ATTACHMENT B — THERMODYNAMICS

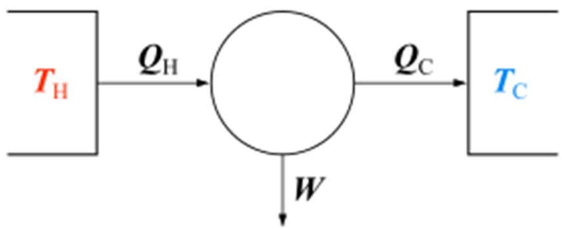
Homer Simpson with daughter Lisa's Perpetual Motion Machine. "In this house we obey the laws of thermodynamics!"

Many of the issues discussed in this book can be understood in terms of the laws of thermodynamics. For example,

- Energy neither be created nor destroyed (except through the use of nuclear reactions). Hence any proposal to "save energy" cannot work. Nor can energy be "renewed". We can transform energy from one form to another. For example, we can burn gasoline in an automobile engine to create forward motion. But the total amount of energy involved remains the same.
- Whenever energy is converted from one form to another the overall system entropy — a measure of disorder or randomness — always increases. For example, when we burn gasoline in the engine of an automobile some of the energy generated moves the vehicle forward. But more of the energy is discarded as waste heat from the automobile's tail pipe. Nothing that we do is "sustainable" — every action leads to an increase in overall entropy. It also means that no machine can have "zero emissions".
- There is really no such thing as "clean energy". Energy is simply energy. Some ways of transforming energy into useful work create generate less entropy than others. But none of them are "clean".

Nicolas Carnot (1796-1832)

Nicolas Carnot, who served in the post-Napoleonic French army, developed the concepts that lie behind the discipline of thermodynamics. He recognized that, in the early 19th century, the French were falling behind the British both technically and in industrial capacity. His interest in thermodynamics was triggered by a desire to close the gap between the two countries. He explained thermodynamic basics with the concept of "thermal engine".



The sketch shows a modern concept of his thermal engine. On the left is a source of heat at high temperature, T_H. (This could be steam from a boiler or it could be the explosive force created by the burning of gasoline in an internal combustion engine.) The heat source supplies energy in the form of a heat flow, Q_H, to an engine which creates useful work, W, defined as motion against an opposing force. Using the steam engine example, the thermal engine could be a piston moving up and down or it could be a spinning turbine wheel. That motion can then be used to drive the wheels of a locomotive or to generate electricity.

Not all of the heat, Q_H, is converted to work — some of it (actually most of it) is discarded to a "cold sink" which has a temperature T_C. The quantity of discarded energy is Q_C. In the case of a steam engine, the cold sink could be a condenser that turns the exhaust steam into water; in the case of an automobile engine the cold sink is atmospheric air that cools the water in the radiator.

Carnot's fundamental insight that the concept of a heat engine provides is that, whenever we use energy to create useful work (where the word 'Work' is used in its narrow, thermodynamic sense), then much of that energy that will be wasted. It is not possible to have perfectly efficient machines, nor is a perpetual motion machine possible, regardless of Lisa Simpson's claim. Indeed, much of the work carried out by engineers is directed toward creating systems that minimize Q_c — the amount of heat that is discarded.

There are four laws of thermodynamics, starting at Zero and finishing at Three. (The reason for this confusing numbering system is that the Zeroth law was developed after laws One through Three, but its logical position is to be ahead of them.) The laws are thoroughly explained in the book *Four Laws that Drive the Universe* by Peter Atkins (Atkins, 2007).

THE ZEROTH LAW

The Zeroth Law defines temperature. Hence it is fundamental to understanding the other laws because they are all to do with temperature and the associated flows of energy. This law provides the theoretical basis for the Carnot engine.

Using the simple sketch Carnot stated that the efficiency of a heat engine can be determined by the following equations.

$$\eta = \frac{W}{Q_H} \qquad \text{..(1)}$$

$$= 1 - \frac{T_C}{T_H} \qquad \text{..(2)}$$

where η is the thermal efficiency of the engine and all temperatures are absolute values.

The first equation states that the efficiency of the system, η, is simply the ratio of useful work divided by the amount of heat added to the system. This value will always be less than 100%. The value of W will always be less than Q_H — usually much less.

The second equation provides a means for calculating how much of the heat is converted into useful work and how much goes to waste. It shows that we can calculate the efficiency of the Carnot engine knowing just the source and sink temperatures of the heat engine.

To get some idea of the practical upshot of the second equation, let us plug in some numbers for the temperature values. In thermodynamics all temperatures are in absolute values, with the most commonly used scale being degrees Kelvin (K). A temperature of zero Kelvin is as low as it possible to go — it is the temperature of outer space, the temperature when all of the atoms in a crystal cease to vibrate. It is the sound of silence.

The Table below provides some typical temperature values (all numbers are rounded, and various approximations have been made; degrees Fahrenheit are also shown.)

Temperature Celsius/Centigrade, C	Temperature Fahrenheit, F	Temperature Kelvin, K	Typical Environment Conditions
-273	-459	0	Outer space
0	32	273	Freezing point of water
20	68	293	Cooling water — say in the radiator of a car
100	212	373	Boiling point of water at sea level
140	284	413	Superheated steam
300	572	573	High pressure superheated steam

Using the above numbers, we can calculate efficiencies for various systems using the second of Carnot's equations.

- If the heat source is saturated steam at 100 C and the sink is cooling water at 20 C, then the efficiency of the engine is (1 – (293 / 373)) = 0.21, or 21%.
- If we use superheated steam as the heat source then the efficiency increases to (1 – (293 / 413)) = 0.29, or 29%.
- If we use the higher temperature superheated steam the efficiency increases to 49%.
- If the temperature of the heat sink (say the cooling water in a condenser) is reduced by 10 C to 283 K, and if we use saturated steam at 100 C, then the efficiency increases from 21% to nearly 24%. (To improve thermodynamic efficiency, it is usually more effective to reduce the temperature of the heat sink than to raise the temperature of the heat source.)

These figures are for a system that is thermodynamically reversible in which there no losses. In fact there are many losses such as friction and steam leaks. Hence the actual efficiencies will be lower than the theoretical values.

The crucial point here is that the efficiency, even of a perfect system, will always be lower, usually much lower, than 100%. Every time we do 'Work' we waste most of the energy that we use. So, for example, even the most efficient modern, gasoline-powered automobile has an efficiency of only about 35%. About 65% of the energy supplied by the gasoline is lost either through the radiator or at the engine's tail pipe. It may be possible to tweak the efficiency of the engine to gain a few points of efficiency. But Carnot tells us that that is about the best that we are going to do. The only way to achieve 100% efficiency is to have a heat sink that is at zero degrees Kelvin — an impracticality here on Earth.

The First Law

The first law of thermodynamics states that energy can neither be created nor destroyed. More formally: the internal energy of an isolated system is constant.

Mathematically, the first law is expressed as,

$$\Delta U = Q - W \qquad \text{(3)}$$

where ΔU is the change in the internal energy of a closed system, Q is the heat added to the system, and W is the work done by the system. From the point of view of this book, the above equation tells us that that the total amount of energy in a closed system is constant. We cannot "save energy", nor can we "waste energy" (leaving aside the special case of nuclear reactions).

The standard unit for measuring energy is the joule; calories and British Thermal Units (BTUs) are also used.

The Second Law

The First Law is to do with the *quantity* of energy within a closed system; the second law is to do with the *quality* of that energy. It states that as energy is transferred or transformed then some of that energy will be dissipated as high entropy waste. (We saw this in the Carnot heat engine — most of the heat added to the system, Q_H, is dissipated as Q_C.) There is a natural tendency of any isolated system to degenerate into a more disordered state. For most people, the first law is fairly straightforward — they grasp that there is something called energy, and that the amount of energy within a closed system cannot be either increased or decreased.

The second law, however, is more tricky, although we see it in action all the time.

Humpty Dumpty sat on a wall,
Humpty Dumpty had a great fall.
All the king's horses and all the king's men
Couldn't put Humpty together again.

In other words, you can't unscramble a scrambled egg.

Place a cup of hot coffee on a table. Gradually the coffee cools down until it reaches room temperature. This action is spontaneous — it does not require that anyone do anything. But when did you last see a cup of coffee spontaneously heat up? Why does the coffee always cool down? Continuing with the domestic theme, if you drop a plate on the floor it breaks. The plate will never spontaneously remake itself. When we go to a restaurant, we convert a low entropy system (the meal that we order) into one that has a higher entropy.

Another way of looking at the Second Law is to imagine two glass jars that are connected to one another, but their contents cannot mix because there is a plate inserted between them. One container contains a gas at high temperature, which means that the gas molecules are moving quickly. The second container contains a gas at a lower temperature, so its molecules are moving relatively slowly. If the plate between the two jars is removed the two gases mix such that the temperature of the mixture will be the mean of the two separate systems. In other words, if you mix a hot gas with a cold gas you wind up with a warm gas. Some of the molecules in the mixture will continue to move quickly, and others will move slowly, but over time they will form a Gaussian distribution or bell curve around the average molecular speed. It is theoretically possible that the molecules could spontaneously separate into two groups and form hot gas on one side of the container and cold gas on the other side. But the chances of this happening are infinitesimally low for the same reason that a scrambled egg will never unscramble itself or that a cup of coffee will spontaneously draw energy from its surroundings so that it becomes hotter.

The concept of entropy can also be explained by looking at the various possible states of water. At or below the freezing the water forms ice; the water molecules are in a well-ordered structure. If the temperature of the ice is increased the water melts, which means that its molecules move around freely with respect to one another — the entropy of the system has increased. If the water is then heated to its boiling point, water vapor is formed. Now the water molecules can move even more freely so their entropy is even higher.

Some consequences of the second law are:

- Any action to transfer or convert energy is irreversible.
- Heat cannot flow from a cooler to a hotter body.
- No system is "sustainable". The transfer of energy always increases entropy.
- There is a thermodynamic arrow of time — the Second Law gives a direction to time's arrow. Other laws of physics remain the same regardless of the flow of time, but the second law does not.

- Eventually, a very, very long time from now, the entire universe will eventually experience its own 'heat death' — a time when everything is at the same temperature and when no work can be done.

It might be thought that a household refrigerator does not conform to the requirements of the Second Law. If we put a glass of warm water into the fridge it cools down, *i.e.,* it moves to a lower entropy state. But the fridge is not an isolated system. It takes low entropy electricity provided by the power plant down the street and uses it to drive a compressor that not only cools the inside of the fridge but also discharges high entropy warm air from the coils at the back of the fridge. If the thermodynamic system includes not only the fridge but also the room in which it stands then overall entropy *does* increase.

Mathematically the second law can be expressed by the following two equations.

$$dS = \delta Q / T \qquad \text{..} (4)$$

$$dS \geq 0 \qquad \text{..} (5)$$

where S is the symbol for entropy, and Q and T represent energy (heat) and absolute temperature, as we saw when we looked at Carnot's equation.

Equation (4) shows that an infinitesimal change in entropy of a system (dS) is calculated by measuring how much heat has entered a closed system (δQ) divided by the common temperature (T) at the moment where the heat transfer took place.

Equation (5) states that, whenever heat is transferred, the value of S always increases, regardless of the direction of flow of that heat. The value of dS can never be negative. Entropy always increases.

Pollution

The examples that I have used so far have had a somewhat domestic flavor — we have looked at scrambled eggs, broken plates and cups of coffee. But let's look at these laws in the context of this book. Consider this all too common sight.

We see piles of trash and refuse despoiling what would otherwise be an attractive beach. And it is likely that many of the sea creatures that live on or around that beach are going to be either killed or driven away by the presence of so much trash.

This is a high entropy situation. We have used low entropy fossil fuels to manufacture those plastic bottles and tires, which are then discarded to the environment. The people involved have thrown those items away. But actually there is no "away". The beach is not "away" — it is part of the overall environment, a thermodynamically closed system.

Now we could use a backhoe, or a team of people to clean up this mess, and so lower the entropy on that beach. But the use of a machine or people will increase the overall entropy of the system that includes not only the beach but the environment around it. The exhaust from the backhoe's engine will contribute toward global warming (another example of a high entropy system). And moving the trash from the beach means that it will have to be disposed of somewhere else — to another "away". To repeat: there is no "away".

The Third Law

The third law of thermodynamics provides a mathematical foundation for the second law. It can be expressed in various ways:

- The entropy of a system approaches a constant value as its temperature approaches zero.

- It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations.
- The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0K).

This law does not have much application in the context of this book, except to say that it is impossible to achieve perfection — something most of us know already.