

Heat Engines, Entropy and the Second Law of Thermodynamics

Physics Enhancement Programme

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Review: First Law

- First law: Conservation of Energy.
- Change in internal energy in a system can occur as a result of energy transfer by heat and/or by work.
- Makes no distinction between processes that occur spontaneously and those that do not.

Examples of Irreversible Process 1

- When two objects at different temperatures are placed in thermal contact with each other, the net transfer of energy by heat is always from the hotter object to the cooler object, never from the cooler to the hotter.
- Can liquid water lose its internal energy to become ice?



Examples of Irreversible Process 2

- A rubber ball dropped to the ground bounces several times and eventually comes to rest, but a ball lying on the ground never gathers internal energy from the ground and begins bouncing on its own.
- Can a stationary ball gain the kinetic energy of air molecule random motion to bounce?

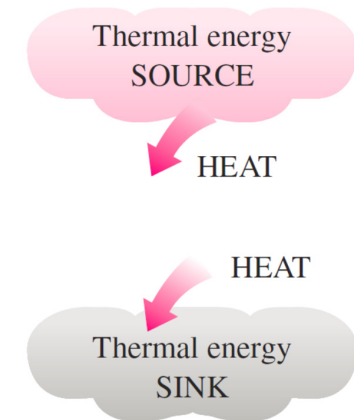


Examples of Irreversible Process 3

- An oscillating pendulum eventually comes to rest because of collisions with air molecules and friction at the point of suspension. The mechanical energy of the system is converted to internal energy in the air, the pendulum, and the suspension.
- All these reverse conversion of energy never occurs.

Thermal Energy Reservoir, Source, and Sink

- Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.
- A source supplies energy in the form of heat, and a sink absorbs it.



The Second Law of Thermodynamics

- Establishes which processes do and which do not occur.
- Some processes can occur in either direction according to the first law.
- They are observed to occur only in one direction.
- This directionality is governed by the second law.

Heat Engine

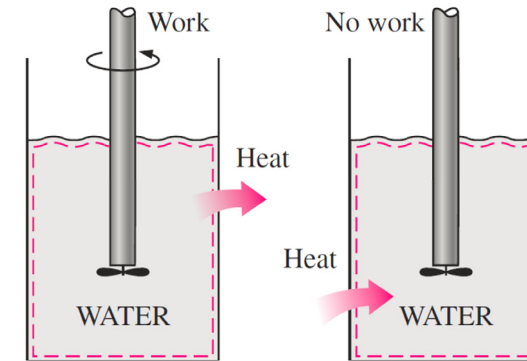
- Irreversible process: occurs naturally in one direction only.
- An important engineering implication is the limited efficiency of heat engines.
- A heat engine is a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work.
- A heat engine carries some working substance through a cyclical process.

Heat Engine

- Heat engines may differ considerably from one another, but all can be characterized by:
 - They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc).
 - They convert part of this heat to work (usually in the form of a rotating shaft).
 - They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc).
 - They operate on a cycle.
- Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle. This fluid is called the working fluid.

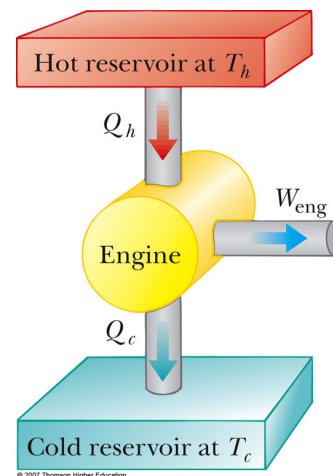
Heat Engine

Work can always be converted to heat directly, and partially or completely, but the reverse is not true.



Heat Engine

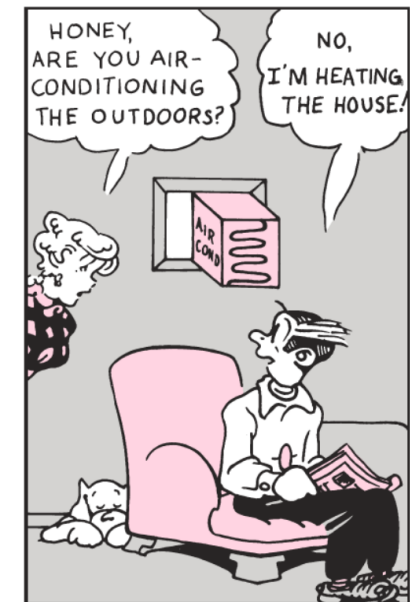
- The working substance absorbs energy by heat from a high temperature energy reservoir (Q_h).
- Work is done by the engine (W_{eng}).
- Energy is expelled as heat to a lower temperature reservoir (Q_c).



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Heat Engine

When installed backward, an air conditioner functions as a heat pump.



Heat Engine

- Since it is a cyclical process, $\Delta E_{\text{int}} = 0$.
 - Its initial and final internal energies are the same.
- Therefore, $Q_{\text{net}} = W_{\text{eng}}$.
- The work done by the engine equals the net energy absorbed by the engine.

Thermal Efficiency of a Heat Engine

- Thermal Efficiency:

$$\eta = \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

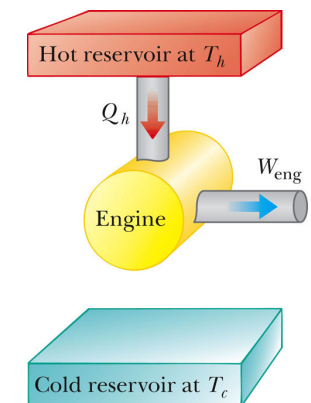
Second Law: Kelvin-Planck Form

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work.

- W_{eng} can never be equal to Q_c .
- Q_c cannot equal 0.
 - Some Q_c must be expelled to the environment.
- Thermal efficiency (η) cannot equal 100%.

Perfect Heat Engine

- No energy is expelled to the cold reservoir.
- It takes in some amount of energy and does an equal amount of work.
- $\eta = 100\%$.
- It is impossible to construct such an engine.



The impossible engine
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Quick Quiz

The energy input to an engine is 3 times greater than the work it performs.

I. What is its thermal efficiency?

- (A) 3.00
- (B) 1.00
- (C) 0.333

II. What fraction of the energy input is expelled to the cold reservoir?

- (A) 0.333
- (B) 0.667
- (C) 1.00

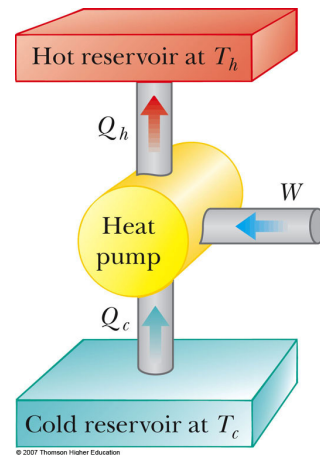
Answers:

Heat Pumps and Refrigerators

- Heat engines can run in reverse.
 - This is not a natural direction of energy transfer.
 - Must put some energy into a device to do this.
 - Devices that do this are called heat pumps or refrigerators.
- Examples
 - A refrigerator is a common type of heat pump.
 - An air conditioner is another example of a heat pump.

Heat Pump Process

- Energy is extracted from the cold reservoir (Q_c).
- Energy is transferred to the hot reservoir (Q_h).
- Work must be done *on* the engine (W).



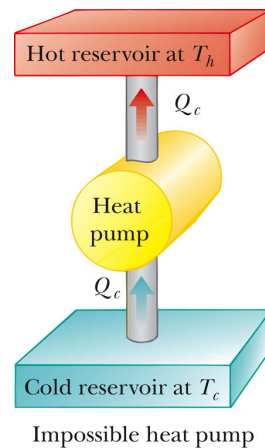
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Second Law – Clausius Form

- It is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from one object to another object at a higher temperature without the input of energy by work.
- Or – energy does not transfer spontaneously by heat from a cold object to a hot object.

Perfect Heat Pump

- Takes energy from the cold reservoir.
- Expels an equal amount of energy to the hot reservoir.
- No work is done.
- This is an impossible heat pump.



Coefficient of Performance

- Coefficient of Performance (COP): The effectiveness of a heat pump.
- In heating mode, COP is the ratio of the heat transferred in to the work required:

$$\text{COP} = \frac{\text{Energy Transferred}}{\text{Work Done by Heat Pump}} = \frac{|Q_h|}{W}$$

- Q_h is typically higher than W .
 - Values of COP are generally greater than 1.
 - It is possible for them to be less than 1.

Coefficient of Performance

- In cooling mode, energy removed from a cold temperature reservoir:

$$\text{COP} = \frac{|Q_c|}{W}$$

- A good refrigerator should have a high COP.
 - Typical values are 5 or 6.

Reversible and Irreversible Processes

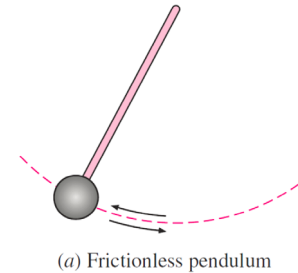
- A reversible process is one in which every point along some path is an equilibrium state.
 - And one for which the system can be returned to its initial state along the same path.
- An irreversible process does not meet these requirements
 - All natural processes are known to be irreversible.
 - Reversible processes are an idealization, but some real processes are good approximations.

Reversible and Irreversible Processes

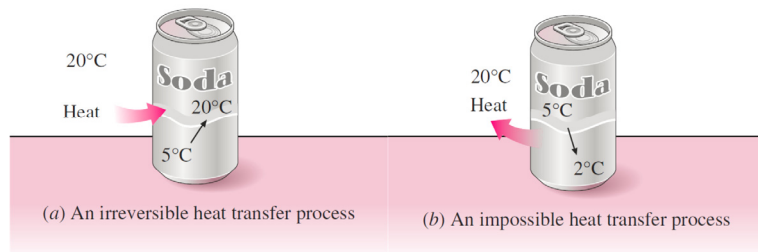
- A real process that is a good approximation of a reversible one will occur very slowly.
 - The system is always very nearly in an equilibrium state.
- A general characteristic of a reversible process is that there are no dissipative effects that convert mechanical energy to internal energy present.
 - Examples: No friction or turbulence.

Reversible and Irreversible Processes

- The reversible process is an idealization.
- All real processes on Earth are irreversible, but we can take approximation.
- Two familiar reversible processes:



Irreversible and Impossible Heat Transfer Process



- (a) Heat transfer through a temperature difference is irreversible.
 (b) The reverse process is impossible.

Sadi Carnot

- 1796 – 1832.
- French engineer.
- First to show quantitative relationship between work and heat.
- Published *Reflections on the Motive Power of Heat*.

Available at:



<https://www3.nd.edu/~powers/ame.20231/carnot1897.pdf>



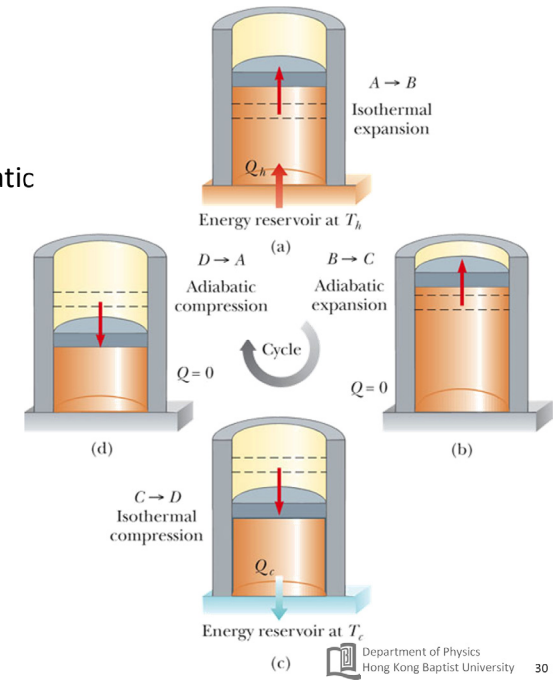
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Carnot Engine

- A theoretical engine developed by Sadi Carnot.
- A heat engine operating in an ideal, reversible cycle between two reservoirs is the most efficient engine possible.
 - This sets an upper limit on the efficiencies of all other engines .
- No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine.
 - All real engines are less efficient than a Carnot engine because they do not operate through a reversible cycle
 - The efficiency of a real engine is further reduced by friction, energy losses through conduction, etc.

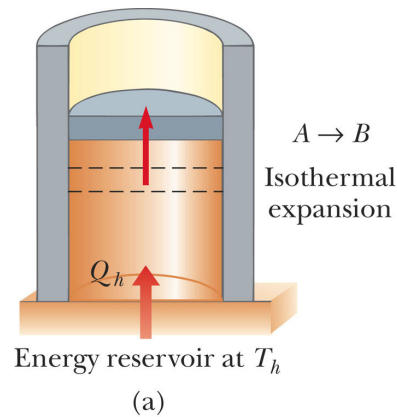
Carnot Cycle

- Two reversible adiabatic processes;
- Two reversible isothermal processes.



Carnot Cycle, Process A → B

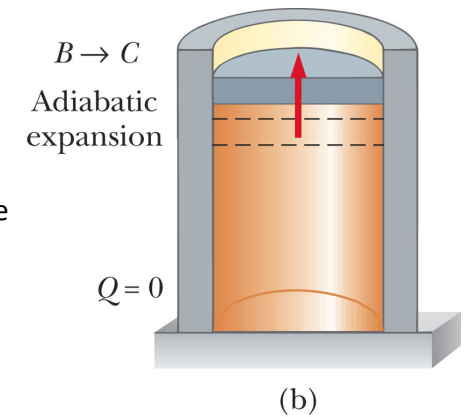
- $A \rightarrow B$ is an isothermal expansion.
- The gas is placed in contact with the high temperature reservoir (T_h).
- The gas absorbs heat $|Q_h|$ from the reservoir.
- The gas does work W_{AB} in raising the piston.



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Carnot Cycle, Process B → C

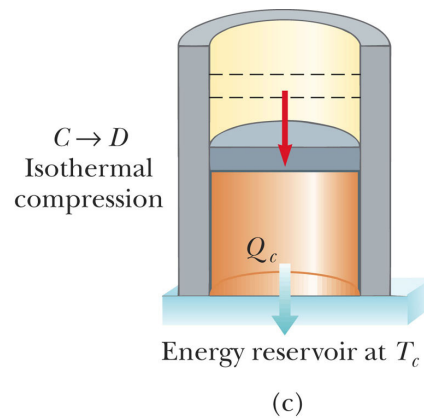
- $B \rightarrow C$ is an adiabatic expansion.
- The base of the cylinder is replaced by a thermally nonconducting wall.
- No heat enters or leaves the system.
- The temperature falls from T_h to T_c .
- The gas does work W_{BC} .



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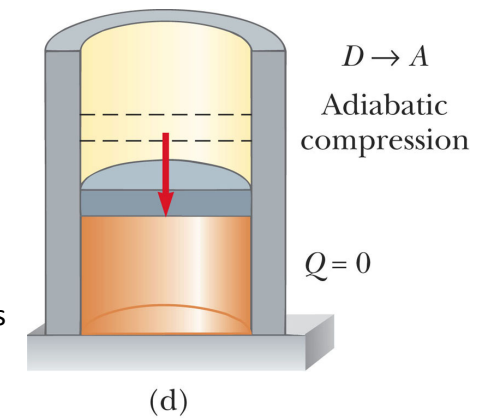
Carnot Cycle, Process C → D

- $C \rightarrow D$ is an isothermal compression.
- The gas is placed in contact with the cold temperature reservoir.
- The gas expels energy Q_c .
- Work W_{CD} is done on the gas.



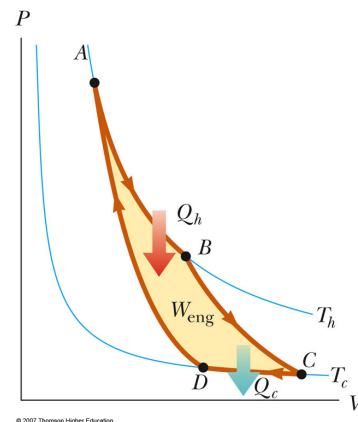
Carnot Cycle, Process D → A

- $D \rightarrow A$ is an adiabatic compression.
- The gas is placed against a thermally nonconducting wall.
- No heat is exchanged with the surroundings.
- The temperature of the gas increases from T_c to T_h .
- The work done on the gas is W_{DA} .



Carnot Cycle, PV Diagram

- The work done = the area enclosed by the curve, W_{eng} .
- The net work = $|Q_h| - |Q_c|$.
- For the entire cycle, $\Delta E_{\text{int}} = 0$.

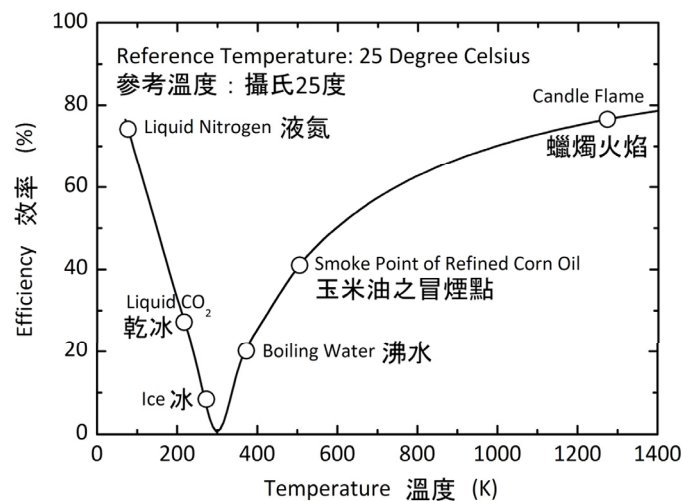


Efficiency of a Carnot Engine

- Efficiency of a Carnot engine depends on the temperatures of the reservoirs:

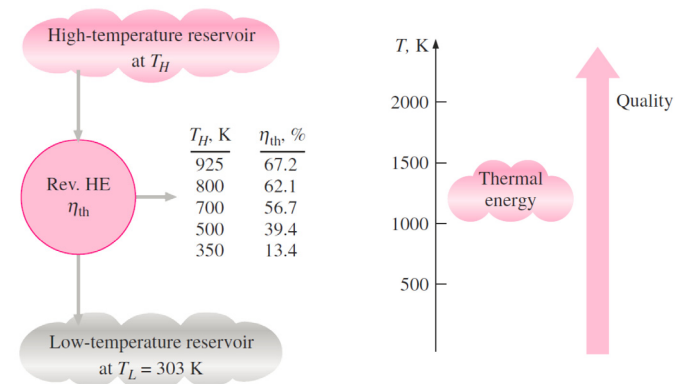
$$\eta = \frac{W_{\text{eng}}}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h}$$

Efficiency of a Carnot Engine



Quality of Thermal Energy

The higher the temperature, the higher the quality of the thermal energy.



Quick Quiz

Three engines operate between reservoirs separated in temperature by 300 K. The reservoir temperatures are as follows:

Engine A: $T_h = 1\,000\text{ K}$, $T_c = 700\text{ K}$;

Engine B: $T_h = 800\text{ K}$, $T_c = 500\text{ K}$;

Engine C: $T_h = 600\text{ K}$, $T_c = 300\text{ K}$.

Rank the engines in order of theoretically possible efficiency from highest to lowest.

Answer:

Exercise: Efficiency of the Carnot Engine

By considering the Carnot Cycle, prove that the Carnot Efficiency is given by:

$$\eta = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h}$$

Carnot Heat Pump COPs

- COP, Heating Mode:

$$\text{COP}_{\text{Carnot, Heating}} = \frac{|Q_h|}{W} = \frac{T_h}{T_h - T_c}$$

- COP, Cooling Mode:

$$\text{COP}_{\text{Carnot, Cooling}} = \frac{|Q_c|}{W} = \frac{T_c}{T_h - T_c}$$

- In practice, the COP value is usually limited to below 10.

Otto Cycle: The Four-Stroke Engine Cycle

- Intake stroke O → A: Piston moves downward and mixture of air and fuel is drawn into the cylinder at atmospheric pressure. Volume increases from V_2 to V_1 .
- Compression stroke A → B: Piston moves upward, the air-fuel mixture is compressed adiabatically from volume V_1 to V_2 , and the temperature increases from T_A to T_B . The work done on the gas is positive (= the negative of the area under the curve AB).

Otto Cycle: The Four-Stroke Engine Cycle

- Process B → C:
 - Combustion occurs when the spark plug fires.
 - Occurs in a very short time interval while the piston is at its highest position.
 - During this time interval, the mixture's pressure and temperature increase rapidly, with the temperature rising from T_B to T_C .
 - Volume remains approximately constant because of the short time interval.
 - To model this process: energy $|Q_h|$ enters the system.

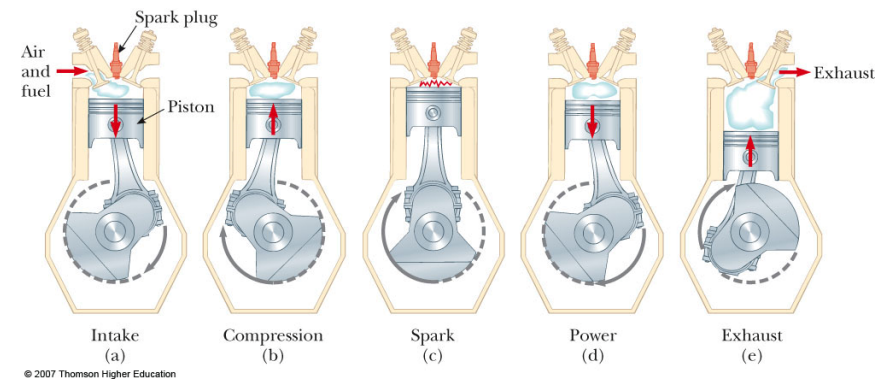
Otto Cycle: The Four-Stroke Engine Cycle

- Power stroke C → D:
 - Gas expands adiabatically from V_2 to V_1 .
 - Expansion causes the temperature to drop from T_C to T_D .
 - Work is done by the gas in pushing the piston downward (= the area under the curve CD).
- Process D → A:
 - Exhaust valve is opened as the piston reaches the bottom.
 - Pressure suddenly drops for a short time interval. During this time interval, the piston is almost stationary and the volume is approximately constant.

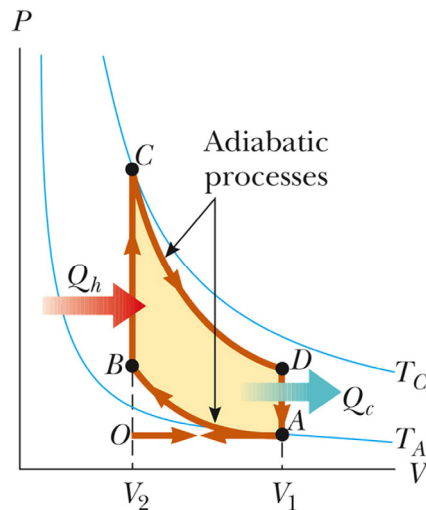
Otto Cycle: The Four-Stroke Engine Cycle

- Exhaust stroke A → O:
 - Piston moves upward while the exhaust valve remains open.
 - Residual gases are exhausted at atmospheric pressure, and the volume decreases from V_1 to V_2 .

Otto Cycle: The Four-Stroke Engine Cycle



Otto Cycle: The Four-Stroke Engine Cycle



Otto Cycle Efficiency

- Assume the air-fuel mixture is an ideal gas,

$$\eta = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

- γ is the ratio of the molar specific heats.
- V_1 / V_2 is the compression ratio.

Otto Cycle Efficiency

- Typical values:
 - Compression ratio of 8;
 - $\gamma = 1.4$;
 - $\eta = 56\%$.
- Efficiencies of real engines: 15% to 20%.
- Mainly due to friction, energy transfer by conduction, incomplete combustion of the air-fuel mixture.

Diesel Engines

- Operate on a cycle similar to the Otto cycle without a spark plug.
- The compression ratio is much greater and so the cylinder temperature at the end of the compression stroke is much higher.
- Fuel is injected and the temperature is high enough for the mixture to ignite without the spark plug.
- Diesel engines are more efficient than gasoline engines .

Exercise: Efficiency of the Otto Cycle

- Show that the thermal efficiency of an engine operating in an idealized Otto cycle is given by:

$$\eta = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

Entropy

- Entropy (S) is a state variable related to the second law of thermodynamics.
- The importance of entropy grew with the development of statistical mechanics.
- A main result is isolated systems tend toward disorder and entropy is a natural measure of this disorder.

Microstates vs. Macrostates

Microstates

The individual constituents of the system.

Macrostates

The macroscopic point of view. For example: macroscopic variables include pressure, density, and temperature for gases.

Microstates vs. Macrostates

- For a given macrostate, a number of microstates are possible.
- It is assumed that all microstates are equally probable.
- When all possible macrostates are examined, it is found that macrostates associated with disorder have far more microstates than those associated with order.

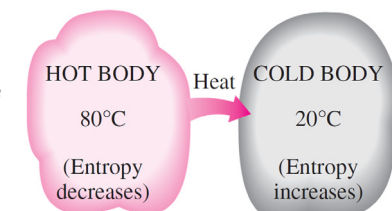
Probabilities: Microstates vs. Macrostates

- The probability of a system from an ordered macrostate to a disordered macrostate is far greater than the probability of the reverse.
 - There are more microstates in a disordered macrostate.
- If we consider a system and its surroundings to include the Universe, the Universe is always moving toward a macrostate corresponding to greater disorder.

Entropy and the Second Law

- Another statement of the second law of thermodynamics:
 - Entropy is a measure of randomness or disorder.
- The entropy of the Universe increases in all real processes
- Increase in Entropy of the Universe is the driving force for a spontaneous processes.

During a heat transfer process, the net entropy increases. (The increase in the entropy of the cold body more than offsets the decrease in the entropy of the hot body.)



Entropy and Heat

- Change in Entropy (dS)

$$dS = \frac{dQ_r}{T}$$

dQ_r = amount of energy transferred by heat when a system follows a reversible path.

Entropy and Heat

- The change in entropy depends only on the endpoints and is independent of the actual path followed.
- The entropy change for an irreversible process can be determined by calculating the change in entropy for a reversible process that connects the same initial and final points.
- For a finite process, the change in entropy is:

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

Change in Entropy

- The change in entropy, from one state to another, has the same value for all paths connecting the two states.
- The finite change in entropy depends only on the properties of the initial and final equilibrium states.
- Therefore we are free to choose a particular reversible path over which to evaluate the entropy the actual path as long as the initial and final states are the same.

ΔS for a Reversible Cycle

- Consider the Entropy change in a Carnot heat engine:

$$\Delta S = \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}$$

* Minus sign represents energy leaving the engine

$$\text{Since } \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c} \Rightarrow \Delta S = 0.$$

- In general, $\Delta S = 0$ for any reversible cycle.

$$\oint \frac{dQ_r}{T} = 0$$

Entropy Changes in Irreversible Processes

- To calculate the change in entropy in a real system, remember that entropy depends only on the state of the system.
- Do not use Q , the actual energy transfer in the process.
 - Distinguish this Q from Q_r , the amount of energy that would have been transferred by heat along a reversible path.
 - Q_r is the correct value to use for ΔS .

Entropy Changes in Irreversible Processes

- In general, the total entropy and therefore the total disorder always increases in an irreversible process.
- The total entropy of an isolated system undergoes a change that cannot decrease.
 - This is another statement of the second law of thermodynamics.

Entropy Changes in Irreversible Processes

- If the process is irreversible, then the total entropy of an isolated system always increases.
 - In a reversible process, the total entropy of an isolated system remains constant.
- The change in entropy of the Universe must be greater than zero for an irreversible process and equal to zero for a reversible process.

Heat Death of the Universe

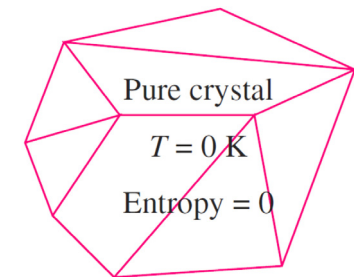
- Ultimately, the entropy of the Universe should reach a maximum value.
- At this value, the Universe will be in a state of uniform temperature and density.
- All physical, chemical, and biological processes will cease.
 - The state of perfect disorder implies that no energy is available for doing work.
 - This state is called the heat death of the Universe.

The Third Law of Thermodynamics

- Molecules in solid phase continually oscillate, creating an uncertainty about their position.
- Degree of oscillations decreases with temperature.
- Expect: molecules become motionless at absolute zero (minimum energy).

The Third Law of Thermodynamics

Third Law: The Entropy of a pure crystalline substance at absolute zero temperature is zero, because there is no uncertainty about the state of the molecules at that instant.



A pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero.

Quick Quiz #1 on Entropy

Which of the following is true for the entropy change (ΔS)?

A system undergoes a reversible and adiabatic process.

- a) $\Delta S < 0$.
- b) $\Delta S = 0$.
- c) $\Delta S > 0$.

Answer:

Quick Quiz #2 on Entropy

The entropy change in an adiabatic process must be zero because $Q = 0$.

- a) True.
- b) False.

Answer:

Quick Quiz #3 on Entropy

An ideal gas is taken from an initial temperature T_i to a higher final temperature T_f along two different reversible paths. Path A is at constant pressure and path B is at constant volume. What is the relation between the entropy changes of the gas for these paths?

Answer:

- (A) $\Delta S_A > \Delta S_B$
- (B) $\Delta S_A = \Delta S_B$
- (C) $\Delta S_A < \Delta S_B$

Entropy Generation in Daily Life



Entropy Change in Thermal Conduction

- Consider a system, which consists of a hot reservoir and a cold reservoir:
 - in thermal contact with each other; and
 - isolated from the rest of the Universe.
- A process occurs:
 - energy Q is transferred by heat from the hot reservoir (T_h) to the cold reservoir (T_c).

Entropy Change in Thermal Conduction

- Change in Entropy of the system and the Universe:

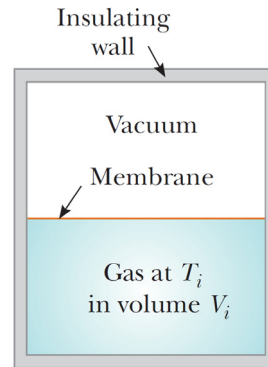
$$\Delta S = \underbrace{\frac{Q}{T_c}}_{\text{Absorb Heat}} + \underbrace{\frac{-Q}{T_h}}_{\text{Lose Heat}} > 0$$

Entropy Change in Free Expansion

Consider the adiabatic free expansion of gas:

- Initial volume V_i ;
- Membrane separating the gas from vacuum;
- Gas expands to volume V_f ;
- The process is neither reversible nor quasi-static.

What is the Entropy changes of the gas and of the Universe during this process?



Entropy Change in Free Expansion

- Entropy Change: $\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$
- To apply The equation of Entropy change, we cannot take $Q = 0$ for the irreversible process;
- Instead find Q_r , an equivalent reversible path that shares the same initial and final states;
- Simple Choice: an isothermal reversible expansion, where the gas pushes slowly against a piston while energy enters the gas by heat from a reservoir to hold the temperature constant.
- Exercise: What is the Entropy change ΔS ?

Entropy on a Microscopic Scale

- Entropy \leftrightarrow Microscopic Viewpoint (through statistical analysis of molecular motions).
- Connection between Entropy and the number of microstates (W) for a given macrostate is:

Boltzmann's Entropy Formula: $S = k_B \ln W$

- The more microstates that correspond to a given macrostate, the greater the entropy of that macrostate.
- This shows that entropy is a measure of disorder.

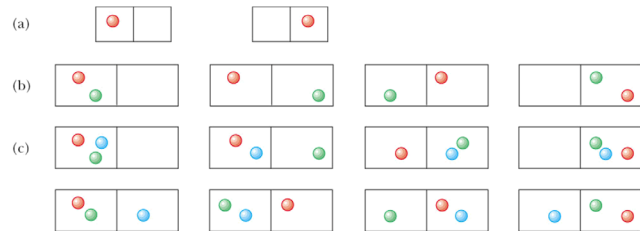
[From Wikipedia]

The equation ($S = k_B \ln W$) was originally formulated by Ludwig Boltzmann between 1872 and 1875, but later put into its current form by Max Planck in about 1900. To quote Planck, "the logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases".



Entropy: Molecule Example

- One molecule in a two-sided container has a 1-in-2 chance of being on the left side.
- Two molecules have a 1-in-4 chance of being on the left side at the same time.
- Three molecules have a 1-in-8 chance of being on the left side at the same time.



Entropy: Molecule Example

- Consider 100 molecules in a container.
- The probability to separate 50 fast molecules on one side and 50 slow molecules on the other side is $(\frac{1}{2})^{100}$.
- If we have one mole of gas, this is found to be extremely improbable.

Entropy: Marble Example

- Suppose you have a bag with 50 red marbles and 50 green marbles.
- You draw a marble, record its color, return it to the bag, and draw another.
- Continue until four marbles have been drawn.
- What are possible macrostates and what are their probabilities?

Entropy: Marble Example

- The most ordered are the least likely.
- The most disorder is the most likely.

TABLE 22.1

Possible Results of Drawing Four Marbles from a Bag

Macrostate	Possible Microstates	Total Number of Microstates
All R	RRRR	1
1G, 3R	RRRG, RRGR, RGRR, GRRR	4
2G, 2R	RRGG, RGRG, GRRG, RGGG, GRGR, GGRR	6
3G, 1R	GGGR, GGGR, GRGG, RGGG	4
All G	GGGG	1

Clausius–Clapeyron Relation

- For characterizing a discontinuous phase transition between two phases a single constituent.
- On a P–T diagram, the Clausius–Clapeyron relation gives the slope of the coexistence curve.

$$\frac{dP}{dT} = \frac{L}{T \Delta v} = \frac{\Delta S}{\Delta v}$$

dP/dT = the slope of the coexistence curve,

L is the specific latent heat,

T is the temperature,

Δv is the specific volume change of the phase transition, and

ΔS is the specific entropy change of the phase transition.

Entropy Balance

- Increase in Entropy for any system is expressed as:

$$\left(\begin{array}{c} \text{Total} \\ \text{Entropy} \\ \text{Entering} \end{array} \right) - \left(\begin{array}{c} \text{Total} \\ \text{Entropy} \\ \text{Leaving} \end{array} \right) + \left(\begin{array}{c} \text{Total} \\ \text{Entropy} \\ \text{Generated} \end{array} \right) = \left(\begin{array}{c} \text{Change in the} \\ \text{Total Entropy} \\ \text{of the System} \end{array} \right)$$

$$S_{\text{in}} - S_{\text{out}} + S_{\text{Gen}} = \Delta S_{\text{system}}$$

- The Entropy change of a system during a process is equal to the net Entropy transfer through the system boundary and the Entropy generated within the system.

Mechanisms of Entropy Transfer

Entropy transferred to or from a system:

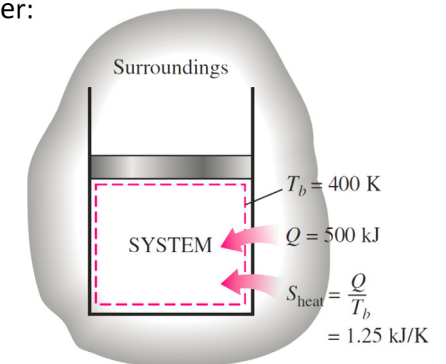
- Heat Transfer;
- Mass Flow.

Heat Transfer

- Entropy transfer by heat transfer:

$$S_{\text{heat}} = \frac{Q}{T} \quad (T = \text{Constant})$$

$$S_{\text{heat}} = \int \frac{dQ}{T} \quad (T \neq \text{Constant})$$



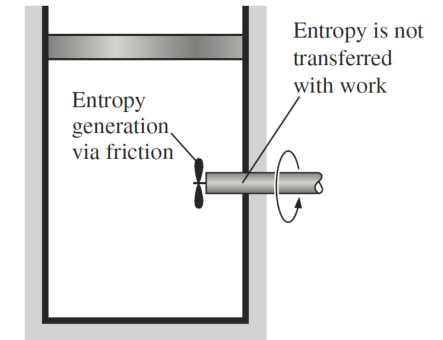
Heat transfer is always accompanied by entropy transfer in the amount of Q/T , where T is the boundary temperature.

Notes on Entropy Transfer

- When two systems are in contact, the Entropy transfer from the warmer system = the Entropy transfer into the cooler one at the point of contact.
- No entropy can be created or destroyed at the boundary, since the boundary has no thickness and occupies no volume.
- No Entropy is transferred by work.
- Comparison:
 - Energy is transferred by both heat and work;
 - Entropy is transferred only by heat.

Notes on Entropy Transfer

- No entropy is exchanged during a work interaction between a system and its surroundings.
- Only energy is exchanged during work interaction.
- Energy and Entropy are exchanged during heat transfer.



No entropy accompanies work as it crosses the system boundary. But entropy may be generated within the system as work is dissipated into a less useful form of energy.

Mass Flow

- Mass: Contains Entropy and Energy.
- Entropy and Energy of a system are proportional to the mass.
- The rates of entropy and energy transport into or out of a system are proportional to the mass flow rate.
- Closed systems do not involve any mass flow.

Mass Flow

Entropy transfer by mass flow:

$$S_{\text{mass}} = ms$$

m = mass; and

s = the specific entropy (entropy per unit mass entering or leaving a system).

Mass Flow

When the properties of the mass change during the process:

$$\dot{S}_{\text{mass}} = \int_A s \rho v dA$$

$$S_{\text{mass}} = \int s dm = \int_{\Delta t} \dot{S}_{\text{mass}} dt$$

A = cross-sectional area of the flow;

ρ = density; and

v = velocity normal to dA .

Entropy Generation

- Entropy generation is a measure of the entropy created by an irreversible process.
- Irreversible processes: friction, mixing, chemical reactions, heat transfer through a finite temperature difference, unrestrained expansion, nonquasiequilibrium compression/expansion.
- Reversible process: the Entropy generation = 0,
 \Rightarrow Entropy change of a system = Entropy transfer.

Entropy Generation

- Entropy balance for any system undergoing any process:

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{Net Entropy Transfer by heat and mass}} + \underbrace{S_{\text{Gen}}}_{\text{Entropy Generation}} = \underbrace{\Delta S_{\text{system}}}_{\text{Change in Entropy}} \quad [\text{J/K}]$$

- In the rate form:

$$\underbrace{\dot{S}_{\text{in}} - \dot{S}_{\text{out}}}_{\text{Rate of Net Entropy Transfer by heat and mass}} + \underbrace{\dot{S}_{\text{Gen}}}_{\text{Rate of Entropy Generation}} = \underbrace{dS_{\text{system}}/dt}_{\text{Rate of Change in Entropy}} \quad [\text{W/K}]$$

Closed System

- No mass flow across its boundaries.
- The Entropy change is simply the difference between the initial and final entropies of the system.
- The Entropy change of a closed system is due to the Entropy transfer accompanying heat transfer and the entropy generation within the system boundaries.

Closed System

Entropy balance equation:

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = \Delta S_{\text{system}}$$

Heat transfer to the system: positive

The entropy balance relation can be stated as:

The entropy change of a closed system during a process is equal to the sum of the net entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries.

Adiabatic Closed System ($Q = 0$)

The Entropy change of the adiabatic closed system equals the Entropy generation within the system boundaries:

$$S_{\text{gen}} = \Delta S_{\text{adiabatic system}}$$

Closed System: System + Surroundings

- Any closed system and its surroundings can be treated as an adiabatic system.
- The total Entropy change of a system = The sum of the Entropy changes of its parts.
- Entropy balance equation for a closed system and its surroundings:

$$S_{\text{gen}} = \sum \Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Exercise: Entropy Generation in a Wall

Consider steady heat transfer through a brick wall (5m×7m, thickness 30 cm) of a house. When the outdoor temperature is 10°C, the house is maintained at 20°C. The temperatures of the inner and outer surfaces of the brick wall are measured to be 18°C and 15°C, respectively. The rate of heat transfer through the wall is 1035 W.

Determine:

- the rate of entropy generation in the wall, and
- the rate of total entropy generation associated with this heat transfer process.

Exercise: Entropy Generation in a Wall

