

Chapter 20 Entropy and the 2nd Law of Thermodynamics

- A one-way processes are processes that can occur only in a certain sequence and never in the reverse sequence, like time.
- these one-way processes are **irreversible**, meaning that they cannot be reversed by means of only small changes in their environment.

Irreversible Processes and Entropy

- Changes in energy within a closed system do not set the direction of irreversible processes. Rather, that direction is set by the *change in entropy* ΔS of the system.
- the **entropy postulate**:

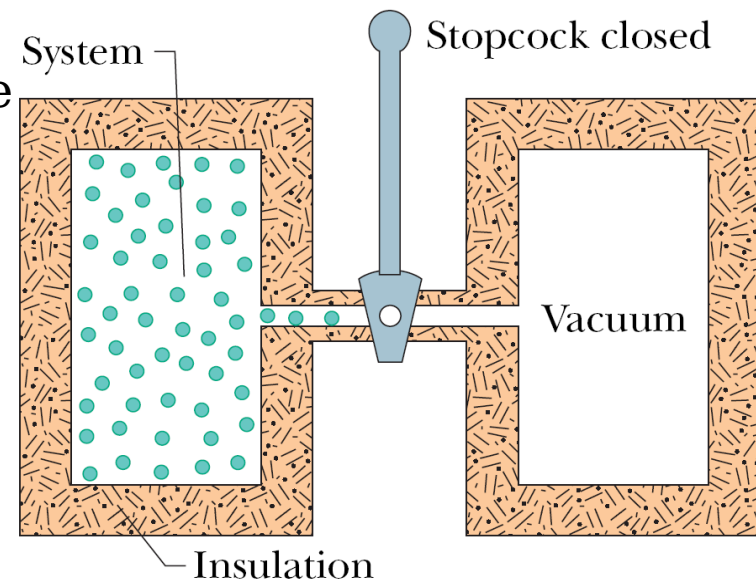
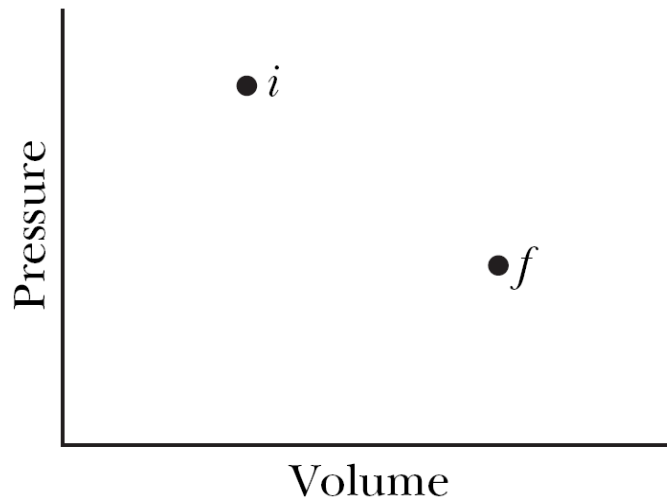
If an irreversible process occurs in a *closed* system, the entropy S of the system always increases; it never decreases.

- Because of this property, the change in entropy is sometimes called “the arrow of time”.
- 2 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.

Change in Entropy

- A free expansion is an irreversible process; all the molecules of the gas will never return to the left half of the container.

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



(a) Initial state i

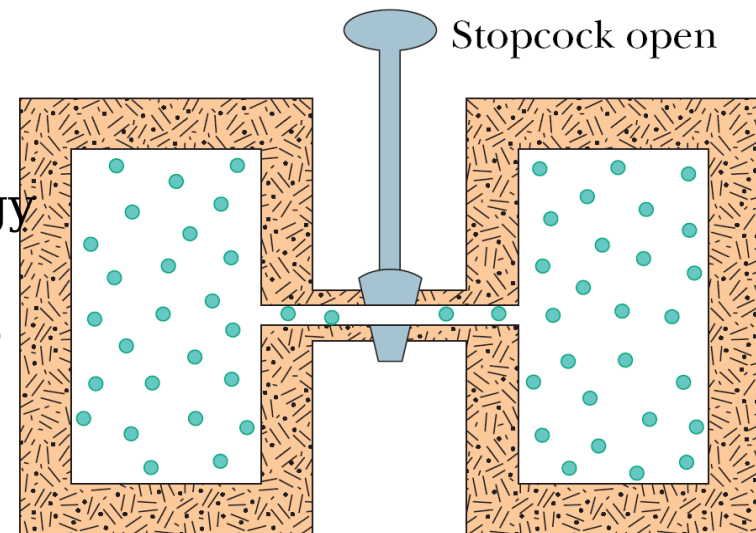
- Define the **change in entropy** ΔS of a system during a process that takes the system from an initial state i to a final state f as

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad \text{change in entropy defined}$$

- An entropy change depends not only on the energy transferred as heat but also on the temperature at which the transfer takes place. Because T is always positive, the sign of ΔS is the same as that of Q .

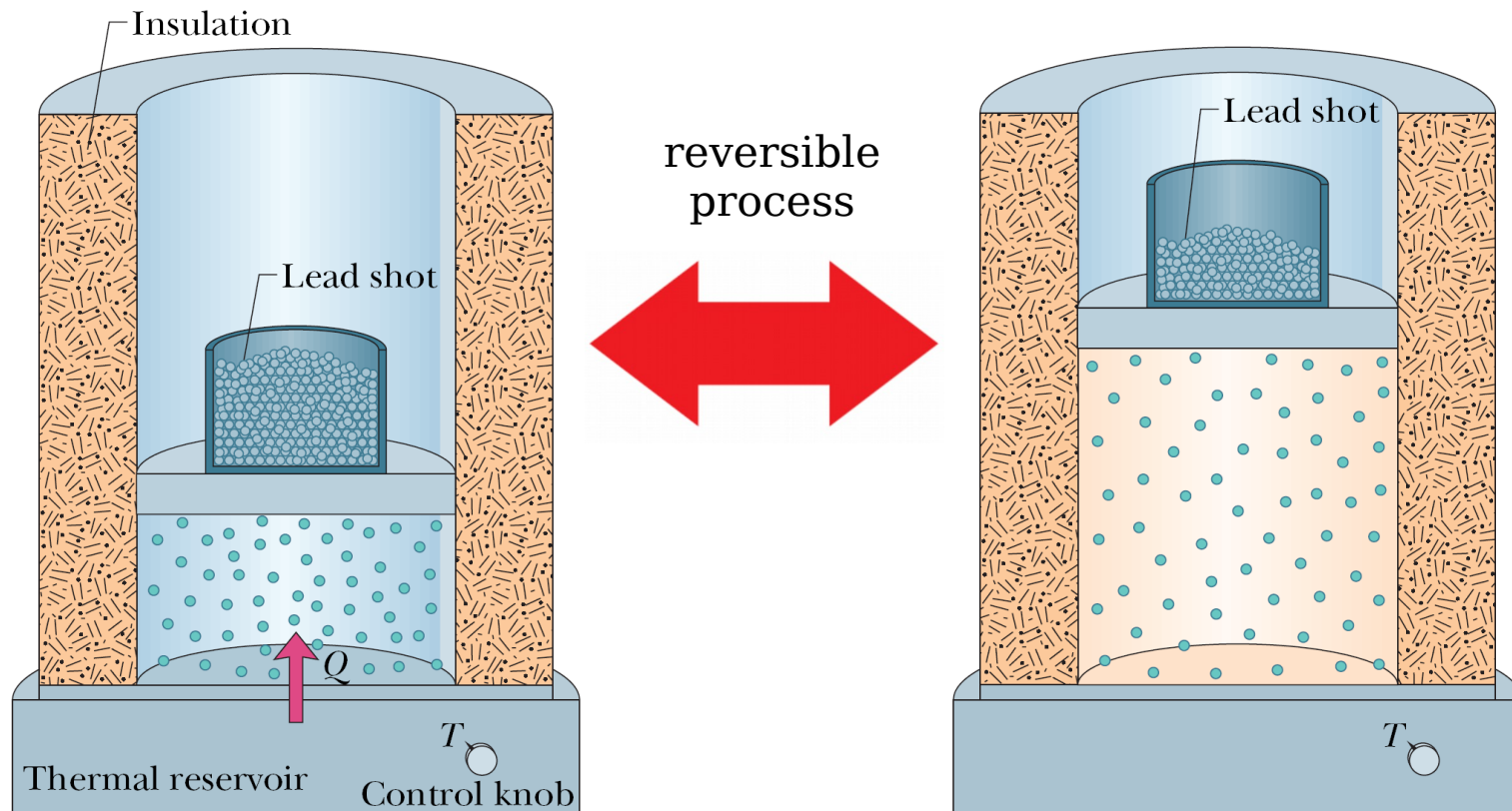
- The SI unit for entropy and entropy change is the joule per kelvin.

Irreversible process



(b) Final state f

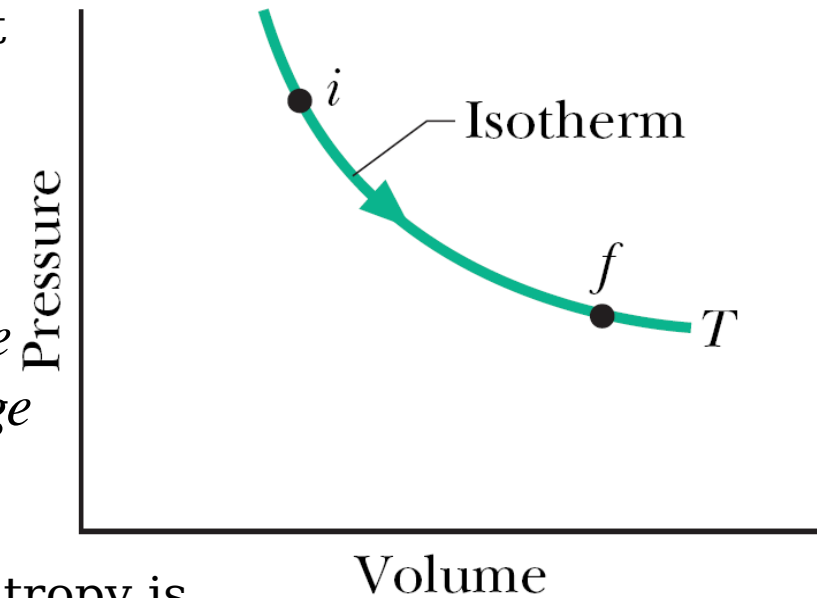
- In a free expansion, we cannot find a relation between Q and T that allows us to integrate the equation.
- However, entropy is a *state property*, the difference in entropy between states i and f depends only on those states and not on the way the system went from one state to the other.
- we can replace the irreversible free expansion with a *reversible* process that connects states i and f , such that we can find a relation between Q and T that allows us to use integrate the equation to obtain the entropy change.



(a) Initial state i

(b) Final state f

- During a free expansion, $T_i=T_f=T$, a convenient replacement process is a reversible isothermal expansion from state i to state f , which actually proceeds along the isotherm.



- Both processes have the same initial state and the same final state and thus must have the same change in entropy.

- In the isothermal process, the change of the entropy is

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{Q}{T} \quad \text{change in entropy, isothermal process}$$

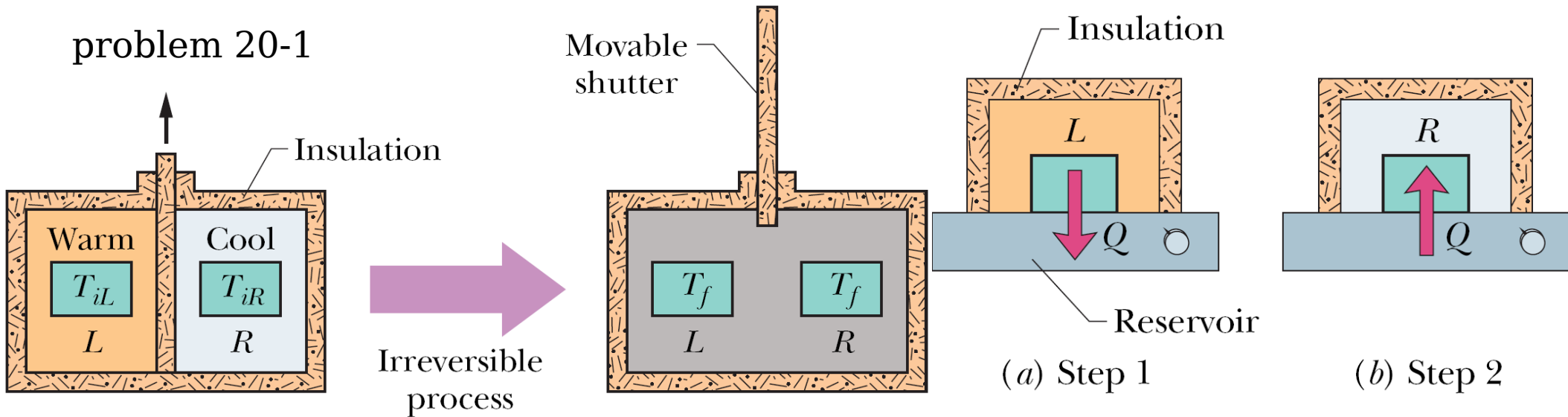
- Q is positive and the entropy of the gas *increases* during the isothermal process and during the free expansion.

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 the above equation.

- If ΔT is small before and after the process, then $\Delta S = S_f - S_i \approx \frac{Q}{T_{\text{avg}}}$

- $dS = \frac{dQ}{T} \Rightarrow dQ = T dS \Rightarrow d\mathcal{E} = dQ - dW = T dS - p dV$

problem 20-1



problem 20-2

Entropy as a State Function

- For a reversible process, the 1st law of thermodynamics can be written in the

differential form $d \mathcal{E}_{\text{int}} = dQ - dW \Rightarrow dQ = p dV + n C_V dT$

- Using the ideal gas law, and dividing each term by T , we obtain

$$\int_i^f \frac{dQ}{T} = \int_i^f n R \frac{dV}{V} + \int_i^f n C_V \frac{dT}{T} \Leftarrow \frac{dQ}{T} = n R \frac{dV}{V} + n C_V \frac{dT}{T}$$

$$= n R \ln \frac{V_f}{V_i} + n C_V \ln \frac{T_f}{T_i} \Rightarrow \Delta S = S_f - S_i = n R \ln \frac{V_f}{V_i} + n C_V \ln \frac{T_f}{T_i}$$

does not depend on the process!

The 2nd Law of Thermodynamics

- If we include the reservoir, along with the gas, as part of the system, then we have a closed system. Let's check the change in entropy of the enlarged system *gas + reservoir* for the process considered above.

- During this reversible process, energy is transferred as heat between the gas and the reservoir. we can then calculate separately the entropy changes for the gas and the reservoir,

$$\Delta S_{\text{gas}} = \pm \frac{|Q|}{T} \quad \text{and} \quad \Delta S_{\text{rev}} = \mp \frac{|Q|}{T}$$

- The entropy change of the closed system is the sum of these 2 quantities, *which is 0*.

- The modification of the entropy postulate:

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.

- 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.

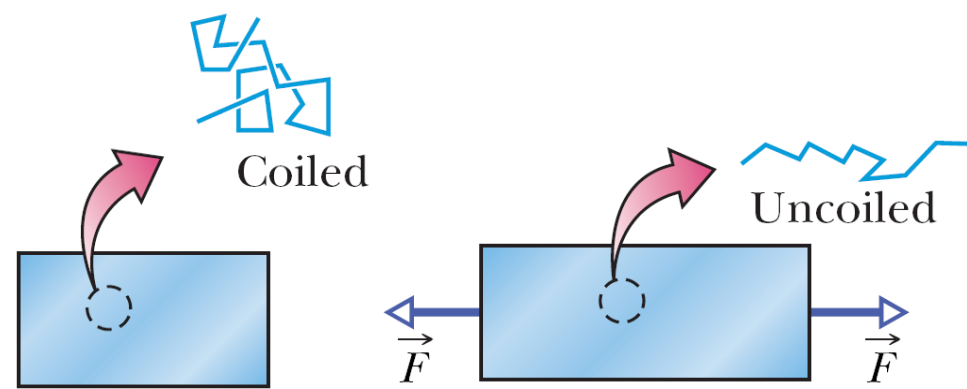
- **the 2nd law of thermodynamics** $\Delta S \geq 0$

- In the real world almost all processes are irreversible to some extent, so the entropy of real closed systems undergoing real processes always increases.

Force Due to Entropy

- To understand why rubber resists being stretched, consider the 1st law of thermodynamics

$$d\mathcal{E} = dQ - dW$$



- For the increase dx , the force is directed inward, and does work $dW = -F dx$
- Small changes in Q and S at constant T are related by

$$dQ = T dS \Rightarrow d\mathcal{E} = T dS + F dx$$

- To good approximation, the change $d\mathcal{E} = 0 \Rightarrow F = -T \frac{dS}{dx}$
- The force is proportional to the rate $\frac{dS}{dx}$ at which the rubber band's entropy changes during a small change dx .
- The alignment decreases the disorder, the entropy of the stretched rubber band is less. The force is due to the tendency of the polymers to return to their former disordered state and higher value of entropy.

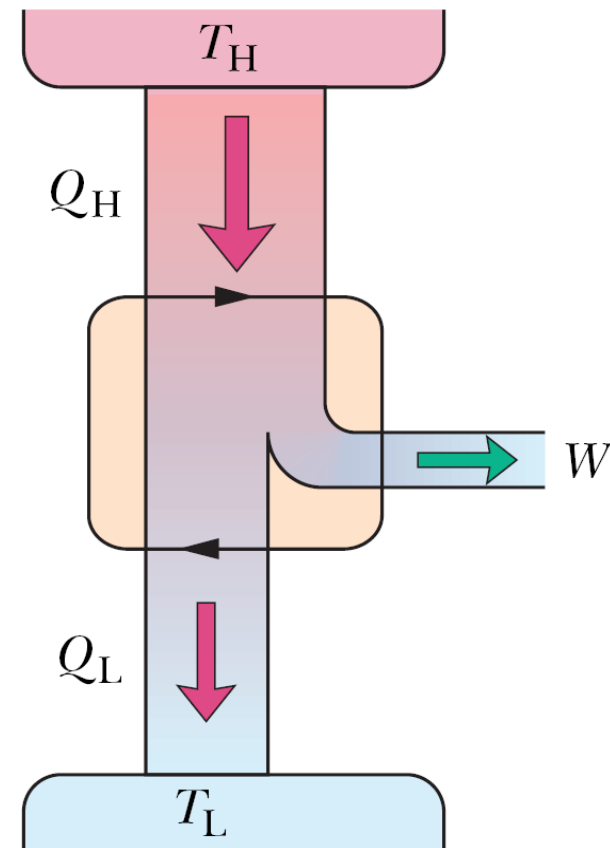
Entropy in the Real World: Engines

- A **heat engine** is a device that extracts energy from its environment in the form of heat and does useful work.
- If an engine is to do work on a sustained basis, the working substance must operate in a *cycle*; that is, the working substance must pass through a closed series of thermodynamic processes, called *strokes*, returning again to each state in its cycle.

A Carnot Engine

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

- A Carnot engine is an ideal engine which is the best (in principle) at using energy as heat to do useful work.
- During each cycle of a Carnot engine, 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 2nd thermal reservoir at a constant lower temperature T_L .



- *Carnot cycle* – the cycle followed by the working substance:

processes *ab* & *cd*: (reversible) isothermal;
 processes *bc* & *da*: (reversible) adiabatic.

- The net work per cycle W is a positive quantity equal to the area enclosed by cycle *abcd*.

The Work

- If X represents any state property of the working substance, such as p , T , V , \mathcal{E}_{int} , or S , we must have $\Delta X = 0$ for every cycle, thus

$$\Delta \mathcal{E}_{\text{int}} = 0 \Rightarrow W = |Q_H| - |Q_L|$$

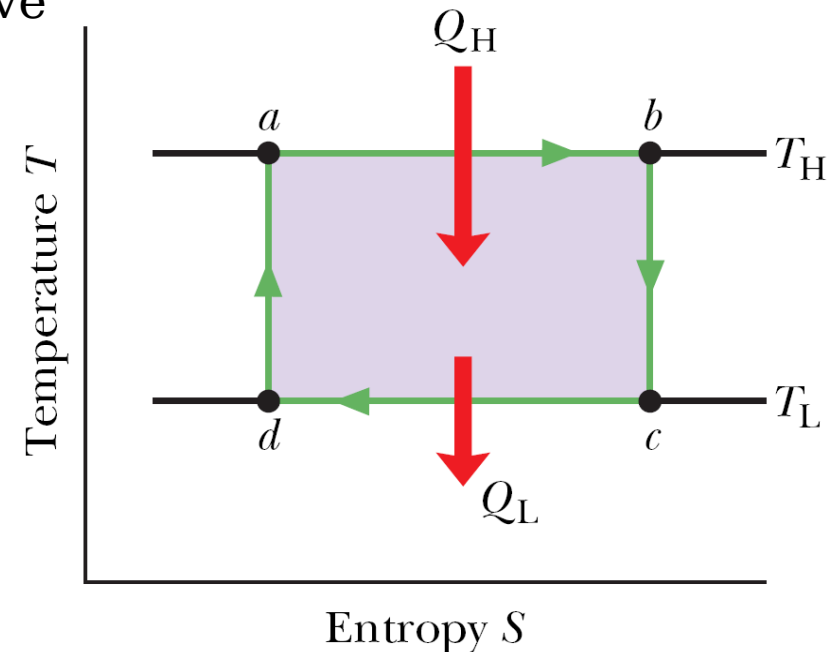
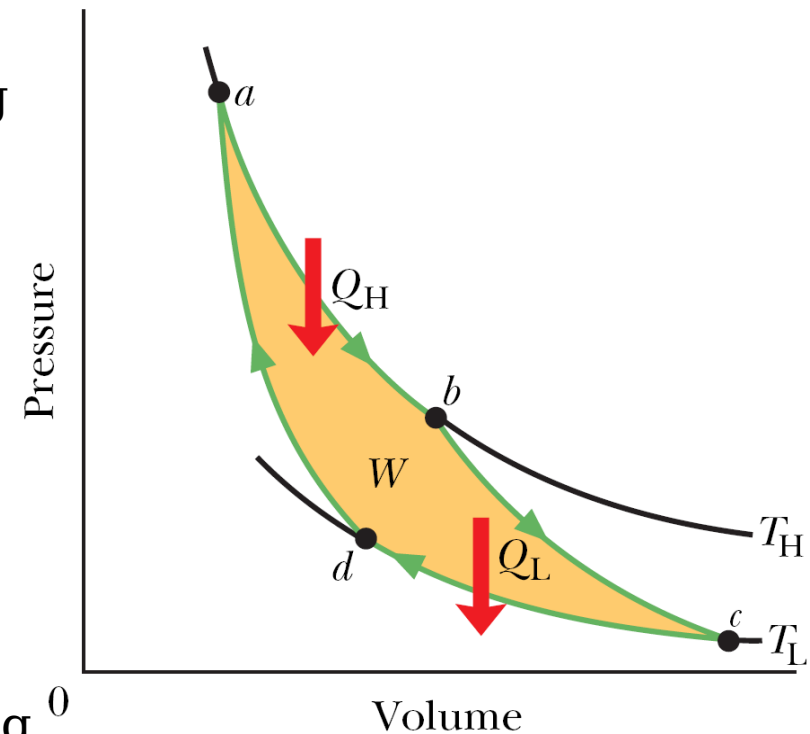
Entropy Changes

- The net entropy change per cycle is

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

Because entropy is a state function, $\Delta S = 0$ for a complete cycle, thus

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L} \Rightarrow |Q_H| > |Q_L| \text{ for } T_H > T_L$$



Efficiency of a Carnot Engine

- The purpose of any engine is to transform as much of the extracted energy Q_H into work as possible.
- **thermal efficiency** ε , defined as the work the engine does per cycle divided by the energy it absorbs as heat per cycle:

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|} \quad \text{efficiency, any engine}$$

- For a Carnot engine

$$\varepsilon_C = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H} \Rightarrow \varepsilon_C = 1 - \frac{T_L}{T_H} \quad \text{efficiency, Carnot engine}$$

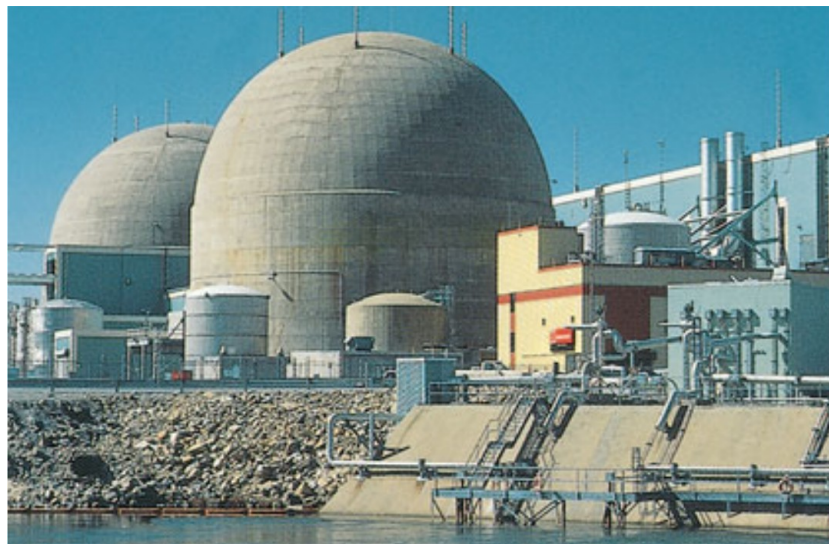
Because $T_L < T_H$, the Carnot engine has a thermal efficiency less than 100%.

- A perfect engine is an engine in which $|Q_L|$ is reduced to 0 and $|Q_H|$ is converted completely into work.
- We can achieve 100% engine efficiency (that is, $\varepsilon=1$) only if $T_L=0$ or $T_H \rightarrow \infty$, requirements that are impossible to meet.
- Practical engineering experience has led to the following alternative version of the 2nd law of thermodynamics:

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.

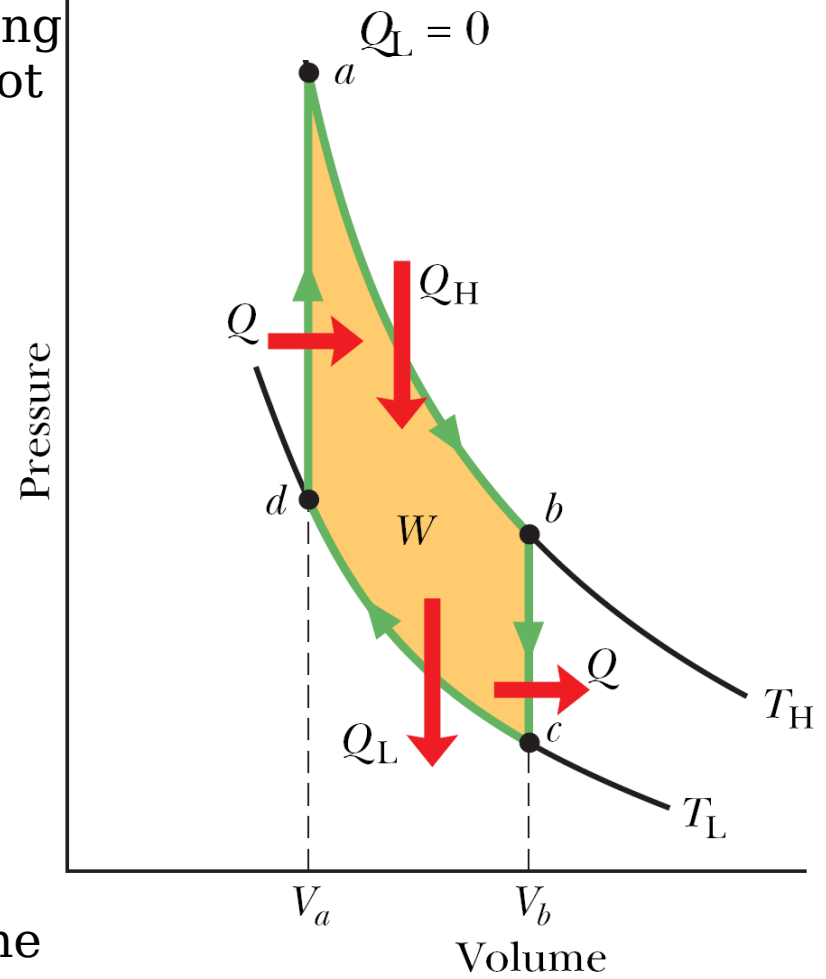
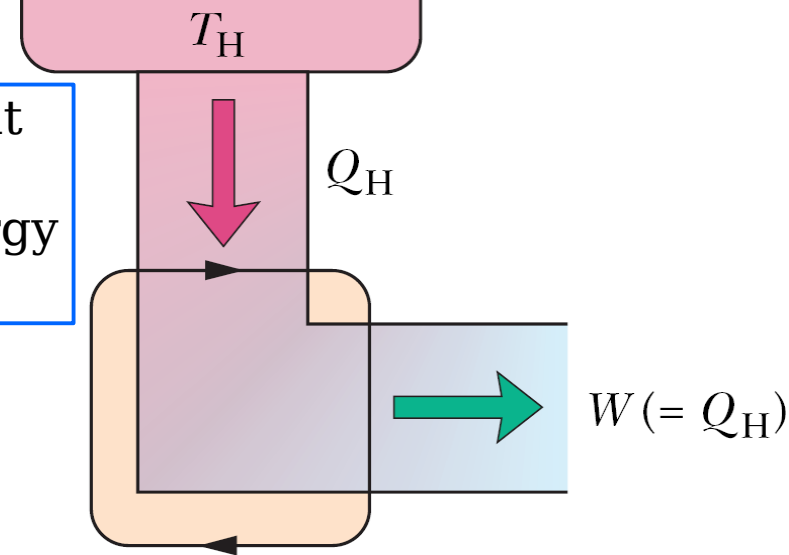
In short, *there are no perfect engines.*

- Real engines, in which the processes that form the engine cycle are not reversible, have lower efficiencies than a Carnot engine. In designing engines of any type, the efficiency of a Carnot engine is simply the efficiency limitation.



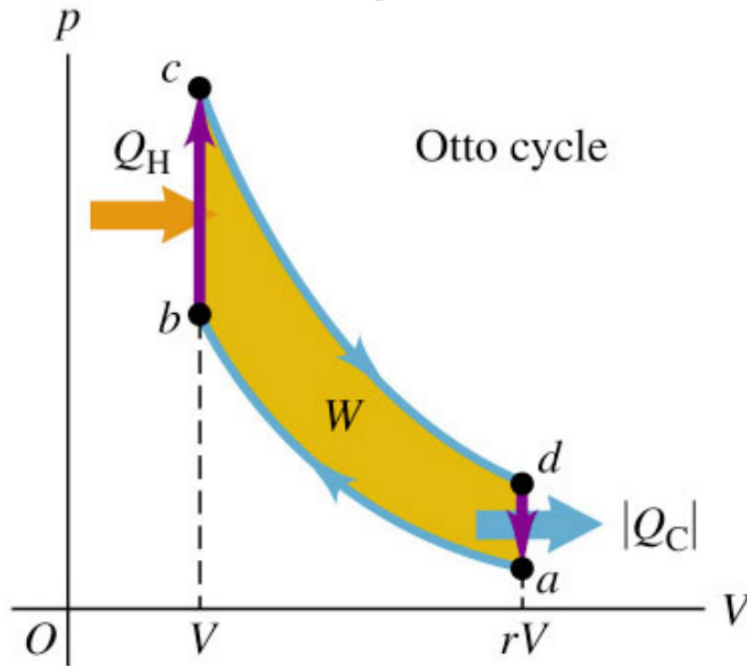
Stirling Engine

process ab & cd : (reversible) isothermal
 process bc & da ; (reversible) constant-volume



- Reversible heat transfers occur in all 4 of the processes that form the cycle of a Stirling engine, not just 2 processes as in a Carnot engine.

Otto cycle – for an ideal gasoline engine



- $a \rightarrow b$: Compression stroke (adiabatic compression)
- $b \rightarrow c$: Ignite fuel (heating at constant volume)
- $c \rightarrow d$: Power stroke (adiabatic expansion)
- $d \rightarrow a$: Reject heat to environment (cooling at constant volume)

- Process bc & da are constant volume

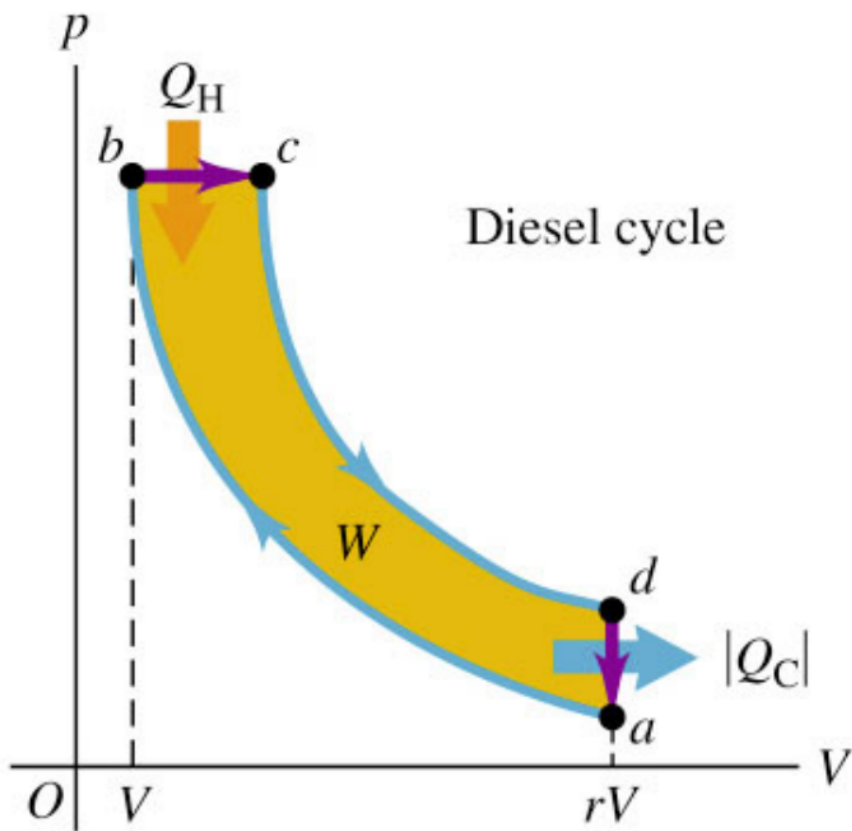
$$Q_H = n C_V (T_c - T_b) > 0, \quad Q_C = n C_V (T_a - T_d) < 0$$

- For the 2 adiabatic processes ab & cd

$$T_a (rV)^{\gamma-1} = T_b V^{\gamma-1}, \quad T_d (rV)^{\gamma-1} = T_c V^{\gamma-1}$$

$$\epsilon_O = \frac{|Q_H| - |Q_C|}{|Q_H|} = \frac{T_c - T_b + T_a - T_d}{T_c - T_b} = \frac{T_d r^{\gamma-1} - T_a r^{\gamma-1} + T_a - T_d}{T_d r^{\gamma-1} - T_a r^{\gamma-1}} = \frac{(T_a - T_d)(r^{\gamma-1} - 1)}{(T_a - T_d)r^{\gamma-1}}$$

$$\Rightarrow \epsilon_O = 1 - \frac{1}{r^{\gamma-1}} \quad \text{thermal efficiency in Otto cycle}$$



Diesel cycle

- $a \rightarrow b$: Compression stroke
(adiabatic compression)
- $b \rightarrow c$: Ignite fuel
(heating at constant pressure)
- $c \rightarrow d$: Power stroke
(adiabatic expansion)
- $d \rightarrow a$: Reject heat to environment
(cooling at constant volume)

Diesel cycle $\epsilon_D = 1 - \frac{\left(\frac{V_c}{V_a}\right)^\gamma - \left(\frac{V_b}{V_a}\right)^\gamma}{\gamma \left(\frac{V_c}{V_a} - \frac{V_b}{V_a}\right)}$

problem 20-3

problem 20-4

Diesel cycle:

$$\text{b-c: } Q_H = n C_P (T_c - T_b), \quad \text{c-d: } T_c V_c^{\gamma-1} = T_d V_d^{\gamma-1}$$

$$\text{d-a: } Q_C = n C_V (T_d - T_a), \quad \text{a-b: } T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1}$$

$$\varepsilon_D = 1 - \frac{Q_C}{Q_H}, \quad \text{where } \frac{Q_C}{Q_H} = \frac{C_V}{C_P} \frac{T_d - T_a}{T_c - T_b} = \frac{1}{\gamma} \frac{T_d - T_a}{T_c - T_b} \Leftarrow \gamma \equiv \frac{C_P}{C_V}$$

$$P V_c = n R T_c, \quad P V_b = n R T_b \Rightarrow T_c - T_b = \frac{P}{n R} (V_c - V_b)$$

$$\Rightarrow \frac{Q_C}{Q_H} = \frac{1}{\gamma} \frac{T_c (V_c/V_d)^{\gamma-1} - T_b (V_b/V_a)^{\gamma-1}}{P (V_c - V_b)/n R}$$

$$= \frac{n R T_c (V_c/V_a)^{\gamma-1} - n R T_b (V_b/V_a)^{\gamma-1}}{\gamma P (V_c - V_b)} \Leftarrow V_d = V_a$$

$$= \frac{V_c (V_c/V_a)^{\gamma-1} - V_b (V_b/V_a)^{\gamma-1}}{\gamma (V_c - V_b)} \Leftarrow P V_c = n R T_c, \quad P V_b = n R T_b$$

$$= \frac{V_c^\gamma / V_a^{\gamma-1} - V_b^\gamma / V_a^{\gamma-1}}{\gamma (V_c - V_b)}$$

$$\Rightarrow \varepsilon_D = 1 - \frac{Q_C}{Q_H} = 1 - \frac{(V_c/V_a)^\gamma - (V_b/V_a)^\gamma}{\gamma (V_c/V_a - V_b/V_a)}$$

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 as the device continuously repeats a set series of thermodynamic processes.

● An *ideal refrigerator*:

In an ideal refrigerator, all processes are reversible and no wasteful energy transfers occur as a result of, say, friction and turbulence.

● In other words, all the energy transfers, as either heat or work, are reversed from those of a Carnot engine.

— **Carnot refrigerator.**

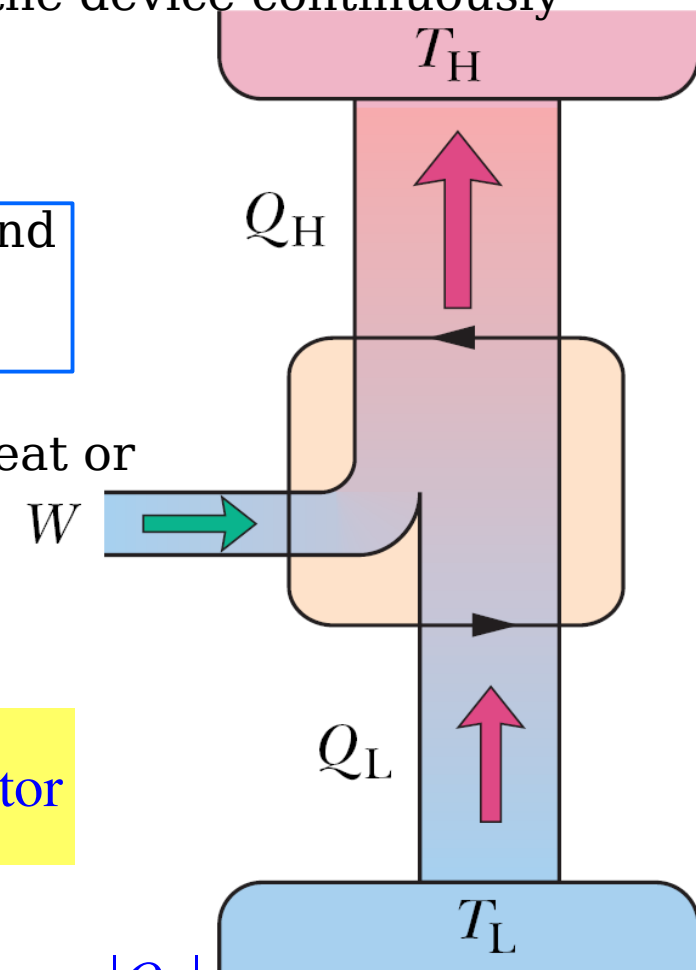
● The efficiency of a refrigerator:

$$K = \frac{\text{what we get}}{\text{what we pay for}} = \frac{|Q_L|}{|W|} \quad \text{efficiency, any refrigerator}$$

K is called the *coefficient of performance*.

● For a Carnot refrigerator $|W| = |Q_H| - |Q_L| \Rightarrow K_C = \frac{|Q_L|}{|Q_H| - |Q_L|}$

$$\Rightarrow K_C = \frac{T_L}{T_H - T_L} \quad \text{efficiency, Carnot refrigerator}$$

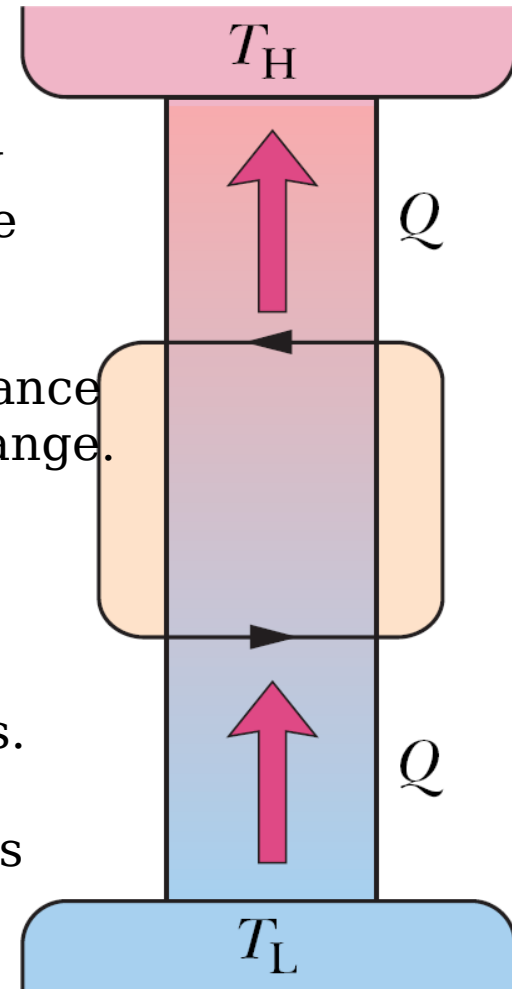


- For typical room air conditioners, $K \sim 2.5$. For household refrigerators, $K \sim 5$.
- The value of K is higher the closer the temperatures of the 2 reservoirs are to each other.
- A *perfect refrigerator* is a refrigerator that transfers energy as heat from a cold reservoir to a warm reservoir without the need for work.
- During a complete cycle, the entropy of the working substance does not change, but the entropies of the 2 reservoirs do change. Thus, the net entropy change for the entire system is

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

- $T_L < T_H \Rightarrow \Delta S < 0 \Rightarrow$ violate the 2nd law of thermodynamics.
- An equivalent formulation of the 2nd law of thermodynamics

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.

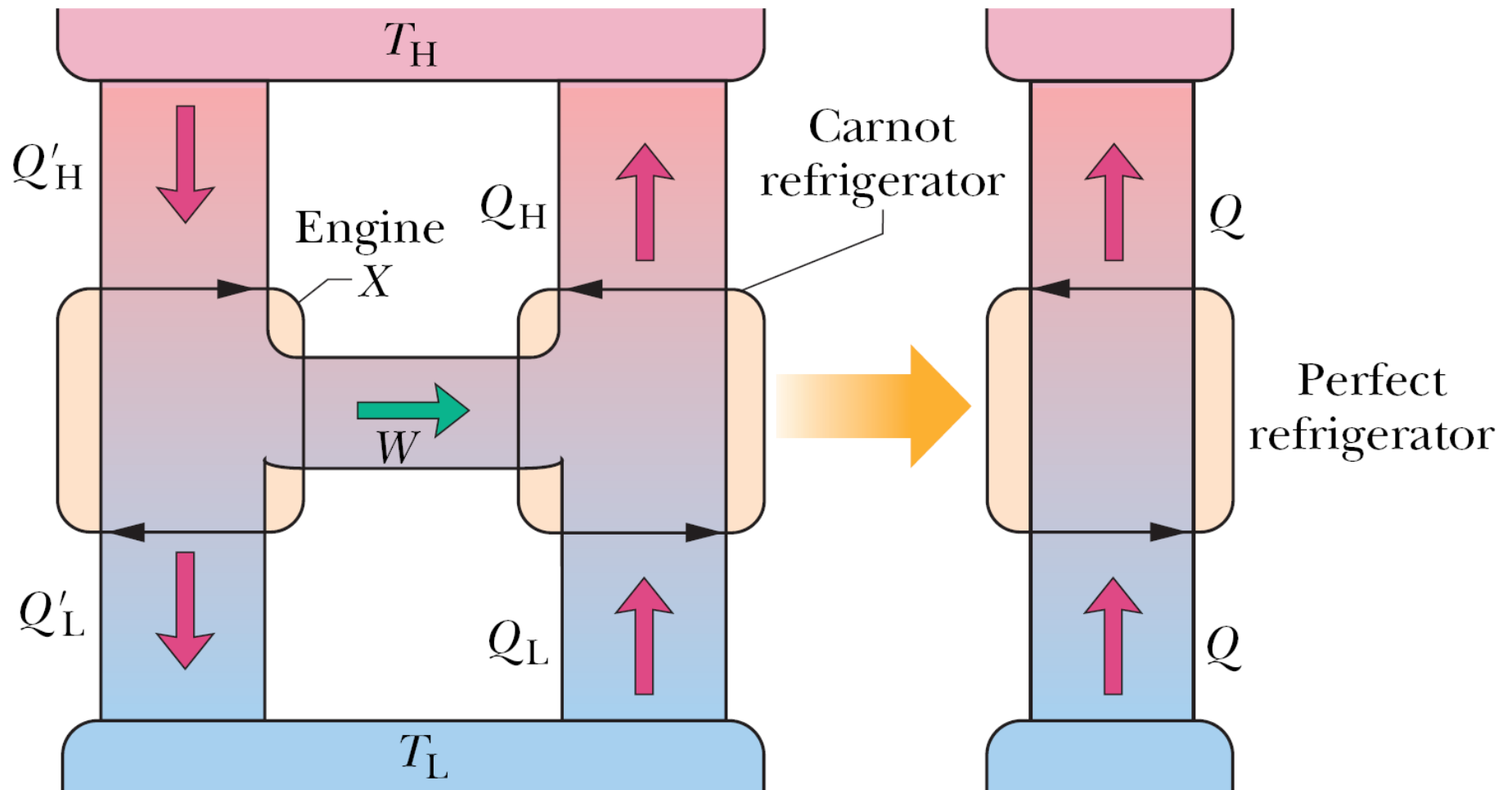


In short, *there are no perfect refrigerators.*

The Efficiencies of Real Engines

- Assume there is an engine X , and its efficiency ε_X is greater than ε_C , the efficiency of a Carnot engine:
$$\varepsilon_X > \varepsilon_C \quad (\text{a claim})$$

- Let us couple engine X to a Carnot refrigerator, then adjust the strokes of the Carnot refrigerator so that the work it requires per cycle is just equal to that provided by engine X .



● From the definition of efficiency $\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|} \Rightarrow |Q_H| > |Q'_H|$

● From the 1st law of thermodynamics

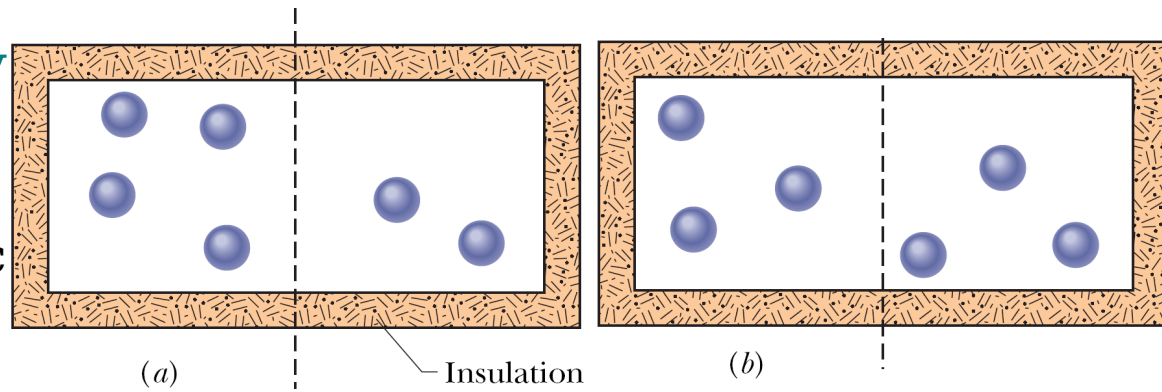
$$|Q_H| - |Q_L| = |Q'_H| - |Q'_L| = W \Rightarrow |Q_H| - |Q'_H| = |Q_L| - |Q'_L| \Rightarrow Q$$

● Thus net effect of engine X and the Carnot refrigerator working in combination is to transfer energy Q as heat from a low-temperature reservoir to a high-temperature reservoir without the requirement of work. And it is a violation of the 2nd law of thermodynamics.

● We conclude that *no real engine can have an efficiency greater than that of a Carnot engine when both engines work between the same two temperatures.*

A Statistical View of Entropy

● **Statistical mechanics:** explain the macroscopic properties of gases in terms of their microscopic behavior.



- Consider a box that contains 6 identical (thus indistinguishable) molecules of a gas.
- *Microstates:* different arrangements of the molecules.

6 Molecules in a Box

Configuration		n_1	n_2	Multiplicity W	Calculation of W	Entropy ($10^{-23} J/K$)
Label						
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
Total =				64		

- Suppose we have N molecules, distributed with n_1 molecules in one half of the box and n_2 in the other. Thus $n_1+n_2=N$.

- The total number of ways in which we can select all N molecules is $N!$. Because the molecules are indistinguishable, the order of the molecules in both halves of the box do not matter.

- Define the *multiplicity* W of a configuration as $W = \frac{N!}{n_1! n_2!}$ multiplicity of configuration

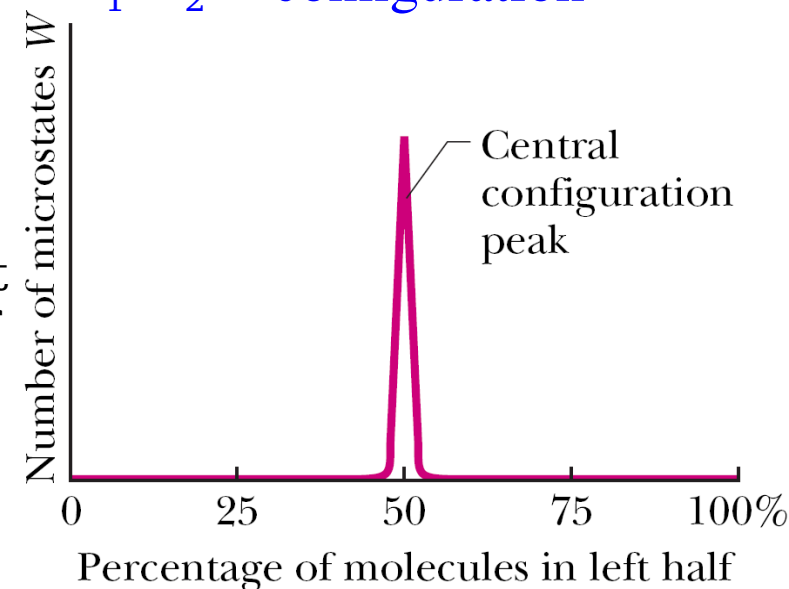
- The basic assumption of statistical mechanics is

All microstates are equally probable.

- Because all microstates are equally probable but different configurations have different numbers of microstates, the configurations are not all equally probable.

- For large values of N , nearly all the microstates belong to the configuration in which the molecules are divided equally between the 2 halves of the box.

- Therefore, we might assume that the gas molecules are always divided equally between the 2 halves of the box.



Probability and Entropy

- In 1877, Ludwig Boltzmann derived a relationship between the entropy S of a configuration of a gas and the multiplicity W of that configuration:

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

- The total entropy of 2 systems is the *sum* of their separate entropies. The probability of occurrence of 2 independent systems is the *product* of their separate probabilities:

$$W_{\text{tot}} = W_1 W_2 \Rightarrow S_{\text{tot}} = k \ln W_{\text{tot}} = k \ln (W_1 W_2) = k (\ln W_1 + \ln W_2) = S_1 + S_2$$

- For N is large, we can use the Stirling's approximation to calculate the entropy:

$$\ln N! \approx N (\ln N) - N = \ln \left(\frac{N}{e} \right)^N \quad \text{Stirling's approximation}$$

$$N! = 1 \times 2 \times \cdots \times N$$

$$\begin{aligned} \Rightarrow \ln N! &= \ln 1 + \ln 2 + \cdots + \ln N = \sum_{k=1}^N \ln k \approx \int_1^N \ln x \, dx = x \ln x - x \Big|_1^N \\ &= N \ln N - N + 1 \approx N \ln N - N \quad \text{as } N \rightarrow \infty \end{aligned}$$

problem 20-6

Selected problems: 18, 21, 24, 37