# Chapter R

The Laws of Thermodynamics

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R.1 - Work and the First Law

Thermodynamic Work

As we saw in Chapter F, the work done in one dimension is $W = \sum F \Delta x$. Consider a gas at a pressure P expanding in a piston. If the piston has a cross-sectional area of A and it expands by the infinitesimal amount dx, then the infinitesimal work done by the gas is $F \Delta x = P A \Delta x = P \Delta V$. Here we have used $F = P A$ and $\Delta V = A \Delta x$.
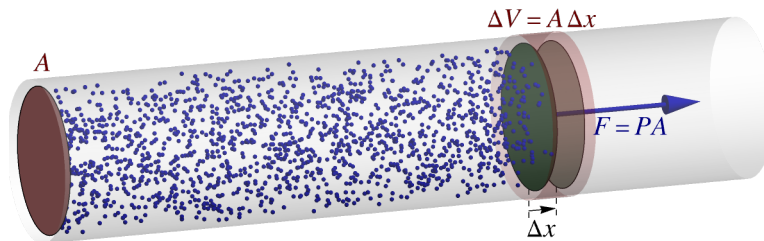
One-dimensional work: An expanding gas in a piston does work on the environment.

This result is more general; if any system at a pressure P expands by ΔV, the small amount of work is $P \Delta V$.
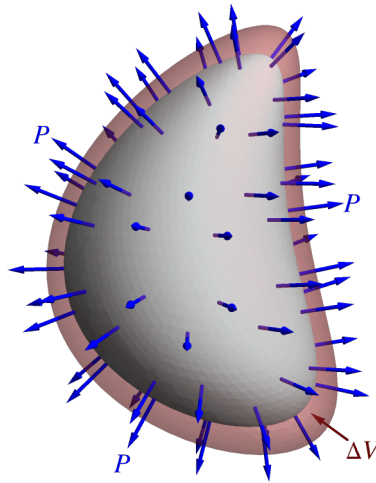
Three-dimensional case: Generally, an expanding thermodynamic system does work as it expands.

The work done *by* a thermodynamic system is

$$W = \sum P \Delta V.$$

When a system expands it does work on the environment. Our sign convention is that W is the work done *by* the system, where positive work decreases the energy of the system. The work done *on* the system is $-W$. The historical reason for this convention is that the focus was on getting work from engines, where the engine was the system.

For the simple case of expansion with a constant pressure we get

$$W = P\,\Delta V.$$

Generally, when the volume increases the work is positive; it is negative when volume decreases.
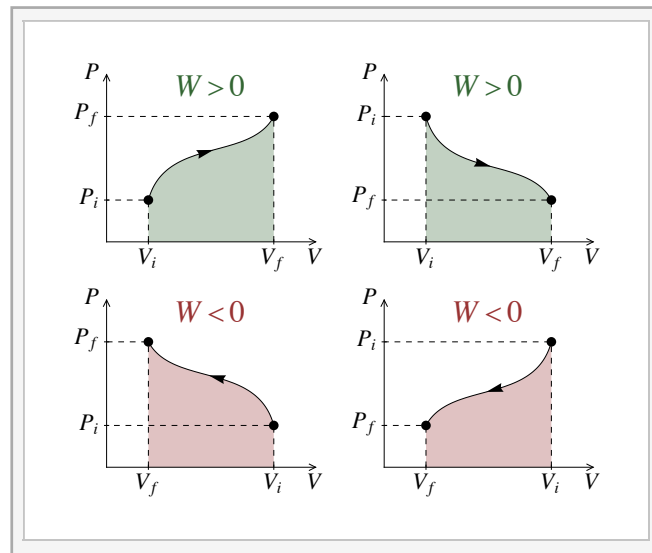
PV-Diagrams and Thermodynamic States

Suppose there is some thermodynamic system, for instance a fixed quantity of some substance. Knowledge of the pressure P and volume V uniquely specifies the thermodynamic state. For example, one could find the temperature uniquely from P and V. The equation that relates P, V and T is called the *equation of state*. For complex thermodynamic systems this is not a simple function that one can write down, but for an ideal gas it is just the ideal gas law.

A *PV*-diagram is a graph of P vs. V (P is the *y*-axis and V is the *x*-axis.) Work has a simple interpretation in terms of *PV*-diagrams; it is the area under the curve.
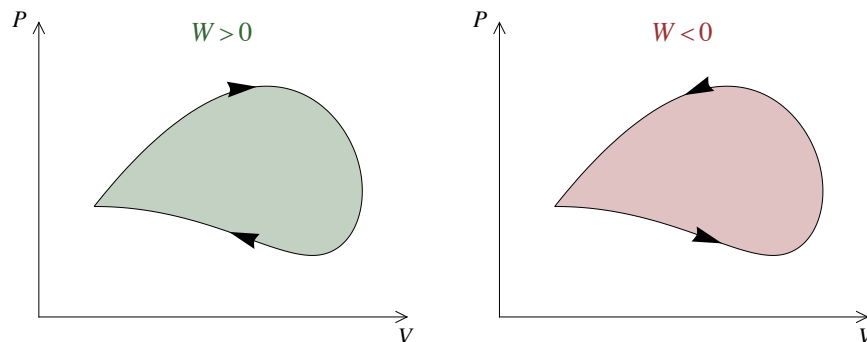
$$W = \sum P\,\Delta V = \pm\,\text{Area Under}$$

Since P is always positive the sign of $P\,\Delta V$ is the same as on the sign of ΔV.


Interactive Figure

In thermodynamics we often deal with cycles. A cycle is a closed path in a *PV*-diagram. For a cycle there is a positive and a negative contribution. If the path is clockwise the positive contribution dominates and the result is positive and it just then enclosed area. When the path is counterclockwise the result is negative.

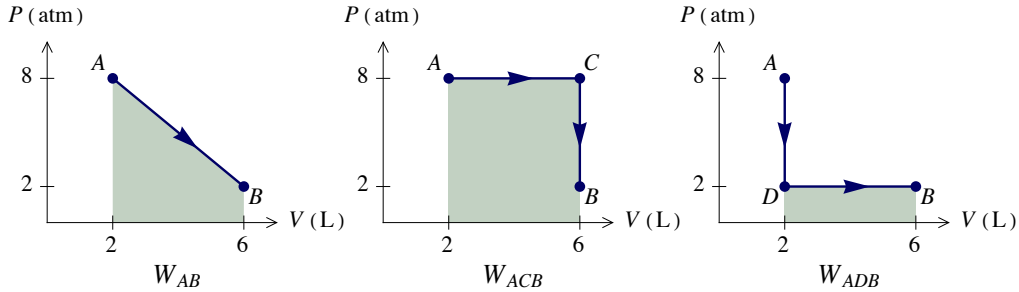$$W_{\text{cycle}} = \pm\,\text{Area Enclosed}$$

Example R.1 - The PV-Diagram

P (atm)
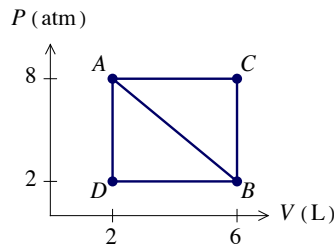
(a) What is the work for different processes taking a system from point A to point B? Find W_{AB} (the direct path), W_{ACB} and W_{ADB}.

Solution

Since all three cases correspond to increasing volumes we have $W = +$(Area under).

W_{AB}

W_{ACB}

W_{ADB}

The SI unit of work is Joule, where $J = Pa\,m^3$. Our axes have the units of atmospheres and liters. We need to convert the units of our areas from atm L to J.

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \quad \text{and} \quad 1 \text{ L} = 10^{-3} \text{ m}^3 \quad \Longrightarrow \quad 1 \text{ atm L} = 101.3 \text{ J}$$

For W_{AB} we have a trapezoid. The area of a trapezoid with a base width of b and sides with heights of h_1 and h_2 is Area $= \frac{1}{2} b\ (h_1 + h_2)$. It follows that

$$W_{AB} = +\frac{1}{2}\ 4 \text{ L } (2 \text{ atm} + 8 \text{ atm}) = +20 \text{ atm L} = +2026 \text{ J}$$
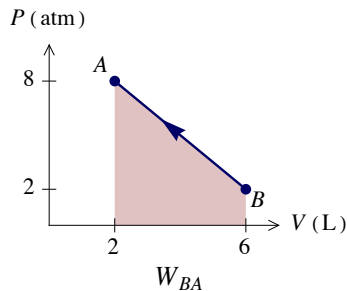
For W_{ACB} and W_{ADB} we have rectangles.

$$W_{ACB} = +4 \text{ L} \times 8 \text{ atm} = +32 \text{ atm L} = +3242 \text{ J} \quad \text{and} \quad W_{ADB} = +4 \text{ L} \times 2 \text{ atm} = +8 \text{ atm L} = +810 \text{ J}$$

This shows the path-dependent nature of work explicitly.

(b) What is the work for a process that takes the system from point B to point A, W_{BA}?

Solution

Here we have a process with decreasing volume, so $W = -$(Area under).
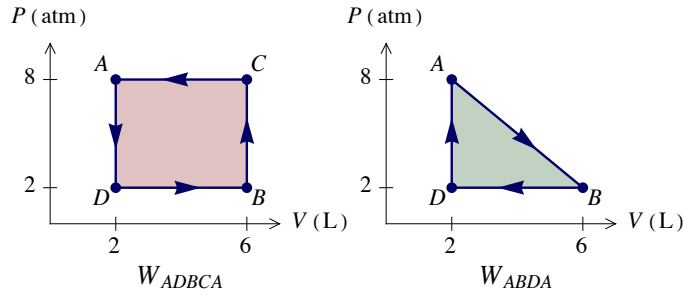
P (atm)

W_{BA}

For W_{AB} we have a trapezoid. The area of a trapezoid with a base width of b and sides with heights of h_1 and h_2 is Area $= \frac{1}{2} b\ (h_1 + h_2)$. It follows that

$$W_{BA} = -W_{AB} = -2026 \text{ J}$$

(c) What is the work for the cycles $ADBCA$ and $ABDA$?

Solution

For a cycle we have $W = \pm$(Area enclosed), where clockwise gives positive and counterclockwise gives negative.

$$W_{ADBCA}$$

$$W_{ABDA}$$

For W_{ADBCA} there is a counterclockwise path around a rectangle.

$$W_{ADBCA} = -4\,\mathrm{L} \times 6\,\mathrm{atm} = -24\,\mathrm{atm\,L} = -2431\,\mathrm{J}$$

There is a clockwise path around a triangle for W_{ABDA}.

$$W_{ABDA} = +\frac{1}{2}\,4\,\mathrm{L} \times 6\,\mathrm{atm} = +12\,\mathrm{atm\,L} = +1215\,\mathrm{J}$$

Quasi-static Processes

This discussion of clear paths in a *PV*-diagram implies that we are undergoing a *quasi-static* process. A process is quasi-static if it is performed sufficiently slowly, so that at each intermediate state the system stays in thermal equilibrium. As an example of a process that is *not* quasi-static, consider the free expansion of a gas. Start with a container containing two regions separated by a partition. On one side of the partition is a pressurized gas and on the other side is a vacuum. When the partition is removed, the gas undergoes a free expansion. The initial and final states are in equilibrium but the intermediate states are not. When a system is not in equilibrium, pressure and temperature are not well-defined quantities.
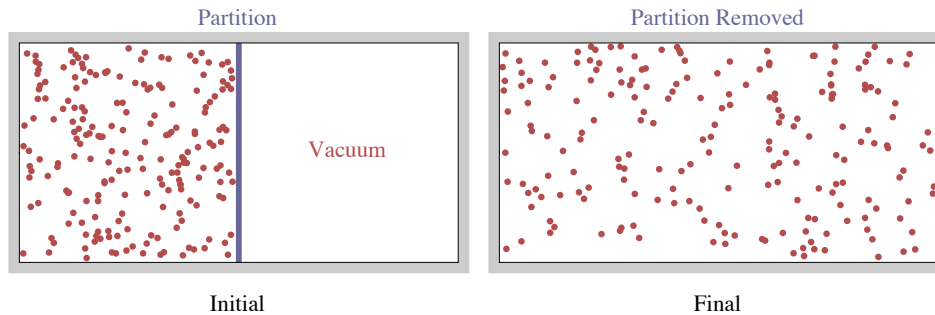
The free expansion of a gas is not quasi-static.

It is possible, theoretically, to do this expansion with a quasi-static process by slowly dragging a piston from initial to final positions.

In this example with an expanding gas, approximating a quasi-static process need not be too slow. To be in thermal equilibrium the system must be at a uniform temperature; there can be no temperature gradients. Suppose heat is added to a solid block. To be in equilibrium every point in the block must be at the same temperature. An approximately quasi-static process here would be very slow; each time after a small amount of heat is added, one must wait for the system to equilibrate.

Adiabatic and Isothermal Processes

A process is said to be adiabatic when it is sufficiently well-insulated so that no heat enters or leaves the system. So for an adiabatic process $Q = 0$. If a process is done quickly, like the free-expansion of a gas discussed above, then there is not enough time for heat to flow and it is adiabatic. The word isothermal implies the temperature is constant, so an isothermal process is at constant temperature.

Work for Isothermal Expansion of an Ideal Gas

For an ideal gas we can use the ideal gas law, the equation of state, to write the pressure as a function of volume. When the gas undergoes an isothermal expansion its temperature stays constant.

$$P(V) = \frac{n\,R\,T}{V} \quad (T \text{ is constant})$$
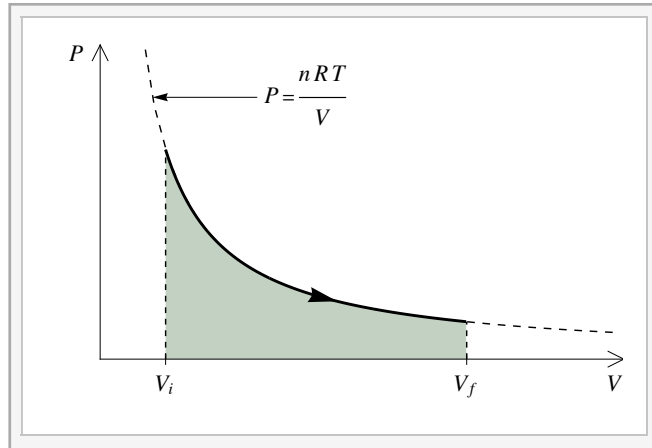
Interactive Figure: Work for an Isothermal Process of an Ideal Gas

The work is the area under this curve. Using integral calculus one can show that this becomes:

$$W = n\,R\,T\,\ln\frac{V_f}{V_i}.$$

Note that the natural log function guarantees that result of the work formula has the correct sign, since the natural log of a ratio less than one is negative.

Example R.2 - Isothermal Expansion

What is the work done by 50-g of oxygen O_2 gas as it is compressed by tripling its pressure at a constant temperature of 20 °C?

Solution

$$m = 0.050 \text{ kg} , \quad T = 20\,°C = 293 \text{ K} \quad \text{and} \quad \frac{P_f}{P_i} = 3$$

The mass of O_2 will tell us the number of moles n. The mass of a molecule in u gives the molar mass

$$m_{O_2} = 2\,m_O = 2\times16\,\text{u} = 32\,\text{u} \implies m_{mol} = 32 \text{ g/mol} = 0.032 \text{ kg/mol}$$

and this gives us the number of moles.

$$m = n\,m_{mol} \implies n = \frac{m}{m_{mol}} = 1.56 \text{ mol}$$

The ideal gas law with constant n and T relates the ratio of the volumes to the ratio of the pressures. This is known as Boyle's law.

$$PV = n\,R\,T \xrightarrow[n,T \text{ const.}]{} P_i V_i = P_f V_f \implies \frac{V_f}{V_i} = \frac{P_i}{P_f} = \frac{1}{3}$$

$$W = n\,R\,T\,\ln\frac{V_f}{V_i} \text{ and } R = 8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}} \implies W = -4180 \text{ J}$$

Note that increasing the pressure will decrease the volume and the work will then be negative.

State Functions

A *state function* is a function of pressure and volume. It has a unique value at each point in a PV-diagram. Temperature is a state function, since it follows from the equation of state.

$$f = f(V, P) \text{ is a state function.}$$

When a system changes from (V_i, P_i) to (V_f, P_f) a function f has a change of Δf given by

$$\Delta f = f(V_f, P_f) - f(V_i, P_i)$$

A cycle is some process that forms a closed loop in a PV-diagram; it follows that for a state function in a cycle: $\Delta f = 0$.

Internal Energy and the First Law

The energy of a thermodynamic system can be increased by adding thermal energy in the form of heat or by adding mechanical energy by doing work on the system. We will write the internal energy of a thermodynamic system as U. The first law of thermodynamics is

$$\Delta U = Q - W.$$

ΔU is the change in the internal energy of the system. Q is the heat *added* to the system. W is the work done *by* the system. It follows that $-W$ is the work done *on* the system. Internal energy is a state function. Since it is a state function then ΔU is independent of the path taken. Since the work is path dependent it follows from the first law that the heat is also path dependent, and not a state function.
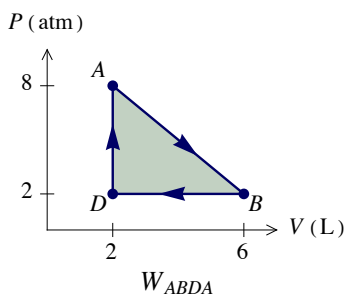

Example R.3 - The PV-Diagram (Continued)

P (atm)
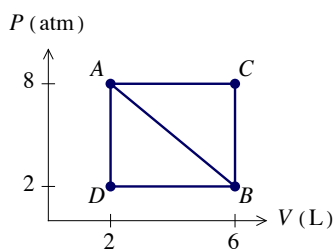
(d) What is the heat added to the system over the *ABDA* cycle?

Solution

First we need the work which we calculated in part (c).

W_{ABDA}

There is a clockwise path around a triangle for W_{ABDA}.

$$W = W_{ABDA} = +12 \text{ atm L} = +1215 \text{ J}$$

Because it is a cycle, $\Delta U = 0$ and the first law implies that $Q = W$.

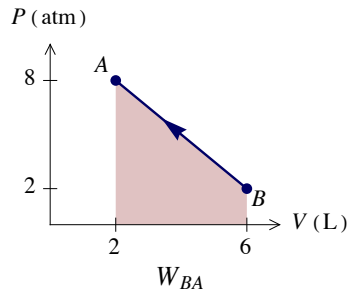$$0 = \Delta U = Q - W \implies Q = W = +1215 \text{ J}$$

(e) If 0.30 kcal of heat flow out of the system as it goes from point B to point A, then what is the change in internal energy for this process?

Solution

We are given the heat that flows out so the heat that flow in is negative and we have to convert kcal to J.

$$Q = -0.30 \text{ kcal} \times \frac{4186 \text{ J}}{\text{kcal}} = -1256 \text{ J}$$

We calculated the work in part (b) as the negative of the area under the trapezoid.

$$W = W_{BA} = -2026 \text{ J}$$

The first law of thermodynamics gives us the change in internal energy.

$$\Delta U = Q - W = +770 \text{ J}$$

R.2 - Entropy

Irreversibility and Reversible Processes

Thermodynamics puts an arrow on time. Take a video of dropping an egg on the floor and run it in reverse. Clearly, the reversed video would show itself as unphysical. All real-world physical processes are irreversible but we can consider idealized reversible processes.

A quasi-static process is *reversible*. As we saw last chapter a quasi-static process is one where we have an equilibrium state for each intermediate state in a process; they are given by clear paths in *PV*-diagrams. By following backward along the path in a *PV*-diagram we can restore the system and its surroundings to their original state. A thermodynamic system undergoing an irreversible process can always be returned to its original state but in both the process and return, a net quantity of heat will flow to the environment; this cannot be undone. Whenever heat flows spontaneously across a temperature gradient we have an irreversible process. The free expansion of a gas, as discussed earlier is not quasi-static and thus not reversible. This chapter will discuss entropy and the second law of thermodynamics. For a system and its environment, a reversible process has zero change in the total entropy and an irreversible process has a net increase in entropy.

A reversible (quasi-static) process is an idealization. When the state of a system is changed by a small amount it moves slightly away from equilibrium, but if done sufficiently slowly the deviations from equilibrium can be negligible and the process can be arbitrarily close to being reversible.

Definition of Entropy

Entropy S is a measure of disorder. One is not used to thinking of disorder as a precise notion that can be quantified, but it turns out that we can give it a precise definition. Doing so is beyond the scope of this course.

If we add heat to a system then we increase its disorder. For example, water at $0\,°C$ is a more disordered state than ice at $0\,°C$; to go from ice to water requires only heat. We define entropy as the state function; for a small Q entropy is defined by

$$\Delta S = \frac{Q}{T}.$$

When heat is added to a system its entropy increases. When it is removed ($Q < 0$) it decreases.

Constant Temperature and Latent Heats

If the temperature T is a constant then summing all the small ΔS above gives the same expression

$$\Delta S = \frac{Q}{T}$$

But now the Q is the total amount of heat added to the system. When some substance changes phase, its temperature stays constant. In that case the heat can be written in terms of the latent heat and mass.

$$Q = \pm m L$$

Temperature Change and Specific Heats

We can find entropy changes in cases of changing temperatures using the specific heat formula $Q = m\,c\,\Delta T$. This can be done with calculus by summing over small changes in temperature ΔT.

$$\Delta S = \sum \frac{m\,c\,\Delta T}{T}$$

The result from calculus becomes.

$$\Delta S = m\,c \ln \frac{T_f}{T_i}$$

Example R.4 - Making Ice Cubes

(a) A tray of water is put in the freezer. What is the change in entropy of an ice tray when 0.45-kg of water initially at 22 °C is frozen to ice at -18 °C?

Solution

The relevant data are the mass, and the temperatures. The constants needed are the specific heats of water and ice and the latent heat of fusion for water.

$$m = 0.45 \text{ kg}, \quad 22 \text{ °C} = 295 \text{ K}, \quad 0 \text{ °C} = 273 \text{ K}, \quad -18 \text{ °C} = 255 \text{ K},$$

$$c_W = 4186 \frac{\text{J}}{\text{kg K}}, \quad c_I = 2100 \frac{\text{J}}{\text{kg K}} \text{ and } L_f = 3.34 \times 10^5 \frac{\text{J}}{\text{kg}}$$

There are three steps we need to consider.

$$\text{Water at } 22 \text{ °C} \xrightarrow{1} \text{ Water at } 0 \text{ °C} \xrightarrow{2} \text{ Ice at } 0 \text{ °C} \xrightarrow{3} \text{ Ice at } -18 \text{ °C}$$

The total change in entropy will be the sum of the changes for each of the three steps. In each step, heat is being removed so the changes must be negative.

$$\Delta S_1 = m\,c \ln \frac{T_f}{T_i} = m\,c_W \ln \frac{273 \text{ K}}{295 \text{ K}} = -146.99 \frac{\text{J}}{\text{K}}$$

$$\Delta S_2 = \frac{\pm m\,L}{T} = \frac{-m\,L_f}{273 \text{ K}} = -550.55 \frac{\text{J}}{\text{K}}$$

$$\Delta S_3 = m\,c \ln \frac{T_f}{T_i} = m\,c_I \ln \frac{255 \text{ K}}{273 \text{ K}} = -64.46 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{ice tray}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -761.0 \frac{\text{J}}{\text{K}}$$

R.3 - The Second Law of Thermodynamics

Statement of the Second Law

A thermally isolated system is one with no heat entering or leaving it. This could consist of smaller systems exchanging heat between them but no heat is allowed to leave or enter the larger system. The total change in entropy for a system is written as ΔS_{tot}.

For a thermally isolated system the total change in entropy cannot be negative.

$$\Delta S_{\text{tot}} \geq 0$$

Heat Reservoirs

In thermodynamics we define a reservoir to be something sufficiently large to maintain a constant temperature given whatever amount of heat exchange as is relevant. If the amount of heat transferred is sufficiently small then a reservoir could be as small as a glass of water. If the amount of heat is large then we must consider reservoirs that are very large.

Example R.5 - Making Ice Cubes (Continued)

(b) The heat that flows out of the ice tray flows into the freezer. What is the total change in entropy of the system consisting of the freezer ice and the ice tray in the "Making Ice Cubes" example above?

Solution

Take the freezer to be a heat reservoir at $-18\,°C = 255\,K$. The total change in entropy of the freezer-ice system is the the ΔS from the the previous part, which we will now refer to as ΔS_{ice}, added to the change in entropy of the freezer, $\Delta S_{freezer}$. The (positive) heat that flows into the freezer $Q_{freezer}$ is the heat flowing out of the ice. Using our convention that Q is the heat added to a system, take the Q_{ice} to be negative.

$$0 = Q_{tot} = Q_{freezer} + Q_{ice\ tray} \implies Q_{freezer} = -Q_{ice}$$

The constants and values used in part (a) are also needed here.

$$m = 0.45\,kg\ ,\quad 22\,°C = 295\,K\ ,\quad 0\,°C = 273\,K\ ,\quad -18\,°C = 255\,K\ ,$$

$$c_W = 4186\ \frac{J}{kg\ K}\ ,\quad c_I = 2100\ \frac{J}{kg\ K}\quad \text{and}\quad L_f = 3.34 \times 10^5\ \frac{J}{kg}$$

Before finding the entropy change of the freezer $\Delta S_{freezer}$ we must first find $Q_{freezer}$ and for that we need to sum the heats for each of the three steps referred to in part (a).

$$Q_1 = m\,c_W\,\Delta T_W = -14\,441\,J$$

$$Q_2 = \pm m\,L = -m\,L_f = -150\,300\,J$$

$$Q_3 = m\,c_I\,\Delta T_I = -170\,010\,J$$

$$Q_{ice} = Q_1 + Q_2 + Q_3 = -208\,751\,J$$

Since the freezer is a reservoir, its entropy change is

$$Q_{freezer} = -Q_{ice}\quad \text{and}\quad \Delta S_{freezer} = \frac{Q}{T} = \frac{Q_{freezer}}{255\,K} = -\frac{Q_{ice}}{255\,K} = 818.6\ \frac{J}{K}$$

The change in entropy of the freezer is positive since heat flows into it. The total change in entropy of the ice tray and freezer combined is the sum of $Q_{freezer}$ with the change in the entropy of the ice, found in part (a) $\Delta S_{ice\ tray} = -761.0\,J/K$.

$$\Delta S_{total} = \Delta S_{freezer} + \Delta S_{ice\ tray} = 57.6\ \frac{J}{K}$$

Since this larger system is thermally isolated, no heat flows out of it or into it, then by the second law our answer had to be positive.

The Second Law and the Direction of Heat Flow

In any spontaneous process, heat flows from hot to cold. This is an immediate consequence of the second law. Consider an amount of heat Q flowing from a reservoir at temperature T_1 to a second reservoir at temperature T_2. Since heat is leaving T_1 its entropy decreases, while the entropy of T_2 increases. The total change in entropy is the sum of these two; by the second law it must be nonnegative.

$$0 \le \Delta S_{tot} = \Delta S_1 + \Delta S_2 = \frac{-Q}{T_1} + \frac{Q}{T_2} \implies \frac{1}{T_1} \le \frac{1}{T_2}$$

Cross-multiplying and remembering that absolute temperatures are always positive gives

$$T_2 \le T_1.$$

Thus, heat flows from a higher to a lower temperature.

Refrigerators, Air Conditioners and Heat Pumps

It is possible however, to have a situation where heat is taken from a cold reservoir and vented to a hotter reservoir. The key phrase in the above discussion is *spontaneous process*. A refrigerator removes heat from a cold interior and vents it to the warm coils behind. The crucial point is that more heat is vented to the back than is removed from the interior. The additional energy is provided by some motor (a compressor) doing work; it pumps the coolant around some cycle.
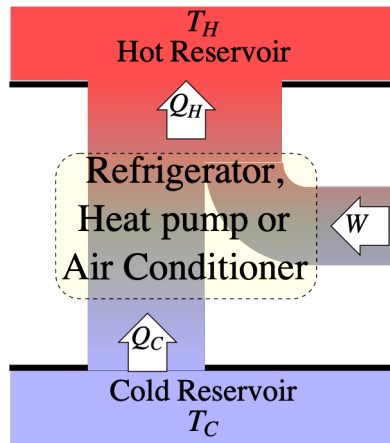
Consider a cold reservoir at temperature T_C and a hot reservoir at T_H. Q_C is removed from T_C and Q_H then is vented to T_H. The conservation of energy implies that

$$Q_H = Q_C + W.$$

This says that the additional energy comes from the work done by the motor. The change in the total entropy is

$$\Delta S_{\text{tot}} = \Delta S_C + \Delta S_H = \frac{-Q_C}{T_C} + \frac{Q_H}{T_H}.$$

It should be clear that if W is large enough that the Q_H may be sufficiently large to cancel any negative ΔS_C. Heat is moved from cold to hot.

An air conditioner is simply a refrigerator operating between the cold interior of a house and the warmer exterior. A heat pump is an air conditioner running in reverse on a cold winter day. The outdoors is air conditioned! Heat Q_C is removed from the cold exterior and more heat Q_H is vented inside. The amount of electrical energy that is used is determined by the work W. The heat vented inside is larger than the amount of electrical energy that is used. The Q_C is essentially a bonus.

R.4 - Heat Engines

Heat Engines and Efficiency
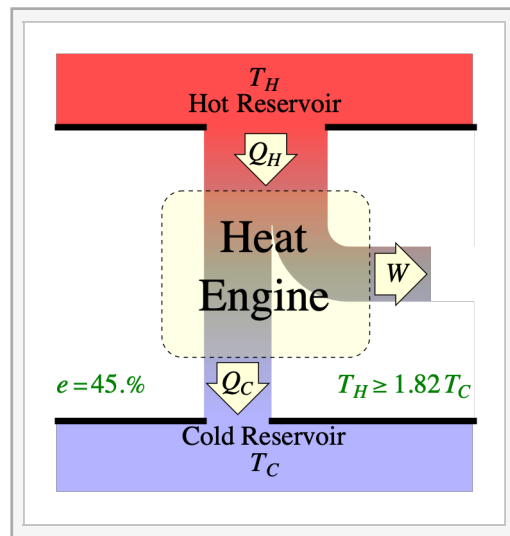
Interactive Figure

A heat engine is essentially an air conditioner running in reverse. Some fuel is burned creating an input heat of Q_H. The point of the engine is to convert this heat to work W. We will define the efficiency of a heat engine to be the energy output of the engine, the work, divided by the energy input, Q_H.

$$e = \frac{W}{Q_H}$$

A perfect heat engine would be 100% efficient. Unfortunately this is, because of the second law, impossible. There is a decrease in entropy without any increase to cancel it.

With a heat engine we have a hot reservoir at temperature T_H producing the input heat Q_H. Some of that heat is converted to work W, but necessarily some of it must be vented to the environment. Take the environment to be a cold reservoir at T_C receiving the vented heat Q_C.

Conservation of energy gives

$$Q_H = Q_C + W.$$

With this we can rewrite the efficiency

$$e = 1 - \frac{Q_C}{Q_H}.$$

The Second Law and Efficiency

The second law has the following form

$$\Delta S_{\text{tot}} = \Delta S_C + \Delta S_H = \frac{Q_C}{T_C} + \frac{-Q_H}{T_H} \geq 0.$$

This gives a fundamental upper limit on the efficiency of a heat engine.

$$\frac{Q_C}{T_C} + \frac{-Q_H}{T_H} \geq 0 \implies \frac{Q_C}{Q_H} \geq \frac{T_C}{T_H} \implies 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

It follows that

$$e \leq e_{\max} \quad \text{where} \quad e_{\max} = 1 - \frac{T_C}{T_H}.$$

A Carnot Engine

A Carnot engine is a theoretical heat engine of maximum efficiency. Its efficiency e_c is then given by

$$e_c = e_{\max} = 1 - \frac{T_C}{T_H}.$$

Example R.6 - Heat Engine

A heat engine takes 3800 kcal of heat from a hot reservoir at 350 °C and vents 2400 kcal of heat to the environment at 40 °C.

(a) What is the efficiency of this heat engine?

Solution

First list what is given, remembering that temperatures must be in Kelvin.

$$Q_H = 3800 \,\text{kcal} , \quad Q_C = 2400 \,\text{kcal} , \quad T_H = 350\,°\text{C} = 623\,\text{K} \quad \text{and} \quad T_C = 40\,°\text{C} = 313\,\text{K}$$

The efficiency involves only the heats.

$$e = 1 - \frac{Q_C}{Q_H} = 0.368 = 36.8\ \%$$

(b) What is the total change in the entropy for this process?

Solution

We are removing Q_H from T_H and adding Q_C to T_C. The total change in entropy is the sum of the negative change in the hot reservoir's entropy and the positive change in the cold reservoir.

$$\Delta S_{\text{tot}} = \Delta S_H + \Delta S_C = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = -6.0996 \ \frac{\text{kcal}}{\text{K}} + 7.6673 \ \frac{\text{kcal}}{\text{K}} = +1.568 \ \frac{\text{kcal}}{\text{K}}$$

(c) What is the maximum efficiency a heat engine could have when operating between these two reservoirs?

Solution

The maximum efficiency will depend only on the temperatures.

$$e_{\text{max}} = 1 - \frac{T_C}{T_H} = 0.498 = 49.8 \ \%$$