# PHYSICS 2: FLUID MECHANICS AND THERMODYNAMICS

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# 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

# What is Physics?

- Time has direction, from the past to the future

- One-way processes that can occur only in a certain sequence and never in the reverse sequence are <span style="color:red">irreversible,</span> meaning that they can not be reversed.

<u>Examples:</u> a pizza is baked, water flows from high level to low level, current moves from high potential to low potential, etc.

Irreversible

incubation & hatch
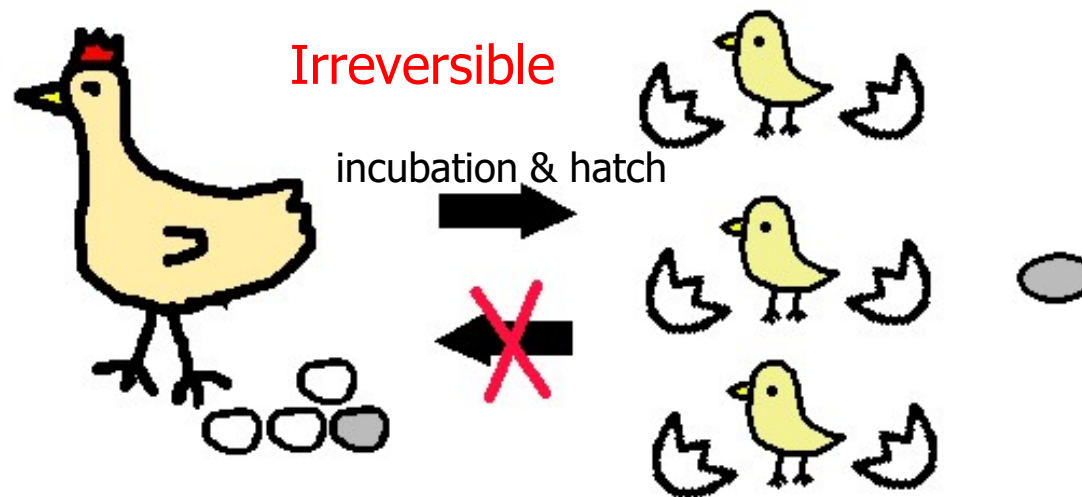
**Evolution**
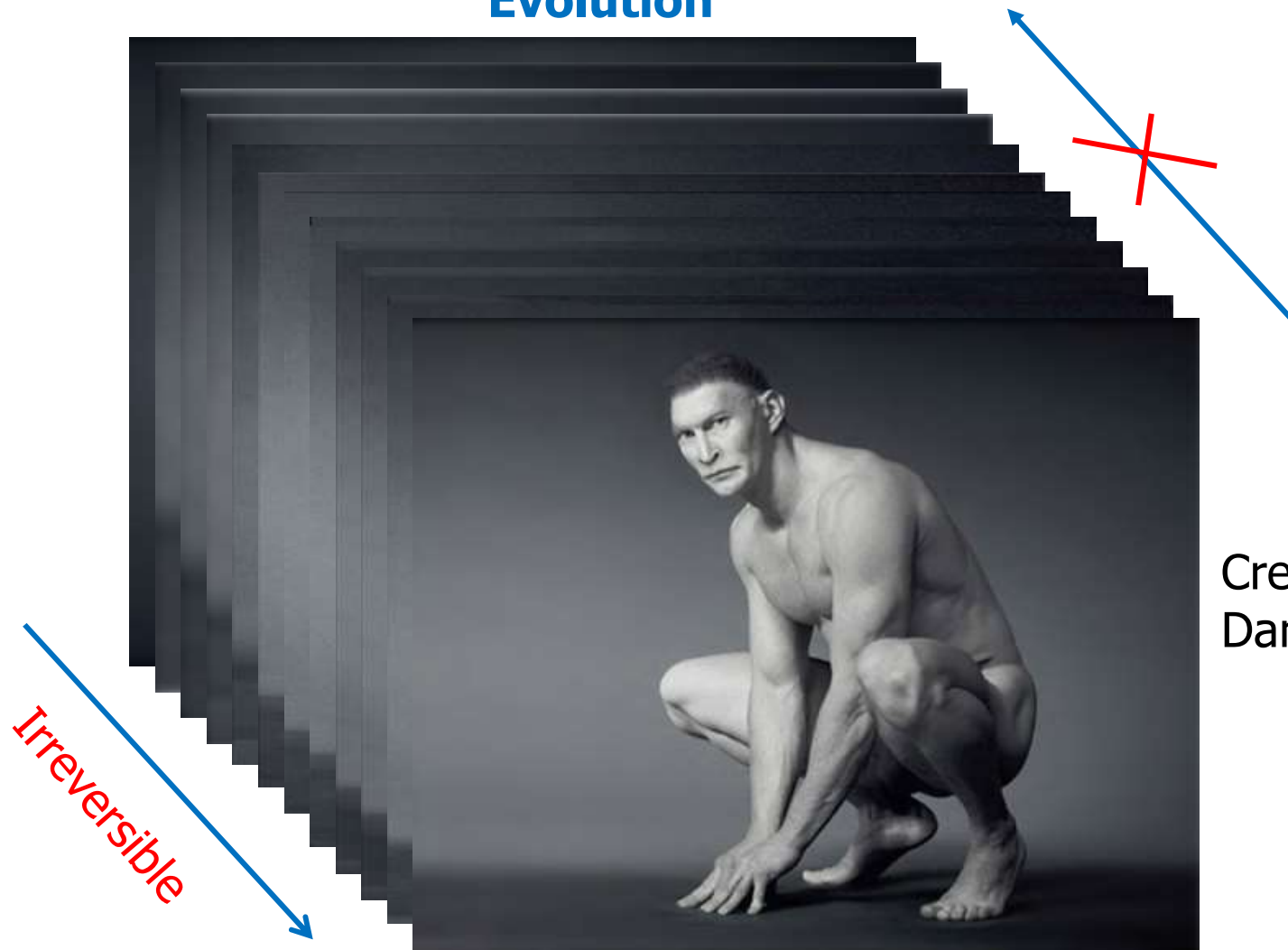


Irreversible

Credit: Daniel Lee

- In this chapter, we study why one-way processes are irreversible
- The key to understand why one-way processes cannot be reversed involves a quantity known as Entropy

# What is Entropy?

Entropy is the extensive property of the system (depends on the mass of the system) and its unit of measurement is J/K. Entropy is heat or energy change per degree Kelvin temperature. Entropy is denoted by 'S'. (Clausius, 1855)

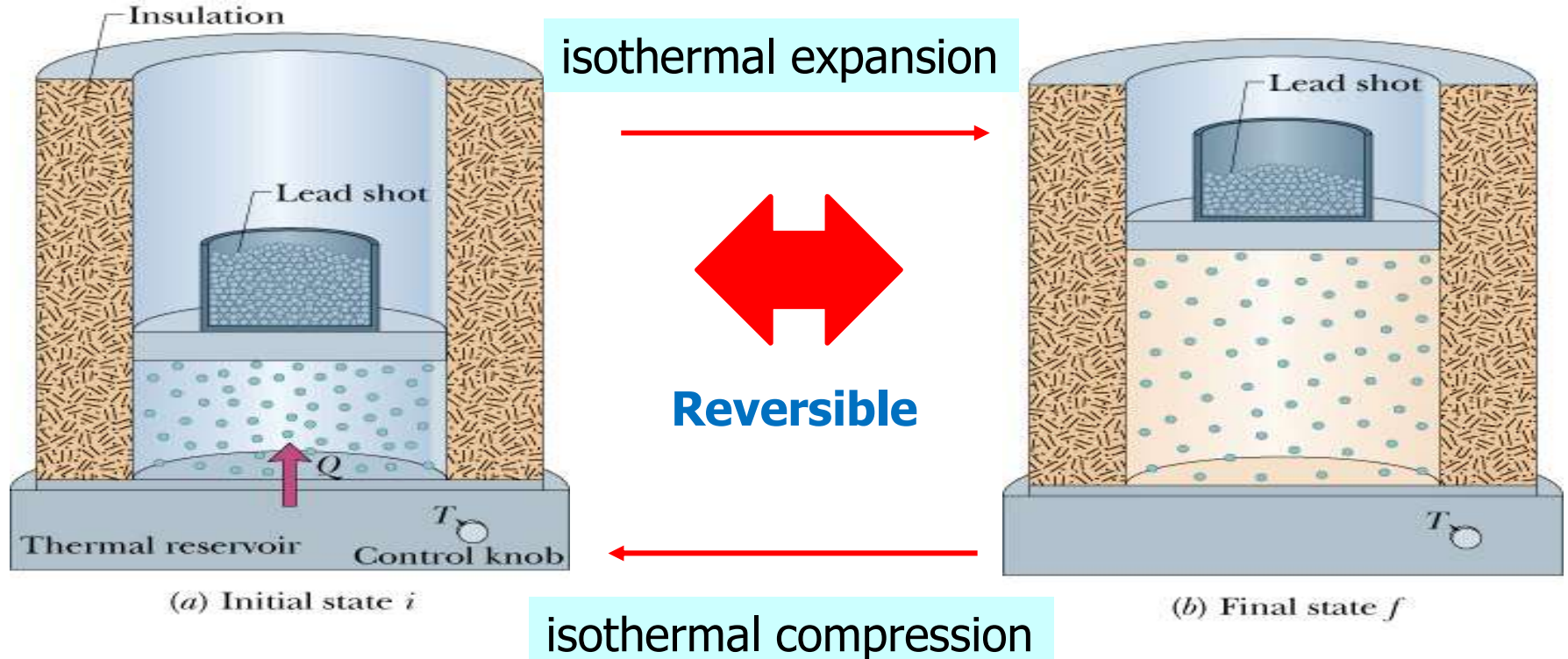## Interdisciplinary applications of entropy

Although the concept of entropy was originally a thermodynamic construct, it has been adapted in the other following fields of study:

- information theory
- psychodynamics
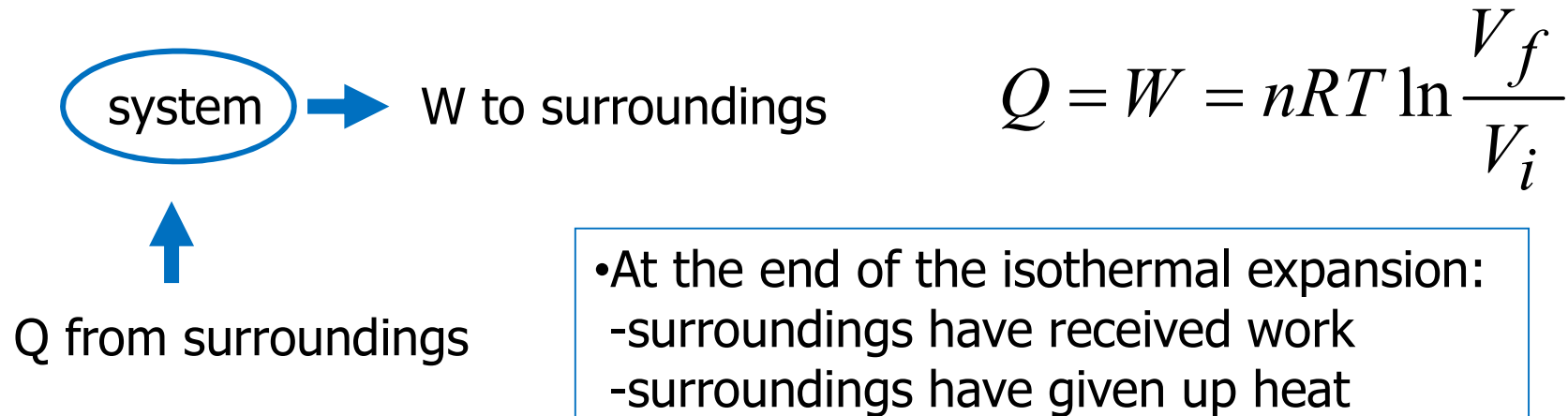- thermo-economics
- evolution

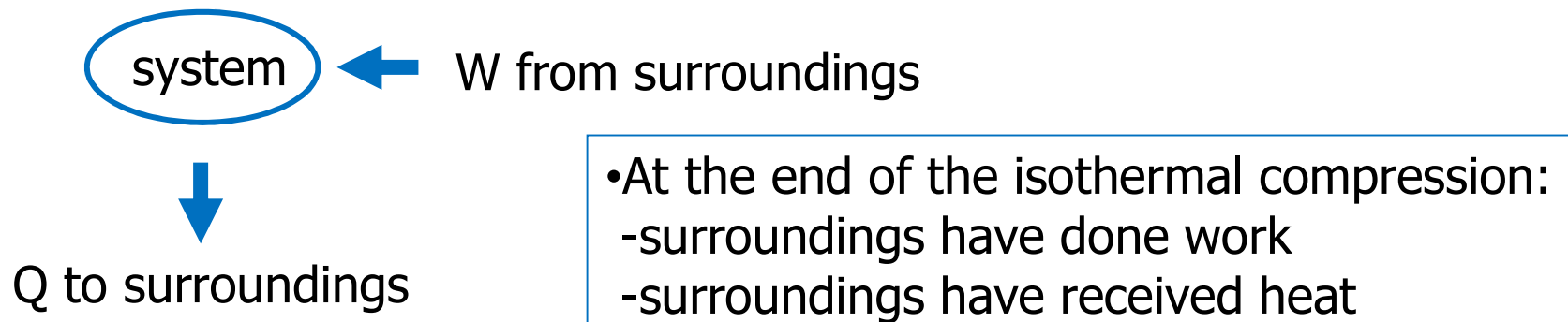# 4.1. Reversible, Irreversible Processes and Entropy

## a. Reversible processes:

A reversible process is a process that, after it has taken place, can be reversed and causes no change in either the system or its surroundings (i.e. without loss or dissipation of energy)

isothermal expansion

**Reversible**

isothermal compression

(a) Initial state i

(b) Final state f

## isothermal expansion

system → W to surroundings

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

↑ Q from surroundings

•At the end of the isothermal expansion:
 -surroundings have received work
 -surroundings have given up heat

## isothermal compression

system ← W from surroundings

↓ Q to surroundings

•At the end of the isothermal compression:
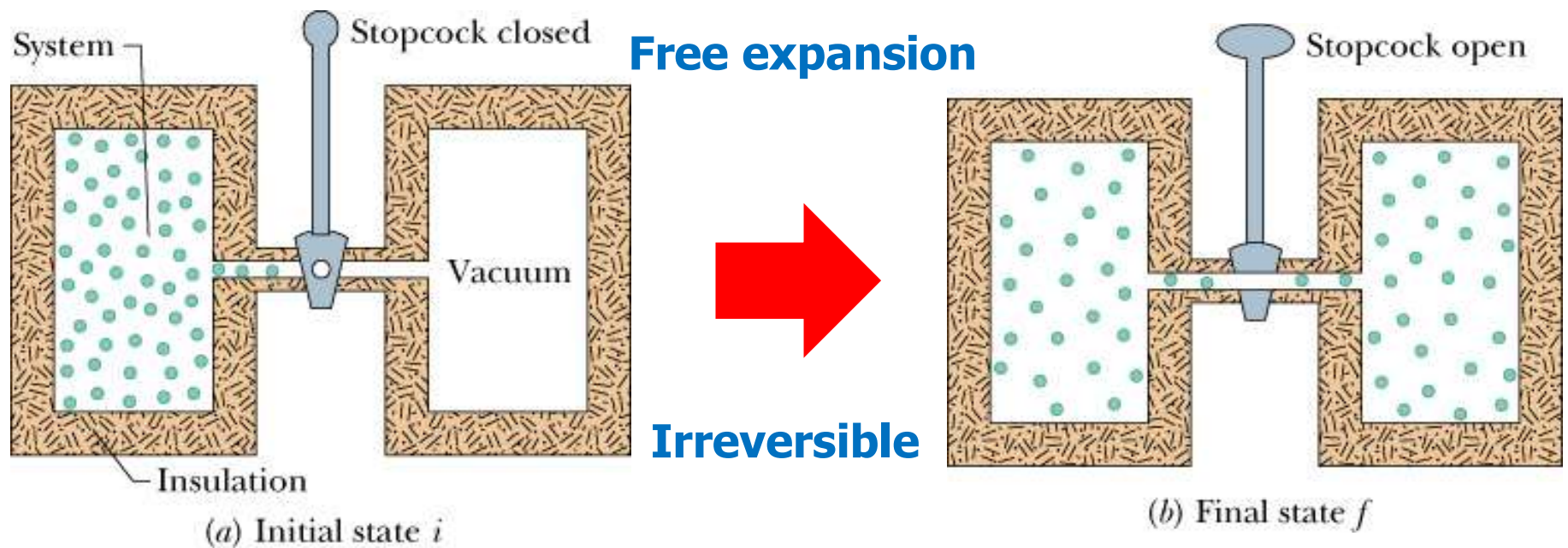 -surroundings have done work
 -surroundings have received heat

Net result: the system and the surroundings back to the initial state without any change → the process is reversible
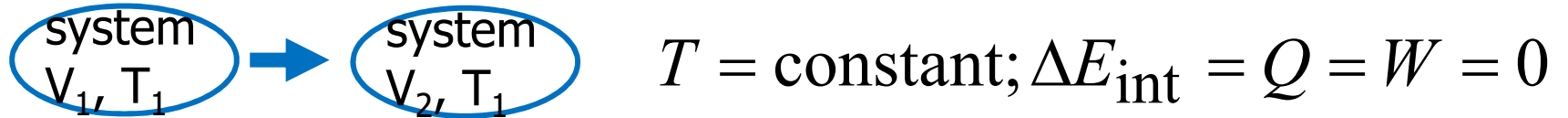
However, the presence of friction always results in the output work of the system being smaller than the work transferred into the system. Therefore, it is practically impossible to realize reversible processes (i.e. ideal ones). But the concept of a reversible process proves to be very useful in studying irreversible processes.

b. Irreversible processes:
- A process that is not reversible is called irreversible.
- In irreversible processes, both the system and the surroundings can not return to their initial state on their own.
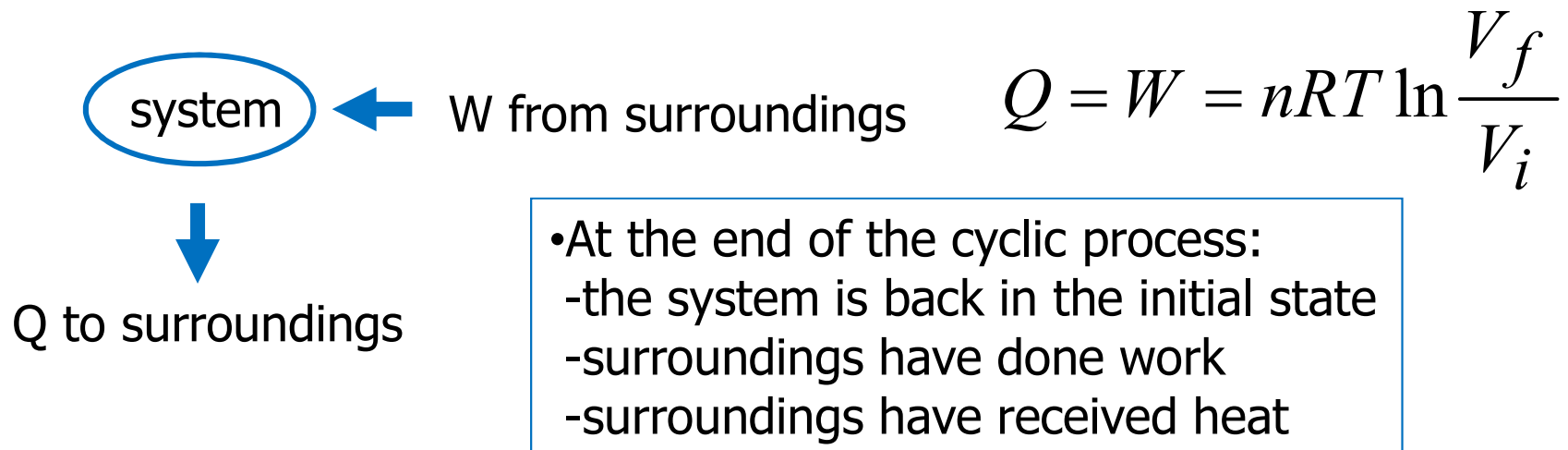
System — Stopcock closed **Free expansion** Stopcock open

Vacuum

**Irreversible**

Insulation
(a) Initial state *i*

(b) Final state *f*

## Free expansion

system $V_1, T_1$ → system $V_2, T_1$

$$T = \text{constant}; \Delta E_{\text{int}} = Q = W = 0$$

- To restore the system to the initial state at constant T, we compress isothermally by some external agency:

## isothermal compression

system ← W from surroundings

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

↓

Q to surroundings

- At the end of the cyclic process:
  - the system is back in the initial state
  - surroundings have done work
  - surroundings have received heat

Net result: the system is the same and the surroundings have changed (W converted to Q) → the process is irreversible

- For irreversible processes, the entropy S of a closed system always increases, because of this property, the change in entropy ΔS is sometimes called "the arrow of time".

  Examples:    eggs → chickens: ΔS > 0

  chickens → eggs: ΔS < 0: it never happens

## c. Change in Entropy:

There are two equivalent ways to define the change in entropy of a system:

1) in terms of the system's temperature and the energy, the system gains or loses as heat

2) by counting the ways in which the atoms or molecules that make up the system can be arranged

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

Q: energy transferred as heat to or from the system during the process

T (K): temperature of the system

Unit: J/K

- For free expansions: p, V and T fluctuate unpredictably, so we cannot find a relation between Q and T to calculate ΔS.

Method to calculate ΔS:

The difference in entropy only depends on the initial and final states, we can therefore replace an irreversible process occurring in a closed system with any reversible one that connects the same initial and final states to calculate the entropy change.

- For the case of free expansions:  $\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f dQ = \frac{Q}{T}$



$T_i = T_f$

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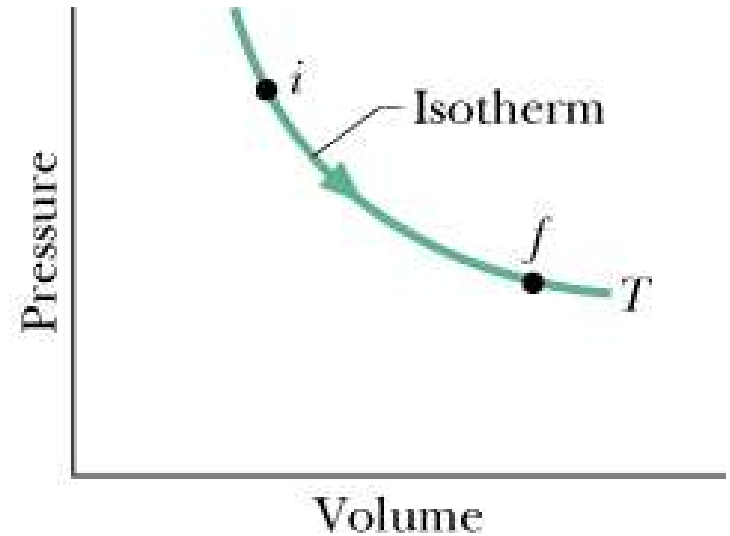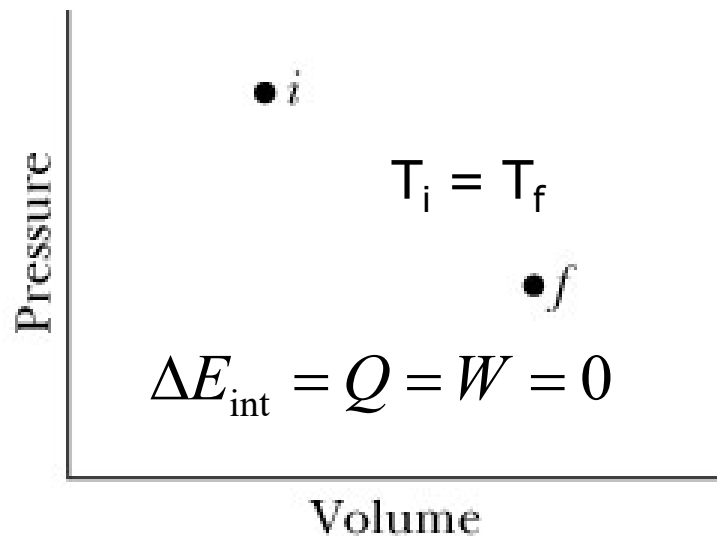


- For isotherms:  $Q = W = nRT \ln \frac{V_f}{V_i}$
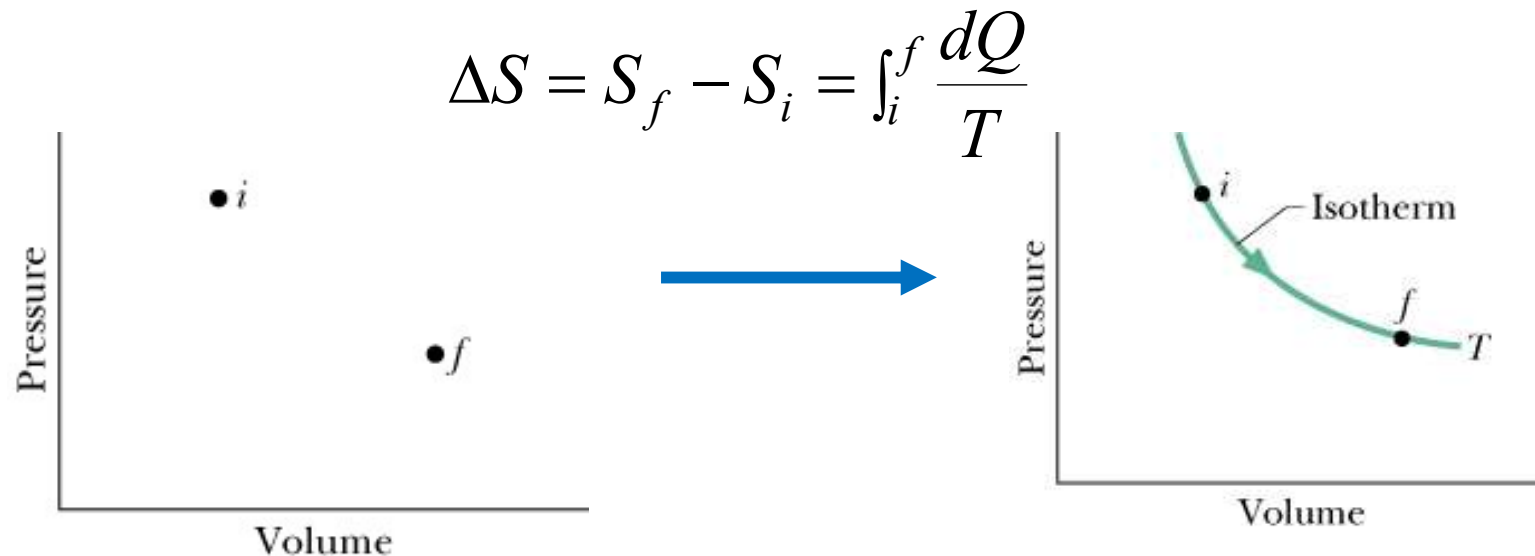
$$\Delta S = nR \ln \frac{V_f}{V_i}$$

• **Special Case:** If the temperature change ΔT of a system is small relative to the temperature (in K) before and after the process, the change in entropy can be computed:

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

Checkpoint: Water is heated on a stove. Rank the entropy changes of the water as its temperature rises (a) from 20⁰C to 30⁰C, (b) from 30⁰C to 35⁰C, and (c) from 80⁰C to 85⁰C, greatest first.

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{avg}} = \frac{cm\Delta T}{T_{avg}} \Rightarrow (a),(b),(c)$$

**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.

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



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

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

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

**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?
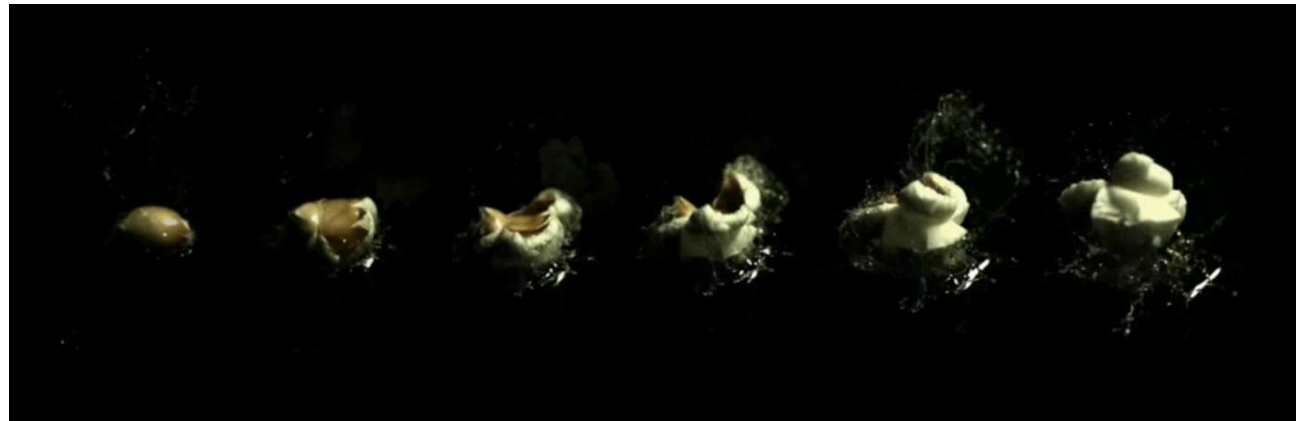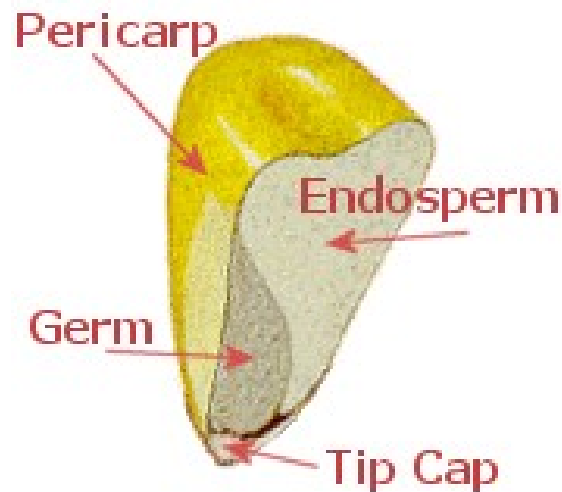


We calculate ΔS of the irreversible process (kernel => popped popcorn) by calculating two reversible processes: (1) vaporization at 180⁰C; (2) adiabatic expansion of the vapor (the process occurs so rapidly, so it is adiabatic)

Process 1: Vaporization, T = constant

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

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

$$\Delta S_1 = \frac{2256 \times 10^3 \times 4 \times 10^{-6}}{453} = 1.99 \times 10^{-2} \, (\text{J/K})$$

Process 2: Adiabatic expansion, dQ = 0

$$\Delta S_2 = 0$$

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.

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

$$nC_V dT \qquad pdV$$

$$dQ = pdV + nC_V dT$$

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

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

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

→ 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 increases for irreversible processes and remains constant for reversible processes. It never decreases.

- Irreversible processes (ex: free expansion):



(a) Initial state $i$

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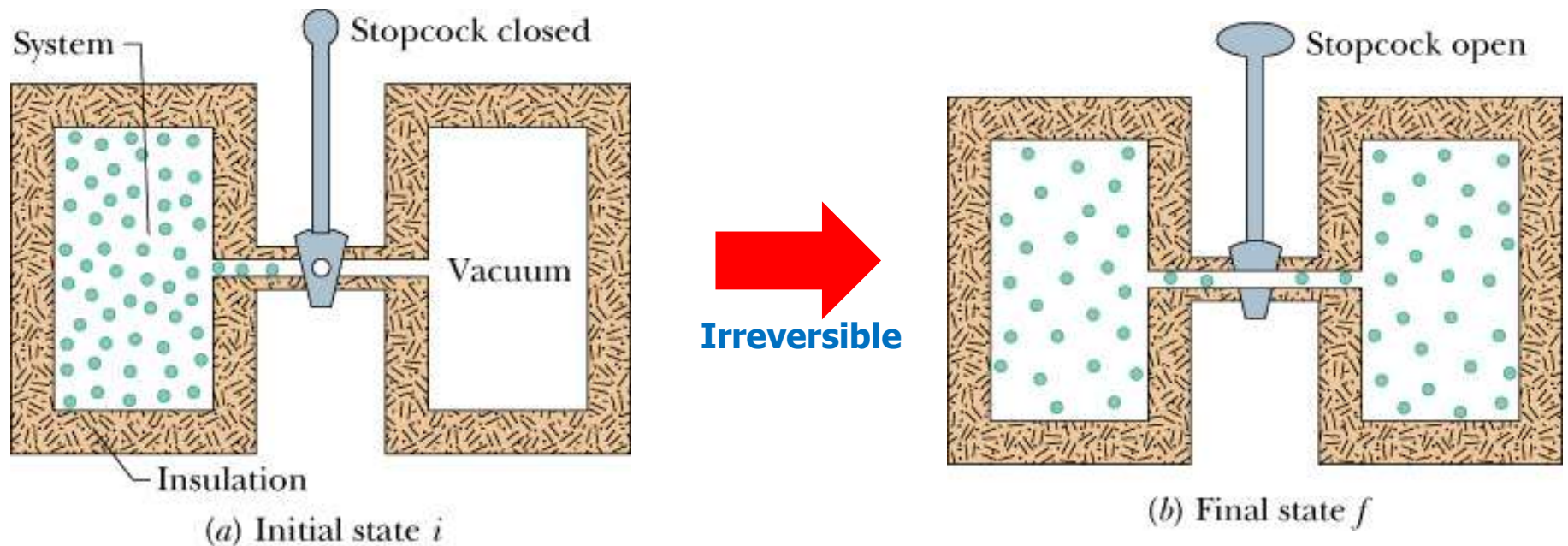
$$\Delta S_{gas} = \frac{Q}{T} > 0 \text{ (gas received energy as heat)}$$

- 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.
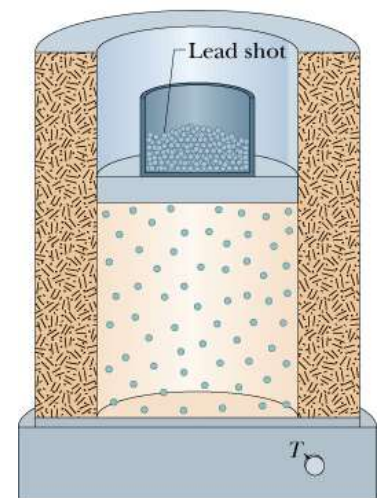
  - We now consider a closed system gas + reservoir:

$$\left.\begin{array}{l} \Delta S_{gas} = -\dfrac{|Q|}{T} \\[2em] \Delta S_{reservoir} = +\dfrac{|Q|}{T} \end{array}\right\} \quad \Delta S_{system} = 0 \,(\text{closed system})$$

The second law of thermodynamics for a closed system:

$$\Delta S \geq 0$$



Insulation

Lead shot

Thermal reservoir    Control knob

$Q$

$T$

(a) Initial state $i$

Reversible process

Lead shot

$T$
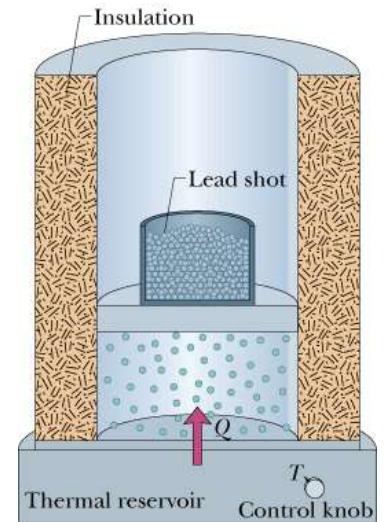
(b) Final state $f$

## 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.
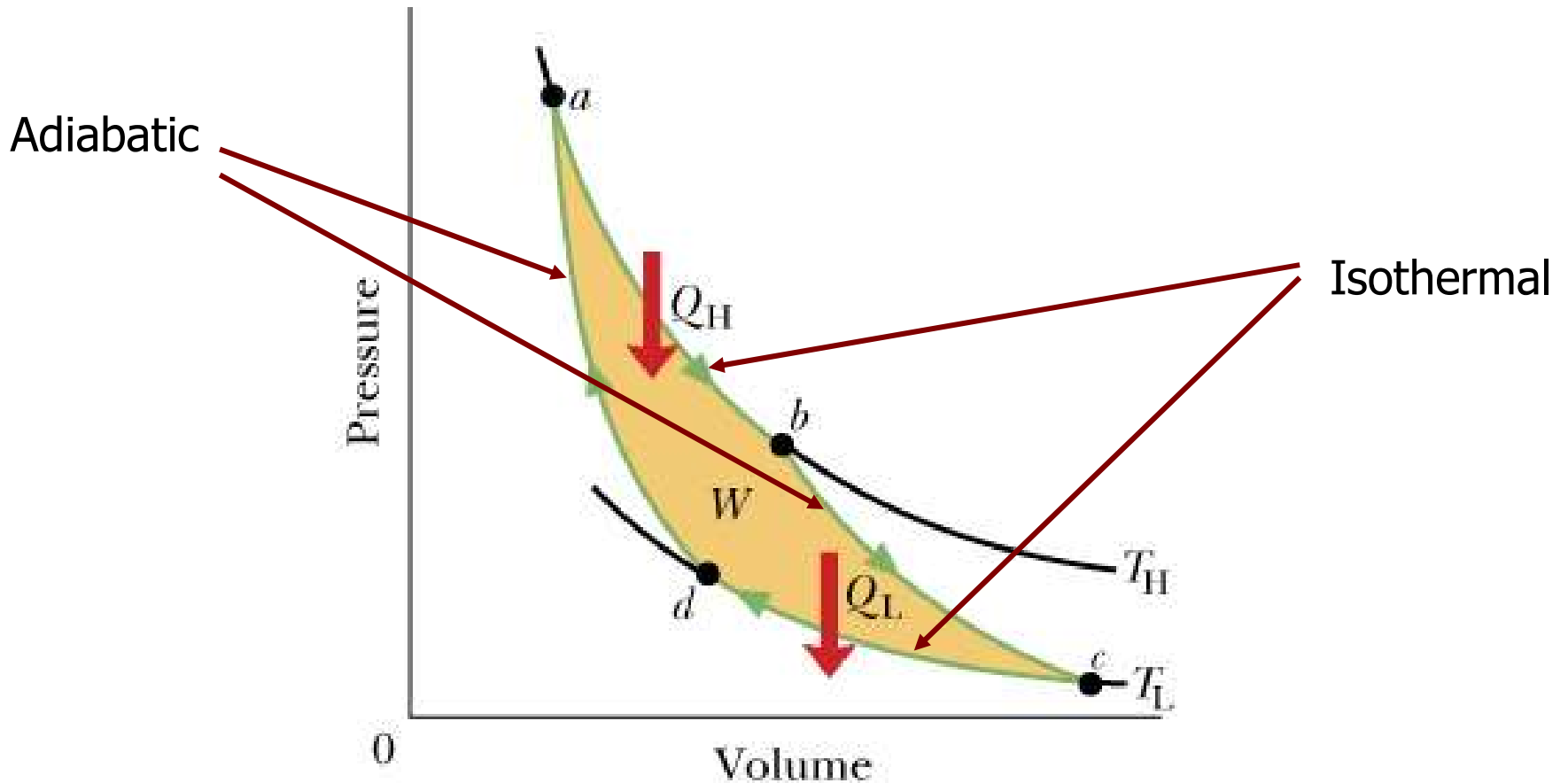
a. A Carnot Engine (an ideal engine):

What is an ideal engine?

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

# The elements of a Carnot engine
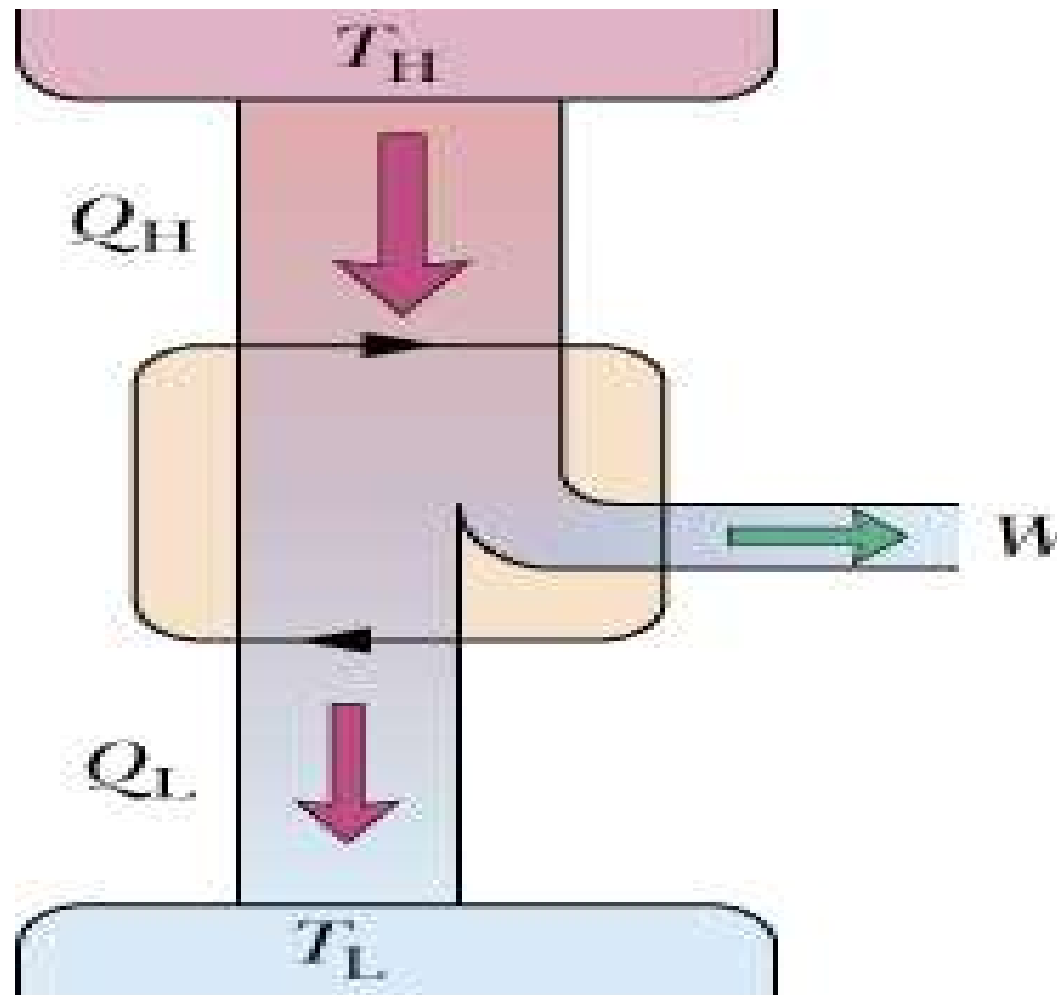
- The Carnot cycle consists of two isothermal (ab and cd) and two adiabatic processes (bc and da).
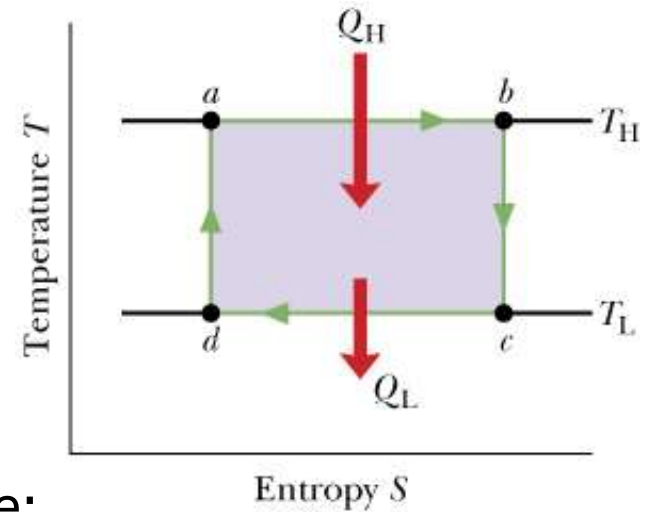


- The working substance absorbs energy $|Q_H|$ from a thermal reservoir at a constant temperature $T_H$ and discharges $|Q_L|$ to a second reservoir at a constant lower temperature $T_L$.

The work in the Carnot cycle:

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

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



Temperature $T$ — Entropy $S$

The entropy change of the working substance:

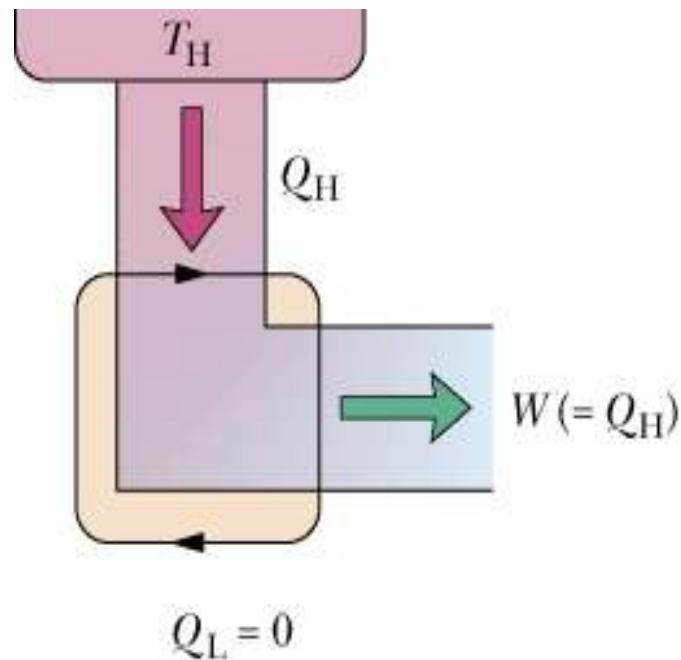$$\Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$

For a closed cycle: $\quad \Delta S = 0 \Rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$

The Efficiency of any engine: $\varepsilon = \dfrac{\text{energy we get}}{\text{energy we pay for}} = \dfrac{|W|}{|Q_H|}$
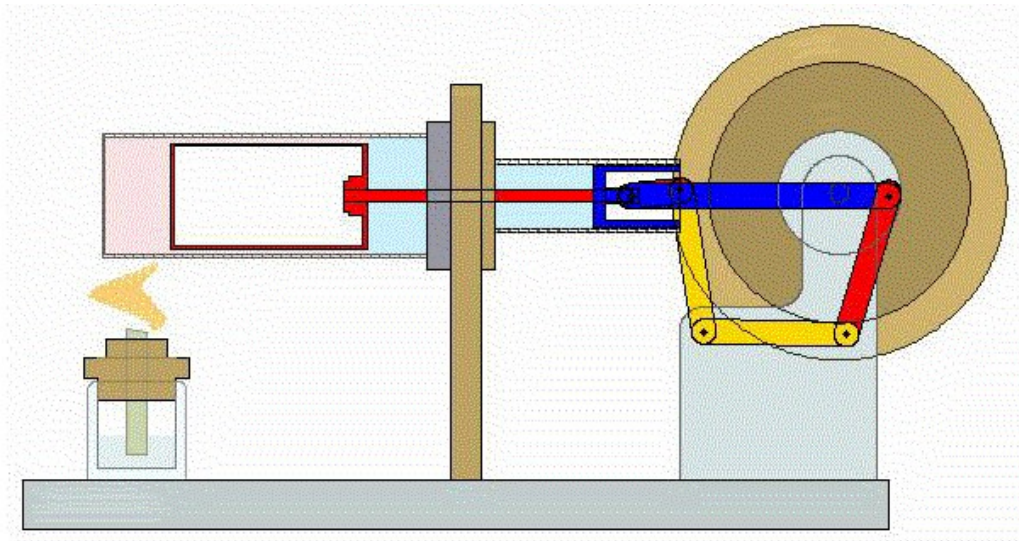
- For a Carnot engine:

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

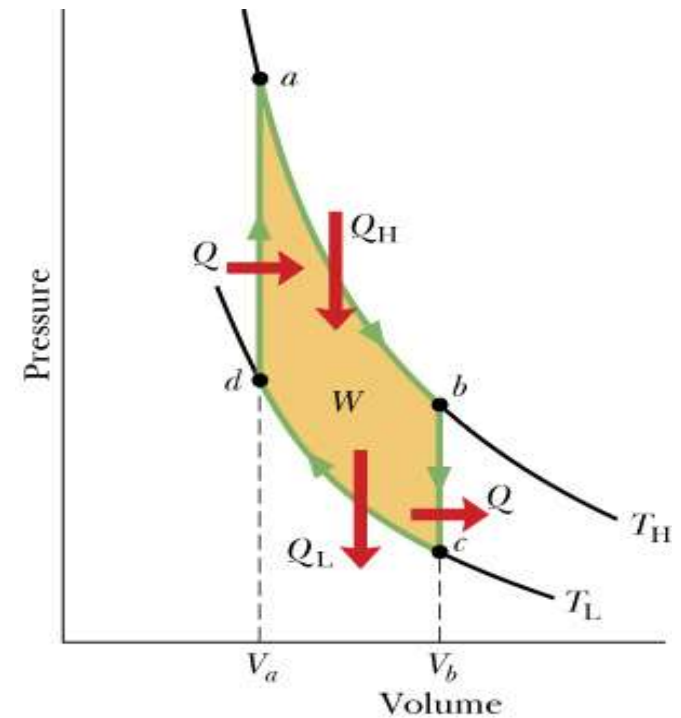- A perfect engine: $Q_L = 0$, $\varepsilon = 1$



$T_H$

$Q_H$

$W (= Q_H)$

$Q_L = 0$

## 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

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

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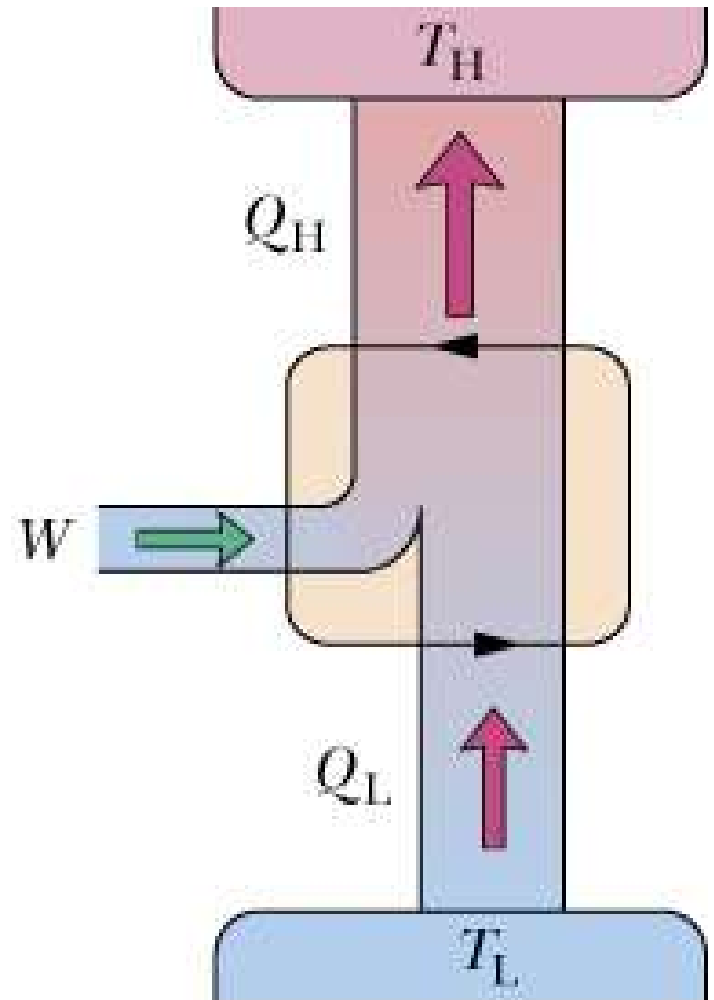
$$K = \frac{|Q_L|}{|W|}$$

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

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

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

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

Element of a Refri.
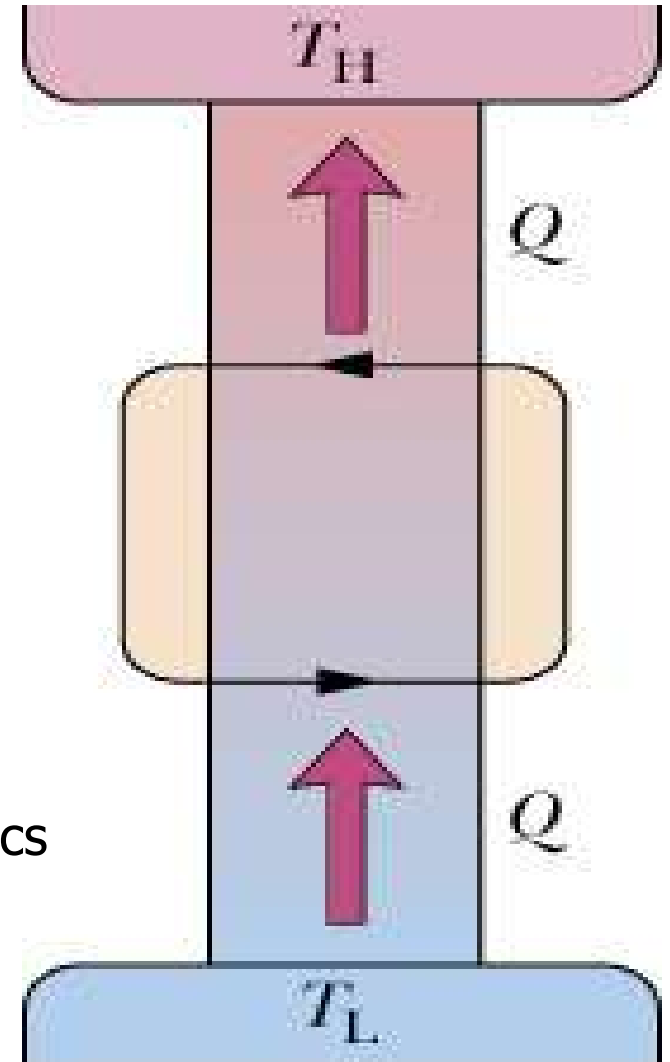
- A Perfect Refrigerator:

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

- We consider a closed system Refrigerator + two Reservoirs:

$$\Delta S = \frac{|Q|}{T_H} - \frac{|Q|}{T_L}$$

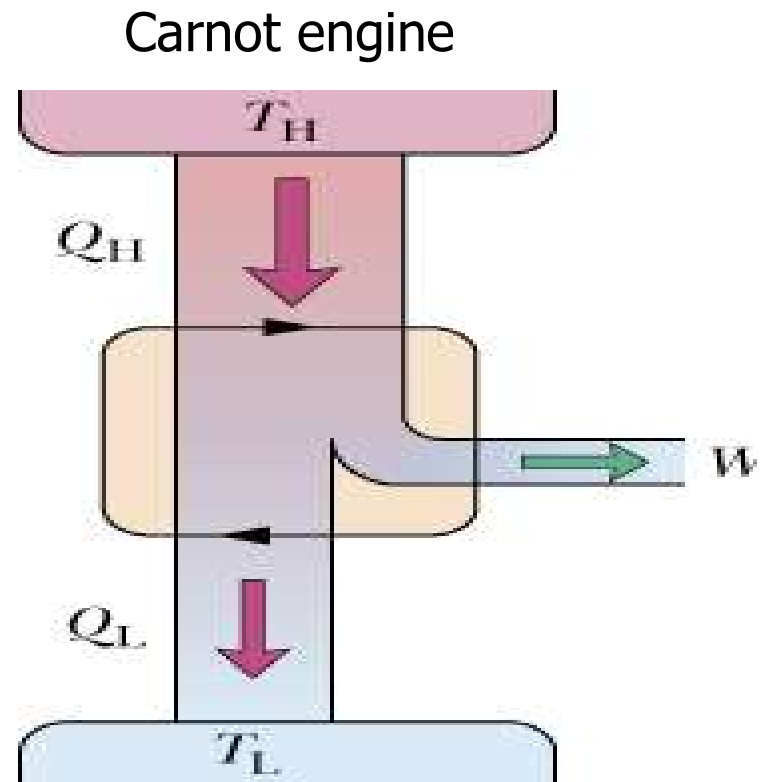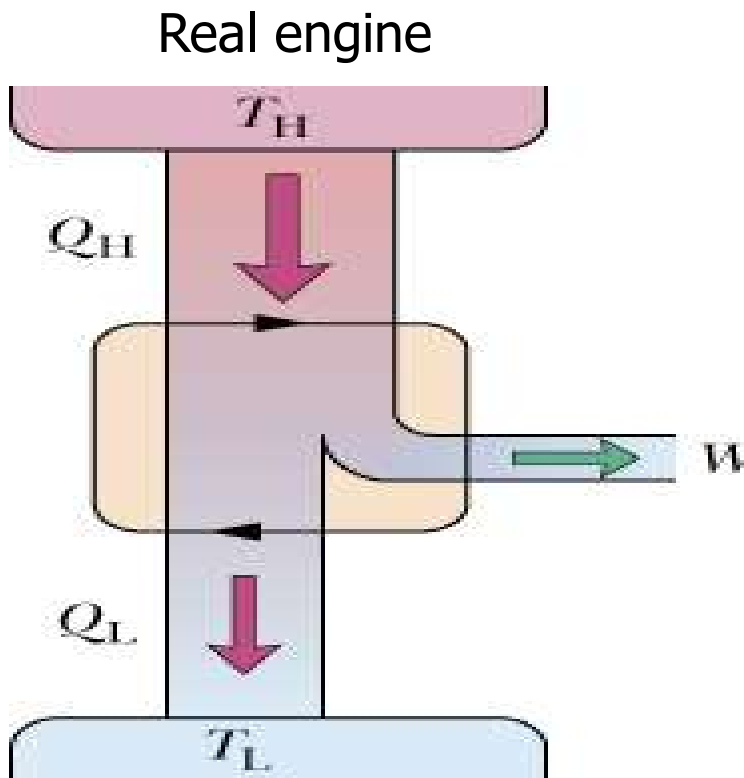$$T_H > T_L \Rightarrow \Delta S < 0$$

→ 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: $\varepsilon_X < \varepsilon_C$

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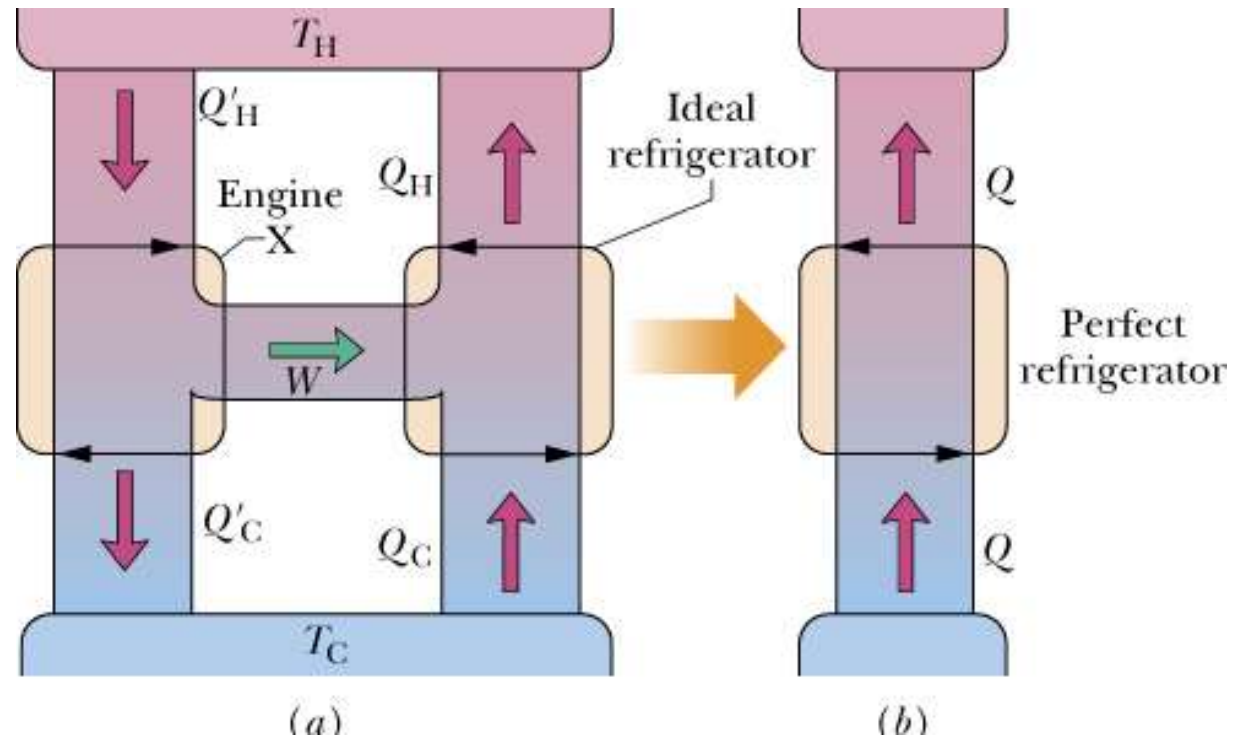


Real engine

Carnot engine

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

We assume: $\varepsilon_X > \varepsilon_C$

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

$\frac{|W|}{|Q_H|}$ is the efficiency of the Carnot refri. when operated as an engine, so

$$|Q_H| > |Q'_H|$$



$(a)$  $(b)$

The 1$^{st}$ law: $\quad |Q_H| - |Q_C| = |Q'_H| - |Q'_C|$

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

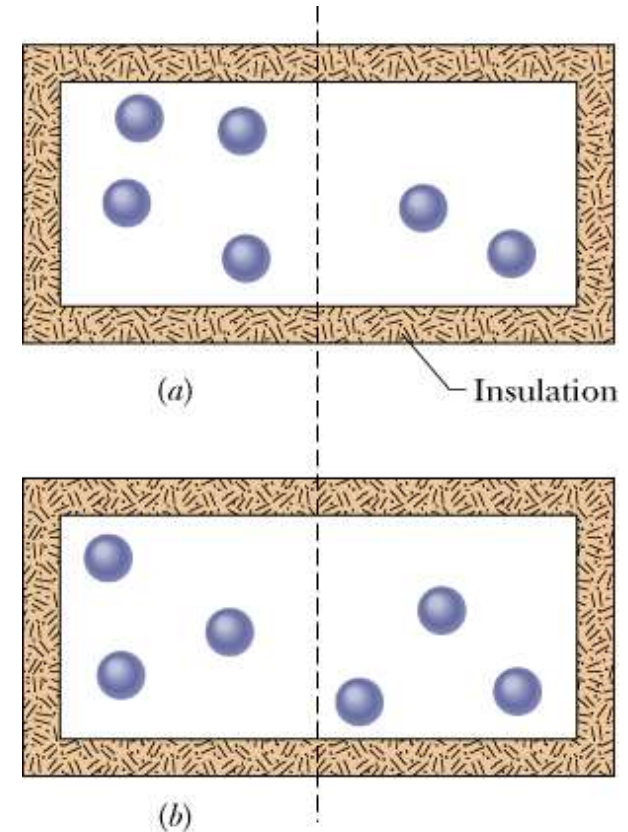→ This coupling acts like a perfect refrigerator! ($\Delta S < 0$)

## 4.4. A Statistical View of Entropy

- 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.



(a)

—Insulation

(b)

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:

$$W_{III} = \frac{6!}{4!2!} = 15$$

(6!: six factorial)

In a general case:

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

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:

$$S_f = Nk \ln 2$$

The entropy change:

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

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

**Homework:**

Problems 1, 2, 3, 5, 8 (page 604 in Chapter 20 Textbook)