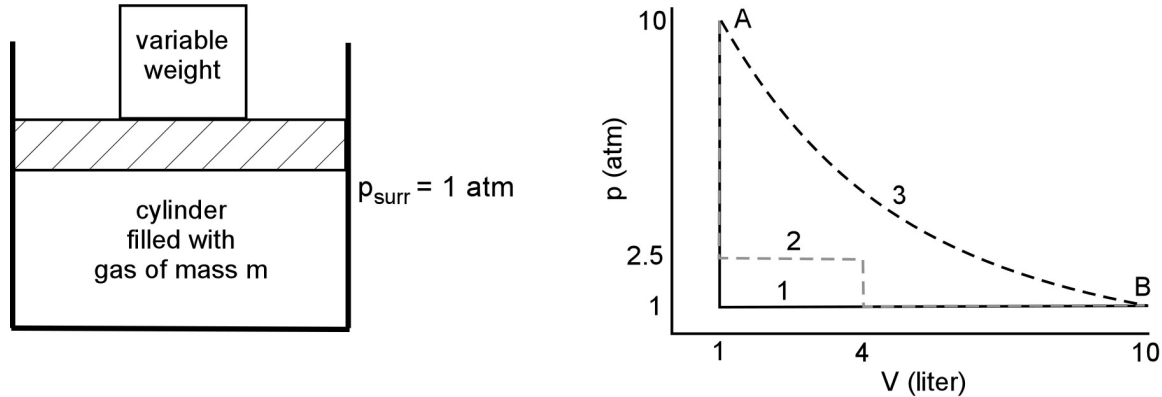


*Fig. 3.2.  Illustration of three processes (1, 2 and 3) discussted in the text.  The "experimental apparatus is shown on the left, and the thermodynamic processes are graphed on the right.*

*Process 1*:  The weight of the piston is reduced to change the cylinder pressure to 1 atm.  The gas will expand until its pressure is 1 atm, and since pV=mRT=const, the final volume $V_f$ will be 10 l (see Fig. 3.1).  The work of expansion is

$$W = \int p dV = p_{surr}(V_f - V_i) = 1 \text{ atm} * (10\text{-}1) \, \ell = 9 \, \ell\text{-atm}.$$

This is the work done on the surroundings.

*Process 2*:  This will be a two-stage process:  (i) Decrease (instantaneously) the cylinder pressure to 2.5 atm; then the volume will be 4 $\ell$, since this is similar to Process 1.  (ii) Then further decrease the pressure (instantaneously)  to 1 atm with a volume of 10 $\ell$.  The work is the sum of these two processes:

$$W = p_1 \Delta V_1 + p_2 \Delta V_2 = 2.5 \text{ atm} * 3 \, \ell + 1 \text{ atm} * 6 \, \ell = 13.5 \, \ell\text{-atm}$$

*Process 3*:  The pressure is *continuously* reduced such that the pressure of the gas is infinitesimally greater than that exerted by the piston at every instant during the process (otherwise no expansion would occur).  Then we must apply the integral form of work to get

$$W = \int p dV = mRT \ln(V_2/V_1) = 23.03 \, \ell\text{-atm}.$$

Note that pV=mRT=10 $\ell$-atm = const in this example.

This last process is reversible and represents the maximum work.  *A reversible process is one in which the initial conditions can be reproduced after a system goes through at least one change in state.* In process 3 above, the initial state of the system can be realized by increasing the pressure continuously until the initial volume is attained.  Note that the value of work for the reversible process depends only on the initial and final states, not on the path.  For the most part, *idealized* atmospheric processes are reversible since parcel pressure is assumed to be equal to (i.e., differs infinitesimally from) the ambient pressure.

Wikipedia definition:
In thermodynamics, a **reversible process**, or *reversible cycle* if the process is cyclic, is a process that can be "reversed" by means of infinitesimal changes in some property of the system without loss or dissipation of energy.[1] Due to these infinitesimal changes, the system is at rest during the whole process. Since it would take an infinite amount of time for the process to finish, perfectly reversible processes are impossible. However, if the system undergoing the changes responds much faster than the applied change, the deviation from reversibility may be negligible. In a reversible cycle, the system and its surroundings will be exactly the same after each cycle.[2]

An alternative definition of a *reversible process* is a process that, after it has taken place, can be reversed and causes no change in either the system or its surroundings. In thermodynamic terms, a process "taking place" would refer to its transition from its initial state to its final state.

http://en.wikipedia.org/wiki/Reversible_process_%28thermodynamics%29

### 3.7  Poisson's Equations

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Introduce the adiabatic process (dq=0)
[refer to the table on const. processes - this should be placed in Chap 1 with the
definitions]
Then use the forms of the first law to derive Poisson's Eqs.
A special case yields the potential temperature derivation – Section 3.8.
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An adiabatic process is defined as one in which dq=0.  For an adiabatic process the two advanced forms of the 1$^{st}$ Law, which are related by the equation of state, can be written

$$0 = dq = c_v dT + pd\alpha \qquad \text{[different forms of the same First Law – take your pick!]}$$
$$0 = dq = c_p dT - \alpha dp.$$

Using the equation of state in the form $p\alpha = R_d T$ (dry atmosphere), the above relations can be manipulated to get the following differential equations:

$$0 = c_v \ln T + R_d d\ln\alpha, \qquad [T,\alpha]$$
$$0 = c_p d\ln T + R_d d\ln p, \qquad [T,p]$$
$$0 = c_v d\ln p + c_p d\ln\alpha, \qquad [p,\alpha]$$

where the latter expression was obtained using the equation of state.  Integration yields three forms of the so-called *Poisson's Equations*:

$$T\alpha^{\eta-1} = \text{const} \qquad (T^c{}_v\alpha^R{}_d = \text{const})$$
$$Tp^{-\kappa} = \text{const} \qquad (T^c{}_p p^{-R}{}_d = \text{const}$$
$$p\alpha^\eta = \text{const} \qquad (p^c{}_v\alpha^c{}_p = \text{const})$$

In the above equations, $\kappa = R_d/c_p$ and $\eta = c_p/c_v$.

The last of the three above equations ($p\alpha^\eta = \text{const}$) has a form similar to that of the equation of state for an isothermal atmosphere (in which case the exponent $\eta$ is 1).  These relationships can be expressed in the more general form

$$p\alpha^n = \text{const},$$

which are known as polytropic relations.  The exponent n can assume one of four values:

1.  For n= 0, p = const                                                    isobaric process
2.  For n = 1, p$\alpha$ = const                                           isothermal process
3.  For n = $\eta$, p$\alpha^\eta$ = const                                 adiabatic process
4.  For n = $\infty$                                                       isochoric process

### 3.8    Potential temperature and the adiabatic lapse rate

We now derive a commonly used thermodynamic state variable utilizing the First Law. [I like to think of this as "building" a new variable using our toolkit of fundamental equations, consisting so far of the Equation of State and the First Law.]   Potential temperature $\theta$ is defined as the temperature which an air parcel attains upon rising (expansion) or sinking (compression) adiabatically to a standard reference level of $p_0$ = 100 kPa (1000 mb).  Since we are dealing with an adiabatic process, dq=0, and we can write the (T,p) form of the First Law (3.5) as

$$dq = 0 = c_p dT - \alpha dp.$$

Now we incorporate the equation of state, $p\alpha = R_d T$, to eliminate $\alpha$, and rearrange to get

$$\frac{c_p}{R_d}\frac{dT}{T} - \frac{dp}{p} = 0$$

Next, we integrate over the limits, in which a parcel has a temperature T at pressure p, and then end with a (potential) temperature $\theta$ at the reference pressure $p_0$.  Although not strictly correct, we assume the $c_p$ and $R_d$ are constant.

$$\frac{c_p}{R_d}\int_\theta^T \frac{dT}{T} = \int_{p_0}^p \frac{dp}{p}$$

or

$$\frac{c_p}{R_d}\ln\frac{T}{\theta} = \ln\frac{p}{p_0} \ .$$

We take the antilog of both sides and rearrange to isolate potential temperature ($\theta$):

$$\theta = T\left(\frac{p_0}{p}\right)^\kappa \qquad\qquad (p_o = 1000 \text{ mb}) \qquad\qquad\qquad (3.13a)$$

[This is also called Poisson's equation, since it a form of Poisson's equations.]  For dry air, $\kappa = R_d/c_p = 287/1005.7 = 0.286$ `[= 2/7 for a diatomic gas – from kinetic theory]`. This value changes somewhat for moist air because both $c_p$ and R ($R_d$) are affected by water vapor (more so than by T,p), as we shall see in the Bolton (1980) paper.  Potential temperature has the property of being *conserved* for unsaturated conditions (i.e., no condensation or evaporation), assuming that the process is adiabatic (i.e., no mixing or radiational heating/cooling of the parcel).  For a moist atmosphere, the exponent $\kappa$ in Eq.

(3.13) is multiplied by a correction factor involving the water vapor mixing ratio $r_v$, and $\theta$ is expressed as (see Bolton 1980, eq. 7)

$$\theta = T\left(\frac{p_0}{p}\right)^{\kappa(1-0.28r_v)} \tag{3.13b}*$$

where $r_v$ is the water vapor mixing ratio expressed in kg kg$^{-1}$ and $\kappa = R_d/c_p = 0.286$. [The student is advised to determine how much $\theta$ is adjusted from the dry air value for a very moist atmosphere in which $r_v = 20$ g kg$^{-1}$.]

Next, we will derive an associated quantity, the dry adiabatic lapse rate, which is used to evaluate static stability. The term "lapse rate" refers to a rate of temperature change with height (or vertical temperature gradient), i.e., $\partial T/\partial z$. [Aside: It is important to differentiate the static stability of the atmosphere, as given the the vertical gradient of temperature, $\partial T/\partial z$, from the Lagrangian temperature change that results when a parcel moves adiabatically in the vertical direction. The parcel change of temperature would be $dT/dt = (dT/dz)(dz/dt) = w(dT/dz)$.] Our starting point is once again the First Law (3.5) with $dq = 0$ since we are again considering an adiabatic process.

$$c_p dT - \alpha dp = 0.$$

For a hydrostatic atmosphere (hydrostatic implies no vertical acceleration, and will be defined more fully later) the vertical pressure gradient is

$$dp/dz = \partial p/\partial z = -\rho g = -g/\alpha.$$

Solving the above for $\alpha$ and substituting into the First Law, we obtain

$$c_p dT + g dz = 0.$$

Thus, the value of the dry adiabatic lapse rate ($\Gamma_d$) is

$$(dT/dz)_d = -g/c_p = \Gamma_d = -9.75 \text{ K km}^{-1}. \tag{3.14}$$

Again, one should be aware that this value changes slightly for a moist atmosphere (one with water vapor), since the addition of water vapor effectively yields a modified value of the specific heat at const pressure:

$$c_{pm} = c_{pd}(1+0.887r_v),$$

where $r_v$ is in units of kg kg$^{-1}$ (Bolton, 1980).

Specifically, for moist air,

$$\Gamma_m = \Gamma_d / (1 + 0.887r_v) \approx \Gamma d \, (1-0.887r_v).$$

### 3.9      Heat capacities of moist air; effects on constants

When we assume that the atmosphere consists of water vapor in addition to dry air, we have seen that the exponent of Poisson's equation ($\kappa = R_d/c_p$) requires adjustment. The water vapor molecule is a triatomic and nonlinear molecule, whose position can be described by 3 translational and 3 rotational coordinates. Dry air is very closely approximated as a diatomic molecule. The specific heats for water vapor are therefore quite different from that of dry air:

$c_{wv} = 1463$ J K$^{-1}$ kg$^{-1}$
$c_{wp} = 1952$ J K$^{-1}$ kg$^{-1}$,

where the w subscript designates the water phase. For Poisson's eq. (3.10a) the exponent $R_d/c_p$ is adjusted using the correction term $(R_d/c_p)(1-0.28r_v)$ (Bolton 1980), where the water vapor mixing ratio $r_v$ is expressed in kg kg$^{-1}$. Also the "constants" $R_d$ and $c_p$ can be corrected for moist air as follows:

$c_{pm} = c_{pd}(1+0.887r_v)$,
$c_{vm} = c_{vd}(1+0.97r_v)$,
$R_m = R_d(1+0.608r_v)$.

http://sol.sci.uop.edu/~jfalward/thermodynamics/thermodynamics.html

### 3.10      Diabatic processes, Latent Heats and Kirchoff's equation

For a diabatic process, there is a source of heating, so $dq \neq 0$. Two examples of diabatic heating/cooling are absorption/emission of radiation; and the diabatic heating/cooling associated with water phase changes: condensation (evaporation), freezing (melting) and deposition (sublimation).

When we consider energy exchange processes for the moist atmosphere, we find instances where heat supplied to a parcel occurs without a corresponding change in temperature. Under such conditions, the water substance is changing phase, and the change in internal energy is associated with a change in the molecular configuration of the water molecule, i.e., a change of phase. We thus refer to three such latent heating terms which are shown in Fig. 3.3 below.

The notation on the latent heating terms is such that the two subscripts define the change in phase of the water substance. For example, $L_{vl}$ is the latent of condensation with the subscript vl denoting a change in phase from vapor (v) to liquid (l). Thus, condensation is implied from the order of subscripts: vapor to liquid. For the sake of simplicity we can define the latent heats as follows:

- $L_{vl} = 2.50 \times 10^6$ J kg$^{-1}$  (0 $^o$C)          latent heat of condensation (function of T)
- $L_{vl} = 2.25 \times 10^6$ J kg$^{-1}$ (100 $^o$C)
- $L_{il} = 0.334 \times 10^6$ J kg$^{-1}$              latent heat of melting
- $L_{vi} = 2.83 \times 10^6$ J kg$^{-1}$ (0 $^o$C)          latent heat of deposition

Also, the important relation $L_{vi} = L_{vl} + L_{il}$ should be noted. In general, these terms are defined for p=const, but L does vary with temperature as indicated above. So, why is L a function of temperature? From the First Law, we can show that L is related to an enthalpy change, i.e., $L = \Delta h$.

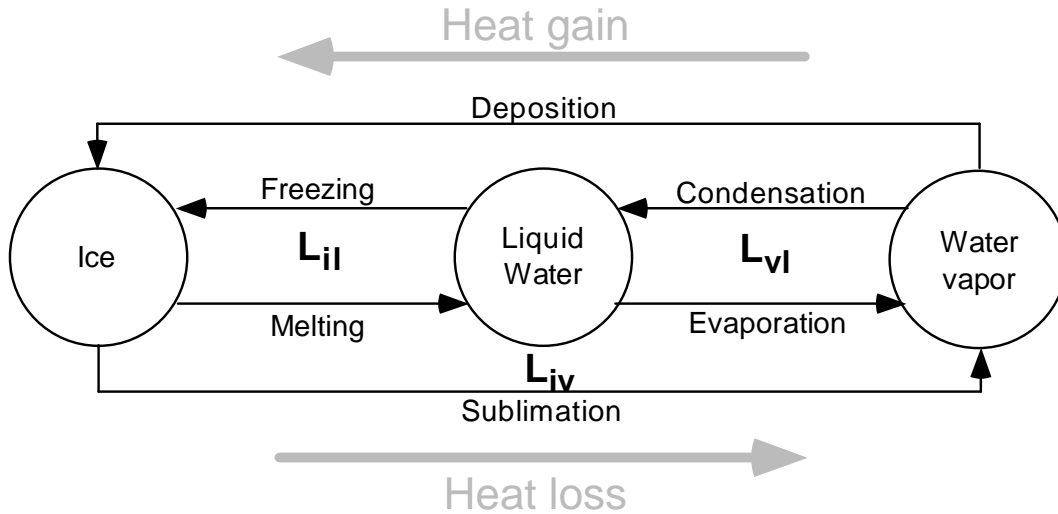[Proof: Since dp=0, the First Law can be written as $dq = c_p dT = dh$.]

*Figure 3.3.  Schematic depiction of latent heating components.*

To examine this temperature dependence, we do the following expansion, based on the definition of the total derivative (note that h = f(T,p):

$$dh = (\partial h/\partial T)_p \, dT + (\partial h/\partial p)_T \, dp \quad \text{(definition of the exact differential)},$$

and apply this to two states a and b ($\Delta h = L = h_b - h_a$):

$$d(\Delta h) = (\partial \Delta h/\partial T)_p \, dT + (\partial \Delta h/\partial p)_T \, dp.$$

For an isobaric process, only the second term vanishes and we have

$$d(\Delta h)_p \equiv dL = (\partial \Delta h/\partial T)_p \, dT = (\partial h_b/\partial T)_p dT - (\partial h_a/\partial T)_p dT$$

$$= (c_{pb} - c_{pa})dT.$$

This latter equivalence is based on the definition of specific heat (see Section 3.4), $c_p \equiv dq/dT = dh/dT$ for an isobaric process.

From the previous equation, we can write

$$(\partial L/\partial T)_p = \Delta c_p, \tag{3.15*}$$

which is *Kirchoff's equation*.  Thus, the temperature dependence of L is related to the temperature dependence of $c_p$.  Bolton (1980) provides an empirical equation that has a linear form for the temperature correction of $L_{vl}$:

$$L_{vl} = (2.501 - aT_c) \times 10^6 \text{ J kg}^{-1}, \tag{3.16}$$

where a = 0.00237 °C$^{-1}$ and $T_c$ is the dry bulb (actual air) temperature in °C.  Table 3.2 includes the values of the latent heats of sublimation, melting, and evaporation for a range of temperature.

*Table 3.2. Temperature dependence of the values of latent heats of sublimation, melting, and evaporation*

| T (°C) | $L_{iv}$ ($10^6$ J kg$^{-1}$) | $L_{il}$ ($10^6$ J kg$^{-1}$) | $L_{lv}$ ($10^6$ J kg$^{-1}$) |
|---|---|---|---|
| -100 | 2.8240 | | |
| -80 | 2.8320 | | |
| -60 | 2.8370 | | |
| -40 | 2.8387 | 0.2357 | 2.6030 |
| -20 | 2.8383 | 0.2889 | 2.5494 |
| 0 | 2.8345 | 0.3337 | 2.5008 |
| 20 | | | 2.4535 |
| 40 | | | 2.4062 |

**3.11 Equivalent potential temperature and the saturated adiabatic lapse rate**

*3.11.1  Equivalent potential temperature (approximate form)*

When an air parcel becomes saturated, and condensation takes place upon further cooling, then we must consider the latent heating by condensation, $L_{vl}$, multiplied by the mass of water vapor condensed during the process.  This heating can be expressed by a change in the saturation mixing ratio, $r_{vs}$, in this saturated state.  [Question:  Is this an adiabatic process since dq ≠ 0?]  Our starting point is the same as for the potential temperature derivation, with the exception that dq is now nonzero due to latent heating.  The magnitude of dq is the latent heat $L_{vl}$ (J kg$^{-1}$) multiplied by an incremental change in saturation mixing ration, $dr_{vs}$ (kg kg$^{-1}$ – this is really dimensionaless).  The units are therefore J kg$^{-1}$.

$$dq = -L_{vl}dr_{vs} = c_p dT - \alpha dp. \tag{3.17}$$

Substituting the equation of state $p\alpha = RT$ for $\alpha$, and rearranging terms in the above yields

$$-L_{vl}\frac{dr_{vs}}{T} = c_p \frac{dT}{T} - R_d \frac{dp}{p}.$$

Taking a log differential of Poisson's eq. (3.10a), we can write

$$d\ln\theta = d\ln T - \frac{R_d}{c_p}d\ln p$$

or      $$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R_d \frac{dp}{p} \qquad \text{(we will see this a lot!)*}$$

Combining this with eq (3.14) yields

$$-\frac{L_{vl}}{c_p T}dr_{vs} = \frac{d\theta}{\theta}$$

Our physical interpretation at this point is that the latent heating changes the potential temperature of the parcel, such that a reduction in $r_{vs}$ ($dr_{vs} < 0$) corresponds to a positive $d\theta$.

The LHS of the preceding equation would be cumbersome to integrate, as it currently stands, because $L_{vl} = L_{vl}(T)$. With the use of a graphical (thermodynamic) diagram, it will later be shown that

$$\frac{L_{vl}}{c_p T} dr_{vs} \approx d\left[\frac{L_{vl} r_{vs}}{c_p T}\right]$$       (this is an approximation, but it provides an exact differential)

Thus we have

$$d\left[\frac{L_{vl} r_{vs}}{c_p T}\right] = \frac{d\theta}{\theta},$$

which can be integrated, assuming that $\theta \rightarrow \theta_e$ as $r_{vs}/T \rightarrow 0$, to get

$$-\left[\frac{L_{vl} r_{vs}}{c_p T}\right] = \ln\left(\frac{\theta}{\theta_e}\right),$$

or

$$\theta_e = \theta \exp\left(\frac{L_{vl} r_{vs}}{c_p T_{sp}}\right)$$       (approximate form) ($r_{vs}$ in kg kg$^{-1}$)       (3.18)

which is an *approximation* for equivalent potential temperature, $\theta_e$. Note the approximations used here: (1) we assumed that $c_p$ and $L_{vl}$ are independent of $r_v$ and/or T and p; and (2) we made the approximation in the differential $(L_{vl}/c_p T)dr_{vs} \approx d(Lr_{vs}/c_p T)$. In essence, we have assumed that $L_{vl}$ is independent of temperature, which sacrifices precision in the integrated form. $T_{sp}$ in Eq (3.18) is the temperature of the parcel's saturation point (SP), traditionally called the lifting condensation level or LCL, and $r_{vs}$ is the mixing ratio at the LCL (or alternatively, the actual water vapor mixing ratio of the parcel). These terms/processes will be further defined and exemplified in a subsequent chapter, "Atmospheric Thermodynamical Processes."

A semi-empirical formula for $\theta_e$, superior to Eq. (3.15) and accurate to within ~0.5 K, is

$$\theta_e = \theta \exp\left(\frac{2675 r_{vs}}{T_{sp}}\right)$$       (within 0.5 K)  ($r_{vs}$ in kg kg$^{-1}$)       (3.19)*

(I don't recall the source of this, but it is given as Eq. (2.36) in Rogers and Yau 1989. Note that the numerical value 2675 replaces the ratio $L_{vl}/cp$, so this implies some constant values for $c_p$, and especially $L_{vl}$. This form is good for quick, relatively accurate calculation of $\theta_e$.)

An accurate calculation of $\theta_e$ requires an accurate determination of $T_{sp}$, $\theta$, $c_p$, and an integrated form that does not assume that $L_{vl}$ is consant.

*3.11.2 Equivalent potential temperature (accurate form)*

Because $\theta_e$ is conserved for moist adiabatic processes, it is widely used, and its accurate calculation has received much effort. An analytic solution is not possible. The approximate form derived in the previous section may produce errors of 3-4 K under very humid conditions (i.e., large $r_v$). Please refer to the paper of Bolton (1980) for a presentation of the accurate calculation of $\theta_e$. We will consider this in some detail. [Assignment: Read the paper by Bolton (1980).]

http://ams.allenpress.com/pdfserv/i1520-0493-108-07-1046.pdf

Bolton's curve-fitted form of $\theta_e$ is

$$\theta_e = \theta \exp\left[\left(\frac{3.376}{T_{sp}} - 0.00254\right) \times r_v (1 + 0.81 \times 10^{-3} r_v)\right] \quad \text{(within 0.04 K) } (r_v \text{ in g kg}^{-1}) \quad (3.20)$$

*3.11.3 Saturated (psuedo) adiabatic lapse rate – preliminary form*

The derivation of the saturated adiabatic lapse rate is complicated and requires advanced tools that are developed in later chapters. The derivation below is first order. A complete derivation is presented in Chapter 6 (my notes).

When water droplets condense within an ascending parcel, two limiting situations can be assumed: (a) the condensed water immediately leaves the parcel (the irreversible *pseudo-adiabatic* process), or (b) all condensed water remains within the parcel (the reversible *saturated-adiabatic* process). In reality, the processes acting within clouds lie somewhere in between. Here we consider the pseudo-adiabatic process. With the addition of latent heating, one may anticipate that a rising parcel undergoing condensation will cool less rapidly that an unsaturated parcel. Our starting point is (3.14), but with the hydrostatic equation term gdz substituted for $\alpha$dp in (3.14). We can then write

$-L_{vl}dr_{vs} = c_p dT + gdz.$          (remember dp/dz = -$\rho$g)

We will ignore the effects of water vapor being heated along with the dry air and write the above as

$$\frac{dT}{dz} = \frac{-L_{vl}}{c_p}\frac{dr_{vs}}{dz} - \frac{g}{c_p}.$$

Applying the chain rule to $dr_{vs}/dz$ yields

$$\frac{dT}{dz} = \frac{-L_{vl}}{c_p}\frac{dr_{vs}}{dT}\frac{dT}{dz} - \frac{g}{c_p},$$

which is similar to the definition of the dry adiabatic lapse, with the addition of the somewhat messy water vapor term (first term on the RHS). Solving the above for dT/dz, the approximate saturated adiabatic lapse rate is given as

$$\left(\frac{dT}{dz}\right)_s = \Gamma_s = \frac{\Gamma_d}{1 + \dfrac{L_{vl}}{c_p}\dfrac{dr_{vs}}{dT}} \tag{3.21}$$

In order to use this quantitatively, one needs to know the function $r_{vs}(p,T)$ to determine $dr_{vs}/dT$. A functional relationship for $r_{vs}$ is obtained from the Clausius-Clapeyron equation, to be considered in a subsequent chapter. We also note that the magnitude of $\Gamma_s$ is not constant, but decreases (nonlinearly) as T increases. This is not obvious from Eq. (3.21), but will become more apparent when we understand the Clausius-Clapeyron equation. On a thermodynamic diagram, lines depicting constant $\Gamma_s$ therefore have a variable slope, and are called saturated adiabats. Equivalent potential temperature is constant along pseudo adiabats; thus they can be labeled according to their value of $\theta_e$.

Note that the pseudo adiabatic process is irreversible, because all condesed water leaves the parcel (immediately) and is not available for evaporation should the parcel later descend. The derivation of an expression for the *reversible* saturated adiabatic process is given in Chap. 6.

## 3.12  Atmospheric Thermodynamic Diagrams

Refer to Chapter 9 in Tsonis.

A thermodynamic diagram serves as a valuable tool to illustrate the relationship between dry adiabats, saturated adiabats and other thermodynamic variables.  A number of thermodynamic diagrams used for atmospheric applications have been constructed.  We have considered only the simple p-V diagram so far (e.g., Fig. 3.1).   Any diagram is based on two thermodynamic coordinates.  With two thermodynamic variables being defined, other variables and processes can be determined based on the Equation of State, First Law, and ancilliary relations that we have considered, or will consider.  For example, the dry and saturated adiabatic lapse rates can (and must) be drawn on an atmospheric thermodynamic diagram to illustrate static stability. Once the coordinates are defined, then other isolines (e.g., saturation mixing ratio, dry/saturated adiabats, isotherms, isobars) can be defined and drawn on the diagram to graphically represent atmospheric processes and evaluate static stability.   Some examples include:
- skew-T, ln p diagram (T (skewed), ln p - our favorite)
- tephigram (T,s - Rogers and Yau)
- pseudo adiabatic chart (T,p - Wallace and Hobbs)
- Stuve diagram
- Clapeyron diagram (-p,$\alpha$; not desirable, but listed for sake of illustration)

The most commonly used diagrams are the skew-T and the tephigram.  Interestingly, it seems as though the "tropical" meteorologists favor the tephigram (with the exception of Rogers and Yau, who are Canadians).  The skew-T is most widely used in the research and operational sectors in the U.S.  An ideal atmospheric thermodynamic diagram has the following features:
1. area equivalence: the area traced out by some process, e.g., the Carnot cycle, is proportional to energy;
2. a maximum number of straight lines;
3. coordinate variables that are easily mearured in the atmosphere;
4. a large angle between adiabats and isotherms;
5. a vertical coordinate that is approximately linear with height.

The tephigram and skew-T closely satisfy nearly all these criteria.  The table below summarizes the imporant aspects for some diagrams.  Note that the skew-T, which we will use in this class, exhibits most of the ideal properties.  See Irabarne and Godson (1973, pp. 79-90) and Tsonis (Chapter 9) for a more complete discussion.

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*Table 3.3.  Summary of  thermodynamic  diagram properties.*

| Diagram | Abscissa | Ordinate | Straight line characteristics | | | Angle between adiabats/isotherms |
|---|---|---|---|---|---|---|
| | | | isobars | adiabats | isotherms | |
| Skew-T, ln P | T | ln p | yes | no | yes | nearly 90 $^o$ (variable) |
| Tephigram | T | ln $\theta$ | no | yes | yes | 90 $^o$ |
| Stuve | T | $p^k$ | yes | yes | yes | |
| Psueo-adiabatic | T | $-p\kappa_d$ | yes | yes | yes | ~45 $^o$ |
| Clapeyron | $\alpha$ | -p | yes | no | no | small |
| Emagram | T | -ln p | yes | no | yes | ~45 $^o$ |
| Refsdal | ln T | -Tlnp | no | no | yes | ~45 $^o$ |

_____

| Diagram | Abscissa | Ordinate | Straight line characteristics | | | Angle between adiabats and isotherms |
| | | | isobars | adiabats | isotherms | |
|---|---|---|---|---|---|---|
| Skew-T, ln P | T | ln p | Yes | no | Yes | nearly 90 $^o$ (variable) |
| Tephigram | T | ln $\theta$ | no | Yes | Yes | 90 $^o$ |
| Stuve | T | $p^{\kappa}$ | Yes | Yes | Yes | |
| Psueo-adibatic | T | $-p\kappa_d$ | Yes | Yes | Yes | ~45 $^o$ |
| Clapeyron | $\alpha$ | -p | Yes | No | No | small |
| Emagram | T | -ln p | yes | No | Yes | ~45 $^o$ |
| Refsdal | ln T | -Tlnp | no | No | yes | ~45 $^o$ |

Various isolines are drawn on thermodynamic diagrams, including isobars, isotherms, lines of constant saturation mixing ratio, dry adiabats and saturated adiabats.  Applications include:
- representation of vertical profiles of temperature and moisture (i.e., soundings)
- evaluation of static stability and potential thunderstorm intensity
- quick estimation of derived thermodynamic quantities such as:
    - relative humidty, given the temperature (T) and dewpoint temperature ($T_d$)
    - mixing ratio, given $T_d$ and pressure p,
    - potential temperature and equivalent potential temperature, given p, T and $T_d$
- determination of cloud/environment mixing processes
- determination of thickness (1000-500 mb thickness)
- mixing processes (advanced application)

Some web links:

http://meted.ucar.edu/mesoprim/cape/print.htm

http://meteora.ucsd.edu/weather/cdf/text/how_to_read_skewt.html

A good tutorial with bad graphics:
http://www.ems.psu.edu/Courses/Meteo200/lesson5/demos/skew_plot.htm

## Sources of skew-T diagrams (real-time and historical)

1) NCAR/RAP – the best Skew-T on the web:
http://www.rap.ucar.edu/weather/upper/

2) University of Wyoming – flexible site, data, skew-T or Stuve diagram; historical data
http://weather.uwyo.edu/upperair/sounding.html

3) Unisys
http://weather.unisys.com/upper_air/skew/

## Other valuable information:

GOES satellite sounding page – good information on skew-T's and their applications.  We will examine many of these during this course.
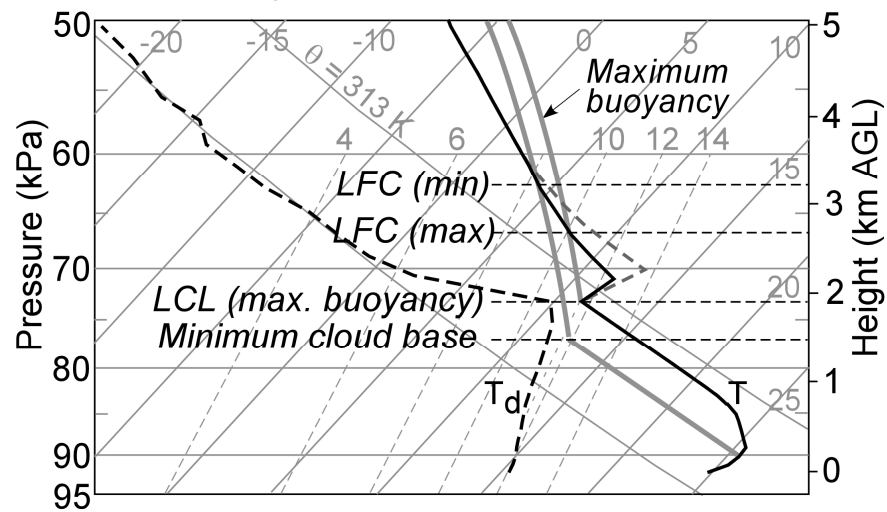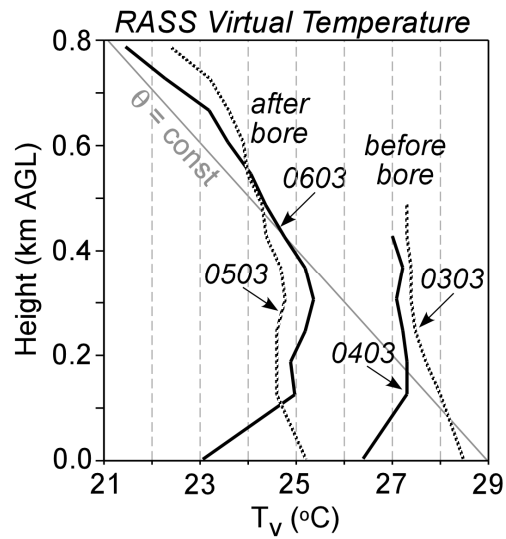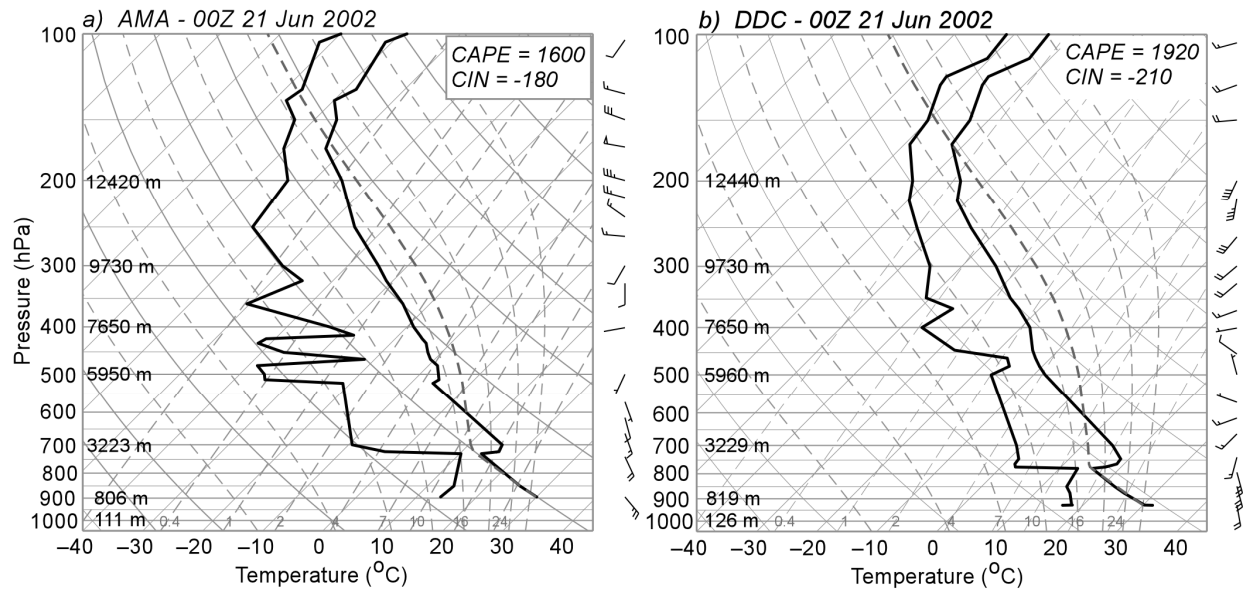http://orbit-net.nesdis.noaa.gov/goes/soundings/skewt/html/skewtinf.html

RAOB program:
http://www.raob.com/

**Buoyancy and CAPE**

http://meted.ucar.edu/mesoprim/cape/index.htm

http://meted.ucar.edu/mesoprim/cape/print.htm

a) AMA - 00Z 21 Jun 2002

CAPE = 1600
CIN = -180

Pressure (hPa)

12420 m

9730 m

7650 m

5950 m

3223 m

806 m

111 m

Temperature (°C)

b) DDC - 00Z 21 Jun 2002

CAPE = 1920
CIN = -210

12440 m

9730 m

7650 m

5960 m

3229 m

819 m

126 m

Temperature (°C)

## RASS Virtual Temperature

Height (km AGL)

θ = const

after bore

0603

before bore

0503

0303

0403

$T_v$ (°C)

Pressure (kPa)

θ = 313 K

Maximum buoyancy

LFC (min)

LFC (max)

LCL (max. buoyancy)

Minimum cloud base

$T_d$

T

Height (km AGL)

## Problems

Solve problems 1-7 below.  ATS 441 students may waive problem 1.

1.  Calculate the work and internal energy for an isothermal compression (isothermal change, which may or may not be brought about by an isothermal process) of an ideal gas from $A_i$ to $A_f$ (see diagram below) for each of the following processes:
    a)  isothermal reversible compression;
    b)  sudden compression from $p_{ext}$ to $p_f$ (e.g., dropping a weight on the piston of a cylinder containing a gas) and the subsequent contraction;
    c)  adiabatic reversible compression to $p_f$, followed by reversible isobaric cooling;
    d)  reversible increase of the temperature at constant volume until $p = p_f$, followed by reversible decrease of T at constant p until $V = V_f$.
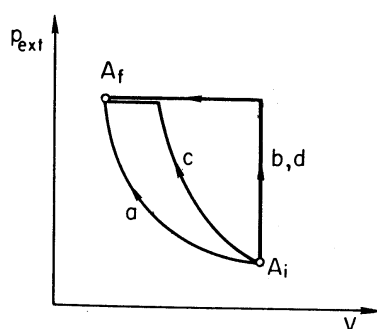


2.  A dry air mass ascends in the atmosphere from 1000 mb to 700 mb.  Assume no mixing or heat exchange, and an initial temperature of 10 °C.  <u>Trace out</u> this process on a skew-T, ln p diagram, and then find the following:
    a)  the initial specific volume;
    b)  the final temperature and specific volume;
    c)  the change in internal energy;
    d)  the work of expansion by 1 km³ of the air (volume taken at initial pressure).

3.  Recall that the specific enthalpy of a gas is defined by $h = u + p\alpha$.
    a)  Prove that dh for an ideal gas is an exact differential.  (See Section 2.1, Tsonis).
    b)  Calculate the change in enthalpy of a unit mass of dry air as it is compressed adiabatically from 700 mb and a temperature of 10 °C, to a pressure of 1000 mb  (as in the previous problem).

4.  Compute $\theta_e$ using the approximate form given by Eq. (3.18), the semi-empirical form given by (3.19), and the accurate form given by Eq. (3.20) (Eq. 43 in Bolton 1980).  Assume the following *extreme* conditions, the first for a very cold day, and the second for an extremely hot and humid day in the Southeast.   Any conclusions?

| Case | p (mb) | T (°C) | $T_d$ (°C) |
|---|---|---|---|
| (a) Cold day | 1020 | -20 | -40 |
| (b) Hot day | 1005 | 40 | 27 |

5.  We have considered four different kinds of processes:  isobaric (p = const), isothermal (T = const), isochoric (α = const), and adiabatic (dq = 0).    We defined heat capacities for only  two of these processes, namely at const pressure and volume.  Why did we not consider heat capacities for the other two processes?

6.  Commercial jet aircraft fly at cruising altitudes of 30,000 – 40,000 ft.  Yet such aircraft carry heat exchangers to cool cabin air at these altitudes.

    a)  Estimate the temperature at such cruising altitudes.  (Hint: Use the skew-T, ln p diagram to estimate a representative temperature and pressure at this altitude.)
    b)  Explain why the air must be cooled.  (Assume that the cabin pressure is 85 kPa.)
    c)  How much heat much be added to the air to achieve a cabin temperature of 23 °C? (Assume the cabin pressure is 85 kPa.)

7.  Explain the following dilemna:  a) Heated air expands.  b) When air expands, it cools.


Solve the following problems in Petty:
5.4
5.7
5.10