

Chapter 5: The Second Law

Rudolph Clausius is kind enough in his 1879 work “The Mechanical Theory of Heat” (Clausius, 1879) to indicate where we have been in our discussion of thermodynamics, as well as where we are going.

“The fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat.

- 1. The energy of the universe is constant.*
- 2. The entropy of the universe tends to a maximum.”*

— Rudolf Clausius, [The Mechanical Theory Of Heat](#)

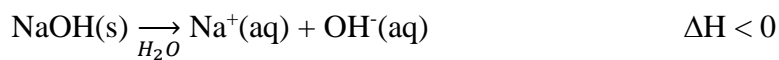
The **second law of thermodynamics**, which introduces us to the topic of entropy, is amazing in how it constrains what we can experience and what we can do in the universe. As Sean M. Carroll, a CalTech Theoretical physicist, suggests in a 2010 interview with Wired Magazine (Biba, 2010),

I’m trying to understand how time works. And that’s a huge question that has lots of different aspects to it. A lot of them go back to Einstein and spacetime and how we measure time using clocks. But the particular aspect of time that I’m interested in is the arrow of time: the fact that the past is different from the future. We remember the past but we don’t remember the future. There are irreversible processes. There are things that happen, like you turn an egg into an omelet, but you can’t turn an omelet into an egg.

We, as observers of nature, are time travelers. And the constraints on what we can observe as we move through time step from the **second law of thermodynamics**. But more than just understanding what the second law says, we are interested in what sorts of processes are possible. And even more to the point, what sorts of processes are **spontaneous**.

A spontaneous process is one that will occur without external forces pushing it. A process can be spontaneous even if it happens very slowly. Unfortunately, Thermodynamics is silent on the topic of how fast processes will occur, but it provides us with a powerful toolbox for predicting which processes will be spontaneous. But in order to make these predictions, a new thermodynamic law and variable is needed since the first law (which defined ΔU and ΔH) is insufficient.

Consider the following processes:



Both reactions will occur spontaneously, but one is exothermic and the other endothermic. So while it is intuitive to think that an exothermic process will be spontaneous, there is clearly more to the picture than simply the release of energy as heat when it comes to making a process spontaneous. The Carnot cycle (a theoretical cyclical heat engine) is a useful thought construct which can guide an exploration of the answer the question of why a process is spontaneous.

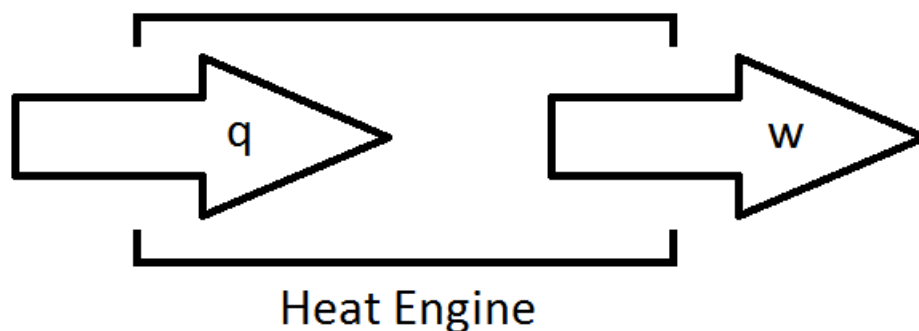
Heat Engines

Sadi Carnot (1796 – 1832) (Mendoza, 2016), a French physicist and engineer was very interested in the improvement of steam engines to perform the tasks needed by modern society.



Figure 1. Sadi Carnot (1796 - 1832)

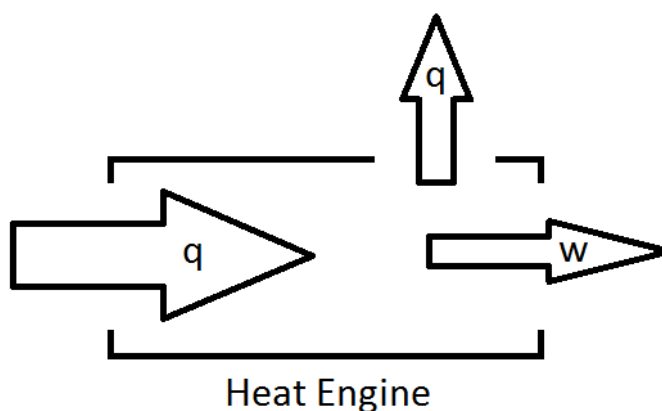
In order to simplify his analysis of the inner workings of an engine, Carnot devised a useful construct for examining what affect engine efficiency. His construct is the **heat engine**. The idea behind a heat engine is that it will take energy in the form of heat, and transform it into an equivalent amount of work.



Unfortunately, such a device is impractical. As it turns out, nature prevents the complete conversion of energy into work with perfect efficiency. This leads to an important statement of the **Second Law of Thermodynamics**.

It is impossible to convert heat into an equivalent amount of work without some other changes occurring in the universe.

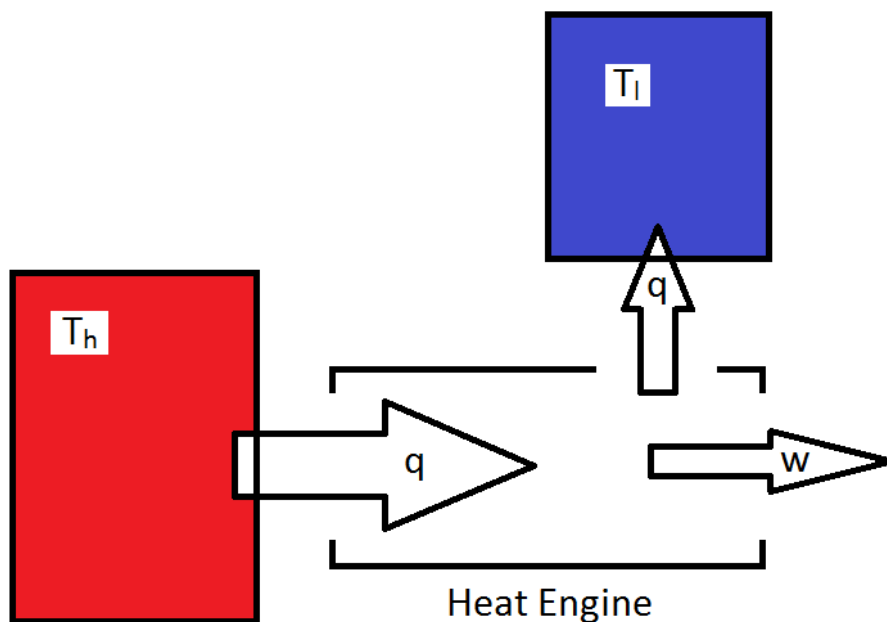
As such, a more reasonable picture of the heat engine is one which will allow for losses of energy to the surroundings.



The fraction of energy supplied to the engine that can be converted to work defines the efficiency of the engine.

The Carnot Cycle

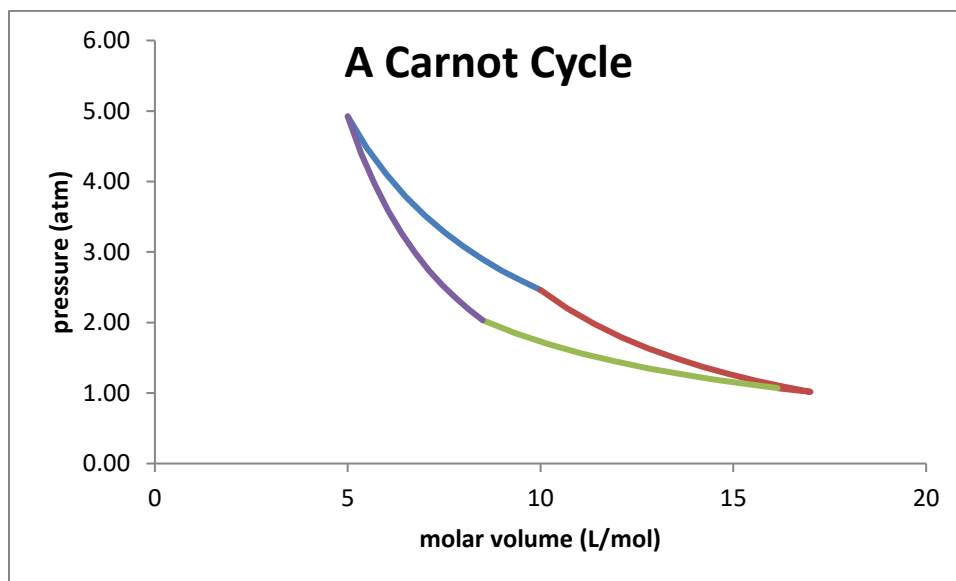
The Carnot cycle is a theoretical cyclic heat engine that can be used to examine what is possible for an engine for which the job is convert heat into work. For simplicity, all energy provided to the engine occurs isothermally (and reversibly) at a temperature T_h and all of the energy lost to the surroundings also occurs isothermally and reversibly at temperature T_l . In order to insure this, the system must change between the two temperatures adiabatically.



Thus, the cycle consists of four reversible legs, two of which are isothermal, and two of which are adiabatic.

- I. Isothermal expansion from p_1 and V_1 to p_2 and V_2 at T_h .
- II. Adiabatic expansion from p_2 , V_2 , T_h to p_3 , V_3 , T_l .
- III. Isothermal compression from p_3 and V_3 to p_4 and V_4 at T_l .
- IV. Adiabatic compression from p_4 , V_4 , T_l to p_1 , V_1 , T_h .

Plotted on a pressure-volume diagram, the Carnot cycle looks as follows:



Because this is a closed cycle (the ending state is identical initial state) any state function must have a net change of zero as the system moves around the cycle. Furthermore, the efficiency of the engine can be expressed by the net amount of work the engine produces per unit of heat supplied to power the engine.

$$\epsilon = \frac{w_{net}}{q_h}$$

In order to examine this expression, it is useful to write down expressions for the heat and work flow in each of the four legs of the engine cycle.

Leg	Heat	Work
I	$q_h = nRT_h \ln(V_2/V_1)$	$-nRT_h \ln(V_2/V_1)$
II	0	$C_v(T_l - T_h)$
III	$q_l = nRT_l \ln(V_4/V_3)$	$-nRT_l \ln(V_4/V_3)$
IV	0	$C_v(T_h - T_l)$

The total amount of work done is given by the sum of terms in the third column. Clearly the terms for the two adiabatic legs cancel (as they have the same magnitude, but opposite signs.) So the total work done is given by

$$w_{tot} = -nRT_h \ln\left(\frac{V_2}{V_1}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

The efficiency of the engine can be defined as the total work produced per unit of energy provided by the high temperature reservoir.

$$\epsilon = \frac{|w_{tot}|}{q_h}$$

or

$$\epsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)}$$

That expression has a lot of variables, but it turns out that it can be simplified dramatically. It turns out that by the choice of pathways connecting the states places a very important restriction on the relative values of V_1 , V_2 , V_3 and V_4 . To understand this, we must consider how the work of adiabatic expansion is related to the initial and final temperatures and volumes. In Chapter 3, it was shown that the initial and final temperatures and volumes of an adiabatic expansion are related by

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$$V_i T_i^{\frac{C_V}{R}} = V_f T_f^{\frac{C_V}{R}}$$

or

$$\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^{\frac{C_V}{R}}$$

Using the adiabatic expansion and compression legs (II and IV), this requires that

$$\frac{V_2}{V_3} = \left(\frac{T_l}{T_h}\right)^{\frac{C_V}{R}} \quad \text{and} \quad \frac{V_1}{V_4} = \left(\frac{T_h}{T_l}\right)^{\frac{C_V}{R}}$$

Since the second terms are reciprocals of one another, the first terms must be as well!

$$\frac{V_2}{V_3} = \frac{V_4}{V_1}$$

A simple rearrangement shows that

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

This is very convenient! It is what allows for the simplification of the efficiency expression.

$$\varepsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)}$$

becomes

$$\varepsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) - nRT_l \ln\left(\frac{V_2}{V_1}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)}$$

Canceling $nR \ln\left(\frac{V_2}{V_1}\right)$ in the numerator and denominator yields

$$\varepsilon = \frac{T_h - T_l}{T_h}$$

This expression gives the maximum efficiency and depends only on the high and low temperatures!

Also, it should be noted that the heat engine can be run backwards. By providing work to the engine, it can be forced to draw heat from the low temperature reservoir and dissipate it into the high temperature reservoir. This is how a refrigerator or heat pump works. The limiting efficiency of such a device can also be calculated using the temperatures of the hot and cold reservoirs.

Example:

What is the maximum efficiency of a freezer set to keep ice cream at a cool -10°C , which it is operating in a room that is 25°C ? What is the minimum amount of energy needed to remove 1.0 J from the freezer and dissipate it into the room?

Solution:

The efficiency for the refrigerator is given by

$$\varepsilon = \frac{T_h - T_l}{T_l}$$

Converting the temperatures to an absolute scale, the efficiency can be calculated as

$$\varepsilon = \frac{298\text{ K} - 263\text{ K}}{263\text{ K}} = 0.1331$$

This value can be used in the following manner

$$\text{energy}_{\text{transferred}} = \varepsilon(\text{work}_{\text{required}})$$

So

$$1.0\text{ J} = 0.1331(w)$$

or

$$w = 7.5\text{ J}$$

It is interesting to note that any arbitrary closed cyclical process can be described as a sum of infinitesimally small Carnot cycles, and so all of the conclusions reached for the Carnot cycle apply to any cyclical process.

Entropy

In addition to learning that the efficiency of a Carnot engine depends only on the high and low temperatures, more interesting things can be derived through the exploration of this system. For example, consider the total heat transferred in the cycle:

$$q_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

Making the substitution

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

the total heat flow can be seen to be given by

$$q_{tot} = -nRT_h \ln\left(\frac{V_4}{V_3}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

It is clear that the two terms do not have the same magnitude, unless $T_h = T_l$. This is sufficient to show that q is not a state function, since its net change around a closed cycle is not zero (as any value of a state function must be.) However, consider what happens when the sum of q/T is considered:

$$\begin{aligned} \sum \frac{q}{T} &= \frac{-nRT_h \ln\left(\frac{V_4}{V_3}\right)}{T_h} + \frac{nRT_l \ln\left(\frac{V_4}{V_3}\right)}{T_l} \\ &= -nR \ln\left(\frac{V_4}{V_3}\right) + nR \ln\left(\frac{V_4}{V_3}\right) \\ &= 0 \end{aligned}$$

This is the behavior expected for a state function! It leads to the definition of entropy in differential form,

$$dS \equiv \frac{dq_{rev}}{T}$$

In general, dq_{rev} will be larger than dq (since the reversible pathway defines the maximum heat flow.) So, it is easy to calculate entropy changes, as one needs only to define a reversible pathway that connects the initial and final states, and then integrate dq/T over that pathway. And since ΔS is defined using q for a reversible pathway, ΔS is independent of the actual path a system follows to undergo a change.

Calculating entropy changes

Entropy changes are fairly easy to calculate so long as one knows initial and final state. For example, if the initial and final volume are the same, the entropy can be calculated by assuming a reversible, isochoric pathway and determining an expression for $\frac{dq}{T}$. That term can then be integrated from the initial condition to the final conditions to determine the entropy change.

Isothermal Changes

If the initial and final temperatures are the same, the most convenient reversible path to use to calculate the entropy is an isothermal pathway. As an example, consider the isothermal expansion of an ideal gas from V_1 to V_2 . As was derived in Chapter 3,

$$dq = nRT \frac{dV}{V}$$

So dq/T is given by

$$\frac{dq}{T} = nR \frac{dV}{V}$$

and so

$$\Delta S = \int \frac{dq}{T} = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \left(\frac{V_2}{V_1} \right)$$

Example:

Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.

Solution:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) \ln \left(\frac{48.8 \text{ L}}{24.4 \text{ L}} \right)$$

$$\Delta S = 5.76 \frac{\text{J}}{\text{K}}$$

Isobaric Changes

For changes in which the initial and final pressures are the same, the most convenient pathway to use to calculate the entropy change is an isobaric pathway. In this case, it is useful to remember that

$$dq = nC_p dT$$

So

$$\frac{dq}{T} = nC_p \frac{dT}{T}$$

Integration from the initial to final temperature is used to calculate the change in entropy. If the heat capacity is constant over the temperature range

$$\int_{T_1}^{T_2} \frac{dq}{T} = nC_p \int_{T_1}^{T_2} \frac{dT}{T} = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. For example, if C_p can be expressed as

$$C_p = a + bT + \frac{c}{T^2}$$

ΔS takes the form

$$\int_{T_1}^{T_2} \frac{dq}{T} = n \int_{T_1}^{T_2} \left(\frac{a + bT + \frac{c}{T^2}}{T} \right) dT$$

which simplifies to

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a}{T} + b + \frac{c}{T^3} \right) dT$$

or

$$\Delta S = n \left[a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) - \frac{c}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \right]$$

Isochoric Changes

Similarly to the case of constant pressure, it is fairly simple to calculate ΔS . Since

$$dq = nC_V dT$$

$\frac{dq}{T}$ is given by

$$\frac{dq}{T} = nC_V \frac{dT}{T}$$

And so for changes over which C_V is independent of the temperature ΔS is given by

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

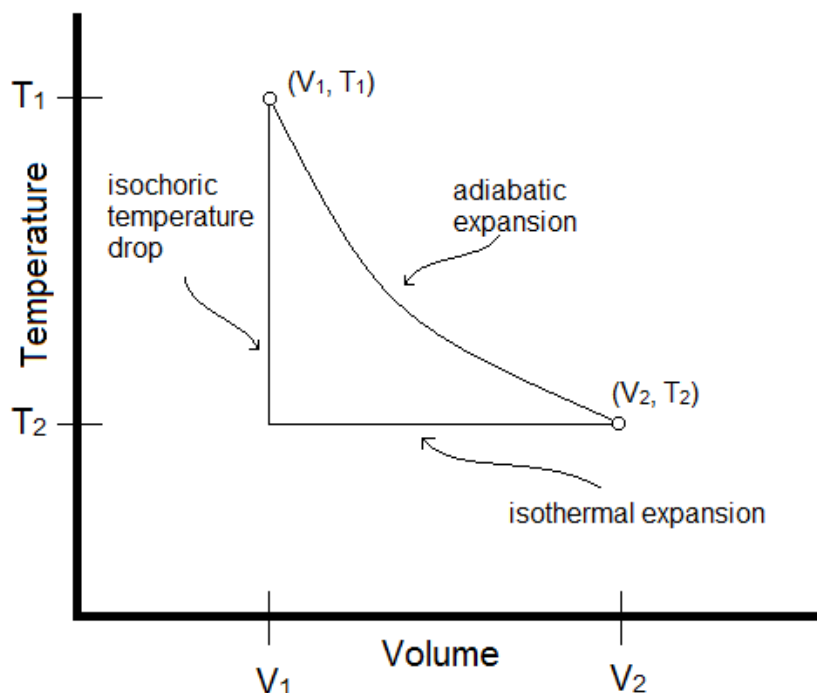
Adiabatic Changes

The easiest pathway for which to calculate entropy changes is an adiabatic pathway. Since $dq = 0$ for an adiabatic change, $dS = 0$ as well. But what if we forget this? Is there another way to show that the entropy change for an adiabatic expansion (for example) will be zero?

The answer, of course, is that because entropy is a state function, we can define a more convenient step-wise pathway, calculate the entropy change for each step, and show that they add to a total entropy change of zero. Since we know the relationship between the temperatures and volumes associated with an adiabatic expansion of an ideal gas

$$V_1 T_1^{\frac{C_V}{R}} = V_2 T_2^{\frac{C_V}{R}}$$

a very convenient step-wise pathway will be an isochoric temperature drop followed by an isothermal expansion. Graphically, this kind of a break down might look as follows:



The entropy change for the isothermal expansion of an ideal gas from V_1 to V_2 is given by

$$\Delta S_T = nR \ln \left(\frac{V_2}{V_1} \right)$$

And for an isochoric temperature drop, the entropy can be calculated from

$$\Delta S_V = nC_V \ln \left(\frac{T_2}{T_1} \right)$$

It will be useful if both terms ΔS_T and ΔS_V can be expressed in terms of either the temperature change or the volume change. Using the relationship between volume and temperature derived earlier for an adiabatic expansion, it can easily be shown that

$$\frac{V_2}{V_1} = \left(\frac{T_1}{T_2} \right)^{\frac{C_V}{R}}$$

Substituting this into the expression for ΔS_T produces

$$\Delta S_T = nR \ln \left(\frac{T_1}{T_2} \right)^{\frac{C_V}{R}}$$

$$\begin{aligned}
 &= nR \ln \left(\frac{T_2}{T_1} \right)^{-\frac{C_V}{R}} \\
 &= -(nR) \left(\frac{C_V}{R} \right) \ln \left(\frac{T_2}{T_1} \right)
 \end{aligned}$$

or

$$\Delta S_T = -nC_V \ln \left(\frac{T_2}{T_1} \right)$$

Finally adding the two together

$$\Delta S_{tot} = \Delta S_T + \Delta S_V$$

or

$$\Delta S_{tot} = -nC_V \ln \left(\frac{T_2}{T_1} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right) = 0$$

which is exactly what we expected since $dq = 0$ must hold at all points along the adiabatic expansion pathway, and

$$\Delta S = \int \frac{dq}{T}$$

Phase Changes

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{\Delta H_{phase}}{T}$$

Example:

The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

Solution:

$$\begin{aligned}
 \Delta S &= \frac{(1.0 \text{ mol}) \left(6010 \frac{\text{J}}{\text{mol}} \right)}{273 \text{ K}} \\
 \Delta S &= 22 \frac{\text{J}}{\text{K}}
 \end{aligned}$$

Comparing the System and the Surroundings

It is oftentimes important (for reasons that will be discussed in the next section) to calculate both the entropy change of the system as well as that of the surroundings. Depending on the size of the surroundings, they can provide or absorb as much heat as is needed for a process without changing temperature. As such, it is oftentimes a very good approximation to consider the changes to the surroundings as happening isothermally, even though it may not be the case for the system (which is generally smaller.)

Example:

Consider 18.02 g (1.00 mol) of ice melting at 273 K in a room that is 298 K. Calculate ΔS for the ice, the surrounding room, and of the universe. ($\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$)

Solution:

For the process, $q_{\text{ice}} = -q_{\text{room}}$

$$q = n\Delta H_{\text{fus}} = (1.00 \text{ mol}) \left(6010 \frac{\text{J}}{\text{mol}} \right) = 6010 \text{ J}$$

For the ice:

$$\Delta S_{\text{ice}} = \frac{q_{\text{ice}}}{T_{\text{ice}}} = \frac{6010 \text{ J}}{273 \text{ K}} = 22.0 \frac{\text{J}}{\text{K}}$$

For the room:

$$\Delta S_{\text{room}} = \frac{q_{\text{room}}}{T_{\text{room}}} = \frac{-6010 \text{ J}}{298 \text{ K}} = -20.2 \frac{\text{J}}{\text{K}}$$

For the universe:

$$\Delta S_{\text{univ}} = \Delta S_{\text{ice}} + \Delta S_{\text{room}}$$

$$\Delta S_{\text{univ}} = 22.0 \frac{\text{J}}{\text{K}} - 20.2 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{univ}} = 1.8 \frac{\text{J}}{\text{K}}$$

Note: ΔS_{univ} is positive, which is characteristic of a spontaneous change!

Example:

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A 10.0 g piece of metal ($C = 0.250 \text{ J/g } ^\circ\text{C}$) initially at 95°C is placed in 25.0 g of water initially at 15°C in an insulated container. Calculate the final temperature of the metal and water once the system has reached thermal equilibrium. Also, calculate the entropy change for the metal, the water, and the entire system.

Solution:

Heat will be transferred from the hot metal to the cold water. Since it has nowhere else to go, the final temperature can be calculated from the expression

$$q_w = -q_m$$

where q_w is the heat absorbed by the water, and q_m is the heat lost by the metal. And since

$$q = mC\Delta T$$

it follows that

$$(25.0 \text{ g}) \left(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (T_f - 15^\circ\text{C}) = -(10.0 \text{ g}) \left(0.250 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (T_f - 95^\circ\text{C})$$

A bit of algebra determines the final temperature to be:

$$T_f = 16.9^\circ\text{C}.$$

To get the entropy changes, use the expression:

$$\Delta S = mC \ln \left(\frac{T_f}{T_i} \right)$$

So, for the water:

$$\Delta S_{\text{water}} = (25.0 \text{ g}) \left(4.184 \frac{\text{J}}{\text{g K}} \right) \ln \left(\frac{289.9 \text{ K}}{288 \text{ K}} \right)$$

$$\Delta S_{\text{water}} = 0.689 \frac{\text{J}}{\text{K}}$$

And for the metal:

$$\Delta S_{\text{metal}} = (10.0 \text{ g}) \left(0.250 \frac{\text{J}}{\text{g K}} \right) \ln \left(\frac{289.9 \text{ K}}{368 \text{ K}} \right)$$

$$\Delta S_{\text{metal}} = -0.596 \frac{\text{J}}{\text{K}}$$

For the system:

$$\Delta S_{sys} = \Delta S_{water} + \Delta S_{metal}$$

$$\Delta S_{sys} = 0.689 \frac{J}{K} - 0.596 \frac{J}{K}$$

$$\Delta S_{sys} = 0.093 \frac{J}{K}$$

Note: The total entropy change is positive, suggesting that this will be a spontaneous process. This should make some sense since one expects heat to flow from the hot metal to the cool water rather than the other way around. Also, note that the sign of the entropy change is positive for the part of the system that is absorbing the heat, and negative for the part losing the heat.

In summary, ΔS can be calculated for a number of pathways fairly conveniently.

Pathway	$\Delta S_{sys} = \int \frac{dq_{rev}}{T_{sys}}$		$\Delta S_{surr} = -\frac{q_{sys}}{T_{surr}}$
Adiabatic	0		$\Delta S_{surr} = -\frac{q_{sys}}{T_{surr}}$
Isothermal	$\frac{q_{rev}}{T}$	$nR \ln \left(\frac{V_2}{V_1}\right)^*$	
Isobaric	$nC_p \ln \left(\frac{T_2}{T_1}\right)$		
Isochoric	$nC_V \ln \left(\frac{T_2}{T_1}\right)$		
Phase Change	$\frac{\Delta H_{phase}}{T}$		

*for an ideal gas

And

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}.$$

This calculation is important as ΔS_{univ} provides the criterion for spontaneity for which we were searching from the outset. This also suggests a new way to state the second law:

The entropy of the universe increases in any spontaneous change.

If we think of “the direction of spontaneous” to be the natural direction of chance, we can see that entropy and the second law are tied inexorably with the natural direction of the flow of time. Basically, we can expect the entropy of the universe to continue to increase as time flows into the future. We can overcome this natural tendency to greater entropy by doing work on a system. This is why it requires such great effort, for example, to straighten a messy desk, but little effort for the desk to get messy over time.

The Second Law can be summed up in a very simple mathematical expression called the **Clausius Inequality**.

$$\Delta S_{\text{universe}} \leq 0$$

which must be true for any spontaneous process. It isn't the most convenient criterion for spontaneity, but it will do for now. In the next chapter, we will derive a criterion which is more useful to us as chemists, who would rather focus on the system itself rather than both the system and its surroundings. Another statement of the Clausius theorem is

$$\oint \frac{dq}{T} \leq 0$$

with the only condition of the left hand side equaling zero is if the system transfers all heat reversibly.

Entropy and Chaos

A common interpretation of entropy is that it is somehow a measure of chaos or randomness. There is some utility in that concept. Given that entropy is a measure of the dispersal of energy in a system, the more chaotic a system is, the greater the dispersal of energy will be, and thus the greater the entropy will be.

Ludwig Boltzmann (1844 – 1906) (O'Connor & Robertson, 1998) understood this concept well, and used it to derive a statistical approach to calculating entropy. Boltzmann proposed a method for calculating the entropy of a system based on the number of energetically equivalent ways a system can be constructed.



Figure 2. Ludwig Boltzmann (1844 - 1906)

Boltzmann proposed an expression, which in its modern form is:

$$S = k_B \ln(W)$$

This rather famous equation is etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics.



Example:

Calculate the entropy of a carbon monoxide crystal, containing 1.00 mol of CO, and assuming that the molecules are randomly oriented in one of two equivalent orientations.

Solution:

Using the Boltzmann formula

$$S = N k_B \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$S = \left(1.00 \text{ mol} \cdot \frac{6.022 \times 10^{23}}{\text{mol}} \right) \left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) \ln(2)$$

$$S = 5.76 \frac{\text{J}}{\text{K}}$$

The Third Law of Thermodynamics

One important consequence of Boltzmann's proposal is that a perfectly ordered crystal (i.e. one that has only one energetic arrangement in its lowest energy state) will have an entropy of 0. This makes entropy qualitatively different than other thermodynamic functions. For example, in the case of enthalpy, it is impossible to have a zero to the scale without setting an arbitrary reference (which is that the enthalpy of formation of elements in their standard states is zero.) But entropy has a natural zero! It is the state at which a system has perfect order. This also has another important consequence, in that it suggests that there must also be a zero to the temperature scale. These consequences are summed up in the **Third Law of Thermodynamics**.

The entropy of a perfectly ordered crystal at 0 K is zero.

This also suggests that absolute molar entropies can be calculated by

$$S = \int_0^T \frac{C}{T} dT$$

where C is the heat capacity. An entropy value determined in this manner is called a **Third Law Entropy**.

Naturally, the heat capacity will have some temperature dependence. It will also change abruptly if the substance undergoes a phase change.

Unfortunately, it is exceedingly difficult to measure heat capacities very near zero K. Fortunately, many substances follow the **Debye Extrapolation** in that at very low temperatures, their heat capacities are proportional to T^3 . Using this assumption, we have a temperature dependence model that allows us to extrapolate absolute zero based on the heat capacity measured at as low a temperature as can be found.

Example:

SiO₂ is found to have a molar heat capacity of 0.777 J mol⁻¹ K⁻¹ at 15 K (Yamashita, et al., 2001). Calculate the molar entropy of SiO₂ at 15 K.

Solution:

Using the Debye model, the heat capacity is given by

$$C_p = aT^3$$

The value of a can be determined by

$$0.777 \frac{\text{J}}{\text{mol K}} = a (15 \text{ K})^3$$

$$a = 0.000230 \frac{J}{mol K^4}$$

The entropy is then calculated by

$$S = \int_0^{15 K} \left(\frac{aT^3}{T} \right) dT$$

$$S = 0.000230 \frac{J}{mol K^4} \int_0^{15 K} T^2 dT$$

$$S = 0.000230 \frac{J}{mol K^4} \left[\frac{T^3}{3} \right]_0^{15 K}$$

$$S = \frac{0.000230}{3} \frac{J}{mol K^4} (15 K)^3$$

$$S = 0.259 \frac{J}{mol K}$$

Calculating a third Law Entropy

Start at 0 K, and go from there!

Adiabatic Compressibility

In Chapter 4, we learned about the isothermal compressibility, κ_T , which is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

κ_T is a very useful quantity, as it can be measured for many different substances and tabulated. Also, as we will see in the next chapter, it can be used to evaluate several different partial derivatives involving thermodynamic variables.

In his seminal work, *Philosophiae Naturalis Principia Mathematica* (Newton, 1723), Isaac Newton (1643 - 1727) (Doc) calculated the speed of sound through air, assuming that sound was carried by isothermal compression waves. His calculated value of 949 m/s was about 15% smaller than experimental determinations. He accounted for the difference by pointing to “non-ideal effects”. But it turns out that his error, albeit an understandable one (since sound waves do not appear to change bulk air temperatures) was that the compression waves are adiabatic, rather than isothermal. As such, there are small temperature oscillations that occur due

to the adiabatic compression followed by expansion of the gas carrying the sound waves. The oversight was correct by Pierre-Simon Laplace (1749 – 1827) (O'Connor & Robertson, Pierre-Simon Laplace, 1999).

Laplace modeled the compression waves using the **adiabatic compressibility**, κ_S defined by

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

Since the entropy is defined by

$$dS = \frac{dq_{rev}}{T}$$

it follows that any adiabatic pathway ($dq = 0$) is also **isentropic** ($dS = 0$), or proceeds at constant entropy.

A couple of interesting conclusions can be reached by following the derivation of an expression for the speed of sound where the sound waves are modeled as adiabatic compression waves. We can begin by expanding the description of κ_S by using Partial Derivative Transformation Type II. Applying this, the adiabatic compressibility can be expressed

$$\kappa_S = \frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_p \left(\frac{\partial S}{\partial p} \right)_V$$

or by using transformation type I

$$\kappa_S = \frac{1}{V} \frac{\left(\frac{\partial S}{\partial p} \right)_V}{\left(\frac{\partial S}{\partial V} \right)_p}$$

Using a simple chain rule, the partial derivatives can be expanded to get something a little easier to evaluate:

$$\kappa_S = \frac{1}{V} \frac{\left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial p} \right)_V}{\left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial T}{\partial V} \right)_p}$$

The utility here is that

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$$

This means that

$$\kappa_S = \frac{C_V}{C_p} \left(\frac{1}{V} \frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p} \right)$$

Simplifying what is in the parenthesis yields

$$\begin{aligned} \kappa_S &= \frac{C_V}{C_p} \left(\frac{1}{V} \frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p} \right) \\ &= \frac{C_V}{C_p} \left(-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \right) \\ &= \frac{C_V}{C_p} \kappa_T \end{aligned}$$

As will be shown in the next chapter, C_p is always bigger than C_V , so κ_S is always smaller than κ_T .

But there is more! We can use this methodology to revisit how pressure affects volume along an adiabat. In order to do this, we would like to evaluate the partial derivative

$$\left(\frac{\partial V}{\partial p}\right)_S = ?$$

This can be expanded in the same way as above

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial S}\right)_V}$$

And further expand

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V}$$

And as before, noting that $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ and $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$, this can be simplified to

$$\begin{aligned}\left(\frac{\partial V}{\partial p}\right)_s &= -\frac{C_v}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_v \\ &= \frac{C_v}{C_p}\left(\frac{\partial V}{\partial p}\right)_T\end{aligned}$$

Or defining $\gamma = C_p/C_v$, this can be easily rearranged to

$$\gamma\left(\frac{\partial V}{\partial p}\right)_s = \left(\frac{\partial V}{\partial p}\right)_T$$

The right-hand derivative is easy to evaluate if we assume a specific equation of state. For an ideal gas,

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2} = -\frac{V}{p}$$

Substitution yields

$$\gamma\left(\frac{\partial V}{\partial p}\right)_s = -\frac{V}{p}$$

which is now looking like a form that can be integrated. Separation of variables yields

$$\gamma \frac{dV}{V} = \frac{dp}{p}$$

And integration (assuming that γ is independent of volume) yields

$$\gamma \int_{V_1}^{V_2} \frac{dV}{V} = \int_{p_1}^{p_2} \frac{dp}{p}$$

or

$$\gamma \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{p_2}{p_1}\right)$$

which is easily manipulated to show that

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad \text{or} \quad pV^\gamma = \text{constant}$$

which is what we previously determined for the behavior of an ideal gas along an adiabat.

Finally, it should be noted that the correct expression for the speed of sound is given by
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$$v_{\text{sound}} = \sqrt{\frac{1}{\rho \kappa_S}}$$

where ρ is the density of the medium. For an ideal gas, this expression becomes

$$v_{\text{sound}} = \sqrt{\frac{\gamma RT}{M}}$$

where M is the molar mass of the gas. Isaac Newton's derivation, based on the idea that sound waves involved isothermal compressions, would produce a result which is missing the factor of γ , accounting for the systematic deviation from experiment which he observed.

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Vocabulary and Concepts

adiabatic compressibility	119	Clausius theorem.....	115
Carnot cycle	100	criterion for spontaneity	115

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Learning Objectives

After mastering the material presented in this chapter, one will be able to:

1. Describe a Carnot engine and derive a relationship for its efficiency of converting heat into work, in terms of the two temperatures at which the engine operates.
2. Define entropy and be able to calculate entropy changes for systems (and the surroundings) undergoing changes which are definable as following various pathways, including constant temperature, constant pressure, constant volume, and adiabatic pathways.
3. Relate entropy to disorder in a crystal based on the number of equivalent orientations a single formula unit may take within the crystal.
4. State the Third Law of Thermodynamics, and use it to calculate total entropies for substances at a given temperature.
5. Understand how isothermal compressibility differs from adiabatic compressibility and relate that difference to the measurement of the speed of sound waves traveling through a gas medium.

Problems

1. What is the minimum amount of work needed to remove 10.0 J of energy from a freezer at -10.0 °C, depositing the energy into a room that is 22.4 °C?
2. Consider the isothermal, reversible expansion of 1.00 mol of a monatomic ideal gas ($C_V = 3/2 R$) from 10.0 L to 25.0 L at 298 K. Calculate q , w , ΔU , ΔH , and ΔS for the expansion.
3. Consider the isobaric, reversible expansion of 1.00 mol of a monatomic ideal gas ($C_p = 5/2 R$) from 10.0 L to 25.0 L at 1.00 atm. Calculate q , w , ΔU , ΔH , and ΔS for the expansion.
4. Consider the isochoric, reversible temperature increase of 1.00 mol of a monatomic ideal gas ($C_V = 3/2 R$) occupying 25.0 L from 298 K to 345 K. Calculate q , w , ΔU , ΔH , and ΔS for the process.

5. Consider the adiabatic expansion of 1.00 mol of a monatomic ideal gas ($C_V = 3/2 R$) from 10.0 L at 273 K to a final volume of 45.0 L. Calculate ΔT , q , w , ΔU , ΔH , and ΔS for the expansion.
6. 15.0 g of ice ($\Delta H_{\text{fus}} = 6.009 \text{ kJ/mol}$) at 0 °C sits in a room that is at 21 °C. The ice melts to form liquid at 0 °C. Calculate the entropy change for the ice, the room, and the universe. Which has the largest magnitude?
7. 15.0 g of liquid water ($C_p = 75.38 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$) at 0 °C sits in a room that is at 21 °C. The liquid warms from 0 °C to 21 °C. Calculate the entropy change for the liquid, the room, and the universe. Which has the largest magnitude?
8. Calculate the entropy change for taking 12.0 g of H_2O from the solid phase ($C_p = 36.9 \text{ J mol}^{-1} \text{ K}^{-1}$) at -12.0 °C to liquid ($C_p = 75.2 \text{ J mol}^{-1} \text{ K}^{-1}$) at 13.0 °C. The enthalpy of fusion for water is $\Delta H_{\text{fus}} = 6.009 \text{ kJ/mol}$.
9. Using data found at http://chem.libretexts.org/Reference/Reference_Tables/Thermodynamics_Tables/T1%3A_Standard_Thermodynamic_Quantities, calculate the standard reaction entropies (ΔS°) for the following reactions at 298 K.
 - a. $\text{CH}_3\text{CH}_2\text{OH(l)} + 3 \text{ O}_2\text{(g)} \rightarrow 2 \text{ CO}_2\text{(g)} + 3 \text{ H}_2\text{O(l)}$
 - b. $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)} + 12 \text{ O}_2 \rightarrow 12 \text{ CO}_2\text{(g)} + 11 \text{ H}_2\text{O(l)}$
 - c. $2 \text{ POCl}_3\text{(l)} \rightarrow 2 \text{ PCl}_3\text{(l)} + \text{O}_2\text{(g)}$
 - d. $2 \text{ KBr(s)} + \text{Cl}_2\text{(g)} \rightarrow 2 \text{ KCl(s)} + \text{Br}_2\text{(l)}$
 - e. $\text{SiH}_4\text{(g)} + 2 \text{ Cl(g)} \rightarrow \text{SiCl}_4\text{(l)} + 2 \text{ H}_2\text{(g)}$
10. 1.00 mole of an ideal gas is taken through a cyclic process involving three steps:
 - I. Isothermal expansion from V_1 to V_2 at T_1
 - II. Isochoric heating from, T_1 to T_2 at V_2
 - III. Adiabatic compression from V_2 to V_1
 - a. Graph the process on a V-T diagram.
 - b. Find q , w , ΔU , and ΔS for each leg. (If you want, you can find ΔH too!)
 - c. Use the fact that ΔS for the entire cycle must be zero (entropy being a state function and all ...), determine the relationship between V_1 and V_2 in terms of C_V , T_1 and T_2 .
11. 2.00 moles of a monatomic ideal gas ($C_V = 3/2 R$) initially exert a pressure of 1.00 atm at 300.0 K. The gas undergoes the following three steps, all of which are reversible: I. isothermal compression to a final pressure of 2.00 atm, II. Isobaric temperature increase to a final temperature of 400.0 K, and III. A return to the initial state along a pathway in which

$$p = a + bT$$

where a and b are constants. Sketch the cycle on a pressure-temperature plot, and calculate ΔU and ΔS for each of the legs. Are ΔU and ΔS zero for the sum of the three legs?

12. A 10.0 g piece of iron ($C = 0.443 \text{ J/g } ^\circ\text{C}$) initially at $97.6 \text{ }^\circ\text{C}$ is placed in 50.0 g of water ($C = 4.184 \text{ J/g } ^\circ\text{C}$) initially at $22.3 \text{ }^\circ\text{C}$ in an insulated container. The system is then allowed to come to thermal equilibrium. Assuming no heat flow to or from the surroundings, calculate
- the final temperature of the metal and water
 - the change in entropy for the metal
 - the change in entropy for the water
 - the change in entropy for the universe
13. Consider a crystal of CHFCIBr as having four energetically equivalent orientations for each molecule. What is the expected residual entropy at 0 K for 2.50 mol of the substance?
14. A sample of a certain solid is measured to have a constant pressure heat capacity of $0.436 \text{ J mol}^{-1} \text{ K}^{-1}$ at 10.0 K. Assuming the Debye extrapolation model

$$C_p(T) = aT^3$$

holds at low temperatures, calculate the molar entropy of the substance at 12.0 K.