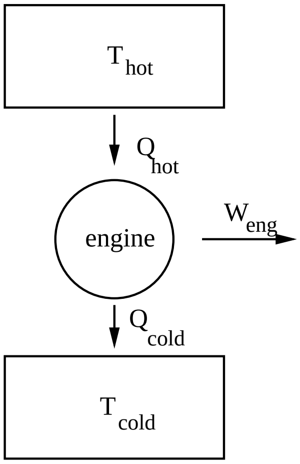
Lecture on Chapter 18: Heat Engines, Entropy, and the Second Law of Thermodynamics

The first law of thermodynamics basically states that energy is conserved. But that doesn't mean that all processes that conserve energy can happen. For example, when a hot object is put in contact with a cold object, heat does not flow from the cold object to the hot object even though energy is conserved. Or, a pond does not suddenly freeze on a hot summer day by giving up heat to its environment, even though this does not violate energy conservation. If these things did occur, they would violate the second law of thermodynamics. It tells us that processes happen in one direction and not the other. These are called irreversible processes. In this lecture and the next one, we will talk about the second law of thermodynamics, which is probably the most famous law of thermodynamics, as well as the closely related topics of heat engines and entropy.

Heat Engines

A heat engine converts heat into useful work. For example in a steam engine, heat can be used to convert water into steam that in turn turns the wheel to power a locomotive or a steam ship or an electric generator. The advent of the industrial revolution in the 1700's led people to study the basic principles of heat engines and establish the laws of thermodynamics.

Heat engines go through a cycle, i.e., they do the same thing over and over again. In each cycle, (1) heat is transferred from a high temperature reservoir, (2) work is done by the engine, and (3) heat is expelled to a lower temperature reservoir. For example in a steam engine, heat is absorbed by water which becomes steam, the steam does work by driving a turbine, then the steam is condensed by giving up its heat to cooling water.



Real Engine $W_{eng} = |Q_{hot}| - |Q_{cold}|$

Let's examine this using the first law of thermodynamics. Let the net heat absorbed by the engine be $Q_{net} = |Q_{hot}| - |Q_{cold}|$ where Q_{hot} is the amount of heat absorbed by the engine from the hot reservoir and Q_{cold} the amount of heat released to the cold reservoir. The engine does work W_{eng} which is negative because negative work is done *on* the engine and this reduces the internal energy of the engine. So $W = -W_{eng}$. Because the engine goes through a cycle, the initial and final energies are the same and $\Delta E_{int} = 0$. So the first law becomes

$$\Delta E_{int} = Q + W = 0 \quad \Longrightarrow \quad Q_{net} = -W = W_{eng} \tag{1}$$

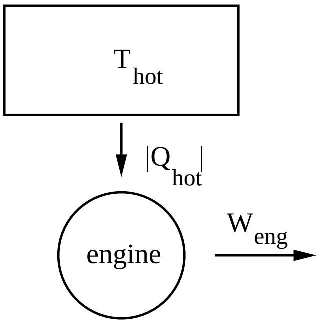
So the work done by the engine equals the net heat transferred to the engine. In other words

$$W_{eng} = |Q_{hot}| - |Q_{cold}| \tag{2}$$

The thermal efficiency e of a heat engine is defined as the ratio of the net work done by the engine to Q_{hot}, the heat absorbed from the high temperature reservoir during one cycle:

$$e = \frac{W_{eng}}{|Q_{hot}|} = \frac{|Q_{hot}| - |Q_{cold}|}{|Q_{hot}|} = 1 - \frac{|Q_{cold}|}{Q_{hot}|} \tag{3}$$

Think of efficiency as the ratio of what you gain (work=W_{eng}) to what you give ($|Q_{hot}|$). Notice that the efficiency $e \leq 1$. A perfect engine has 100% efficiency, i.e., $e = 1$. In a perfect engine all the heat absorbed from the high temperature reservoir is converted into work and no heat is released to the cold reservoir, i.e., $W_{eng} = Q_{hot}$.



Perfect Engine $W_{eng} = |Q_{hot}|$

Kelvin's formulation of the second law of thermodynamics states that **it is impossible to construct a perfect heat engine.**

Reversible and Irreversible Processes

Have you ever let the cat of the bag and told someone a secret? There's no way you can take back what you said. You can't erase their knowledge of the secret. In some crude sense, letting the cat out of the bag is an irreversible process. In terms of physics, a **reversible** process is one for which the system is in equilibrium every step of the way. The system can be returned to its initial state by retracing its steps along this reversible path. An **irreversible** process is one that doesn't satisfy these requirements. Most natural processes are irreversible. For example, if you let air out of a balloon, it never spontaneously returns to fill up the balloon. Or if you pour milk into coffee, it gets mixed with the coffee. The milk never separates out from the coffee as a little white pool.

Reversible processes tend to proceed very slowly since you have to maintain equilibrium (or quasi-equilibrium) at every step along the way. So if you compress a gas reversibly with a piston, you can imagine doing it by dropping grains of sand one by one onto the piston.

Carnot Engine

The most efficient engine you can have is a Carnot engine. The Carnot cycle is a reversible cycle run between a hot and a cold reservoir. To illustrate a Carnot cycle, let's assume that we have an ideal gas contained in a cylinder with a movable piston. The Carnot engine then goes through a cycle consisting of 4 steps, all performed reversibly.

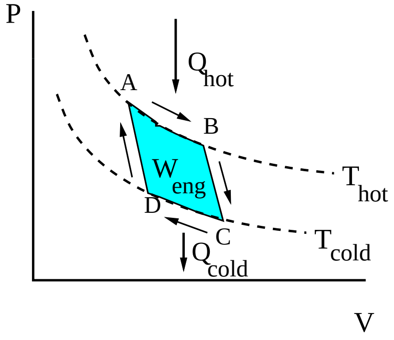
- The process A $\longrightarrow$ B is an isothermal expansion at temperature T_{hot} in which the gas is placed in thermal contact with an energy reservoir at temperature T_{hot}. The gas absorbs energy Q_{hot} from the reservoir and expands. In expanding, it does work W_{AB} by raising the piston.

- In the process B $\longrightarrow$ C, the base of the cylinder thermally insulated and the gas is allowed to expand adiabatically ($Q = 0$). No heat is transferred. In expanding the gas does work W_{BC} in raising the piston. The temperature of the gas falls from T_{hot} to T_{cold}.

- In the isothermal process C $\longrightarrow$ D, the gas is placed in thermal contact with the reservoir at temperature T_{cold} and is isothermally compressed. It transfer heat Q_{cold} to the reservoir and the work done on the gas is W_{CD}.

- In the final adiabatic process D $\longrightarrow$ A, the base of the cylinder is thermally insulated to prevent heat transfer and the gas is compressed adiabatically. The temperature of the gas increases from T_{cold} to T_{hot}, and the work done on the gas is W_{DA}. By the end of this process, we are back to where we started, namely state A.

If we plot the Carnot cycle on a PV diagram, it looks like this:



The work W_{eng} done by the engine corresponds to the area enclosed by the curve.

$$W_{eng} = \int_{A\rightarrow B\rightarrow C\rightarrow D\rightarrow A} pdV \tag{4}$$

By energy conservation,

$$W_{eng} = |Q_{hot}| - |Q_{cold}| \tag{5}$$

Since we start at state A and we end at state A, there is no net change in the internal energy $\Delta E_{int} = 0$.

It turns out that for a Carnot cycle

$$\frac{|Q_{cold}|}{|Q_{hot}|} = \frac{T_{cold}}{T_{hot}} \tag{6}$$

You can view this as way of defining absolute temperature, i.e., temperature measured in Kelvin. We explicitly prove this relation for an ideal gas in the appendix. We can use eq. (6) to compute the efficiency of the engine:

$$e = 1 - \frac{|Q_{cold}|}{|Q_{hot}|} = 1 - \frac{T_{cold}}{T_{hot}} \tag{7}$$

From this equation we see that all Carnot engines operating between the same 2 temperatures will have the same efficiency, independent of the details of the engines. Of course, you wouldn't want to buy a Carnot engine because it runs very, very slowly. In order to make sure that it's always in equilibrium, everything happens very slowly. For example, when we compress the gas, we do so by dropping grains of sand on the piston one grain at a time.

Example: Quiz 18.2 Three engines operate between reservoirs separated in temperature by 300 K. The reservoir temperatures are as follows:

Engine A: $T_{hot} = 1000$ K, $T_{cold} = 700$ K

Engine B: $T_{hot} = 800$ K, $T_{cold} = 500$ K

Engine C: $T_{hot} = 600$ K, $T_{cold} = 300$ K

Rank the engines in order of theoretically possible efficiency, from highest to lowest.

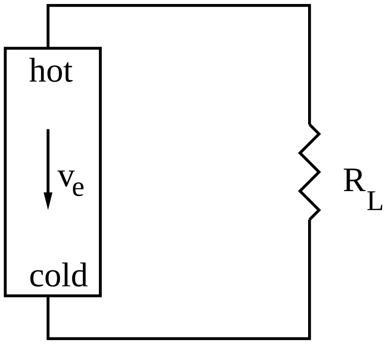
Assume the engines are Carnot engines to get the best theoretically possible efficiency. Take the ratios T_{cold}/T_{hot}. The smallest ratio corresponds to the most efficient engine because the efficiency $e = 1 - T_{cold}/T_{hot}$. So

Engine A: $T_{cold}/T_{hot} = 0.7$, $e = 0.3$, least efficient.

Engine B: $T_{cold}/T_{hot} = 0.625$, $e = 0.375$

Engine C: $T_{cold}/T_{hot} = 0.5$, $e = 0.5$, most efficient

We are used to gasoline powered engines in our car, steam engines, nuclear powered generators, etc. One type of engine you may not be aware of is a solid state engine with no moving parts. If you take a bar of a metal or a semiconductor, heat one end and cool the other, you can get electrons to flow from the hot end to the cold end and these electrons do work.

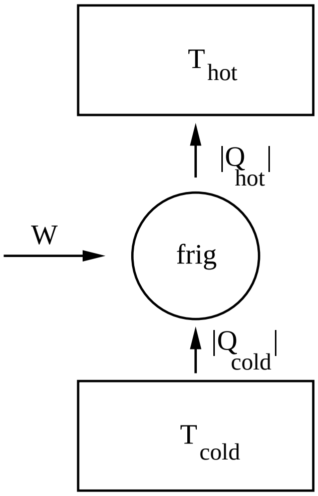


Solid state engines are used in deep space probes where moving parts would wear out after a few years. The heat source can be a radioactive substance like plutonium.

Refrigerators

Heat flows naturally from a hot reservoir to a cold reservoir. If we want to reverse the direction of flow, we use a refrigerator. An air conditioner is an example of a refrigerator. We want to remove hot air from inside the house and dump it outside the house. The outside is hotter than the inside.

A refrigerator is just a heat engine run in reverse.



Real Refrigerator $|Q_{hot}| = |Q_{cold}| + W$

Energy $|Q_{cold}|$ is absorbed from the cold reservoir and work W is done in dumping heat $|Q_{hot}|$ into the high temperature reservoir. By energy conservation,

$$|Q_{hot}| = |Q_{cold}| + W \tag{8}$$

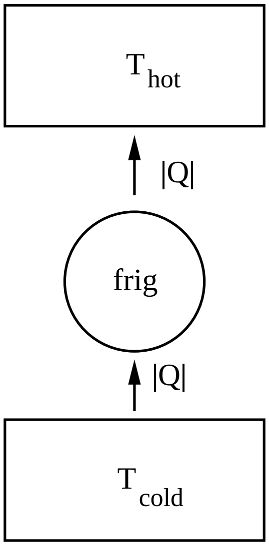
The purpose of a refrigerator is to cool something down. The operation of a heat pump is the same as that of a refrigerator, but the goal is to heat up something by dumping the heat $|Q_{hot}|$ into it. So if it is cold outside, and you want to heat your house with a heat pump, then the heat pump pumps heat from the outside (cold reservoir) into the inside of the house (hot reservoir).

Rather than efficiency, we talk about the coefficient of performance (COP) of refrigerators and heat pumps. The coefficient of performance for a refrigerator is the ratio of the heat removed from the cold reservoir to the work done:

$$\mathrm{COP(refrigerator)} = \frac{|Q_{cold}|}{W} \tag{9}$$

The bigger the COP, the better the refrigerator. The COP is the figure of merit.

A perfect refrigerator could do the heat transfer without doing any work ($W = 0$). This would correspond to a COP=∞. But it is impossible for heat to flow from a cold reservoir to a hot reservoir without doing any work. This leads us to the Clausius formulation of the second law of thermodynamics which states that **it is impossible to make a perfect refrigerator**.



Perfect Refrigerator

The best refrigerator we can make is one using the Carnot cycle. Just take the Carnot engine and run it in reverse to get a refrigerator. For a Carnot refrigerator the coefficient of performance is

$$\mathrm{COP(Carnot\ refrigerator)} = \frac{|Q_{cold}|}{|Q_{hot}| - |Q_{cold}|} = \frac{|T_{cold}|}{|T_{hot}| - |T_{cold}|} \tag{10}$$

Here we used eq. (6) which tells us that the heat ratio equals the temperature ratio $|Q_{hot}|/|Q_{cold}| = T_{hot}/T_{cold}$.

For a heat pump we care about the heat Q_{hot} dumped into the hot reservoir, so the coefficient of performance for a heat pump is the ratio of $|Q_{hot}|$ to the work W done:

$$\mathrm{COP(heat\ pump)} = \frac{|Q_{hot}|}{W} \tag{11}$$

The most efficient heat pump is one that uses a Carnot cycle. In that case

$$\text{COP(Carnot heat pump)} = \frac{T_{hot}}{T_{hot} - T_{cold}} \tag{12}$$

Example: If a refrigerator is be maintained at -3^o C, and the outside air is at 27^o C, what minimum amount of work has to be done to remove a joule of heat from inside the refrigerator?

The minimum amount of work will be done by the most efficient refrigerator. That is a Carnot refrigerator. For a Carnot refrigerator, $|Q_{hot}|/|Q_{cold}| = T_{hot}/T_{cold}$ or $|Q_{hot}| = (T_{hot}/T_{cold})|Q_{cold}|$ and we know that $|Q_{cold}| = 1$ Joule. The work done by the refrigerator is

$$W_{frig} = |Q_{hot}| - |Q_{cold}| = \frac{T_{hot}}{T_{cold}}|Q_{cold}| - |Q_{cold}| = \left(\frac{T_{hot}}{T_{cold}} - 1\right)|Q_{cold}|. \tag{13}$$

Converting the temperatures to Kelvin ($T_{cold} = -3^o$ C $= 270$ K and $T_{hot} = 27^o$ C $= 300$ K), we find $W_{frig} = 0.11$ J.

Entropy

The key concept behind the second law of thermodynamics is entropy. The symbol S is usually used to denote entropy. You've probably heard that entropy is a measure of disorder and that's correct. But we'd like to define entropy more precisely. Like energy and temperature, entropy is a state variable, i.e., it just depends on the state of the system, and not on its history. There is a macroscopic and a microscopic definition of entropy. They turn out to be equivalent, though it's not obvious.

First let's go over the macroscopic definition. If a heat reservoir at temperature T absorbs heat Q, the entropy change of the reservoir is

$$\Delta S = \frac{Q}{T} \tag{14}$$

We can write this in differential form. If a tiny bit of heat dQ is added to a system at temperature T, the heat won't really change the temperature and the entropy change dS of the system is

$$dS = \frac{dQ}{T} \tag{15}$$

This equation holds when the initial and final states are in equilibrium and the process of adding heat dQ is a reversible process. It turns out that this is part of the statement of the second law of thermodynamics. You can also write this as

$$dQ = TdS \tag{16}$$

This is a good equation to remember. If the system goes from one state to another along a reversible path, staying in equilibrium at each tiny step along the way, then the change in entropy from the initial to the final state is given by the integral

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ}{T} \tag{17}$$

We put the temperature inside the integral because the temperature may change along this path.

For a Carnot cycle the entropy change is zero: $\Delta S = 0$. This is certainly true for the engine because it returns to its initial state after 1 cycle, and entropy is solely a function of the state. During the 2 adiabatic parts of the Carnot cycle, $Q = 0$, so $\Delta S = 0$ during the adiabatic processes. (A process where $\Delta S = 0$ is called an **isentropic** process.) So the only entropy change occurs in the heat reservoirs during the isothermal processes when the temperature is fixed.

$$\Delta S = \frac{Q_{hot}}{T_{hot}} + \frac{Q_{cold}}{T_{cold}} \tag{18}$$

The first term is the entropy decrease of the high temperature reservoir. $Q_{hot} < 0$ because the heat flows out of the high temperature reservoir. The second term is the entropy change of the low temperature reservoir. Since heat is added to the low temperature reservoir, $Q_{cold} > 0$ and the entropy of the low temperature reservoir increases.

Now recall from eq. (6) that

$$\frac{|Q_{cold}|}{|Q_{hot}|} = \frac{T_{cold}}{T_{hot}} \tag{19}$$

or

$$\frac{Q_{cold}}{T_{cold}} = -\frac{Q_{hot}}{T_{hot}} \tag{20}$$

We've removed the absolute value signs. The minus sign is because Q_{hot} leaves the high temperature reservoir and according to our sign convention, that means that $Q_{hot} < 0$ and hence that $-Q_{hot} > 0$. So both sides of the equation are positive. This equation tells us that the two terms in eq. (18) cancel out and that $\Delta S = 0$ for a Carnot cycle. In general for any reversible cycle

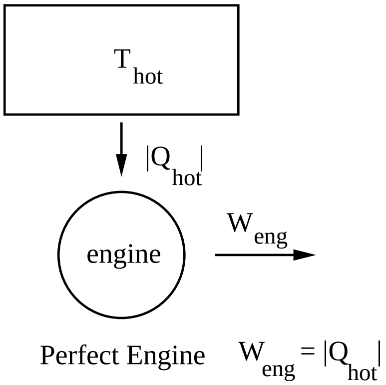
$$\Delta S = \oint \frac{dQ}{T} = 0 \tag{21}$$

where the circle on the integral sign means that the integration is over a closed path or cycle.

Of course the Carnot engine is an ideal engine (though not perfect). Engines we meet in the real world are not as efficient. In those engines the change in entropy is greater than zero. One way of stating the second law of thermodynamics is to say that in an isolated system, i.e., one in which no heat or work can enter or leave, the entropy never decreases. It always increases or stays the same. Mathematically we write

$$\Delta S \geq 0 \qquad \text{for an isolated system} \tag{22}$$

Let's consider a perfect engine again.

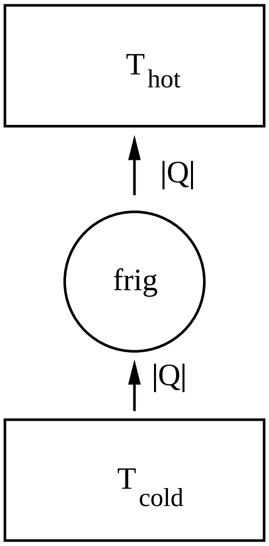


Heat Q leaves the reservoir which is at temperature T. So $Q < 0$. So the entropy change of the temperature reservoir is negative. That implies that the total entropy change is

$$\Delta S = \frac{Q}{T} < 0 \tag{23}$$

which violates the second law of thermodynamics. So a perfect engine is impossible.

Similarly for a perfect refrigerator,



Perfect Refrigerator

the entropy change is

$$\Delta S = \frac{|Q|}{T_{hot}} - \frac{|Q|}{T_{cold}} \tag{24}$$

The minus sign is because heat leaves the cold reservoir. So the entropy change of the cold reservoir is negative. Since $T_{cold} < T_{hot}$, $\Delta S < 0$ which violates the second law of thermodynamics. So a perfect refrigerator is impossible.

$\Delta S = Q/T$ is the macroscopic definition of entropy. Actually we've only been considering the entropy change. Now let's consider the microscopic definition. With the microscopic definition we can define the absolute value of the entropy, not just the change in entropy.

Let's begin by defining microstates versus macrostates of a system. A macrostate is specified by macroscopic variables such as temperature, pressure, energy, number of particles, etc. To specify a microstate, we need to specify the positions and velocities of all the particles. So if we have an ideal gas, we can specify its macrostate by its temperature, pressure (or volume), number of particles, etc. There are a lot of microstates which have the same temperature, pressure, and particle number. And since the particles are moving around, the system is changing from one microstate to another.

Your book gives the example of dice. The macrostate corresponds to the sum of the 2 dice. The microstate corresponds to the particular combination of die. Any particular combination is as likely as any other. So the microstates are equally likely. But some macrostates are more likely than others. The macrostate of 7 has 6 combinations of the dice while the macrostate of 2 has only 1 combination. So throwing a 7 is much more probable than throwing a 2.

Similarly, all the microstates of a physical system are equally likely when the system is in equilibrium. But if a given macrostate A has more microstates associated with it than some other macrostate B, then the system is more likely to be in macrostate A than in macrostate B. The more microstates a macrostate has associated with it, the more disordered we consider the macrostate to be. Suppose that a given macrostate has only one microstate associated with it. That macrostate would be very ordered. Suppose that each object in your bedroom could only be in one place; each object has its place and there is no other place you can put it. Then your room would be very ordered. On the other hand, suppose your stuff could be anywhere. Then there are a lot of arrangements that are possible. If we look at any single arrangement chosen at random, then your room will probably look messy and disordered. So the more microstates a macrostate has, the more likely it is that the system will be in that macrostate and the more disordered the system will tend to be. Disordered macrostates are more likely than ordered macrostates.

Notice that we are talking in terms of probabilities. In physics 3A when you studied Newtonian mechanics, you were usually talking about a single object and you could use Newton's equations of motion to determine its motion and trajectory. But the world has more than just one object. In fact most things have something like Avogadro's number of atoms and molecules. When we talk about an ideal gas, we think of it as having of order 6×10^{23} particles. It would be hopeless to try to calculate the trajectory of each and every particle. And, besides, that's not really what we want. We want to know macroscopic quantities like temperature and pressure. We want to know what the macrostate is, not the microstate. So rather than talk in terms deterministic equations of motion, we talk in terms of probabilities.

So each macrostate, which is specified by certain values of the macroscopic variables like temperature, pressure, etc., has a number of microstates that have these values of the macroscopic variables. Let Ω be the number of microstates for a given macrostate. (Your book uses W instead of Ω, but we already use W for work.) Ω is a number of order

Avogadro's number. To make the number more managable, let's take the logarithm. The entropy S is proportional to the logarithm of Ω. The proportionality constant is k_B, Boltzmann's constant.

$$S = k_B \ln \Omega \tag{25}$$

Notice that the entropy is a macroscopic variable that is a property of a given macrostate. It doesn't depend on how the system got to that macrostate. The bigger Ω is, the bigger the number of microstates, the more disordered the macrostate is, and the more likely the system is to be in that macrostate. In some sense eq. (25) is a microscopic definition of entropy because it depends on the number of microstates.

So we have a microscopic and a macroscopic definition of entropy. They look very different but they are in fact equivalent. We can illustrate this using an ideal gas (what else?). Suppose an ideal gas goes from an initial macrostate with volume V_i to a final macrostate with volume V_f. The temperature stays the same: $T_i = T_f$. What is the change of entropy ΔS?

The entropy change will depend only on the initial and final macrostates of the system, not on the path between them. So we can choose any path that's convenient. First let's use the macroscopic definition, eq. (14). We will choose an isothermal path in which the system stays at temperature T. In the notes on Chapter 17, we showed that for an isothermal process, $\Delta T = 0$, so $\Delta E_{int} = 0$, so $Q = -W$. We calculated the work W and hence the heat Q with the help of the ideal gas law:

$$Q = -W = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right) \tag{26}$$

Now from eq. (14), the entropy change is

$$\Delta S = \frac{Q}{T} = nR \ln\left(\frac{V_f}{V_i}\right) \tag{27}$$

Now let's see what we get with the microscopic definition of entropy. In this case it's easier to choose a different path. Let's choose the free expansion process. So initially the gas is confined to a volume V_i that is separated from the rest of the container by a partition. The volume of the entire container is V_f. The container has perfectly thermally insulating walls so no heat enters or leaves the system. When we remove the partition, the gas expands to fill the entire box and its final volume is V_f. No work is done, so $W = 0$. Since $Q = 0$ and $W = 0$, $\Delta E_{int} = 0$ and hence $\Delta T = 0$. So $T_i = T_f$ as stipulated in the problem. In order to use the microscopic definition of entropy in eq. (25), we need to count microstates. To do this, let's assume that a gas molecule takes up a tiny volume V_m. When the gas is initially confined to the volume V_i, there are (V_i/V_m) places to put a molecule. Suppose we have 2 molecules. Then there are $(V_i/V_m)^2$ ways to arrange the 2 molecules. (The molecules in an ideal gas do not interact, so they can sit on top of each other. So there is no excluded volume.) Extrapolating, we see that there are $(V_i/V_m)^N$ ways to arrange N molecules. $(V_i/V_m)^N$ is the number of microstates. Similarly in the final state there are $(V_f/V_m)^N$ arrangements of N molecules. So using eq. (25), we find that the entropy in the initial state is

$$S_i = k_B \ln \Omega_i = k_B \ln \left[\left(\frac{V_i}{V_m} \right)^N \right] = N k_B \ln \left(\frac{V_i}{V_m} \right) \tag{28}$$

Similarly for the final state

$$S_f = k_B \ln \Omega_f = k_B \ln \left[\left(\frac{V_f}{V_m} \right)^N \right] = N k_B \ln \left(\frac{V_f}{V_m} \right) \tag{29}$$

So the entropy change between the initial and final states is

$$\Delta S = S_f - S_i = N k_B \left[\ln \left(\frac{V_f}{V_m} \right) - \ln \left(\frac{V_i}{V_m} \right) \right] = N k_B \ln \left(\frac{V_f}{V_i} \right) = nR \ln \left(\frac{V_f}{V_i} \right) \tag{30}$$

where we used $N k_B = n N_A k_B = nR$ and n is the number of moles of the ideal gas. We see that eqs. (27) and (30) agree which means that the microscopic and macroscopic definitions of the entropy give the same answer.

Notice that even though $Q = 0$ for the free expansion process, $\Delta S \neq 0$. This is because $\Delta S = Q/T$ only holds for a reversible process and free expansion is not a reversible process. If I start with a box that has one side with gas and the other side empty, then I take out the partition, gas fills the whole box. If I put the partition back, gas does not go to one side of the box, leaving the other side empty. So free expansion is not a reversible process.

Let me summarize the second law of thermodynamics in terms of entropy: An equilibrium macrostate of a system can be characterized by a quantity S (called "entropy") which has the properties that

1. In any process in which a thermally *isolated* system goes from one macrostate to another, the entropy tends to increase, i.e.,

$$\Delta S \geq 0 \tag{31}$$

2. If the system is not isolated and undergoes a reversible infinitesimal process in which it absorbs heat dQ, then

$$dS = \frac{dQ}{T} \tag{32}$$

where T is a quantity characteristic of the macrostate of the system. T is called the "absolute temperature" of the system.

Example: Problem 18.22. An airtight freezer holds 2.50 mol of air at 25.0^o C and 1.00 atm. The air is then cooled to -18^o C. (a) What is the change in entropy of the air if the volume is held constant? (b) What would be the change if the pressure were maintained at 1 atm during the cooling?

a) We want to find ΔS. So start with $\Delta S = \int dQ/T$. T changes, so we need to keep it inside the integral. We need dQ in terms of T. Notice that the volume = constant which means that W=0. So $\Delta E_{int} = Q + W = Q$. So $dQ = dE_{int}$. Now recall that for an ideal gas that undergoes a temperature change, $\Delta E_{int} = nC_V \Delta T$. This is true even is the volume changes, though it's fixed in this case. Recall that E_{int} just depends on the state of the system, not on how the system got to that state. For an ideal gas, all that matters is the temperature of the system. So I can choose any path I want as long as the initial and final states have the correct initial and final temperatures. So I choose a fixed volume path and get $\Delta E_{int} = nC_V \Delta T$. If the temperature just changes a little, then $dE_{int} = nC_V dT$. So $dQ = dE_{int} = nC_V dT$ and we can write

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{dE_{int}}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T} = nC_V \ln\left(\frac{T_f}{T_i}\right) \tag{33}$$

Air consists of diatomic oxygen and nitrogen. Looking at table 17.3, C_V is very close to $5R/2$, so we will use $C_V = 5/R/2$. $T_i = 25.0^o$ C = 298 K and $T_f = 255$ K. Plugging in numbers, we get $\Delta S = -8.10$ J/K.

(b) We want ΔS at constant pressure. Again we use $\Delta S = \int dQ/T$. We can express dQ in terms of known variables using the first law of thermodynamics. For any infinitesimal step in a process on an ideal gas,

$$\begin{aligned} dE_{int} &= dQ + dW \\ dQ &= dE_{int} - dW = nC_V dT + pdV \\ dS &= \frac{dQ}{T} = nC_V\frac{dT}{T} + \frac{p}{T}dV = nC_V\frac{dT}{T} + nR\frac{dV}{V} \end{aligned} \tag{34}$$

where we used the ideal gas law in the last step. So

$$\begin{aligned} \Delta S &= \int_i^f \left(nC_V\frac{dT}{T} + nR\frac{dV}{V}\right) \\ &= nC_V \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right) \end{aligned} \tag{35}$$

Since the pressure is constant, the ideal gas law tells us that $V_f/V_i = T_f/T_i$. So

$$\begin{aligned} \Delta S &= nC_V \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{T_f}{T_i}\right) \\ &= n(C_V + R)\ln\left(\frac{T_f}{T_i}\right) \\ &= n\left(\frac{5}{2}R + R\right)\ln\left(\frac{T_f}{T_i}\right) \\ &= \frac{7}{2}nR\ln\left(\frac{T_f}{T_i}\right) \end{aligned} \tag{36}$$

Plugging in numbers gives $\Delta S = -11.3$ J/K.

Example: Problem 18.27. The temperature at the surface of the Sun is approximately 5700 K, and the temperature at the surface of the Earth is approximately 290 K. What entropy change occurs when 1000 J of energy is transferred by radiation from the Sun to the Earth?

1000 J of energy is such a small amount of energy that the temperature of the Sun and Earth don't change. We use $\Delta S = Q/T$. The Sun loses heat, so $Q_{sun} < 0$, which means that its entropy decreases. $\Delta S_{Sun} = Q_{Sun}/T_{Sun} = -$ 1000 J/5700 K. The Earth gains heat, so $Q_{Earth} > 0$, which means that the Earth's entropy increases. $\Delta S_{Earth} = Q_{Earth}/T_{Earth}$ = 1000 J/290 K. The net change in entropy is the sum of the changes (which winds up being a difference since the Sun loses entropy and the Earth gains entrtopy):

$$\Delta S = \Delta S_{Sun} + \Delta S_{Earth} = \frac{Q_{Sun}}{T_{Sun}} + \frac{Q_{Earth}}{T_{Earth}} = \frac{-1000 \text{ J}}{5700 \text{ K}} + \frac{1000 \text{ J}}{290 \text{ K}} = 3.27 \;\; \text{J/K} \tag{37}$$

Example: Problem 18.28. A 1.00 kg iron horseshoe is taken from a forge at 900^o C and dropped into 4.00 kg of water at 10.0^o C. Assuming that no energy is lost by heat to the surroundings, determine the total entropy change of the horseshoe–water system.

We use

$$\Delta S = \Delta S_{water} + \Delta S_{iron} = \int \frac{dQ_{water}}{T} + \int \frac{dQ_{iron}}{T} \tag{38}$$

We leave the temperature under the integral sign because the temperature changes as the iron cools and the water heats up. We can express dQ as follows. Recall that $Q = mC\Delta T$. So $dQ_{water} = m_{water}C_{water}dT$ and $dQ_{iron} = m_{iron}C_{iron}dT$.

$$\begin{aligned}
\Delta S &= \Delta S_{water} + \Delta S_{iron} \\
&= \int \frac{dQ_{water}}{T} + \int \frac{dQ_{iron}}{T} \\
&= \int_{T_i,water}^{T_f} \frac{m_{water}C_{water}dT}{T} + \int_{T_i,iron}^{T_f} \frac{m_{iron}C_{iron}dT}{T} \\
&= m_{water}C_{water} \ln\left(\frac{T_f}{T_{i,water}}\right) + m_{iron}C_{iron} \ln\left(\frac{T_f}{T_{i,iron}}\right) \qquad (39)
\end{aligned}$$

where T_f is the final temperature. Both the iron and the water reach the same final temperature. To calculate the final temperature, we use $Q_{cold} = -Q_{hot}$. This leads to

$$\begin{aligned}
m_{water}C_{water}\Delta T_{water} &= -m_{iron}C_{iron}\Delta T_{iron} \\
m_{water}C_{water}(T_f - 10.0^o \text{ C}) &= -m_{iron}C_{iron}(T_f - 900^o \text{ C}) \qquad (40)
\end{aligned}$$

Using C_{water} = 4186 J/kg$-^oC$ and C_{iron} = 448 J/kg$-^oC$, we find T_f = 33.2^o C = 306.2 K. Plugging this into eq. (39) yields ΔS = 718 J/K.

Note that since the volume of the water and iron don't change much in this process, there isn't much difference between C_V and C_p. We just call the specific heat C.

Appendix

In this appendix we will show that for a Carnot engine which uses an ideal gas,

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}} \tag{41}$$

Along the isothermal path A ⟶ B, the temperature, and hence the internal energy of an ideal gas, remains constant. According to the first law of thermodynamics, the heat Q_{hot} absorbed by the gas in its expansion must be equal to the work $-W_{hot}$ done in this expansion. We showed in the lectures on chapter 17 that

$$Q_{hot} = -W_{hot} = nRT_{hot} \ln\left(\frac{V_B}{V_A}\right) \tag{42}$$

This also follows from eq. (26). Similarly, in the isothermal compression along the path CD, we have

$$Q_{cold} = -W_{cold} = nRT_{cold} \ln\left(\frac{V_D}{V_C}\right) = -nRT_{cold} \ln\left(\frac{V_C}{V_D}\right) \tag{43}$$

$Q_{cold} < 0$ because the gas gives up heat along the path C ⟶ D. The signs get confusing so let's use absolute values. The ratio

$$\frac{|Q_{hot}|}{|Q_{cold}|} = \frac{T_{hot} \ln\left(\frac{V_B}{V_A}\right)}{T_{cold} \ln\left(\frac{V_C}{V_D}\right)} \tag{44}$$

Now we want to show that the ratio of the heats equals the ratio of the temperatures. So we proceed as follows. From the ideal gas law we have for the isothermal processes

$$\begin{aligned} p_A V_A &= p_B V_B = nRT_{hot} \\ p_C V_C &= p_D V_D = nRT_{cold} \end{aligned} \tag{45}$$

For the adiabatic processes along paths B ⟶ C and D ⟶ A:

$$\begin{aligned} p_B V_B^\gamma &= p_C V_C^\gamma \\ p_D V_D^\gamma &= p_A V_A^\gamma \end{aligned} \tag{46}$$

Multiplying these 4 equations together and cancelling the factor $p_A p_B p_C p_D$ on both sides, we obtain

$$V_A V_B^\gamma V_C V_D^\gamma = V_B V_C^\gamma V_D V_A^\gamma \tag{47}$$

We can simplify this a little by grouping factors together:

$$(V_B V_D)^{\gamma-1} = (V_C V_A)^{\gamma-1} \tag{48}$$

or

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \tag{49}$$

Now plug this into eq. (44) to obtain the desired result:

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}} \tag{50}$$