Chapter 20

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

1. Introduction

A piece of ice at room temperature will eventually melt. The reversed process (a spot of water freezes) will never occur, however.

The melting of the piece of ice is an example of a **one-way process**, or **irreversible process**.

The fact that there is a preferred direction for the "time arrow" has to do with one of the most fundamental quantities in physics; **entropy**.

2. Irreversible Process and Entropy

Many processes never occur spontaneously in the reversed way.

Heat will never gather to heat up a coffee cup in a room. Perfume in a room will never gather near the perfume bottle. None of these "wrong-way" processes would violate the law of conservation of energy.

The direction of an irreversible process is set by a property of the system; the change in entropy ΔS of the system. We state the entropy postulate as follows:

"If an irreversible process occurs in a closed system, the entropy of the system always increases; it never decreases."

There are two ways to define the change in entropy of a system: (1) In terms of the system's temperature and heat gained or lost, and (2) By counting the ways in which atoms or molecules that make up the system can be arranged. We will discuss the first approach only.

3. Change in Entropy

We approach the definition of **change in entropy** by considering the free expansion process.
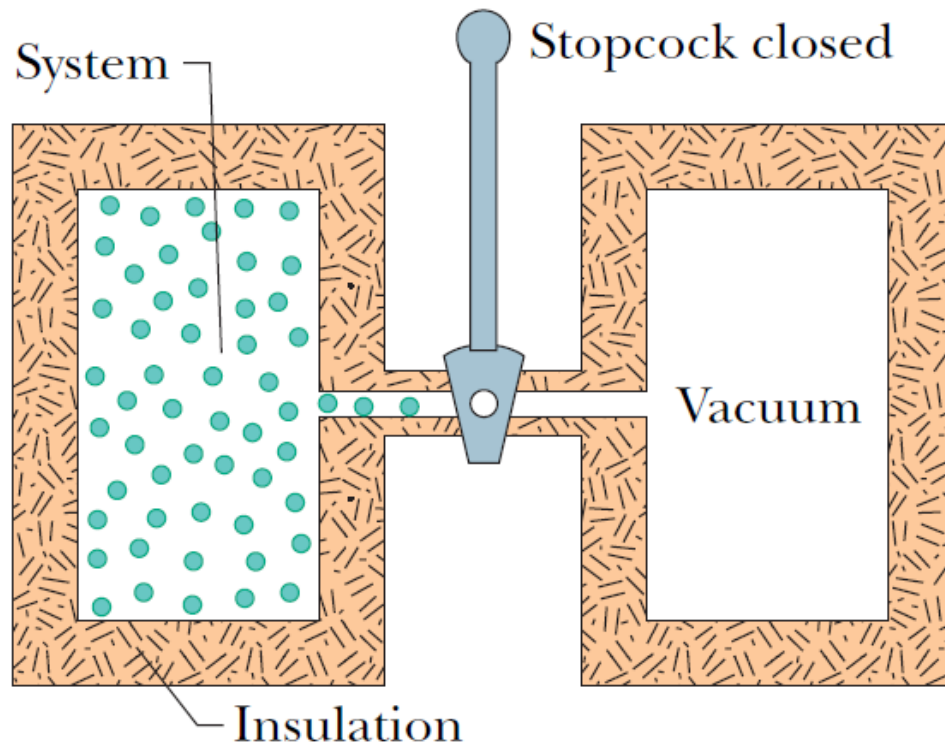
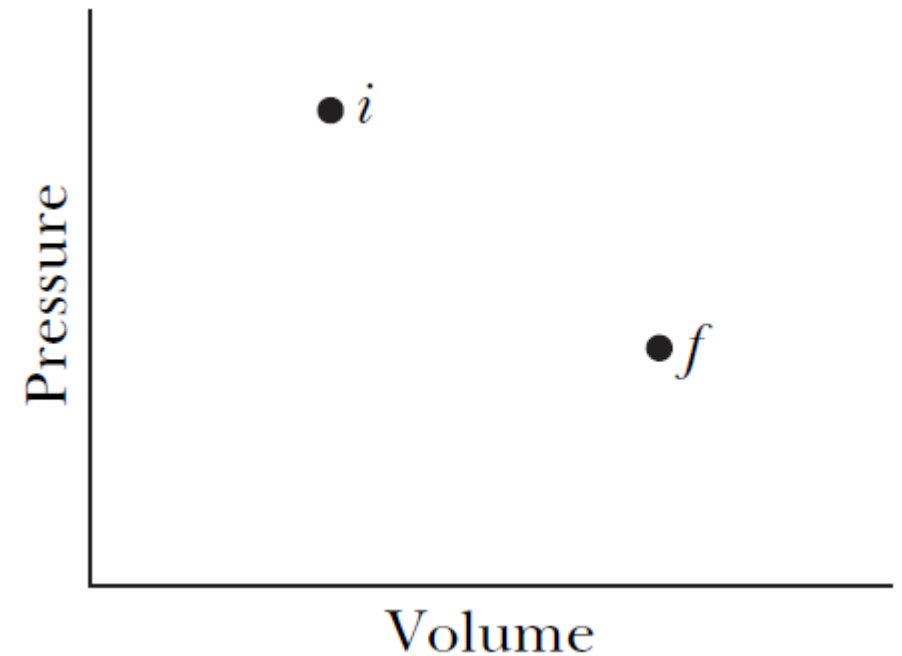(a) Initial state i
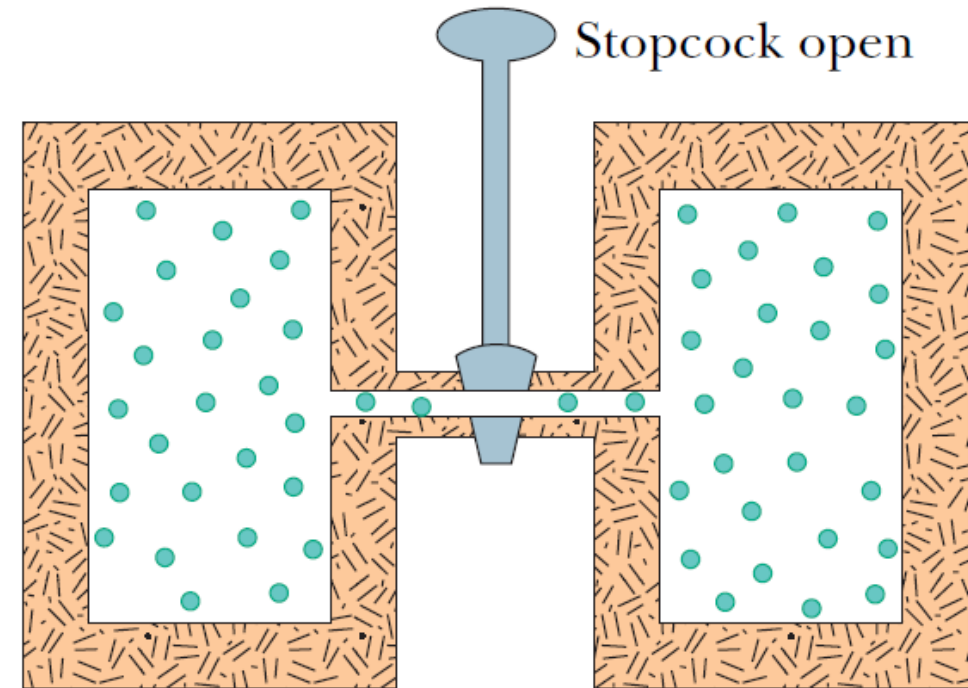
(b) Final state f

3. Change in Entropy

This process is irreversible: the gas molecules will never return to the left half of the container.

The figure shows the p-V plot of the process; the pressure and volume of the gas in the initial state i and final state f.

Pressure and volume are **state properties**: they depend only on the state of the gas, not on how it reached that state.

Temperature and internal energy are other state properties.

We assume that the gas has still another state property: entropy.

3. Change in Entropy

We define the change in entropy $S_f - S_i$ of a system during a <u>reversible</u> process that takes the system from an initial state i to a final state f as

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T},$$

where Q is the energy transferred as heat to or from the system during the process. ΔS has the same sign as that of Q. The SI unit of entropy is J/K.

We cannot use the expression above to calculate ΔS for the free expansion process since it is irreversible.

However, if the entropy is a state property, the change in entropy ΔS between states i and state f must depend only on these states.
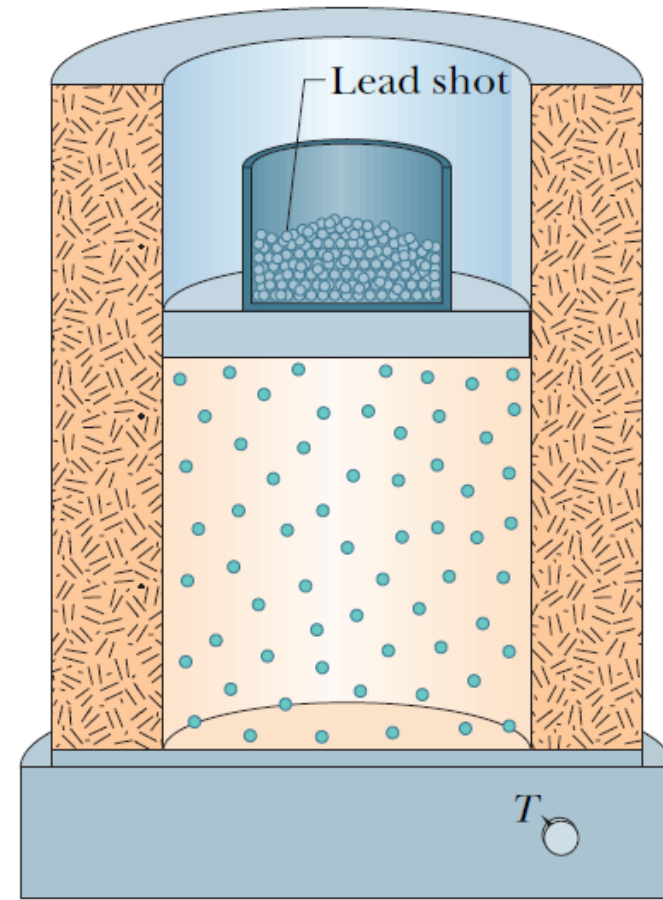
3. Change in Entropy

Let us replace the irreversible free expansion with a reversible process that connects states i and f. We will then trace a pressure-volume path on a p-V plot, and find a relation between Q and T that enables us to find ΔS.

We know that the temperature of an ideal gas does not change during a free expansion ($T_i = T_f$). Thus, points i and f are both on the same isotherm. We therefore choose to replace the process with an isothermal process which proceeds along an isotherm connecting states i and f.
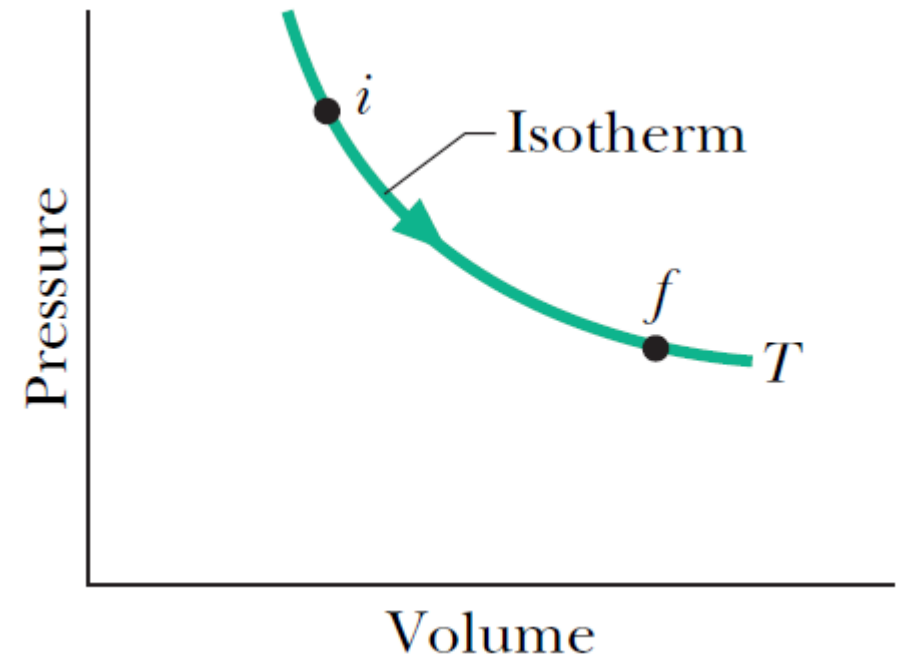
3. Change in Entropy
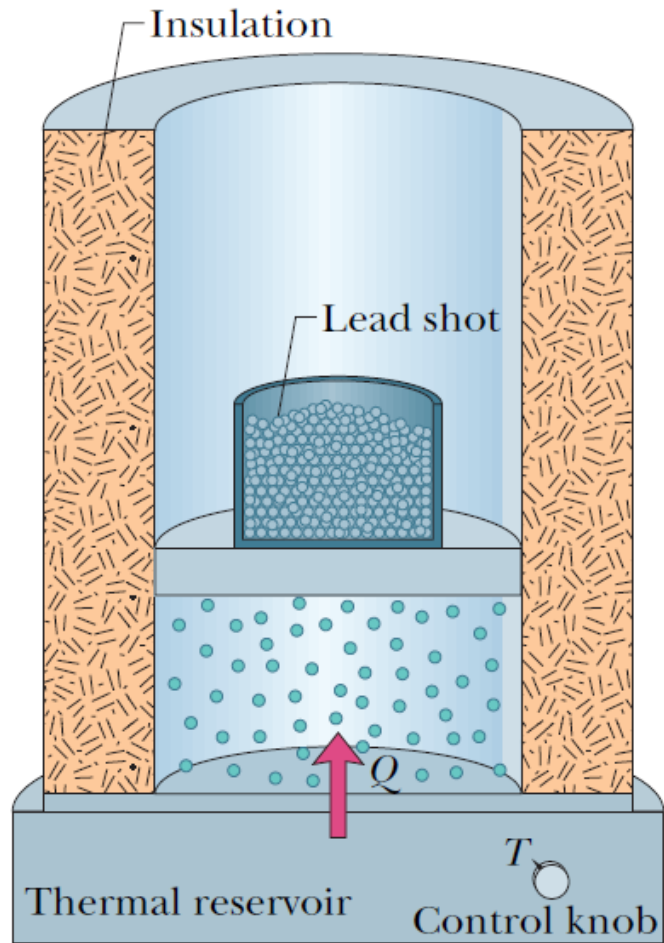
(a) Initial state i

(b) Final state f

3. Change in Entropy

The reversible isothermal process and irreversible free expansion are quite different processes. However, because both processes have the same initial and final states, they must have the same change in entropy.

The isothermal expansion proceeds smoothly as we remove lead shot slowly. The intermediate states of the gas are therefore equilibrium states and we can plot them on the p-V diagram.

3. Change in Entropy

We now evaluate the integral $\left(\int_i^f dQ/T\right)$ for the isothermal process:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f dQ = \frac{Q}{T}.$$

Heat Q has been added to the gas to keep it at constant temperature. Thus, Q is positive and the entropy of the gas increases during the process.

To sum up:

To find the entropy change for an irreversible process occurring in a closed system, replace that process with any reversible process that connects the same initial and final states. Calculate the entropy change for this reversible process with $\int_i^f dQ/T$.

3. Change in Entropy

When $\Delta T \ll T$ (in kelvins), the entropy change can be approximated as

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{avg}},$$

where T_{avg} is the average temperature of the system in kelvins during the process.

3. Change in Entropy

Water is heated on a stove. Rank the entropy changes of the water as its temperature rises (a) from 20°C to 30°C, (b) from 30°C to 35°C, and (c) from 80°C to 85°C, greatest first.

(a), (b) then (c).

$$Q = C\Delta T$$

$$\Delta S \approx \frac{Q}{T_{avg}}$$

3. Change in Entropy

Entropy as a State Function

We want to prove that the entropy is indeed a state function for the case in which an ideal gas is taken through a reversible process.

To make the process reversible, it is done slowly in a series of small steps, with the gas in an equilibrium state at the end of each step. In every step, heat dQ is transferred to or from the gas, work dW is done by the gas, and the change in internal energy is dE_{int}. According to the first law of thermodynamics,

$$dE_{\text{int}} = dQ - dW.$$

Using $dW = pdV$, $dE_{\text{int}} = nC_V dT$ and rearranging gives

$$dQ = pdV + nC_V dT.$$

3. Change in Entropy

Entropy as a State Function

We then replace p with nRT/V and divide both sides by T to get

$$\frac{dQ}{T} = nR\frac{dV}{V} + nC_V\frac{dT}{T}.$$

Integrating between arbitrary initial and final states, we have

$$\int_i^f \frac{dQ}{T} = nR\int_i^f \frac{dV}{V} + nC_V\int_i^f \frac{dT}{T}.$$

The quantity on the left hand side is ΔS $(= S_f - S_i)$, which can be written as

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i} + nC_V\ln\frac{T_f}{T_i}.$$

3. Change in Entropy

Entropy as a State Function

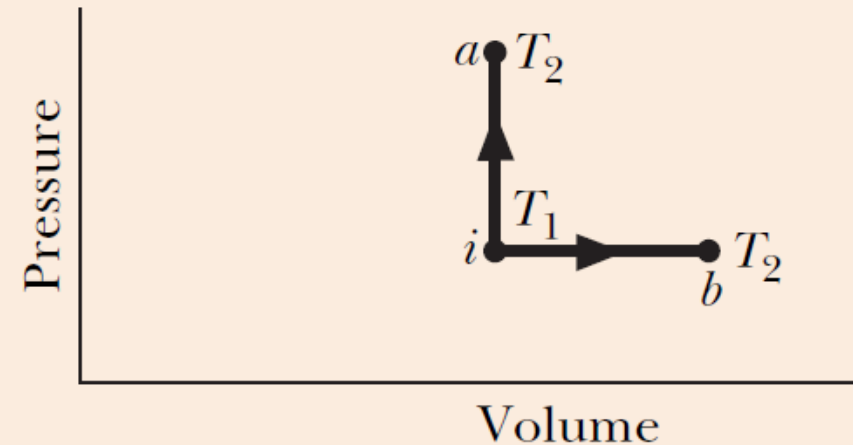$$\Delta S = S_f - S_i = nR \ln\frac{V_f}{V_i} + nC_V \ln\frac{T_f}{T_i}.$$

This result holds for all reversible processes that take the gas from state i to state f. We can see that ΔS depends only on the properties of the initial state (V_i, T_i) and final state (V_f, T_f). ΔS does not depend on how the gas changes between the two states.

3. Change in Entropy

An ideal gas has temperature T_1 at the initial state i shown in the p-V diagram here. The gas has a higher temperature T_2 at final states a and b, which it can reach along the paths shown. Is the entropy change along the path to state a larger than, smaller than, or the same as that along the path to state b?


Smaller.

$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}$$

3. Change in Entropy

Example 1: The figure shows two identical copper blocks of mass $m = 1.5$ kg: block L at temperature $T_{iL} = 60°C$ and block R at temperature $T_{iR} = 20°C$. The blocks are in a thermally insulated box and are separated by an insulating shutter. When we lift the shutter, the blocks eventually come to the equilibrium temperature $T_f = 40°C$. What is the net entropy change of the two-block system during this irreversible process? The specific heat of copper is 386 J/kg · K.
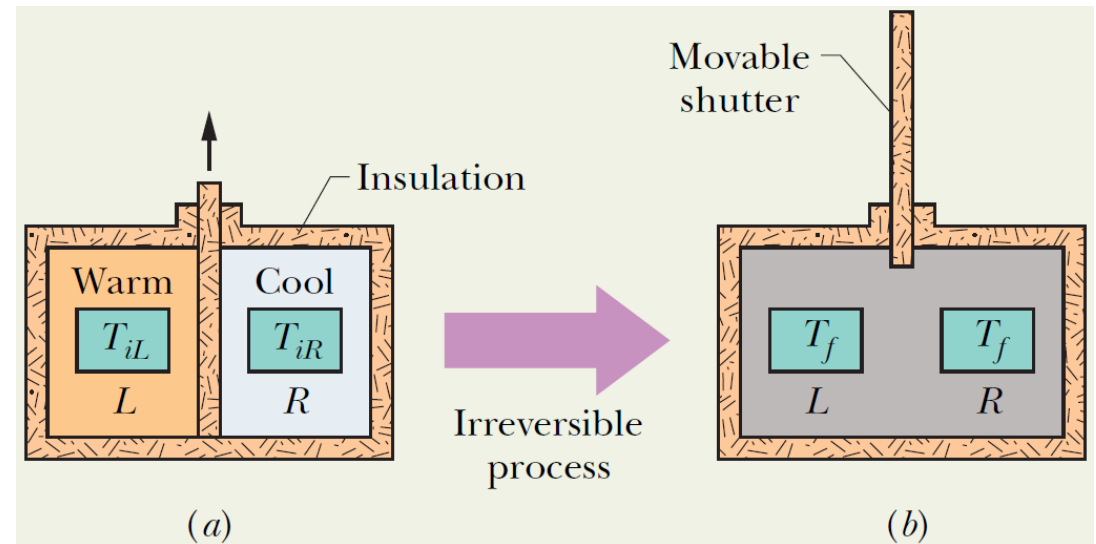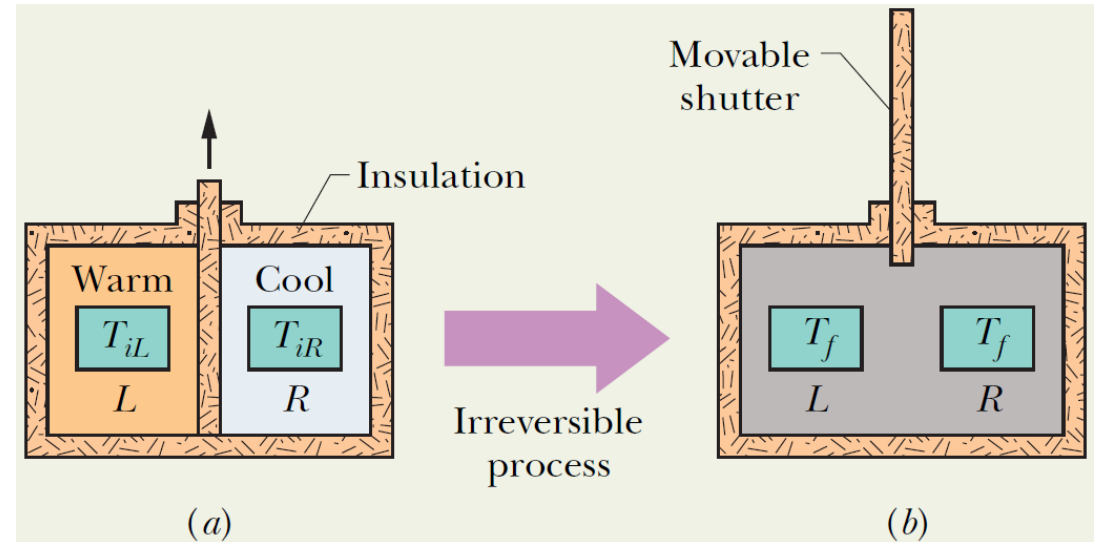
3. Change in Entropy

To calculate the entropy change, we must find a reversible process that takes the system from the initial state (a) to the final state (b).

We can calculate the net entropy change ΔS_{rev} of the reversible process using

$$\Delta S_{rev} = \int_i^f \frac{dQ}{T},$$

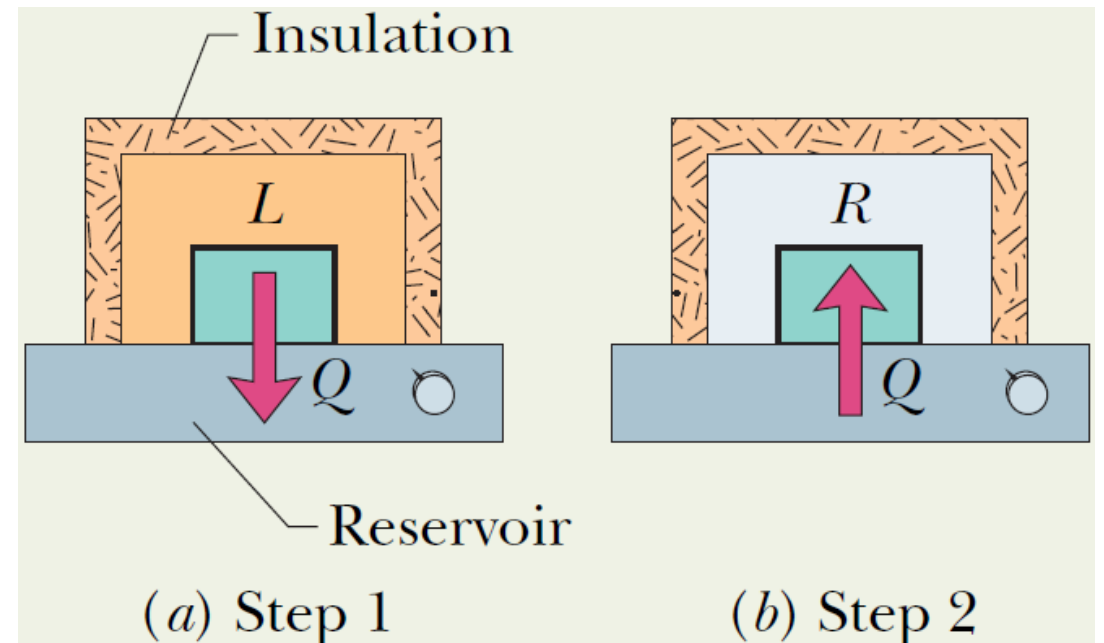and then the entropy change for the irreversible process is equal to ΔS_{rev}.

3. Change in Entropy

Consider the alterative process shown in the figure. The blocks can proceed from their initial state to their final state in a reversible way if we use a reservoir with a controllable temperature (a) to extract heat reversibly from block L and (b) to add heat reversibly to block R.

For block L

$$\Delta S_L = \int_i^f \frac{dQ}{T} = \int_{T_{iL}}^{T_f} \frac{mcdT}{T} = mc \int_{T_{iL}}^{T_f} \frac{dT}{T}$$

$$= mc \ln \frac{T_f}{T_{iL}} = (1.5 \text{ kg})(386 \text{ J/kg} \cdot \text{K}) \ln \frac{313\text{K}}{333\text{K}}$$
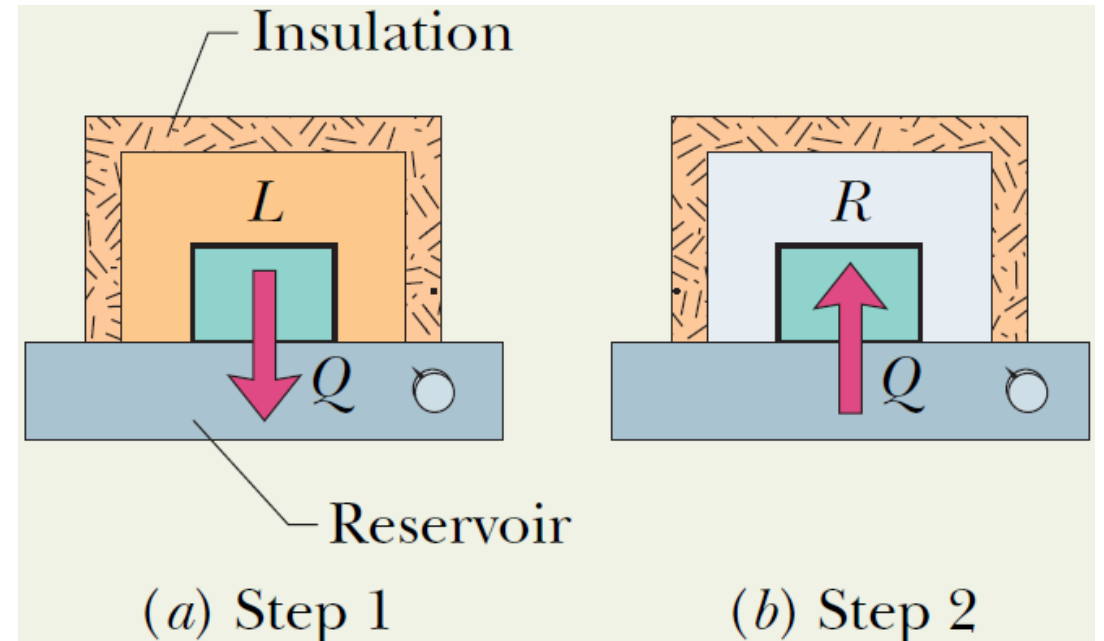
$$= -35.86 \text{ J/K}.$$

Insulation

L

R

Q

Q

Reservoir

(a) Step 1

(b) Step 2

3. Change in Entropy

For black R

$$\Delta S_R = mc \ln \frac{T_f}{T_R}$$

$$= (1.5 \text{ kg})(386 \text{ J/kg} \cdot \text{K}) \ln \frac{313\text{K}}{293\text{K}}$$

$$= 38.23 \text{ J/K}.$$

$$\Delta S = \Delta S_L + \Delta S_R = -35.86 \text{ J/K} + 38.23\text{J/K}$$

$$= 2.4 \text{ J/K}.$$

ΔS is positive, in accordance with the entropy postulate.

Insulation

L

Q

Reservoir

(a) Step 1

R

Q

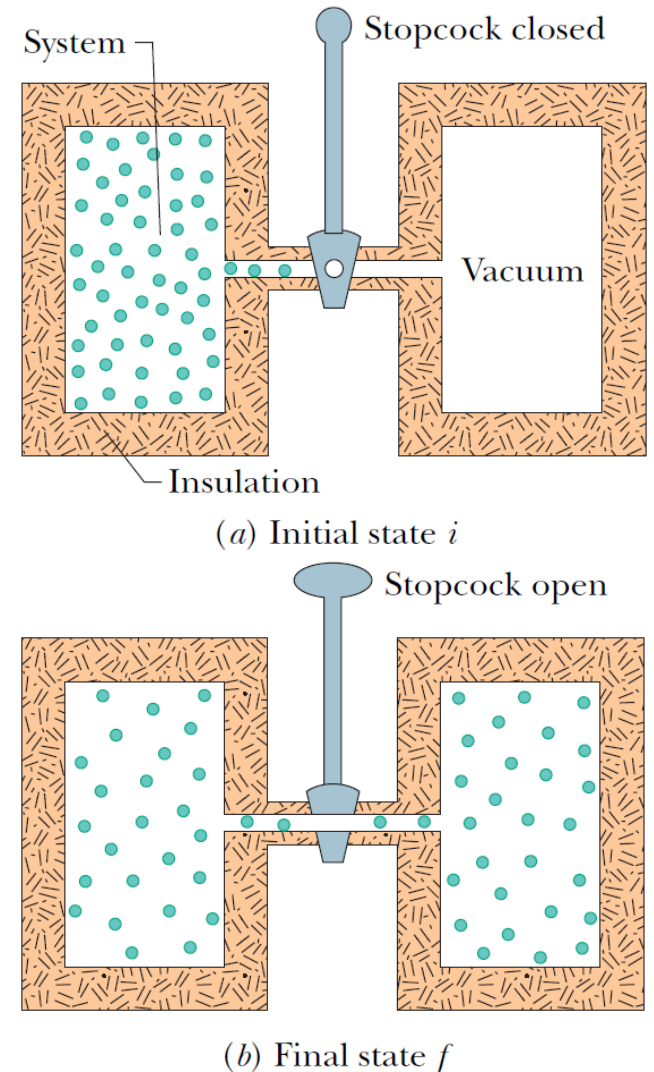(b) Step 2

3. Change in Entropy

Example 2: Suppose 1.00 mol of nitrogen gas is confined to the left side of the container of the figure. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process? Treat the gas as ideal.

$$\Delta S_{irr} = \Delta S_{rev} = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}.$$

In the free expansion $T_i = T_f$ and $2V_i = V_f$. Thus,

$$\Delta S_{irr} = \Delta S_{rev} = nR \ln 2 + nC_V \ln 1$$

$$= (1.00 \text{ mol}) \left(8.31 \frac{J}{\text{mol} \cdot K} \right) \ln 2 = 5.76 \text{ J/K}.$$

ΔS is positive, in accordance with the entropy postulate.

System — Stopcock closed

Vacuum

Insulation

(*a*) Initial state *i*

Stopcock open

(*b*) Final state *f*

4. The Second Law of Thermodynamics

We have seen that when the system (see slide 8) proceeds from (a) to (b), the change in the entropy of the gas (which we take as our system) is positive. However, because the process is reversible, we can make the system (gas) proceeds from (b) to (a). In this reversible process, energy must be extracted as heat from the gas to keep it at a constant temperature. Therefore, Q is negative and the entropy of the gas must decrease.

This does not violate the entropy postulate, which states that entropy always increases, because it holds only for <u>irreversible processes</u> occurring in <u>closed systems</u>. The process here is not irreversible and the system is not closed (it exchanges heat with the reservoir).

The enlarged system of the gas + reservoir is closed. Let us calculate ΔS of the enlarged system for the process that takes it from (b) to (a).

4. The Second Law of Thermodynamics

During this process, an amount of heat Q is transferred from the gas to the reservoir. The gas loses $|Q|$ and the reservoir gains heat $|Q|$. Therefore,

$$\Delta S_{\text{gas}} = -\frac{|Q|}{T}$$

and

$$\Delta S_{\text{res}} = +\frac{|Q|}{T}.$$

The entropy change of the closed system is therefore zero.

We can modify the entropy postulate to include both reversible and irreversible processes:

"If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases."

4. The Second Law of Thermodynamics

The entropy may decrease in part of a closed system, but there will always be an equal or larger entropy increase in another part of the system. The entropy of the system as a whole never decreases. This fact is one form of the second law of thermodynamics which can be written as

$$\Delta S \geq 0.$$

The greater-than sign applies to irreversible processes and the equal sign to reversible processes. This inequality applies only to <u>closed systems</u>.

In the real world almost all processes are irreversible, so the entropy of real closed systems undergoing real processes always increases. Processes in which the system's entropy remains constant are always idealization.

5. Entropy in the Real World: Engines

A **heat engine** (or simply **engine**) is a device that extracts energy from its environment in the form of heat and does useful work.

In every engine, there is a *working substance*. Water (vapor) is the working substance in steam engines, and gasoline-air mixture is the working substance in an automobile engine.

If the engine is to do work on a sustained basis, the working substance must operate in a *cycle*: the working substance must pass through a closed series of thermodynamic processes, called *strokes*, returning repeatedly to each state in its cycle.

We want to see what the law of thermodynamics tells us about the operation of engines.

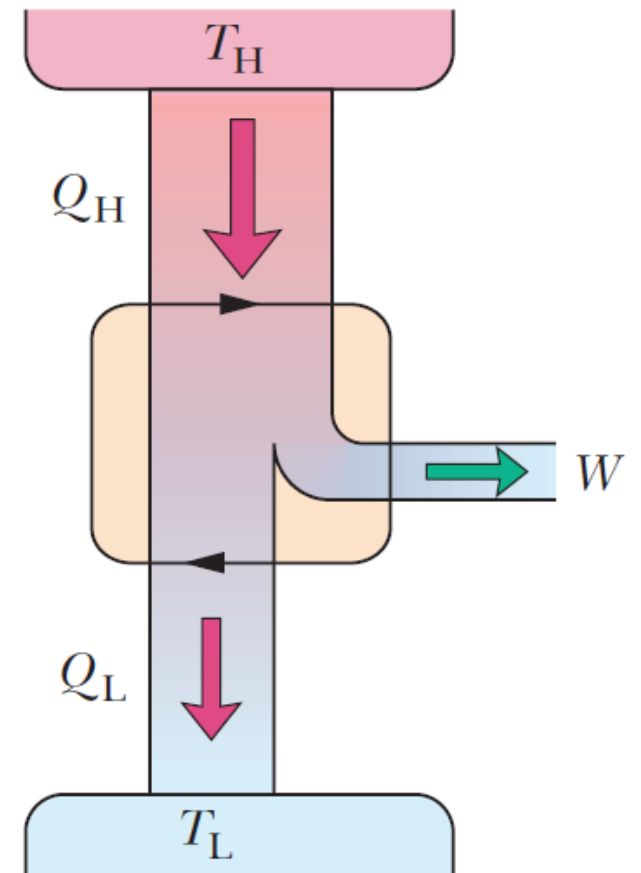# 5. Entropy in the Real World: Engines

A Carnot Engine

To study real engines we need to analyze an **ideal engine** first.

In an ideal engine, all processes are reversible and no wasteful energy transfers occur.

We will focus on a particular ideal gas engine called the **Carnot engine**. It turns out to be the best at using energy as heat to do useful work.

The figure shows schematically the operation of a Carnot engine. During each cycle, the working substance absorbs energy $|Q_H|$ as heat from a thermal reservoir at constant temperature T_H and discharges energy $|Q_L|$ as heat to a second thermal reservoir at constant lower temperature T_L.
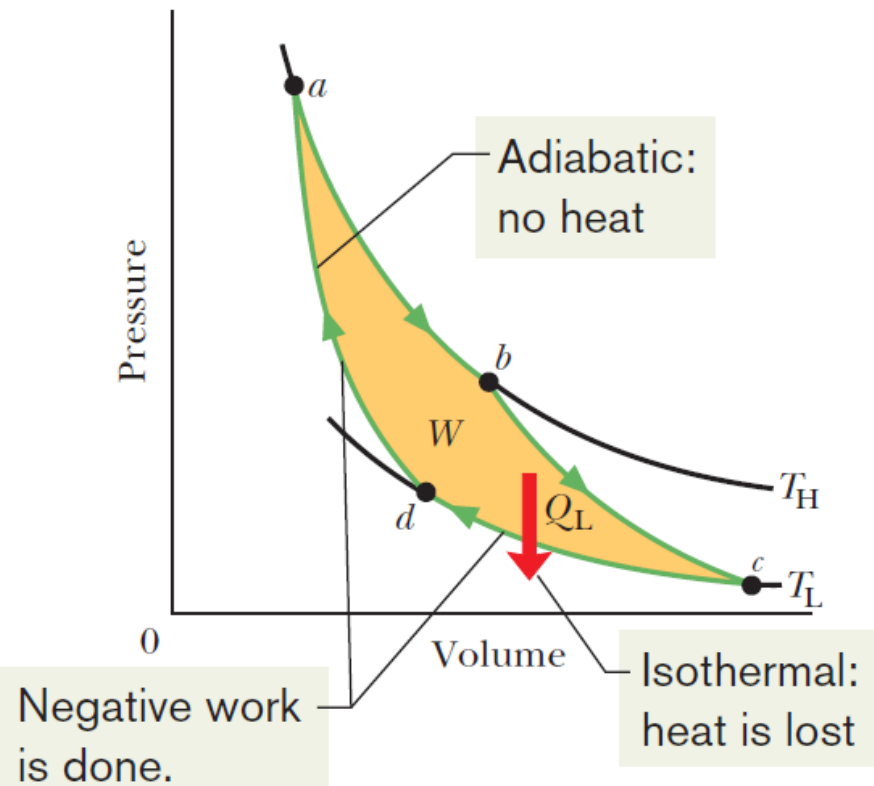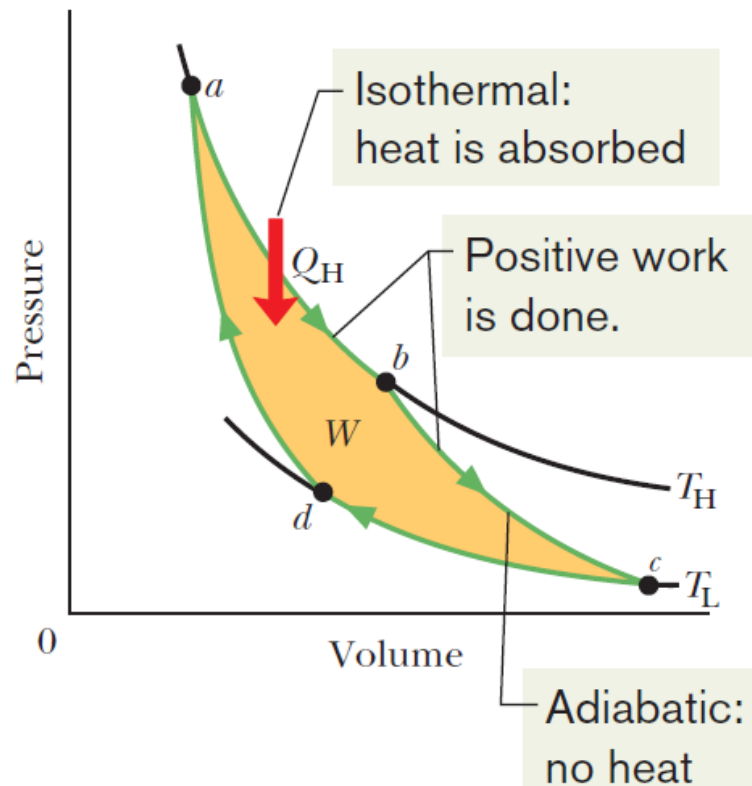
5. Entropy in the Real World: Engines

https://www.youtube.com/watch?v=s3N_QJVucF8

A Carnot Engine

The p-V plot of Carnot cycle followed the working substance is shown in the figure.

5. Entropy in the Real World: Engines

A Carnot Engine:

THE WORK: For every complete cycle of the working substance $\Delta E_{int} = 0$. Using the first law of thermodynamics $(\Delta E_{int} = Q - W)$, the net work per cycle is

$$W = Q = |Q_H| - |Q_L|.$$

ENTROPY CHANGE: There are two reversible isothermal heat transfers, and thus two changes in the entropy of the working substance: one at temperature T_H and one at temperature T_L. The net entropy change per cycle is

$$\Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}.$$

The entropy is a state variable and for a complete cycle $\Delta S = 0$. This implies that

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}.$$

5. Entropy in the Real World: Engines

A Carnot Engine:

EFFICIENCY OF A CARNOT ENGINE: The **thermal efficiency** ε of an engine is the ratio of the work the engine does (energy we get) to the energy absorbed as heat (energy we pay) in a cycle:

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay}} = \frac{|W|}{|Q_H|}.$$

For a Carnot engine

$$\varepsilon_C = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|},$$

or equivalently,

$$\varepsilon_C = 1 - \frac{T_L}{T_H}.$$
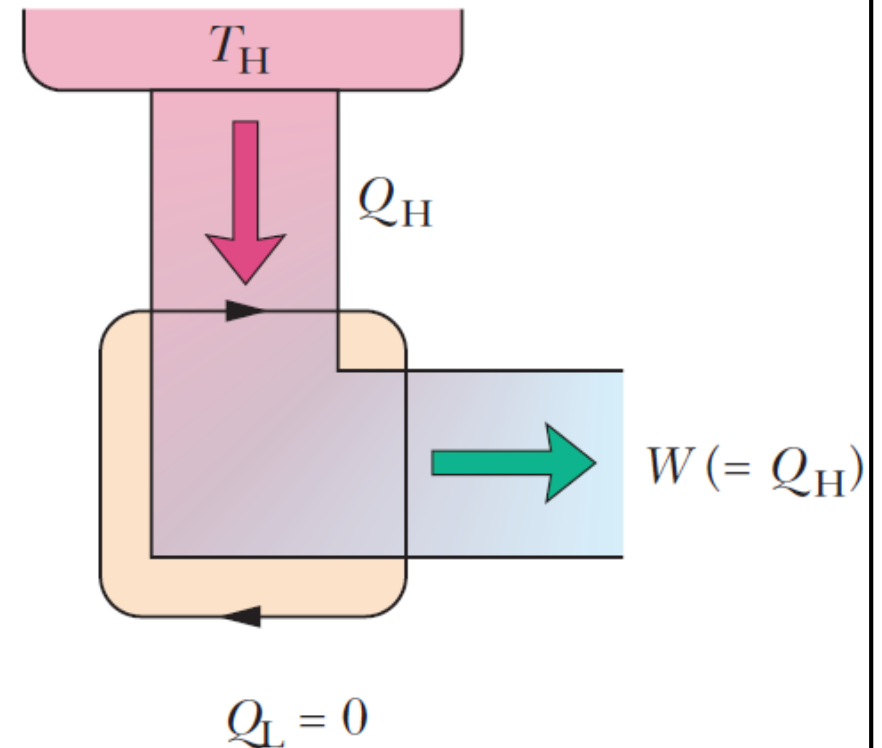
5. Entropy in the Real World: Engines

A Carnot Engine:

A perfect engine (with $|Q_L| = 0$) is shown in the figure.

Such a 100% efficiency is achieved when $T_L = 0$ or $T_H \rightarrow \infty$, which are impossible.

This fact gives an alternative version of the second law of thermodynamics, which says in short, *there are no perfect engines*:

"No series of processes is possible whose sole result is the transfer of energy as heat from a thermal reservoir and the complete conversion of this energy to work."

T_H

Q_H

$W (= Q_H)$

$Q_L = 0$

5. Entropy in the Real World: Engines

Stirling Engine:
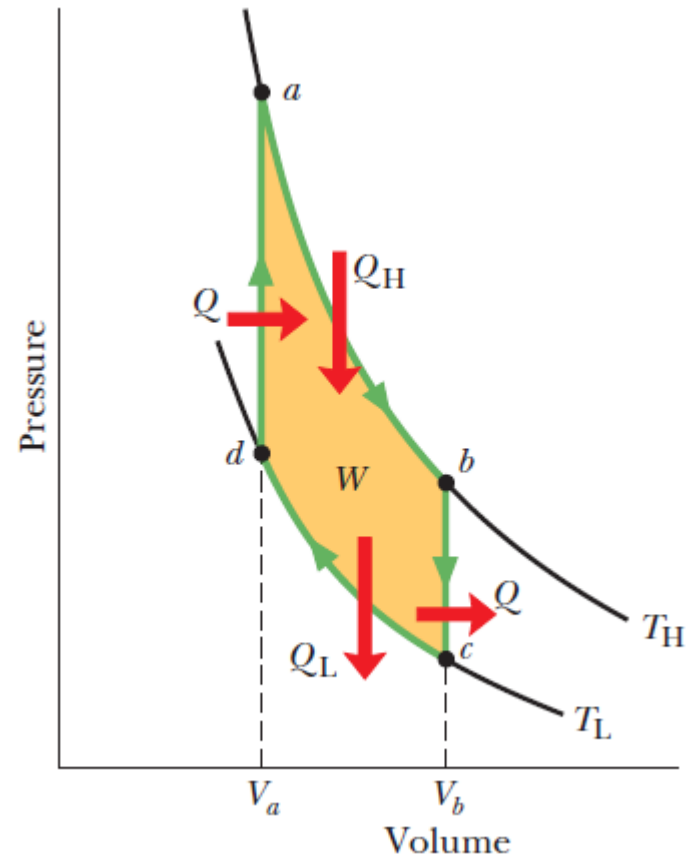
5. Entropy in the Real World: Engines

c, b and then a.

$$\varepsilon_C = 1 - \frac{T_L}{T_H}.$$

3. Change in Entropy

Example 3: Imagine a Carnot engine that operates between the temperatures T_H = 850 K and T_L = 300 K. The engine performs 1200 J of work each cycle, which takes 0.25 s.

(a) What is the efficiency of this engine?

$$\varepsilon_C = 1 - \frac{T_L}{T_H} = 1 - \frac{300 \text{ K}}{850 \text{ K}} = 0.647 = 64.7\%.$$

(b) What is the average power of this engine?

$$P = \frac{W}{t} = \frac{1200 \text{ J}}{0.25 \text{ s}} = 4.8 \text{ kW}.$$

3. Change in Entropy

(c) How much energy $|Q_H|$ is extracted as heat from the high-temperature reservoir every cycle?

We know that $\varepsilon_C = W/|Q_H|$. Thus,

$$|Q_H| = \frac{W}{\varepsilon_C} = \frac{1200\text{ J}}{0.647} = 1.85\text{ kJ.}$$

(d) How much energy $|Q_L|$ is delivered as heat to the low temperature reservoir every cycle?

$$|Q_L| = |Q_H| - W = 1855\text{ J} - 1200\text{ J} = 655\text{ J.}$$

3. Change in Entropy

(e) By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{1855 \text{ J}}{850 \text{ K}} = 2.18 \text{ J/K.}$$

$$\Delta S_L = \frac{-Q_L}{T_L} = \frac{-655 \text{ J}}{300 \text{ K}} = -2.18 \text{ J/K.}$$

$$\Delta S = \Delta S_H + \Delta S_L = 0,$$

as it should be for a reversible process.

3. Change in Entropy

Example 4: An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and freezing points of water. Is this possible?

The efficient of any engine cannot exceed the efficiency of a Carnot engine.

$$\varepsilon_C = 1 - \frac{273 \text{ K}}{373 \text{ K}} = 0.268 = 26.8\%.$$

The claimed engine is impossible.

6. Entropy in the Real World: Refrigerators

A **refrigerator** is a device that uses work to transfer energy from a low-temperature reservoir to a high-temperature reservoir on a sustained basis.

Let us consider an ideal refrigerator. In an ideal refrigerator, all processes are reversible and no wasteful energy transfers occur.

The figure shows the basic elements of an ideal refrigerator.

Its operation is the reverse of how the Carnot engine operates. We call such an ideal refrigerator, a **Carnot refrigerator**.
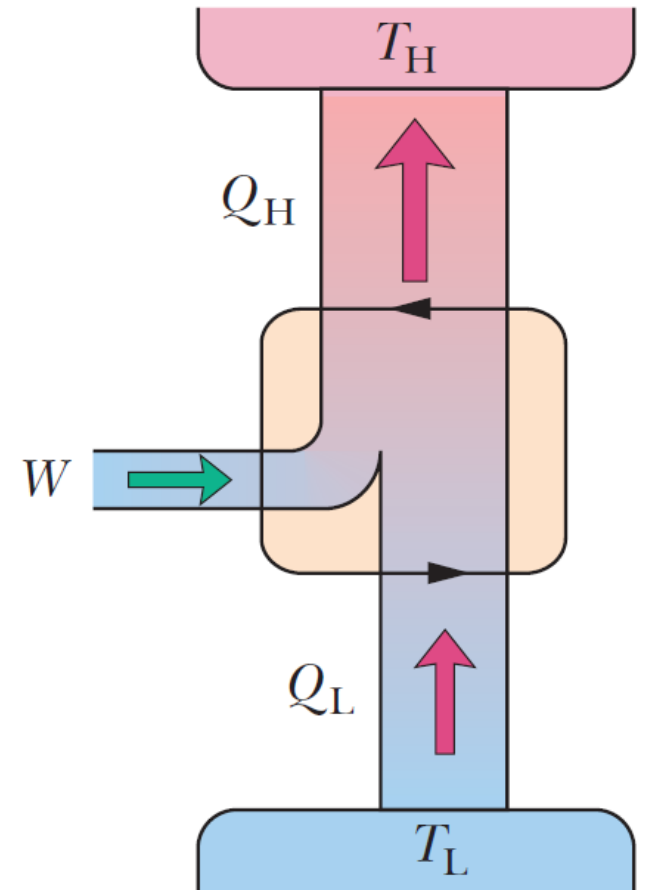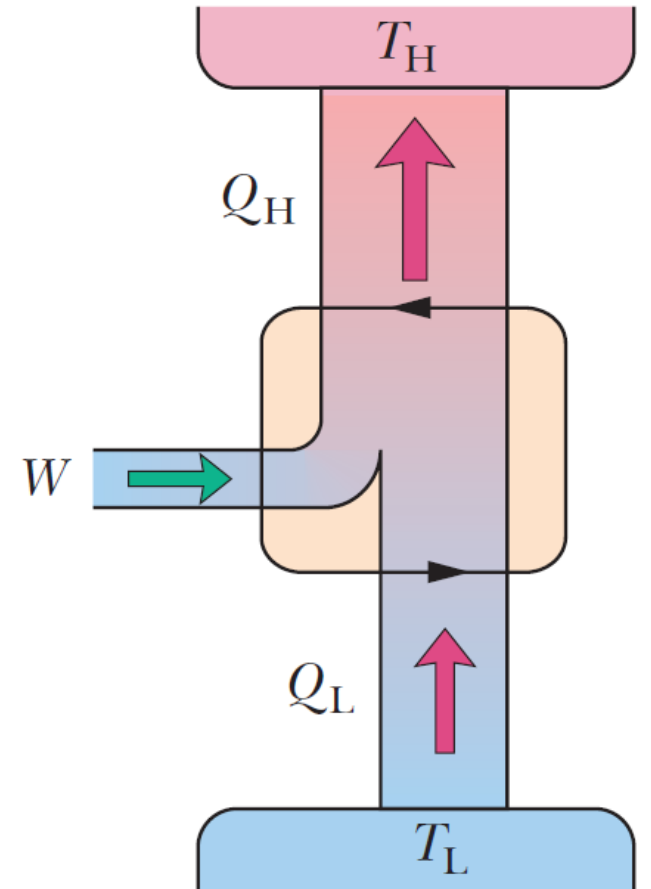
6. Entropy in the Real World: Refrigerators

We would like to extract as much energy $|Q_L|$ as possible from the low temperature reservoir (what we want) for the least amount of work $|W|$ (what we pay for). A measure of the efficiency of a refrigerator is then

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|}.$$

K is called the **coefficient of performance**. The first law of thermodynamics for a Carnot refrigerator gives $|W| = |Q_H| - |Q_L|$. We then write
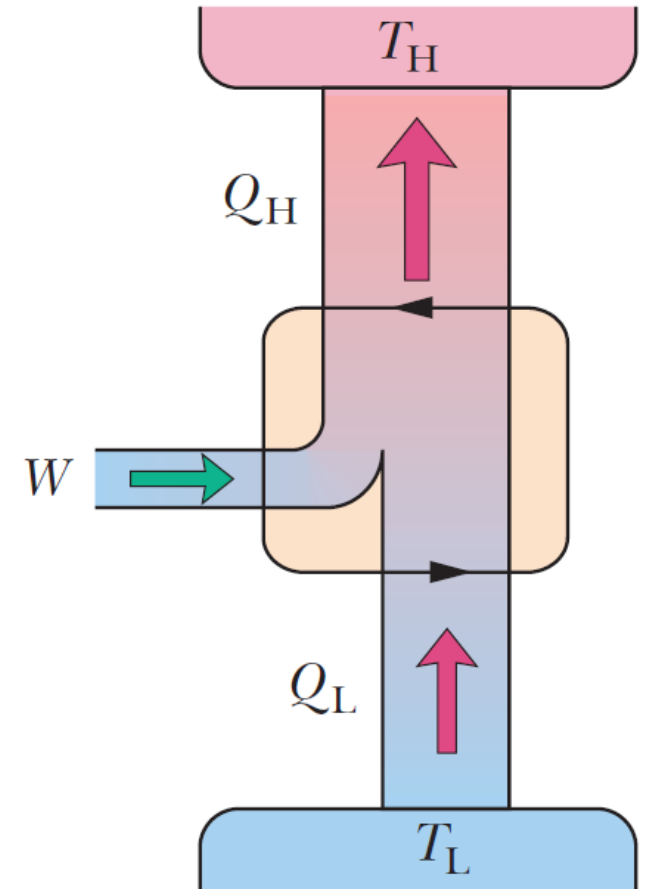
$$K = \frac{|Q_L|}{|Q_H| - |Q_L|}.$$

6. Entropy in the Real World: Refrigerators

The second law of thermodynamics requires that $\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$.

K can be rewritten as

$$K = \frac{T_L}{T_H - T_L}.$$

6. Entropy in the Real World: Refrigerators

The figure shows a **perfect refrigerator** that transfers heat Q from a cold reservoir to a warm reservoir without the need for work.

The entropy of working substance does not change because the unit is working in cycles. The entropy of the reservoirs, however, do change:

$$\Delta S = \Delta S_H + \Delta S_L = \frac{|Q|}{T_H} - \frac{|Q|}{T_L}.$$

Because $T_H > T_L$, ΔS is negative and the change of entropy of the closed system of the refrigerator + reservoirs is negative. Therefore, a perfect refrigerator does not exist.
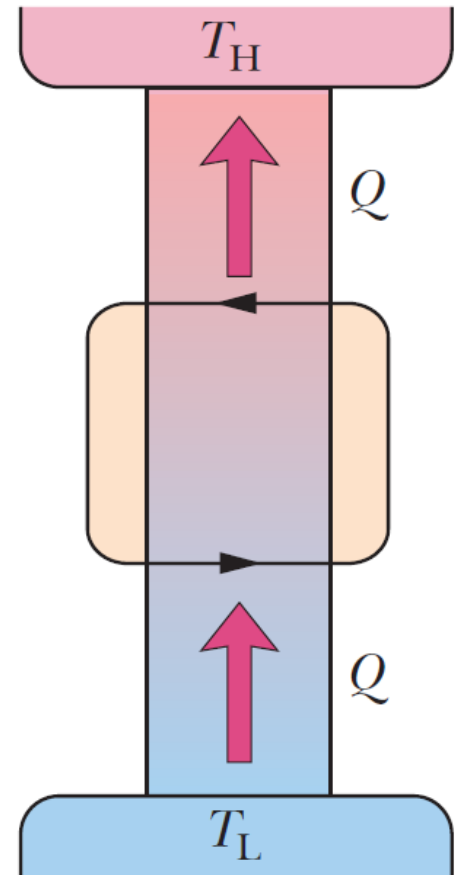
6. Entropy in the Real World: Refrigerators

This result leads to another formulation of the second law of thermodynamics, which says in short, *there are no perfect refrigerators*:

"No series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature."