Chap. 3

First Law of Thermodynamics

General Form

Atmospheric Science Applications

Some general statements

- The energy of the universe is constant
- The First Law:
  - defines internal energy
  - states that heat is a form of energy.
  - states that energy is conserved
- The First Law is the second fundamental principle in (atmospheric) thermodynamics, and is used extensively.

Work of expansion

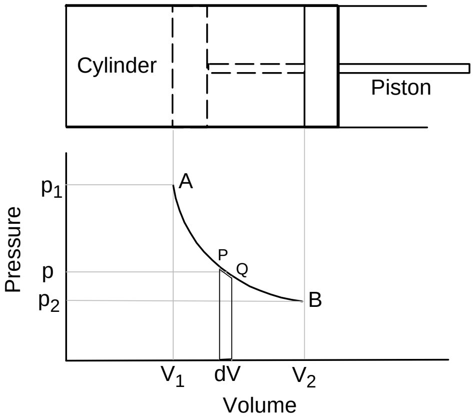
- Work is part of the First Law, but it can be considered independently
- What is work?
  - If a system (parcel) is not in mechanical (pressure) equilibrium with its surroundings, it will expand or contract. This involves "work".
- Work is defined by the differential $dw \equiv \mathbf{f} \cdot d\mathbf{s}$

Illustration:

- $dW = pAdx = pdV$ (shaded region of the graph)
- Specific work (work per unit mass):

  $dw = pd\alpha$
- work is found by integrating this differential over the initial and final volumes V_1 and V_2:

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



$W \propto$ area under the curve AB

This thermodynamic diagram (p-V) represents the state of the system at every point along the line. (Recall that the p-V diagram is a simple thermodynamic diagram.)

Example 3.1

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

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

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

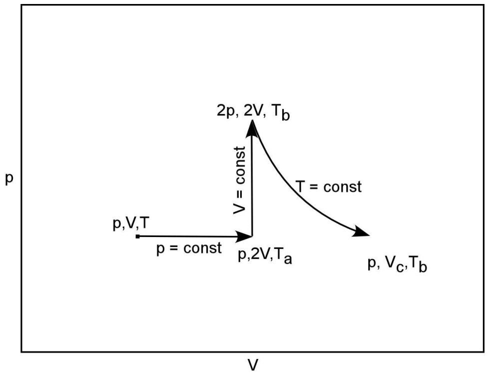
Then $W = mR_dT \int d\ln V = mR_dT\ln(V_2/V_1)$
(remember the process is isothermal)
$= (287\ \mathrm{J\ K^{-1}\ kg^{-1}})(288.15\ \mathrm{K})(2\ \mathrm{kg})(\ln 0.1)$
$= -3.81 \times 10^5\ \mathrm{J}$.

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

Work, cont.

- The quantity of work done depends on the path taken; work is not an exact differential. If it was, work would depend only on the beginning and end points (or initial and final conditions.
- Reconsider Eq. (3.a) above, rewriting it as follows (noting that the displacement dx = vdt, where v is the magnitude of the velocity vector):
- $dW = pA(dx) = pA(vdt)$
- 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
- or $dW/dt = dK/dt$ $(K = ½\ mv^2)$
- Hmmmm, we just can’t escape dynamics!

Example 3.2 (from problem 3.7 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 on the right. In the first process, the work is

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

In the second process, the work is zero since volume does not change.

In the third process, the value of work is similar 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_%28thermodynamics%29

Internal energy and a mathematical statement of the First Law

1. Consider a system which undergoes a change from some **heat input q per unit mass (q=Q/m).**
2. The system responds through the **work** of expansion, **w** (work per unit mass).
3. The excess energy beyond the work done by the system is **q-w**.
4. 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 (Δu - per unit mass) of the system must increase according to:

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

General form of the First Law in terms of various energy terms:

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 (LHS) and non-thermal (RHS) forms of energy:

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

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.

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

What is thermal energy (q)?

- At this point, it is instructive to define thermal energy.
- In the atmosphere, thermal energy can include heating/cooling by
  - Radiation (heating by absorption of SW or LW; cooling by emission of LW)
  - latent heating (associated with water phase changes).

Joule's Law: *u depends only on T* *OK, prove it!*

From statistical mechanics, for an ideal monatomic gas, the kinetic energy of translations is given by (refer to Chap 2 of Knupp's notes)

$$pV = (1/3)N_o mu^2 = \boxed{(2/3)E_{kin} = RT,}$$

where N_0 is Avogadro's number (6.023×10^{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 more generally for air).

$$\boxed{u = f(T)}$$

(Is this a proof?)

A general form of the First Law (in the differential form)

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

[What has happened to the Σe_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., $\oint Dw \neq 0.$

[see http://en.wikipedia.org/wiki/Inexact_differentials]

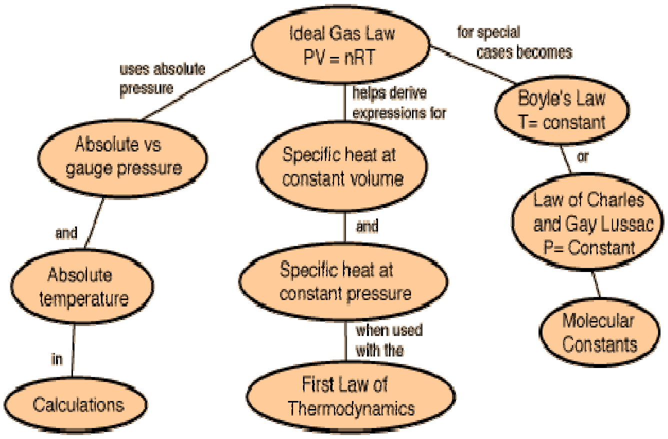
The first law requires that du be an exact differential -- one whose value depends only on the initial and final states, and not on the specific path. However, from here on, we will ignore (but not forget) this formal distinction between exact and inexact differentials.

Illustrate with p-V diagram

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

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

Review and applications



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

Review and example problems

Review the information and example problems at the following web site:

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

3.4 Specific heats

Consider the case where an incremental amount of heat dq is added to a system.

The temperature of the system increases by an incremental amount dT (assuming that a change of phase does not occur).

The ratio dq/dT (or Dq/DT) is defined as the specific heat, whose value is dependent on how the system changes as heat is input.

$c = dq/dT$ [note that $C = mc = m(dq/dT)$]

Two atmospheric scenarios: constant volume and constant pressure.

For constant volume: $c_v \equiv (dq/dT)_{\alpha=const}$

Since specific volume is constant, no work is done. According to the First Law, Eq. (3.1), dq = du (since $d\alpha = 0$) and

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

Then $du=c_v dT$

and $\boxed{\mathbf{dq = c_v dT + p d\alpha}}$. (3.6)*

For the isobaric process, the specific heat is

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

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

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

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

$$\mathbf{dq = (c_v+R)dT - \alpha dp = c_p dT - \alpha dp.} \qquad (3.8)^*$$

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:

$$\mathbf{c_p = c_v + R.} \qquad (3.9)^*$$

For dry air, the values are:

$c_v = 717\ \mathrm{J\ K^{-1}\ kg^{-1}}$

$c_p = 1005.7\ \mathrm{J\ K^{-1}\ kg^{-1}}$ [= f(T,p); 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} ($\mathrm{J\ K^{-1}\ kg^{-1}}$) 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*

Relative variation: (1007.4 – 1004.0) / 1007.4
= 3.4/1007.4 = 0.0034

Why is c_p not constant?

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 α change, then the First Law ($dq = du + pd\alpha$) can be integrated 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 enthalpy h is defined as

$$h = u + p\alpha. \qquad (3.10)$$

Upon differentiation, we obtain

$$dh = du + pd\alpha + \alpha dp \quad [= dq + \alpha dp]$$

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

Comparing this with (3.8) we can redefine dh as

$$dh = c_p dT. \qquad (3.11)$$

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

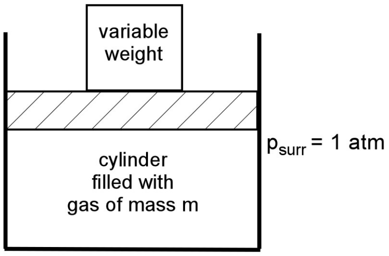
$$\mathbf{dq = dh - \alpha dp = c_p dT - \alpha dp}. \qquad (3.12)^*$$

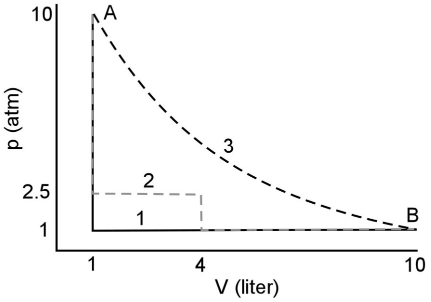
Three useful forms of the first law: (3.6), (3.8) and (3.12).

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 (L).

Consider three different processes in going from A to B (below 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

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

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 L, since this is similar to Process 1. (ii) Then further decrease the pressure (instantaneously) to 1 atm with a volume of 10 L. The work is the sum of these two processes:

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

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

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

Note that pV=mRT=10 L-atm = const in this example.

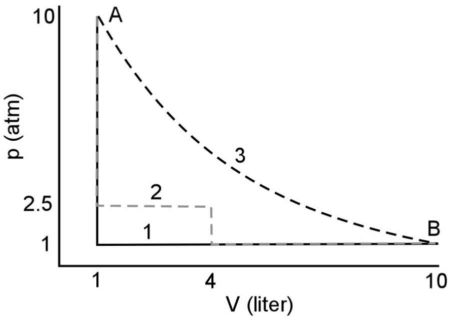
This last process is reversible and represents the maximum work.

Definition: ***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 of reversibility

- 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. 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

An **adiabatic process is defined as one in which dq=0**. The two advanced forms of the 1st Law (which are related by the equation of state) become

$$0 = dq = c_v dT + p d\alpha$$

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

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:

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

$0 = c_p d\ln T + R_d d\ln p,$ $[T, p]$ (let's look at this one)

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

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

$T\alpha^{\eta-1} = \text{const}$ $(T^{cv}\alpha^{Rd} = \text{const})$

$Tp^{-\kappa} = \text{const}$ $(T^{cp}p^{-Rd} = \text{const}$

$p\alpha^{\eta} = \text{const}$ $(p^{cv}\alpha^{cp} = \text{const})$

$\kappa = R_d/c_p = 0.286$ and $\eta = c_p/c_v = 1.403$

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 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:

For $n = 0$, $p = \text{const}$	isobaric process
For $n = 1$, $p\alpha = \text{const}$	isothermal process
For $n = \eta$, $p\alpha^{\eta} = \text{const}$	adiabatic process
For $n = \infty$	isochoric process

Refer to Tsonis, pp. 34-36.

3.8 Potential temperature and the adiabatic lapse rate

Potential temperature θ 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).

We use the (T,p) form of the First Law (3.5) , assuming an adiabatic process (dq=0)

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

Incorporate the equation of state, $p\alpha = R_d T$, to eliminate α, and rearrange to get

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

Now integrate over the limits, in which a parcel has a temperature T at pressure p, and then end with a (potential) temperature q 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

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

.

Take the antilog of both sides and rearrange to isolate potential temperature (θ):

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

[This is also called Poisson's equation, since it a form of Poisson’s equations, e.g., $Tp^{-\kappa}$ = const] 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 κ in Eq. (3.13a) is multiplied by a correction factor involving the water vapor mixing ratio rv, and q is expressed as (see Bolton 1980, eq. 7)

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

where r_v is the water vapor mixing ratio expressed in kg kg^{-1}.

Dry Adiabatic Lapse Rate

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., ∂T/∂z.

[Aside: It is important to differentiate the static stability of the atmosphere, as given the the vertical gradient of temperature, ∂T/∂z, from the Lagrangian temperature change that results when a parcel moves adiabically 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 (adiabatic process).

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

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

$$dp/dz = \partial p/\partial z = -\rho g = -g/\alpha \qquad \text{(hydrostatic equation)}$$

Solving the above for α and substituting into the First Law, we obtain

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

Thus, the value of the dry adiabatic lapse rate (Γ_d) is

$$(dT/dz)_d = -g/c_p = \Gamma_d = -9.81 \text{ m s}^{-2} / 1005.7 \text{ J K}^{-1} \text{ kg}^{-1} \quad [\text{J} = \text{kg m}^2 \text{ s}^{-2}]$$
$$= -9.75 \text{ K km}^{-1}. \qquad (3.14)$$

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

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

where r_v is in units of kg kg^{-1} (Bolton, 1980). (We will see this difference in graphical form later.)

Specifically, for moist air,

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

Some uses of θ

- Atmospheric structure; conserved for subsaturated motion; atmospheric bores
- Vertical cross sections
- Analysis of static stability

3.9 Heat capacities of moist air; effects on constants

The exponent of Poisson's equation ($\kappa = R_d/c_p$) requires adjustment when water vapor is present. Why?

The water vapor molecule (H_2O) 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 (N_2, O_2)
(See web site http://sol.sci.uop.edu/~jfalward/thermodynamics/thermodynamics.html.)
The specific heats for water vapor are therefore quite different from (much larger than) that of dry air:

$c_{wv} = 1463 \text{ J K}^{-1} \text{ kg}^{-1}$ (w subscript designates the water phase)
$c_{wp} = 1952 \text{ J K}^{-1} \text{ kg}^{-1}$,

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:

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

3.10 Diabatic processes, Latent Heats and Kirchoff's equation

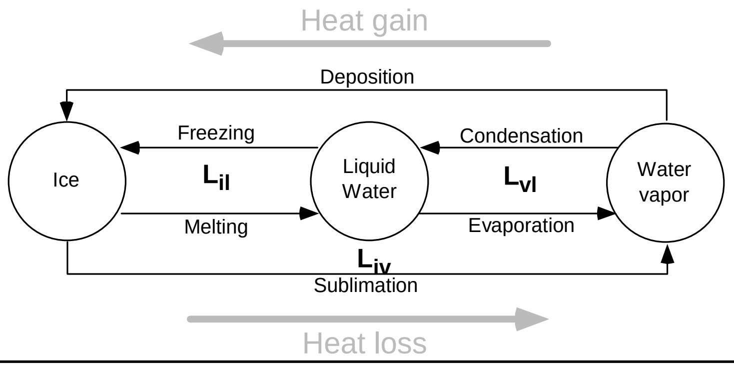
diabatic process → $dq \neq 0$.

Two examples of diabatic heating/cooling

1. absorption/emission of radiation;
2. heating/cooling associated with water phase changes

In the moist atmosphere, there are cases where heat supplied to a parcel 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. (latent heating)



Notation on the latent heating terms: the two subscripts define the change in phase of the water substance.

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 °C)	latent heat of condensation (function of T)
$L_{vl} = 2.25 \times 10^6$ J kg^{-1} (100 °C)	(yes, L_{vl} does vary by 10% between 0-100 °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 °C)	latent heat of deposition

Note: $L_{vi} = L_{vl} + L_{il}$

In general, these terms are defined for p=const . . .

but L_{vl} does vary with temperature!

Why is L a function of temperature?

From the First Law: L is related to an enthalpy change, i.e., $L = \Delta h$.

[Proof: Since dp=0, the First Law can be written as $dq = c_p dT = dh$. Also recall that enthalpy can be derived from the First Law.]

To examine this temperature dependence, expand the differential dh, based on the definition of the total derivative (note that $h = f(T,p)$:

$$dh = (\partial h/\partial T)_p \, dT + (\partial h/\partial p)_T \, dp$$ (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 ***Kirchoff's equation***

$$(\partial L/\partial T)_p = \Delta c_p, \qquad (3.15)^*$$

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}:

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

where a = 0.00237 °C^{-1} and T_c is the dry bulb (actual air) temperature in °C.

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)

Saturation → condensation → latent heating by condensation (L_{vl}, multiplied by the mass of water vapor condensed)

Expressed by a change in the saturation mixing ratio, r_{vs}

[Question: Is this an adiabatic process since dq ≠ 0?]

Starting point – First Law (dq is now nonzero due to latent heating)

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

Substitute the equation of state $p\alpha = RT$ for α, and rearrange terms:

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

Take the log differential of Poisson's eq. (3.10a):

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

or

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

Combine the preceding with eq (3.14):

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

Physical interpretation: 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 is 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)

Then we can integrate the following

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

assuming that $\theta \to \theta_e$ as $r_{vs}/T \to 0$, 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, θ_e.

Note the **approximations** used here:

(1) assumed that c_p and L_{vl} are independent of r_v and/or T and p;

(2) made the approximation in the differential $(L_{vl}/c_p T) dr_{vs} \approx d(L r_{vs}/c_p T)$.

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).

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

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

Better!

(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 θ_e. An accurate calculation of θ_e requires an accurate determination of T_{sp}, θ, c_p, and an integrated form that does not assume that L_{vl} is consant. These steps are detailed in the paper by Bolton (1980).

Note: $L/c_p = 2.5 \text{ x}10^6 / 1005 = 2488$

$L/c_p = 2675$; $L = 2675\ c_p = 2675 \text{ x } 1005.7$
$= 2.69 \text{ x } 10^6$

3.11.2 *Equivalent potential temperature (accurate form)*

Because θ_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).

Refer to the paper of Bolton (1980) for a presentation of the accurate calculation of θ_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 θ_e is (more clumsy with the calculator, but is easily coded)

$$\boxed{\theta_e = \theta \exp\left[\left(\frac{3.376}{T_{sp}} - 0.00254\right) \times r_v (1 + 0.81 \times 10^{-3} r_v)\right]} \qquad (3.20)$$

(within 0.04 K) (r_v in g kg^{-1})

3.11.3 Saturated (psuedo) adiabatic lapse rate – preliminary form

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

When water droplets condense within an ascending parcel, two limiting situations can be assumed:

1) the condensed water immediately leaves the parcel (the irreversible *pseudo-adiabatic* process), or
2) 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 αdp in (3.14). We can then write

$-L_{vl}d_{rvs} = c_pdT + gdz.$ (remember $dp/dz = -\rho g$)

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

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

The second term g/c_p defines the dry adiabatic lapse rate. The first term is new, and is 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

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

A functional relationship for r_{vs} is obtained from the Clausius-Clapeyron equation, to be considered Chapter 5 (my notes). We also note that the magnitude of Γ_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 examine and analyze the Clausius-Clapeyron equation.

More on the saturated adiabatic lapse rate

- Pseudo adiabatic process – all condensed water leaves the parcel; irreversible
- Saturated adiabatic process – all condensed water is carried with the parcel; reversible
- More on this in Chap. 6

More on θ_e

- Recall the approximate form (for illustrative puroses only):

$$\theta_e = \theta \exp\left(\frac{L_{vl} r_{vs}}{c_p T_{sp}}\right)$$

- r_{vs} is the initial parcel water vapor mixing ratio (r_v)
- T_{sp} is the so-called “saturation point” temperature. Bolton defines this is T_L.

How is T_{sp} determined?

- T_{sp} will be derived in Chap. 6
- For now, use Bolton's formula:

$$T_{sp} = \frac{2840}{3.5\ln T - \ln e - 4.805} + 55.$$

e is water vapor pressure; T is temperature in K

$$T_{sp} = \frac{1}{\frac{1}{T-55} - \frac{\ln(f/100)}{2840}} + 55$$

f is relative humidity

3.12 Atmospheric Thermodynamic Diagrams

Refer to Chapter 9 in Tsonis.

thermodynamic diagram - 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.

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:

- area equivalence: the area traced out by some process, e.g., the Carnot cycle, is proportional to energy;
- a maximum number of straight lines;
- coordinate variables that are easily mearured in the atmosphere;
- a large angle between adiabats and isotherms;
- 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 important 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; handout) and Tsonis (Chapter 9) for a more complete discussion.

Table 3.3. Summary of thermodynamic diagram properties.

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° (variable)
Tephigram	T	ln θ	no	Yes	Yes	90°
Stuve	T	p^κ	Yes	Yes	Yes	
Psueo-adibatic	T	-pκd	Yes	Yes	Yes	~45°
Clapeyron	α	-p	Yes	No	No	small
Emagram	T	-ln p	yes	No	Yes	~45°
Refsdal	ln T	-Tlnp	no	No	yes	~45°

Various isolines are drawn on thermodynamic diagrams, including isobars, isotherms, lines of constant saturation mixing ratio, dry adiabats and saturated adiabats.

On-line references:
Skew-T diagram:
http://www.sundogpublishing.com/AtmosThermo/Resources/SkewT.html

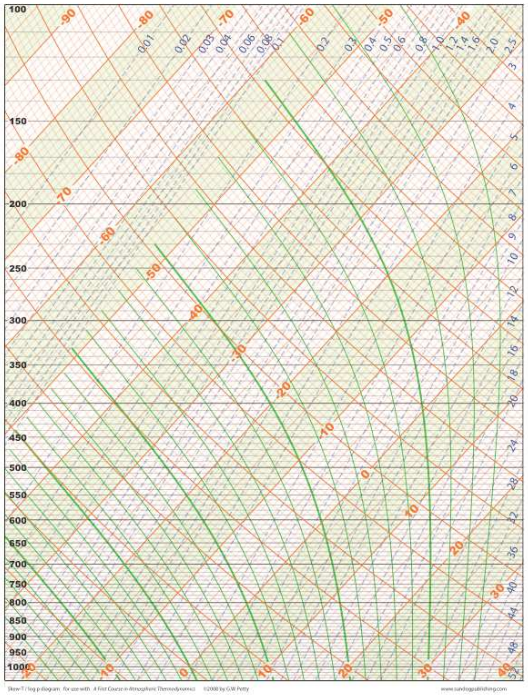
http://meteora.ucsd.edu/weather/cdf/text/how_to_read_skewt.html

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

Another one:
http://www.personal.psu.edu/jaz158/Skew-T%20Manual.pdf#search=%22use%20of%20the%20skew-t%22

An excellent resource to access recent and archived soundings (U. Wyoming):
http://weather.uwyo.edu/upperair/sounding.html

Available commercially:
http://www.raob.com/



Applications

- 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 humidity, 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
  - others
- determination of cloud/environment mixing processes
- determination of thickness (1000-500 mb thickness)
- mixing processes (advanced application)

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

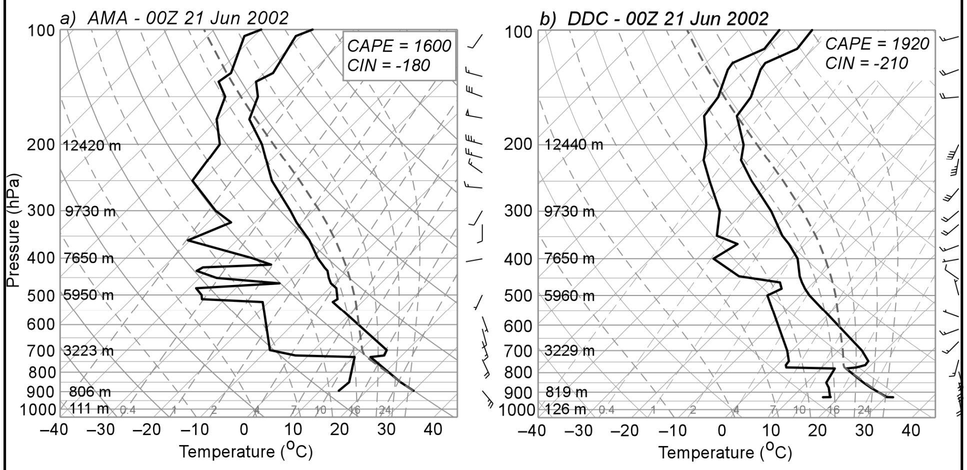
3) Unisys
http://weather.unisys.com/upper_air/skew/

Other valuable information:

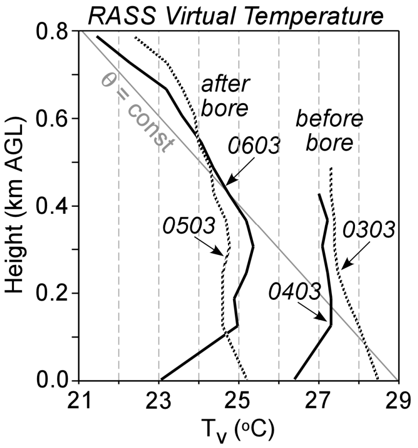
GOES satellite sounding page – good information on skew-T's and their applications. We will examine many of these during this course.
http://orbit-net.nesdis.noaa.gov/goes/soundings/skewt/html/skewtinf.html

RAOB program:
http://www.raob.com/RAOB5.htm

Soundings plotted on a skew-T, ln p diagram

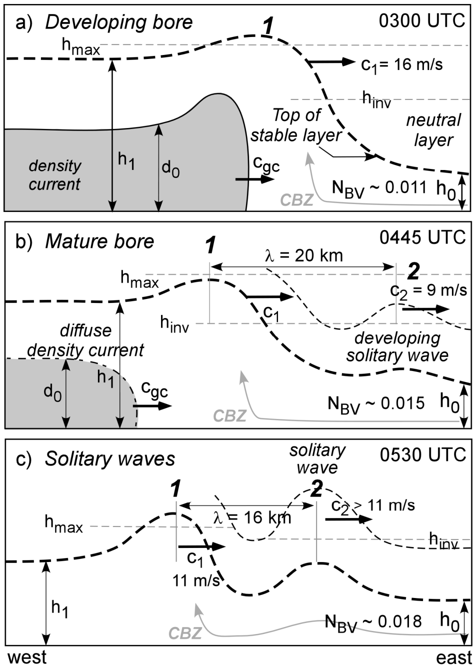


Variations in T_v vertical profiles around an atmospheric bore

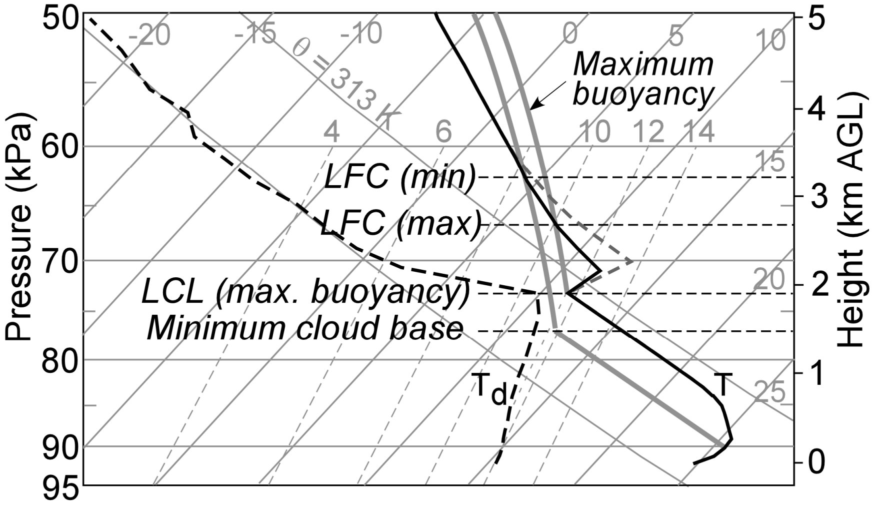


So what is a bore?

Schematic of a bore



A more detailed analysis on the skew-T



Animation of parcel ascent

- **Buoyancy and CAPE**

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

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

Chap. 3 HW

- Problems 1-7 in notes, plus Petty 5.4, 5.7, 5.10
  - – ATS 441 students may waive number 1

Examples

3.39 (W&H) A person perspires. How much liquid water (as a percentage of the mass of the person) must evaporate to lower the temperature of the person by 5 ℃? (Assume that the latent heat of evaporation of water is 2.5×10^6 J kg^{-1}, and the specific heat of the human body is 4.2×10^3 J K^{-1} kg^{-1}.)

3.38 (W&H) Consider a parcel of dry air moving with the speed of sound, $c_s = (\gamma R_d T)^{1/2}$, where $\gamma = c_p c_v = 1.40$, R_d is the gas constant for a unit mass of dry air, and T is the temperature of the air in degrees kelvin.
(a) Derive a relationship between the macroscopic kinetic energy of the air parcel K_m and its enthalpy H.
(b) Derive an expression for the fractional change in the speed of sound per degree Kelvin change in temperature in terms of c_v, R_d, and T.