4. THE SECOND LAW OF THERMODYNAMICS AND RELATED ITEMS

4.1 General statement of the law

Recall that the First Law is an empirical statement regarding the conservation of energy. The Second Law is concerned with the maximum fraction of heat that can be converted into useful work. The second law may be stated in several different ways, such as :

a) Thermal energy will not spontaneously flow from a colder to a warmer object.

b) The ***entropy*** (defined below) of the universe is constantly increasing.

Thus, the second law is not a conservation principle, but rather is a law defining the direction of flow of energy. In the following we will see that entropy and energy are closely related `[Note: The second law is a statement of macroscopic probability. Can refer to elementary kinetic theory.]`

4.2 Entropy

Entropy is a *state* function defined by (per unit mass)

$$ds \equiv \frac{dq_{rev}}{T}\,. \tag{4.1a}$$

The second law defines entropy as a state function and permits the following statements:

a) For a <u>reversible</u> process the entropy of the universe remains <u>constant</u>.

b) For an <u>irreversible</u> process the entropy of the universe will <u>increase</u>.

Thus, a more general definition of entropy is

$$ds \geq \frac{dq}{T} \qquad \text{(4.1b)*}$$

Note that the Second Law does not address anything specifically about the entropy of the *system*, but only that of the *universe* (system + surroundings).

A system process is defined as reversible if a system, after having experienced several transformations, can be returned to its original state without alteration of the system itself or the system's surroundings. A reversible transformation will take place when a system moves by infinitesimal amounts, and infinitesimally slowly, between equilibrium states such that the direction of the process can be reversed at any time. Remember that in a reversible process the deviation from equilibrium is infinitesimal. [Refer to the work of expansion problem considered previously in Section 3.6.] In a reversible process, the entropy of the universe (i.e., the system plus surroundings) remains constant.

In principle, a thermodynamic process can be classified into one of three categories: (a) natural, (b) reversible, and (c) impossible. Natural processes are more or less irreversible. For example, the following general processes are irreversible:

- friction - associated heating warms the surroundings (frictional heating in a hurricane)
- unrestrained expansion (expansion of a gas into a vacuum) - again the surroundings are modified
- heat conduction in the presence of a temperature gradient (surface heating/cooling)
- chemical reactions (e.g., the combination of H and O in the production of H_20; many others)
- turbulent mixing and molecular diffusion of pollutants and aerosols
- freezing of supercooled water
- precipitation formation - removes water and heat from an air parcel
- mixing between a cloud and the subsaturated atmosphere

Consider the p-V diagram below, on which both isotherms (lines of constant temperature) and adiabats (lines of constant potential temperature) are drawn. The isotherms are distinguished by differences in temperature and the adiabats by differences in potential temperature. There is another way of distinguishing differences between adiabats. In passing from one of the adiabats (θ_1 or θ_2) to another along an isotherm (this is actually one leg of the Carnot cycle, see also the appendix), heat is absorbed or rejected, where the amount of heat Δq_{rev} depends on the temperature of the isotherm. It can be shown that the ratio $\Delta q_{rev}/T$ is the same no matter what isotherm is chosen in passing from one adiabat to another. Therefore, the ratio $\Delta q_{rev}/T$ is a measure of the difference between the adiabats – and this is also the difference in entropy s. [This suggests that θ and s are related, which is shown in the following.]

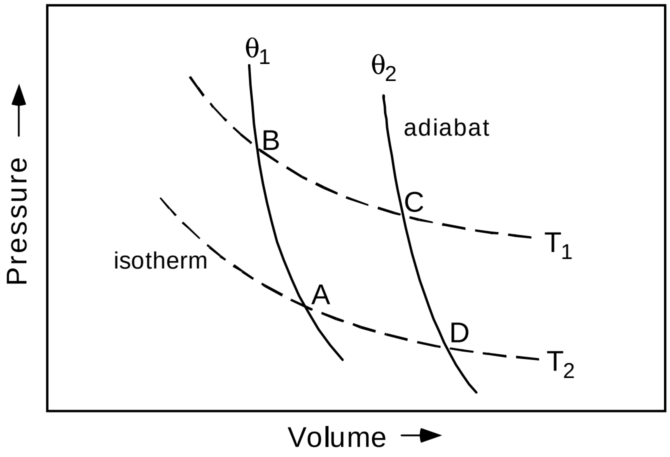


Figure 4.1. Isotherms (dashed) and adiabats (solid) on a p-V diagram. The line segments A-B-C-D-A define a Carnot cycle on this diagram. Adapted from Fig. 2.15 of Wallace and Hobbs (1977).

Using the definition of entropy from Eq. (4.1), the first law can be expressed as

$$dq = Tds = du + pd\alpha.$$

When a substance passes from state 1 to state 2, the change in entropy is found by integrating (4.1):

$$\Delta s = s_2 - s_1 = \int_1^2 \frac{dq_{rev}}{T}$$

It is desirable to express entropy in terms of more commonly-used atmospheric variables. To do this, we combine the equation of state

$$p\alpha = RT$$

with the first law in the form

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

We can then write

$$\frac{dq}{T} = c_p \frac{dT}{T} - R\frac{dp}{p} \qquad (4.2)$$

Taking the log differential of Poison's Eq. (potential temperature) we can write

$$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R\frac{dp}{p} \qquad (4.3)$$

Since (4.2) and (4.3) have identical right-hand sides (RHS), they can be equated:

$$\frac{dq}{T} = c_p \frac{d\theta}{\theta}$$

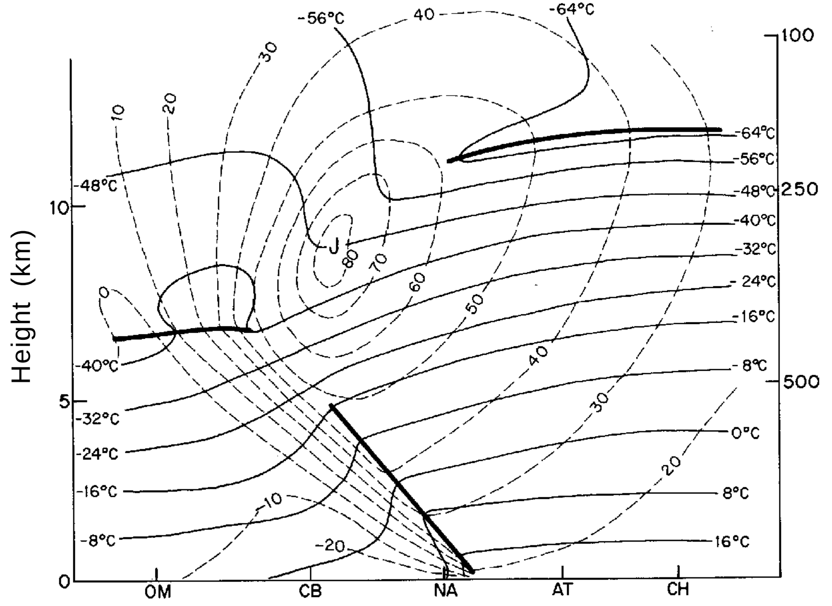
Thus the entropy function can be expressed in terms of potential temperature as

$$ds = c_p \frac{d\theta}{\theta}$$

or $s = c_p \ln\theta + \text{const}$.

From this we can see that transformations in which entropy is constant are also processes in which the potential temperature of an air parcel is constant. Such processes are called *isentropic* (adiabatic) processes. Analyses using the variable θ are similarly called *isentropic analyses*, and lines of constant θ are termed *isentropes*. An example of an isentropic analysis, and a corresponding temperature analysis, is shown in Fig. 4.2.

a) Temperature analysis



b) Isentropic analysis

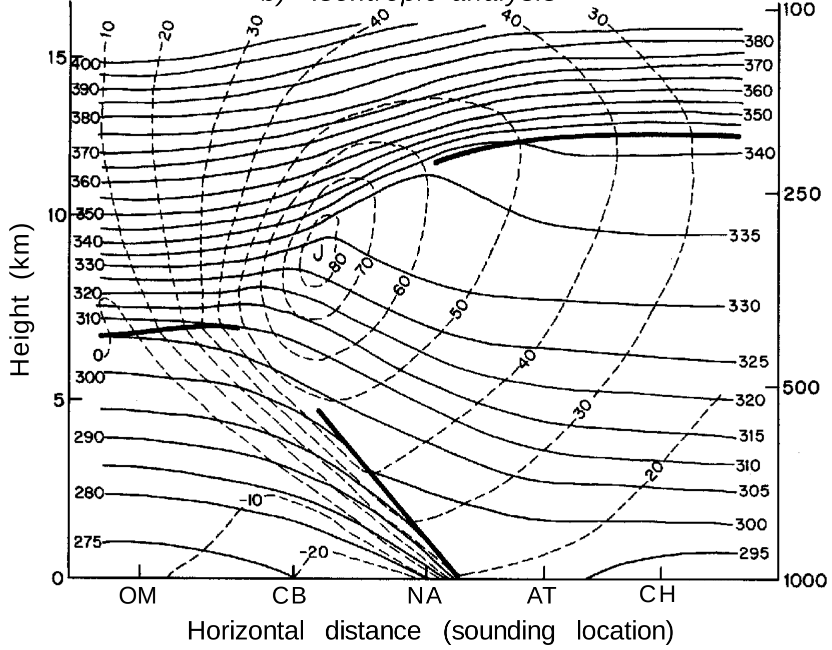


Fig 4.2. Analysis of (a) temperature and (b) potential temperature along a vertical section between Omaha, NE and Charleston, SC, through the core of a jet stream. In each panel, wind speed in m s^{-1} is indicated by the dashed contours. Taken from Wallace and Hobbs (1977).

4.3 A generalized statement of the second law

To this point we have considered only reversible processes in which a system moves through a series of equilibrium states. However, all natural processes are irreversible since they move a system from a nonequilibrium state toward a condition of equilibrium. The second law can be stated more generally in terms of the following postulates:

1. There exists a function of state for a system called entropy s.

2. s may change as the system: (a) comes into thermal equilibrium with its environment or (b) undergoes internal changes within the body. The total entropy change ds can be written as the sum of external (e) and internal (i) changes

$$ds = (ds)_e + (ds)_i$$

3. The external change $(ds)_e$ is given by $(ds)_e = dq/T$.

4. For reversible changes, $(ds)_i = 0$, and for irreversible changes, $(ds)_i > 0$. Thus,

$$ds = dq/T \text{ for reversible changes}$$

$$ds > dq/T \text{ for irreversible changes.}$$

Combining these two gives the generalized form of the first law as

$$Tds \geq du + pd\alpha, \qquad (4.4)^*$$

where the equality refers to reversible (equilibrium) processes and the inequality to irreversible (spontaneous) transformations.

[Note: For those interested, a simple treatment of thermodynamic probability and entropy is provided in Fleagle and Businger (1980), pp 54-59.]

4.4 Determination of entropy changes: some examples

The change in entropy for any process in going from an initial to a final state is measured by dq/T, using Eq. (4.4) or an equivalent. Consider the following processes.

4.4.1 Some idealized entropy change processes

[Note: in the examples below we are beginning with the first law $dq = du + pd\alpha$ or $dq = c_p dT - \alpha dp$]

<u>a) isothermal expansion of an ideal gas</u>

For an isothermal process du = 0 and the work of expansion (determined previously) is

$$\int pd\alpha = nRT\ln(\alpha_2/\alpha_1).$$

Thus, $\Delta s = nR\ln(\alpha_2/\alpha_1)$.

[Proof: Since $\alpha = RT/p$, $d\alpha = (R/p)dT - (RT/p^2)dp$. Then $-pd\alpha$ (=dw) = $-RdT + RTd\ln p$]

If the final specific volume α_2 is greater than the initial α_1 then the entropy change is positive, while for a compression it is negative.

b) adiabatic expansion of an ideal gas

For a reversible adiabatic expansion $dq=0$ and the entropy change is $ds=0$. This is the isentropic process defined previously.

c) heating of an ideal gas at constant volume

For a reversible process, and $d\alpha=0$. Then

$$ds = dq_{rev}/T = c_v dT/T = c_v d\ln T.$$

d) heating of an ideal gas at constant pressure

For a reversible process

$$ds = dq_{rev}/T = c_p dT/T = c_p d\ln T.$$

e) entropy changes during phase transitions

For a phase transition carried out reversibly, we have

$$\Delta s = \Delta h_{transition}/T_{transition}.$$

[Recall that $\Delta h = L = c_p \Delta T$ for a phase change, assumed to occur at constant pressure.]

4.4.2 *Example*: *The entropy change in an irreversible process*

Consider the isothermal expansion of an ideal gas with an initial value of pressure = 1 atm, temperature = 273.1 K, and volume = 22.412 liters per mole. Let this system expand isothermally against a constant external pressure of 0.5 atm. The final volume is 44.824 liters (L) and the work done is $p_{ext}(V_2-V_1) = 0.5(22.412) = 11.206$ L atm = 271.04 cal = 1135 J (1 cal = 4.187 J). This is the heat that must be supplied from an external reservoir to maintain isothermal conditions. Since this process is irreversible, the entropy change of the system is not dq/T. Rather, we must find a reversible process from the initial to final state. In this case we refer to Example (a) above in which $\int dq_{rev} = RT\ln 2 = 1573$ J. The change in entropy of the reversible process is thus $\Delta q/T = 1573\ \text{J} / 273.1\ \text{K} = 5.76\ \text{J K}^{-1}$.

4.4.3 *The phase change entropy*

At 273.15 K (0 °C) the entropy of melting of water is $L_{il}/T_f = 3.34 \times 10^5\ \text{J kg}^{-1} / 273.1\ \text{K} = 1223\ \text{J K}^{-1}\ \text{kg}^{-1}$, while at 373.1 K the entropy of vaporization is $L_{lv}/T = 2.25 \times 10^6\ \text{J kg}^{-1} / 373.1\ \text{K} = 6031\ \text{J K}^{-1}\ \text{kg}^{-1}$. This entropy change is due primarily to two effects: (1) the entropy associated with the intermolecular energy and (2) configurational entropy.

`Further explanation:` For the conversion of ice into water there is little change in the intermolecular entropy term and an increase in configuration entropy in transforming to a slightly less ordered system. However, in evaporation there is a large change in intermolecular entropy (the molecules in the gas are spaced far apart and are subject to little interaction compared to molecules in the liquid phase) as well as a large change in configurational entropy in going from a somewhat ordered liquid to a nearly completely disordered gas.
`[Can include the statistical treatment of entropy here.]`

Example: Calculate the change in entropy when 5 g of water at 0 °C are raised to 100 °C and then converted to steam at that temperature. We will assume the latent heat of vaporization is 2.253×10^6 J kg^{-1} at 100 °C. (Note that we will use the extensive forms – capital letters – since mass is involved.)

Step 1: Compute the increase in entropy resulting from increasing the water temperature from 0 to 100 °C:

$$\Delta S_1 = S_{373} - S_{273} = \int_{273}^{373} dQ_{rev} / T$$

Here, $dQ_{rev} = m(dq_{rev}) = mc_w dT$ where m is mass and c_w is the specific heat of water. It we assume c_w to be constant at 4.18×10^3 J kg^{-1} K^{-1} we have

$$\Delta S_1 = S_{373} - S_{273} = (0.005\,kg)(4.18 \times 10^3\ J\ kg^{-1}\ K^{-1}) \int_{273}^{373} dT/T$$

$$= 20.9 \ln(373/273) = 6.58 \text{ J K}^{-1}$$

Step 2: Compute the change in entropy from conversion of 5 g of water to steam, which involves a latent heat term. This is

$$\Delta S_2 = mL_{vl}/T = (.005 \text{ kg})(2.253 \times 10^6 \text{ J kg}^{-1})/373 \text{ K}$$
$$= 30.2 \text{ J K}^{-1}.$$

The sum of these components gives the total increase ΔS

$$\Delta S = \Delta S_1 + \Delta S_2 = 6.58 + 30.2 = 36.78 \text{ J K}^{-1}.$$

4.5 The free energy functions

The first law is a conservation statement, while the second law governs the directions of thermal energy transfer and also permits the determination of the reversibility of a process. It is desirable to have a function or set of functions which will describe for a system the likelihood of a given process and the conditions necessary for equilibrium. Since there are really only two basic thermodynamic functions (u and s), we can on the basis of convenience define additional functions that may be based on u or s `[Wait a minute -- It may not be clear why u and s are so basic. Think about this.]`. These functions can then be used to define equilibrium conditions for processes to be considered later.

4.5.1 *Helmholtz free energy*

The Helmholtz free energy is defined as

$$f \equiv u - Ts.$$

In differential form, we have

$$df = du - Tds - sdT \tag{4.5}$$

Combining this with Eq (4.4) ($Tds=du+pd\alpha$ -- recall that the equality implies the reversible condition here) gives

$$df = -sdT - pd\alpha$$

If a system is in equilibrium and both T and α are constant, then df = 0. For a system which undergoes a spontaneous (irreversible) process, we have

$$df < -sdT - pd\alpha$$

and df < 0. Thus, a system at constant T and volume (α) is in a stable equilibrium when f attains a minimum value. For this reason, the Helmholtz free energy is sometimes called the thermodynamic potential at constant volume.

4.5.2 *Gibbs free energy*

In this case we will derive the Gibbs free energy from the First Law, using the form

$$dq = du + pd\alpha.$$

Integration between the limits associated with a phase change, we get

$$L \equiv \int dq = \int du + \int pd\alpha$$

Assuming p=const and through some simple rearrangement we can obtain

$$L = T\int_{q_1}^{q_2} dq/T = T(s_2 - s_1) = u_2 - u_1 + p(\alpha_2 - \alpha_1)$$

where the subscripts 1 and 2 denote the two phases. Rearranging to combine like subscripts yields the following equality regarding the energy between the two phases:

$$u_1 + p\alpha_1 - Ts_1 = u_2 + p\alpha_2 - Ts_2$$

Based on the above, the Gibbs free energy is defined as (per unit mass)

$$g = u - Ts + p\alpha \qquad [= f + p\alpha]$$

In differential form,

$$dg = du - Tds - sdT + pd\alpha + \alpha dp. \tag{4.6}$$

Again, we can use (4.4) to obtain

$$dg = -sdT + \alpha dp.$$

In this case, if T and p are constant, for a body in equilibrium we have $dg = 0$. For an irreversible process,

$$dg < -sdT + \alpha dp.$$

Thus, $dg < 0$ in an irreversible, isobaric, isothermal transformation. Gibbs free energy is also called the thermodynamic potential at constant pressure. We will find that g is very useful for phase changes which occur at constant T (isothermal) and p (isobaric).

4.5.3 The free energy functions and total work

At this point it is instructive to relate g and f to the external work that a system can perform under various conditions. So far we have assumed that the only work term is that of expansion, $pd\alpha$. There are other forms of work that we will consider, however. [Recall the strange $\sum e_i$ term in Eq. (3.3) at the top of page 3, Chapter 3: $\Delta u = q + \Sigma e_i$]
For example, the creation of a surface in the nucleation (formation) of water droplets and ice crystals will be of interest to us. In this more general form, the First Law can be written as

$$dq = du + dw_{tot},$$

and for a reversible transformation

$$Tds = du + dw_{tot} \tag{4.7}$$

where the total work is dw_{tot}. If we combine the above with (4.5) and assume an isobaric condition, we find

$$dw_{tot} = -df - sdT.$$

Furthermore, for an isothermal process,

$$dw_{tot} = -df.$$

Thus, the total external work done by a body in a reversible, isothermal, isobaric process is equal to the decrease in Helmholtz free energy of the body.

Now, if da (this variable *is* a and not α) is the external work done by a unit mass of a body over and above any work of expansion ($pd\alpha$), i.e.,

$$da \equiv dw_{tot} - pd\alpha \ ,$$

then we can use (4.6), (4.7) and the above to write

$$da = -dg - sdT + \alpha dp.$$

For an isothermal, isobaric process,

$$da = -dg.$$

The thermodynamic functions f and g have important applications in problems involving phase changes in the atmosphere. In particular, these functions will be utilized later in this course when we consider the formation (nucleation) of water droplets from the vapor phase. [In other words, don't forget about g!]

Problems

1. One gram of water is heated from 0 to 20 °C, and then evaporated at const T. Compute the following (also assuming isobaric conditions):
   a) the change in internal energy
   b) the change in enthalpy
   c) the change in entropy

2. Calculate the change in entropy of 2 g of ice initially at -10 °C which is converted to steam at 100 °C due to heating. [ans: 17.3 J K^{-1}]

3. A 200 g sample of dry air is heated isobarically. Its entropy increases by 19.2 J K^{-1}, and the work done by expansion is 1.61 x 10^3 J. Solve for the final temerature of the air.

4. We are so accustomed to thinking of energy as being conserved and entropy as increasing that we may lose sight of the fact that the converse is possible. In what kind of general process is the entropy of a system conserved but its internal energy is not? This is a simple and straightforward question, not a trick. [Taken from Bohren and Albrecht.]

5. (a) Sketch the Carnot cycle on a skew-T diagram (make a copy of your large diagram, or find a skew-T on the web). (b) Prove that for any reversible heat engine, the work done in one cycle is proportional to the area enclosed by the cycle when represented on a graph of θ against p^κ.

6. A refreigerator is the reverse of a heat engine: Work is done *on*, rather than *by*, the working fluid in a refrigerator. Devise an energy efficiency for a refrigerator. Keep in mind that such an efficiency (call the coefficient of performance) is the ratio of what is desired to what this costs (in energy). After you have obtained this efficiency for any refrigerator, determine what it is for an ideal *Carnot refrigerator* (one that operates on a Carnot cycle). Estimate the Carnot coefficient of performance for a typical refrigerator.

Appendix: The Carnot Cycle: Highlights

Note: Refer to Petty, Section 5.5.2 (pp. 143-149)

The Carnot cycle may be one the the most popular examples used in the study of (general) Thermodynamics. Tsonis discusses it in disproportionate detail on pp. 49-56, and the student is encouraged to read this. The Carnot cycle illustrates several aspects of the Second Law, and also defines thermodynamic efficiency.

The Carnot cycle is a sequence of 4 component processes, two being isothermal, and the other two being adiabatic. These component cycles are interlaced as follows:

a. reversible isothermal expansion at $T = T_1$
b. reversible adiabatic compression at $\theta = \theta_1$
c. reversible isothermal compression $T = T_2$
d. reversible adiabatic expansion $\theta = \theta_2$

Fig. A.1 illustrates these paths as they would appear on a skew-T, ln p diagram. (Tsnonis uses a p-V diagram.)

The quantitative measures of work, internal energy change, and heat input along each leg are detailed in Tsnonis, pp. 50-52. Take some time to examine these.

From the Carnot cycle, the thermodynamic efficiency can be defined as

$$E_{thermo} = 1 - \frac{T_2}{T_1}.$$

Efficiency is zero when $T_1 = T_2$, and is maximized when $T_2 << T_1$.

Tsnonis mentions two postulates that originate from this, and these are alternate statements of the Second Law:

1) Kelvin's postulate: It is impossible for a thermal engine to accomplish work at only one temperature (p. 52, Tsnois).
2) Clausius's postulate: A transformation that permits heat transfer from a cold body to a hot body is impossible (p. 53, Tsonis). Recall that the First Law does not address the possibility of transformations; it only quantifies them, even if they are impossible. (Think of the First Law as the smart person who has no common sense, and the Second Law as the wise person who has abundant common sense.)

Question for discussion: How does the Carnot Cycle illustrate the way in which a heat pump (or refrigerator) works.

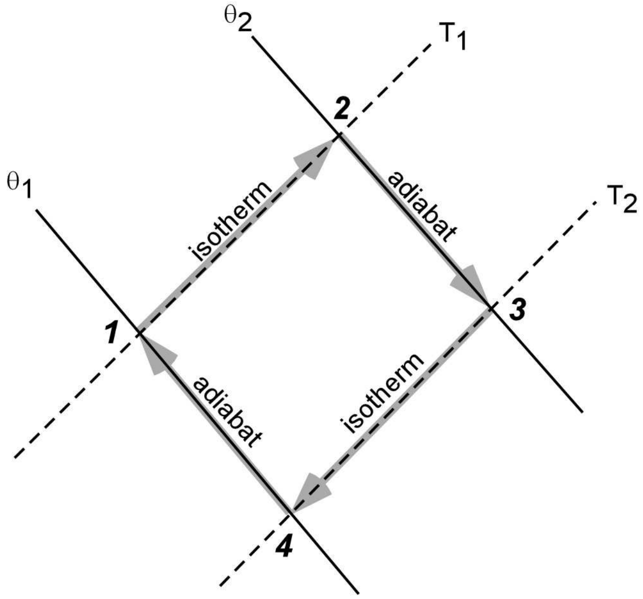


Figure A.1. Illustration of the Carnot Cycle as it would appear in graphical form on the skew-T, ln p diagram. The process is cyclic, begins at points 1, and then proceeds through points 2, 3, 4, and back to 1.