



### 4.2 Entropy

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

$$ds \equiv \frac{dq_{rev}}{T}$$
 (defined for a reversible process)  
Note: entropy is also represented by the symbol  $\phi$ 

The <u>second law defines entropy as a state function</u> (see Petty, Section 6.1) 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

$$ds \ge \frac{dq}{T}$$

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

http://en.wikipedia.org/wiki/Second\_law\_of\_thermodynamics

Chap. 6 in Petty is short and sweet. He has a good explanation of the second law and its relation to thermodynamic equilibrium in Section 6.2. Read this carefully.

Key Fact: Within any isolated system that is not at equilibrium, the net effect of any active process is always to increase the total entropy of the system. A state of equilibrium in therefore reached when the total entropy of the system has achieved it maximum possible value. At this point, no further evolution of the system state variables is possible.

# Definition of reversibility (revisited)

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.

- 1. 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.
- 2. 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.]
- 3. In a reversible process, the entropy of the universe (i.e., the system plus surroundings) remains constant.

We can examine reversible processes theoretically, but do reversible processes actually take place in the atmosphere?

Thermodynamic process can be classified into one of three categories:

- 1. natural
- 2. reversible
- 3. impossible.

Natural processes are more or less irreversible. Examples include:

- friction associated heating warms the surroundings (frictional heating in a hurricane is real)
- 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 two atoms of H and and one atom of O in the production of H<sub>2</sub>0)
- 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
- deliquescence behavior of NaCL

#### A closer look at entropy:

In the p-V diagram below , isotherms are distinguished by differences in temperature and the adiabats by differences in potential temperature  $\theta$ . There is another way of distinguishing differences between adiabats. In passing from one of the adiabats ( $\theta_1$  or  $\theta_2$ ) 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  $\Delta q_{rev}$  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.





The relation between s and  $\theta$  -- Another cool derivation

How is entropy related to the more commonly-used atmospheric variables?

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

$$ds = \frac{dq}{T} = c_p \frac{dT}{T} - R \frac{dp}{p}$$

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

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

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

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

Now we have a more intuitive definition of entropy!

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

$$ds = c_p \frac{d\theta}{\theta}$$
 (differential entropy)

or 
$$s = c_p \ln \theta + const.$$

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  $\theta$  are similarly called *isentropic analyses*, and lines of constant  $\theta$  are termed *isentropes*. An example of an isentropic analysis, and a corresponding temperature analysis, is shown in Fig. 4.2.



4.3 A generalized statement of the second law (review)

Calculation of entropy requires an equivalent reversible process. [But 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

 $ds = (ds)_e + (ds)_l$ 

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 for reversible changes ds > dq/T for irreversible changes

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

$$Tds \ge du + pd\alpha$$
, (4.4)\*

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

# **Examples** 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<sub>p</sub>dT - $\alpha$ dp] a) isothermal expansion of an ideal gas For an isothermal process du = 0 and the work of expansion (determined previously) is $\int pd\alpha = nRTln(\alpha_2/\alpha_1).$ $\Delta s = \Delta q/T = nRln(\alpha_2/\alpha_1).$ [Proof: Since $\alpha = RT/p$ , $d\alpha = (R/p)dT - (RT/p^2)dp$ . Then -pd $\alpha$ (=dw) = -RdT + RTdlnp] If the final specific volume $\alpha_2$ is greater than the initial $\alpha_1$ 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

By defintion,  $d\alpha$ =0. Then

 $ds = dq_{rev}/T = c_v dT/T = c_v dlnT.$ 

d) heating of an ideal gas at constant pressure

For a reversible process

 $ds = dq_{rev}/T = c_p dT/T = c_p dInT.$ 



4.4.2 A more comprehensive example: The entropy change in an irreversible process
Consider the isothermal expansion of an ideal gas: p = 1 atm, T = 273.1 K, and V = 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 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  $\underline{not} dq/T$ . Rather, we must find a reversible process from the initial to final state.

In this case we refer to Example (a) above (isothermal expansion) in which

 $\int dq_{rev} = RT \ln 2 = 1573 J.$ 

The change in entropy of the reversible process is thus  $\Delta q/T$  = 1573 J / 273.1 K = 5.76 J K  $^{-1}.$ 

#### 4.4.3 The phase change entropy

At 273.15 K (0 °C) the entropy of melting of water is

 $L_{ii}/T_{f} = 3.34 \text{ x} 10^{5} \text{ J} \text{ kg}^{-1} / 273.1 \text{ K} = 1223 \text{ J} \text{ K}^{-1} \text{ kg}^{-1}$ ,

while at 373.1 K the entropy of vaporization is

 $L_{\rm b}/T = 2.25 \text{ x } 10^6 \text{ J kg}^{-1} / 373.1 \text{ K} = 6031 \text{ J K}^{-1} \text{ kg}^{-1}.$ 

Note the large difference between these two entropies. Why?

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.

#### 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  $2.253 \times 106$  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  $4.18 \times 10^3$  J kg<sup>-1</sup> K<sup>-1</sup> then

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

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

This is

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

The sum of these components gives the total increase  $\Delta S$ 

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

## 4.5 The free energy functions

The first law is a conservation statement . . .

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.] **Is this true???** 

These functions can then be used to define equilibrium conditions for processes to be considered later.

4.5.1	Helmholtz free energy	
The <u>Helmholtz free energy</u> is defined as		
	f≡u-Ts.	
In differential form, we have		
	df = du - Tds - sdT	(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 $\alpha$ are constant, then df = 0. For a system which undergoes a spontaneous (irreversible) process, we have		
	df < -sdT - pdα	
and df < 0. Thus, a system at constant T and volume ( $\alpha$ ) 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 (after all, let's see how fundamental Gibbs free energy is):

 $dq = du + pd\alpha$ .

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

$$L \equiv \int dq = \int du + \int p d\alpha$$

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

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

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)

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

In differential form,

$$dg = du - Tds - sdT + pd\alpha + \alpha dp.$$
(4.6)

Again, we can use (4.4) (Tds = du +  $pd\alpha$ , in reversible form) 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:  $Du = q + \sum e_i$ ]

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  $\begin{array}{l} dq = du + dw_{tot}, \\ and for a reversible transformation \\ Tds = du + dw_{tot} \\ where the total work is dw_{tot}. \\ If we combine the above with (4.5) and assume an isobaric condition, we find \\ dw_{tot} = -df - sdT. \\ Furthermore, for an isothermal process, \\ dw_{tot} = -df. \end{array}$ 

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.

If da (this variable *is* a and not  $\alpha$ ) 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!]



The quantitative measures of work, internal energy change, and heat input along each leg are detailed in Petty, pp. 143-149. 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  $T_2 \ll T_1$ .



Another example problem:

Calculate the change in entropy when 1 mol of an ideal diatomic gas initially at 13  $^\circ\!\!C$  and 1 atm changes to a temperatu re of 100  $^\circ\!\!C$  and a pressure of 2 atm.

Find the change in air pressure if the specific entropy decreases by 50 J kg<sup>-1</sup> K<sup>-1</sup> and the air temperature decreases by 5%.

$$\begin{split} ds &= c_p dT/T - Rdp/p \\ Rearrange: \ dp/p &= (c_p/R) dT/T - ds/R \\ Integrate: \ ln(p_i/p_i) &= (c_p/R) ln(0.95T_i/T_i) - \Delta s/R \\ Insert values: \ ln(p_i/p_i) &= (1005.7/287.05) ln(0.95T_i/T_i) - (-50)/287.05 \\ &= 3.504 \ (-0.0513) - 0.174 = -0.00576 \\ p_f/p_i &= 0.994 \end{split}$$

p<sub>f</sub> = 0.994p<sub>i</sub>

