

Heat and Work

Now we want to discuss the material covered in chapter 8 of K&K. This material might be considered to have a more classical thermodynamics rather than statistical mechanics flavor. We've already discussed a lot of this material in bits and pieces throughout the term, so we will try to focus on the material not yet covered and just hit the highlights of the remaining material.

Heat and work occur during processes. They are energy transfers. Work is an energy transfer by macroscopic means and heat is an energy transfer by microscopic means. We've discussed reversible processes several times and we'll assume reversible processes unless we explicitly state otherwise. When work is done to or by a system, the macroscopic parameters of the system are changed—for example changing the volume causes $p dV$ work to be performed. Performing work changes the energy, U , of a system. But work does not change the entropy. Heat transfer changes the entropy as well as the energy:

$$dU = dQ = \tau d\sigma .$$

A very important activity in any modern society is the conversion of heat to work. This is why we have power plants and engines, etc. Basically all forms of mechanical or electrical energy that we use involve heat to work conversion. Not all of them involve fossil fuels, and in some cases it may be hard to see where the heat enters. For example, what about hydro-electric power? This is the storage of water behind a dam and then releasing the gravitational potential energy of the water to run an electric generator. Where is the heat supplied? Heat is supplied in the form of sunlight which keeps the weather going which provides water in the atmosphere to make rain to fill the lake behind the dam. Of course, the economics of this process are quite different from the economics of an oil fired electrical generating plant.

It was the steam engine (conversion of heat, obtained by burning coal, into work) that allowed the industrial revolution to proceed. The desire to make better steam engines produced thermodynamics!

With an irreversible process you can turn work completely into heat. Actually, this statement is not well defined. What we really mean to say is that with an irreversible process we can use work to increase the internal energy of a system and leave that system in a final configuration that would be exactly the same as if we had reversibly heated the system. For example, consider a viscous fluid in an insulating container. Immersed in the fluid is a paddle wheel which is connected by a string running over various pulleys and whatever to a weight. The weight is allowed to fall under the influence of gravity. Because the fluid is so viscous, the weight drops at a constant slow speed. Once the weight reaches the end of its travel, we wait for the fluid to stop sloshing and the temperature and pressure in the fluid to become uniform. Thus essentially all of the mechanical gravitational

potential energy is converted to internal energy of the fluid. We can take the fluid from the same initial state to the same final state by heating slowly (reversibly!) until we have the same temperature rise.

There is no known way to convert (reversibly or non-reversibly) heat (more properly, internal energy, U) entirely into work with no other change. This is one of the ways of stating the second law of thermodynamics.

It is certainly possible to convert heat into work. (I'm getting tired of trying to say it exactly correctly, so I'll just use the vernacular and you know what I mean, right?) The constraints are that you can't convert all of it to work or there must be some permanent change in the system or both. For example, suppose we reversibly add heat to an ideal gas while we keep the volume constant. Then we insulate the gas and allow it to reversibly expand until its temperature is the same as when we started. Then the internal energy of the gas is the same as when we started, so we have completely converted the heat into work, but the system is not the same as when we started. The gas now occupies a bigger volume and has a lower pressure.

The problem is that when we reversibly add heat to a system we add internal energy $dU = dQ$ and we also add entropy $d\sigma = dQ/\tau$, but when we use the system to perform work, we remove only the energy $dU = dW$ and leave the entropy! If we want to continue using the system to convert heat to work, we have to remove the entropy as well as the energy, so there is no accumulation of entropy. The only way to remove entropy (reversibly) is to remove heat. We want to remove less heat than we added (so we have some energy left over for work) so we must remove the heat at a lower temperature than it was added in order to transfer the same amount of entropy.

To make this a little more quantitative, consider some time interval (perhaps a complete cycle of a cyclic engine) during which heat Q_h is transferred into the system at temperature τ_h , heat $-Q_l$ is transferred into the system at temperature τ_l , and energy $-W$ in the form of work is transferred into the system. (So heat $Q_l > 0$ leaves the system and work $W > 0$ is performed on the outside world.) At the end of this time interval we want the system to be in the same state it was when we started. This means

$$\Delta U = 0 = Q_h - Q_l - W ,$$

and

$$\Delta\sigma = 0 = \frac{Q_h}{\tau_h} - \frac{Q_l}{\tau_l} .$$

We find

$$\frac{Q_h}{Q_l} = \frac{\tau_h}{\tau_l} ,$$

and

$$\eta_C = \frac{W}{Q_h} = 1 - \frac{\tau_l}{\tau_h} .$$

The ratio of the heat input and output is the same as the ratio of the temperatures of the input and output reservoirs. The *energy conversion efficiency* or just efficiency, η is defined as the work output over the heat input, W/Q_{input} . For the ideal engine we've been considering, the efficiency is η_C , the *Carnot efficiency*, and is the upper limit to the efficiency of any real (i.e. non-reversible) engine operating between temperature extremes τ_h and τ_l . Carnot might be called the father of thermodynamics. He worked in the early 1800's and understood the second law. This was before heat was recognized as a form of energy!

Of course, this definition of efficiency is motivated by the fact that if you're an electric power company, you can charge your customers based on W but you have to pay your suppliers based on Q_h and you want to maximize profits!

We live on the surface of the Earth and any engine must dump its waste heat, Q_l , at what amounts to room temperature, about 300 K. This is roughly the equilibrium temperature of the surface of the Earth and is set by radiation equilibrium between the Sun and Earth and between the Earth and space ($T = 3$ K). See problem 5 in chapter 4 of K&K. Aside: are you surprised that room temperature and the surface temperature of the Earth are about the same? Anyway, the waste heat goes into the environment and usually generates thermal pollution. There may come a time when a cost is associated with Q_l . In this case it's still desirable to maximize η , because that minimizes Q_l .

Because waste heat must be dumped at room temperature, improving the Carnot efficiency requires increasing the high temperature, τ_h . But this is not so easy to do, especially in an economically viable power plant that's supposed to last for many years,

Comment 1: no real engine is reversible, so all real engines operating between temperature extremes τ_h and τ_l will have an efficiency less than the Carnot efficiency.

Comment 2: many practical engines are designed in such a way that heat is exchanged at intermediate temperatures as well as the extremes. Such engines, even if perfectly reversible, frictionless, etc. have an efficiency less than the Carnot efficiency. However, if one assumes a perfect, reversible engine operating according to the specified design, one can calculate an efficiency (lower than the Carnot efficiency) which is the upper limit that can be achieved by that engine design.

A reversible refrigerator uses work supplied from the outside to remove heat from a low temperature reservoir and deposit that heat plus the work used as heat in a high temperature reservoir. Such a refrigerator is basically the reversible engine just discussed, but run backwards! The signs of Q_h , Q_l , and W all change but anything involving their ratios remains the same. (Note if you wanted to "derive" refrigerators you could start from the same idea we used with the engine—entropy is only transferred when there's a heat transfer and entropy must not be allowed to accumulate in the refrigerator.) With refrigerators, one uses a *coefficient of performance*, this is defined as the ratio of the heat

removed from the low temperature reservoir to the work required. This is

$$\gamma = \frac{Q_l}{W},$$

and for a reversible refrigerator operating between temperatures τ_l and τ_h , the Carnot coefficient of performance is

$$\gamma_C = \frac{\tau_l}{\tau_h - \tau_l},$$

and this is an upper limit to the performance of any refrigerator operating between the same temperature extremes.

Aside: If you go to a department store and look at air conditioners, you will find something called an energy efficiency rating (EER) which is basically the coefficient of performance. But, I believe these are given in BTU per hour per watt. That is they have dimensions instead of being dimensionless! To convert to a dimensionless number you must multiply by

$$\frac{1055 \text{ Joules}}{1 \text{ BTU}} \cdot \frac{1 \text{ Hour}}{3600 \text{ Seconds}} = 0.29 \frac{\text{J Hour}}{\text{BTU s}}.$$

A typical EER you'll find on an air conditioner is roughly 10, so the "real" γ is about 3!

Note that all reversible engines operating between the same two temperature reservoirs must have the same efficiency. Similarly, all reversible refrigerators operating between the same two temperature reservoirs must have the same coefficients of performance.

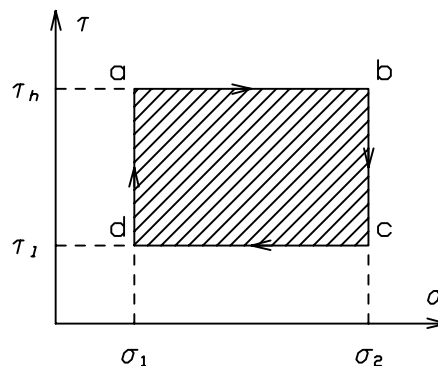
To see this, suppose that one has two reversible engines operating between the same two temperature reservoirs but they have different efficiencies. Run the high efficiency engine for some time, taking heat Q_h from the high temperature reservoir, producing work W , and dumping heat $Q_l = Q_h - W$ in the low temperature reservoir. Now run the other engine in reverse (it's reversible!) as a refrigerator removing heat Q_l from the low temperature reservoir, so the low temperature reservoir is exactly the same as when we started. To do this, the refrigerator is supplied with work W' and it dumps heat $Q'_h = Q_l + W'$ to the high temperature reservoir. Since this is the less efficient of the two reversible engines, $W' < W$. So the net effect of running the two engines is to extract heat from the high temperature reservoir and turn it completely into work. This is a violation of the second law of thermodynamics, and it does not happen. Therefore all reversible engines operating between the same two reservoirs must have the same efficiency.

Similar kinds of arguments can be used to show that all reversible refrigerators operating between the same two reservoirs must have the same coefficients of performance, that reversible engines are more efficient than irreversible engines, and that reversible refrigerators have higher coefficients of performance than irreversible refrigerators.

The Carnot Cycle

We've mentioned the Carnot efficiency and we've talked about heat engines, but how would one make a heat engine that (were it reversible) would actually have the Carnot efficiency? Simple, make an engine that uses the Carnot cycle.

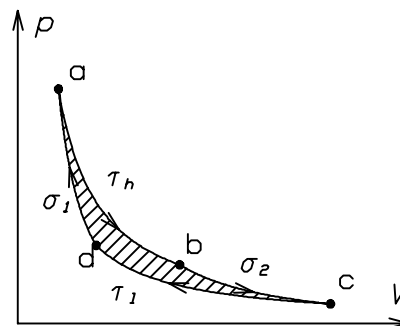
The Carnot cycle is most conveniently plotted on a temperature-entropy diagram. We plot the entropy of the "working substance" in an engine on the horizontal axis and the temperature of the working substance on the vertical axis. The working substance might be an ideal gas. It's whatever component actually receives the heat and undergoes changes in its entropy and internal energy and performs work on the outside world. There are four steps in a Carnot cycle. In step ab , the temperature is constant at τ_h while the entropy is increased from σ_1 to σ_2 . This is the step in which the system is in contact with the high temperature reservoir and heat $Q_h = \tau_h(\sigma_2 - \sigma_1)$ is added to the system. If the system is an ideal gas, then it must expand to keep the temperature constant, so it does work on the outside world. In step bc , the temperature is lowered at constant entropy. No heat is exchanged, the gas expands and does more work on the outside world. In step cd , entropy is removed at constant temperature by placing the system in contact with the low temperature reservoir. The heat removed is $Q_l = \tau_l(\sigma_2 - \sigma_1)$. In this step, the gas is compressed in order to maintain constant temperature, so the outside world does work on the gas. In step da , the system is returned to the starting temperature, τ_h , by isentropic compression, so more work is done on the system. The hatched area within the path followed by the system is the total heat added to the system in one cycle of operation,



$$Q = Q_h - Q_l = \oint \tau d\sigma.$$

Since the system returns to its starting configuration (same U) this is also the work done in one cycle.

Whatever the working substance, a Carnot cycle always looks like a rectangle on a $\tau\sigma$ diagram. (It has two isothermal segments and two isentropic segments.) Given a working substance we can plot the Carnot cycle on a pV diagram. The figure shows the Carnot cycle for a monatomic ideal gas. The vertices $abcd$ in this diagram are the same as the vertices $abcd$ in the $\tau\sigma$ diagram. So paths ab and cd are the constant temperature paths with $\tau = \tau_h$ and $\tau = \tau_l$. Along these paths $pV = \text{const}$. Paths bc and da are the constant entropy paths with $\sigma = \sigma_2$ and $\sigma = \sigma_1$.

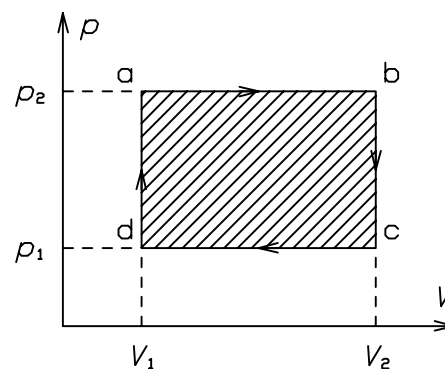


Along these paths $pV^{5/3} = \text{const}$. The work done on the outside world in one cycle is the hatched area within the path,

$$W = \oint p dV .$$

The arrows on the paths indicate clockwise traversal. In this direction, the Carnot cycle is a Carnot engine producing work and waste heat from high temperature input heat. If the cycle is run in reverse—counterclockwise—one has a Carnot refrigerator using work to move heat to a higher temperature reservoir.

As an example of a non-Carnot cycle, suppose we have a monatomic ideal gas which is the working substance of a reversible engine and it follows the rectangular path on the pV diagram shown in the figure. Along da , heat is added at constant volume V_1 . On ab , heat is added at constant pressure p_2 , and work is performed. On bc heat is removed at constant volume V_2 , and on cd , heat is removed at constant pressure p_1 , while the outside world does some work on the system. As before the total work done on the outside world is the area within the path and in this case,



$$W = (p_2 - p_1)(V_2 - V_1) .$$

The heat added is

$$\begin{aligned} Q_{\text{in}} &= \frac{3}{2}N(\tau_a - \tau_d) + \frac{5}{2}N(\tau_b - \tau_a) , \\ &= \frac{3}{2}(p_2V_1 - p_1V_1) + \frac{5}{2}(p_2V_2 - p_2V_1) , \\ &= \frac{5}{2}p_2V_2 - p_2V_1 - \frac{3}{2}p_1V_1 . \end{aligned}$$

The actual efficiency of this reversible engine is

$$\eta = \frac{W}{Q_{\text{in}}} = \frac{p_2V_2 - p_2V_1 - p_1V_2 + p_1V_1}{\frac{5}{2}p_2V_2 - p_2V_1 - \frac{3}{2}p_1V_1} ,$$

while the Carnot efficiency is

$$\eta_C = 1 - \frac{p_1V_1}{p_2V_2} .$$

These formulae aren't all that illuminating so let's consider a numerical example: suppose $p_2 = 2p_1$ and $V_2 = 2V_1$. Then the temperature at the hottest (upper right) vertex is 4 times the temperature at the lowest (lower left) vertex, so the Carnot efficiency is

$$\eta_C = \frac{3}{4} .$$

The actual efficiency is

$$\eta = \frac{2}{13}.$$

If you're actually trying to build a heat engine that operates on this cycle, then as you improve the engine by reducing friction, heat losses, etc., you will approach an efficiency of $2/13$ and this should be your goal, not the Carnot efficiency.

If you want to approach the Carnot efficiency, you must redesign the cycle to be more like a Carnot cycle. In the cycle shown, the extreme temperatures are reached only at the upper right and lower left vertices. Most heat transfers are at less extreme temperatures and this is why the actual efficiency is so much less than the Carnot efficiency .

Other Thermodynamic Functions

We have concentrated on the internal energy, U , in the preceding discussion. If we consider a constant temperature process, then the work done on the system is the change in the Helmholtz free energy. This is because at constant temperature, $d(\tau\sigma) = \tau d\sigma$, so

$$dW = dU - d(\tau\sigma) = dF \quad (\text{constant temperature}).$$

Many processes occur at constant pressure, such as all processes open to the atmosphere. If a process occurs at constant pressure, then we are letting the system adjust its volume "as necessary," so we cannot really use or supply any $p dV$ work performed by or on the system. The $p dV$ work "just happens." If the system can perform work in other ways, then we can divide the work into the $p dV$ work and other work,

$$dW = dW_{\text{other}} + dW_{pV},$$

and

$$\begin{aligned} dW_{\text{other}} &= dU - dW_{pV} - dQ, \\ &= dU + p dV - dQ, \\ &= dU + d(pV) - dQ, \\ &= dH - dQ \quad (\text{constant pressure}), \end{aligned}$$

where

$$H = U + pV,$$

is called the enthalpy. In any constant pressure process the heat added plus the non- $p dV$ work done is the change in enthalpy. In particular, if there is no non- $p dV$ work done, the change in enthalpy is just the heat added. Note that dW_{other} is what K&K call the "effective" work in a constant pressure process.

In the event that we have a reversible process that occurs at constant temperature and constant pressure, the Gibbs free energy is useful. This is defined as

$$G = F + pV = H - \tau\sigma = U + pV - \tau\sigma .$$

It should be clear that

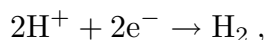
$$dW_{\text{other}} = dG \quad (\text{constant temperature and pressure}) .$$

Also, a system which is allowed to come to equilibrium at constant temperature and pressure will come to equilibrium at a minimum of the Gibbs free energy.

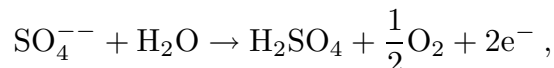
As an example of the use of the Gibbs free energy, consider a system (cell) of two noninteracting electrodes in an electrolyte consisting of sulfuric acid dissolved in water. The sulfuric acid becomes two hydrogen ions and one sulfate ion,



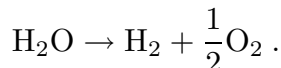
When current is forced through the system in the direction to supply electrons to the cathode, the reaction at the cathode is



and the reaction at the anode is



and the net reaction is



If the current is passed through the cell slowly and the cell is open to the atmosphere and kept at constant temperature, then the process occurs at constant τ and p . The “other” work is electrical work.

$$W_{\text{other}} = G(\text{H}_2\text{O}) - G(\text{H}_2) - \frac{1}{2}G(\text{O}_2) ,$$

where the Gibbs free energies can be looked up in tables and it is found that the difference is

$$\Delta G = -273,000 \text{ J mol}^{-1} .$$

The other work done is electrical work equal to the charge times the voltage. Since we have two electrons per mole,

$$W_{\text{other}} = -2eN_0V_0 ,$$

or

$$V_0 = -\frac{\Delta G}{2N_0e} = 1.229 \text{ Volts} ,$$

where N_0 is Avogadro’s number and e is the charge on an electron. V_0 is the voltage that is established with no current flowing. At higher voltage, current flows and the cell liberates hydrogen and oxygen (electrolysis). If these gases are kept in the cell and allowed to run the reactions in reverse, one obtains a fuel cell in which the reaction of hydrogen and oxygen to form water generates electricity “directly.”