

Chapter 20

The Second Law of Thermodynamics

When we previously studied the *first law of thermodynamics*, we observed how conservation of energy provided us with a relationship between ΔU , Q , and W , namely $\Delta U = Q - W$. However, it's still possible to have "heat flow" from a cold body to a warmer body and not violate the first law of thermodynamics. We need another guiding principle that we can apply to thermodynamic systems that will describe why heat should flow from "hot" objects to "cold" objects.

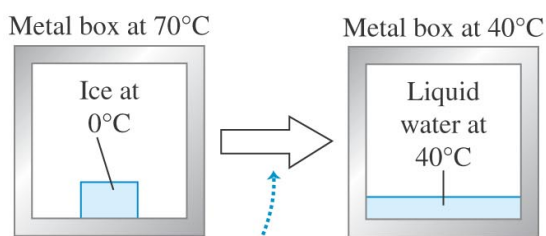
In this chapter we will discover a new state variable called *entropy* and learn how changes in entropy will unambiguously determine the heat flow "in" or "out" of a thermodynamic system.

1 Directions of Thermodynamic Processes

Thermodynamic processes that occur in nature are all **irreversible processes**. These are processes that proceed spontaneously in one direction but not the other. The flow of heat from a *hot* body to a *cold* body is irreversible.

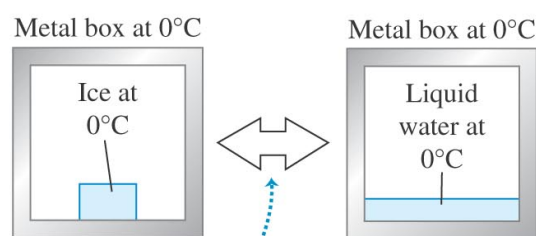
However, we can think of a class of idealized processes that would be reversible. An idealized **reversible process** is always very close to being in thermodynamic equilibrium within itself and with its surroundings. For example, heat flow between two bodies whose temperatures differ only infinitesimally can be reversed by making only a very small change in one temperature or the other.

(a) A block of ice melts *irreversibly* when we place it in a hot (70°C) metal box.



Heat flows from the box into the ice and water, never the reverse.

(b) A block of ice at 0°C can be melted *reversibly* if we put it in a 0°C metal box.



By infinitesimally raising or lowering the temperature of the box, we can make heat flow into the ice to melt it or make heat flow out of the water to refreeze it.

While a reversible process is an idealization that can never be precisely attained in the real world, making temperature gradients and the pressure differences in the substance very small, we can keep the system very close to equilibrium states and make the process nearly reversible. For this reason, reversible processes are called **equilibrium processes**, with the system always in thermodynamic equilibrium.

2 Heat Engines

Any device that transforms heat partly into work or mechanical energy is called a **heat engine**. The simplest kind of engine to analyze is one in which the working substance undergoes a **cyclic process**. In summary, a heat engine absorbs thermal energy from a high-temperature reservoir, performs some mechanical work, and discards or rejects heat to a low-temperature reservoir. Applying the first law of thermodynamics to a cyclic process, we see that $Q = W$.

A typical heat engine can be described by the following picture.

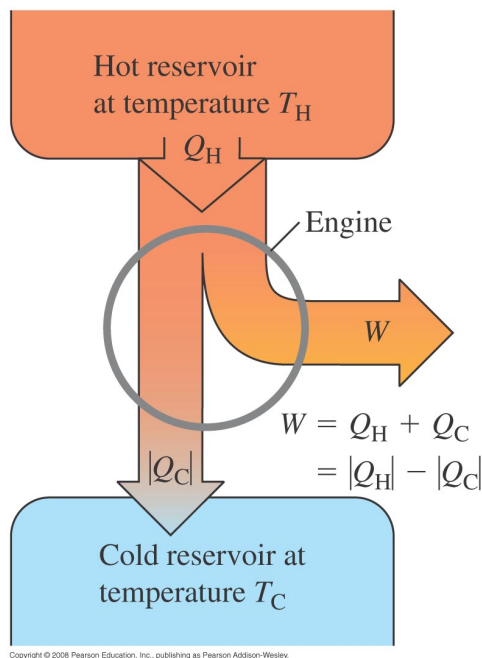


Figure 1: Schematic energy-flow diagram for a heat engine. Figure 20.3 from University Physics 15th edition.

The **thermal efficiency** of an engine, denoted by e , is the quotient:

$$e = \frac{W}{Q_H} \quad (1)$$

Ex. 1 A diesel engine performs 2200 J of mechanical work and discards 4300 J of heat each cycle. a) How much heat must be supplied to the engine in each cycle? What is the thermal efficiency of the engine?

Ex. 34 A heat engine takes 0.350 mol of a diatomic ideal gas around the cycle shown in the pV -diagram of **Fig. P20.34**. Process 1→2 is at constant volume, process 2→3 is adiabatic, and process 3→1 is at a constant pressure of 1.00 atm. The value of γ for this gas is 1.40. a) Find the pressure and volume at points 1, 2, and 3. b) Calculate Q , W , and ΔU for each of the three processes. c) Find the net work done by the gas in the cycle. d) Find the net heat flow into the engine in one cycle. e) What is the thermal efficiency of the engine? How does this compare to the efficiency of a Carnot-cycle engine operating between the same minimum and maximum temperatures T_1 and T_2 ? We'll come back and answer this last question later once we've investigated the Carnot cycle.

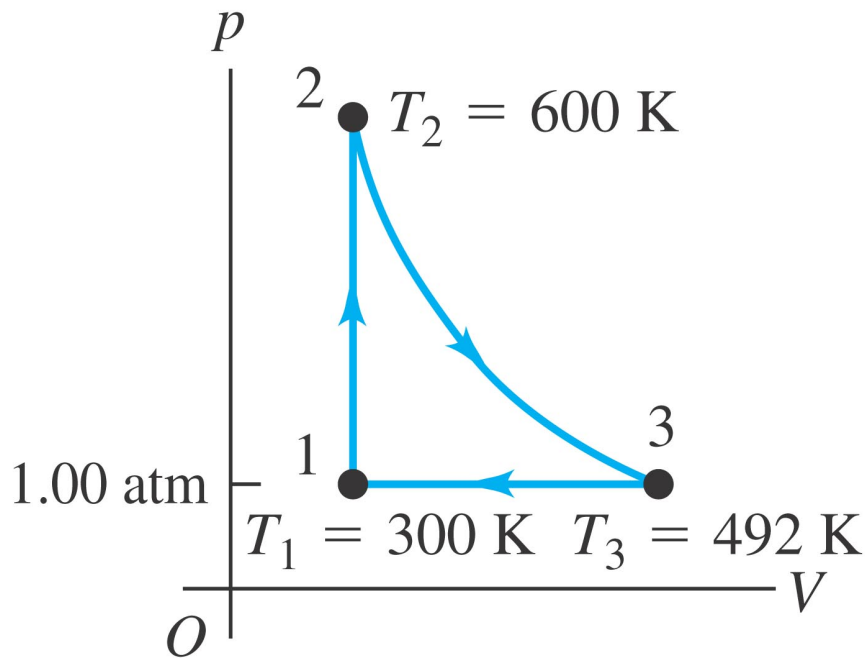


Figure 2: Figure P20.34 from University Physics 15th edition.

3 Internal-Combustion Engines

The gasoline engine is an example of a heat engine. In this section we determine the thermal efficiency for two cyclic processes, the Otto cycle and the Diesel cycle.

3.1 The Otto Cycle

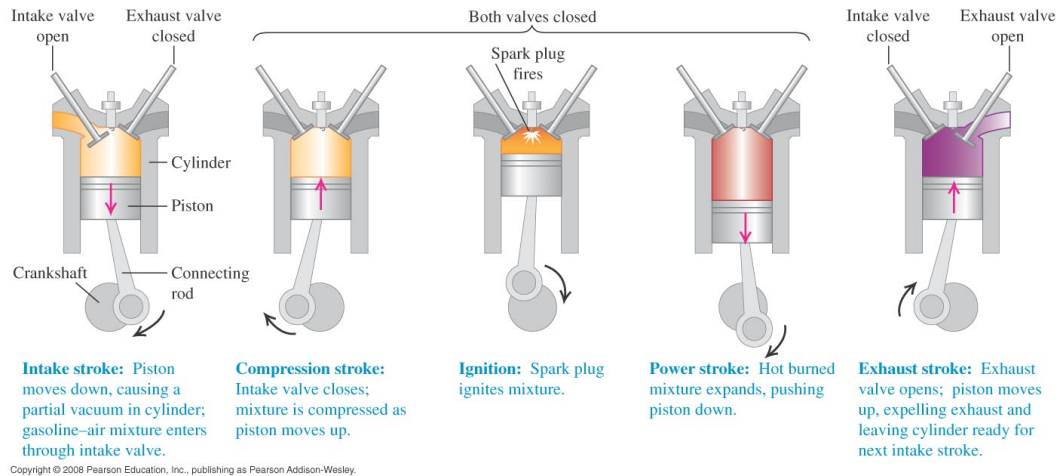


Figure 3: Cycle of a four-stroke internal-combustion engine. Figure 20.5 from University Physics 15th edition.

Using the definition of thermal efficiency (Eq. 1) we have:

$$e = \frac{Q_H + Q_C}{Q_H}$$

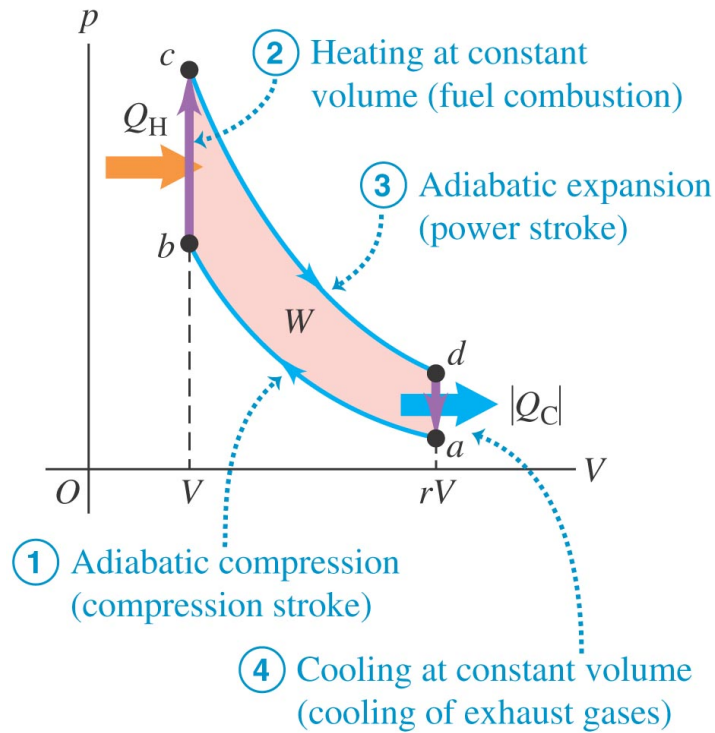
Using the p - V diagram for the Otto cycle on the next page, we find the *thermal efficiency* for the Otto cycle to be:

$$\text{eff} = \frac{W}{Q_H} = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 + \frac{n C_V (T_a - T_d)}{n C_V (T_c - T_b)} = 1 - \frac{(T_d - T_a)}{(T_c - T_b)}$$

On the two adiabats, we have the following relations:

$$(c \rightarrow d) \quad V_c T_c^{\gamma-1} = (r V_c) T_d^{\gamma-1} \quad \Rightarrow \quad T_c^{\gamma-1} = r T_d^{\gamma-1} \quad \Rightarrow \quad T_d = \frac{1}{r^{\gamma-1}} T_c$$

Otto cycle



$$(a \rightarrow b) \quad V_b T_b^{\gamma-1} = (rV_b) T_a^{\gamma-1} \Rightarrow T_b^{\gamma-1} = r T_a^{\gamma-1} \Rightarrow T_a = \frac{1}{r^{\gamma-1}} T_b$$

Substituting T_d and T_a into the *efficiency* equation above, the thermal energy becomes:

$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (\text{thermal efficiency in the Otto cycle})$$

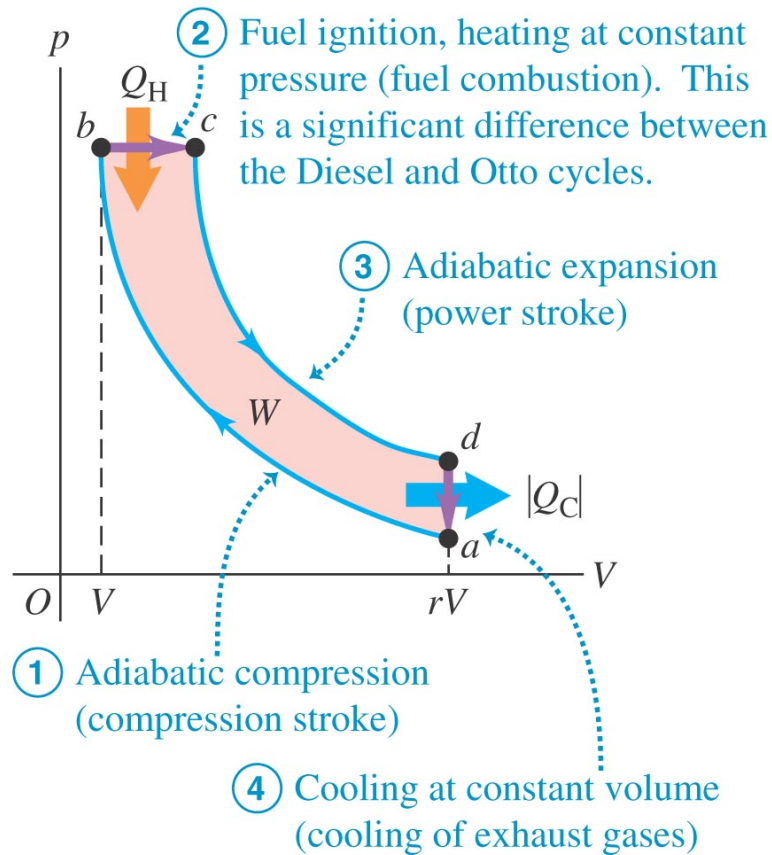
Typical r values for the Otto cycle are ~ 8 while the theoretical efficiency is $e = 0.56$.

Ex. 8 Calculate the theoretical efficiency for an Otto-cycle engine with $\gamma = 1.40$ and $r = 9.50$. (b) If this engine takes in 10,000 J of heat from burning its fuel, how much heat does it discard to the outside air?

3.2 The Diesel Cycle

The Diesel engine is similar in operation to the gasoline engine, however, there is no fuel in the cylinder at the beginning of the compression stroke. Typical r values in a Diesel engine are 15-20 while theoretical efficiencies are about 0.65 to 0.70.

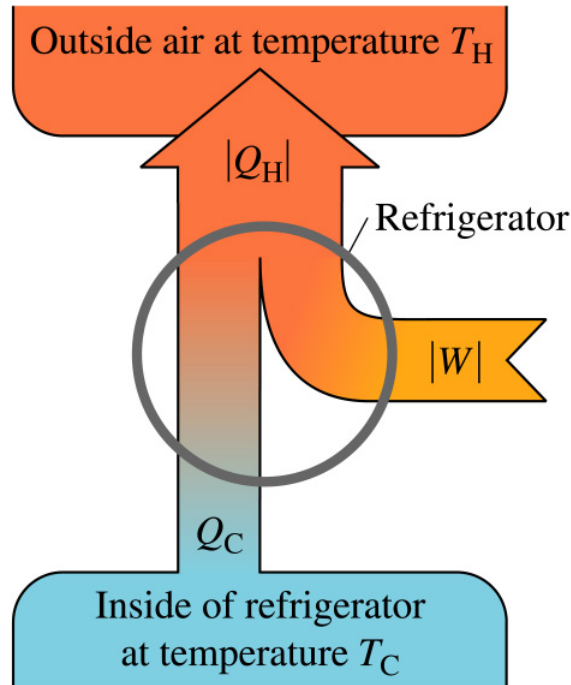
Diesel cycle



4 Refrigerators

We can think of a **refrigerator** as a heat engine operating in reverse. It takes heat from a cold place (inside the refrigerator) and ejects it to a warmer place (usually the air in the room where the refrigerator is located).

The work required to extract the heat $|Q_C|$ from the cold reservoir (the refrigerator) can be found from conservation of energy:



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$$W + |Q_C| = |Q_H|$$

or

$$W = |Q_H| - |Q_C|$$

The **coefficient of performance** (K) describes how much heat is extracted per unit work:

$$K = \frac{|Q_C|}{W} = \frac{|Q_C|}{|Q_H| - |Q_C|} \quad (\text{coefficient of performance of a refrigerator})$$

where K is a dimensionless number. The value K is also called the **energy efficiency rating**. The bigger the value, the more efficient the refrigerator.

Ex. 12 A refrigerator has a coefficient of performance of 2.10. In each cycle it absorbs 3.10×10^4 J of heat from the cold reservoir. (a) How much mechanical energy is required each cycle to operate the refrigerator? (b) During each cycle, how much heat is discarded to the high-temperature reservoir?

5 The Second Law of Thermodynamics

There is experimental evidence that strongly suggests that it is *impossible* to build a heat engine that converts heat completely into work—that is, an engine with 100% thermal efficiency. This impossibility is stated in the 2nd law of thermodynamics.

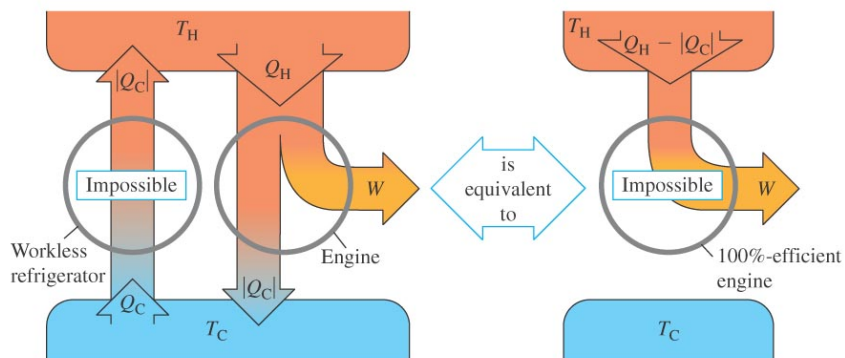
2nd Law of Thermodynamics

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.

or

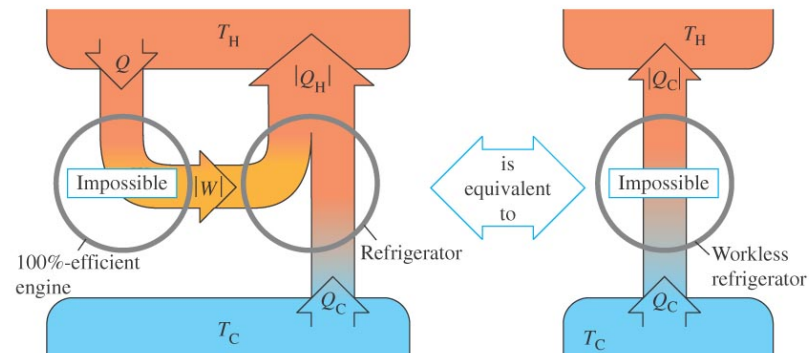
It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.

(a) The “engine” statement of the second law of thermodynamics



If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $Q_H - |Q_C|$ completely to work.

(b) The “refrigerator” statement of the second law of thermodynamics



If a 100%-efficient engine were possible, it could be used in conjunction with an ordinary refrigerator to form a workless refrigerator, transferring heat Q_C from the cold to the hot reservoir with no input of work.

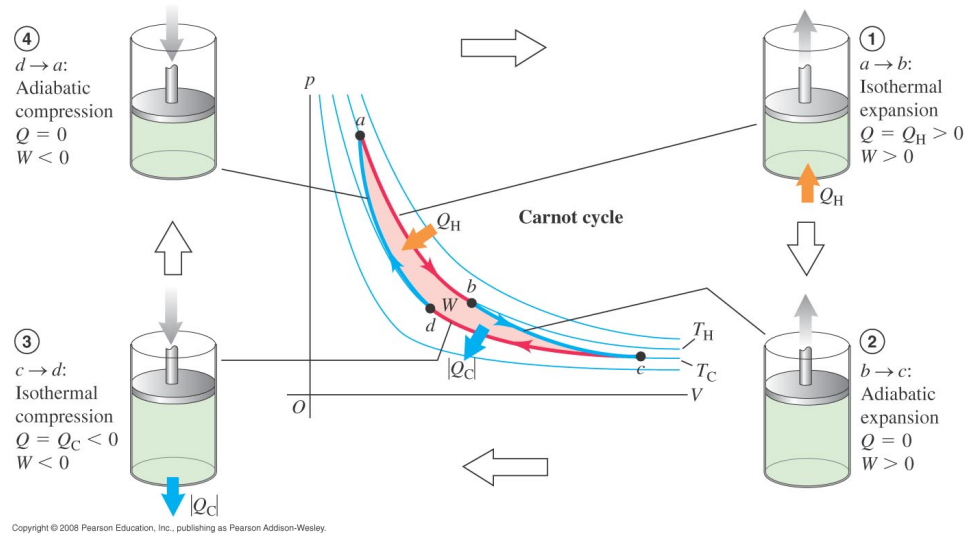
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6 The Carnot Cycle

Sadi Carnot (1796-1832) developed a hypothetical, idealized heat engine that has the maximum possible efficiency consistent with the 2nd law of thermodynamics. No heat engine can have 100% efficiency. The Carnot cycle determines the greatest efficiency that an engine can have operating between two heat reservoirs at temperatures T_H and T_C .

The Carnot cycle consists of the following steps:

1. The gas expands isothermally at temperature T_H , absorbing heat Q_H (a→b).
2. It expands adiabatically until its temperature drops to T_C (b→c).
3. It is compressed isothermally at T_C , rejecting heat $|Q_C|$ (c→d).
4. It is compressed adiabatically back to its initial state at temperature T_H (d→a).



$$Q_H = W_{ab} = nRT_H \ln \left(\frac{V_b}{V_a} \right)$$

$$Q_C = W_{cd} = nRT_C \ln \left(\frac{V_d}{V_c} \right) = -nRT_C \ln \left(\frac{V_c}{V_d} \right)$$

$$\text{eff} = \frac{W}{Q_H} = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \frac{T_C \ln\left(\frac{V_c}{V_d}\right)}{T_H \ln\left(\frac{V_b}{V_a}\right)} \quad (2)$$

However, we know that for an adiabatic process:

$$PV^\gamma = \text{constant} \quad \text{and} \quad TV^{\gamma-1} = \text{constant}'$$

Going back to our figure up above, the two adiabats give the following relations:

$$\begin{aligned} b \rightarrow c & \quad T_C V_c^{\gamma-1} = T_H V_b^{\gamma-1} \\ d \rightarrow a & \quad T_C V_d^{\gamma-1} = T_H V_a^{\gamma-1} \end{aligned}$$

Taking the ratio of these two equations, we find that $V_c/V_d = V_b/V_a$. Substituting this result into Eq. 2, we find that:

$$\text{eff} = 1 - \frac{T_C}{T_H} \quad (\text{Carnot efficiency}) \quad (3)$$

Ex. 15 A Carnot engine whose high-temperature reservoir is at 620 K takes in 550 J of heat at this temperature in each cycle and gives up 335 J to the low-temperature reservoir. (1) How much mechanical work does the engine perform during each cycle? What is (b) the temperature of the low-temperature reservoir; (c) the thermal efficiency of the cycle?

7 Entropy

The 2nd law of thermodynamics, as stated above, is in a different form compared to other physical laws we have encountered. Instead of an equation, it is a statement of *impossibility*. In order to put this law into the form of an equation, we need to introduce a new state variable called the *entropy*, S .

For an Isothermal Process: If we increase the volume while keeping the temperature (i.e., the internal energy) constant, we find that:

$$dQ = dW = p dV = \frac{nRT}{V} dV \quad \text{so} \quad nR \frac{dV}{V} = \frac{dQ}{T}$$

The measure of randomness, which we will call *entropy*, is related to the number of states accessible by the ensemble of molecules in a volume. If we “double” the volume, we should somehow “increase” the number of accessible states and, as a result, increase the randomness or *entropy*. If we define *entropy* in the following manner:

$$dS = \frac{dQ}{T} \quad \text{units of} \quad \left[\frac{J}{K} \right] \quad (4)$$

we see that the entropy “increases” by a factor of $\ln(2)$ when the volume “doubles.”

What if the process is not isothermal?

We can still use Eq. 4 to define the infinitesimal change in entropy. However, when the system *acquires* or *loses* energy on a thermodynamical path other than an isothermal path, we need to integrate the infinitesimal changes to find the total “change in entropy,” ΔS :

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} \quad (\text{for non-isothermal paths})$$

Ex. 23 A sophomore with nothing better to do adds heat to 0.350 kg of ice at 0.0°C until it is all melted. a) What is the change in entropy of the water? b) The source of heat is a very massive body at a temperature of 25.0°C. What is the change in entropy of this body? c) What is the total change in entropy of the water and the heat source?

8 Microscopic Interpretation of Entropy

Imagine you have 10 coins and you want to calculate the “number of microscopic states” for the given “macroscopic state” that all 10 coins will have their “heads up.” Obviously, there is only one way (or one combination) by which this can be done. Suppose you want to calculate the total number of “microscopic states” for the “macroscopic state” where there is only 1 coin with its “head” facing up and the other 9 coins having their “heads” facing down. Well, there are 10 “microscopic states” (or combinations) that can give that result. And, so on. The number of combinations is given by the binomial coefficients $\binom{n}{m}$. In other words, “If I had n coins, how many ways could I rearrange them (i.e., how many *microstates* are there) such that I would have m coins with **heads up**.”

This is a simple program to write using [Mathematica](#). The results are as follows for 4 coins, 10 coins, 100 coins, and 1,000 coins.

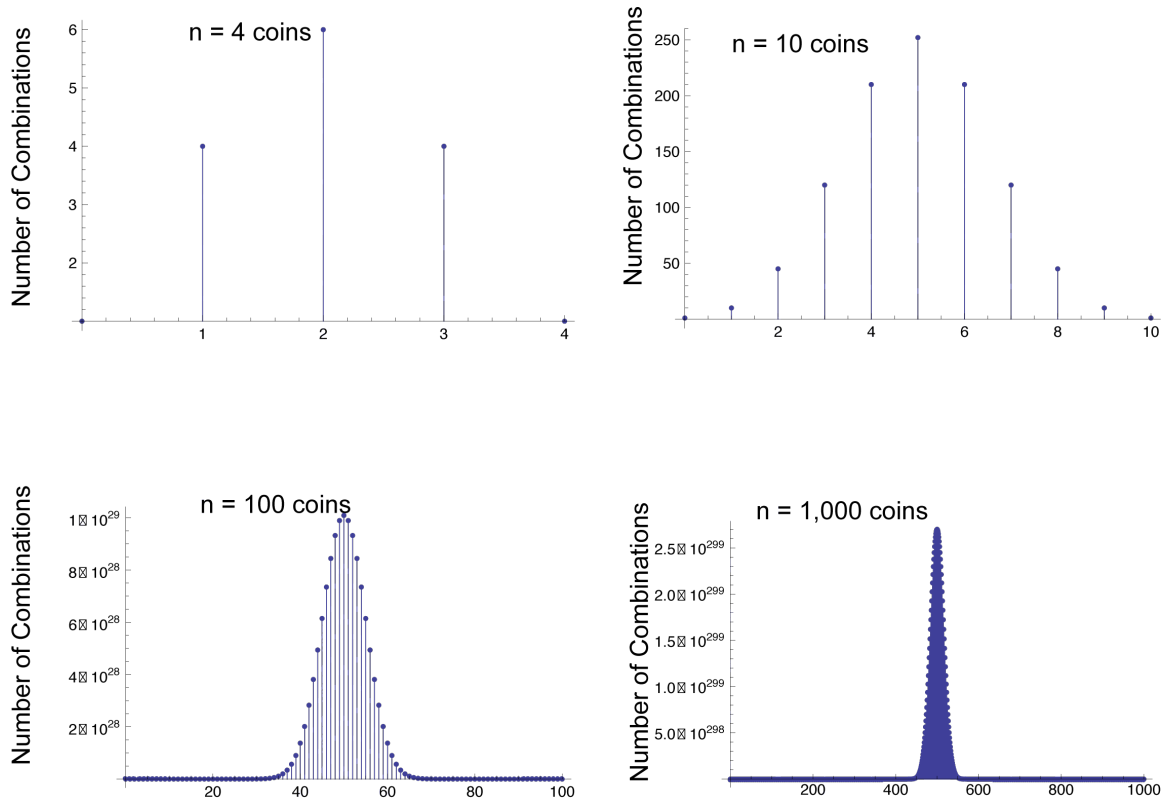


Figure 4: These four figures show the number of combinations possible for m “heads up” for $n = 4, 10, 100,$ and $1,000$ coins. In statistical mechanics jargon, these four figures show the number of *microstates* as a function of *macrostate* “ m ” for n coins. The *macrostate* “ m ” is the number along the x axis. For example, for 100 coins the greatest number of microstates occurs at the macrostate of $m = 50$. Notice that the widths of these distributions get smaller when the number of objects (i.e., coins) increases. The probability for the system to deviate from the average value gets increasingly small as the number of objects increases.

The fraction of coins with all “heads up“ are:

Table 1: A list of probabilities for “all heads up” for n number of coins

n	fraction of combinations with all “heads up”
4 coins	0.0625
10 coins	0.00097656
100 coins	7.88861×10^{-31}
1,000 coins	9.33264×10^{-302}

As you can see, the possibility of having 1,000 coins with all their “heads up” is astronomically small. This analysis can also be applied to the molecules in this room. Suppose that there are only 1,000 molecules in this room, and you wait for all 1,000 of them to be in the “left half” of the room. The probability of that happening is 9.33×10^{-302} . Now, imagine how astronomically small that probability would be if we require many times Avogadro’s number of molecules to be in the “left half” of the room. We would be waiting many times longer than the lifetime of the universe.

The microscopic definition of entropy

If we let Ω represent the number of possible microscopic states for a given macroscopic state, then the entropy S of the macroscopic state is given by:

$$S = k_B \ln(\Omega) \quad (\text{microscopic expression for entropy})$$

where k_B is the Boltzmann constant (1.38×10^{-23} J/K). Notice that the Boltzmann constant has the same units as entropy. This is not a coincidence. The Boltzmann constant is inextricably linked to the definition of *entropy*. Also note that our textbook uses the symbol w to represent the # of microstates for a given macrostate. $W = \text{Wahrscheinlichkeit} = \text{german for probability}$.

In practice, the system must be able to occupy at least *one* accessible state (i.e., microstate), in which case, the entropy of the system would be zero. The entropy can never be negative. Using this definition of entropy, we can plot the entropy as a function of the macrostates m , similar to what we did for the figures above. The entropy as a function of the macrostates is shown in Fig. 5.

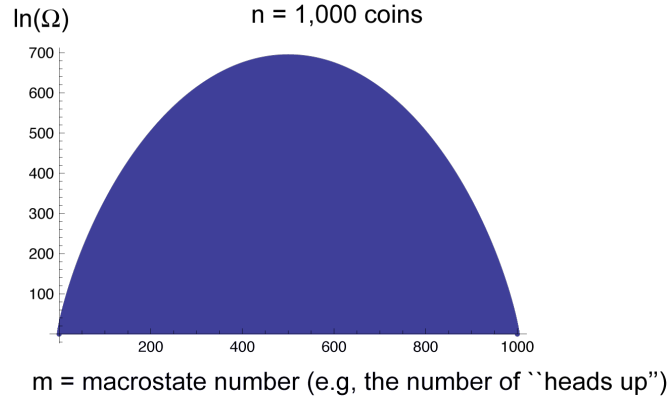


Figure 5: The $\ln(\Omega)$ as a function of the macrostate number m for $n = 1,000$ coins. The \ln of the number of microstates is directly proportional to the entropy.

Consider a system that undergoes a thermodynamic process that takes it from a macroscopic state 1, for which there are Ω_1 possible microscopic states, to a macroscopic state 2, which has Ω_2 microscopic states. The change in entropy in this process is:

$$\Delta S = S_2 - S_1 = k_B \ln(\Omega_2) - k_B \ln(\Omega_1) = k_B \ln\left(\frac{\Omega_2}{\Omega_1}\right)$$

For example, if we use Fig. 5, the differences in entropy can be read off the vertical axis where Ω_1 is the number of microstates in macrostate $m_1 = 500$, and Ω_2 is the number of microstates in macrostate $m_2 = 600$. In this case, the change in entropy would be:

$$\Delta S = k_B \ln(\Omega_2) - k_B \ln(\Omega_1) = k_B(669.352 - 689.467) = -k_B(20.1151)$$

where $k_B = 1.38 \times 10^{-23}$ J/K, the Boltzmann constant.