# Topic 7: The Second Law of Thermodynamics and Entropy

## 7.1 Introduction

In section 6.4 we said that no heat engine can possibly be more efficient than a Carnot engine, and in section 1.1 we said that when we place two bodies of different temperature in thermal contact, heat flows from the hotter body to the cooler body. These are, in fact, two statements of the **Second Law of Thermodynamics**:

**The Clausius statement:  
No process can have as its sole result the transfer of heat from a colder to a hotter body.**

In other words, heat does not flow spontaneously from cold to hot.

**The Carnot engine statement:  
No engine working between two given temperatures TH and TC can be more efficient than a Carnot engine.**

There is also a third statement of the Second Law:

**The Kelvin statement:  
No process can have as its sole result the complete conversion of heat into work.**

The Clausius and Kelvin statements of the Second Law are in fact precisely equivalent, though this is not obvious at first glance, and the Carnot statement can be proved from the Clausius statement. Notice that both the Clausius and the Kelvin statements imply an **arrow of time**: if we were to consider a time-reversed version of Clausius’ statement, we would see heat flowing from the hotter body to the cooler, which is perfectly legitimate, and likewise a time-reversed version of the Kelvin statement would involve the complete conversion of work into heat, which is also legitimate.

## 7.2 Equivalence of the Clausius and Kelvin statements of the Second Law

In order to prove that two statements A and B are equivalent, we need to prove that A implies B *and* B implies A. If that is the case, then whenever A is true, B is true, and vice versa, so they are equivalent. For the Clausius and Kelvin statements, we can prove both implications by contradiction.

### Clausius implies Kelvin

TH

TC

QK

QH

QC

W

Suppose that Clausius’ statement is true but Kelvin’s is not. If Kelvin’s state­ment is not true, we can build an engine K that converts heat into work. We connect this to a Carnot engine working in reverse, as shown in figure 7.1.

By the First Law, , and also . Therefore . Therefore the composite engine has the effect of taking heat from the cold reservoir and transferring it to the hot reservoir. But this is in violation of Clausius’ statement, which contradicts our initial assumption. Therefore Clausius’ statement implies Kelvin’s statement.

*Figure 7.1: if Kelvin is false, so is Clausius.*

### Kelvin implies Clausius

We can use the same approach here. Assume that Clausius’ statement is not true, and that we can there­fore build a machine that simply transports heat from a cold reservoir to a hot reservoir. Connect this to a Carnot engine running forwards, which takes heat from a hot reservoir, does work *W*, and rejects heat . If we adjust the Clausius machine so that , then the combined engine takes in heat and converts it completely to work, which violates Kelvin’s statement. Therefore, if Kelvin’s statement is true, Clausius’ statement must also be true.

### Clausius implies Carnot

Assume that Carnot’s statement is not true, and we can therefore build an engine E that has a higher efficiency than a Carnot engine. We connect this super-efficient engine to a Carnot engine running in reverse. Engine E takes in heat , does work *W*, and ejects heat ; the Carnot engine takes in heat and the work done by engine E, and ejects heat . Since , and we have assumed that , it follows that . The First Law tells us that (taking all the *Q*’s to be positive). Therefore , and the net effect of the combined engine is to take heat from the cold reservoir and eject it into the hot reservoir, which violates Clausius’ statement. Therefore, Clausius’ statement of the Second Law implies that engine E cannot exist.

*Figure 7.2: Clausius’ statement implies Carnot’s.*

TH

TC

Q’H

QH

QC

W

Q’C

## 7.3 The Third Law of Thermodynamics

If we could run a Carnot engine with its cold reservoir at 0 K, we could violate Kelvin’s statement, because such an engine would have , and would therefore convert all the input heat into work. This is forbidden by the **Third Law of Thermodynamics**, Nernst’s statement of which is

**It is impossible for any procedure to lead to the isotherm T = 0 in a finite number of steps.**

## 7.4 Entropy

From the Carnot cycle definition of thermodynamic temperature, equation 6.9, we know that   
Accounting properly for the signs, i.e. recognising that , we also have

We can generalise this sum to an integral around a closed loop (imagine lots of little mini Carnot cycles working between temperatures and , all satisfying equation 7.1):   
This holds only if the loop consists entirely of *reversible* processes, which is why we put the label ‘rev’ on the đ*Q*.

It follows from this that the quantity *is an exact differential*, i.e. the value of the integral between two states A and B is independent of the path taken.

A

B

*P*

*V*

To see this, consider states A and B in figure 7.3. The two paths connecting A and B are both reversible. We can integrate from A to B along path 1 and get   
or we can integrate along path 2 and get

2

1

But we can also reverse the direction of path 2, since we have defined it to be reversible, and integrate from B to A, which must give us   
where the minus sign indicates that path 2 is taken in reverse.

*Figure 7.3: two arbitrary paths between states A and B.*

Now, if we integrate from A to B via path 1, and then from B to A via path 2, we have completed a closed reversible cycle, and equation 7.2 tells us that

Therefore, since paths 1 and 2 were arbitrary, we must have for *any* reversible path. Therefore is an exact differential. It follows that the quantity *S* defined by   
is a function of state. We call *S* the **entropy** of the state.

This definition only allows us to calculate *changes* in entropy, : if we try to calculate the absolute value of *S* we have an undetermined integration constant. To calculate absolute values of *S*, we need a microscopic definition of *S* in terms of individual particles. You will meet this definition (and show that it is equivalent to the definition in equation 7.2) when you study statistical mechanics next year.

## 7.5 Entropy and the First Law

We can write equation 7.3 as . If we also assume that we are dealing with an ideal gas, such that , we can write the differential form of the First Law as   
But now a miracle has occurred: *everything* in equation 7.4 is a function of state, and therefore equa­tion 7.4 holds *irrespective* of the path taken. This can be very useful: if you want to calculate for an irreversible process, and you know the start and end states, you can apply equation 7.4 to *any* re­versible path between the start and end states and the result will be the same as for the irreversible process. (This doesn’t mean that the heat supplied and the work done will be the same: đ*Q* and đ*W* are still inexact differentials. But the changes in internal energy, entropy and volume will be the same.)

## 7.6 Entropy in reversible and irreversible processes

So far, we have considered entropy in the context of reversible processes. What about irreversible processes?

Irreversible processes are irreversible because energy is dissipated in a way that cannot be reversed, e.g. friction. This is clearly not work: as we noted in section 1, work is energy transfer associated with ordered motion, and is therefore reversible. Hence, if we suppose that the maximum work that can be extracted from a reversible transition between state A and state B is (i.e. , since here we’ve defined as work done *by* the system), we expect that an irreversible transition between the same two states will extract work .

If we make this transition infinitesimal, such that states A and B are very close together, we can write  
(again, recall that the minus sign here is because the work is done *by*, not *on*, the system). So we have  
This emphasises that the definition of *S* refers to the heat supplied in a *reversible* process. If you have an *irreversible* process, the definition does not apply. This means that if we wish to cal­culate the entropy change associated with an irreversible process, we cannot simply integrate . Fortunately, there is a solution to this, because entropy is a function of state: if we can define a *rever­sible* path with the same initial and final state, we can use this to calculate Δ*S*.

### *Example 7.1*

Suppose that we connect a small system with temperature *TS* to a very large heat reservoir with tem­perature *TR*. The two will reach equilibrium at temperature *TR* (we assume that the heat transfer to or from the small system has negligible effect on the temperature of the reservoir). What is the change in entropy (i) of the small system, (ii) of the large reservoir, (iii) of the Universe? Assume that the volume of the small system does not change, and that the combined system of the small system plus the reservoir is thermally isolated from the rest of the Universe.

### *Answer*

This is an irreversible process, since reversing it would require heat to flow from cold to hot without doing any work, which contravenes the Second Law. However, we can replace it with a reversible transfer of heat at constant temperature for the reservoir, and constant volume for the small system.

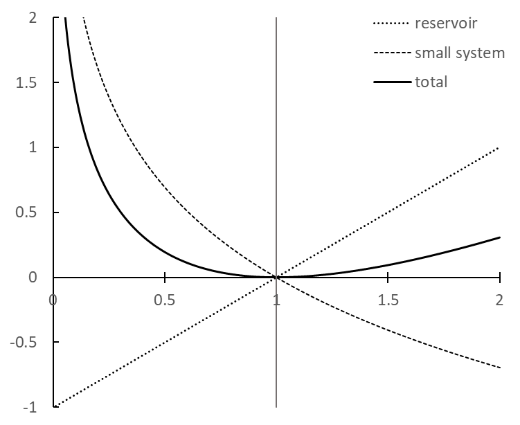
The heat transferred to or from the small system is , where *CV* is the heat capacity of the small system at constant volume. is positive if the small sys­tem was initially cooler than the reservoir (heat is supplied *to* the small system) and negative if the small system was initially warmer (heat is lost *from* the small system). Since the combined system is thermally isolated, and no work is being done, we must have .

As the reservoir is at constant temperature throughout, the entropy change is

For the small system, . We integrate this from *TS* to *TR*:

The total entropy change is

There are various points to note here:

1. Although the temperature of the reservoir does not change, its entropy does.
2. Although the heat flow into or out of the   
   two subsys­tems is the same (apart from   
   the sign), the entropy change is not.
3. is always greater than zero if .

Point 3 is illustrated in figure 7.4. We can also   
deduce it by differentiating equation 7.6.   
If we write , we have   
which is equal to zero when , at which point   
. This must be a   
minimum, because the derivative is positive (curve   
rising) for and negative (curve falling) for   
. Hence for all values of ,   
and is zero only if and there is no heat flow.

*TR* < *TS*

*TR* > *TS*

*Figure 7.4: entropy changes for example 7.1.*

In the above example, the entropy change of the small system is negative when the system cools to equilibrium and positive when it warms, as we would expect since the heat flow is negative when it cools (heat is transferred *from* the small system) and positive when it warms (heat is transferred *to* the small system). However, the *total* change in entropy, taking the surroundings into account, is al­ways positive (except in the case where the two systems were already in equilibrium before being brought into contact). In contrast, if we have a *reversible* process, the entropy change in the sur­roundings will always balance the entropy change in the small system:   
This is necessarily so if the process is quasistatic, since—by definition—we are assuming in a quasi­sta­tic process that the system is essentially in equilibrium with its surroundings, i.e. at the same tempera­ture. So if the system receives heat from its surroundings at temperature *T*, its entropy change is , and the entropy change of the surroundings is .

This leads to yet another statement of the Second Law:

**The entropy of a thermally isolated system cannot decrease.**

Note the key qualifier: not just any system, but a *thermally isolated* system. If the system is not ther­mally isolated, by definition heat can flow into and out of the system, and this will be accompanied by a change in entropy which can be positive *or* negative. This explains why we see many processes in nature, e.g. crystal growth, which appear to be associated with a decrease in entropy: in such cases the entropy of the system may indeed decrease, but it is not a thermally isolated system, and the decrease is compensated by an increase in the entropy of the surroundings, as in example 7.1.

The Universe is the ultimate thermally isolated system, so the entropy statement of the Second Law implies that the entropy of the Universe cannot decrease.

### *Example 7.2*

Calculate the entropy change in the system and its surroundings for each stage of a Carnot cycle.

### *Answer*

A Carnot cycle consists of four stages: (1) isothermal compression at temperature *TC*; (2) adiabatic com­pression increasing the temperature to *TH*; (3) isothermal expansion at temperature *TH*; (4) adiabatic expansion decreasing the temperature back to *TC*.

We can do the adiabatic steps 2 and 4 immediately: by definition, in an adiabatic process no heat is transferred, so .

In step 1, work is done *on* the gas, but the internal energy of the gas does not change (in an isothermal process ), so heat must be expelled by the gas, hence . The entropy change of the system is (we do not need to do an integration because the temperature is con­stant). Conversely, the surroundings (the cold reservoir) *receive* heat , so the entropy change is .

In step 3, work is done *by* the gas, so it must take in heat (). The entropy change of the system is , and the entropy change of the surroundings (the hot reservoir) is But from equation 6.9 we know that , and so we can write these as and .

From this we see that (1) the *total* entropy change of the system is zero, as it must be, since this is a closed cycle and entropy is a function of state; (2) the entropy change of *system plus surroundings* is zero not only for the cycle as a whole but also for each individual step. This is what we would expect for reversible processes.

## 7.7 Entropy as a measure of disorder

Total entropy increases in irreversible processes, but is zero in reversible processes. We saw that what makes a process irreversible is the dissipation of energy—in essence, some of the energy that would, in a reversible system, be released as work (ordered motion) is instead dissipated in some disordered fashion. Also, the entropy of a system increases when heat flows *into* it, and decreases when heat flows *out of* it, and we saw that heat is energy associated with *disordered* (i.e. random) motion. These observations suggest that entropy is in some way associated with disorder. This is indeed true, and you will quantify this when you explore the microscopic definition of entropy next year.

### *Example 7.3*

**This is a sneak preview of next year, and is not examinable.**

How many ways are there of arranging a pack of 52 playing cards?

A new pack of playing cards is arranged in suits, with the cards in each suit arranged in order. How many ways are there of doing this?

Which would you say is “more disordered”, the new pack as described above, or a pack which has been thoroughly shuffled? Can you relate this to your previous answers? Which state—new or shuf­fled—do you think has higher entropy?

### *Answer*

There are 52 possibilities for the first card, 51 for the second, and so on, so in total there are 52! ≈ 8.067×1067 different orderings.

The suits can be ordered in 4! = 24 ways, and the cards could be in ascending or descending order, so there are 48 ways of meeting this description (one assumes that either all the suits would be in ascending order, or they’d all be in descending order).

I think that everyone would agree that the shuffled pack is more disordered. There are a couple of ways we can think about this:

1. We could describe the arrangement of our new pack very easily, just by specifying the order of the suits and whether the cards are in ascending order or descending order: if I say “with the pack oriented such that the faces of the cards are visible, the cards in each suit are ordered from Ace to King, and the suits are ordered Spades, Hearts, Clubs, Diamonds”, then you can immediately reproduce the exact same ordering with a different pack of cards. On the other hand, to allow you to reproduce the order of the shuffled pack, I’d have to tell you the identity of 51 of the 52 cards (the 52nd is the only one left!)—that’s a lot more information than is needed to describe the new pack.
2. The number of arrangements of the cards that are “equivalent” to our new pack is quite small (we might grant more than 48, in the sense that there are other ways of arranging the cards that would also look “ordered”, e.g. all four aces in the order ♠♥♣♦, followed by all four 2’s in the same order, and so on to four Kings, but that would still be a very tiny fraction of 8.067×1067), whereas the number of arrangements that are “equivalent” to the shuffled pack is very large—one shuffled pack looks very much like another, even though the detailed order of the cards is not the same[[1]](#footnote-1).

So we could define a “highly ordered” arrangement as one which requires only a small amount of in­formation to specify it, or as one which has only a small number of equivalent states.

The act of shuffling the cards is effectively irreversible: taking the shuffled pack and attempting to re­verse the moves you made when shuffling them is not going to result in a pack sorted back into suit and value order. So we conclude that the shuffled pack has higher entropy.

In fact, our explanations 1 and 2 both correspond (when made more mathematically rigorous) to def­i­ni­tions of entropy. Explanation 2, in terms of the number of equivalent **microstates**, is the one you will study next year. Explanation 1, in terms of the amount of information needed to specify the state, is the basis of **information entropy** or **Shannon entropy**, which is a key concept in information theory. The mathematical definitions of thermodynamic entropy and Shannon entropy are essentially identi­cal.

1. This is why people are inclined to regard a sequence of Lottery numbers such as 123456 as being somehow less probable than 2 5 13 14 22 38, even though each number has an equal chance of being drawn and so each of these sequences is just as (im)probable as any other. The chance of drawing a sequence that is *as well ordered* as 123456 is small, because such sequences represent only a tiny fraction of all possible 6-number sequences. [↑](#footnote-ref-1)