

# Second Law of Thermodynamics and Entropy

## Reversibility and the Second Law

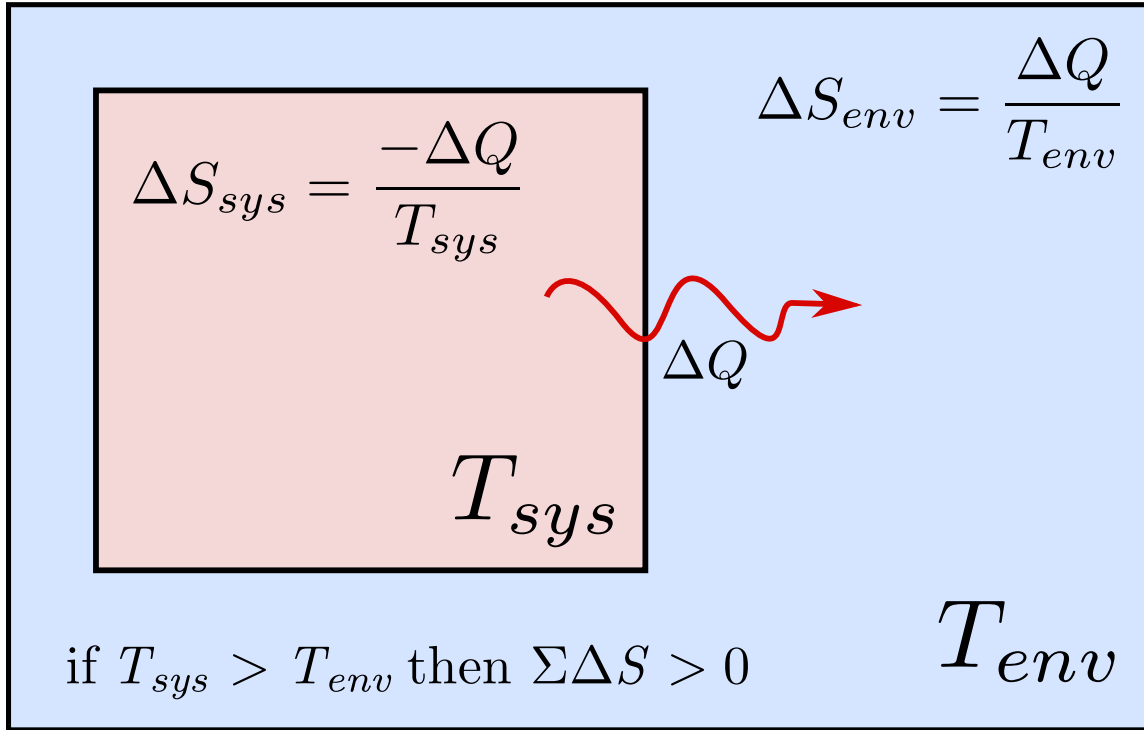


Figure 1: Transfer of heat from the system to its environment is spontaneous if entropy production is positive, requiring that the system has a higher temperature.

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. Lets 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.

$$\Delta S = \frac{\Delta Q_{rev}}{T}$$

or per unit mass

$$\Delta s = \frac{\Delta q_{rev}}{T}$$

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.

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

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

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

$$Tds = dh - \alpha dp = c_p dT - \alpha dp$$

or

$$ds = c_p d \ln T - R d \ln p$$

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

$$ds = c_p d \ln T - R d \ln p$$

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!

$$\left(\frac{\partial s}{\partial t}\right)_T = \frac{1}{T} \left(\frac{\partial w}{\partial t}\right)_T = -R \left(\frac{\partial \ln p}{\partial t}\right)_T$$