

The Second Law of Thermodynamics

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1 Introduction

Last week, we looked at the first law of thermodynamics, which was a statement of the conservation of energy. We can also view the first law as a statement of the impossibility of a particular sort of perpetual motion machine which produces a quantity of work greater than the energy it absorbs. This is known as a perpetual motion machine of the first kind, and is clearly in violation of the principle of energy conservation. This week, we will consider the second law of thermodynamics, which likewise can be viewed as a statement about perpetual motion machines of the second kind. Such machines are more subtle than the first kind: they are perfectly in accord with conservation of energy, but they perform work by extracting heat from a reservoir. Since the Earth is essentially an infinite heat reservoir, a machine that could convert heat into work would be, for all intents and purposes, a perpetual motion machine. We will see how thermodynamics rejects this possibility.

2 Statements of the Second Law

We are generally familiar with the idea that the second law of thermodynamics assures that the entropy of a closed system will never decrease. This, of course, requires a definition of entropy which is a notoriously difficult concept; we will work up to this definition by starting with simpler statements. One of these is Kelvin's postulate, which states that *a transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible*. Another statement, Clausius's Postulate, states that *a transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible*. We defined temperature last week in a statistical way, which is not suitable for a thermodynamic discussion; we can rephrase the Clausius postulate by stating that *if heat flows spontaneously from body A to body B, then a transformation whose only final result is to transfer heat from body B to body A is impossible*.

These two statements are, in fact, equivalent. We can prove here that Clausius's postulate implies Kelvin's postulate by proving the contrapositive. If Kelvin's postulate were not true, then we could take heat from a body at temperature t_1 and transform it into work. This work could then be transformed through friction into heat in another body with temperature $t_2 > t_1$. The only final result would be to transfer heat from the body at temperature t_1 to a body at temperature t_2 , which would imply that Clausius's postulate is false.

3 The Carnot Cycle

Kelvin's postulate tells us that we cannot extract work from a body at uniform temperature; therefore, in order to build a heat engine, we need two separate heat reservoirs. Let the temperatures of these reservoirs be T_1 and T_2 , with $T_2 > T_1$. With these two heat sources, the following process will transform heat into work:

1. The container of gas at temperature T_2 is attached to the heat source with temperature T_2 , and allowed to expand isothermally, absorbing a heat Q_2 .

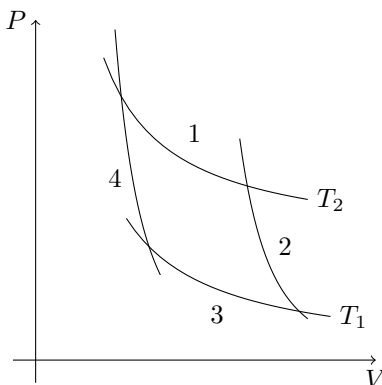


Figure 1: The Carnot cycle illustrated on a pressure-volume diagram. The numbers on the lines correspond to the steps in the cycle given above.

2. The container is detached from the first heat source and expands adiabatically (without gain nor loss of heat) until it reaches the temperature T_1 .
3. The container is placed on the heat source with temperature T_1 , and is compressed isothermally, delivering a heat Q_1 to the heat source.
4. The container is detached from the second heat source and compressed adiabatically until its temperature reaches T_2 .

This process is called the *Carnot cycle*. It is depicted in Figure 1. The efficiency of this cycle is equal to the work performed divided by the heat absorbed from the higher temperature reservoir. Since the process is cyclic, internal energy does not change; the first law therefore implies that the work done is equal to the net heat gained, or $Q_2 - Q_1$. Therefore, the efficiency is

$$\eta = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}.$$

For a short digression, we can use the Carnot cycle to finish the proof of the equivalence of Kelvin's and Clausius's postulates. Assume that Clausius's postulate is false, and we can transfer a heat Q_2 from the reservoir at T_1 to the reservoir at T_2 with no other effects. We can then use the Carnot cycle to extract this heat Q_2 from the reservoir at T_2 , deliver a heat Q_1 to the reservoir at T_1 , and perform some work W . There was no net heat change in the reservoir at T_2 , the reservoir at T_1 suffered some heat loss since $Q_2 > Q_1$, and work was performed. This is in violation of Kelvin's postulate, since we have extracted heat from the reservoir at T_1 and converted it into work with no side effects.

4 Carnot's Theorem

The Carnot cycle is important because it achieves the theoretical maximum efficiency. Consider another cycle operating between the same two reservoirs, which extracts a heat Q'_2 from the reservoir at T_2 , delivers a heat Q'_1 from the reservoir at T_1 , and performs a work W' . We seek to show that the efficiency of the Carnot cycle has a higher efficiency than this cycle; i.e.,

$$\frac{Q_2}{Q_1} \geq \frac{Q'_2}{Q'_1}.$$

The following argument is due to Enrico Fermi¹. We can approximate the ratio Q'_2/Q_2 to arbitrary accuracy by a rational number, so that

$$\frac{Q'_2}{Q_2} \approx \frac{N}{N'}$$

Now consider a process composed of N' forward turns of the second cycle and N reverse turns of the first cycle. This is valid because the first cycle is a reversible Carnot cycle; we make no assumptions about the reversibility of the second cycle. The forward process performs a work $W'_{tot} = N'Q'_2 - N'Q'_1$, and the reverse process performs work $W_{tot} = NQ_1 - NQ_2$. Adding the two portions, we find that the total work is equal to

$$W'_{tot} + W_{tot} = (N'Q'_2 - NQ_2) + NQ_1 - N'Q'_1.$$

As the approximation N'/N grows in accuracy, the first part of this expression vanishes. Therefore, the total work performed is

$$W = NQ_1 - N'Q'_1 = -Q_{1,tot}$$

where we have indicated that this work is equal to the heat absorbed by the engine processes from the reservoir at T_1 . Now, assume W is positive. Then we have succeeded in extracting heat from the reservoir at T_1 and converting it to work while the other reservoir suffers no gain nor loss of heat; this is in violation of Kelvin's postulate. Therefore, $W \leq 0$, or

$$N'Q'_1 \geq NQ_1.$$

Recalling that $N'/N \approx Q'_2/Q_2$, we can rewrite this as

$$\begin{aligned} Q_2Q'_1 &\geq Q'_2Q_1 \\ \frac{Q_2}{Q_1} &\geq \frac{Q'_2}{Q'_1} \end{aligned}$$

This is the desired result, and it directly follows that $\eta \geq \eta'$. Additionally, if the second cycle is reversible, then we could follow the argument in reverse and obtain the opposite inequality. Therefore, the efficiencies of all reversible cycles between reservoirs at T_2 and T_1 have the same efficiency $1 - Q_1/Q_2$. We can use this fact to define an absolute temperature, as opposed to the empirical measurements of temperature we have used previously. Given two reservoirs, the ratio of the heats exchanged with them by a Carnot cycle is well defined according to the Carnot theorem.

5 Entropy as a State Function

When we discuss the second law of thermodynamics, we operate under a more qualitative definition. In this section we will develop a more quantitative understanding of what is meant by entropy. There is really no way to start other than to straight away introduce the definition

$$dS = \left(\frac{dq}{T} \right)_{rev} \quad (1)$$

Notice that entropy is a state variable. For a reversible process on the PV diagram, one can show that the net change in entropy is 0 around a closed loop. In general, one can determine the entropy by integrating infinitesimal bits of heat added to the system, over the temperature the system is at. However, one caveat exists: we must specify a reversible path.

This is most easily seen through the following example: consider a box, half filled with gas. The gas is prevented from diffusing to the other side when the barrier is suddenly lifted (see Figure 2). Assuming the gas expands in a vacuum, what would the change in entropy be for this process?

¹From his excellent book on thermodynamics: <http://www.amazon.com/Thermodynamics-Dover-Books-Physics-Enrico/dp/048660361X>

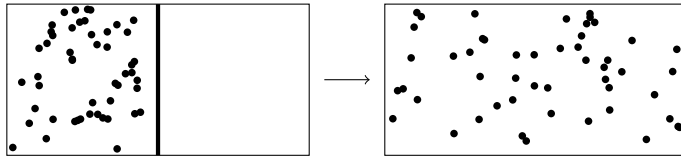


Figure 2: A gas gains entropy as it expands to fill a larger volume.

In this case, the box is insulated from the environment, so the process is adiabatic. As a result, one might say that the heat transferred to the system is 0, and the entropy change is 0. This reasoning, however, is wrong. This is because such a process is not reversible (it is spontaneous in fact). Instead, we must choose a reversible process that goes from the initial to final point, and then calculate the entropy difference between the two points. Because the gas expands into a vacuum, it doesn't do any work on its environment, so the change in internal energy of the system is 0. This just means that the system's temperature is constant. In fact, we can choose an isothermal path (which is reversible) from the starting point to the ending point. Our entropy change is thus

$$\Delta S = \int_V^{2V} \frac{PdV}{T} = \int_V^{2V} \frac{nRdV}{V} = nR \ln(2) \quad (2)$$

This is a more sensible answer. Since the process is spontaneous, we would expect the entropy change to be positive. (Technically, the previous statement is incorrect because spontaneity is determined through the Gibbs Free Energy. However, Entropy and spontaneity are very similar concepts too.) With this new definition, we can land ourselves in a whole host of problems. A good check to determine whether our answers make sense is to check the sign for the change in entropy.

6 The Clapeyron Equation

Last week, we used the first law to derive an expression for differential charge,

$$\delta Q = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV.$$

This immediately gives a differential expression for entropy:

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV$$

We know that entropy is an exact differential. This means that if we write it as $M dx + N dy$, then

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}.$$

Applying this condition to the equation above gives

$$\frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V \right] = \frac{\partial}{\partial T} \left[\frac{1}{T} \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) \right].$$

Now we can simply perform the derivatives:

$$\begin{aligned} \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} &= -\frac{1}{T^2} \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) + \frac{1}{T} \left(\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial P}{\partial T} \right)_V \right) \\ \left(\frac{\partial U}{\partial V} \right)_T &= T \left(\frac{\partial P}{\partial T} \right)_V - P \end{aligned}$$

We will use this important result to analyze systems in which a liquid and gas coexist (i.e., the liquid is boiling). Let m_1 and m_2 be the masses of the liquid and gas parts, respectively. Then we can write the total mass, volume, and internal energy as

$$\begin{aligned} m &= m_1 + m_2 \\ V &= m_1 v_1(T) + m_2 v_2(T) \\ U &= m_1 u_1(T) + m_2 u_2(T). \end{aligned}$$

Now consider an isothermal transformation in which a mass dm passes from the liquid state to the gas state. Then we will have

$$\begin{aligned} dV &= (v_2(T) - v_1(T)) dm \\ dU &= (u_2(T) - u_1(T)) dm. \end{aligned}$$

According to the first law,

$$\begin{aligned} \delta Q &= dU + p dV = dm(u_2(T) - u_1(T) + P(v_2(T) - v_1(T))) \\ \frac{\delta Q}{m} &= u_2(T) - u_1(T) + P(v_2(T) - v_1(T)) = \lambda \end{aligned}$$

where we have defined the latent heat of vaporization, λ , as the heat required to vaporize a unit mass of the liquid.

Now, since we used an isothermal transformation above,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{dU}{dV} = \frac{u_2(T) - u_1(T)}{v_2(T) - v_1(T)}.$$

We can also rewrite this in terms of λ , like so:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\lambda}{v_2 - v_1} - P.$$

Comparing to the equation we derived before, we have

$$\begin{aligned} T \left(\frac{\partial P}{\partial T}\right)_V - P &= \frac{\lambda}{v_2 - v_1} - P \\ \frac{dP}{dT} &= \frac{\lambda}{T(v_2 - v_1)}. \end{aligned}$$

The last equation is called Clapeyron's equation, and it gives the slope of a coexistence curve in a phase diagram. Note that we have replaced the partial derivative with a total derivative, since the pressure is a function of temperature alone in this system.

7 Gibbs' Phase Rule

Consider the sketch of a pressure-temperature phase diagram in Figure 3. We know that a thermodynamic system can be described generally by three parameters, usually taken to be the pressure, volume, and temperature. However, the ideal gas law removes a degree of freedom, so we are left with two parameters. However, if we specify that the state is in two simultaneous phases – for example, a liquid is boiling – then it is confined to one of the coexistence curves on the diagram, and so has only one degree of freedom. If we specify that there are three coexistent states, then the system has no degrees of freedom and is confined to the triple point.

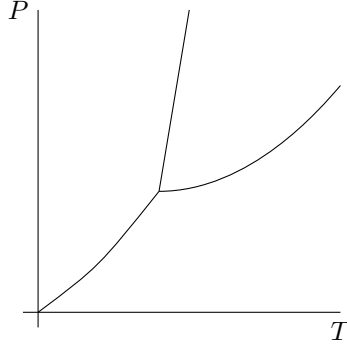


Figure 3: The phase diagram shows two-dimensional regions for single phases, one-dimensional regions for coexistence of two phases, and a single triple point.

Gibbs' phase rule gives a simple general expression for the degrees of freedom of a thermodynamic system. Before we can develop this rule, though, we will need a quick discussion of thermodynamic potentials. Recall from the section on entropy that

$$\int_A^B \frac{\delta Q}{T} \leq S_B - S_A.$$

If heat is added to a system from a source at constant temperature, then we can factor the temperature out of the integral and obtain

$$\Delta Q \leq T \Delta S.$$

The first law then gives us a corresponding upper bound on the work done by the system.

$$W = -\Delta U + \Delta Q \leq -\Delta U + T \Delta S$$

Now we can define the Helmholtz free energy, $F = U - TS$. In terms of the Helmholtz free energy, we have

$$W \leq F(A) - F(B) = -\Delta F$$

This relationship shows some of the utility of the free energy. It becomes more useful when we consider a system that is dynamically insulated; i.e., it cannot perform any work on its environment. Therefore,

$$\begin{aligned} 0 &\leq F(A) - F(B) \\ F(B) &\leq F(A) \end{aligned}$$

Therefore, for such a system, the Helmholtz free energy can never increase. This implies that if a dynamically insulated system is at a minimum of its Helmholtz free energy, then it is in a stable equilibrium.

Of course, most systems are not dynamically insulated: they are performing pressure-volume work. In general, this work is given by an integral and can't be simplified. However, if a process takes place at constant pressure P , then the work is simply $P\Delta V$. Therefore, we have

$$\begin{aligned} P\Delta V &\leq -\Delta F \\ \Delta(F + PV) &\leq 0 \end{aligned}$$

We call the quantity $F + PV = U - TS + PV = H - TS$ the Gibbs free energy G . We have defined G so that $\Delta G \leq 0$ for an isobaric, isothermal transformation. This means that if a system has its temperature and pressure held constant, the Gibbs free energy can only decrease. If the Gibbs free energy is at a local minimum, then the system is in stable equilibrium.

Armed with this result concerning the Gibbs free energy, we can derive the phase rule. Consider a system which has n components (i.e., chemical constituents) and f phases. Let m_{ik} be the mass of the k th

constituent present in the i th phase. If the system is in equilibrium, then any infinitesimal change must have no first-order effect on the Gibbs free energy. Consider a transformation in which a mass δm of the k th constituent transitions from the i th phase to the j th phase. Then the first-order change in free energy is

$$\delta G = \frac{\partial G}{\partial m_{jk}} \delta m - \frac{\partial G}{\partial m_{ik}} \delta m = 0$$

$$\frac{\partial G}{\partial m_{ik}} = \frac{\partial G}{\partial m_{jk}}$$

This gives us a set of equations relating the partials.

$$\frac{\partial G}{\partial m_{11}} = \frac{\partial G}{\partial m_{21}} = \dots = \frac{\partial G}{\partial m_{f1}}$$

$$\frac{\partial G}{\partial m_{12}} = \frac{\partial G}{\partial m_{22}} = \dots = \frac{\partial G}{\partial m_{f2}}$$

$$\vdots$$

$$\frac{\partial G}{\partial m_{1n}} = \frac{\partial G}{\partial m_{2n}} = \dots = \frac{\partial G}{\partial m_{fn}}$$

Each row contains $f - 1$ independent equations, for a total of $(f - 1)n$ independent equations. Now we need to count the number of independent variables. Only the ratios of the constituents of the phase are important, which gives $(n - 1)f$ variables, plus 2 for T and P . The degrees of freedom, v , is the difference between the number of variables and number of equations:

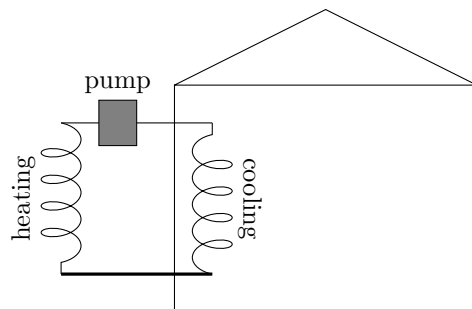
$$v = (n - 1)f + 2 - (f - 1)n = n - f + 2$$

$$v - n + f = 2$$

This is Gibbs' phase rule. You can verify that it gives the correct results for any of the examples considered before. It also gives sensible results for systems with more than one component, such as a mixture of two gases. The phase rule gives three degrees of freedom, which are the temperature, pressure, and the relative amounts of the gases.

8 Problems

1. Prove the Clausius Inequality: $\oint \frac{dq}{T} \leq 0$. Hint: the equal sign works for a reversible process. Prove that for the irreversible process, the less than sign holds.
2. The heat of vaporization of water is 44.01 kJ/mol and the normal boiling point of water is 100°C. Calculate the atmospheric pressure in Denver where the boiling point is 97.1°C.
3. Consider two gases in a container. One gas n_A is contained in a volume V_A , and the other gas n_B is contained in a volume V_B . The barrier is lifted and the gases mix together (all at a constant temperature). Determine the change in entropy of the system in terms of their respective mole fractions χ_A and χ_B . Choose a reversible path!
4. (USAPHO 2014) A room air conditioner is modeled as a heat engine run in reverse: an amount of heat Q_L is absorbed from the room at a temperature T_L into cooling coils containing a working gas; this gas is compressed adiabatically to a temperature T_H ; the gas is compressed isothermally in a coil outside the house, giving off an amount of heat Q_H ; the gas expands adiabatically back to a temperature T_L ; and the cycle repeats. An amount of energy W is input into the system every cycle through an electric pump. This model describes the air conditioner with the best possible efficiency.



Assume that the outside air temperature is T_H and the inside air temperature is T_L . The air-conditioner unit consumes electric power P . Assume that the air is sufficiently dry so that no condensation of water occurs in the cooling coils of the air conditioner.

- a. Derive an expression for the maximum rate at which heat is removed from the room in terms of the air temperatures T_H , T_L , and the power consumed by the air conditioner P .
 - b. The room is insulated, but heat still passes into the room at a rate $R = k\Delta T$, where ΔT is the temperature difference between the inside and the outside of the room and k is a constant. Find the coldest possible temperature of the room in terms of T_H , k , and P .
5. Consider a heat engine with an efficiency ϵ_1 attached to another with an efficiency ϵ_2 . That is, the exhaust of the first engine is used to power the second one. Determine the effective efficiency of the configuration.
 6. A mass m of water is initially at the same temperature as the surrounding air (both at a temperature T_1 .) You wish to cool the water to a temperature T_2 by transferring heat from the water to the air. What is the minimum work required to do this? Assume that the specific heat of water is c .