11

Thermodynamic Processes

Nothing in life is certain except death, taxes and the second law of thermodynamics. All three are processes in which useful or accessible forms of some quantity, such as energy or money, are transformed into useless, inaccessible forms of the same quantity. That is not to say that these three processes don't have fringe benefits: taxes pay for roads and schools; the second law of thermodynamics drives cars, computers and metabolism; and death, at the very least, opens up tenured faculty positions.

Seth Lloyd, American professor of mechanical engineering and physics (1960–)

In this chapter we will discuss thermodynamic processes, which concern the consequences of thermodynamics for things that happen in the real world.

The original impetus for thermodynamics, aside from intellectual curiosity, was the desire to understand how steam engines worked so that they could be made more efficient. Later, refrigerators, air conditioners, and heat pumps were developed and were found to be governed by exactly the same principles as steam engines.

The main results in this chapter rely on the temperature being positive, which would be consistent with Optional Postulate 6: Monotonicity (Subsection 9.7.2). This is usually, but not always, true. We will call attention to the results that depend on $T > 0$ as they are derived, and later in the chapter, we will explain the changes necessary to take negative temperatures into account.

11.1 Irreversible, Reversible, and Quasi-Static Processes

If we release a constraint in a composite system, the new equilibrium state maximizes the total entropy so that the change in entropy is non-negative for all processes in an isolated system,

$$dS \geq 0. \tag{11.1}$$

The change in the total entropy is zero only when the system had already been in equilibrium.

When the total entropy increases during some isolated thermodynamic process, the process is described as 'irreversible'. Running the process backwards is impossible,

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since the total entropy in an isolated system can never decrease. All real processes are accompanied by an increase in the total entropy, and are irreversible.

On the other hand, if the change ΔX in some variable X is small, the change in entropy can also be small. Since the dependence of the entropy on a small change in conditions is quadratic near its maximum, the magnitude of the increase in entropy goes to zero quadratically, as $(\Delta X)^2$, while the number of changes grows linearly, as $1/\Delta X$. The sum of the small changes will be proportional to $(\Delta X)^2/\Delta X = \Delta X$, which goes to zero as ΔX goes to zero. Consequently, a series of very small changes will result in a small change of entropy for the total process. In the limit of infinitesimal steps, the increase of entropy can vanish. Such a series of infinitesimal steps is called a quasi-static process.

A quasi-static process is reversible. Since there is no increase in entropy, it could be run backwards and return to the initial state.

The concept of a quasi-static process is an idealization, but a very useful one. The first applications of thermodynamics in the nineteenth century concerned the design of steam engines. The gases used in driving steam engines relax very quickly because of the high speeds of the molecules, which can be of the order of $1000\, m/s$. Even though the approximation is not perfect, calculations for quasi-static processes can give us considerable insight into the way real engines work.

Quasi-static processes are not merely slow. They must also take a system between two equilibrium states that differ infinitesimally. The classic example of a slow process that is not quasi-static occurs in a composite system with two subsystems at different temperatures, separated by a wall that provides good but not perfect insulation. Equilibration of the system can be made arbitrarily slow, but the total entropy will still increase. Such a process is not regarded as quasi-static.

Although the word ‘dynamics’ appears in the word ‘thermodynamics’, the theory is primarily concerned with transitions between equilibrium states. It must be confessed that part of the reason for this emphasis is that it is easier. Non-equilibrium properties are much more difficult to analyze, and we will only do so explicitly in Chapter 22, when we discuss irreversibility.

11.2 Heat Engines

As mentioned above, the most important impetus to the development of thermodynamics in the nineteenth century was the desire to make efficient steam engines. Beginning with the work of Sadi Carnot (French scientist, 1792–1832), scientists worked on the analysis of machines to turn thermal energy into mechanical energy for industrial purposes. Such machines are generally known as heat engines.

An important step in the analysis of heat engines is the conceptual separation of the engine itself from the source of heat energy. For this reason, a heat engine is defined to be ‘cyclic’; whatever it does, it will return to its exact original state after going through a cycle. This definition ensures that there is no fuel hidden inside the heat engine—a condition that has been known to be violated by hopeful inventors of perpetual-motion machines. The only thing a heat engine does is to change energy from one form (heat) to another (mechanical work).

11.2.1 Consequences of the First Law

The simplest kind of heat engine that we might imagine would be one that takes a certain amount of heat $đQ$ and turns it directly into work $đW$. Since we are interested in efficiency, we might ask how much work can be obtained from a given amount of heat. The First Law of Thermodynamics (conservation of energy) immediately gives us a strict limit:

$$đW \leq đQ. \tag{11.2}$$

A heat engine that violated eq. (11.2) could be made into a perpetual-motion machine; the excess energy ($đW - đQ$) could be used to run the factory, while the rest of the work would be turned into heat and fed back into the heat engine. Because such a heat engine would violate the First Law of Thermodynamics, it would be called a Perpetual Motion Machine of the First Kind.

Perpetual Motion Machines of the First Kind do not exist.

A pessimist might express this result as: 'You can't win.' Sometimes life seems like that.

11.2.2 Consequences of the Second Law

The limitations due to the Second Law are considerably more severe than those due to the First Law *if the temperature is positive*.

If a positive amount of energy in the form of heat $đQ$ is transferred to a heat engine, the entropy of the heat engine increases by $dS = đQ/T > 0$. If the heat engine now does an amount of work $đW = đQ$, the First Law (conservation of energy) is satisfied. However, the entropy of the heat engine is still higher than it was at the beginning of the cycle by an amount $đQ/T > 0$. The only way to remove this excess entropy so that the heat engine could return to its initial state would be to transfer heat out of the system (at a lower temperature), but this would cost energy, lowering the amount of energy available for work.

A machine that could transform heat directly into work, $đW = đQ$, could run forever, taking energy from the heat in its surroundings. It would be called a Perpetual Motion Machine of the Second Kind because it would violate the Second Law of Thermodynamics.

Perpetual Motion Machines of the Second Kind do not exist.

A pessimist might express this result as: 'You can't break even.' Sometimes life seems like that, too.

It is unfortunate that perpetual-motion machines of the second kind do not exist, since they would be very nearly as valuable as perpetual-motion machines of the first kind. Using one to power a ship would allow you to cross the ocean without the need of fuel, leaving ice cubes in your wake.

11.3 Maximum Efficiency

The limits on efficiency imposed by the First and Second Laws of Thermodynamics lead naturally to the question of what the maximum efficiency of a heat engine might be. The main thing to note is that after transferring heat into a heat engine, heat must also be transferred out again before the end of the cycle to bring the net entropy change back to zero. The trick is to bring heat in at a high temperature and take it out at a low temperature.

We do not need to be specific about the process, but we will assume that it is quasi-static (reversible). Simply require that heat is transferred into the heat engine from a reservoir at a high temperature T_H, and heat is removed at a low temperature $T_L < T_H$. If the net work done by the heat engine during an infinitesimal cycle is $đW$, conservation of energy gives us a relationship between the work done and the heat exchanged,

$$đW = đQ_H + đQ_L. \tag{11.3}$$

Sign conventions can be a tricky when there is more than one system involved. Here we have at least three systems: the heat engine and the two reservoirs. In eq. (11.3), work done by the heat engine is positive, and both $đQ_H$ and $đQ_L$ are positive when heat is transferred to the heat engine. In practice, the high-temperature reservoir is the source of energy, so $đQ_H > 0$, while wasted heat energy is transferred to the low-temperature reservoir, so $đQ_L < 0$.

Because a heat engine is defined to be cyclic, the total entropy change of the heat engine for a completed cycle must be zero:

$$dS = \frac{đQ_H}{T_H} + \frac{đQ_L}{T_L} = 0. \tag{11.4}$$

The assumption of a quasi-static process (reversibility) is essential to eq. (11.4). While $dS = 0$ in any case because of the cyclic nature of the heat engine, a violation of reversibility would mean that a third (positive) term must be added to $(đQ_H/T_H + đQ_L/T_L)$ to account for the additional generation of entropy.

If we use eq. (11.4) to eliminate $đQ_L$ from eq. (11.3), we obtain a relationship between the heat in and the work done,

$$đW = \left(1 - \frac{T_L}{T_H}\right) đQ_H. \tag{11.5}$$

We can now define the efficiency of a heat engine, η,

$$\eta = \frac{đW}{đQ_H} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H}. \tag{11.6}$$

The efficiency η is clearly less than 1, which is consistent with the limitation due to the Second Law of Thermodynamics. Actually, the Second Law demands that the efficiency given in eq. (11.6) is the maximum possible thermal efficiency of any heat engine, whether it is reversible (as assumed) or irreversible. The proof of this last statement will be left as an exercise.

11.4 Refrigerators and Air Conditioners

Since ideal heat engines are reversible, you can run them backwards to either cool something (refrigerator or air conditioner) or heat something (heat pump). The equations derived in the previous section do not change.

First consider a refrigerator. The inside of the refrigerator can be represented by the low-temperature reservoir, and the goal is to remove as much heat as possible for a given amount of work. The heat removed from the low-temperature reservoir is positive for a refrigerator, $đQ_L > 0$, and the work done *by* the heat engine is negative, $đW < 0$, because you have to use power to run the refrigerator.

We can define a coefficient of performance ϵ_R and calculate it from eqs. (11.3) and (11.4):

$$\epsilon_R = \frac{đQ_L}{-đW} = \frac{T_L}{T_H - T_L}. \tag{11.7}$$

This quantity can be much larger than 1, which means that you can remove a great deal of heat from the inside of your refrigerator with relatively little work; that is, you will need relatively little electricity to run the motor.

An air conditioner works the same way as a refrigerator, but $đQ_L$ is the heat removed from inside your house or apartment. The coefficient of performance is again given by eq. (11.7).

The coefficient of performance for a refrigerator or an air conditioner is clearly useful when you are thinking of buying one. Indeed, it is now mandatory for new refrigerators and air conditioners to carry labels stating their efficiency. However, the labels do not carry the dimensionless quantity ϵ_R; they carry an 'Energy Efficiency Ratio' (EER) which is the same ratio, but using British Thermal Units (BTU) for $đQ_L$ and Joules for $đW$. The result is that the EER is equal to ϵ_R times a factor of about $3.42\,BTU/\mathcal{J}$. A cynic might think that these peculiar units are used to produce larger numbers and improve sales—especially since the units are sometimes not included on the label; I couldn't possibly comment.

11.5 Heat Pumps

Heat pumps also work the same way as refrigerators and air conditioners, but with a different purpose. They take heat from outside your house and use it to heat the inside of your house. The low-temperature reservoir outside your house usually takes the form of pipes buried outside in the yard. The goal is to heat the inside of your house as much as possible with a given amount of work.

We can define a coefficient of performance for a heat pump,

$$\epsilon_{HP} = \frac{-đQ_H}{-đW} = \frac{T_H}{T_H - T_L}. \tag{11.8}$$

This quantity can also be significantly larger than 1, which makes it preferable to use a heat pump rather than running the electricity through a resistive heater to heat your house.

11.6 The Carnot Cycle

The Carnot cycle is a specific model of how a heat engine might work quasistatically between high- and low-temperature thermal reservoirs. The Carnot heat engine is conceived as a closed piston containing gas—usually an ideal gas. To clarify the description of the cycle, we will include two figures: Fig. 11.1, which contains a plot of pressure vs. volume, and Fig. 11.2, which contains a plot of temperature vs. entropy for the same process.

We'll describe the cycle as beginning at pressure P_A and volume V_A in Fig. 11.1 and temperature T_A and entropy S_A in Fig. 11.2, both labelled as point A. The heat engine is assumed to be in contact with a (high-temperature) thermal reservoir at temperature T_A. It expands to a volume of V_B, while remaining in contact with the thermal reservoir and doing work. If Q_{AB} is the amount of heat transferred to the heat engine along the path AB, then the entropy of the heat engine grows by an amount Q_{AB}/T_A. The path from A to B in Fig. 11.2 is consequently a straight, horizontal line. Since the heat engine is expanding, the pressure is steadily reduced, according to the ideal gas law, $P = Nk_BT_A/V$. The heat engine is now at point B in both Fig. 11.1 and Fig. 11.2.

Next, the heat engine is removed from contact with the thermal reservoir. It then continues to expand and do work until it is reaches a volume of V_C. The heat engine has cooled further, according to the adiabatic equation, $P =$ (constant) $V^{-5/2}$ reaching a temperature of T_C. Because there is no transfer of heat along the path BC, and the process is reversible, the entropy remains unchanged. The heat engine is now at point C.

At this point the heat engine is put in contact with a second (low-temperature) thermal reservoir, which is at temperature T_C. The heat engine is then compressed isothermally until it reaches a volume of V_D. Because it requires work to compress the heat engine, the heat engine does negative work on the path between point C and point D. The pressure grows during this part of the cycle according to the ideal gas law, $P = Nk_BT_C/V$, until it

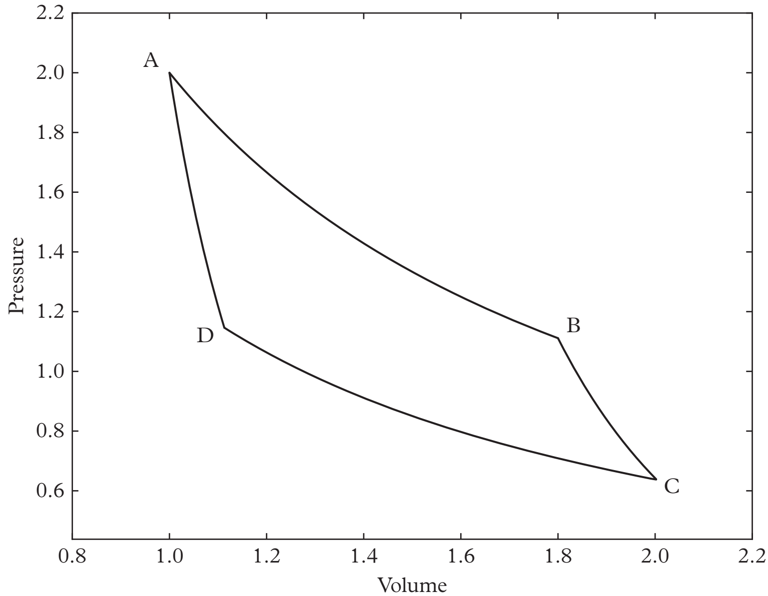

Fig. 11.1 *Pressure vs. volume plot for a Carnot cycle.*

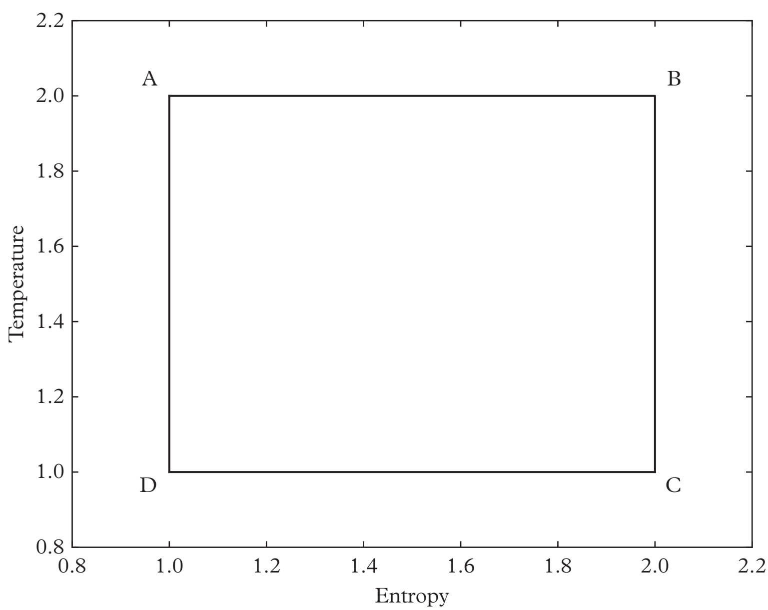

Fig. 11.2 *Temperature vs. entropy plot for a Carnot cycle.*

Table 11.1 *Carnot cycle.*

Path	Process	Temperature change	Volume change	Work done
A to B	isothermal	constant T	expand	positive work
B to C	adiabatic	cooling	expand	positive work
C to D	isothermal	constant T	contract	negative work
D to A	adiabatic	heating	contract	negative work

reaches a pressure of P_D. The entropy decreases because heat is removed from the heat engine. The heat engine is now at point D.

After reaching the point D, the heat engine is removed from the low-temperature reservoir. It continues to be compressed until it reaches a volume of V_A and a pressure of P_A, with temperature T_A and entropy S_A —which is where it started. The Carnot cycle is summarized in Table 11.1.

The Carnot cycle is historically of great importance. It continues to be of great importance to students taking standard national examinations. Its main drawback is that the analysis of the equations is somewhat tedious, and the physical insight is (in my opinion) less than that obtained from the differential forms presented earlier in this chapter.

11.7 Alternative Formulations of the Second Law

There have been nearly as many formulations of the second law as there have been discussions of it.

P. W. Bridgman, American physicist (1882–1961) 1946 Nobel Prize in Physics

Various alternate formulations of the Second Law of Thermodynamics have been suggested in the history of thermodynamics as scientists have wrestled with the meaning of entropy. They have provided simple examples of important consequences of thermodynamics in our lives.

1. The Clausius version of the Second Law
   The original version of the Second Law was phrased by Rudolf Clausius without reference to the entropy.

   Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

   This can be derived easily by considering a hypothetical heat engine (run in reverse) that extracts an amount of heat $đQ_L < 0$ from the lower temperature body, and adds an amount of heat $đQ_H > 0$ to the higher temperature body $(T_L < T_H)$. If $đQ_L + đQ_H = 0$, this is essentially a transfer of heat from a colder to a warmer body, with $đQ_L = -đQ_H < 0$. However, the entropy of the heat engine must change by

$$dS = \frac{đQ_L}{T_L} + \frac{đQ_H}{T_H} = \frac{đQ_L}{T_L} - \frac{đQ_L}{T_H} = đQ_L \left(\frac{T_H - T_L}{T_L T_H} \right) < 0. \tag{11.9}$$

This leaves us with an decrease in the entropy of the heat engine which would violate the Second Law.

2. The Kelvin version of the Second Law
Lord Kelvin (Irish mathematical physicist and engineer, 1824–1907, 1st Baron Kelvin) phrased the second Law as follows.

> *It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

This is clear from the fact that entropy increases from adding heat at a lower temperature which cannot be compensated for by subtracting heat at a higher temperature.

3. The Planck version of the Second Law
Max Planck's version of the second Law was again expressed in terms of a restriction on the construction of a refrigerator.

> *It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and cooling of a heat reservoir.*

Cooling a heat reservoir would add energy to the heat engine, thereby increasing its entropy. The work done by the heat engine would not decrease its entropy, so the process could not be cyclic.

4. The ter Haar and Wergeland version of the Second Law,
Dirk ter Haar (Anglo-Dutch physicist, 1919–2002) and Harald Wergeland (Norwegian physicist, 1912–1987) put the Kelvin and Planck versions of the Second Law together in their textbook on thermodynamics.

> *It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.*

This is again a process which would add heat to the heat engine, raising its entropy with no way to reduce it.

11.8 Positive and Negative Temperatures

If Optional Postulate 6 (Monotonicity, Subsection 9.7.2) does not apply to a particular system, things get considerably more interesting. If the entropy is decreasing in some range of energies, the expression for the temperature, Eq. (8.26), becomes negative.

Negative temperatures have been the subject of considerable debate in recent years. Some workers claim that the temperature is never negative, while others claim that negative temperature states exist, but are unstable. I claim that they exist and are quite interesting.

For many models in statistical mechanics, Optional Postulate 6 (Monotonicity, Subsection 9.7.2) is not valid. These models have an increasing density of states at low energies, but a decreasing density of states for high energies (see Chapter 31). Since the temperature can be expressed as the derivative of the logarithm of the density of states with respect to energy, the temperature is positive at low energies, but negative at high energies.

Although it might seem counterintuitive, negative temperatures are not colder than $T = 0$, but instead hotter than $T = \infty$. This is easier to see if we consider the inverse temperature, $\beta = 1/k_B T$, which has units of inverse energy. Then $T = 0$ corresponds to $\beta = \infty$. Making the system hotter *decreases* β until $T = \infty$ at $\beta = 0$. Making the system even hotter lowers β to negative values.

To describe systems that exhibit both positive and negative temperatures, it is convenient to use a dimensionless entropy, $\tilde{S} = S/k_B$. The differential form of the fundamental equation, expressed in the $\tilde{S}$-representation can be obtained from eq. (10.26),

$$d\tilde{S} = \beta dU + (\beta P)dV - (\beta\mu)dN. \tag{11.10}$$

The parentheses are put around (βP) and $(\beta\mu)$ as a reminder that these products are to be regarded a single variable. We will use this representation again in Chapter 12, Thermodynamic Potentials.

We consider two bodies, one at high temperature (H) and one at low temperature (L). The convention being used is that work done by the heat engine is positive, and heat coming out of any body is positive.

The entropy balance equation for the heat engine reflects the cyclic requirement and the quasi-static limit. In terms of β and $\tilde{S}$, this becomes

$$d\tilde{S} = \beta_H đQ_H + \beta_L đQ_L = 0, \tag{11.11}$$

or

$$\beta_H đQ_H = -\beta_L đQ_L. \tag{11.12}$$

This equation implies that if β_H and β_L have the same sign, $đQ_H$ and $đQ_L$ must have opposite signs. If β_H and β_L have opposite signs, $đQ_H$ and $đQ_L$ must have the same sign.

The energy balance equation is

$$đW = đQ_H + đQ_L. \tag{11.13}$$

In eqs. (11.12) and (11.13), there are three variables and two equations. Eliminating one variable leaves a relationship between the other two, which is what is needed to calculate various measures of efficiency. There are two cases that we will need.

1. Eliminate $đQ_L$.
   Using eq. (11.12) to eliminate $đQ_L$ from eq. (11.13), we find

$$đW = \left(1 - \frac{\beta_H}{\beta_L}\right) đQ_H = \left(\frac{\beta_L - \beta_H}{\beta_L}\right) đQ_H. \tag{11.14}$$

2. Eliminate $đQ_H$.
   Using eq. (11.12) to eliminate $đQ_H$ from eq. (11.13), we find

$$đW = \left(1 - \frac{\beta_L}{\beta_H}\right) đQ_L = \left(\frac{\beta_H - \beta_L}{\beta_H}\right) đQ_L. \tag{11.15}$$

Three ranges of temperatures will be treated: (1) both temperatures are positive, (2) the higher temperature is negative, but the lower temperature is positive, and (3) both temperatures are negative. A summary of the directions of energy flow is given in Table 11.2.

11.8.1 Both temperatures positive, $0 < \beta_H < \beta_L$

11.8.1.1 Heat engines

A heat engine does work, so that $đW > 0$. Consequently, $đQ_H > 0$ and eq. (11.12) tells us that $đQ_L < 0$, which represents the heat exhaust. The signs of these energy flows are indicated in the second line of Table 11.2.

The work performed, $đW$, and the heat extracted from the higher-temperature body are both positive. Their ratio gives a measure of the efficiency of the heat engine:

Table 11.2 *Signs of work and heat flow for various inverse temperature ranges. If $đW > 0$, work is being performed. If $đQ_H > 0$, heat is being extracted from the higher-temperature body. The forward direction of operation is take as that which generates positive work.*

Range of β's	$đW$	$đQ_H$	$đQ_L$	Direction
$0 < \beta_H < \beta_L$	+	+	−	forward
	−	−	+	reverse
$\beta_H < 0 < \beta_L$	+	+	+	forward
	−	−	−	reverse
$\beta_H < \beta_L < 0$	+	−	+	forward
	−	+	−	reverse

$$\eta = \frac{đW}{đQ_H} = 1 - \frac{\beta_H}{\beta_L} = \frac{\beta_L - \beta_H}{\beta_L} < 1. \tag{11.16}$$

For positive temperatures, as the higher of the two temperatures, T_H, increases, β_H decreases, and the efficiency η approaches one.

11.8.1.2 Refrigerators and air conditioners

The essential property of a refrigerator is that heat is removed from the lower-temperature system, $đQ_L > 0$. For positive temperatures, this requires the heat engine to run backwards, as indicated in the third line of Table 11.2. From eq. (11.15), we find the ratio of the heat extracted from the lower-temperature system, $đQ_L$, to the work done on the refrigerator, $-đW$, which is the coefficient of performance for a refrigerator,

$$\epsilon_R = \frac{đQ_L}{-đW} = \frac{\beta_H}{\beta_L - \beta_H} > 0. \tag{11.17}$$

Coefficients of performance are not limited to a maximum value of one. In fact, ϵ_R can be very large if β_H is close in value to β_L.

11.8.1.3 Heat pumps

For positive temperatures, heat pumps are also heat engines running backwards, but with the purpose of adding heat to the higher-temperature body, $đQ_H < 0$. The coefficient of performance for a heat pump is given by the amount of heat added to the higher-temperature body, $-đQ_H$, divided by the work performed on the engine, $-đW$,

$$\epsilon_{HP} = \frac{-đQ_H}{-đW} = \frac{\beta_L}{\beta_L - \beta_H} > 0. \tag{11.18}$$

This quantity can also be significantly larger than 1 if β_H is close to β_L, which makes it preferable to use a heat pump rather than running electricity through a resistive heater. It remains larger than one for all $\beta_L > \beta_H > 0$.

11.8.1.4 Summary for $0 < \beta_H < \beta_L$ (positive temperatures)

Table 11.3 *Thermal efficiencies for $0 < \beta_H < \beta_L$ (positive temperatures).*

Heat engine	$\eta \equiv \frac{đW}{đQ_H}$	$\eta = \frac{\beta_L - \beta_H}{\beta_L} = \frac{T_H - T_L}{T_H}$
Refrigerator	$\epsilon_R \equiv \frac{đQ_L}{-đW}$	$\epsilon_R = \frac{\beta_H}{\beta_L - \beta_H} = \frac{T_L}{T_H - T_L}$
Heat pump	$\epsilon_{HP} \equiv \frac{-đQ_H}{-đW}$	$\epsilon_{HP} = \frac{\beta_L}{\beta_L - \beta_H} = \frac{T_H}{T_H - T_L}$

11.8.2 The lower temperature is positive, but the higher temperature is negative, $\beta_H < 0 < \beta_L$

If $\beta_H < 0$ and $\beta_L > 0$, eq. (11.12) shows that $đQ_H$ and $đQ_L$ have the same sign. If heat is extracted from the higher-temperature body, it must also be extracted from the lower-temperature body. This is indicated in the fourth line in Table 11.2, which also shows that the work is positive, $đW > 0$.

11.8.2.1 Heat engines, $\beta_H < 0 < \beta_L$

The nominal efficiency of a heat engine is $(1 - \beta_H/\beta_L)$, which is greater than one if β_H and β_L have different signs. This gives the (false) impression that the efficiency is greater than one. Actually, energy from the lower-temperature body is also contributing to the work done,

$$đW_L = đQ_L = -\left(\frac{\beta_H}{\beta_L}\right) đQ_H > 0, \tag{11.19}$$

since $\beta_H/\beta_L < 0$.

If both sources of heat are taken into account, the true efficiency is

$$\eta_{true} = \frac{đW}{đQ_H + đQ_L} = 1. \tag{11.20}$$

11.8.2.2 Refrigerators and air conditioners, $\beta_H < 0 < \beta_L$

Since the process we just described in Subsection 11.8.2.1 also extracts heat from the lower-temperature body, identifying a refrigerator as a heat engine running backwards is incorrect in this case. The process generates work, rather than requiring it ($đW > 0$). Consequently, the definition of a coefficient of efficiency is not appropriate.

11.8.2.3 Heat pumps, $\beta_H < 0 < \beta_L$

A heat pump requires $đQ_H < 0$ (heat is added to the higher-temperature body), which means that the heat engine must run in reverse ($đW < 0$ and $đQ_H < 0$), as indicated in the fifth line in Table 11.2. The coefficient of performance for a heat engine is then

$$\epsilon_{HP} = \frac{-đQ_H}{-đW} = \left(\frac{\beta_L}{\beta_L - \beta_H}\right), \tag{11.21}$$

which is exactly the same as eq. (11.18) for positive temperatures. However, $0 < \epsilon_{HP} < 1$ because the temperatures have opposite signs.

11.8.2.4 Summary for $\beta_L > 0 > \beta_H$

Table 11.4 *Thermal efficiencies for $\beta_L > 0 > \beta_H$. The normal definition of the efficiency of a heat engine gives a value greater than one, as shown on the first line of the table. A definition that includes both sources of energy from the bodies is given on the second line.*

Heat engine	If 'η' $\equiv \dfrac{đW}{đQ_H}$	'η' $= \left(1 - \dfrac{\beta_H}{\beta_L}\right) > 1$
	If $\eta_{true} \equiv \dfrac{đW}{đQ_H + đQ_L}$	$\eta_{true} = 1$
Refrigerator	$đW > 0$ and $đQ_L > 0$	No work required for refrigeration
Heat pump	$\epsilon_{HP} \equiv \dfrac{-đQ_H}{-đW}$	$\epsilon_{HP} = \left(\dfrac{\beta_L}{\beta_L - \beta_H}\right) < 1.$

11.8.3 Both temperatures negative, $\beta_H < \beta_L < 0$

If both temperatures are negative, whether the engine is used as a heat engine, a refrigerator, or a heat pump, it is always run in the positive direction, that is, it always generates work, ($đW > 0$, $đQ_H < 0$, and $đQ_L > 0$). This is shown in the second to last line in Table 11.2. Running a heat engine in the reverse direction for this temperature range, as shown in the last line of Table 11.2, does not appear to be useful.

11.8.3.1 Heat engines, $\beta_H < \beta_L < 0$

In this temperature range, eq. (11.12) implies that $đQ_H$ and $đQ_L$ have opposite signs. Since $|\beta_H| > |\beta_L|$, eq. (11.14) requires $đQ_H < 0$. If the heat engine performs work ($đW > 0$), the higher-temperature body must absorb energy rather than supplying it. The energy to run the heat engine comes from the lower-temperature body!

A reasonable measure of the efficiency of this process is given by $đW/đQ_L$, which can be obtained from eq. (11.15),

$$\eta_L = \frac{đW}{đQ_L} = \frac{\beta_H - \beta_L}{\beta_H} = 1 - \frac{\beta_L}{\beta_H} < 1. \tag{11.22}$$

11.8.3.2 Refrigerators, $\beta_H < \beta_L < 0$

The operation of a refrigerator in this temperature range is strange, as eq. (11.15) shows,

$$đW = \left(\frac{\beta_H - \beta_L}{\beta_H}\right) đQ_L = \left(\frac{|\beta_H| - |\beta_L|}{|\beta_H|}\right) đQ_L > 0. \tag{11.23}$$

This refrigerator extracts heat from the lower-temperature body, *and* does work. It would not make sense to try to define a refrigerator coefficient of efficiency.

11.8.3.3 Heat pumps, $\beta_H < \beta_L < 0$

If the engine is operated as a heat pump, $đQ_H < 0$, it must still do work, $đW > 0$. All of the energy to heat the higher-temperature body comes from the lower-temperature body. It would not make sense to try to define a heat pump coefficient of efficiency.

11.8.3.4 Summary, $\beta_H < \beta_L < 0$

Table 11.5 *Thermal efficiency for $\beta_H < \beta_L < 0$. The operation of the engine as a heat engine, a refrigerator, and a heat pump is exactly the same. The work to drive the heat engine comes from the low-temperature body, so a reasonable measure of efficiency uses of heat from the low-temperatures body, η_L, which is shown in the table. Neither a refrigerator nor a heat pump requires work as a source of energy, so it does not make sense to define a coefficient of efficiency.*

Heat engine	$\eta_L \equiv \frac{đW}{đQ_L}$	$\eta_L = \frac{\beta_H - \beta_L}{\beta_H}$
Refrigerator	$đW > 0$ and $đQ_L > 0$	No work required for refrigeration
Heat pump	$đW > 0$ and $đQ_H < 0$	No work required for heat pump

11.9 Problems

PROBLEM 11.1

Efficiency of real heat engines

We showed that the efficiency of an ideal heat engine is given by

$$\eta_{\text{ideal}} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}.$$

Real heat-engines must be run at non-zero speeds, so they cannot be exactly quasi-static. Prove that the efficiency of a real heat engine is less than that of an ideal heat engine,

$$\eta < \eta_{\text{ideal}}.$$

PROBLEM 11.2

Maximum work from temperature differences

Suppose we have two buckets of water with constant heat capacities C_A and C_B, so that the relationship between the change in temperature of bucket A and the change in energy is

$$dU_A = C_A dT$$

with a similar equation for bucket B.

The buckets are initially at temperatures $T_{A,0}$ and $T_{B,0}$.

The buckets are used in conjunction with an ideal heat engine, guaranteed not to increase the world's total entropy (FBN Industries, patent applied for).

1. What is the final temperature of the water in the two buckets?
2. What is the maximum amount of work that you can derive from the heat energy in the buckets of water?
3. If you just mixed the two buckets of water together instead of using the heat engine, what would be the final temperature of the water?
4. Is the final temperature in this case higher, lower, or the same as when the heat engine is used? Explain your answer.
5. What is the change in entropy when the water in the two buckets is simply mixed together?

PROBLEM 11.3

Work from finite heat reservoirs

1. Suppose we have N objects at various initial temperatures. The objects have constant but different heat capacities $\left\{C_j | j = 1, \ldots, N\right\}$. The objects are at initial temperatures $\left\{T_{j,0} | j = 1, \ldots, N\right\}$.

   If we again have access to an ideal heat-engine, what is the maximum work we can extract from the thermal energy in these objects?

   What is the final temperature of the objects?
2. Suppose that the heat capacities of the objects were not constant, but proportional to the cube of the absolute temperature

$$\left\{C_j(T_j) = A_j T_j^3 | j = 1, \ldots, N\right\}$$

   where the A_j are constants.

   What is the maximum work we can extract from the thermal energy in these objects?

   What is the final temperature of the objects?