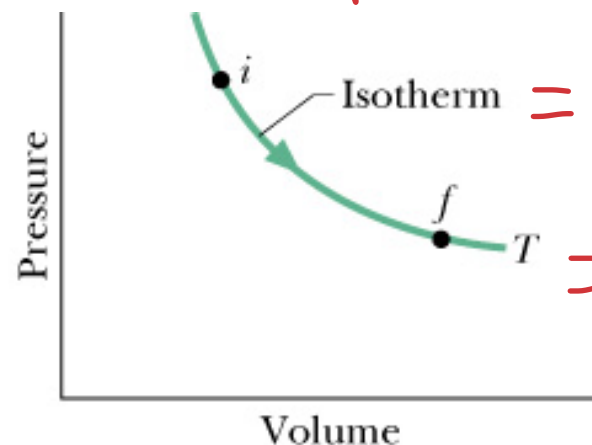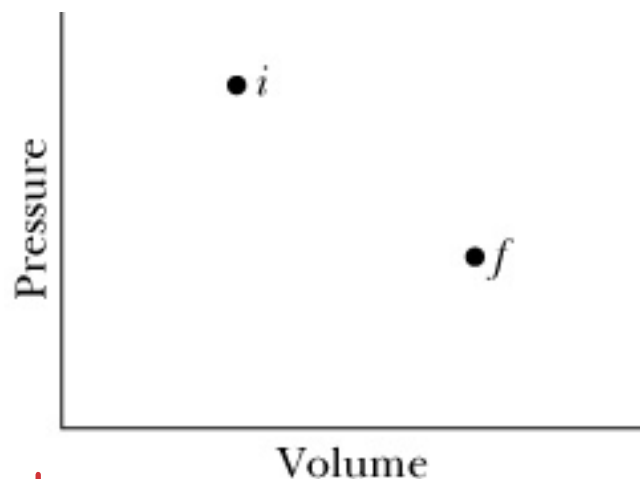Homework: Read Sample Problems page 540 and page 541

Sample Problem (p. 541)

Suppose 1.0 mol of nitrogen gas is confined to the left side of the container of the figure below. 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.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int dQ = \frac{Q}{T} = \frac{nRT}{T}\ln\frac{v_f}{v_i} =$$


$$w = Q = nRT\ln\frac{V_f}{V_i} \Rightarrow \Delta S_{rev} = nR\ln\frac{V_f}{V_i}$$

We have n= 1 mol, V_f/V_i=2: $\Rightarrow \Delta S_{rev} = 1.0 \times 8.31 \times \ln 2 = 5.76$ (J/K)

$$\Delta S_{irrev} = \Delta S_{rev} = +5.76 \text{ (J/K)}$$

Sample Problem:

The pericarp part of a popcorn kernel is a small container of liquid water. When the popcorn is heated to ~180⁰C, the pericarp walls burst, and the liquid vaporizes so rapidly that the vapor explodes the rest of the kernel to many times its original volume. The explosion produces the audible pop of the popcorn. If the water in a pericarp has a mass of about 4 mg, what is the change in entropy of the water due to the vaporization and expansion?
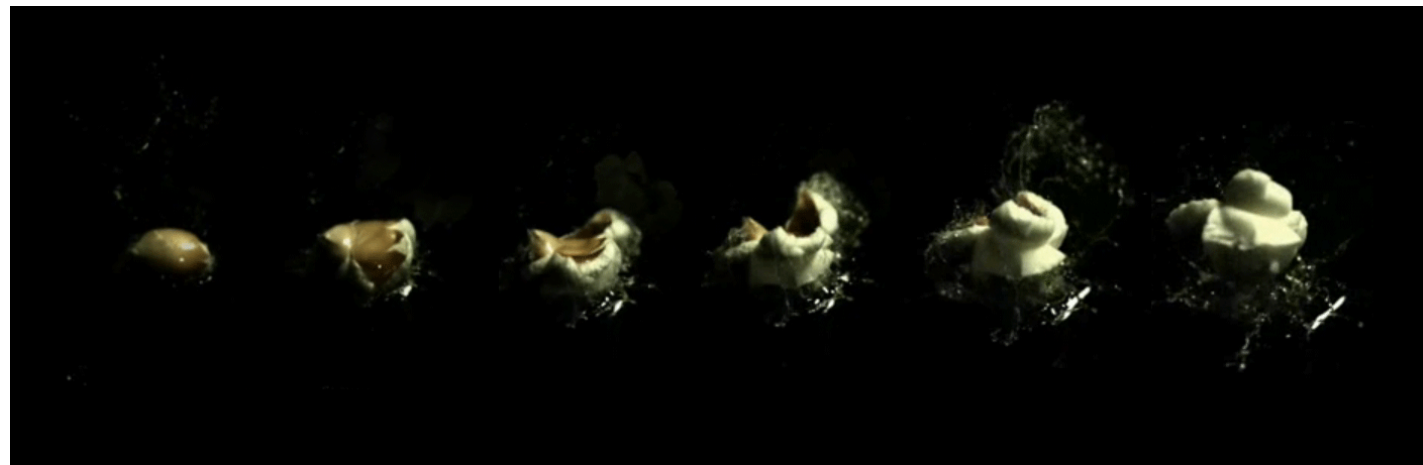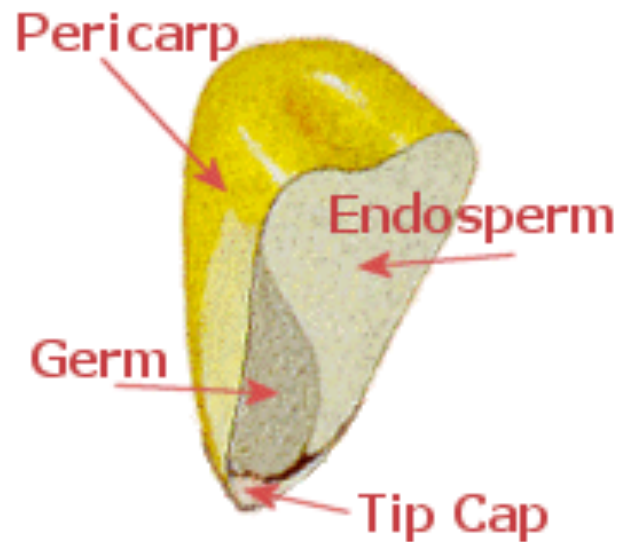
We calculate ΔS of the irreversible process (kernel ⇒ popped popcorn) by calculating two reversible processes: (1) vaporization at 180⁰C; (2) adiabatic expansion of the vapor (the process occurs so rapidly, so it is adiabatic)

Process 1: Vaporization, T = constant

$$mc\int\frac{dt}{T} = mc\ln\frac{T_f}{T_i}$$

$$Q = mc\Delta T$$
$$dQ = mc\,dT$$

$$\Delta S_1 = \int_i^f \frac{dQ}{T} = \frac{Q}{T} = \frac{mL_v}{T}$$

L_v = 2256 kJ/kg: latent heat of vaporization of water

$$\Delta S = \frac{2256\times10^3 \times 4\times10^{-6}}{453} = 1.99\times10^{-2}\,(\text{J/K})$$

Process 2: Adiabatic expansion, dQ = 0

$$\Delta S_2 = 0$$

T const $\Rightarrow Q = mL_v$

$$\frac{1}{T}\int dQ = \frac{Q}{T} = \frac{mL_v}{T}$$

Total change in entropy: $\Delta S = \Delta S_1 + \Delta S_2 \approx 0.02\,(\text{J/K})$

Important Notes:
   • Free expansion process (Q = 0, irreversible): dQ =0 but dS > 0, the formula dS = dQ/T is not applicable.
   • Adiabatic process (Q = 0, reversible): dQ =0, dS = 0

Entropy as a State Function

Key idea: To calculate the entropy change of a process, we need to make that process reversible, which is done slowly in a series of small steps with the gas in an equilibrium state at the end of each step.

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

$$\underbrace{}_{nC_V dT} \qquad \underbrace{}_{pdV}$$

$nC_V dT \qquad\qquad pdV$

$$\boxed{dQ} = pdV + nC_V dT$$

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

$\Delta S = \mathscr{f}(p, V, T)$

State function

isothermal process
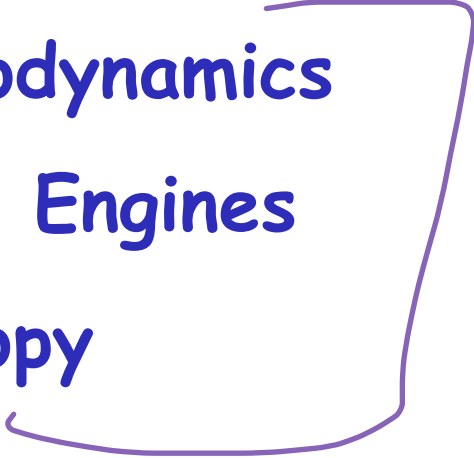
$W = Q = nRT \ln\frac{V_f}{V_i}$

Work done by gas:

$\Delta S = nR\ln\frac{V_f}{V_i}$

The entropy change:

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

$N_\theta T$

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

➡the entropy change only depends on properties of the initial and final states, therefore we say entropy is a state function.
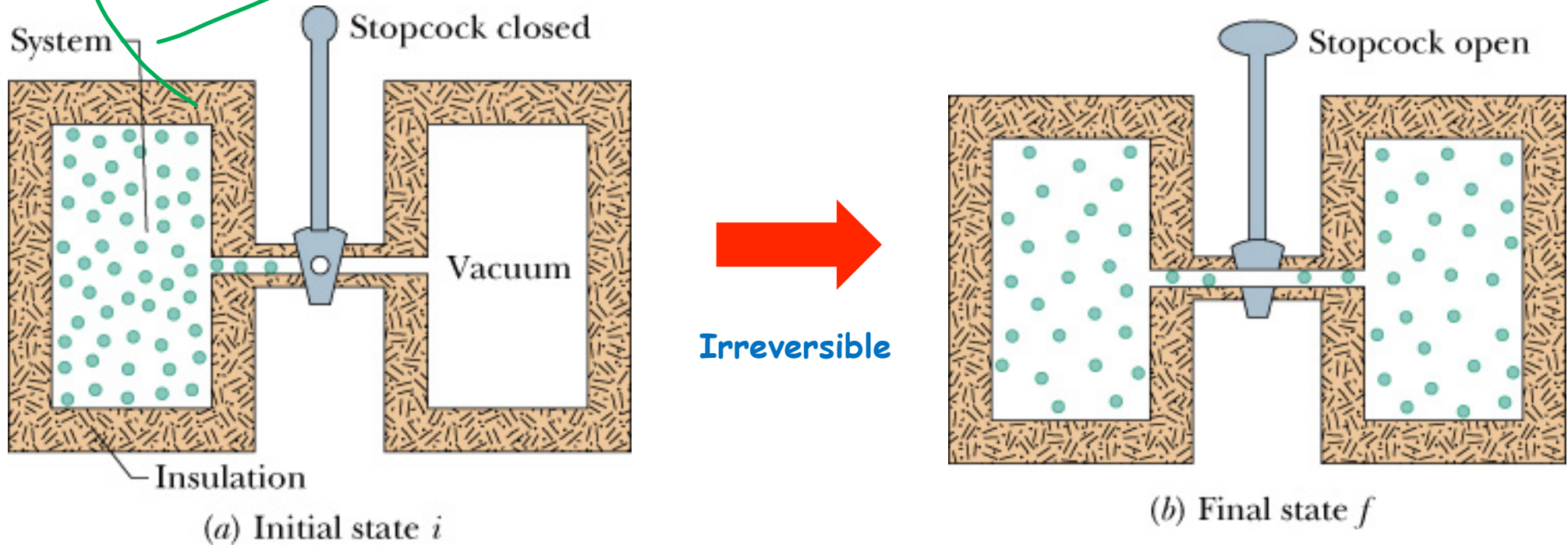
Chapter 4 Entropy and the Second Law of Thermodynamics

4.1. Reversible, Irreversible Processes and Entropy

4.2. The Second Law of Thermodynamics

4.3. Entropy in the Real World: Engines

4.4. A Statistical View of Entropy

4.2. The Second Law of Thermodynamics

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

- **Irreversible processes (ex: free expansion):**

Insulation

(a) Initial state i

(b) Final state f

$$\Delta S_{gas} = \frac{Q}{T} > 0 \ (\text{gas received energy as heat})$$

- **Reversible processes:**

  - (a) to (b): Q > 0, $\Delta S_{gas} = \dfrac{Q}{T} > 0$
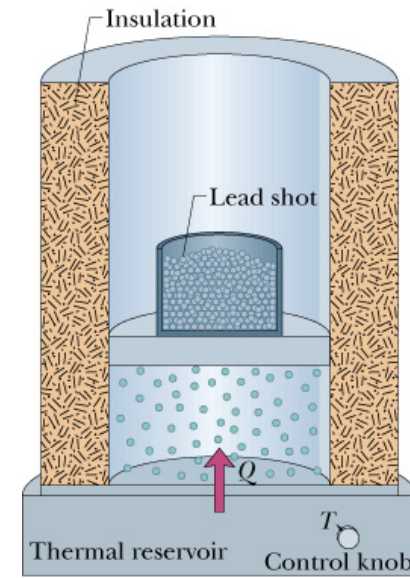
  - (b) to (a): Q < 0, $\Delta S_{gas} = \dfrac{Q}{T} < 0$

  This energy is extracted from the gas and transferred to the reservoir.

  - We now consider a __closed__ system gas + reservoir:

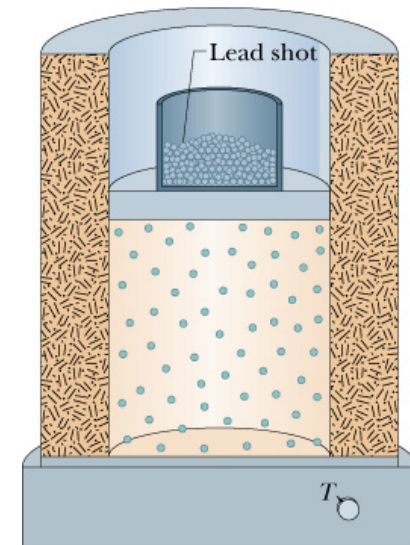$$\left.\begin{array}{l} \Delta S_{gas} = -\dfrac{|Q|}{T} \\[3mm] \Delta S_{reservoir} = +\dfrac{|Q|}{T} \end{array}\right\} \Delta S_{system} = 0 \,(\text{closed system})$$

The second law of thermodynamics for a closed system:

$$\Delta S \geq 0$$

Insulation

Lead shot

Thermal reservoir

Q

T

Control knob

(a) Initial state i

Reversible process

Lead shot

T

(b) Final state f

4.3. Entropy in the Real World: Engines

• A heat engine is a device that extracts energy from its environment in the form of heat and does useful work.

• A working substance is the heart of every engine, e.g., in a steam engine the working substance is water (vapor and liquid).

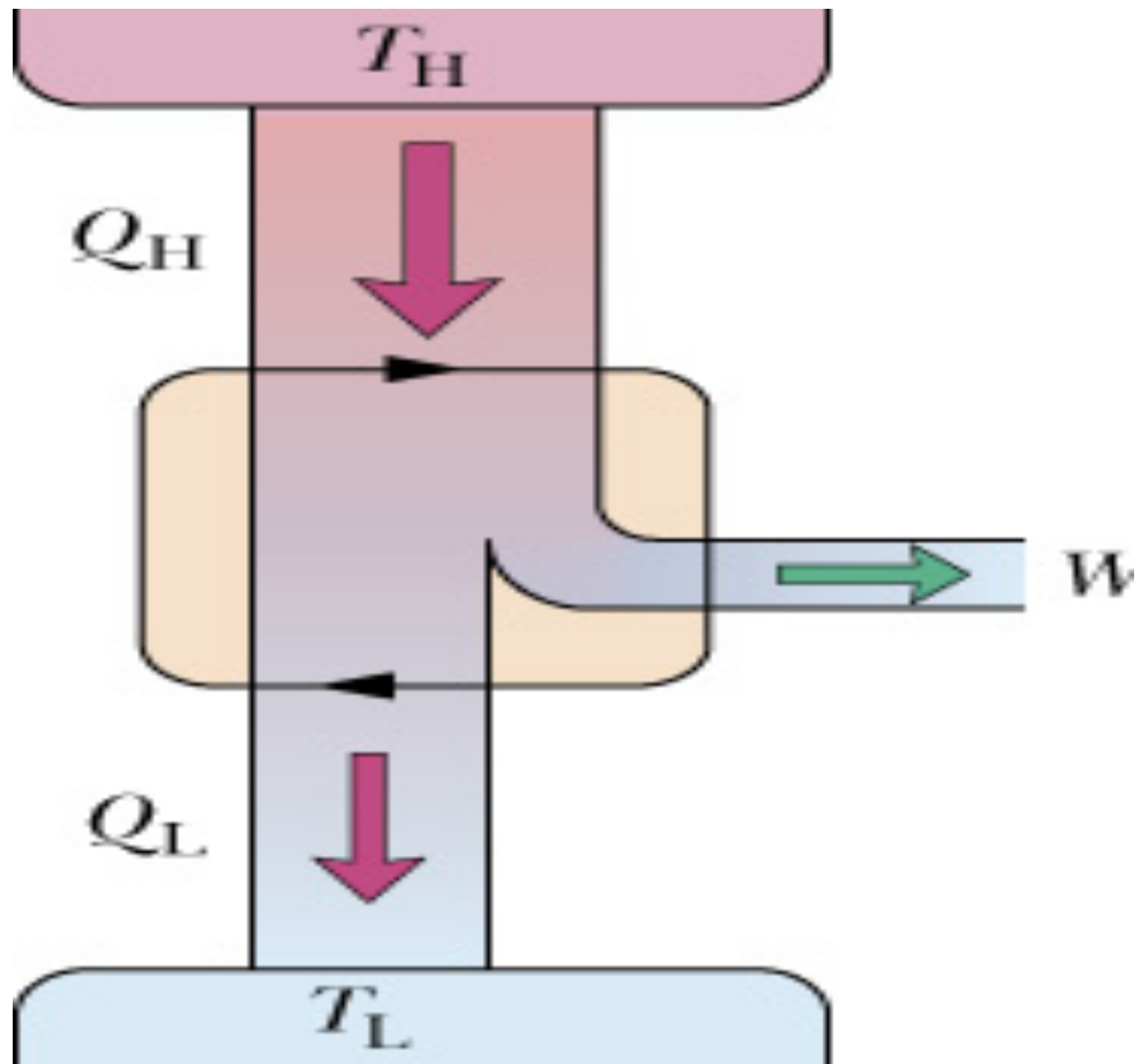• If an engine is to do work, the working substance must operate in a closed cycle.

a. A Carnot Engine (an ideal engine):

→ Not V pwl

What is an ideal engine?
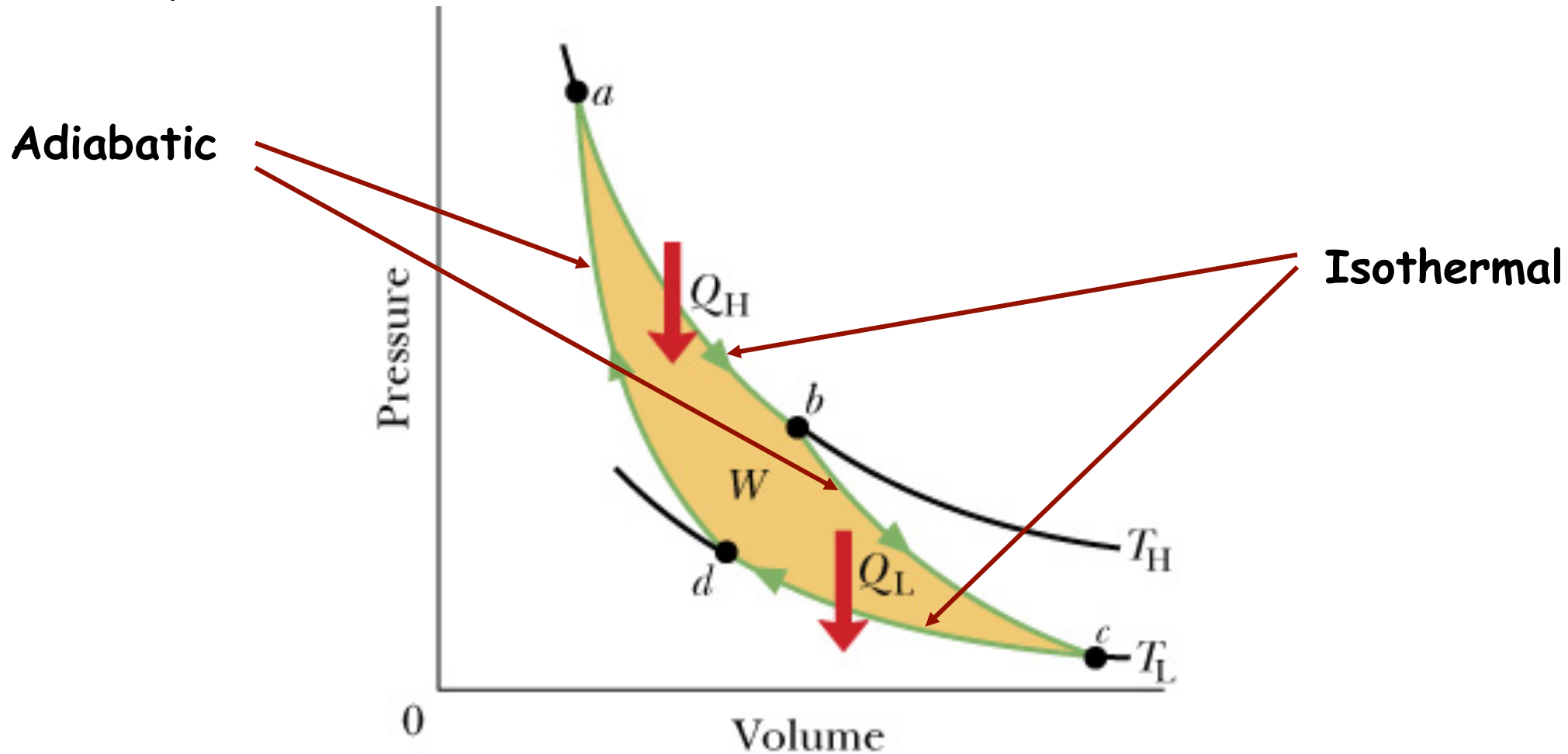
•In an ideal engine, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence.

The elements of a Carnot engine

T_H

Q_H

Q_L

T_L

W

•The Carnot cycle consists of two isothermal (ab and cd) and two adiabatic processes (bc and da).
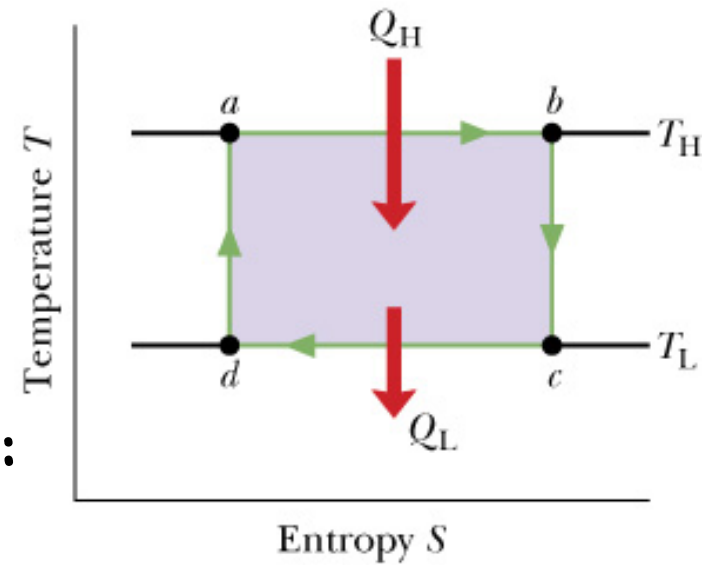
Adiabatic

Isothermal

•The working substance absorbs energy $|Q_H|$ from a thermal reservoir at a constant temperature T_H and discharges $|Q_L|$ to a second reservoir at a constant lower temperature T_L.

The work in the Carnot cycle:

$$\Delta E_{\text{int}} = 0$$

$$W = |Q_H| - |Q_L|$$

The entropy change of the working substance:

$$\Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$
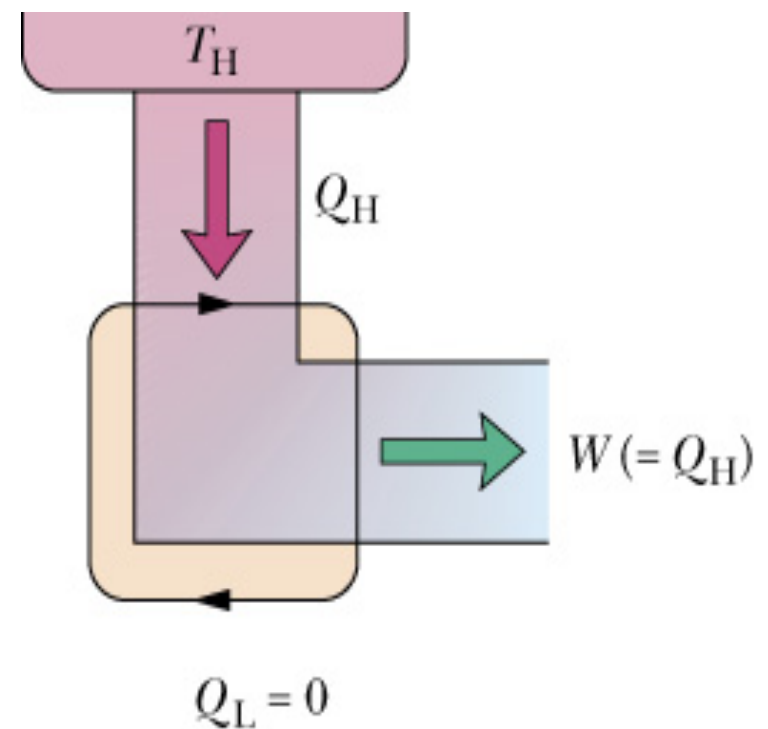
For a closed cycle:

$$\Delta S = 0 \Rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

The Efficiency of any engine:

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|}$$
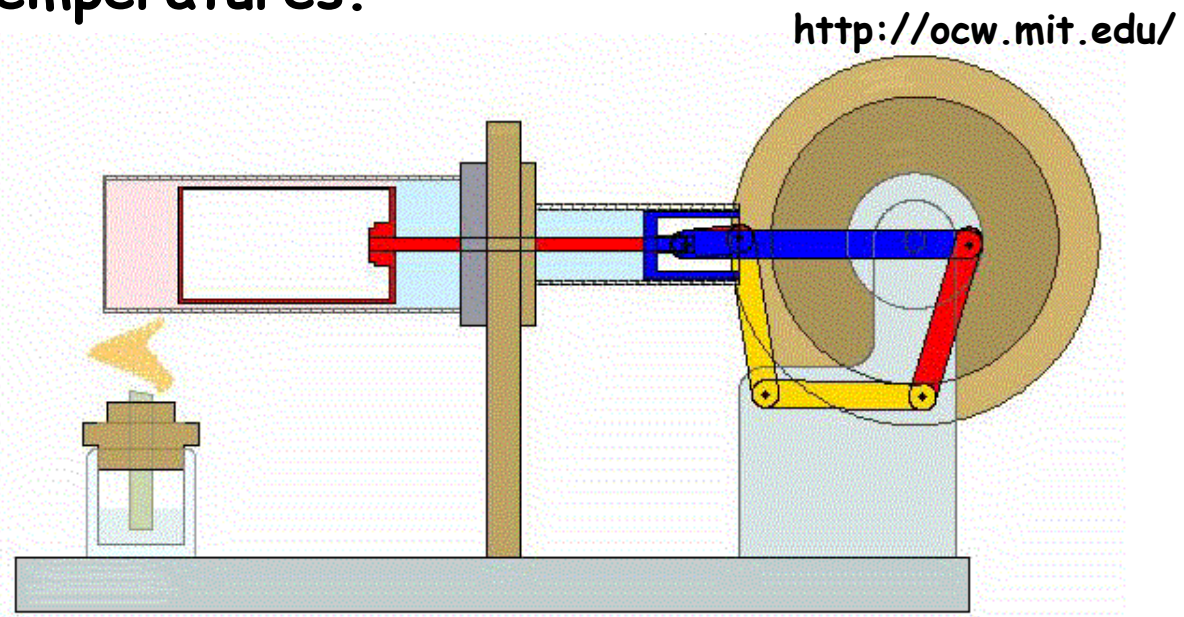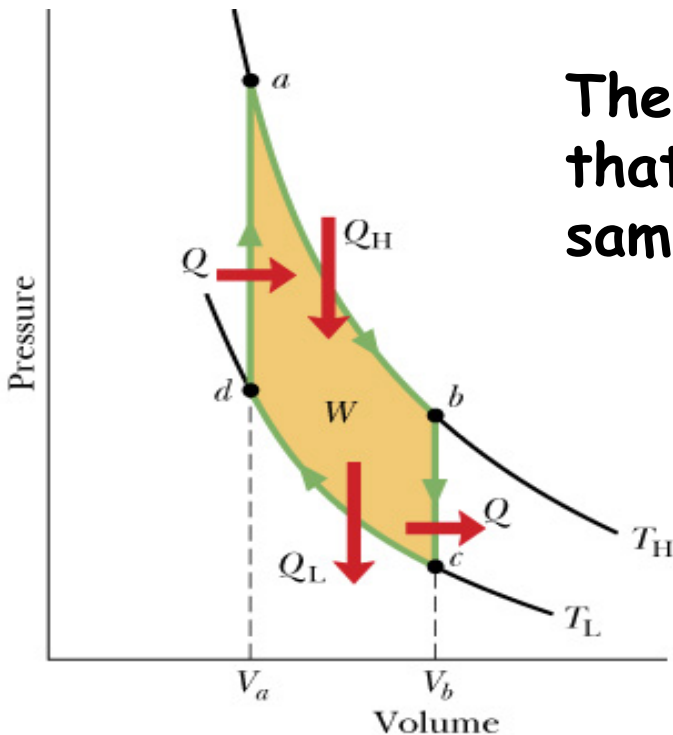
- For a Carnot engine:

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

T_H

Q_H

$W (= Q_H)$

$Q_L = 0$

- A perfect engine: $Q_L = 0$, $\varepsilon = 1$

b. Stirling Engine:

The efficiency of a Stirling engine is lower than that of a Carnot engine operating between the same two temperatures.

http://ocw.mit.edu/

c. Entropy in the Real World: Refrigerators

Element of a Refri.

• In an ideal refrigerator, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence.

• The Efficiency of a refri. (coefficient of performance):
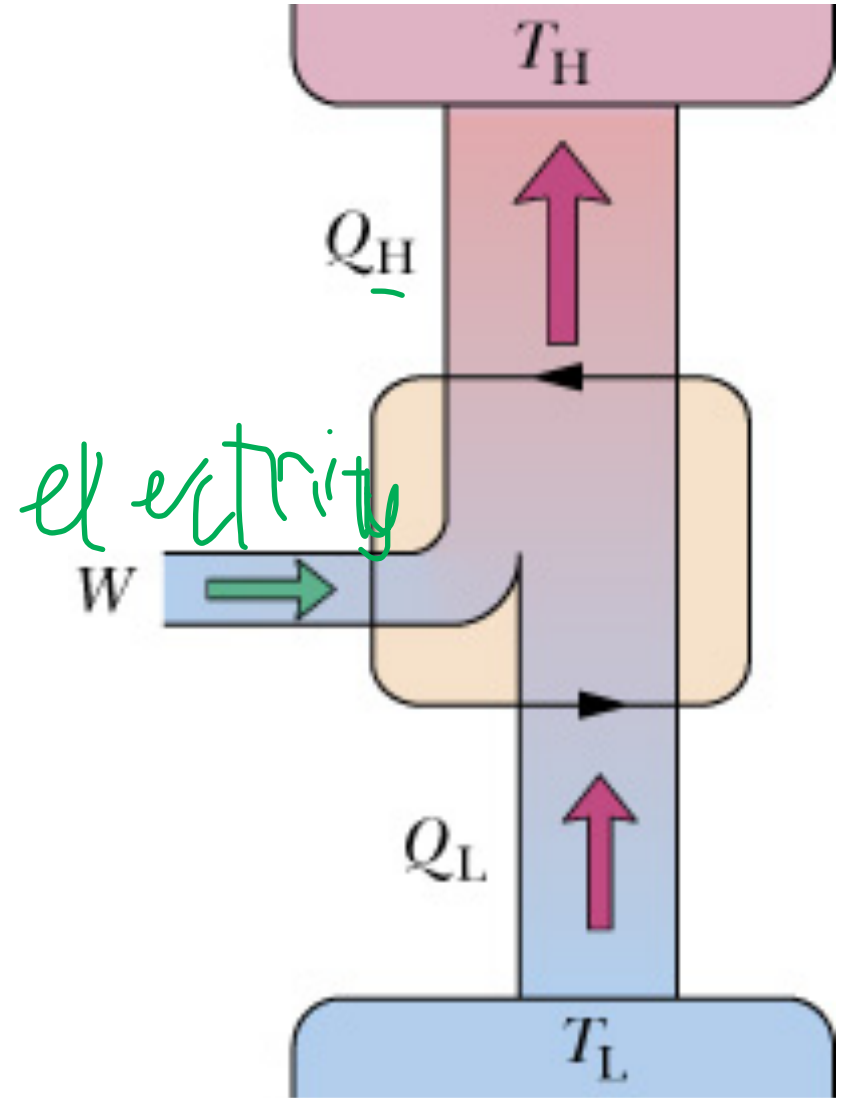
$$K = \frac{|Q_L|}{|W|}$$

For a Carnot refri. (an ideal refri.):

$$|W| = |Q_H| - |Q_L|$$

$$K_C = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

$$K_C = \frac{T_L}{T_H - T_L}$$

T_H

Q_H

electricity

W

Q_L
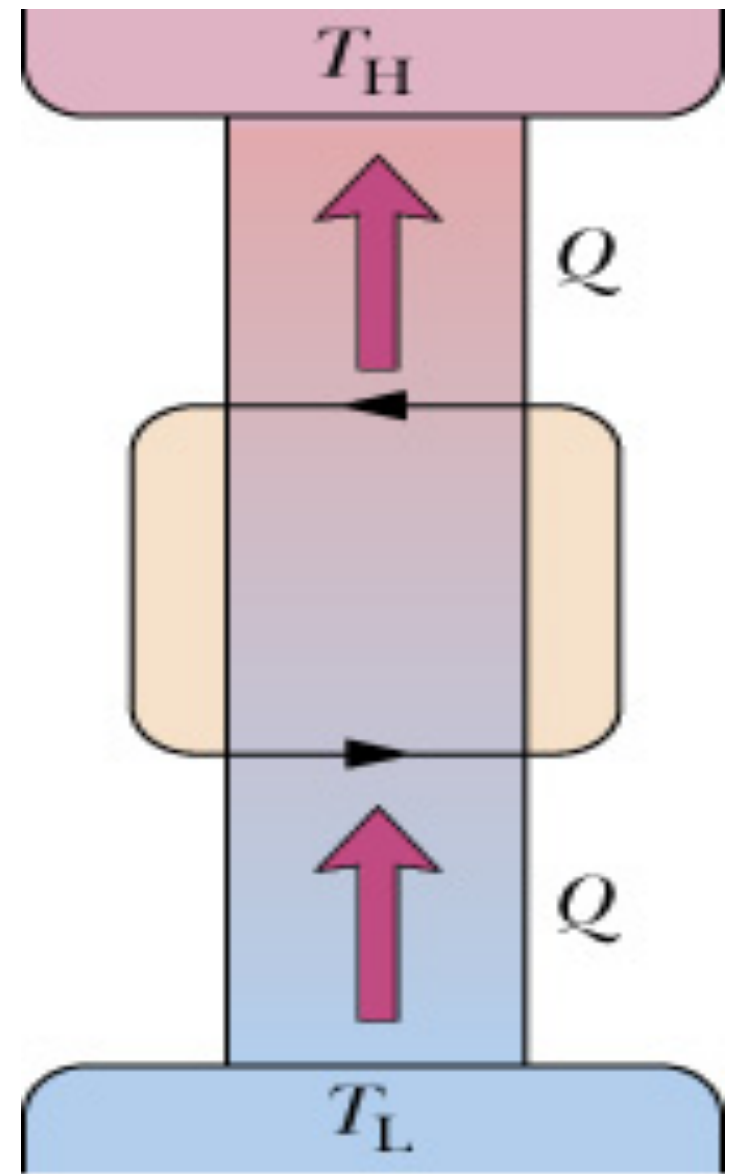
T_L

- **A Perfect Refrigerator:**

$$|W| = |Q_H| - |Q_L| = 0$$

- **We consider a closed system Refrigerator + two Reservoirs:**
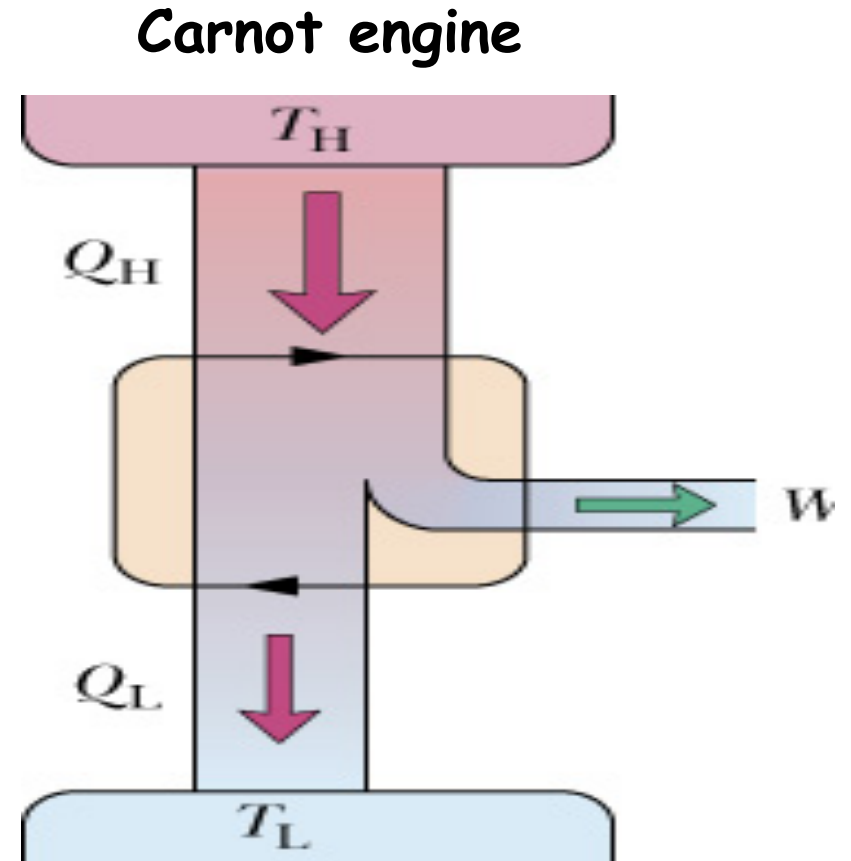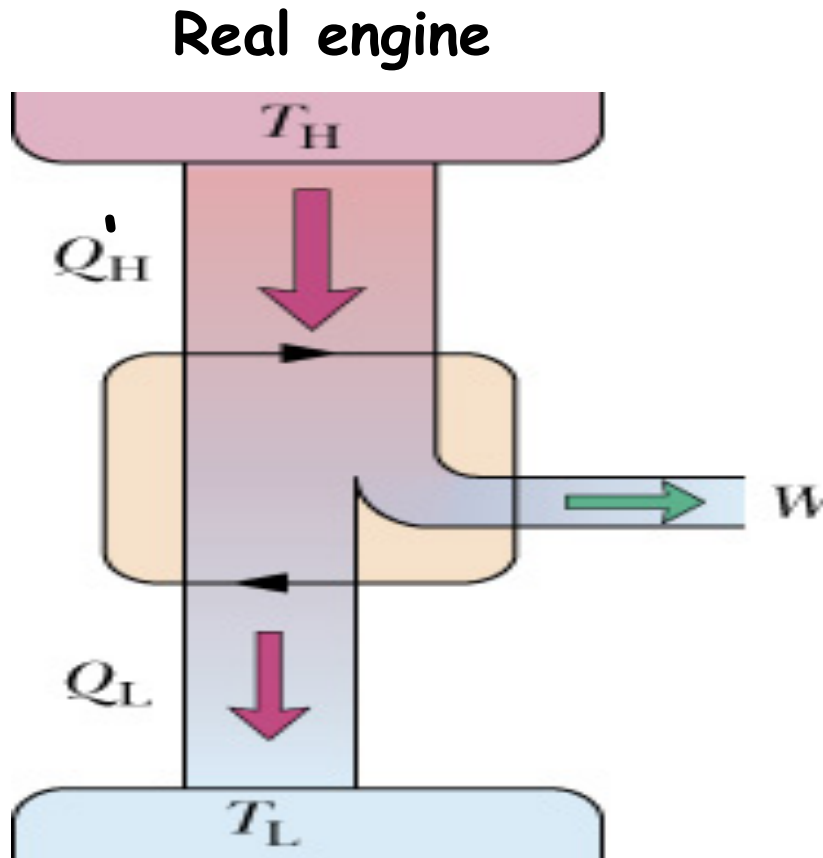
$$\Delta S = \frac{|Q|}{T_H} - \frac{|Q|}{T_L}$$

$$T_H > T_L \Rightarrow \Delta S < 0$$

➡**this violates the 2nd law of thermodynamics or a perfect refrigerator does not exist.**

d. The efficiencies of Real Engines:

• Any real engine X whose efficiency must smaller than that of a Carnot engine: $\varepsilon_X < \varepsilon_C$

Real engine

Carnot engine

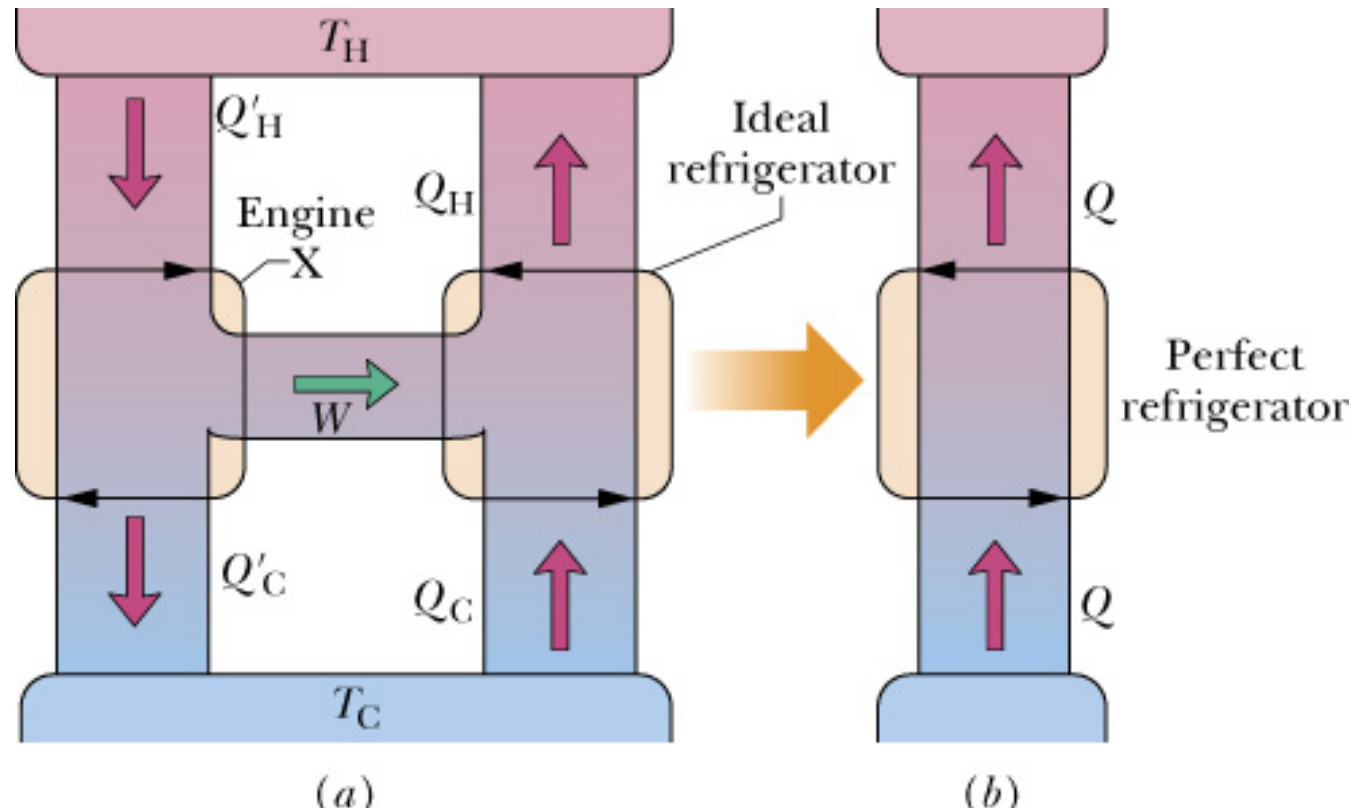$$\frac{|W|}{\left|Q^{'}_H\right|} < \frac{|W|}{\left|Q_H\right|}$$

- To prove the claim above, we couple engine X to a Carnot refrigerator:

We assume: $\varepsilon_X > \varepsilon_C$

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|}$$

$\dfrac{|W|}{|Q_H|}$ is the efficiency of the Carnot refri. when operated as an engine
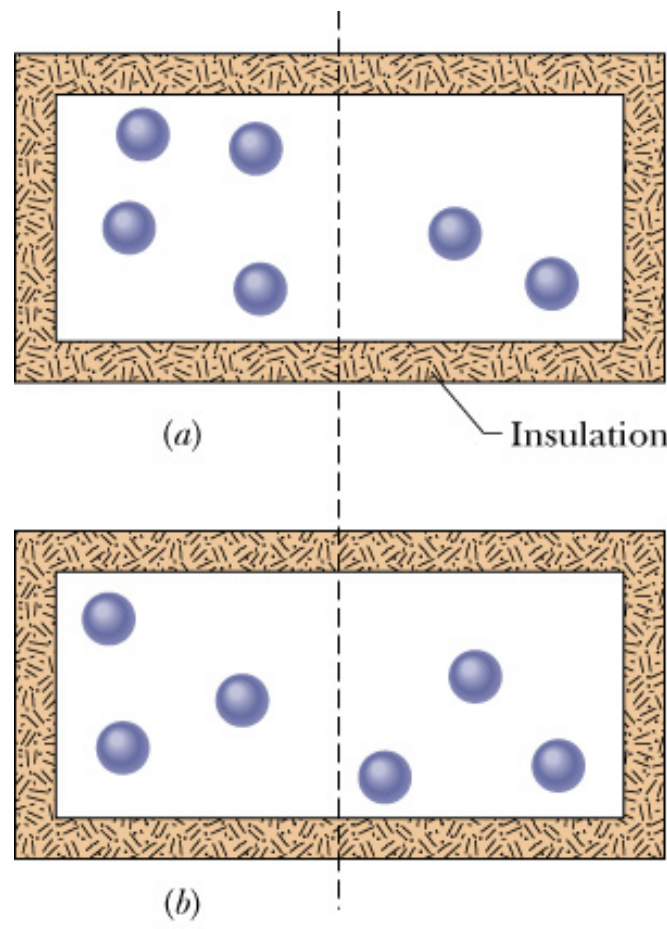
$$\boxed{|Q_H| > |Q'_H|}$$

(a)   (b)

The 1st law:

$$|Q_H| - |Q_C| = |Q'_H| - |Q'_C|$$

Let $\quad Q = |Q_H| - |Q'_H| = |Q_C| - |Q'_C| > 0$

→this coupling acts like a perfect refrigerator! (ΔS<0)

4.4. A Statistical View of Entropy

(a)

Insulation

(b)

•We consider 6 molecules in an insulated box.
•At any instant, a given molecule will be either in the left or the right half of the box.

•Let n_1 be the number of molecules in the left and n_2 be that in the right.
•A set (n_1, n_2) is called a configuration of the six molecules.

For a given configuration, we can have different arrangements of the molecules, which are called microstates.

Example: for Configuration III (4,2), the number of microstates or the multiplicity W:

$$W_{III} = \frac{6!}{4!2!} = 15 \quad \text{(6!: six factorial)}$$

In a general case:

$$W = \frac{N!}{n_1!n_2!} = 15$$

Probability and Entropy:

L. Boltzmann derived a relationship between the entropy S of a configuration of a gas and the multiplicity W of that configuration:

$$S = k \ln W$$

Sample Problem (p. 553)

In Sample (p. 541), we already calculated the entropy change for a free expansion:

$$\Delta S_{irrev} = \Delta S_{rev} = nR \ln \frac{V_f}{V_i} = nR \ln 2$$

Now, using the Boltzmann equation above to calculate ΔS!

Initial state, the configuration is (N,0): $W_i = \dfrac{N!}{N!0!} = 1$

Final state, the configuration is (N/2,N/2): $W_f = \dfrac{N!}{(N/2)!(N/2)!}$

Initial entropy: $S_i = k \ln W_i = k \ln 1 = 0$

Final entropy: $S_f = k \ln W_f = k \ln(N!) - 2k \ln[(N/2)!]$

Using Stirling's approximation: $\ln N! \approx N(\ln N) - N$

$$S_f = Nk \ln 2 \quad = NR \ln 2$$

The entropy change:

$$\boxed{\Delta S = S_f - S_i = nR \ln 2 - 0 = nR \ln 2}$$

→ **The same result as the previous one (sample p.541)**

only use $\Delta S = \int \dfrac{dQ}{T}$

Homework: 1, 2, 3, 5, 8 (page 556)

Final Exam: Chapter 18, 19, and 20 (not including "Engines")

Assignment:
- a group of 5 people
- each group submits ONLY 1 report