

Chapter 22

Heat Engines, Entropy and the Second Law of Thermodynamics



First Law of Thermodynamics – Review

The first law is a statement of Conservation of Energy.

The first law states that a change in internal energy in a system can occur as a result of energy transfer by heat, by work, or by both.

The first law makes no distinction between processes that occur spontaneously and those that do not.

Only certain types of energy-conversion and energy-transfer processes actually take place in nature.

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.

These types of processes are irreversible.

- An irreversible process is one that occurs naturally in one direction only.
- No irreversible process has been observed to run backwards.
- An important engineering implication is the limited efficiency of heat engines.

Lord Kelvin

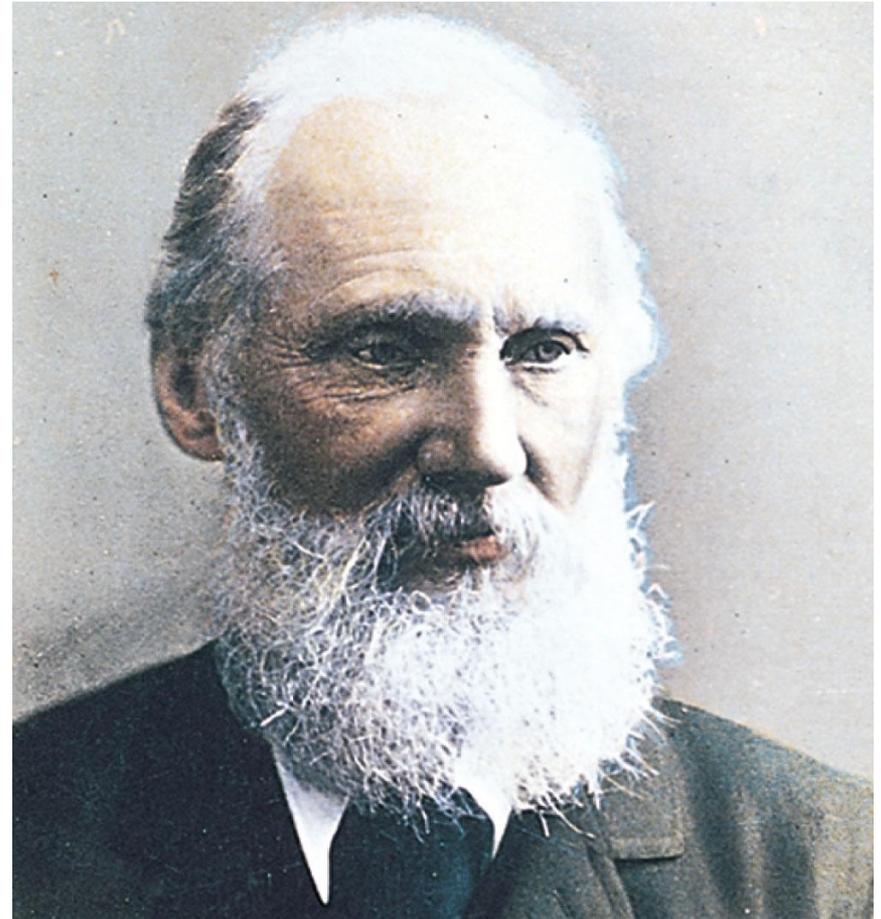
William Thomson, Lord Kelvin

1824 – 1907

British physicist and mathematician

First to propose the use of an absolute scale of temperature

His work in thermodynamics led to the idea that energy cannot pass spontaneously from a colder object to a hotter object.



Heat Engine

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.

Example –

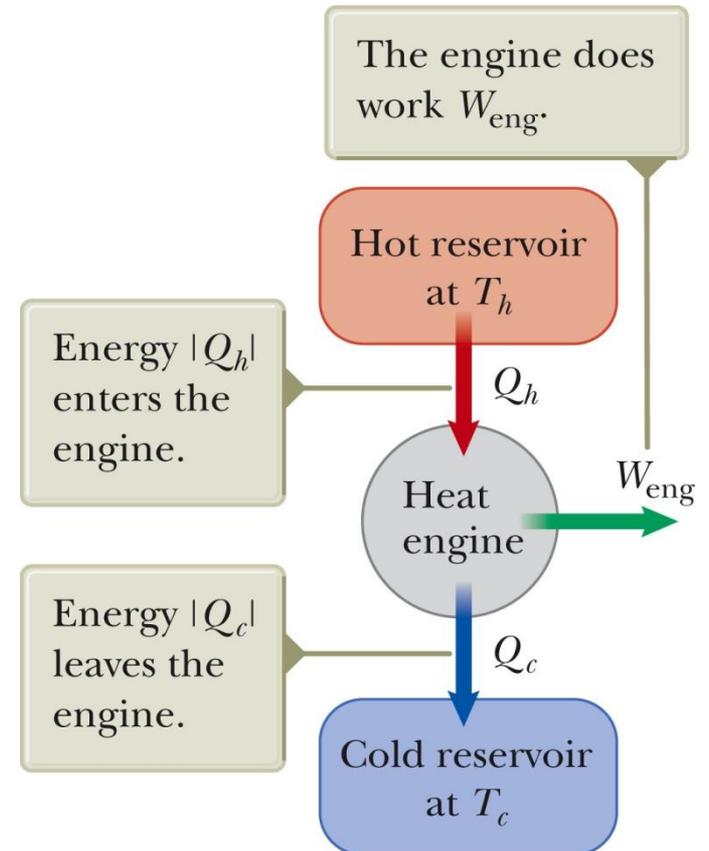
- Power plant produces electricity
- Internal Combustion engine of an automobile

Heat Engine, cont.

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).



Heat Engine, cont.

Since it is a cyclical process, $\Delta E_{\text{int}} = 0$

- Its initial and final internal energies are the same.

So, from 1st Law of Thermodynamics

$$\Delta E_{\text{int}} = Q + W = Q - W_{\text{eng}} = 0$$

Therefore, $W_{\text{eng}} = Q_{\text{net}} = |Q_{\text{h}}| - |Q_{\text{c}}|$

The net work done by a heat engine equals the net energy transferred to it.

Thermal Efficiency of a Heat Engine

Thermal efficiency is defined as the ratio of the net work done by the engine during one cycle to the energy input at the higher temperature.

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

We can think of the efficiency as the ratio of what you gain to what you give.

In practice, all heat engines expel only a fraction of the input energy by mechanical work.

Therefore, their efficiency is always less than 100%.

- To have $e = 100\%$, Q_c must be 0

Second Law: Kelvin-Planck Form

Because efficiencies of real engines are well below 100% - the **Kelvin-Planck Form of the Second Law states -**

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 $|Q_h|$
- Means that Q_c cannot equal 0
 - Some energy $|Q_c|$ must be expelled to the environment
- Means that e cannot equal 100%

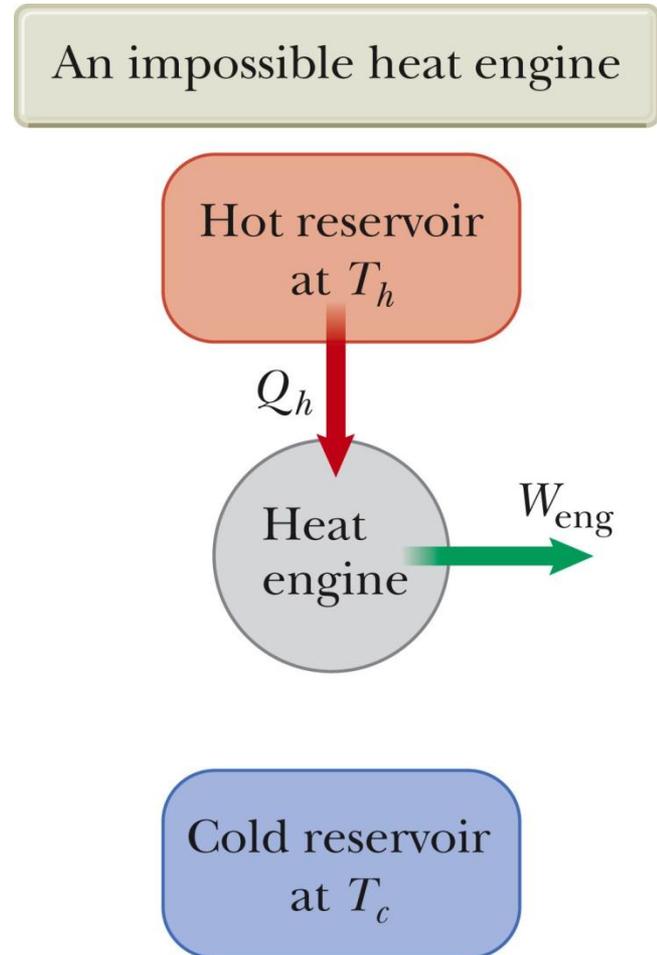
Perfect Heat Engine

No energy is expelled to the cold reservoir.

It takes in some amount of energy and does an equal amount of work.

$$e = 100\%$$

It is impossible to construct such an engine.



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

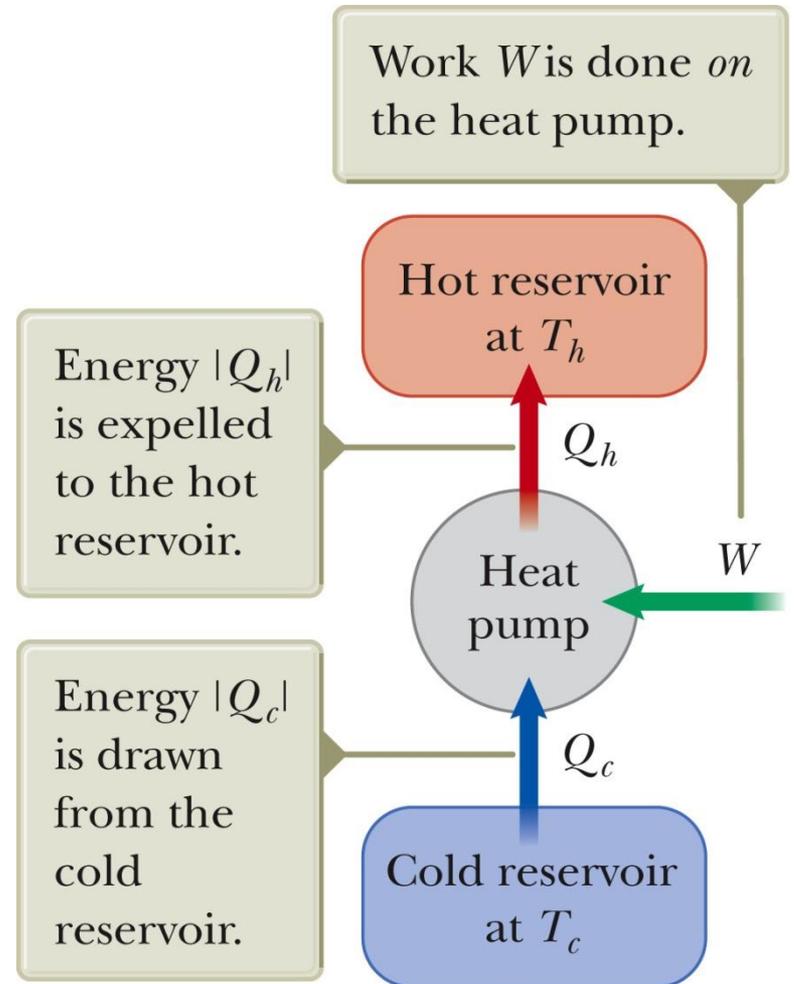
Examples

- 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



Second Law – Clausius Form

Because existence of a perfect pump or refrigerator (i.e, without doing any work) is in violation of second law of thermodynamics, which in the form of **Clausius statement states** -

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

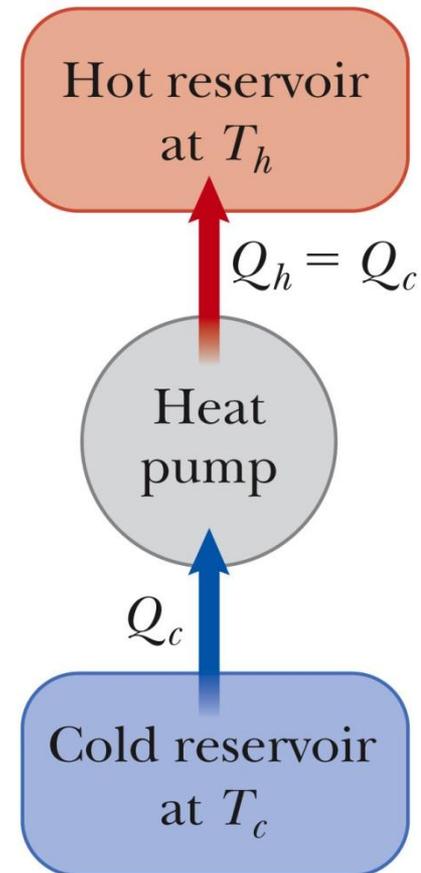
Takes energy from the cold reservoir

Expels an equal amount of energy to the hot reservoir

No work is done

This is an impossible heat pump

An impossible heat pump



Coefficient of Performance

The effectiveness of a heat pump is described by a number called the **coefficient of performance (COP)**.

Similar to thermal efficiency for a heat engine

- It is the ratio of what you gain (energy transferred to or from a reservoir) to what you give (work input).

COP, Cooling Mode

In **cooling mode**, you “gain” energy removed from a cold temperature reservoir.

$$\text{COP (Cooling Mode)} = \frac{\text{energy transferred at low temp}}{\text{work done on the pump}} = \frac{|Q_c|}{W}$$

A good refrigerator should have a high COP.

- Typical values are 5 or 6

COP, Heating Mode

In **heating mode**, the COP is the ratio of the heat transferred in to the work required.

$$\text{COP (Heating Mode)} = \frac{\text{energy transferred at high temp}}{\text{work done by heat pump}} = \frac{|Q_h|}{W}$$

Q_h is typically higher than W

- Values of COP are generally about 4
 - For outside temperature about 25° F

The use of heat pumps that extract energy from the air is most satisfactory in moderate climates.

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, cont

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.

- No friction or turbulence, for example

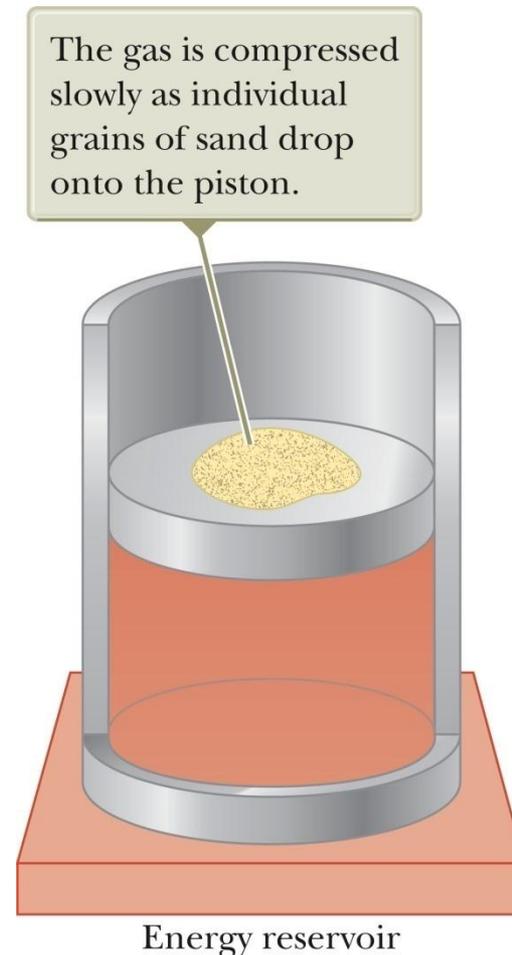
Reversible and Irreversible Processes, Summary

The reversible process is an idealization.

All real processes on Earth are irreversible.

Example of an approximate reversible process:

- The gas is compressed isothermally
- The gas is in contact with an energy reservoir
- Continually transfer just enough energy to keep the temperature constant



Sadi Carnot

1796 – 1832

French engineer

First to show quantitative relationship between work and heat

Published *Reflections on the Motive Power of Heat*

- Reviewed industrial, political and economic importance of the steam engine
- Gave a definition of work



Carnot Engine

A theoretical engine developed by Sadi Carnot

A heat engine operating in an ideal, reversible cycle (now called a Carnot cycle) between two reservoirs is the most efficient engine possible

- This sets an upper limit on the efficiencies of all other engines.

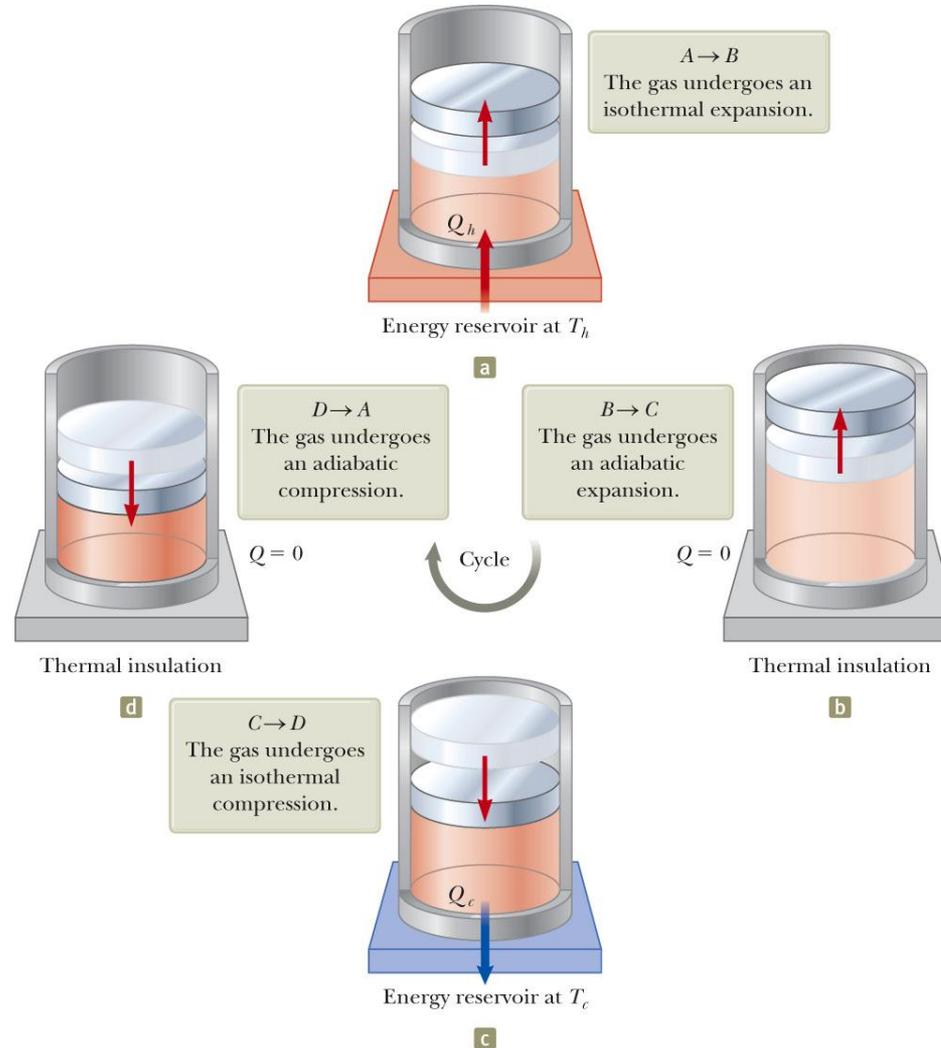
Carnot's Theorem

No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

- 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

Overview of the processes in a Carnot cycle



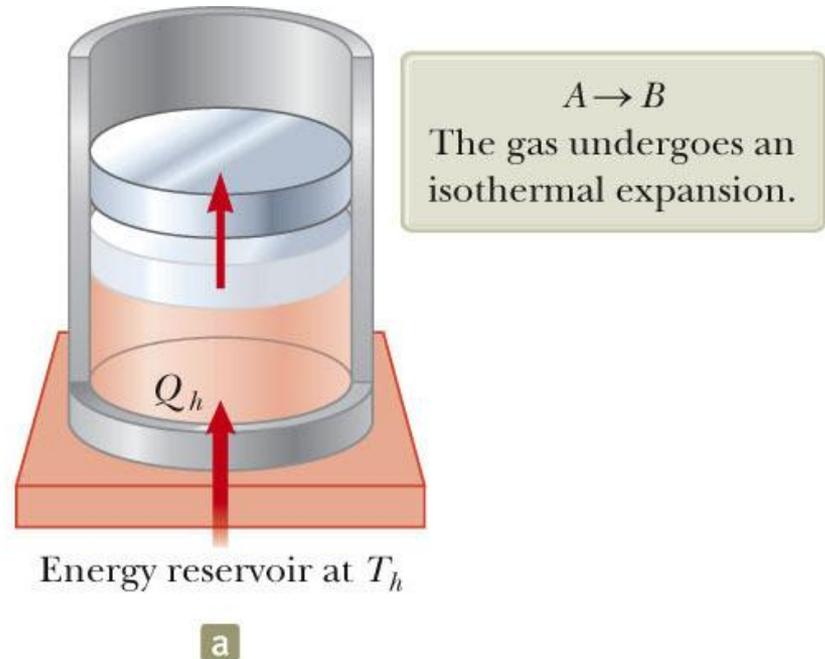
Carnot Cycle, A to B

$A \rightarrow B$ is an isothermal expansion.

The gas is placed in contact with the high temperature reservoir, T_h .

The gas absorbs heat $|Q_h|$.

The gas does work W_{AB} in raising the piston.



Carnot Cycle, B to C

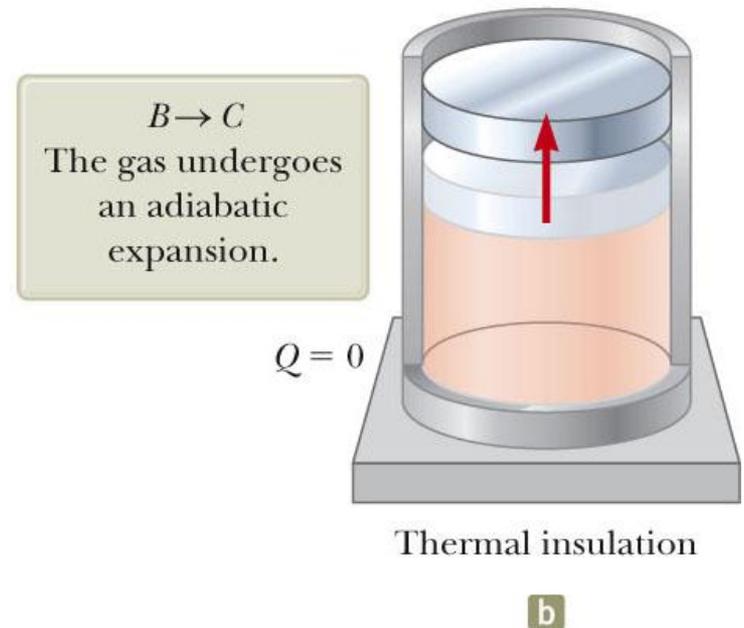
$B \rightarrow C$ is an adiabatic expansion.

The base of the cylinder is replaced by a thermally nonconducting wall.

No energy enters or leaves the system by heat.

The temperature falls from T_h to T_c .

The gas does work W_{BC} .



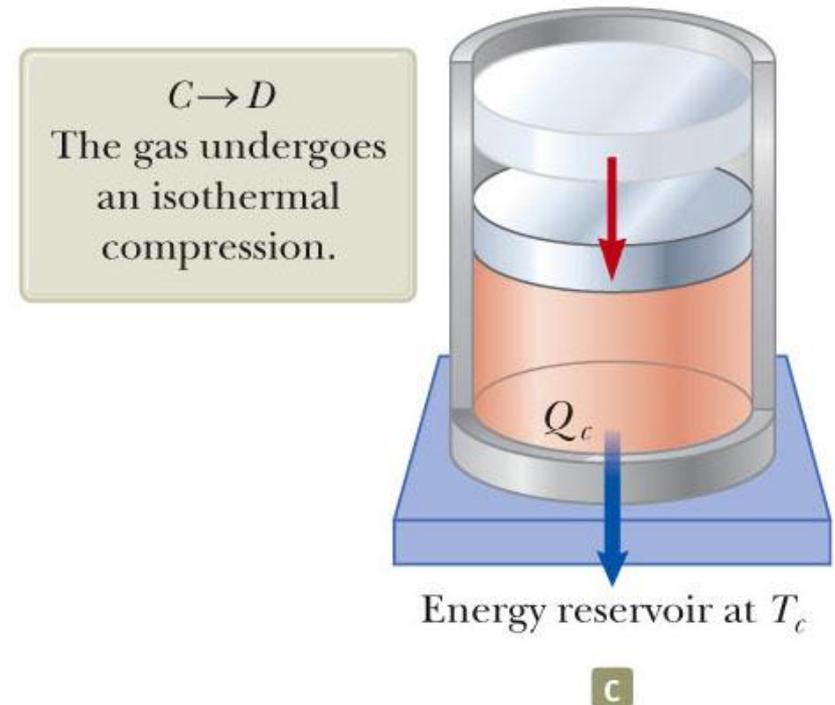
Carnot Cycle, C to D

The gas is placed in thermal contact with the cold temperature reservoir.

$C \rightarrow D$ is an isothermal compression.

The gas expels energy $|Q_c|$.

Work W_{CD} is done on the gas.



Carnot Cycle, D to A

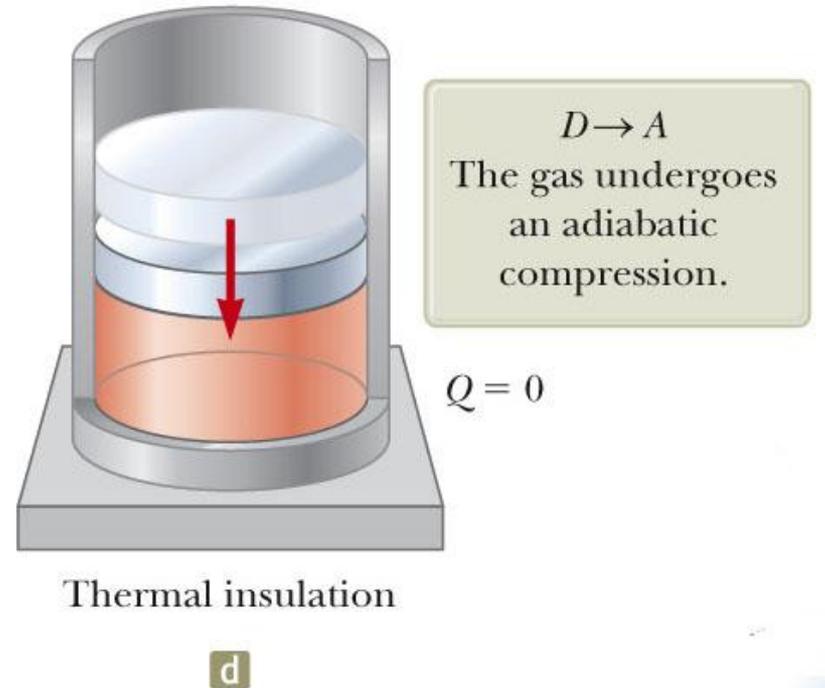
$D \rightarrow A$ is an adiabatic compression.

The base is replaced by a thermally nonconducting wall.

- So 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} .

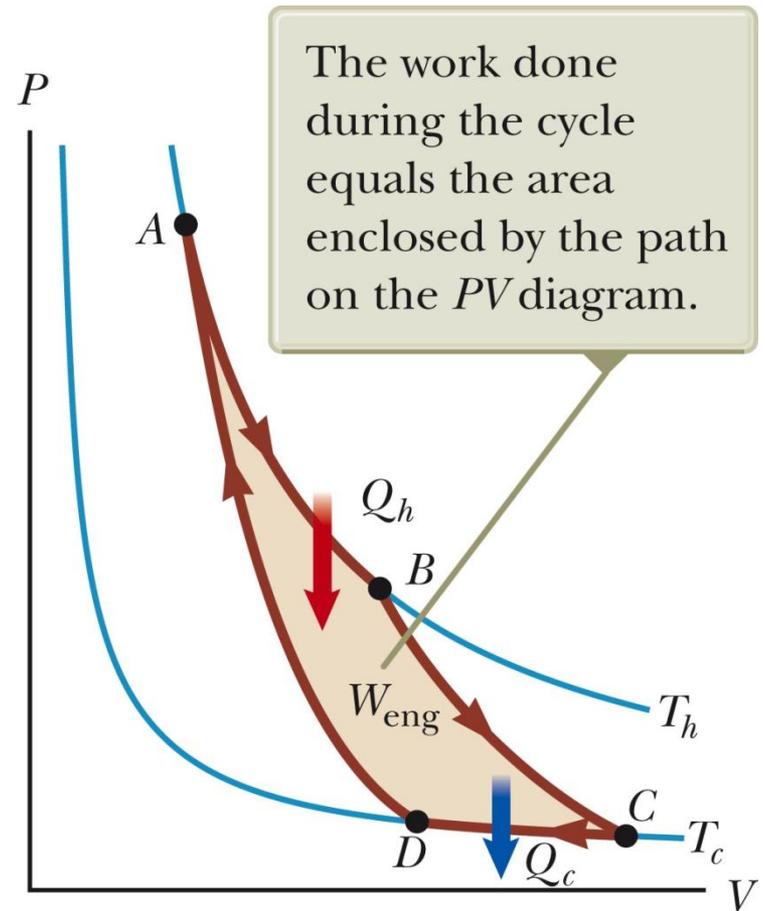


Carnot Cycle, PV Diagram

The work done by the engine is shown by the area enclosed by the curve, W_{eng} .

The net work is equal to $|Q_h| - |Q_c|$.

$\Delta E_{\text{int}} = 0$ for the entire cycle



Efficiency of a Carnot Engine

Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs.

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

Again for Carnot Cycle, $\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$

Hence the thermal efficiency for Carnot engine is

$$e_C = 1 - \frac{T_c}{T_h}$$

Temperatures must be in Kelvins

All Carnot engines operating between the same two temperatures will have the same efficiency.

Notes About Carnot Efficiency

Efficiency is 0 if $T_h = T_c$

Efficiency is 100% only if $T_c = 0 \text{ K}$

- Such reservoirs are not available
- Efficiency is always less than 100%

The efficiency increases as T_c is lowered and as T_h is raised.

In most practical cases, T_c is near room temperature, 300 K

- So generally T_h is raised to increase efficiency.

Carnot Cycle in Reverse

Theoretically, a Carnot-cycle heat engine can run in reverse.

This would constitute the most effective heat pump available.

This would determine the maximum possible COPs for a given combination of hot and cold reservoirs.

Carnot Heat Pump COPs

In heating mode:

$$COP_C = \frac{|Q_h|}{W} = \frac{T_h}{T_h - T_c}$$

In cooling mode:

$$COP_C = \frac{|Q_c|}{W} = \frac{T_c}{T_h - T_c}$$

In practice, the COP is limited to values below 10.

Gasoline Engine

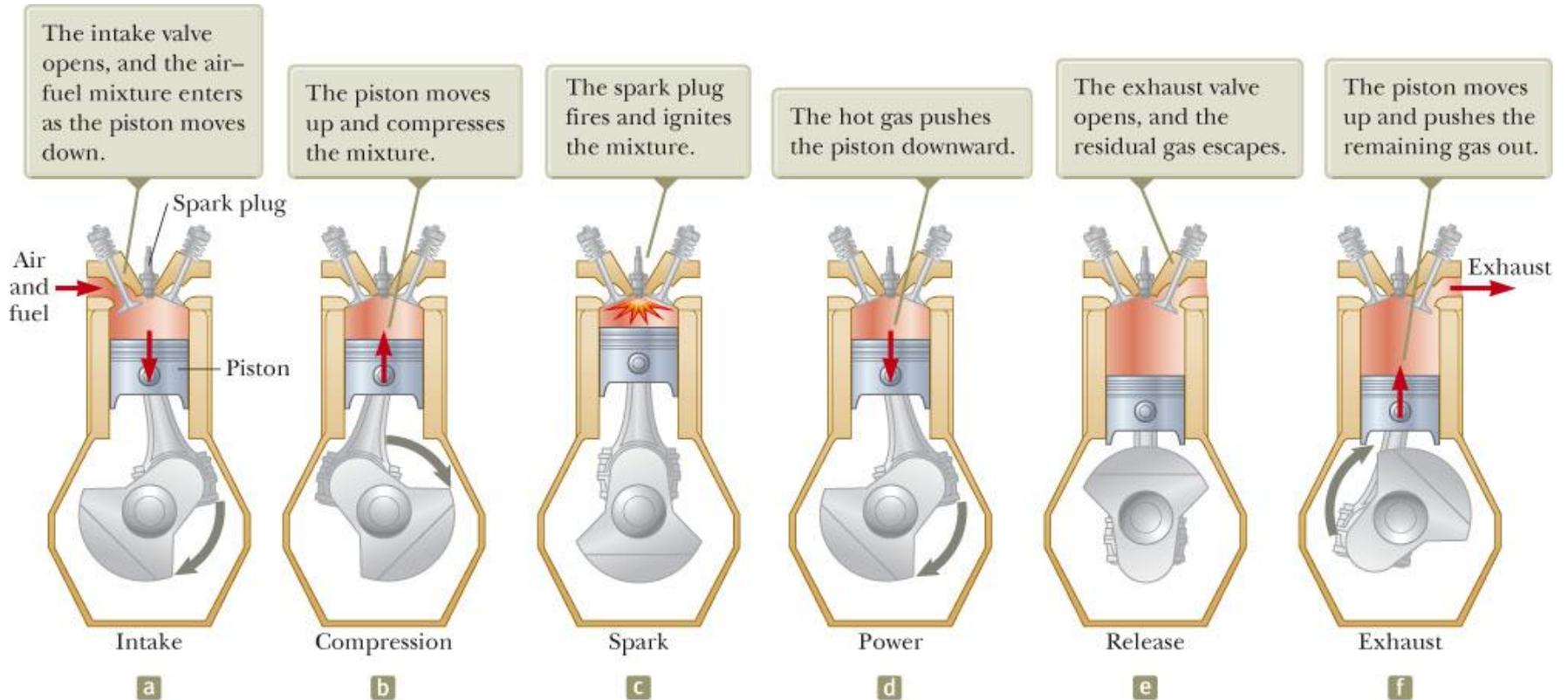
In a gasoline engine, six processes occur during each cycle.

For a given cycle, the piston moves up and down twice.

This represents a four-stroke cycle.

The processes in the cycle can be approximated by the Otto cycle.

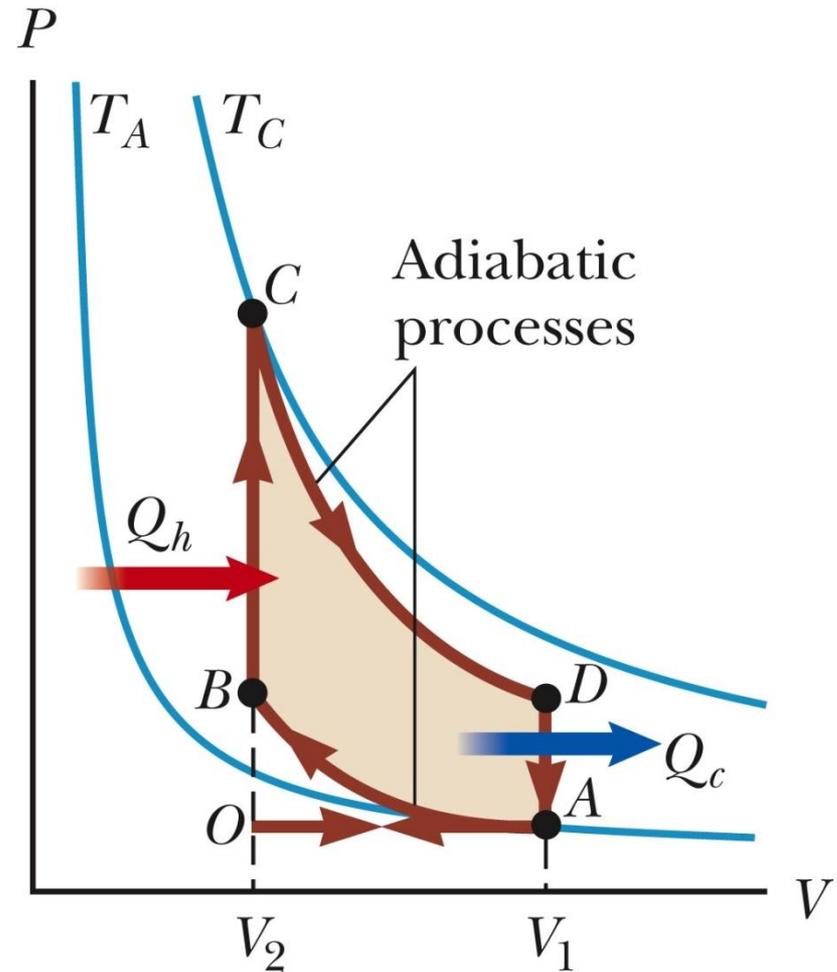
The Conventional Gasoline Engine



Otto Cycle

The PV diagram of an Otto cycle is shown at right.

The Otto cycle approximates the processes occurring in an internal combustion engine.



Gasoline Engine – Intake Stroke

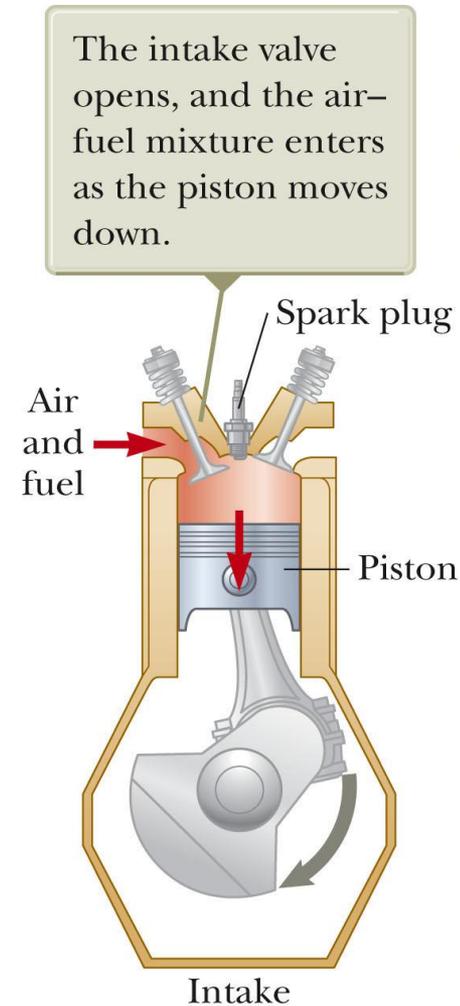
During the intake stroke, the piston moves downward.

A gaseous mixture of air and fuel is drawn into the cylinder.

Energy enters the system by matter transfer as potential energy in the fuel.

The volume increases from V_2 to V_1 .

$O \rightarrow A$ in the Otto cycle PV diagram.



a

Gasoline Engine – Compression Stroke

The piston moves upward.

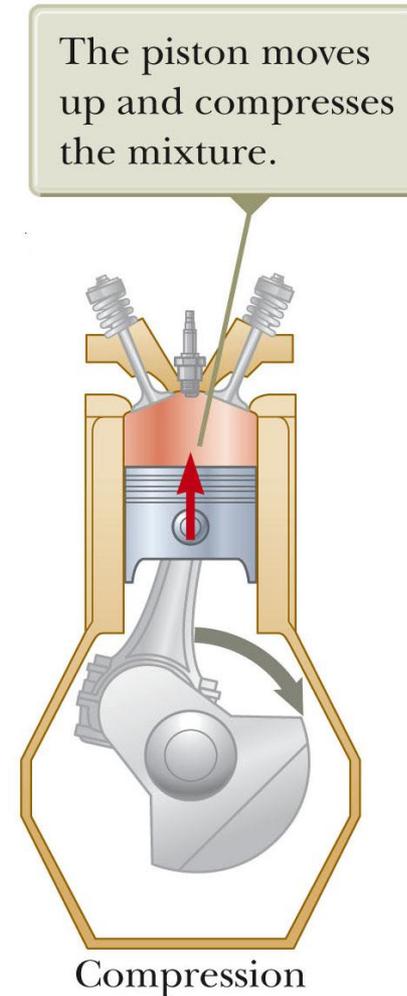
The air-fuel mixture is compressed adiabatically.

The volume changes from V_1 to V_2 .

The temperature increases.

The work done on the gas is positive and equal to the negative area under the curve.

$A \rightarrow B$ in the Otto cycle PV diagram.



b

Gasoline Engine – Spark

Combustion occurs when the spark plug fires.

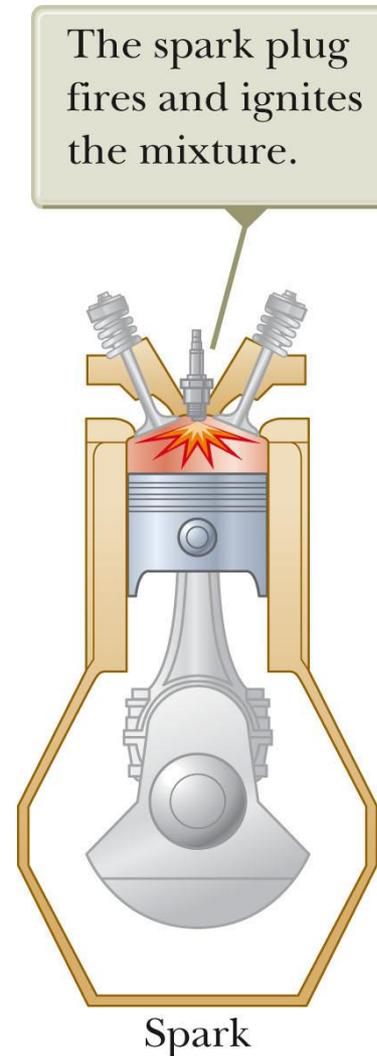
This is not one of the strokes of the engine.

It occurs very quickly while the piston is at its highest position.

The combustion represents a rapid energy transformation from potential energy to internal energy.

The temperature changes from T_B to T_C but the volume remains approximately the same.

$B \rightarrow C$ in the Otto cycle PV diagram.



Gasoline Engine – Power Stroke

In the power stroke, the gas expands adiabatically.

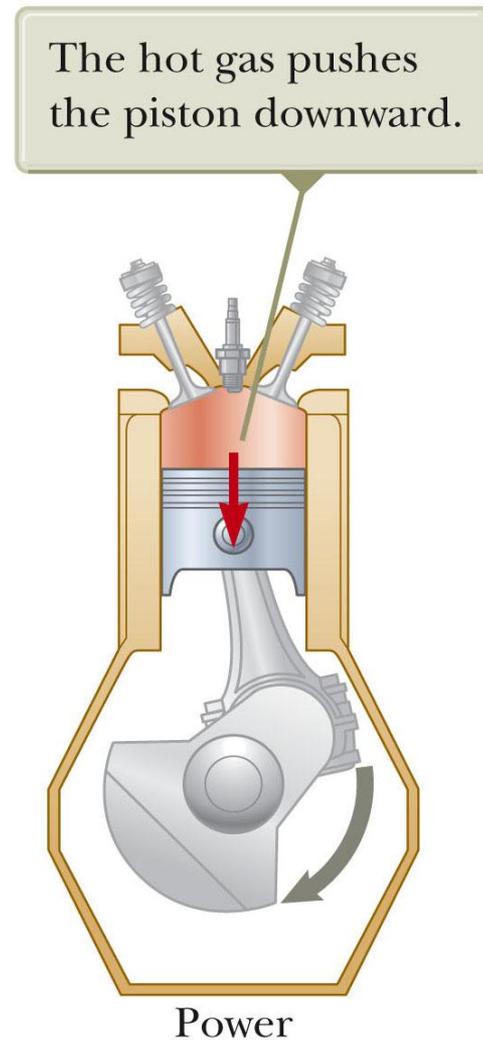
Volume changes from V_2 to V_1

The temperature drops from T_c to T_D .

Work is done by the gas

The work is equal to the area under the curve.

$C \rightarrow D$ in the Otto cycle PV diagram



d

Gasoline Engine – Valve Opens

This is process $D \rightarrow A$ in the Otto cycle PV diagram

An exhaust valve opens as the piston reaches its bottom position.

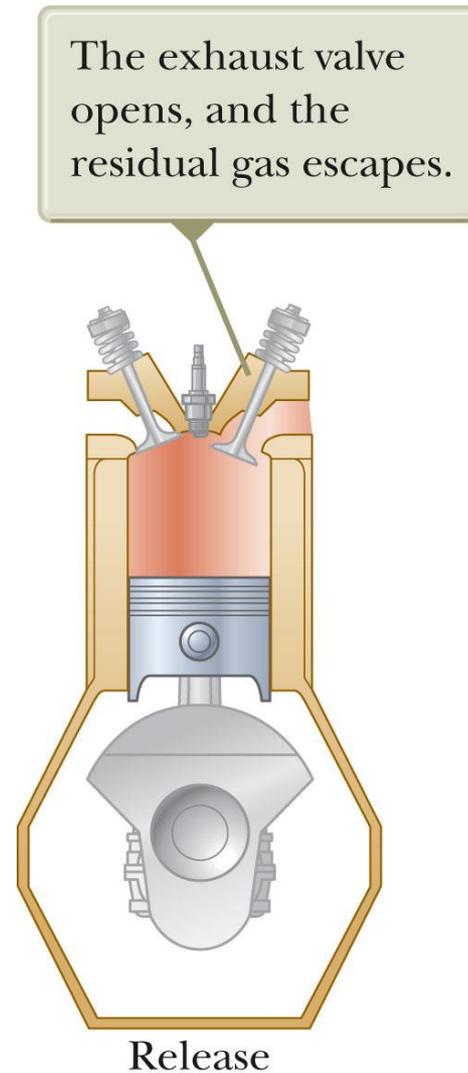
The pressure drops suddenly.

The volume is approximately constant.

- So no work is done

Energy is expelled from the interior of the cylinder.

- It continues to be expelled during the next process.



Gasoline Engine – Exhaust Stroke

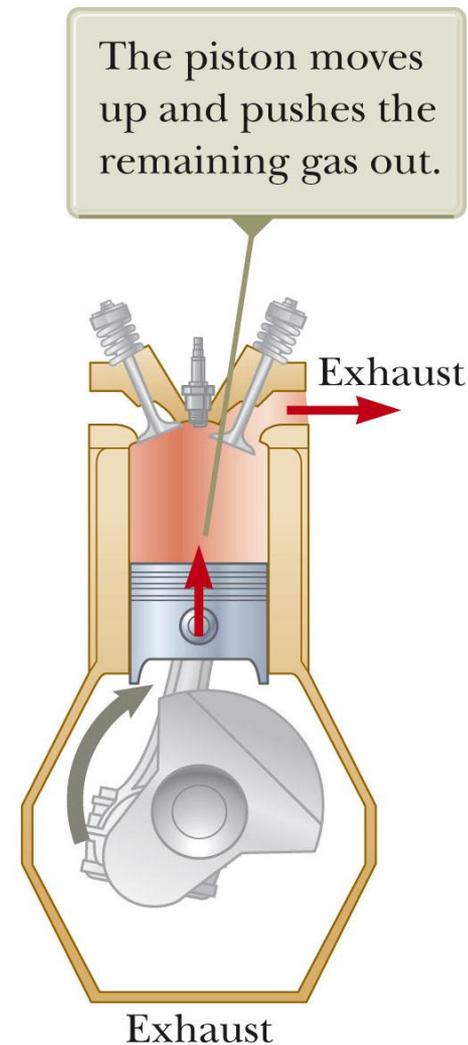
In the exhaust stroke, the piston moves upward while the exhaust valve remains open.

Residual gases are expelled to the atmosphere

The volume decreases from V_1 to V_2 .

$A \rightarrow O$ in the Otto cycle PV diagram

The cycle then repeats



Otto Cycle Efficiency

If the air-fuel mixture is assumed to be an ideal gas, then the efficiency of the Otto cycle is

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

γ is the ratio of the molar specific heats.

V_1 / V_2 is called the compression ratio.

Otto Cycle Efficiency, cont

Typical values:

- Compression ratio of 8
- $\gamma = 1.4$
- $e = 56\%$

Efficiencies of real engines are 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.

Entropy

Entropy, S , is a state variable related to the second law of thermodynamics.

- Do not confuse entropy with energy
 - They are very different concepts

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

A microstate is a particular configuration of the individual constituents of the system.

A macrostate is a description of the conditions from a macroscopic point of view.

- It makes use of macroscopic variables such as pressure, density, and temperature for gases.

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.

Microstates vs. Macrostates, Probabilities

The probability of a system moving in time 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.

The more microstates that belong to a particular macrostate, the higher the probability that macrostate will occur.

Entropy and Heat

The original formulation of entropy dealt with the transfer of energy by heat in a reversible process.

Let dQ_r be the amount of energy transferred by heat when a system follows a reversible path.

The change in entropy, dS is

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

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.

More About Change in Entropy

dQ_r is measured along a reversible path, even if the system may have followed an irreversible path.

The meaningful quantity is the change in entropy and not the entropy itself.

For a finite process, T is generally not constant during process.

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

The change in entropy of a system going 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 rather than the actual path, as long as the initial and final states are the same.

ΔS for a Reversible Cycle

$\Delta S = 0$ for any reversible cycle

In general,

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

- This integral symbol indicates the integral is over a closed path.

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 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 and the Second Law

Entropy is a measure of disorder.

The entropy of the Universe increases in all real processes.

- This is another statement of the second law of thermodynamics.
 - It is equivalent to the Kelvin-Planck and Clausius statements.

Entropy Changes in Non-isolated Systems

The increase in entropy described in the second law is that of the system and its surroundings.

When a system and its surroundings interact in an irreversible process, the increase in entropy of one is greater than the decrease in entropy of the other.

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.

ΔS in Thermal Conduction

The cold reservoir absorbs energy Q and its entropy changes by Q/T_c .

At the same time, the hot reservoir loses Q and its entropy changes by $-Q/T_h$.

Since $T_h > T_c$, the increase in entropy in the cold reservoir is greater than the decrease in entropy in the hot reservoir.

Therefore, $\Delta S_U = Q/T_c + (-Q/T_h) > 0$

- For the system and the Universe

ΔS in a Free Expansion

Consider an adiabatic free expansion.

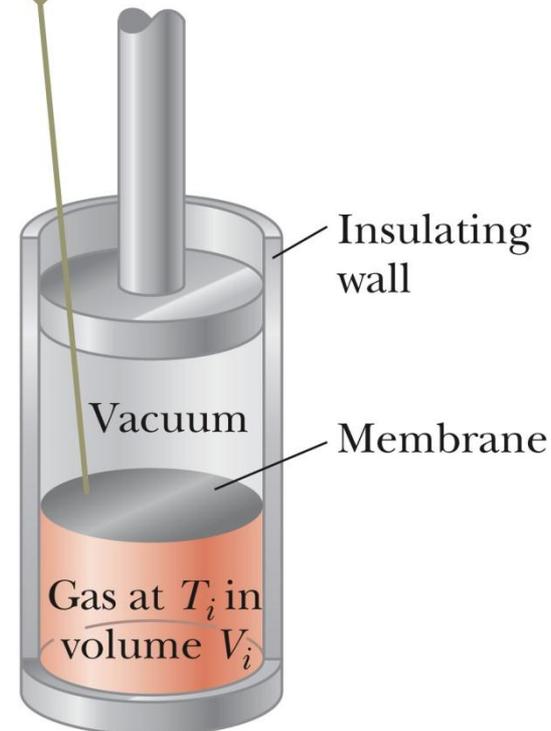
This process is irreversible since the gas would not spontaneously crowd into half the volume after filling the entire volume.

$Q = 0$ but we need to find Q_r

Choose an isothermal, reversible expansion in which the gas pushes slowly against the piston while energy enters from a reservoir to keep T constant.

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

When the membrane is ruptured, the gas will expand freely and irreversibly into the full volume.



ΔS in Free Expansion, cont

For an isothermal process, this becomes

$$\Delta S = nr \ln \frac{V_f}{V_i}$$

Since $V_f > V_i$, ΔS is positive

This indicates that both the entropy and the disorder of the gas increase as a result of the irreversible adiabatic expansion .

Entropy on a Microscopic Scale

We can treat entropy from a microscopic viewpoint through statistical analysis of molecular motions.

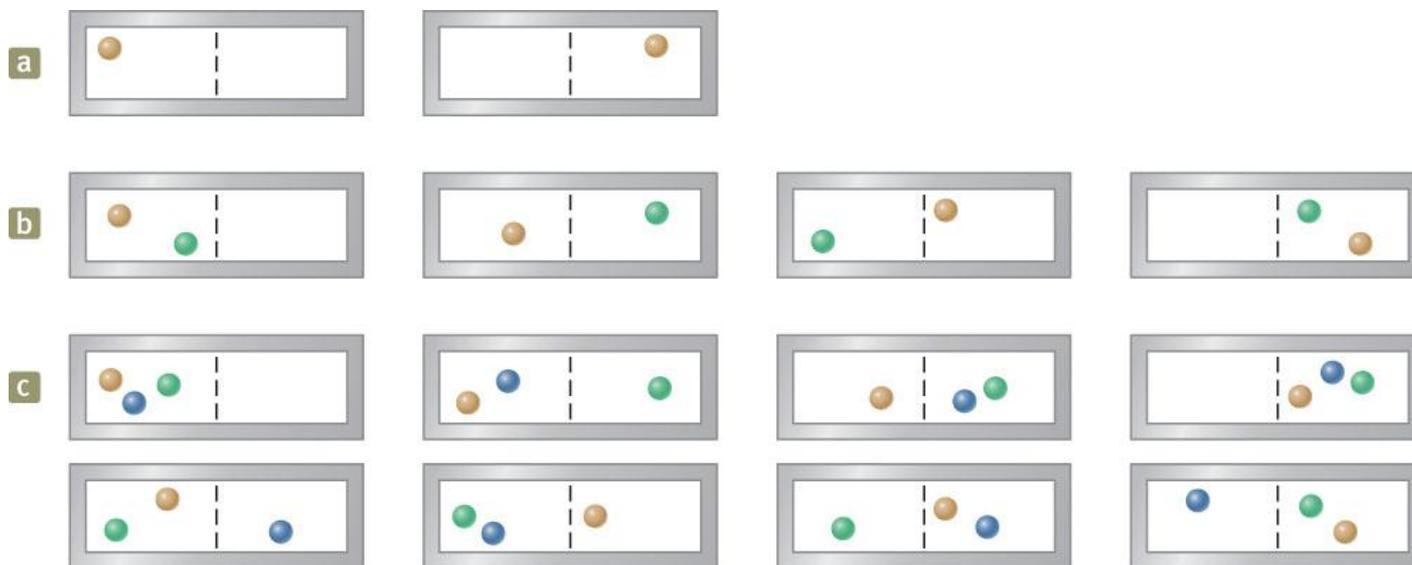
A connection between entropy and the number of microstates (W) for a given macrostate is

$$S = k_B \ln W$$

- 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.

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 Extended

Consider 100 molecules in the container.

The probability of separating 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, Results

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, RGGR, GRGR, GGRR | 6 |
| 3G, 1R | GGGR, GGRG, GRGG, RGGG | 4 |
| All G | GGGG | 1 |

The most likely, and most disordered, macrostate corresponds to the largest number of microstates.

The least likely, and most ordered, macrostate corresponds to the smallest number of microstates.