

4.2 Classical Thermodynamics: The Second Law

4.2.1 A Qualitative Sketch of the Second Law and Entropy

The first law of thermodynamics is concerned with the conservation of energy. The second law of thermodynamics is concerned with how that energy is transferred between systems. Its relevance to everyday experience can be seen from the following examples:

- Ice is placed in a glass of water. It melts.
- A hot metal tray is taken out of the oven and placed on a bench top. It cools.
- A brittle plate is dropped from a height onto a hard floor. It smashes into small pieces.
- A piece of iron is left outside. It rusts.
- A bicycle tyre is pumped to high pressure and punctured. The air rushes out.

The common factor in all these examples is that energy is spreading out *in a certain direction*.

- The energy in more rapidly moving warm air molecules disperses to the ice and breaks the intermolecular hydrogen bonds, allowing the water molecules in the ice to move more freely.
- The hot metal contains a relatively large amount of energy due to its vibrating atoms and this energy is transferred to the surrounding air molecules and thereby dispersed.
- The potential energy in the plate disperses through a heating of the surrounding air, the ground and the plate as it smashes.
- The iron atoms and oxygen molecules in the air have chemical (potential) energy stored in their bonds. When iron and oxygen react, lower energy iron oxide bonds are formed and the energy difference is dispersed as heat¹.
- The relatively large energy of the pressurized air in the tyre disperses when the tyre is punctured.

Very qualitatively, the second law says that *energy tends to spontaneously disperse unless hindered from doing so*.

If any of these processes were filmed and the tape accidentally played backwards, the mistake would immediately be evident. However, no physical law (apart from the second law) would be broken if the events happened in reverse. For example, the plate falls because there is a gravitational force pulling it down. However, beginning at the end and working back, it is theoretically possible for the many billions of air (and ground) molecules, which are now moving more rapidly due to the breaking plate, to interact in such a perfect way that the dispersed heat flows back towards the broken pieces and so provides enough energy for the pieces to fly together and gain a kinetic energy to lift off the ground, rise up and eventually slow until it reaches its precise original position off the ground. The second law says that this will not happen; energy does not spontaneously, that is without outside interference, gather together and concentrate in a small locality.

¹ most spontaneous reactions of this type require a certain energy to get started, the **activation energy**, and this hinders the second law from wreaking havoc

Entropy is closely associated with the second law. Again, qualitatively, entropy is *a measure of how dispersed energy is*. Each system has a certain entropy and as energy disperses, the entropy increases. When the air rushes out of the tyre, the entropy of the air and its surroundings increases. When the hot tray cools, the entropy of the tray and surrounding air increases. When the iron and oxygen react, entropy increases.

Entropy can also be defined in terms of probabilities. To take a classic example, consider a box with a shutter splitting it in two. A gas occupies one half of the box (as in Fig. 4.1.8). The shutter is then removed. What will happen? The gas will of course expand to completely fill the box. What are the chances of this happening in reverse? The gas molecules are constantly moving, but the probability of them moving about the box in such a way that all gas molecules would somehow occupy only one half of the box, with no gas in the other half of the box, is zero. As the gas expands, it moves to a more probable state, and the entropy increases.

The Second Law and Maximum Work

When heat is supplied to the confined gas of Fig. 4.1.9, work is done when the gas expands and raises the weight. However, if the flame is not placed under the apparatus but simply left to burn, the heat energy, according to the second law, will disperse into the air. It will not ever *spontaneously* gather back again in a small locality where it could again be used to do some work. The only way to get it back into a small locality again is to input even more energy. In this sense the second law tells us that if we want to maximize the amount of work we can do, we need to use heat energy productively, and if any heat energy escapes it is not possible to use it again without expending more energy. In this sense, entropy can be regarded as a measure of a system's energy unavailable for conversion into work.

A more formal and quantitative treatment of the second law will now be given.

4.2.2 Entropy and the Second Law

Entropy

The entropy S of a system is a property of that system. The change in entropy dS is due to two quantities. First, define the **entropy supply** $\delta S^{(r)}$ (an increment) through

$$\delta S^{(r)} = \frac{\delta Q}{\theta} \quad (4.2.1)$$

where Q is the heat supply; one can imagine the entropy “flowing” into the system. Define also the **entropy production** $\delta S^{(i)}$ (also an increment) to be the difference between the increment of entropy and the entropy supply:

$$dS = \delta S^{(r)} + \delta S^{(i)} \quad (4.2.2)$$

Thus the entropy change in a material is due to two components: the entropy supply, “carried” into the material with the heat supply, and the entropy production, which is

produced *within* the material. (The reason for the “*r*” and “*i*” superscripts is given further below.)

Note that, whereas the entropy S is a state function (a property), the entropy supply and entropy production are not, since they depend on the particular process by which the state has changed, and hence the use of the symbol “ δ ” for these functions. (Compare 4.2.2 with the first law, $dU = \delta W + \delta Q$.)

The Second Law

The second law of thermodynamics states that the entropy production is a non-negative quantity,

$$\boxed{\delta S^{(i)} \geq 0} \quad \text{The Second Law} \quad (4.2.3)$$

Regarding 4.2.2, the Second Law states that the increase in entropy of a system must be at least as great as the entropy flowing into that system.

In terms of the entropy, the first law can be written as

$$\begin{aligned} dU &= \delta W + \theta \delta S^{(r)} \\ &= \delta W + \theta dS - \theta \delta S^{(i)} \end{aligned} \quad (4.2.4)$$

or, including the second law,

$$\delta W = dU - \theta dS + \theta \delta S^{(i)} \quad \text{with} \quad \delta S^{(i)} \geq 0. \quad (4.2.5)$$

A process is termed **reversible** if the equality holds, $\delta S^{(i)} = 0$, so that there is no entropy production, in which case $dS = \delta S^{(r)}$. Otherwise it is termed an **irreversible** process, in which case $dS = \delta S^{(r)} + \delta S^{(i)}$. The superscript “*r*” on the entropy supply is to indicate that the entropy supply is equivalent to the change of entropy in a *reversible* process. The superscript “*i*” on the entropy production is to indicate that entropy production is associated with *irreversible* processes.

Alternative Statements of the Second Law

There are many different statements of the second law and each can be “derived” from the others (there is no one agreed version). Another useful definition is that *the heat input to the system in transforming from state A to state B is bounded from above*, according to

$$\delta Q \leq \theta dS \quad (4.2.6)$$

The maximum possible heat input is θdS , in which case the entropy change is due entirely to entropy supply, with no entropy production – a reversible process. It can be seen that the statement $\delta Q \leq \theta dS$ is equivalent to the statement $\delta S^{(i)} \geq 0$.

A re-arrangement of Eqn. 4.2.6 gives the classic **Clausius’s inequality**:

$$dS \geq \frac{\delta Q}{\theta} \quad (4.2.7)$$

4.2.3 Reversibility

Pure Heating

As an example of a reversible process, consider a **pure heating** (or cooling) process, where the volume is held constant, Fig. 4.2.1. Taking the two state variables to be θ and V , it follows from 4.2.5 that the work increment can be expressed as

$$\delta W = \left(\frac{\partial U}{\partial V} - \theta \frac{\partial S}{\partial V} \right)_\theta dV + \left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right)_V d\theta + \theta \delta S^{(i)} \quad (4.2.8)$$

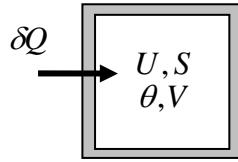


Figure 4.2.1: Pure heating

With $\delta W = dV = 0$, this reduces to

$$\left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right)_V d\theta + \theta \delta S^{(i)} = 0 \quad (4.2.9)$$

Now U and S are state functions, and the partial derivatives and, in particular, the term inside the brackets are also properties of the system. Further, $\delta S^{(i)} \geq 0$, $\theta > 0$, and $d\theta$ can be positive, negative or zero. Since $d\theta$ can be assigned a value completely independently of the value of the term inside the brackets, the equality in Eqn. 4.2.9 can only be satisfied *in general* if both

$$\left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right)_V = 0 \quad \text{and} \quad \delta S^{(i)} = 0 \quad (4.2.10)$$

The second equality shows that *a quasi-static pure heating process is always reversible*. As mentioned, the first equality is a relation between state functions and is not path-dependent and hence holds for *all* processes, not just for pure heating.

In reality there is never any such thing as a completely reversible process – in the case of pure heating, a reversible process would require that the temperature at any instant is uniform throughout the material, which will never be exactly true. It will be shown below that if there is any appreciable temperature gradient within a material then there will be entropy production.

Reversible Processes

To be precise, a process is reversible when both the system *and its surroundings* can be returned to their original states. For example, if the material in a piston-cylinder arrangement is compressed quasi-statically and there is no friction between the piston and cylinder walls, then the process is reversible – the load can be reduced by very small amounts and the material will “push back” on the piston returning it to its original configuration, with no net work done or heat supplied to the system.

Irreversible Processes

An irreversible process is one for which there is entropy production, $\delta S^{(i)} > 0$. In practice, irreversibilities are introduced into systems whenever there is spontaneity:

- unrestrained expansion of a gas/liquid to a lower pressure – for example when the lid is taken off a gas at high pressure, and is allowed to escape into the atmosphere
- heat transfer from one part of a material to another part at a lower temperature (except in the ideal case where the temperature difference is infinitesimal)
- friction (both the sliding friction of solid on solid and the friction that occurs between molecules in the flow of fluids)

The common factor amongst all these is that the system and its surroundings cannot be returned to their original configurations. For example, with the piston-cylinder arrangement, friction between the piston head and cylinder walls means that further work needs to be expended on the return stroke so that, although the piston-cylinder is returned to its original state, a net amount of work needs to be done and so the “surroundings”, or whatever is producing the work, is not back at its original state. Similarly, if the piston was compressed very quickly to its final position, the temperature, momentarily, might well be higher at the piston head than further down in the material. This would produce a spontaneous heat transfer from the upper part of the material to the lower part and it would not be possible to return the system and its surroundings to their original states.

Irreversible Heat Transfer

In the processes studied so far, it has been assumed that all the state functions were uniform throughout the material. In particular, it has been assumed that the temperature is uniform throughout. What if one now has a system whose parts are at different temperatures?

Suppose that a quantity of heat δQ flows from a body at temperature θ_1 to a body at temperature θ_2 , Fig. 4.2.2. One can imagine for the sake of argument that the heat capacities of both bodies are sufficiently large that their temperatures are effectively unchanged by the heat flow. The two bodies are insulated from their surroundings.

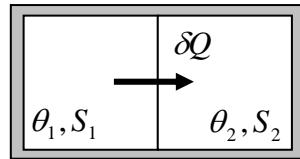


Figure 4.2.2: Heat flow from one body to another

This is pure heating and so the entropy change due to this heat transfer are the entropy supplies $\delta S_1^{(r)} = \delta Q / \theta_1 < 0$ and $\delta S_2^{(r)} = \delta Q / \theta_2 > 0$. Considering now the complete system (both bodies), there is no entropy supply, so any entropy change must be an entropy production

$$\delta S^{(i)} = \frac{\delta Q}{\theta_2} - \frac{\delta Q}{\theta_1} \quad (4.2.11)$$

Since $\delta S^{(i)} \geq 0$, it follows that $\theta_1 > \theta_2$, that is, *heat flows from the warmer body to the colder body*.

In this example there is no work done, no heat transfer and no internal energy change, but there is an entropy change.

If one wants the heat transfer to be very nearly reversible, one can make the entropy production very small. This can be achieved by making the temperature difference between the two bodies very small: by letting $\theta_1 = \theta$, $\theta_2 = \theta + \Delta\theta$, one has

$\delta S^{(i)} \approx -(\delta Q / \theta)(\Delta\theta / \theta)$. Keeping the entropy supply constant, this means that one must make $\Delta\theta / \theta$ as small as possible. Thus heat transfer is reversible *only* if there is an “infinitely small” temperature difference between the two bodies.

Entropy supply is due to heat transfer, but the entropy production here is due to an adiabatic irreversible change.

Entropy Measurements

The entropy of a material can be measured as follows. First, since $dS = \delta Q / \theta + \delta S^{(i)}$, one has $dS = C(d\theta / \theta) + \delta S^{(i)}$ where C is the specific heat capacity. Thus, for a *reversible* process, one has

$$\Delta S = \int_{\theta_1}^{\theta_2} C d\theta / \theta \quad (\text{reversible}) \quad (4.2.12)$$

but one must ensure that the entropy production is zero. In practice, what one does is keep $d\theta / \theta$ small enough so that the entropy production is sufficiently small for the accuracy required. Once the entropy change is found, it of course applies to *all* processes, not just the reversible process used in the experiment.

Thermodynamic Equilibrium

Thermodynamic equilibrium has already been mentioned – it occurs when no changes of the state variables can occur. Thus, one requires that $\delta W = \delta Q = dU = 0$. With $\delta Q = 0$, one has $\delta S^{(r)} = 0$ and $dS = dS^{(i)}$. For full equilibrium, one requires that $dS^{(i)} = 0$ but, since entropy production tends always to increase the entropy, thermal equilibrium can only occur if the entropy has reached its *maximum possible value*.

4.2.4 Free Expansion of an Ideal Gas

It was seen that, for an ideal gas undergoing a quasi-static process (see Eqn. 4.1.25),

$$\Delta S = S_2 - S_1 = C_V \ln(\theta_2 / \theta_1) + mR \ln(V_2 / V_1) \quad (4.2.13)$$

and the entropy production is zero. In other words, any quasi-static process involving an ideal gas is reversible.

Consider an isothermal quasi-static process in which an ideal gas is heated very slowly, so that it does work and expands to twice its original volume. One has $\Delta S = mR \ln 2$. This is the change in entropy in the gas; the surroundings has an equal decrease in entropy as heat leaves it so that, by definition, the total entropy change in this reversible process is zero.

Consider now a thermally insulated container divided by a partition into two parts each of volume V . One of these contains an ideal gas and the other is evacuated. The partition is taken away, so that the gas completely fills the container (see Fig. 4.1.8). During the spontaneous expansion, there is a complex non-equilibrium turbulence. The gas eventually settles down to its new equilibrium position. The initial and final states are as for the reversible heating described above, so the entropy change in the gas must again be $\Delta S = mR \ln 2$. However, here there is no interaction with the surroundings, so this entropy must be entropy production.

4.2.5 Problems

1. A system undergoes a process in which work is done on the system and the heat transfer Q occurs at a constant temperature θ_b . For each case, determine whether the entropy change of the system is positive, negative, zero or indeterminate:
 - (a) reversible process, $Q > 0$
 - (b) reversible process, $Q = 0$
 - (c) reversible process, $Q < 0$
 - (d) irreversible process, $Q > 0$
 - (e) irreversible process, $Q = 0$
 - (f) irreversible process, $Q < 0$

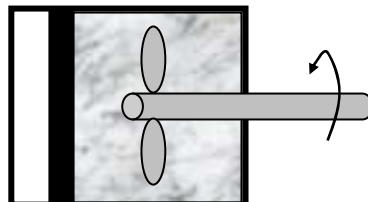
2. A block of lead at temperature 200 K has heat capacity $C = 1000 \text{ J K}^{-1}$, which is independent of temperature in the range 100 – 200 K. It is to be cooled to 100 K in liquid baths, which are large enough that their temperatures do not change. Assume that the only heat transfer which occurs is between the liquid baths and the lead block, and that the lead block changes temperature instantaneously/uniformly (so that there is no entropy production *within* the block). What is the entropy supply for the lead and the liquid bath(s), and the net entropy production, during the following processes: the lead is
- plunged straight into a liquid bath at 100 K
 - first cooled in a bath at 150 K and then in a second bath at 100 K
 - cooled using four baths at temperatures 175 K, 150 K, 125 K and 100 K
 - cooled in an infinite number of temperature baths with a continuous range from 200 K to 100 K

[hint: no work is done; use the lead's heat capacity to evaluate Q]

3. Consider an *insulated* piston-cylinder assembly which initially contains water as a saturated liquid at 100 C (373.15 K), as illustrated below. A paddle wheel acts on the water, which undergoes a process to the corresponding saturated vapour state at the *same* temperature, during which the piston moves freely in the cylinder (no friction). Using the data below, determine
- the net work per unit mass done – which is greater, the work done by the paddle wheel or that done by the expanding water?
 - the specific entropy supply; the specific entropy production – why do you think it is non-zero?

Next, consider the case where the initial and final states are the same as before, but the change is now brought about by the supply of *heat only* (with no paddle wheel). Determine

- the work done per unit mass²
- the heat transfer per unit mass
- the specific entropy supply and the specific entropy production – is this a surprise?



	$u \text{ (kJ / kg)}$	$v \text{ (m}^3 \text{ / kg)}$	$s \text{ (kJ / kg.K)}$	$p \text{ (MPa)}$
Liquid	400	0.001	1.448	0.1014
Gas	2500	1.6	7.510	0.1014

² the initial and final temperatures and pressures are 100 C and 0.1014 MPa – these are the “end-points” for the initial and final *states* – in general, they may not necessarily be constant throughout the process – we do not know (and don’t have to know here) how the temperature and pressure changed *during* the process in parts (a-b); with the paddle wheel, the temperature and pressure are unlikely to be uniform throughout the material. For parts (c-e), it is reasonable to assume that they are constant throughout

4. A certain mass of an ideal gas for which $C_V = 3R/2$, independent of temperature, is taken *reversibly* from $\theta = 100 \text{ K}$, $p = 10^5 \text{ Pa}$ to $\theta = 400 \text{ K}$, $p = 8 \times 10^5 \text{ Pa}$ by two different paths (1) and (2):
- (1) consisting of (a) at constant volume from $\theta = 100 \rightarrow 400 \text{ K}$, (b) isothermally to the final pressure
 - (2) consisting of (a) at constant pressure from $\theta = 100 \rightarrow 400 \text{ K}$, (b) isothermally to the final volume

Calculate the entropy changes and verify that the total entropy change is the same for both paths. Compare this with the heat absorbed or given out for each of paths (1) and (2) – they even turn out to be of opposite sign.

[hint: use the ideal gas law and the fact that for a constant volume process,

$$\delta Q = C_V d\theta ; \text{ also, use Eqn. 4.2.13, the fact that } Q_{\text{rev}} = \int_{S_1}^{S_2} \theta dS , \text{ and the result of Q.8}$$

from section 4.1]