

Course announcement

- The 2nd midterm score has been posted on eLearn today. I will bring the answer sheet to class for review from Friday until 12/30. You can also review it during Monday's office hours. If you have any questions about the score, please contact me.
- The 5th homework set has been posted. And it will be due on (1/3), 5pm.
- The review section 3 on 1/6 will be a pre-recorded section. It will be uploaded on eLearn.

16	12/30(Fri.)	Entropy and the Second Law of Thermal Dynamics: entropy
17	1/3(Tue.)	Entropy and the Second Law of Thermal Dynamics: engines and refrigerator
17	1/6(Fri.)	Review III
18	1/10(Tue.)	Final Exam

GENERAL PHYSICS B1

THE SECOND LAW OF

THERMODYNAMICS

2022/12/30

Entropy

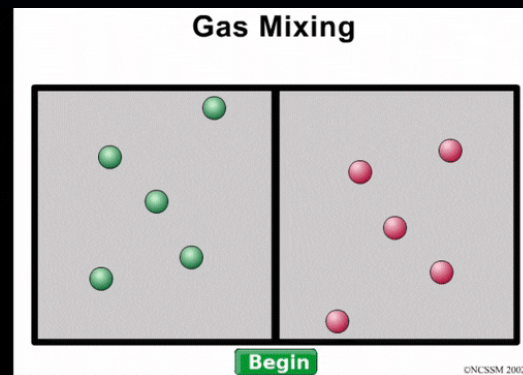
Topic Today

Entropy and the second law of thermodynamics

- **Irreversible Process and Entropy**
- The second law of thermodynamics
- Heat Engine and Refrigerator

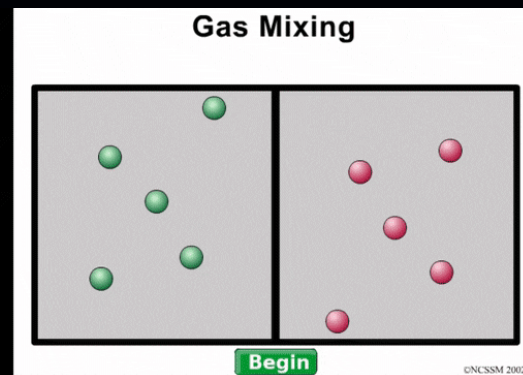
Irreversible process

- We just learned various process of gases. Most of these processes that we learned are reversible process, namely, these process can happen in both directions.
- However, there are many thermodynamics processes are irreversible, which means the process can go with one directions:



Irreversible process

- The one-way character of irreversible processes is so pervasive that we take it for granted. If these processes were to occur spontaneously (on their own) in the wrong way, we would be astonished. Yet none of these wrong-way events would violate the law of conservation of energy.



Entropy Postulate

- In these irreversible processes, physicists found one physical quantity, **entropy**, is always increasing during these irreversible processes.

Entropy postulate:

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

Definition of Entropy

- Entropy is a state property just like pressure and volume that describing the status of a system at a certain state.
- Since we know the change in entropy can tell the direction of a process, we start the definition with changing in entropy:

Change in entropy $S_f - S_i$ of a system during a process that takes the system from an initial state i to a final state f as

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

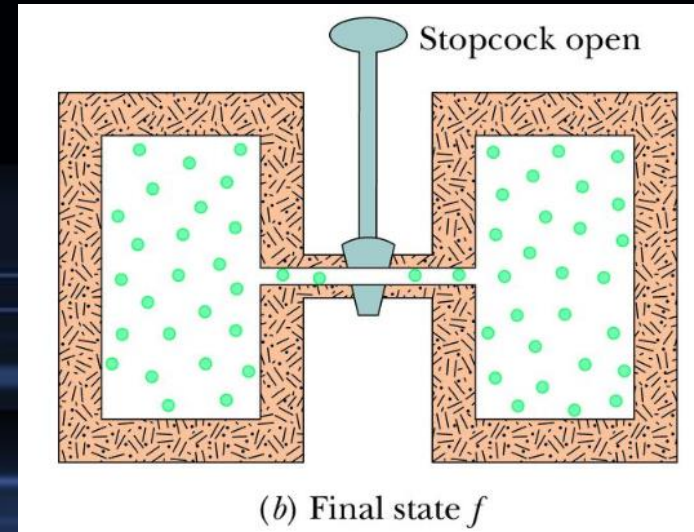
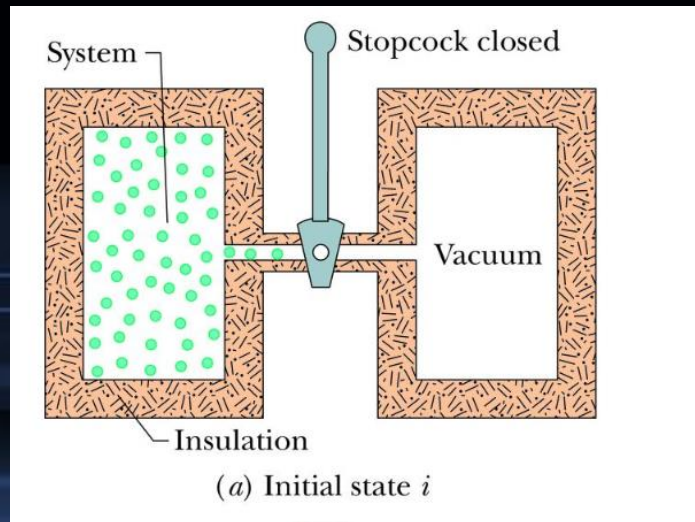
Definition of Entropy

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

Here Q is the energy transferred as heat to or from the system during the process, and T is the temperature of the system in kelvins. Thus, 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.

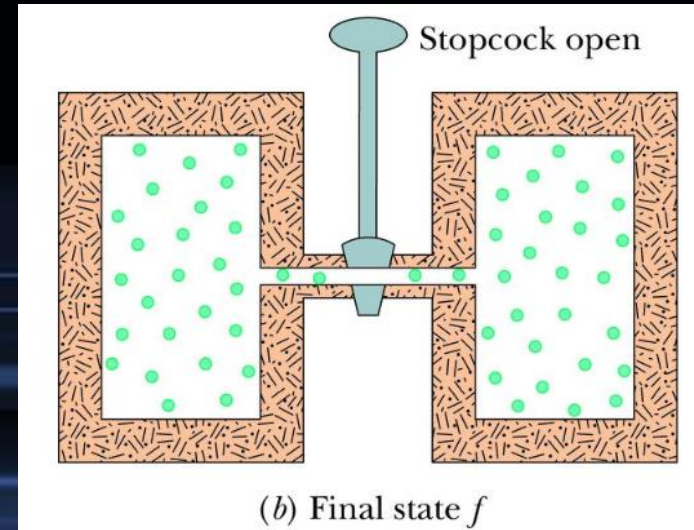
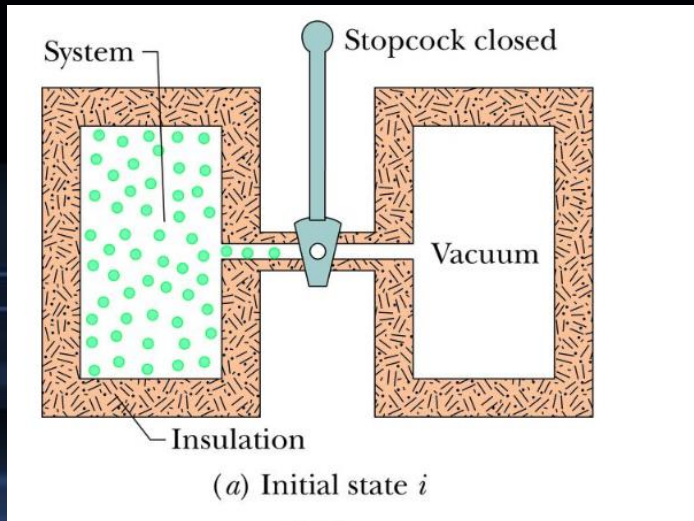
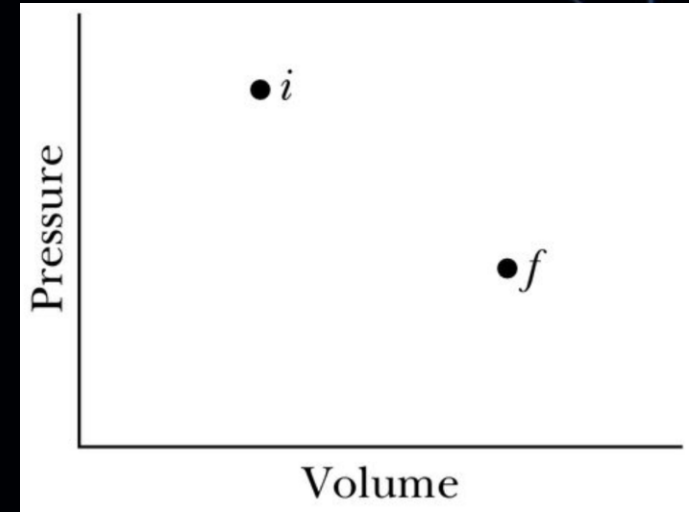
Finding entropy in a process

- Consider a gas free expansion (irreversible): the gas in its initial equilibrium state i , confined by a closed stopcock to the left half of a thermally insulated container. If we open the stopcock, the gas rushes to fill the entire container, eventually reaching the final equilibrium state f .



Finding entropy in a process

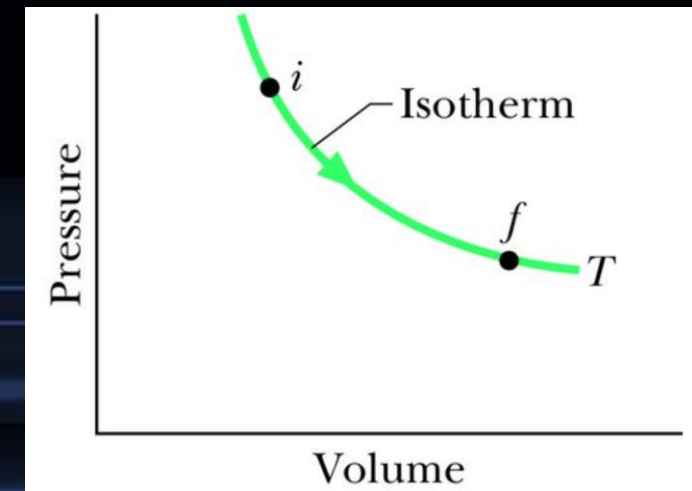
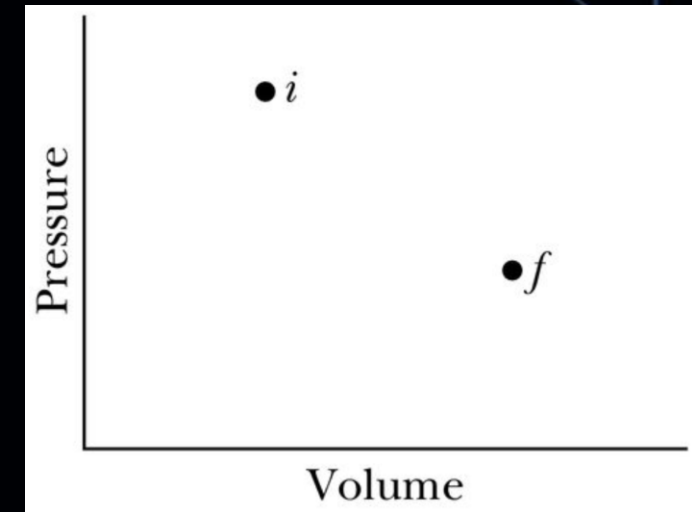
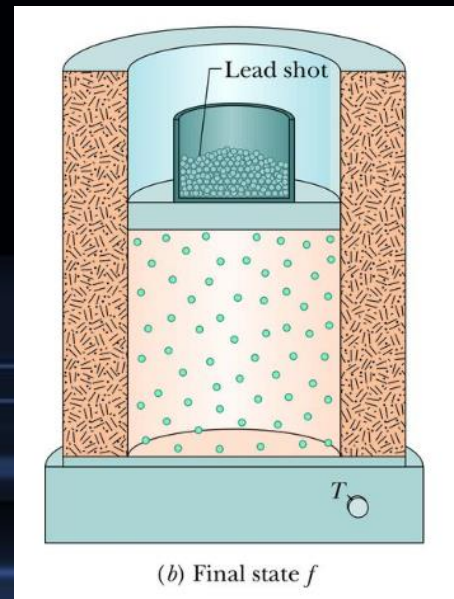
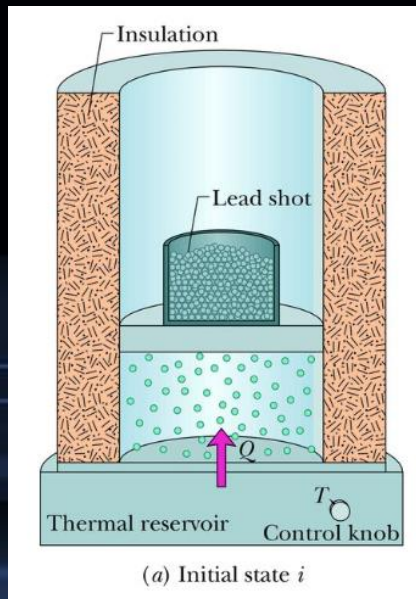
- During this free expansion process, the states are not in equilibrium. The P-V plot looks like:
Cannot find ΔS directly.



Finding entropy in a process

- Since S is a state function, we can find a reversible process to link i to f and find ΔS .

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

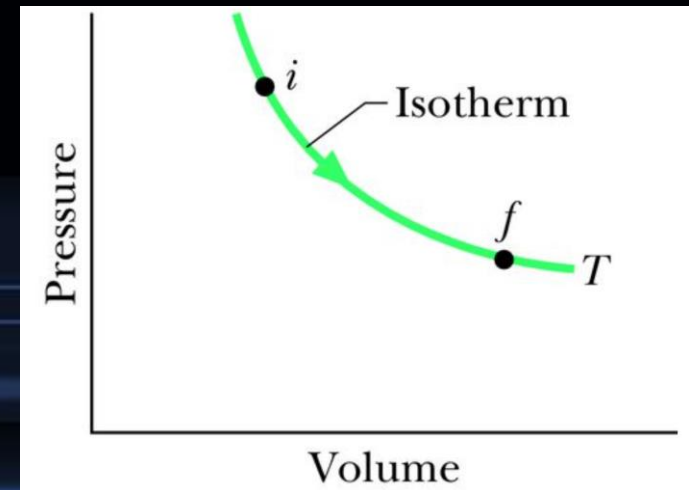
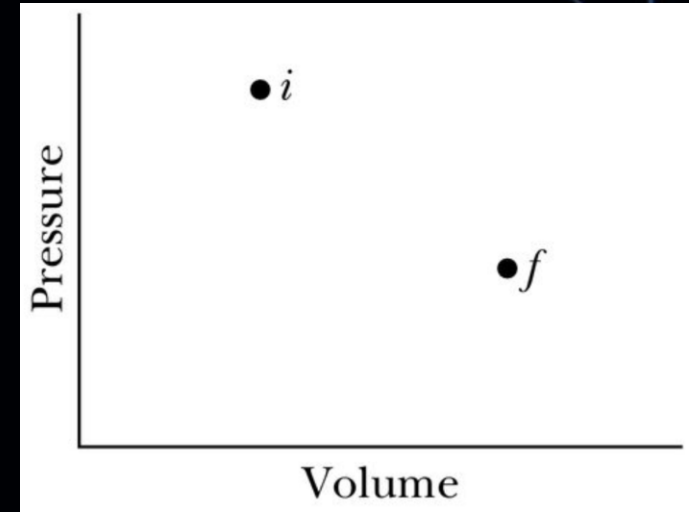


Finding entropy in a process

- In this case, we use an isotherm process to find out change of entropy from state i to f :

$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process})$$

- To keep the temperature T of the gas constant during the isothermal expansion, heat Q must have been energy transferred from the reservoir to the gas. Thus, Q is positive and the entropy of the gas increases during the isothermal process and during the free expansion.



Finding entropy in a process

- To find the entropy change for an irreversible process, replace that process with any reversible process that connects the same initial and final states. Calculate the entropy change for this reversible process with

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

- When the temperature change ΔT of a system is small relative to the temperature (in kelvins) before and after the process, the entropy change can be approximated as

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

Entropy as a State Function

- Entropy is indeed a state function (as state properties are usually called) can be deduced only by experiment. However, we can prove it is a state function for the special and important case in which an ideal gas is taken through a reversible process.
- For ideal gas, we start with 1st law of thermodynamics:

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

And we have

$$dQ = pdV + nC_V dT$$

Entropy as a State Function

- Using the ideal gas law, we replace p in this equation with nRT/V . Then we divide each term in the resulting equation by T :

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

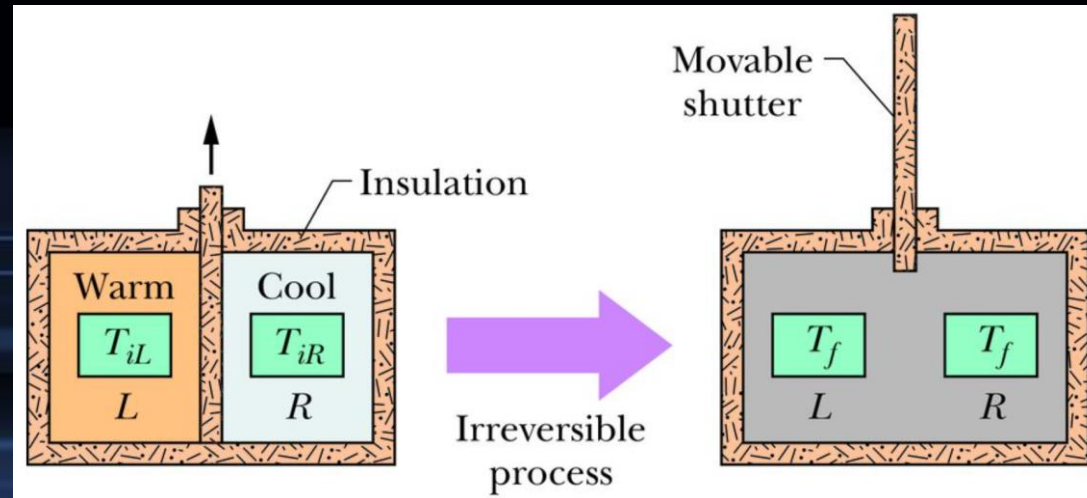
$$\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_V \frac{dT}{T}$$

- We can conclude (all quantities are state functions):

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

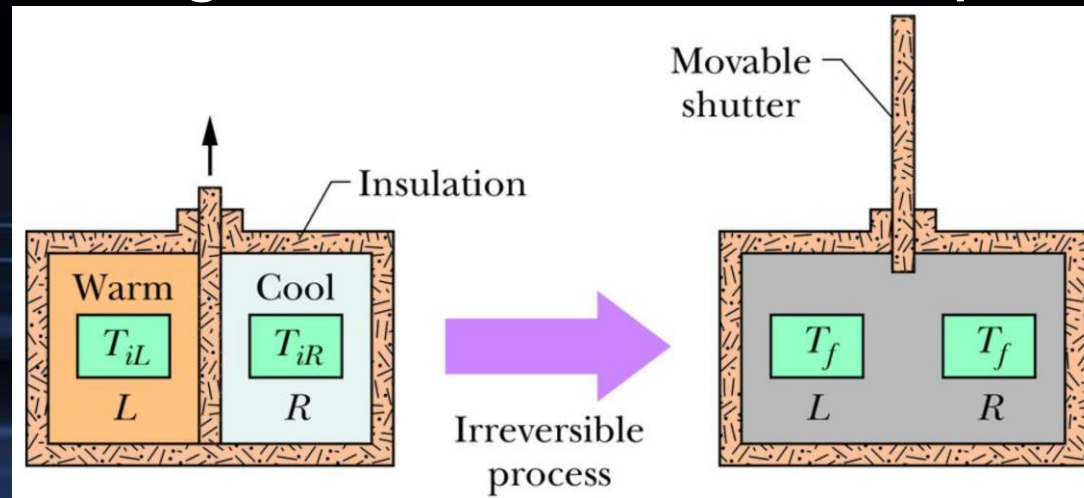
Example: Entropy change of two blocks coming to thermal equilibrium

Two identical copper blocks of mass $m = 1.5 \text{ kg}$: block L at temperature $T_{iL} = 60^\circ\text{C}$ and block R at temperature $T_{iR} = 20^\circ\text{C}$. 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 $T_f = 40^\circ\text{C}$. What is the net entropy change of the two-block system during this irreversible process? The specific heat of copper is $386 \text{ J/kg}\cdot\text{K}$.



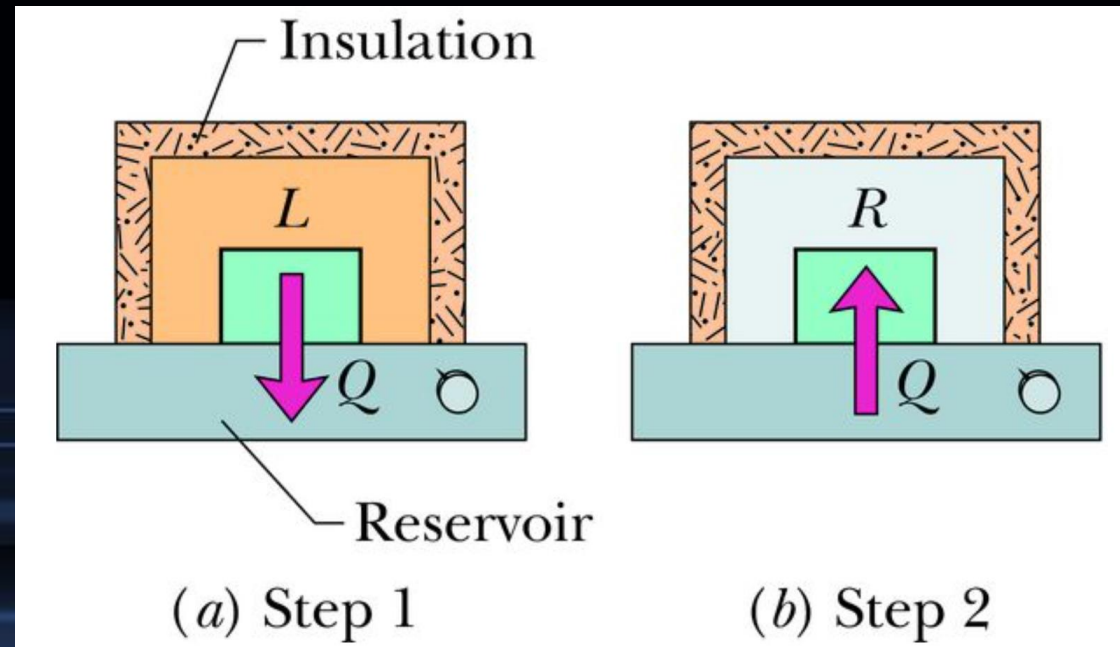
Entropy change of two blocks coming to thermal equilibrium

- Key: To calculate the entropy change, we must find a reversible process that takes the system from the initial state to the final state. We can calculate the net entropy change ΔS_{rev} of the reversible process using, and then the entropy change for the irreversible process is equal to ΔS_{rev} .



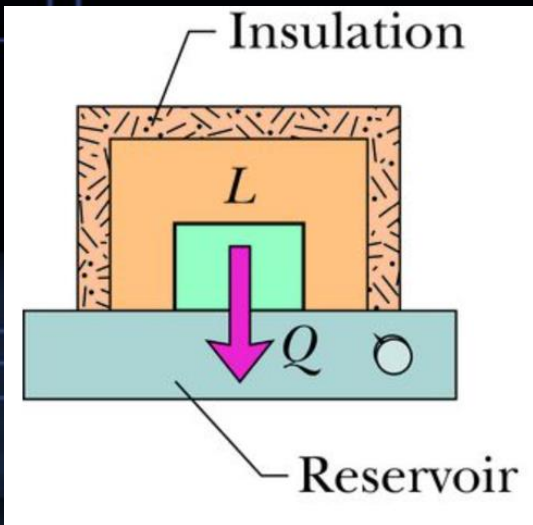
Entropy change of two blocks coming to thermal equilibrium

For the reversible process, we need a thermal reservoir whose temperature can be changed slowly (say, by turning a knob).



Entropy change of two blocks coming to thermal equilibrium

The entropy change ΔS_L of block L during the full temperature change from initial temperature T_{iL} ($= 60^\circ\text{C} = 333\text{ K}$) to final temperature T_f ($= 40^\circ\text{C} = 313\text{ K}$) is

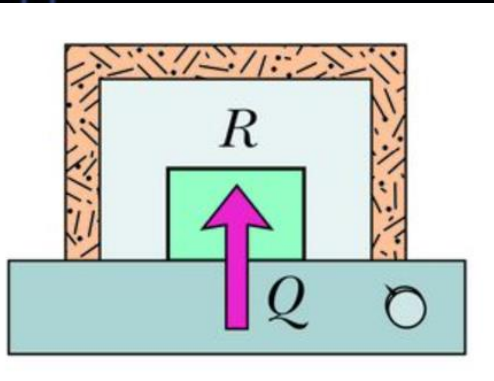


$$\begin{aligned}\Delta S_L &= \int_i^f \frac{dQ}{T} = \int_{T_{iL}}^{T_f} \frac{mc dT}{T} = mc \int_{T_{iL}}^{T_f} \frac{dT}{T} \\ &= mc \ln \frac{T_f}{T_{iL}}.\end{aligned}$$

$$\begin{aligned}\Delta S_L &= (1.5\text{ kg})(386\text{ J/kg}\cdot\text{K}) \ln \frac{313\text{ K}}{333\text{ K}} \\ &= -35.86\text{ J/K}.\end{aligned}$$

Entropy change of two blocks coming to thermal equilibrium

With the same reasoning used to find ΔS_L , you can show that the entropy change ΔS_R of block R during this process is



$$\begin{aligned}\Delta S_R &= (1.5 \text{ kg}) (386 \text{ J/kg} \cdot \text{K}) \ln \frac{313 \text{ K}}{293 \text{ K}} \\ &= +38.23 \text{ J/K}.\end{aligned}$$

Entropy change of two blocks coming to thermal equilibrium

- The net entropy change ΔS_{rev} of the two-block system undergoing this two-step reversible process is then

$$\begin{aligned}\Delta S_{\text{rev}} &= \Delta S_L + \Delta S_R \\ &= -35.86 \text{ J/K} + 38.23 \text{ J/K} = 2.4 \text{ J/K}.\end{aligned}$$

Thus, the net entropy change ΔS_{irrev} for the two-block system undergoing the actual irreversible process is

$$\Delta S_{\text{irrev}} = \Delta S_{\text{rev}} = 2.4 \text{ J/K. (Answer)}$$

This result is positive, in accordance with the entropy postulate.

Topic Today

Kinetic Theory of Gases:

- Adiabatic expansion

Entropy and the second law of thermodynamics

- Irreversible Process and Entropy
- **The second law of thermodynamics**
- Heat Engine and Refrigerator
- A Statistical View of Entropy

The 2nd 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.

$$\Delta S \geq 0 \quad (\text{second law of thermodynamics})$$

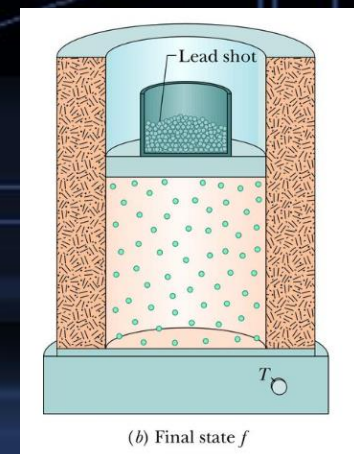
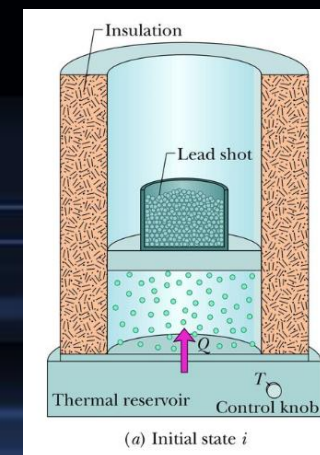
Discussion about close system

Back to example of gas undergoing a reversible expansion in previous example. The calculated gas has a positive change in entropy. Why this process is reversible? **Because the gas is not a close system**, the gas interact with heat reservoir. We can also find that:

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

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

Thus the total change in entropy is 0.



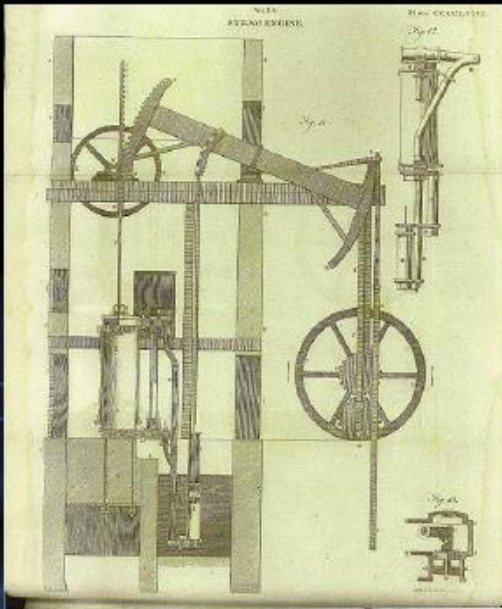
Topic Today

Entropy and the second law of thermodynamics

- Irreversible Process and Entropy
- The second law of thermodynamics
- **Heat Engine and Refrigerator**

Heat Engine

- A heat engine, or more simply, an engine, is a device that extracts energy from its environment in the form of heat and does useful work.
- The invention and improvement of steam engine start the Industrial Revolution.



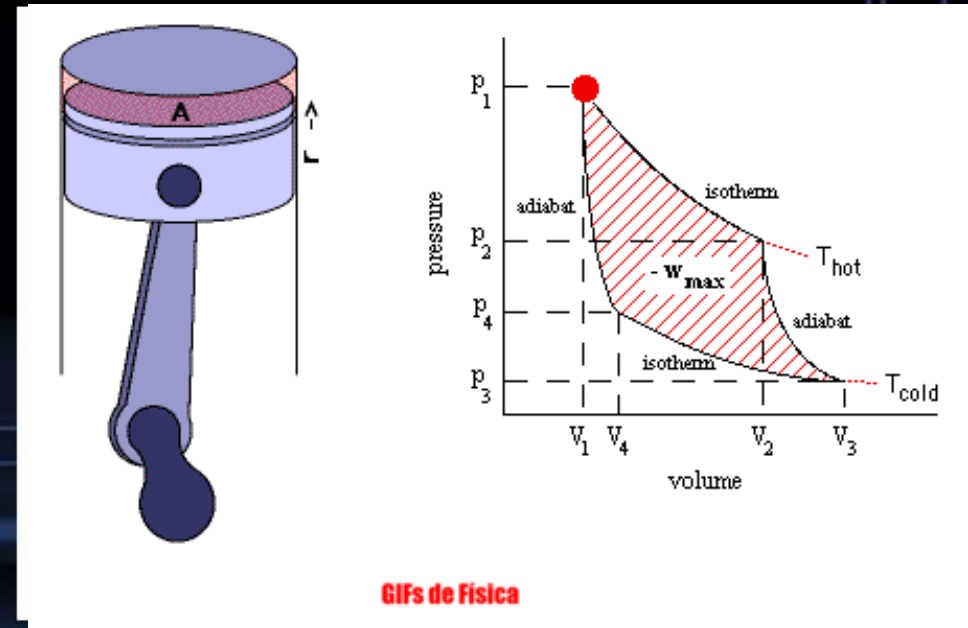
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https://en.wikipedia.org/wiki/Engine#/media/File:Mercedes_V6_DTM_Rennmotor_1996.jpg

Cycle in Heat Engine

- At the heart of every engine is a working **substance**. In a steam engine, the working substance is water, in both its vapor and its liquid form. In an automobile engine the working substance is a gasoline–air mixture.
- The working substance must operate in a **cycle**; that is, the working substance must pass through a closed series of thermodynamic processes (strokes).



Question

- How much work can we get from each cycle?
- What is the efficiency of an engine? Can we maximize it?

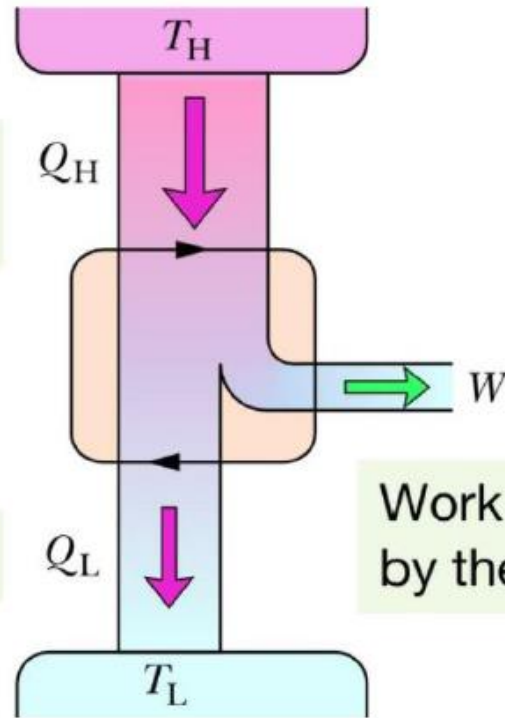
Ideal Engine and Carnot Engine

- Let's use ideal gas as working substance (obeys the simple law $pV = nRT$).
- In an ideal engine, all processes are **reversible** and **no wasteful energy** transfers occur due to friction and turbulence.
- French scientist and engineer N. L. Sadi Carnot who first proposed the engine's concept in 1824. He was able to analyze the performance of this engine before the first law of thermodynamics and the concept of entropy had been discovered.

Scheme of Carnot Engine

Schematic of
a Carnot engine

Heat is
absorbed.

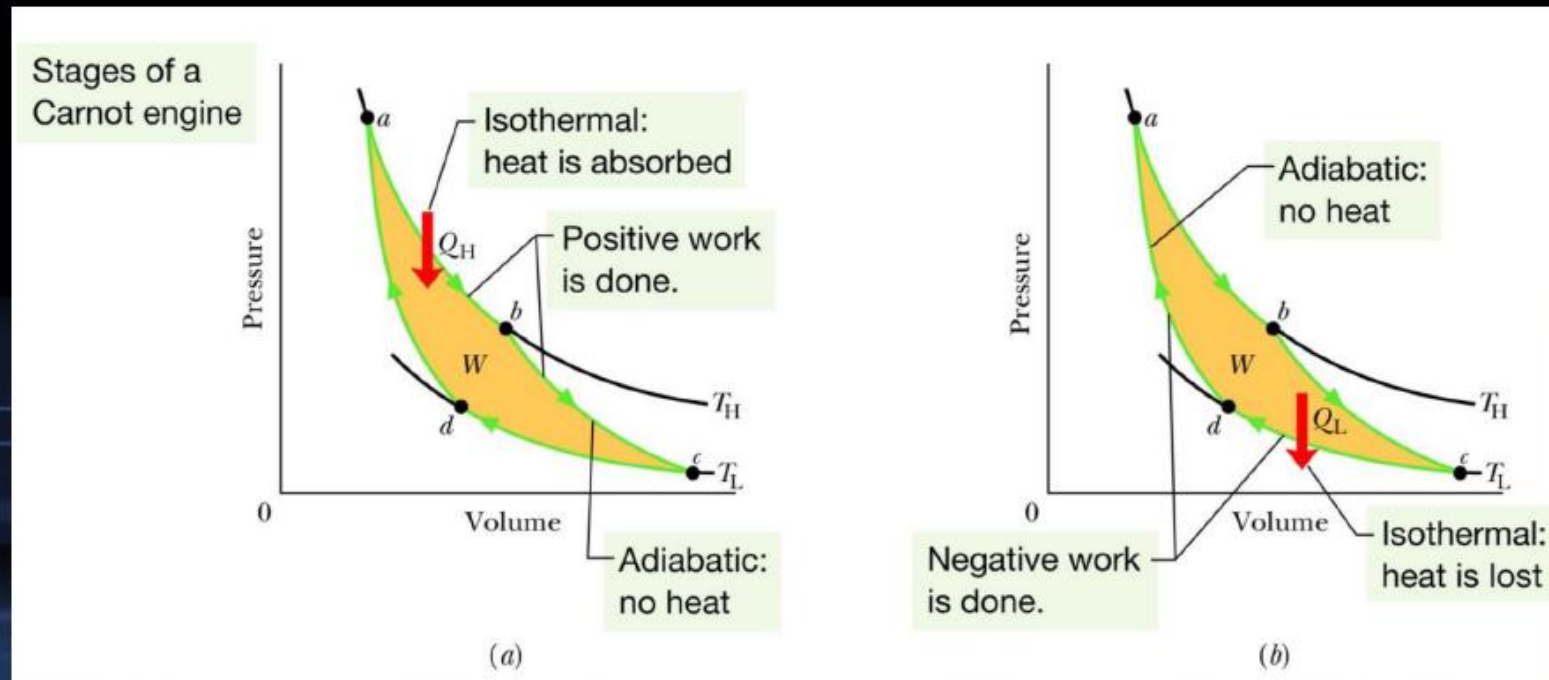


Heat is lost.

Work is done
by the engine.

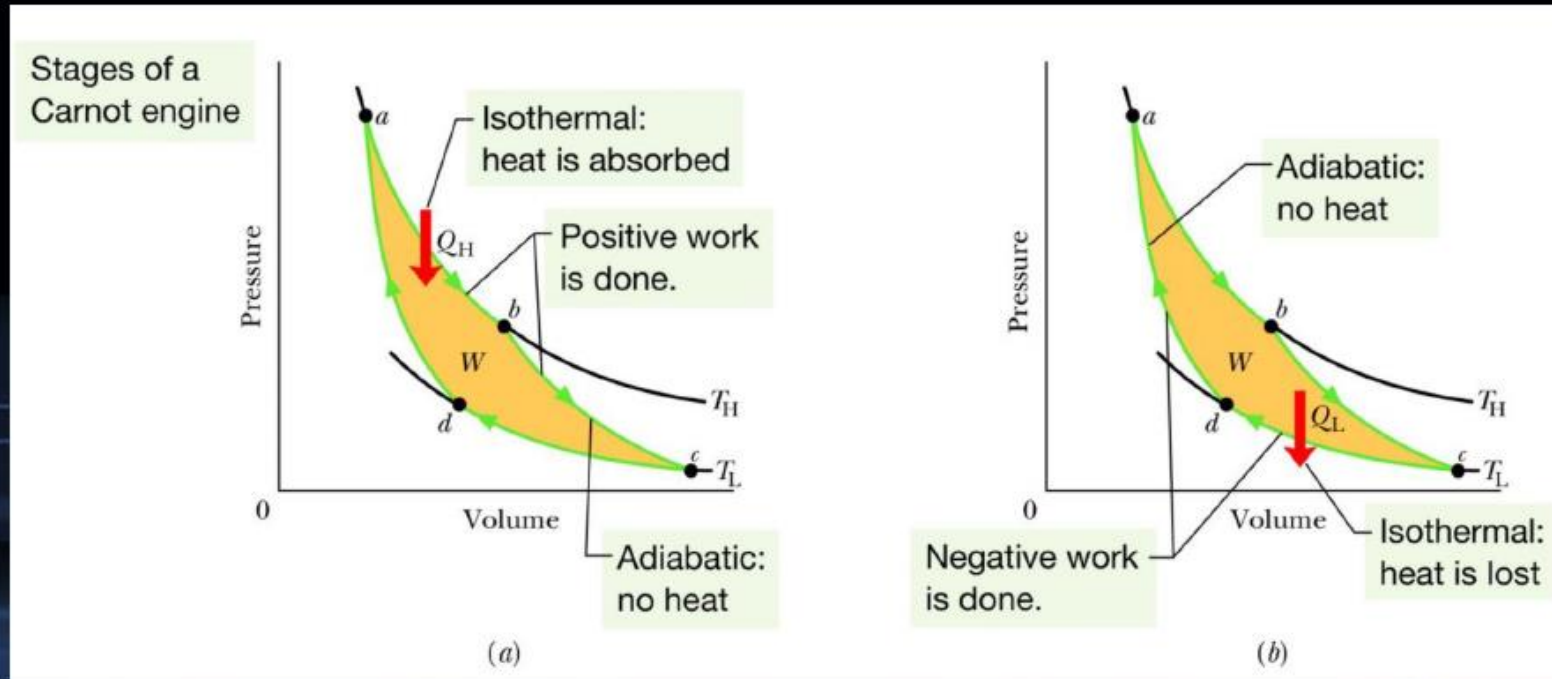
Carnot Cycle

Carnot cycle is how a working substance cycling in a Carnot engine. It contain four steps: Isothermal expansion(ab), adiabatic expansion(bc), isothermal compression(cd), and adiabatic compression(da).



Analysis of Carnot Cycle

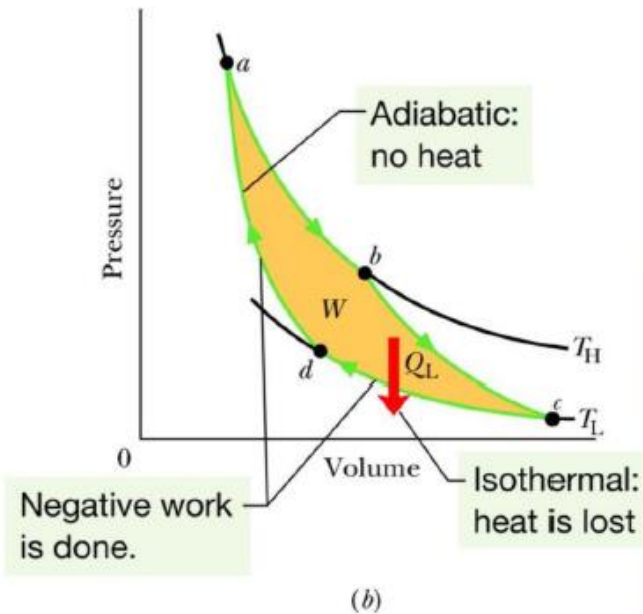
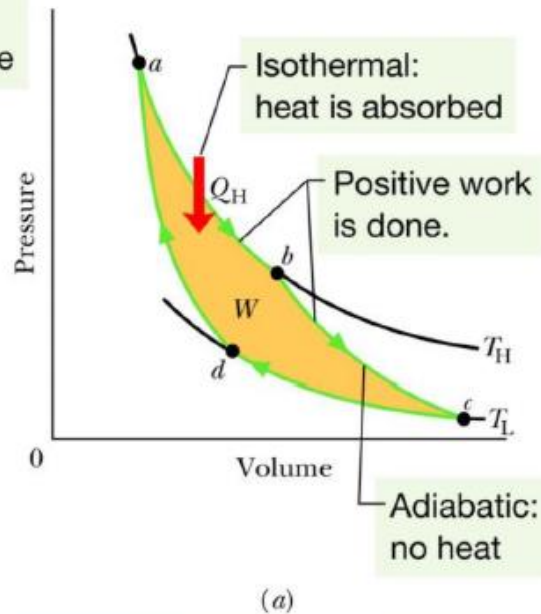
- ab: No change in E_{int} . Absorb heat Q_H . Do positive work.
- bc: Decrease in E_{int} . No heat exchange. Do positive work.
- cd: No change in E_{int} . release heat Q_L . Do negative work.
- da: Increase in E_{int} . No heat exchange. Do negative work.



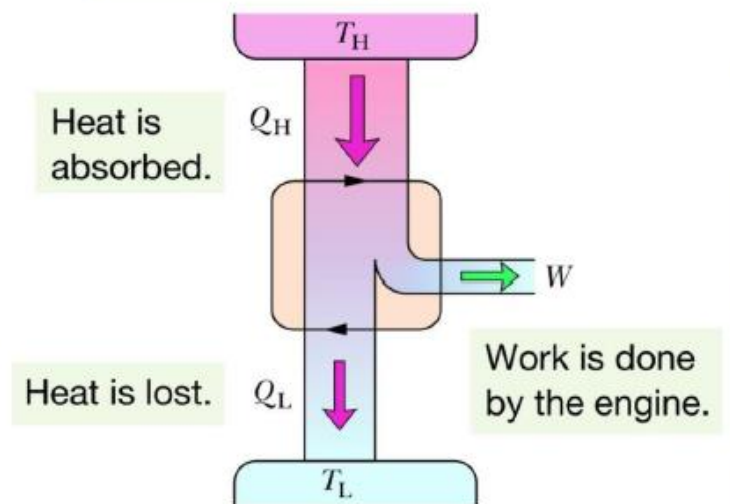
Summing up of Carnot Cycle

- With above analysis, we can see that after one cycle:
Work done W : the colored area in the p - V plot
 $\Delta E_{int} = 0$, since it goes back to a state.
Total heat absorbed: $Q_H - Q_L$.
With 1st law of thermodynamics: $W = Q_H - Q_L$

Stages of a Carnot engine



Schematic of a Carnot engine



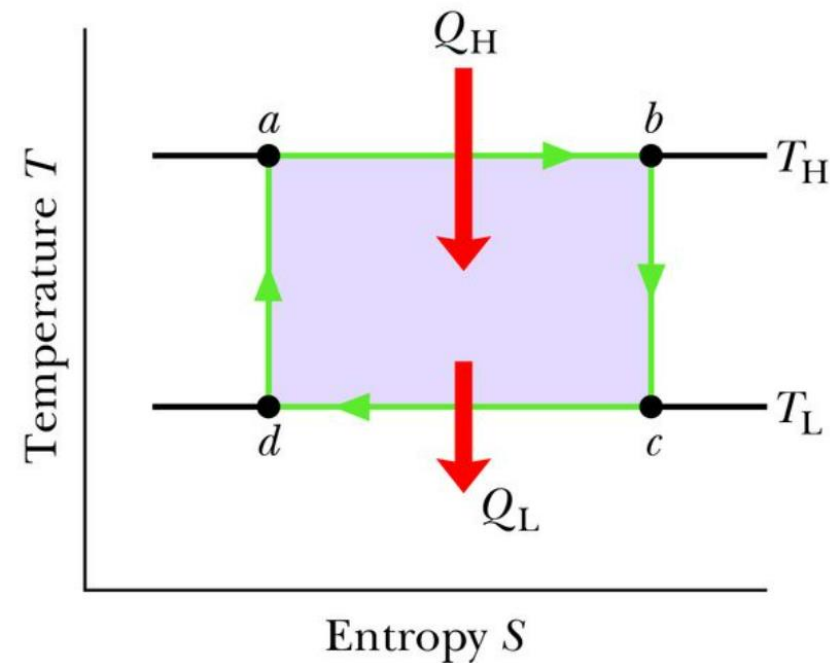
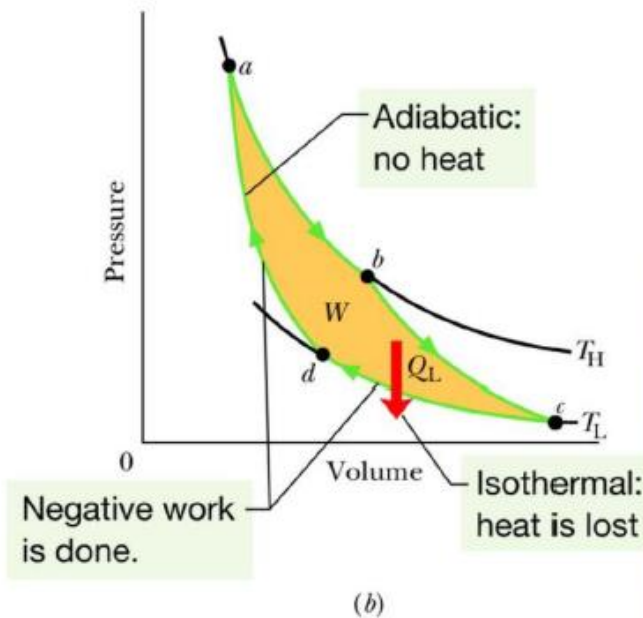
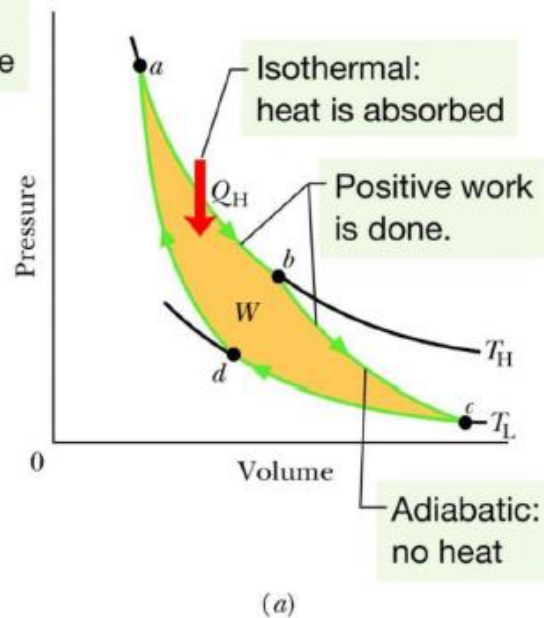
Entropy change in a Carnot Cycle

- The change of entropy:

$$ab: +\frac{Q_H}{T_H}, \quad bc: 0, \quad cd: -\frac{Q_L}{T_L}, \quad da: 0,$$

$$\text{Total entropy change: } \Delta S_{\text{cycle}} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

Stages of a Carnot engine



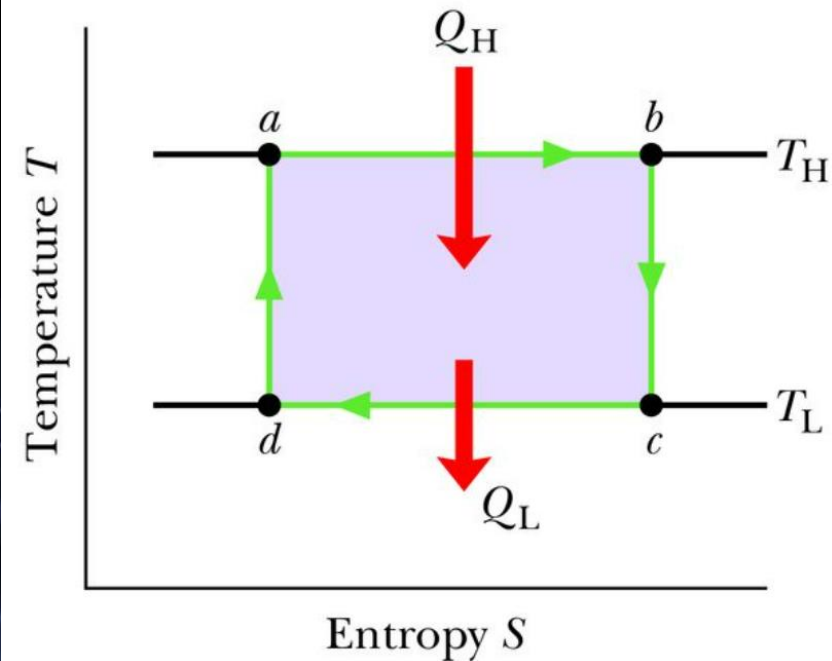
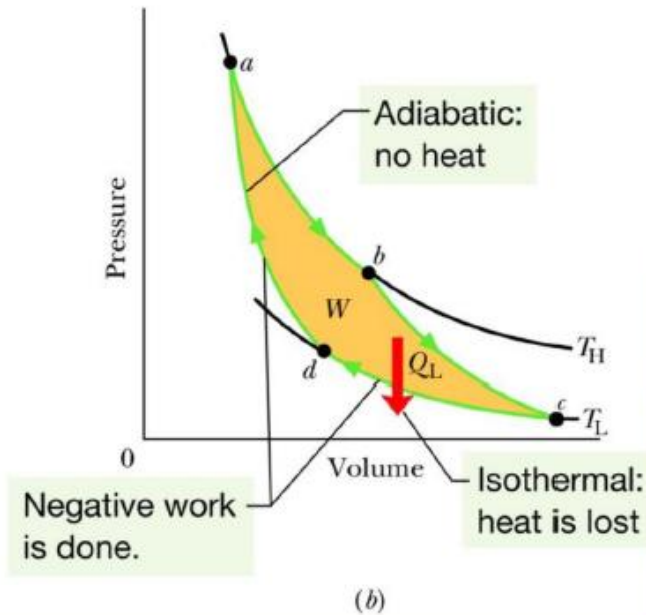
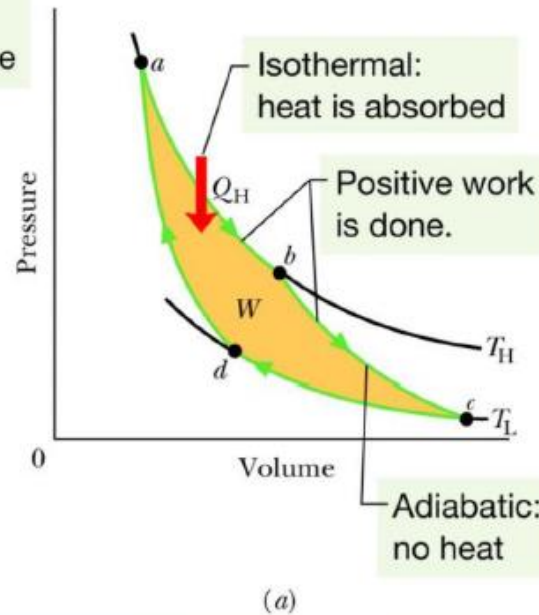
Entropy change in a Carnot Cycle

Total entropy change: $\Delta S_{cycle} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$

Since entropy is a state function and we go back to a ($\Delta S_{cycle} = 0$):

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

Stages of a Carnot engine



Efficiency of a heat engine

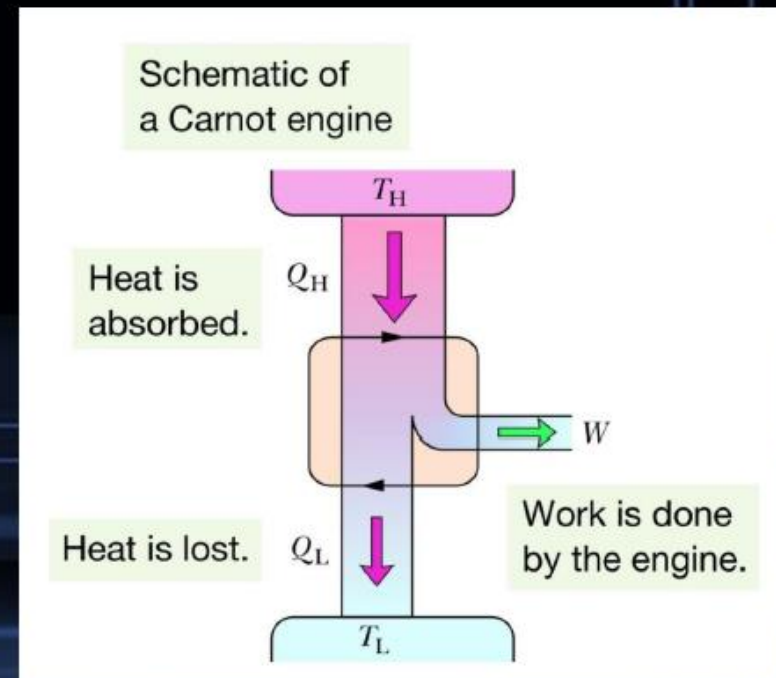
- Let's consider what is efficiency of a heat engine:

We measure its success in doing so by its thermal efficiency ϵ

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

In a cycle:

$$\epsilon = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$



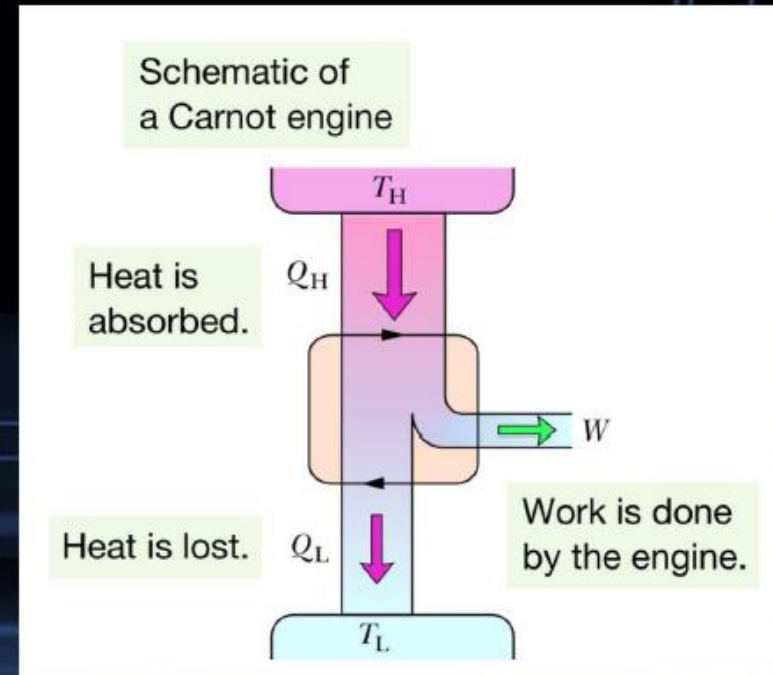
Efficiency of a heat engine

In a Carnot cycle:

$$\varepsilon_C = 1 - \frac{T_L}{T_H} \quad (\text{efficiency, Carnot engine})$$

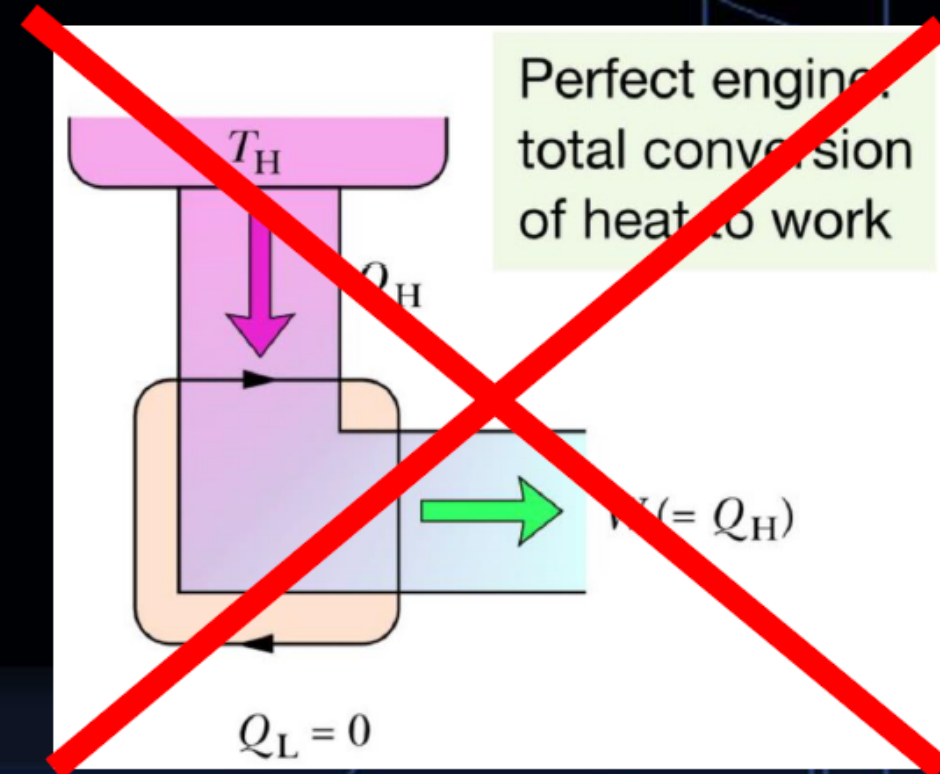
where the temperatures T_L and T_H are in kelvins. Therefore, the efficiency is decided by the thermal reservoirs' temperatures.

Because $T_L < T_H$, the Carnot engine necessarily has a thermal efficiency less than unity—that is, less than 100%.



No perfect engine

- The inventor's dream is to produce the perfect engine, as the figure, in which is reduced to zero and is converted completely into work.
- A perfect engine is only a dream: we can achieve 100% engine efficiency (that is, $\varepsilon = 1$) only if $T_L = 0$ or $T_H \rightarrow \infty$, which is an impossible requirements.
- 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.



The 2nd law of thermodynamics (Kelvin-Planck Statement)

It is impossible to construct a heat engine operating in a cycle that extracts heat from a reservoir and delivers an equal amount of work