

Biology 3550: Physical Principles in Biology

Fall Semester - 2016

Notes on Thermodynamics I

Energy, Work, and Heat

- I. Thermodynamics is the branch of chemistry and physics that is concerned with the interconversion of different forms of energy. The laws of thermodynamics place constraints on how much work can be obtained from different forms of energy and whether or not specific processes will occur spontaneously. Thermodynamics does not tell us how a process will occur, but only whether or not the process will occur spontaneously. Thermodynamics is definitely one of the most challenging subjects for nearly all students, for several reasons:
- A. The ideas are fundamentally abstract and subtle. Even people who have thought about thermodynamics for many years easily get tripped up.
 - B. It uses math! Even if many of the ideas seem to be conceptually simple, a deep and useful understanding depends on mathematics.
 - C. The language can be confusing. Different disciplines sometimes use different terms. In addition, the language has historical origins, and the history is convoluted.
 - D. Historical confusion. Unlike classical mechanics, which almost all came from one person, Newton, over a short period of time, thermodynamics was developed over a long period of time by several generations of scientists, and there were periods of profound confusion.

But, it's worth it! The current issues regarding energy and climate change offer a dramatic examples of how important the interconversion of energy forms can be. In the context of our course, we will use these principles to understand how biological systems become organized and do amazing things.

- II. Units of energy. Before going on, it is worthwhile to think about the definition of energy and the units we use. A general definition of energy is that it is the "ability to do work". We define mechanical work as the integral of force applied over distance:

$$w = \int_{x_1}^{x_2} F dx$$

If the force is constant, then

$$w = F(x_2 - x_1)$$

The units of work must be force times distance. The SI unit of force is the Newton, which is the force required to accelerate a mass of 1 Kg by 1 m/s per s. The SI unit of work or energy is then the Nm, or Joule:

$$1 \text{ Joule} = 1 \text{ Newton} \cdot \text{meter} = 1 \text{ Kg} \cdot \text{m}^2\text{s}^{-2}$$

Another commonly used unit of energy is the calorie, which is defined as the amount of energy required to raise the temperature of 1 g of water by 1 °C, or 1 K. One problem with defining the calorie in this way is that the heat required to raise the temperature of water depends on the starting temperature. 4 °C and 15 °C have been used to define the unit, sometimes with a subscript indicating the temperature. The standard definition now is in terms of the Joule, as defined above:

$$1 \text{ cal} = 4.184 \text{ J}$$

Another source of confusion is that the calorie has been defined at different times in terms of the energy to heat either 1 g of water or 1 Kg. The current convention is to use a lower case “c” to designate the “gram calorie” and an uppercase “C” to designate the “kilogram calorie”. The energy content of foods is expressed in kilogram calories. This is one reason that the idea of losing weight by eating ice cream (which should cool the body and result in negative calorie intake) is doomed to failure!

III. An important distinction: Temperature versus heat.

Before considering some simple examples, it is important to be sure that we are using language carefully. One common cause of confusion is the difference between temperature and heat.

- Temperature has a relatively straight-forward definition. It is a property of a given mass of matter that is directly related to average kinetic energy of the molecules making up the matter. For an ideal gas, the temperature determines the relationship between volume and gas according to the ideal gas law:

$$PV = nRT$$

For an ideal gas temperature is related to the average kinetic energy of the ideal gas molecules according to:

$$E = 3kT/2$$

- Heat is often defined as “a form of energy”. More specifically, heat is the flow of energy from a warm object to a cooler one, with the result that the temperatures become more equal.

At one time, heat was thought to be a massless substance, often called “caloric”, that flowed invisibly between objects. We now understand that heat is not something that objects contain, but the language still seems to imply this. This is one of the historical origins of some of the confusion in thermodynamics.

It is possible to formulate the laws of thermodynamics without invoking “heat”, but that seems rather artificial to me and only shifts the difficulties to other words.

- In summary: temperature is a property of matter that can be directly measured, while heat is a flow of energy associated with temperature changes. The heat flow is always from a warm object to a cooler one.

IV. Some examples based on the expansion and compression of gasses.

Historically, one of the most important motivations for the development of thermodynamics was the invention of the steam engine. Once steam engines started to be used, there was great interest in getting the maximum amount of work from them. Since steam engines work through the expansion of a gas, many of the ideas in thermodynamics were formulated in this context.

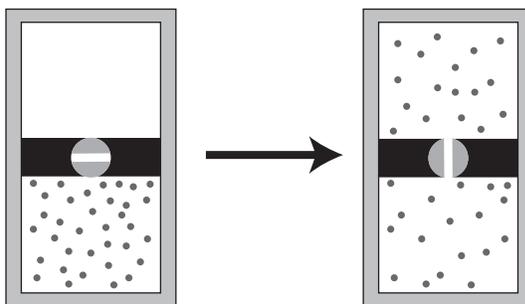
At the time, though, the relationship between the pressure of a gas and the motion of molecules was not understood, and the theory was developed without any explicit model for what actually generated forces or work. This treatment is usually referred to as “classical thermodynamics”. Later, a molecular interpretation was developed, what we now call “statistical mechanics”. Both can stand on their own and are completely consistent with one another. But, I think that it is often easier to merge the two approaches when trying to understand things.

A. Gas expansion without work

Suppose we build an apparatus with the following features:

- It is completely insulated from its surroundings, so that heat can't flow in or out of it.
- There are two chambers separated by a valve that can be opened or closed without perturbing anything else and without any friction.
- One chamber is filled with a gas at some arbitrary pressure, P .
- The other chamber is evacuated.

Once the system has equilibrated, we open the valve. As we have discussed at length, the molecules are moving about due to kinetic energy in random directions. Eventually (quite quickly, actually) we expect the molecules to distribute themselves throughout the vessel, with roughly equal numbers on the two sides.



What can we say about what has changed and what hasn't?

- Nothing has happened to change the average velocities of the molecules. Therefore, the temperature should be the same, and the average kinetic energy is the same.
- The volume has increased. So, by the ideal gas law, $PV = nRT$, the pressure should decrease.
- Because of the insulation, no heat has flowed in or out of the chambers.

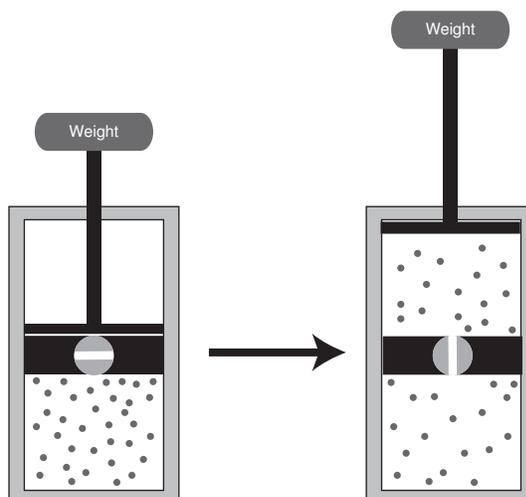
- Nothing, except the molecules, has been moved, so no work has been done.

But, something else has happened. Even though no work was done and the energy has stayed the same, we know that we would have to do work, *i.e.* spend energy, to restore the system to its original state. You probably already know the fancy word for this, “entropy”, but let’s put off discussing this concept. What we can say, though, is that somehow or other we have wasted the potential to do work, even though the total thermal energy has stayed the same.

Processes in which there is no exchange of heat are called “adiabatic”.

B. Gas expansion with work, but without heat flow.

Now, let’s think about another type of apparatus. Again we will keep the apparatus fully insulated. But, now a movable piston has been added to the upper chamber. The upper chamber is still evacuated, and our engineers have made a perfect, frictionless seal to the outside, through which a rod connects the piston to a weight.



When we open the valve, the gas molecules begin to collide with the piston, and the pressure from the gas molecules pushes the piston and the weight upward. Mechanical work is now being done. What is changing as the piston moves?

- Does the temperature change? Consider what happens when the piston is pushed upwards. The gas molecules collide with the piston and transfer some of their energy to it. Unlike when they collide with a fixed wall, their velocity is not quite as great when they bounce off in the other direction. As a consequence the average kinetic energy of the molecules decreases, meaning that the temperature decreases as well.
- If the volume increases by the same amount as in the previous example and the temperature decreases, then the pressure must decrease *more* than in the previous example.

The key point about this example is that some of the kinetic energy of the gas molecules has been converted to mechanical work. From the conservation of momentum, the change in energy should be equal to the amount of work done.

Let's put some labels on the quantities involved:

- E = energy of the molecules. For an ideal gas, this is entirely translational kinetic energy. We will define the change in energy associated with a process as:

$$\Delta E = E_{\text{final}} - E_{\text{start}}$$

It's important to keep track of the signs! We will define the work involved, w , so that it is positive when work is done on the gas (or, more generally the "system"), and negative when the system does work on the outside world, as in this case.

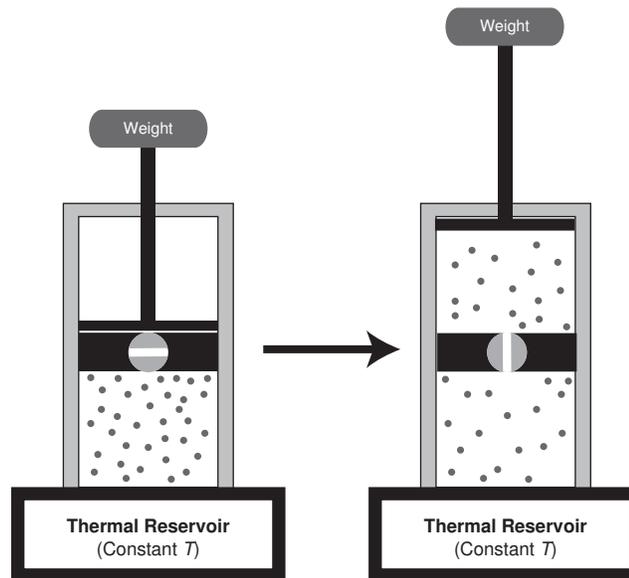
For this example, we know that the amount of work must equal the change in energy:

$$\Delta E = w$$

Is this always true?

C. Gas expansion at constant temperature with work.

Next, we make an even fancier device by adding a thermal reservoir at the bottom of the cylinder:

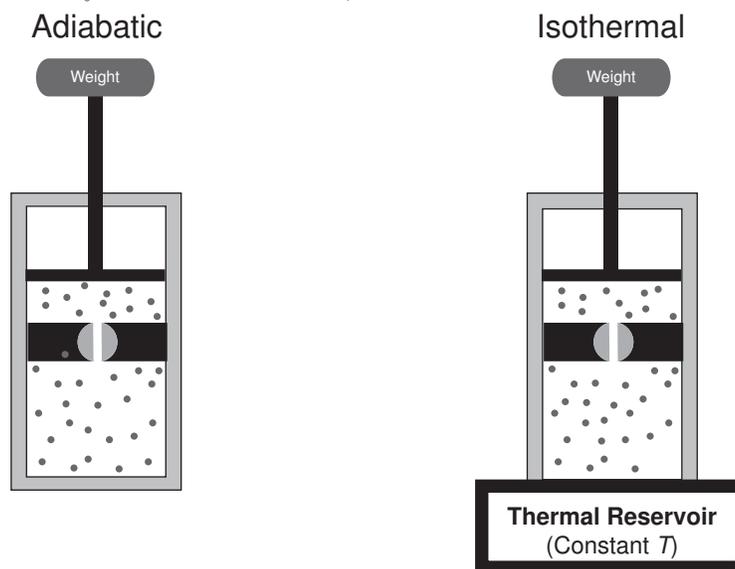


Basically, the reservoir is a large mass equilibrated at the same temperature as the gas. If the temperature of the gas drops, heat will flow to equalize the two temperatures, without significantly lowering the temperature of the reservoir.

What happens, now, when we allow the piston to move and do work?

- As the piston is pushed upwards, the gas molecules lose some energy, and the temperature starts to drop. But, as soon as that happens, heat flows from the reservoir.

- At the end of the process, the temperature is the same as when it started, so the energy must be the same as well. In this respect, the result is the same as in the adiabatic expansion without work.
- Again, work has been done. Is more work done in the adiabatic or isothermal process? Consider a point part wqy through each process, where the volumes have increased by the same amount, as illustrated below:



Because the adiabatic process does not allow heat to flow to the gas, the temperature at this intermediate point must be lower for the adiabatic process than the isothermal one. As a consequence, the pressure must be lower for the adiabatic process. Since pressure represents force divided by the area over which it is exerted, the total force on the piston must also be less for the adiabatic process than for the isothermal one. We can thus conclude that the isothermal process can produce more work than the adiabatic process.

The energy for the additional work from the isothermal process is drawn from the heat of the reservoir.

In this example, $\Delta E = 0$, but work has been done, and there has been a flow of heat.

We represent the heat flow by the symbol q and define it so that it is positive when heat flows from the surroundings into the system of interest. In this case, q is positive and w is negative, and:

$$q = -w$$

V. This brings us to the first law of thermodynamics.

The common statement of the first law is that the energy of the universe is constant. But, the more formal statement is that for any process, the change in energy, E , is the sum of the work done on the system and the heat absorbed from the surroundings:

$$\Delta E = q + w$$

We can see how this applies to the three examples from above:

- Adiabatic expansion without work.

$$\begin{aligned}q &= 0 \\w &= 0 \\ \Delta E &= 0\end{aligned}$$

- Adiabatic expansion with work

$$\begin{aligned}q &= 0 \\w &< 0 \\ \Delta E &< 0 \\ \Delta E &= w\end{aligned}$$

- Isothermal expansion with work

$$\begin{aligned}q &> 0 \\w &< 0 \\ \Delta E &= q + w = 0 \\ q &= -w\end{aligned}$$

Is there a proof of the first law? No! The laws of thermodynamics are postulates, and our confidence in them comes from the fact that no one has ever found an exception.

In 1775 the French Royal Academy of Science effectively made the first law of thermodynamics (before it was called that) a real law by declaring that it would no longer consider patent applications for perpetual motion machines.

VI. State functions versus path functions

The quantities E , on the one hand, and q and w , on the other are fundamentally different. The energy of a system depends only on the state of that system, irrespective of how it got there. For an ideal gas, the energy depends only on the temperature and the number of molecules. A change in energy, ΔE , depends only on the starting and ending states.

But, will we always get the same amount of work for a given change in state? Our examples clearly show that we won't. For both the first and third examples, ΔE is zero, but q and w are different for the two processes.

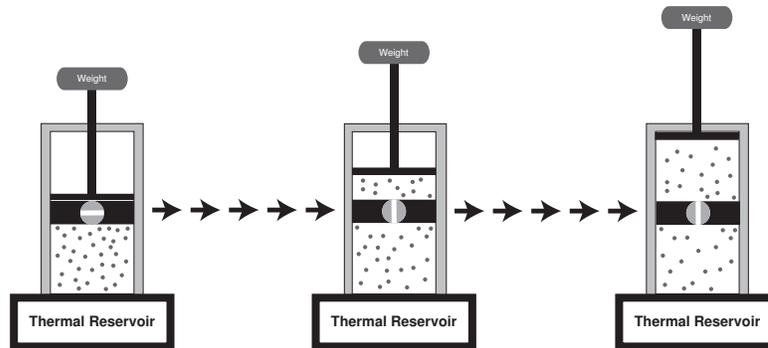
We say that the energy is a "state function", while heat and work are path-dependent functions. For a gas, the pressure, P and volume, V , are also state functions.

VII. How much work can we get out of a process?

We already saw that we can get extra work from the expansion of the gas by allowing it to draw heat from its surroundings as it expands. Even if the temperature is the

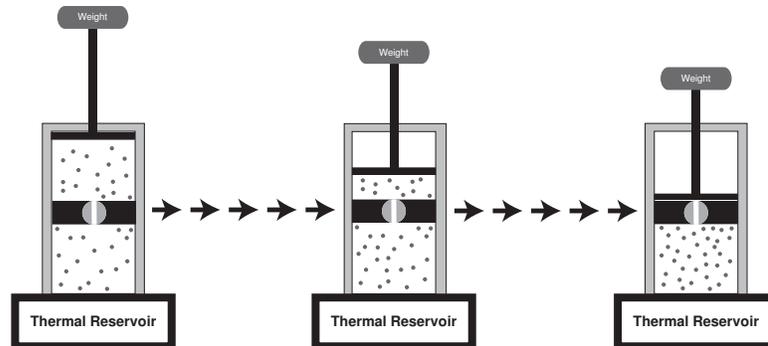
same at the beginning and end of the expansion processes, different paths can lead to different amounts of work being produced and different amounts of heat absorbed.

The maximum amount of work that can be generated from the expansion of a gas is obtained by controlling the movement of the piston so that it is slow enough that the temperature never actually drops. This cannot be done in practice, but it can be approached as a limit, in the sense of limits in calculus, by allowing the piston to move only in infinitesimal steps, as suggested in the drawing below:



Because the piston moves in infinitesimally small steps, the temperature never falls below that of the reservoir. If a larger step ever does take place, the temperature will drop, causing the pressure to drop. As a consequence, less work will be produced by the expansion. This is why we can argue that this is the path that will lead to the maximum production of work (the most negative value of w).

The reverse of this process, diagrammed below, is the one that requires the *least* amount of work to compress the gas to its original volume.



Again, the volume is changed in infinitesimally small steps. As the gas is compressed, the piston imparts extra kinetic energy on the gas molecules, but (in the ideal case) the excess energy is instantly transferred to the thermal reservoir and the temperature remains constant. Because the volume of the gas decreases, the pressure increases, and progressively more work must be done for each decrease in the volume. But, if larger steps were taken, the temperature would increase temporarily, causing a larger increase in pressure and requiring more work for the next step.

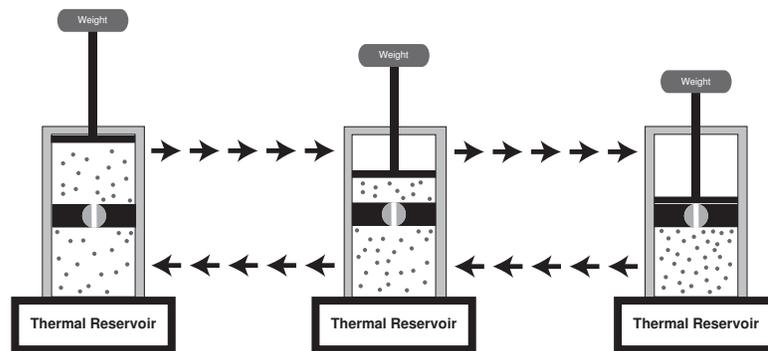
The two processes described above are said to be reversible, and that term can be taken in two senses. In the first sense, the two processes are reversible because they are exact opposites. The maximum work that can be done during expansion is also the minimum amount of work that is required for compression. Thus:

$$w_{\text{exp,rev}} = -w_{\text{comp,rev}}$$

Since $\Delta E = 0$ for both processes, and $q = -w$ for each, we can also conclude that

$$q_{\text{exp,rev}} = -q_{\text{comp,rev}}$$

We can also imagine a cycle formed by the two processes, as illustrated below:



Because $w_{\text{exp,rev}} = -w_{\text{comp,rev}}$ and $q_{\text{exp,rev}} = -q_{\text{comp,rev}}$, w and q for the complete cycle must be zero. Thus, the system is restored to its original volume, pressure, temperature and energy with no net input or output of either work or heat.

Of course, no real process can meet this ideal. As noted above, any real expansion process will produce less work than the ideal, and any real compression will require more work than the ideal. As a consequence, there is a net amount of work applied to the system and w for the cycle will be greater than zero. If the original temperature is restored $\Delta E = 0$ and $q = -w$, and q will be negative, meaning that heat is transferred to the surroundings. This is the general nature of less-than-ideal processes, they require more work (or produce less) than the ideal process and they release more heat.

The ideal expansion and compression processes described above are also reversible in a second sense: Either process can be reversed at a given point by an infinitesimal force in the opposite direction. This is the meaning most commonly implied by the term in thermodynamics.

Although work and heat are not state functions, the changes in these quantities associated with the ideal, reversible process separating two states do represent changes in state function. Thus, there are quantities, w_{rev} and q_{rev} that are associated with any two states that can, in principle, be interconverted by a reversible process.

The quantity w_{rev} is described as being the “free energy change”, ΔF , for the conversion of one state to another. The energy change is “free” in the sense that it is the maximum amount of energy that is available to do work. In a more practical sense, free energy

is anything but free, since it is the kind of energy that we pay for when we buy, for instance, electrical power or gasoline. On the other hand, molecular kinetic energy is “free” in the sense that it is always there, but it can’t actually be used to do any work. The quantity q_{rev} for any two states is also very important, as we will soon see when we discuss the elusive concept of entropy.