

Physics 2: Fluid Mechanics and Thermodynamics

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✓ Midterm exam

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✓ Final exam

(Chapters 14, 18, 19, 20 of Principles of Physics, Halliday et al.)

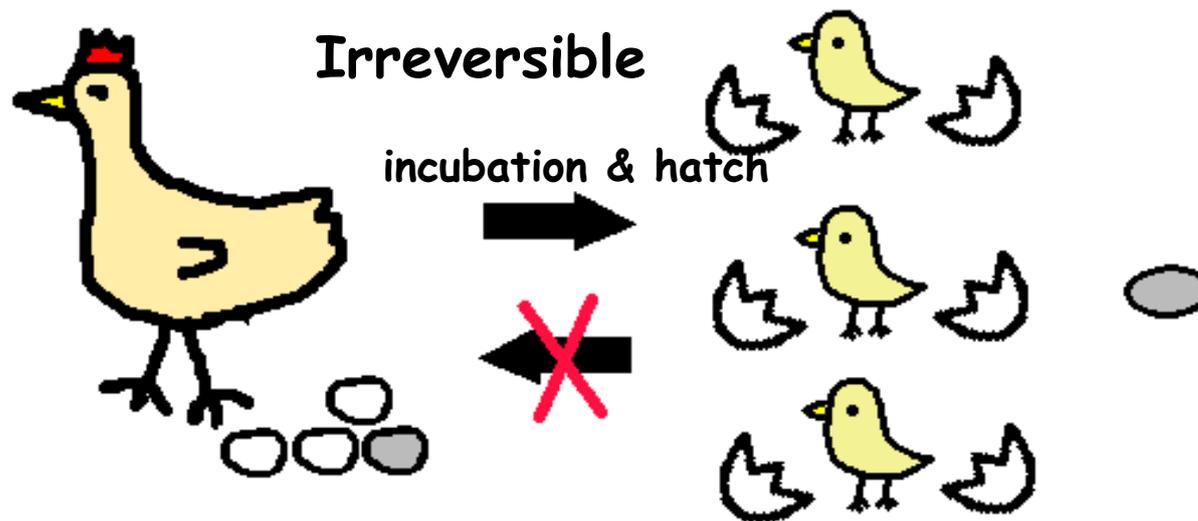
Chapter 4 Entropy and the Second Law of Thermodynamics

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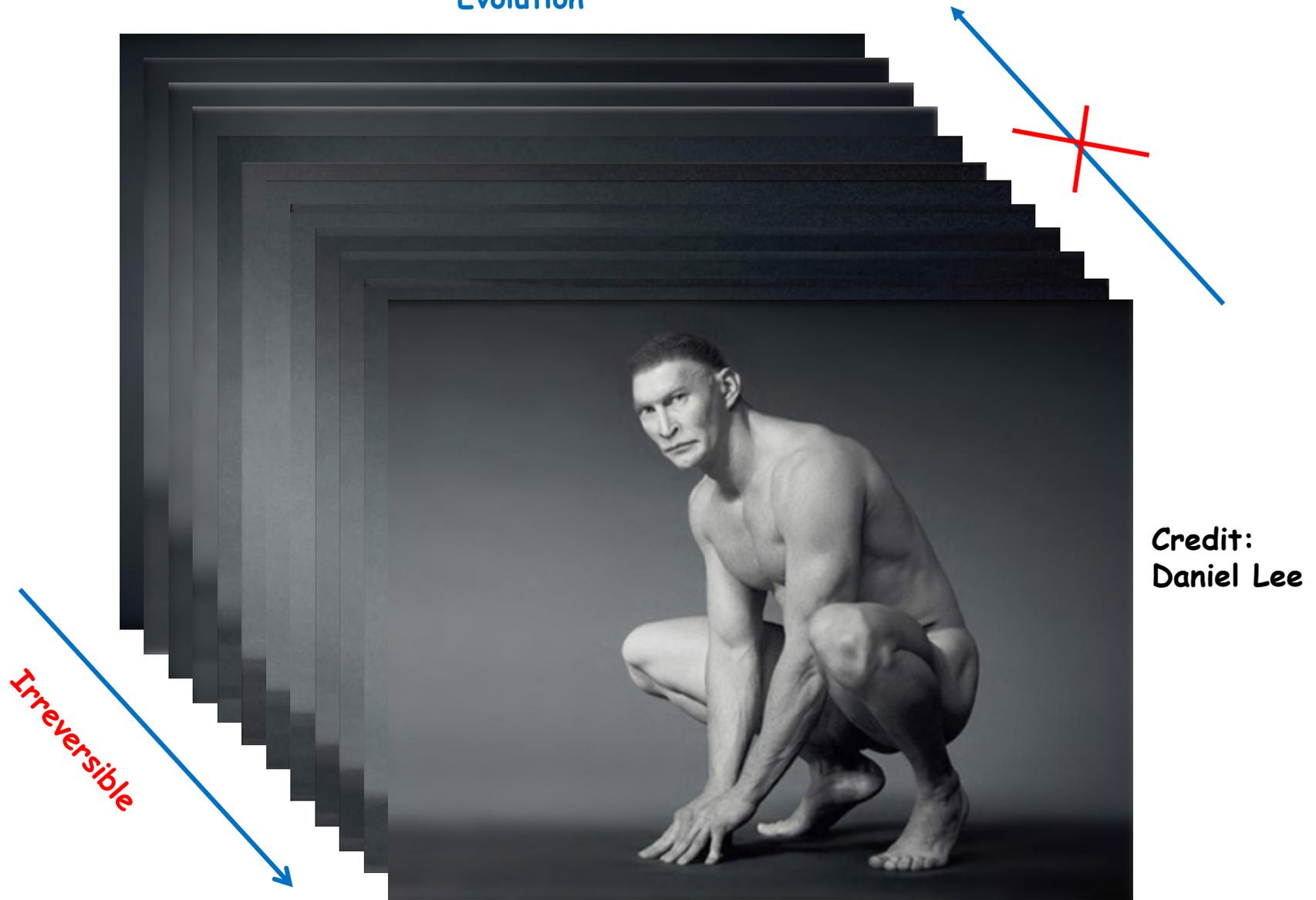
What is Physics?

- 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 **irreversible**, meaning that they can not be reversed.

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



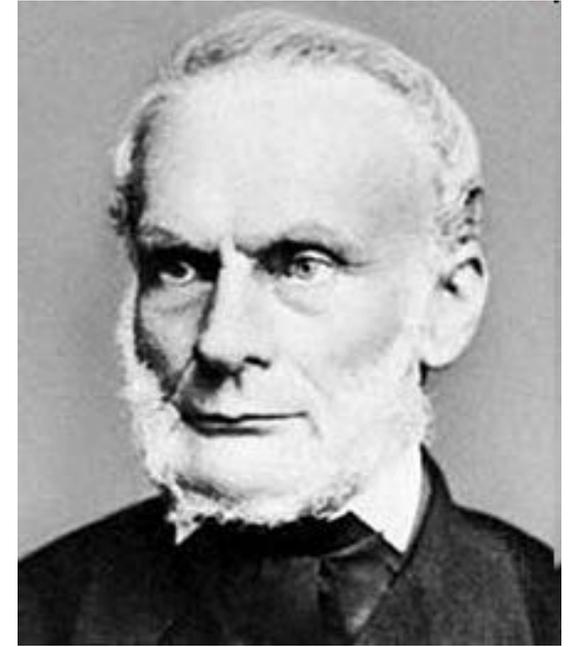
Evolution



- 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 - author of the entropy concept

Interdisciplinary applications of entropy

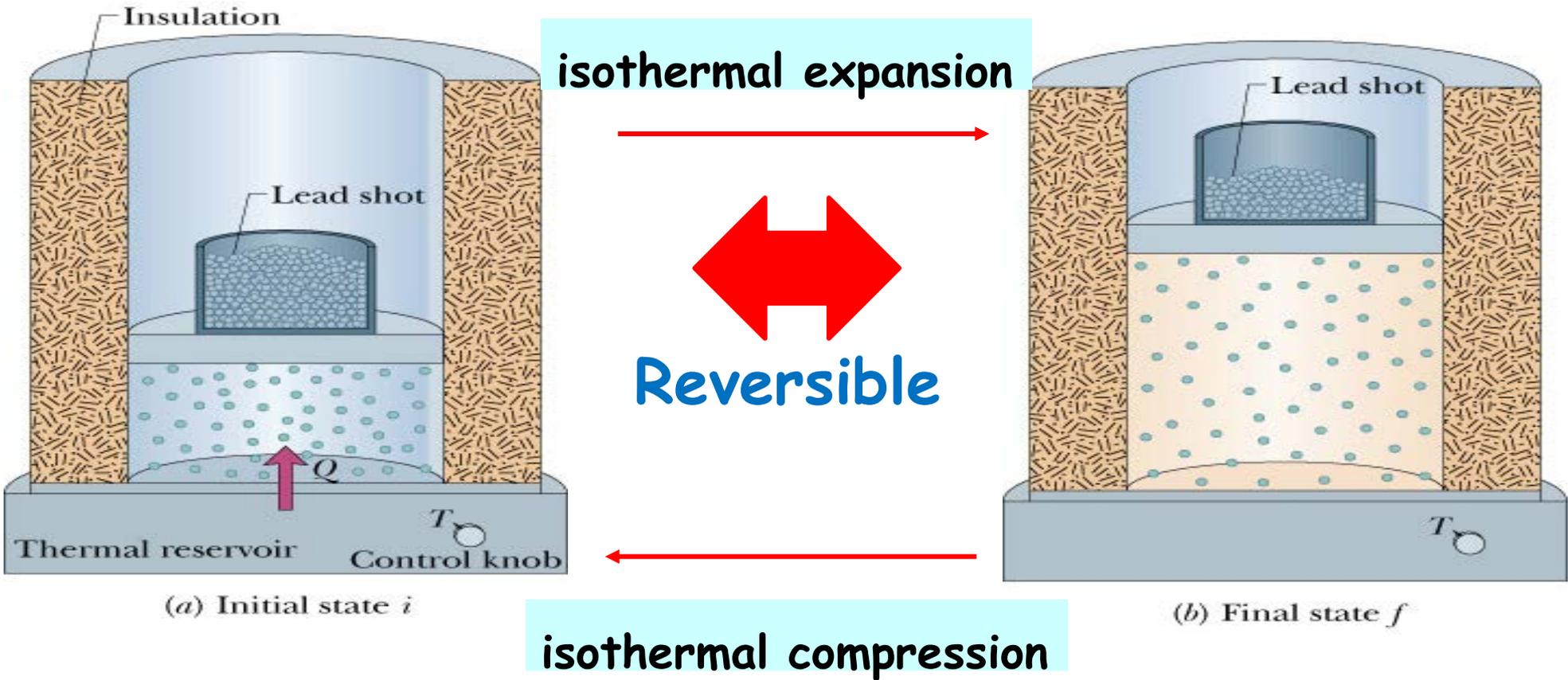
Although the concept of entropy was originally a thermodynamic construct, it has been adapted in the other following fields of study:

- ✓ information theory
- ✓ psychodynamics
- ✓ thermoeconomics
- ✓ evolution

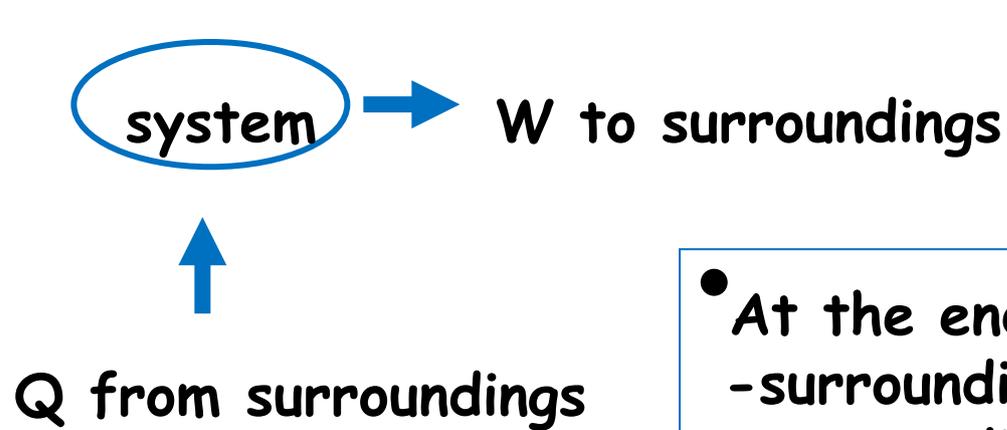
4.1. Reversible, Irreversible Processes and Entropy

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)



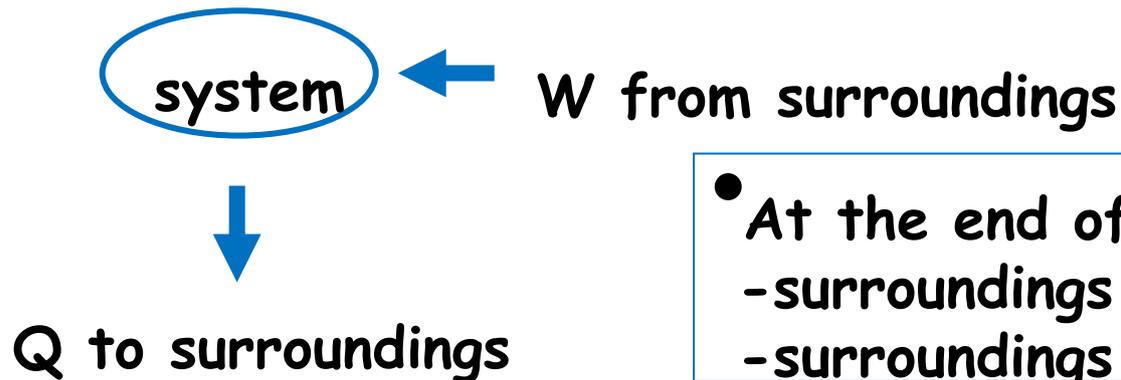
isothermal expansion



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

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

isothermal compression



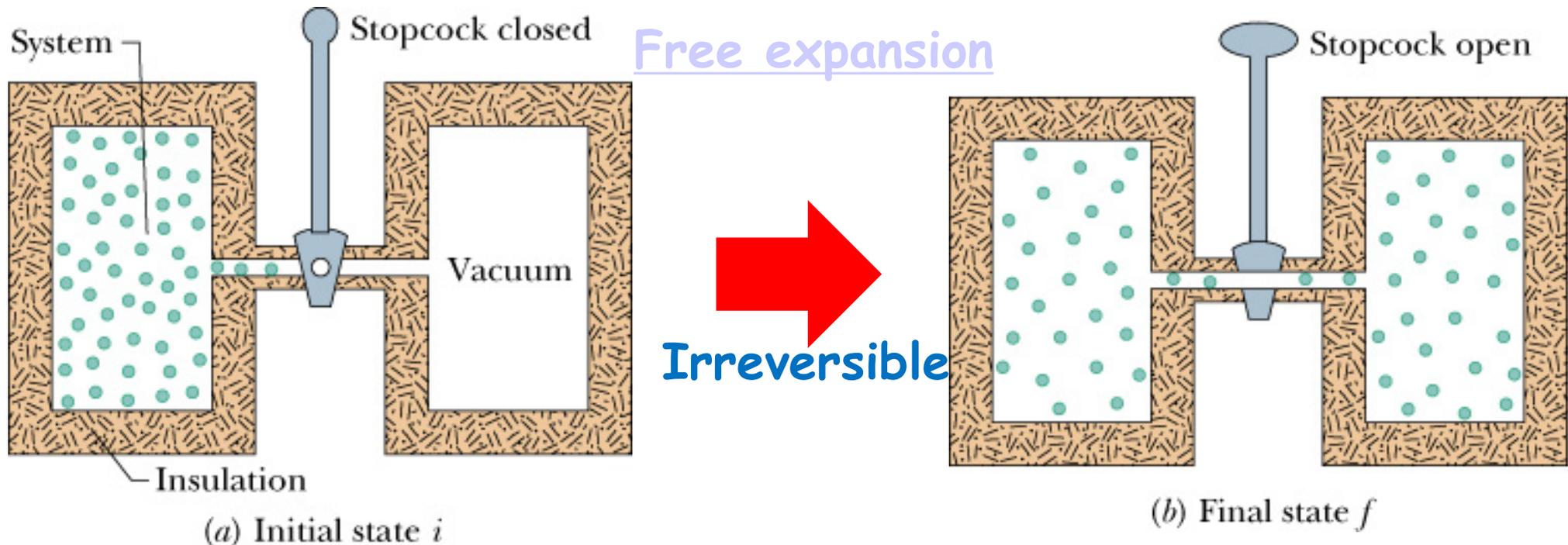
- At the end of the isothermal compression:
 - surroundings have done work
 - surroundings have received heat

Net result: the system and the surroundings back to the initial state without any change \Rightarrow **the process is reversible**

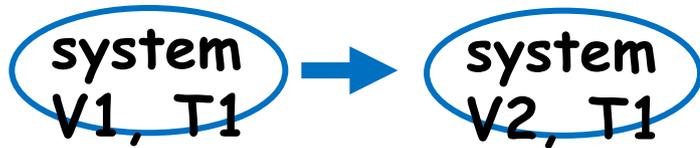
- However, the presence of friction always results in the output work of the system being smaller than the work transferred into the system. Therefore, **it is practically impossible to realize reversible processes** (i.e. ideal ones). But the concept of a reversible process proves to be very useful 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.



Free expansion



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

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

isothermal compression



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



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)

\Rightarrow the universe has changed \Rightarrow **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 \Rightarrow chickens: $\Delta S > 0$

chickens \Rightarrow eggs: $\Delta S < 0$: it never happens

d. 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 (next slide)
2. By **counting** the ways in which **the atoms or molecules** that make up the system can be arranged (see next lecture)

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

Q: energy transferred as heat to or from the system during the process; **T (K)**: temperature of the system;

Unit: **J/K**

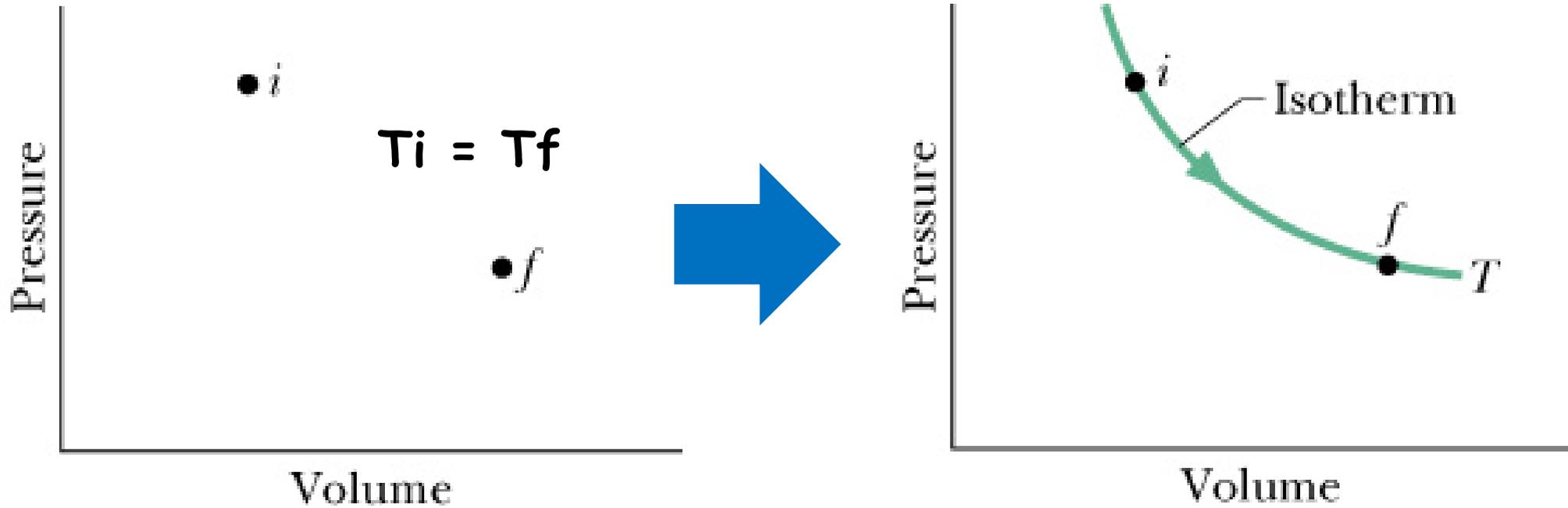
• For free expansions: p , V and T fluctuate unpredictably, so we cannot find a relation between Q and T to calculate ΔS .



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:



$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T}$$

- 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 1 (p. 539):

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 ,
- (c) from 80°C to 85°C , greatest first.

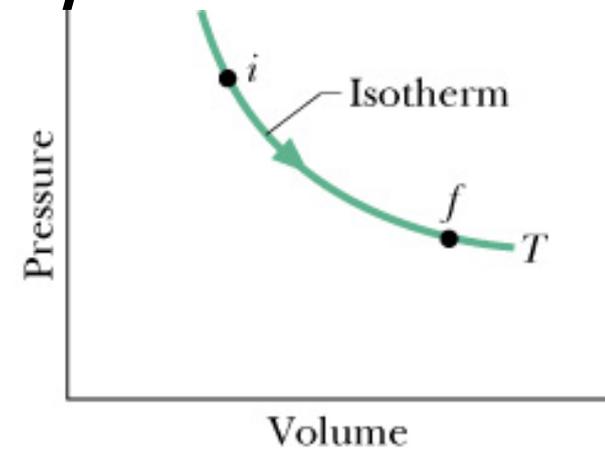
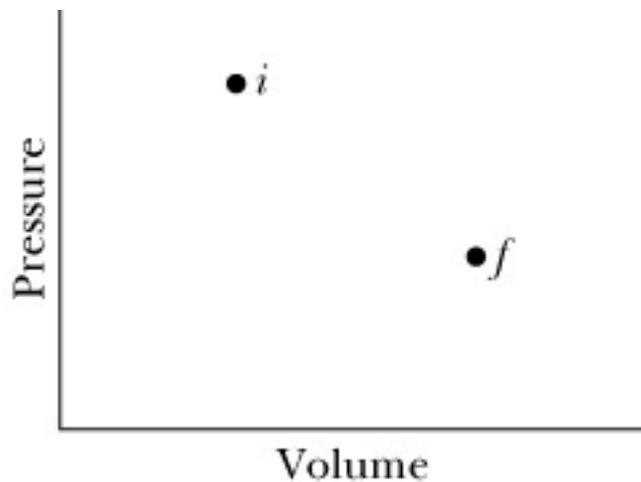
$$\Delta S = S_f - S_i \approx \frac{Q}{T_{avg}} = \frac{cm\Delta T}{T_{avg}}$$

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.

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



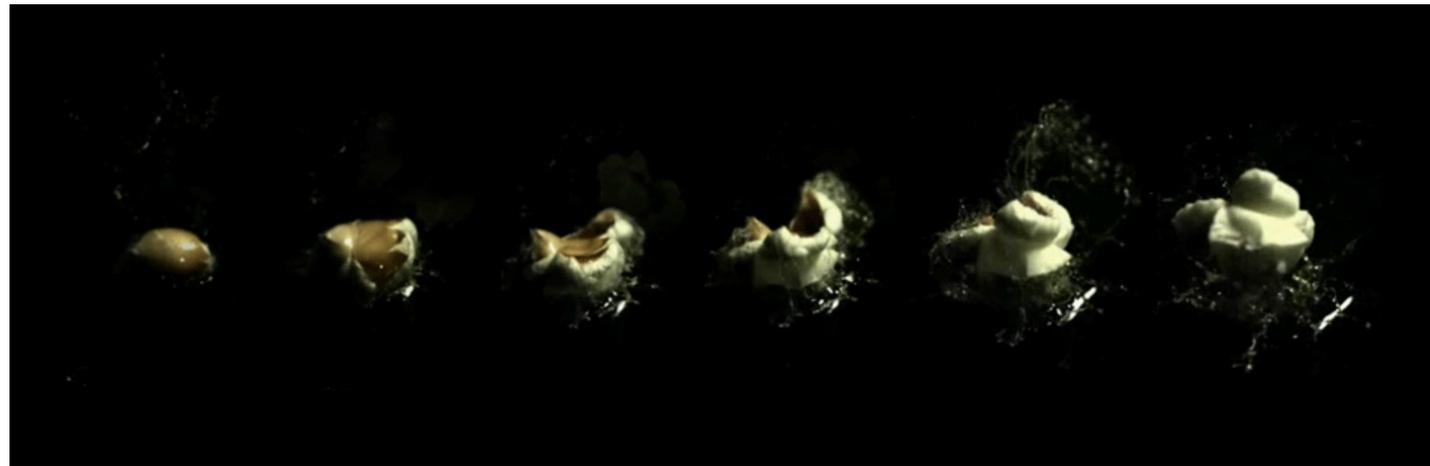
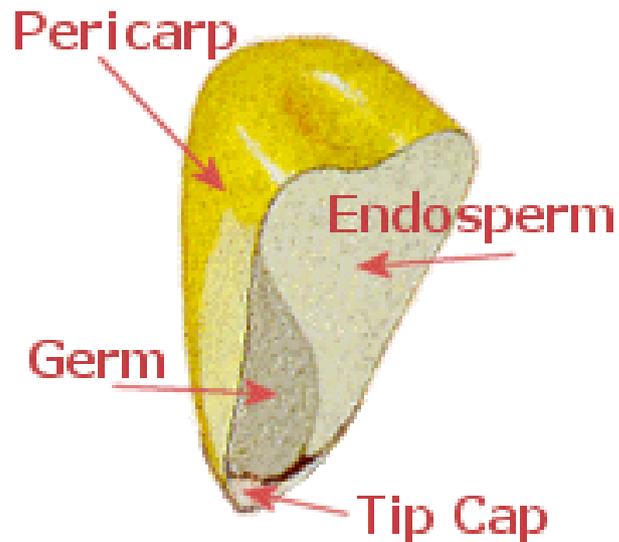
$$Q = nRT \ln \frac{V_f}{V_i} \Rightarrow \Delta S_{rev} = nR \ln \frac{V_f}{V_i}$$

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)

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

Sample Problem:

The pericarp part of a popcorn kernel is a small container of water. When the popcorn is heated to $\sim 180^\circ\text{C}$, the pericarp walls break and the liquid vaporizes so rapidly. The vapor explodes the rest of the kernel to many times of 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 \Rightarrow popped popcorn) by calculating two reversible processes:

(1) vaporization at 180°C ;

(2) adiabatic expansion of the vapor (the process occurs so rapidly, so it is adiabatic)

Process 1: Vaporization, $T = \text{constant}$

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

$L_v = 2256 \text{ kJ/kg}$: latent heat of vaporization of water

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

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.

$$\underbrace{dE_{\text{int}}}_{nC_V dT} = dQ - \underbrace{dW}_{pdV}$$

$$dQ = pdV + nC_V dT$$

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

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

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

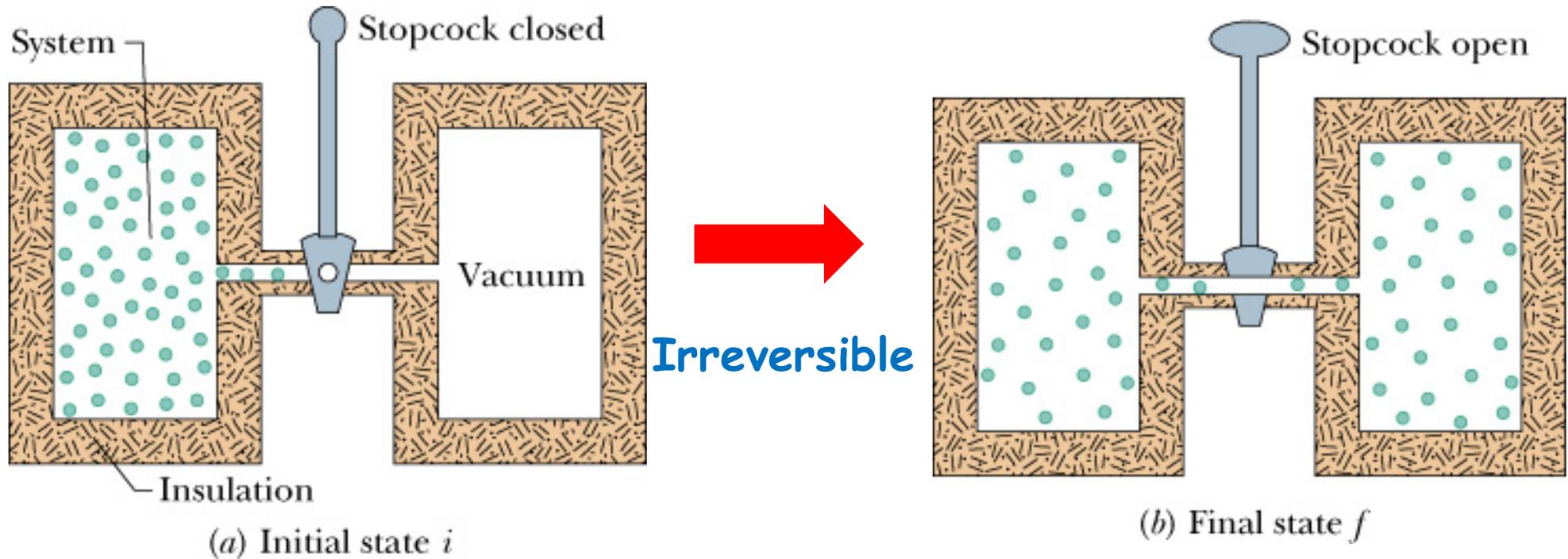
→ the entropy change only depends on properties of the initial and final states, therefore we say entropy is a state function.

Homework: 1, 3, 7, 10, 14, 15, 18 (page 556)

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):



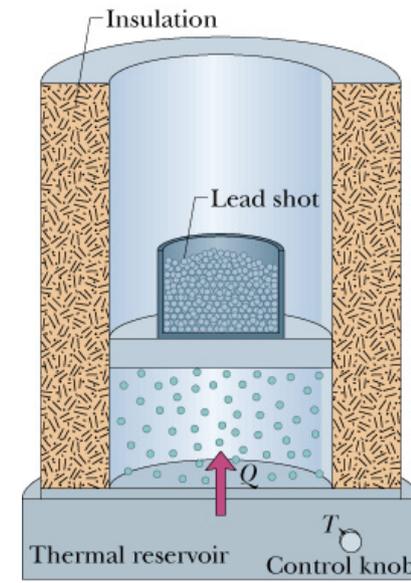
$$\Delta S_{gas} = \frac{Q}{T} > 0 \text{ (gas received energy as heat)}$$

- **Reversible processes:**

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

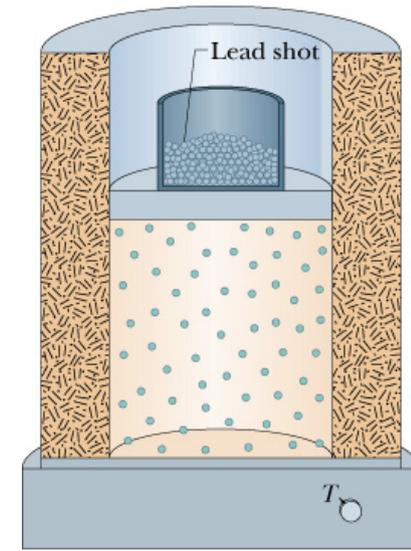
(b) to (a): $Q < 0$, $\Delta S_{gas} = \frac{Q}{T} < 0$

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



(a) Initial state *i*

↕ Reversible process



(b) Final state *f*

We now consider a closed system gas + reservoir:

$$\left. \begin{aligned} \Delta S_{gas} &= -\frac{|Q|}{T} \\ \Delta S_{reservoir} &= +\frac{|Q|}{T} \end{aligned} \right\} \Delta S_{system} = 0 \text{ (closed system)}$$

The second law of thermodynamics for a closed system:

$$\Delta S \geq 0$$

4.3. Entropy in the Real World: Engines

- A **heat engine** is a device that converts internal energy (heat) to other useful forms, such as electrical or mechanical energy (does useful works).
- 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):

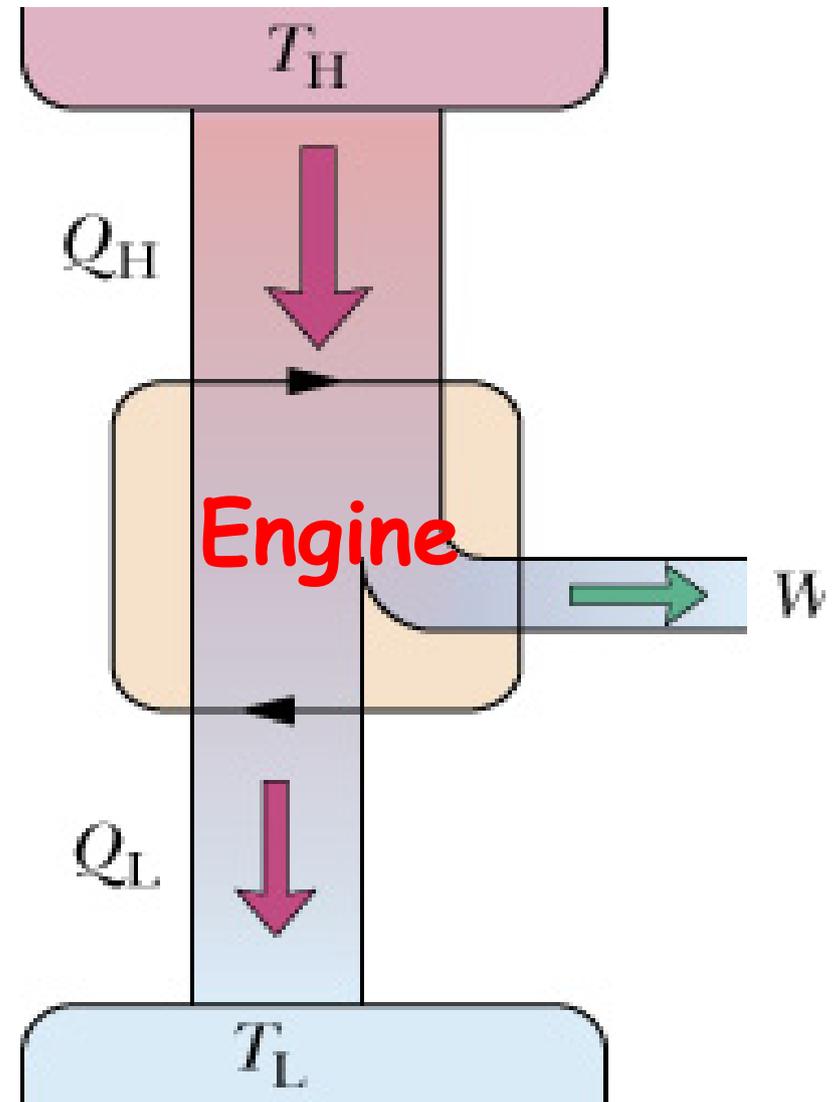
What is an ideal engine?

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

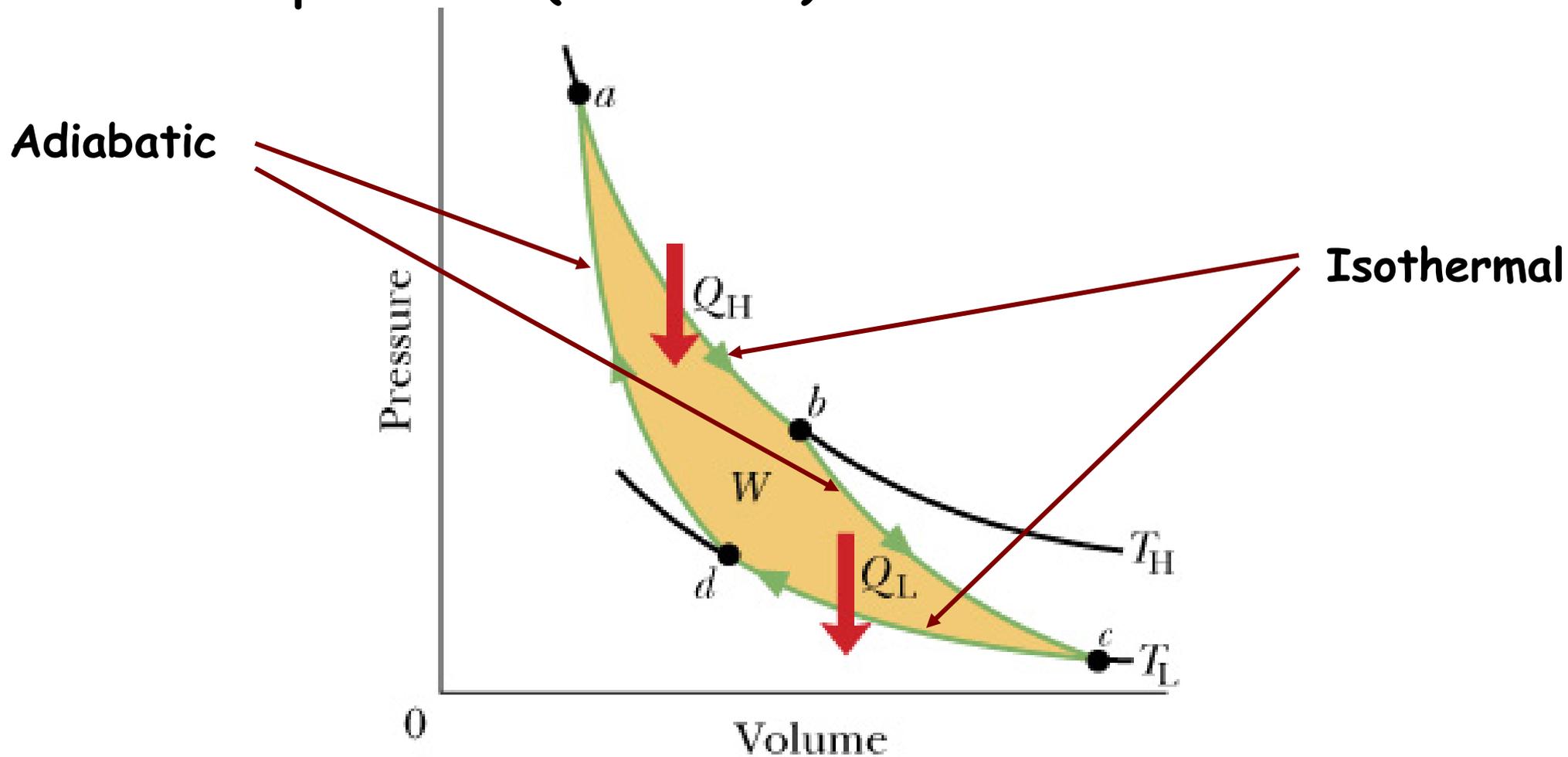
Working principle of a heat engine

- **Energy** is transferred from a source at a high temperature (Q_H)
- **Work** is done by the engine (W)
- **Energy** is expelled to a source at a lower temperature (Q_L)

The elements of a Carnot engine



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



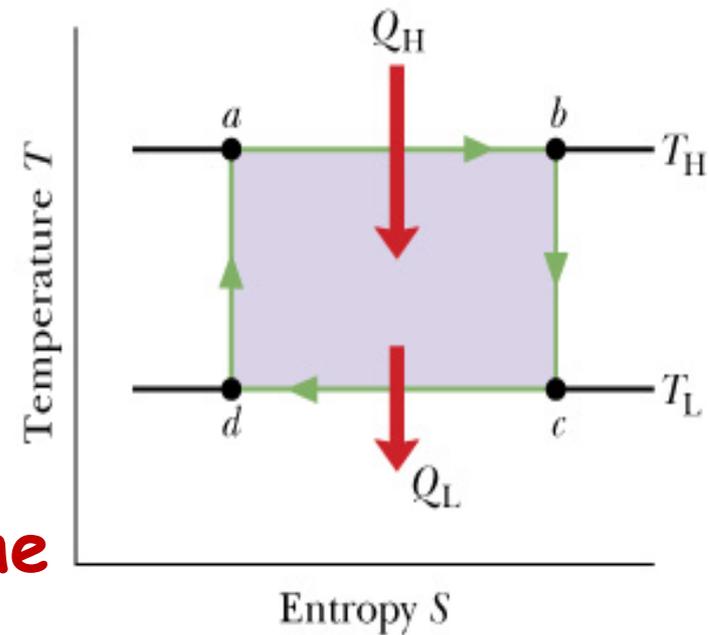
- The working substance **absorbs energy $|Q_H|$** from a thermal reservoir at a constant temperature T_H and **discharges $|Q_L|$** to a second reservoir at a constant lower temperature T_L .

The work in the Carnot cycle:

$$\Delta E_{\text{int}} = 0 \quad (\text{a cyclical process})$$

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

The **work done** by the engine equals the **net energy absorbed by the engine**



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:

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

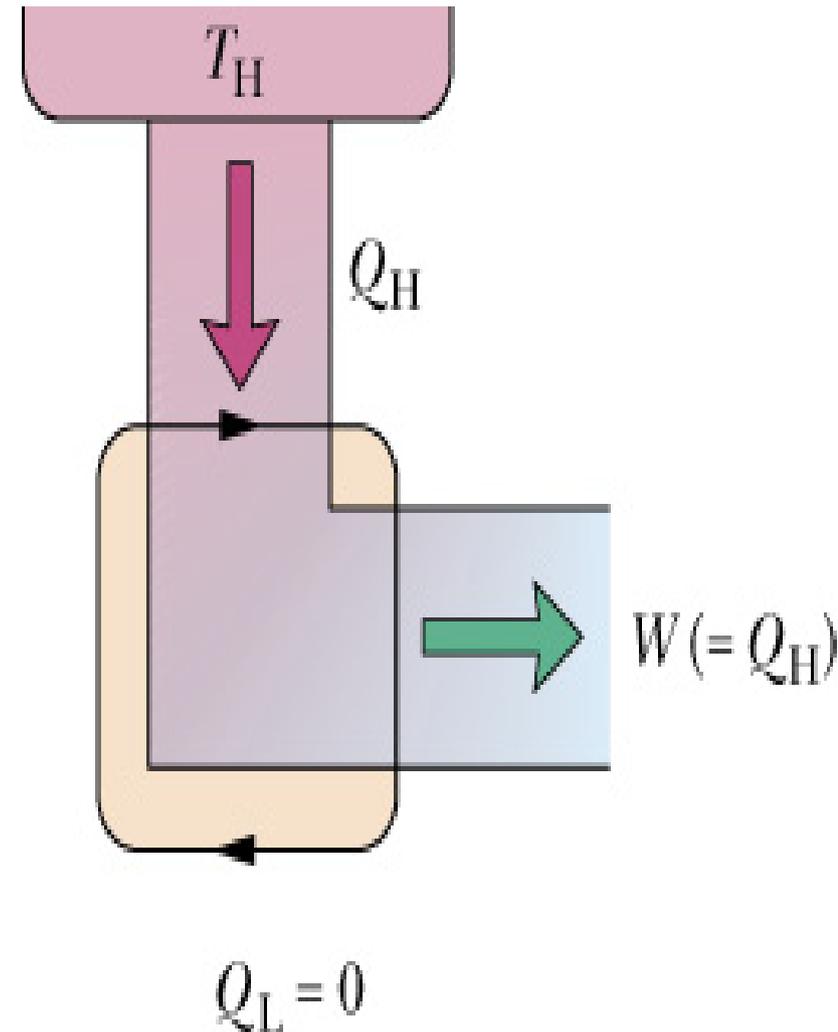
The Efficiency of any engine:

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

• For a Carnot engine:

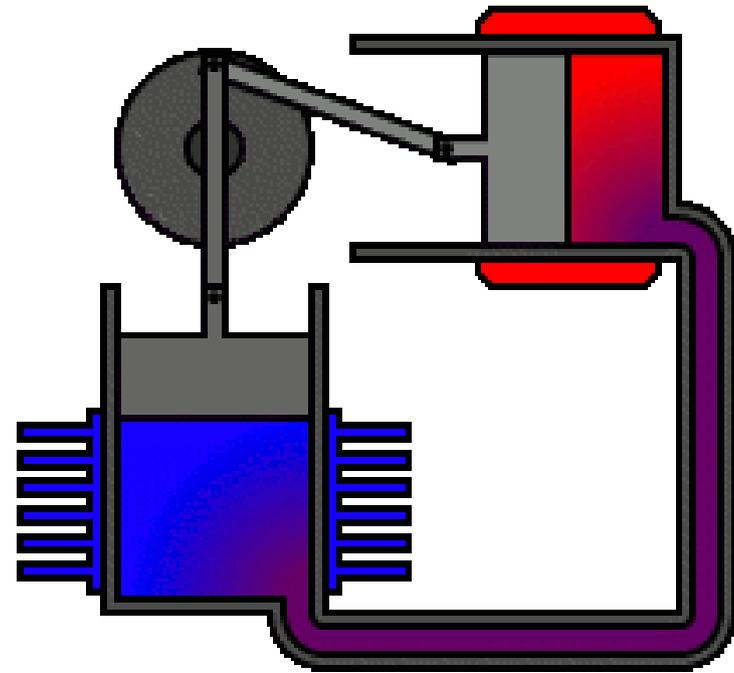
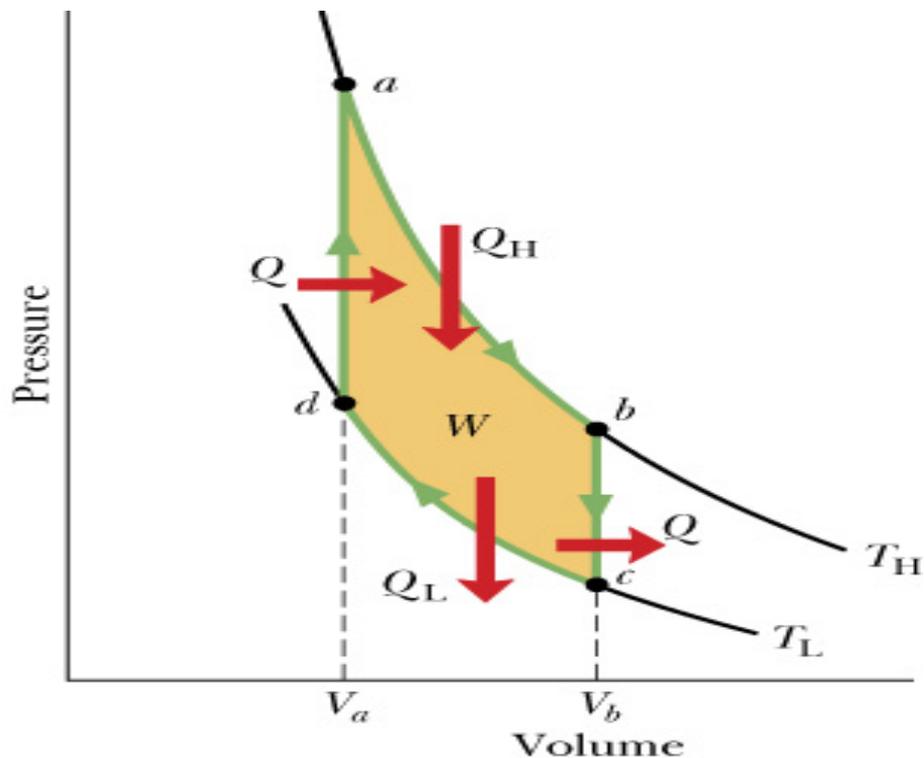
$$\varepsilon_C = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

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



b. Stirling Engine:

A Stirling engine is a **heat engine** that operates **by cyclic compression and expansion** of air or other gas (the working fluid) at different temperatures, such that there is a net conversion of heat energy to mechanical work



https://en.wikipedia.org/wiki/Stirling_engine

Stirling engines have a high efficiency compared to steam engines, being able to reach 50% -80% efficiency.

Example 1:

A diesel engine performs 2200 J of mechanical work and discards 4300 J of heat each cycle.

(a) How much heat must be supplied to the engine in each cycle?

(b) What is the thermal efficiency of the engine?

a) heat must be supplied to the engine

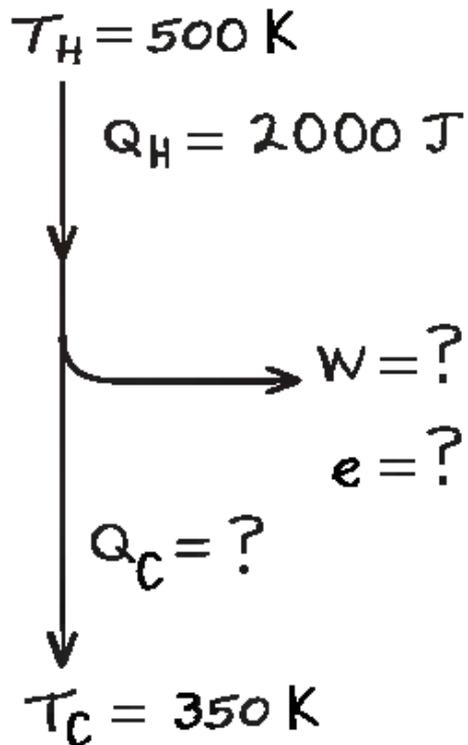
$$Q_H = W + |Q_C| = 6500 \text{ J.}$$

b) the thermal efficiency of the engine

$$e = \frac{2200 \text{ J}}{6500 \text{ J}} = 0.34 = 34\%.$$

Example 2:

A Carnot engine takes 2000 J of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do,
a) how much heat is discarded, and
B) what is the efficiency ?



$$\text{a) } Q_C = -Q_H \frac{T_C}{T_H} = -(2000 \text{ J}) \frac{350 \text{ K}}{500 \text{ K}} = -1400 \text{ J}$$

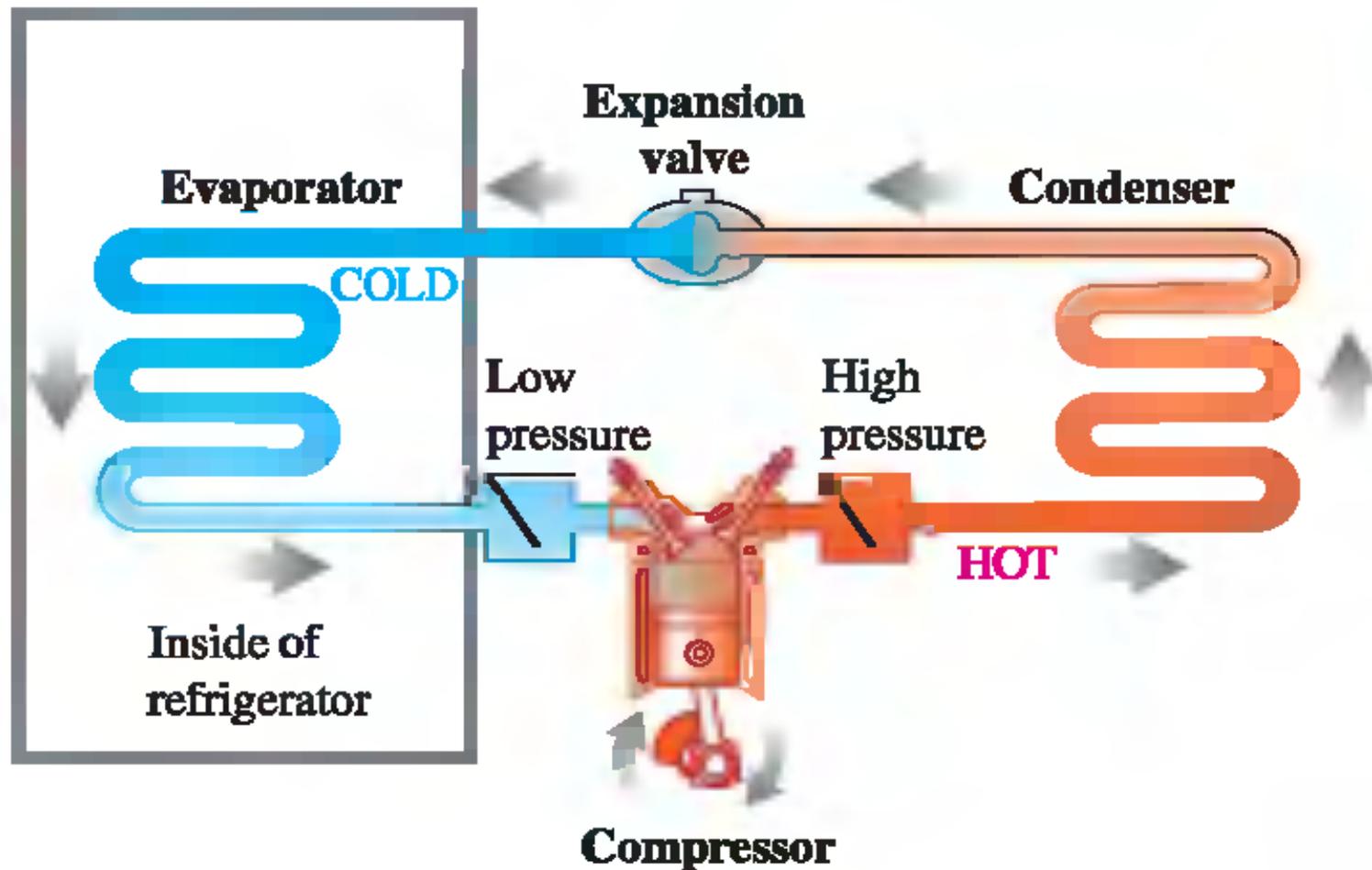
($Q_C < 0$: heat flows out of the engine and into the cold reservoir.)

$$W = Q_H + Q_C = 2000 \text{ J} + (-1400 \text{ J}) = 600 \text{ J}$$

$$\text{b) } e = 1 - \frac{T_C}{T_H} = 1 - \frac{350 \text{ K}}{500 \text{ K}} = 0.30 = 30\%$$

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 refrigerator**
(coefficient of performance):

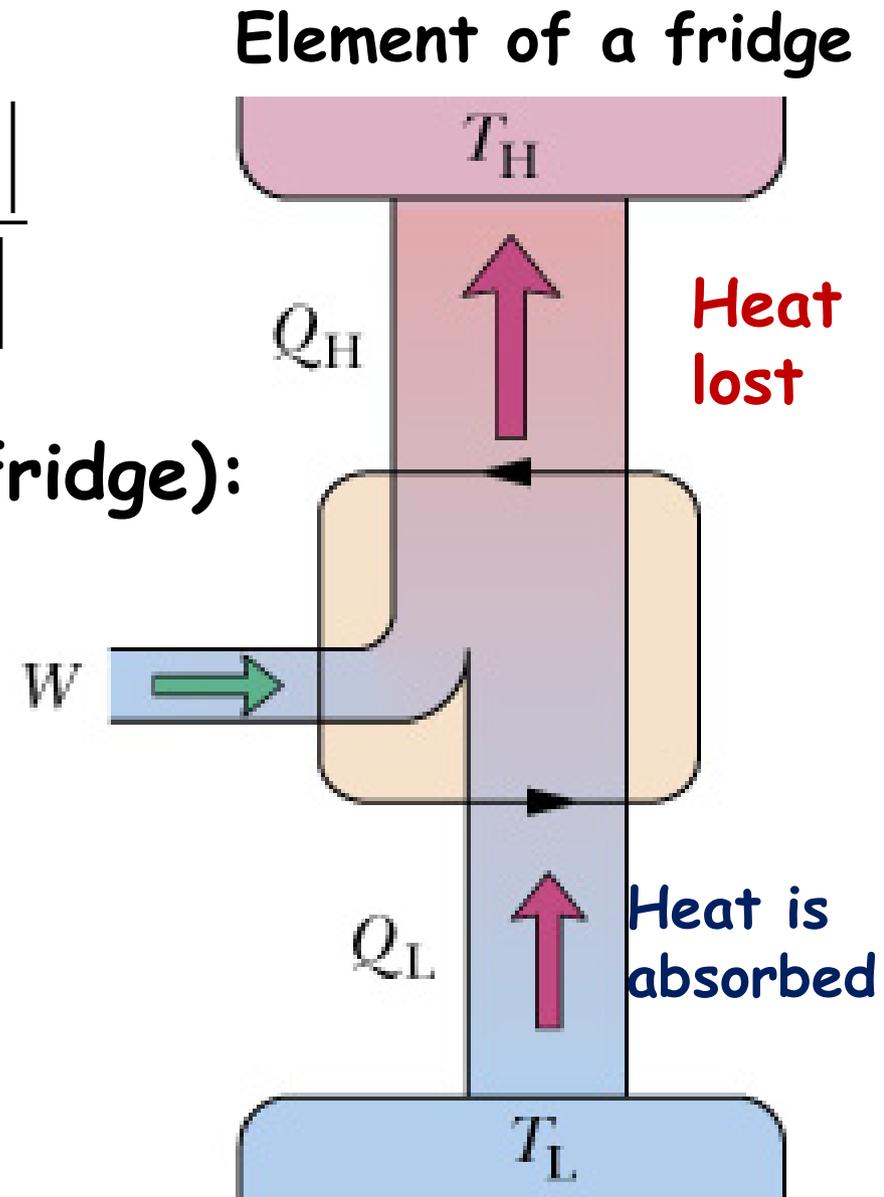
$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|}$$

For a Carnot fridge (an ideal fridge):

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

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

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



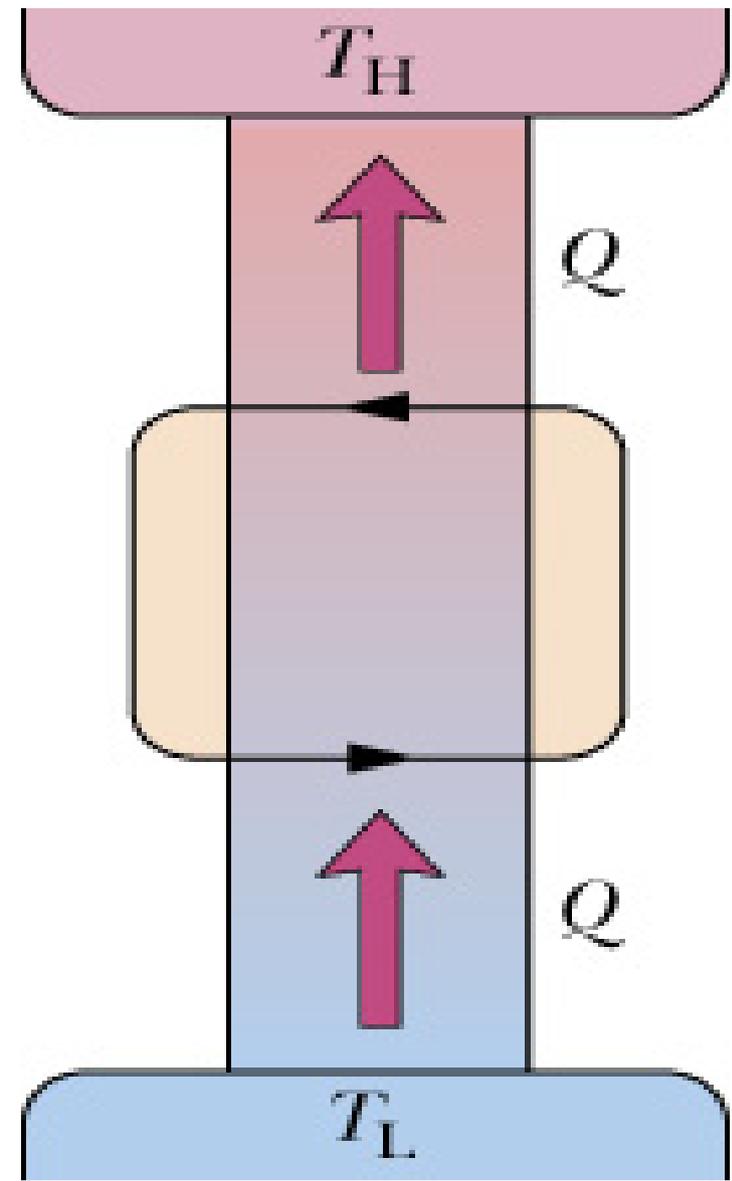
- A Perfect Refrigerator:

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

- We consider a closed system fridge of 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.**

Example 3:

A refrigerator has a coefficient of performance of 0.35. In each cycle it absorbs 3.40×10^4 J of heat from the cold reservoir.

(a) How much mechanical energy is required each cycle to operate the refrigerator?

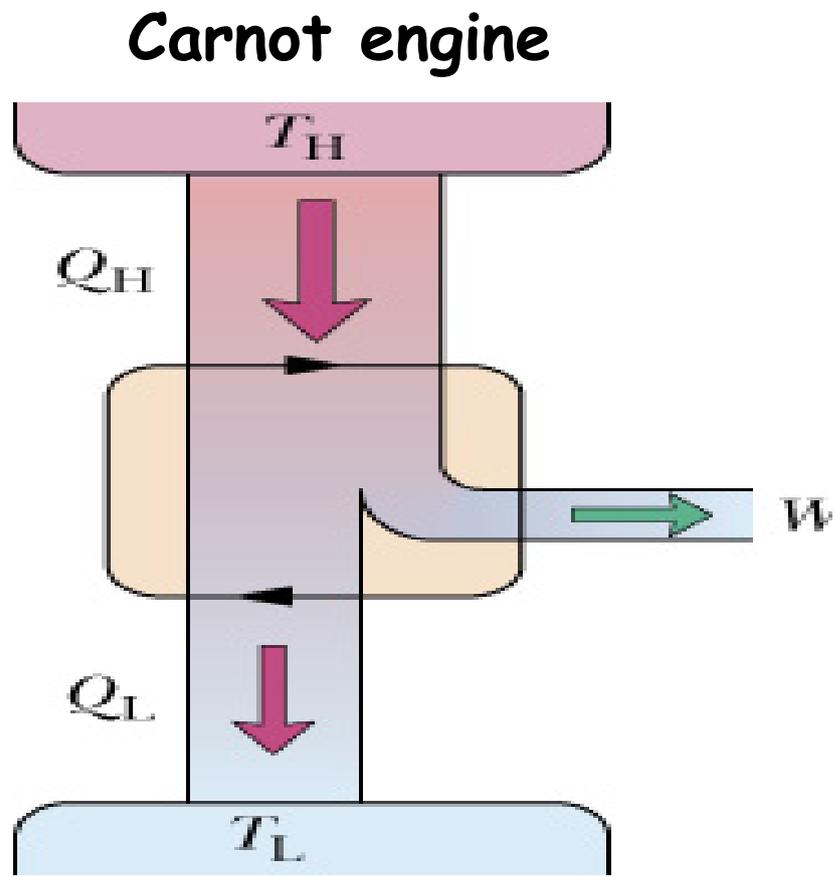
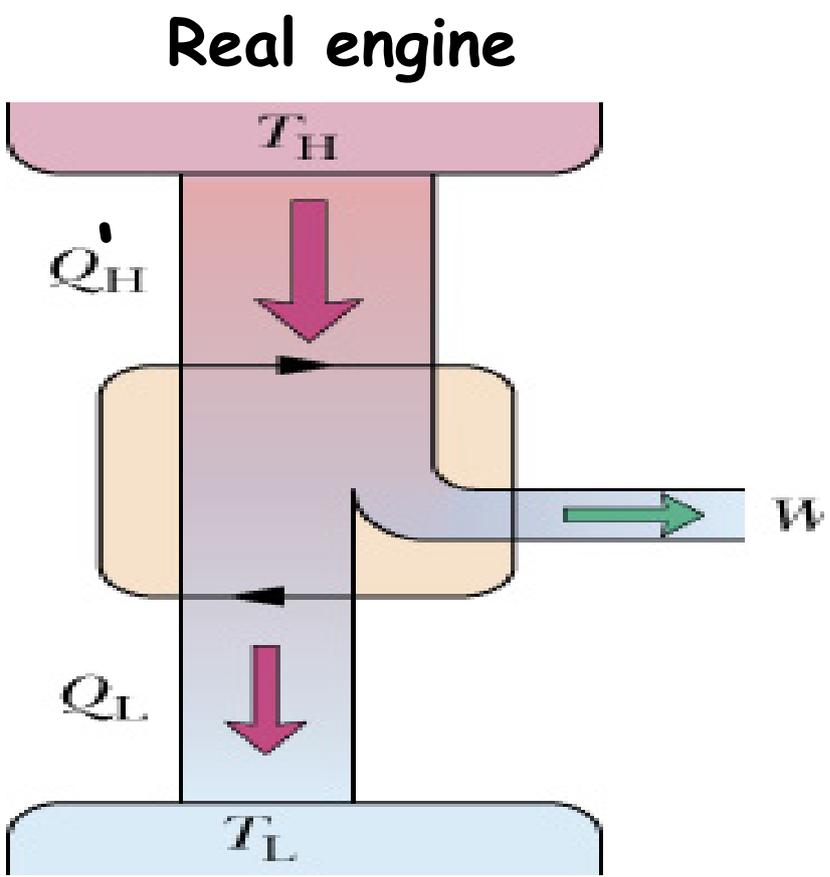
(b) During each cycle, how much heat is discarded to the high-temperature reservoir?

$$\text{a) } K = \frac{|Q_L|}{|W|} \longrightarrow W$$

$$\text{b) } |W| = |Q_H| - |Q_L| \longrightarrow |Q_H|$$

d. The efficiencies of Real Engines:

Any real engine X whose efficiency must smaller than that of a Carnot engine: $\epsilon_X < \epsilon_C$



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

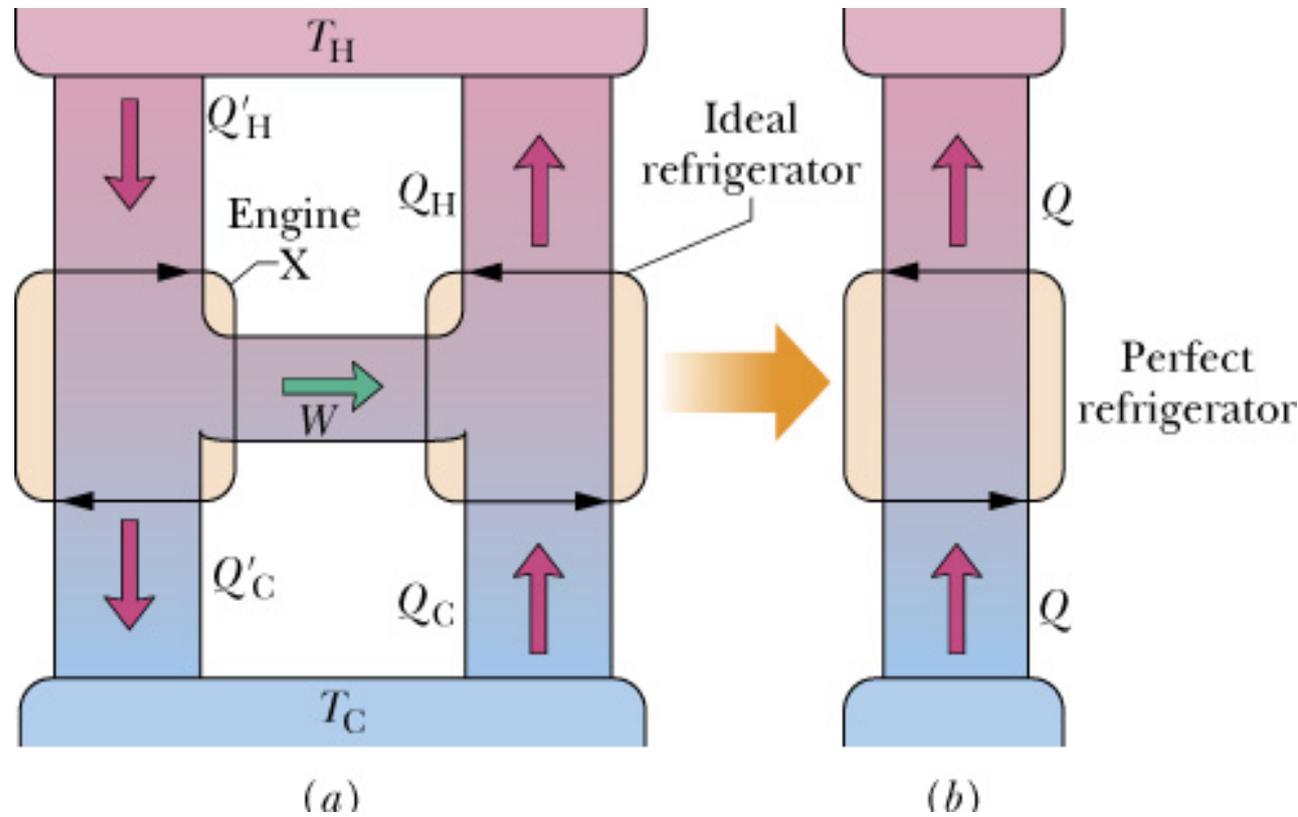
• To prove the claim above, we couple engine X to a Carnot refrigerator:

We assume: $\varepsilon_X > \varepsilon_C$

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

The efficiency of the Carnot refri. when operated as an engine

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



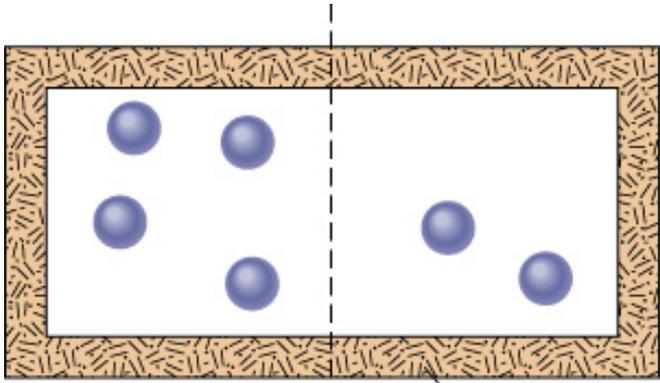
The 1st law:

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

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

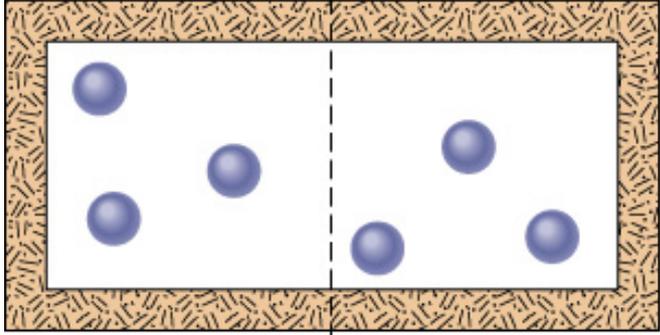
→ this coupling acts like a perfect refrigerator! ($\Delta S < 0$)

4.4. A Statistical View of Entropy



(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 :

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

In a general case:

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

Table 20-1 Six Molecules in a Box

Configuration			Multiplicity W (number of microstates)	Calculation of W (Eq. 20-20)	Entropy 10^{-23} J/K (Eq. 20-21)
Label	n_1	n_2			
I	6	0	1	$6!/(6! 0!) = 1$	0
II	5	1	6	$6!/(5! 1!) = 6$	2.47
III	4	2	15	$6!/(4! 2!) = 15$	3.74
IV	3	3	20	$6!/(3! 3!) = 20$	4.13
V	2	4	15	$6!/(2! 4!) = 15$	3.74
VI	1	5	6	$6!/(1! 5!) = 6$	2.47
VII	0	6	1	$6!/(0! 6!) = 1$	0
			<u>1</u>		
			Total = 64		

Probability and Entropy:

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

$$S = k \ln W \quad (\text{Boltzmann's entropy equation})$$

Sample Problem (p. 553)

The entropy change for a free expansion (sample P. 541):

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

Now, using the Boltzmann equation above to calculate ΔS

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

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

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: 25, 29, 33, 40 (page 558)