Second Law of Thermodynamics and Entropy

Reversibility and the Second Law

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

The second law of thermodynamics states that all natural processes are irreversible. A corollary of the Second Law of Thermodynamics (which we shall not prove) is

*In a reversible transformation, heat can only be converted to work by moving heat from a warmer to a colder body*

Another:

*In the absence of external work done on a body, heat can only move from warm to cold.*
For example, absorbing heat \( Q_2 \) from a cold reservoir and releasing \( Q_1 \) to a hot reservoir gives us a refrigerator, which requires an amount of work \( Q_1 - Q_2 \) to have been done by some outside agency.

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

\[
\Delta S = \frac{\Delta Q_{\text{rev}}}{T}
\]

or per unit mass

\[
\Delta s = \frac{\Delta q_{\text{rev}}}{T}
\]

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

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

\[\Sigma \Delta S > 0\]

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

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

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

However, in the hypothetical situation that a system is reversible (which is an assumption often made in atmospheric sciences)

\[dS = dQ/T\]

Under this assumption, the first law can be written

\[TdS = dh - \alpha dp = c_pdT - \alpha dp\]

or

\[ds = c_p d\ln T - Rd\ln p\]

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

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

from which we can see that

\[ds = c_p d\ln \theta\]

Note, that in the presence of condensation it is better to use \( \theta_e \)

\[ds \geq c_p d\ln \theta_e\]

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

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

\[ Tds = c_p dT - \alpha dp \]
\[ ds = c_p \frac{dT}{T} \]

2. Vaporize or Sublimate an object in its entirety at constant temperature and pressure

\[ Tds = c_p dT - vdp + L \]

where \( L \) is the Latent Heat
\[ ds = \frac{L}{T} \]
zero.

Relationship between entropy changes and pressure changes and work

We showed that
\[ ds = c_p d\ln T - Rd\ln p \]
which implies that, at constant pressure, entropy increases when the temperature increases
\[ \left( \frac{\partial s}{\partial t} \right)_p = c_p \left( \frac{\partial \ln T}{\partial t} \right)_p \]
or at constant temperature, entropy increases when the pressure decreases
\[ \left( \frac{\partial s}{\partial t} \right)_T = -R \left( \frac{\partial \ln p}{\partial t} \right)_T \]

This is very important because it means we can interpret the second law more intuitively as a requirement that, absent some external force, the pressure must decrease with time. Remember that maintaining constant temperature requires that heating equals working, i.e.
\[ \left( \frac{\partial q}{\partial t} \right)_T = \left( \frac{\partial w}{\partial t} \right)_T \]

We showed previously that work is done when, at constant pressure, the volume goes up or the pressure goes down
\[ \left( \frac{\partial w}{\partial t} \right)_T = -RT \frac{d\ln p}{dt} = RT \frac{d\ln \alpha}{dt} \]

So you can see now that entropy goes up when heating enables work to be done so that the pressure goes down!
\[ \left( \frac{\partial s}{\partial t} \right)_T = \frac{1}{T} \left( \frac{\partial w}{\partial t} \right)_T = -R \left( \frac{\partial \ln p}{\partial t} \right)_T \]
Entropy changes in a materially open system at constant pressure and temperature

So entropy increases in a materially closed system as things get hotter at constant pressure, or if there is expansion at constant temperature. The only thing that remains to be changed is the amount of mass at constant temperature and pressure. If the system is materially open, so that matter can flow in and out of the constant $T$ and $p$ surface, this is just the same as saying

$$\left( \frac{dS}{dt} \right)_{T,p} = \frac{(dQ/dt)_{T,p}}{T} = \frac{(dH/dt)_{T,p}}{T} = \frac{c_p T (dm/dt)_{T,p}}{T}$$

$$= c_p \left( \frac{dm}{dt} \right)_{T,p}$$

So, entropy production, provided it is along a surface of constant pressure and temperature, is related to an increase in enthalpy due to an increase in mass! When you (a surface of constant temperature and pressure) get fatter, your entropy goes up not down! There is so much confusion here, since many (including some quite famous physicists) think of us as ordered structures, whose growth must correspond to a decrease in entropy. Quite the opposite! Looking at us, by ourselves, it is an increase in entropy.