# Lecture 13

## Heat Engines

- Thermodynamic processes and entropy
- Thermodynamic cycles
- Extracting work from heat
  - How do we define engine efficiency?
  - Carnot cycle: the best possible efficiency

Reading for this Lecture:
Elements Ch 4D-E, 10A-B

# Review

## Entropy in Macroscopic Systems

Traditional thermodynamic entropy: $S = k \ln\Omega = k\sigma$

We want to calculate S from macrostate information (p, V, T, U, N, *etc.*)
Start with the definition of temperature in terms of entropy:

$$\boxed{\frac{1}{kT} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_{V,N}, \text{ or } \frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{V,N}}$$

The entropy changes when T changes: (We're keeping V and N fixed.)

$$dS = \frac{dU}{T} = \frac{C_V dT}{T} \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T}$$

If $C_V$ is constant:

$$= C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \ln\left(\frac{T_2}{T_1}\right)$$

# Entropy in Quasi-static Heat Flow

When V is constant: $dS \equiv dU/T = dQ/T$ ⇐ W = 0, so dU = dQ

In fact, $dS = dQ/T$ during any reversible (quasi-static) process, even if V changes.

The reason: In a reversible process, $S_{tot}$ (system plus environment) doesn't change:

$$0 = dS_{sys} + dS_E$$

$\Delta S_{tot} = 0$ if process is reversible.

$$= dS_{sys} + \frac{dU_E}{T}$$

The reservoir is supplying (or absorbing) heat.

$$= dS_{sys} - \frac{dQ}{T}$$

The reservoir's energy gain is the system's heat loss. That's how they interact.

$$\boxed{dS = \frac{dQ}{T}, \text{ or } \Delta S = \int_{init}^{final} \frac{dQ}{T}}$$

for any reversible process

# $\Delta S$ in Isothermal Processes

Suppose V & p change but T doesn't.

Work is done ($dW_{by} = pdV$).
Heat must enter to keep T constant: $dQ = dU + dW_{by}$.

So:

$$dS = \frac{dQ}{T} = \frac{dU + dW_{by}}{T} = \frac{dU + pdV}{T}$$

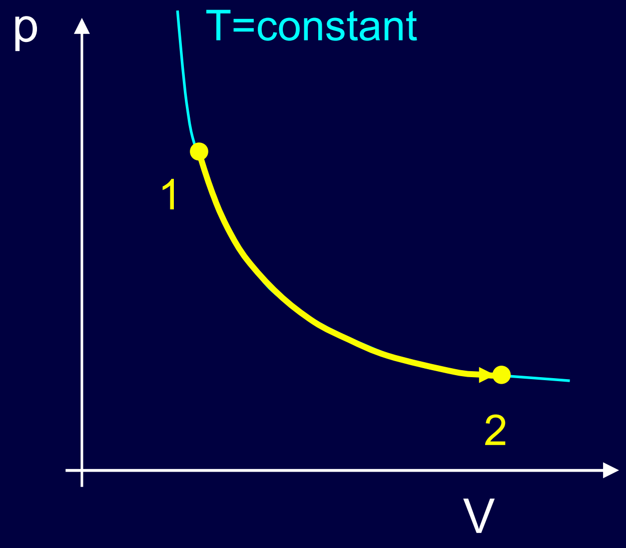
Remember: This holds for quasi-static processes, in which the system remains near thermal equilibrium at all times.

Special case, ideal gas:

For an ideal gas, if $dT = 0$, then $dU = 0$.

$$dS = \frac{pdV}{T} = \frac{NkTdV}{VT} = \frac{NkdV}{V}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{NkdV}{V} = Nk \ln\left(\frac{V_2}{V_1}\right)$$



# ACT 1

1) The entropy of a gas increases during a quasi-static isothermal expansion.
What happens to the entropy of the environment?

a) $\Delta S_{env} < 0$　　b) $\Delta S_{env} = 0$　　c) $\Delta S_{env} > 0$

2) Consider instead the 'free' expansion (*i.e.*, not quasi-static) of a gas.
What happens to the total entropy during this process?

a) $\Delta S_{tot} < 0$　　b) $\Delta S_{tot} = 0$　　c) $\Delta S_{tot} > 0$

Remove the barrier

# Solution

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What happens to the entropy of the environment?

$\boxed{\text{a) } \Delta S_{env} < 0}$ b) $\Delta S_{env} = 0$ c) $\Delta S_{env} > 0$

Energy (heat) leaves the environment, so its entropy decreases.
In fact, since the environment and gas have the same T,
the two entropy changes cancel: $\Delta S_{tot} = 0$. This is a reversible process.

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What happens to the total entropy during this process?

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ $\boxed{\text{c) } \Delta S_{tot} > 0}$

There is no work or heat flow, so $U_{gas}$ is constant. $\Rightarrow$ T is constant.
However, because the volume increases, so does the number of available states,
and therefore $S_{gas}$ increases. Nothing is happening to the environment.
Therefore $\Delta S_{tot} > 0$. This is not a reversible process.

# Quasi-static Adiabatic Processes

$Q = 0$ (definition of an adiabatic process)

V and T both change as the applied pressure changes.

For example, if p increases (compress the system):

- V decreases, and the associated S also decreases.
- T increases, and the associated S also increases.

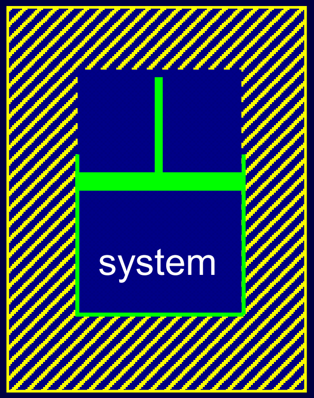
These two effects must exactly cancel !!

Why? Because:

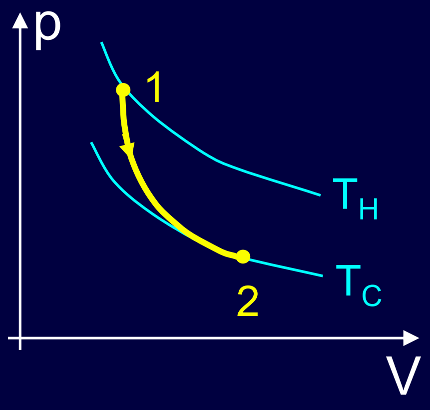
- This is a reversible process, so $S_{tot} = 0$.
- No other entropy is changing.
  ($Q = 0$, and $W_{by}$ just moves the piston.)

So, in a quasi-static adiabatic process, $\boxed{\Delta S = 0.}$

Note: We did not assume that the system is an ideal gas. This is a general result.



Insulated walls

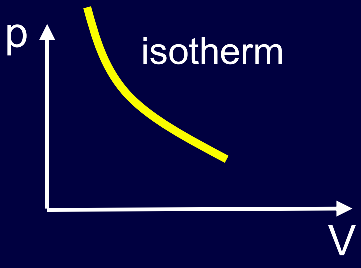


# Irreversible Processes

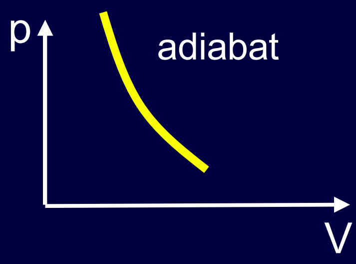
Entropy-increasing processes are irreversible,
because the reverse processes would reduce entropy.
Examples:

- Free-expansion (actually, any particle flow between regions of different density)
- Heat flow between two systems with different temperatures.

Consider the four processes of interest here:
Isothermal: Heat flow but no T difference. Reversible
Adiabatic: $Q = 0$. No heat flow at all. Reversible
Isochoric & Isobaric: Heat flow between different T's. Irreversible
(Assuming that there are only two reservoirs.)



reversible



reversible

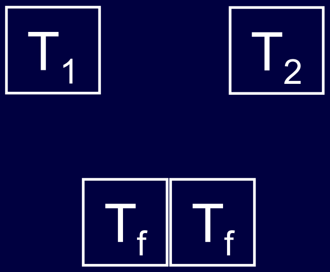
irreversible

irreversible

# ACT 2

Two blocks, each with heat capacity* C = 1 J/K are initially at different temperatures, $T_1 = 250$ K, $T_2 = 350$ K. They are then placed into contact, and eventually reach a final temperature of 300 K. (Why?) What can you say about the total change in entropy $\Delta S_{tot}$?

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ c) $\Delta S_{tot} > 0$



$T_1 = 250$K

$T_2 = 350$K

$T_f = 300$ K

Two masses each
with heat capacity
C = 1J/K*

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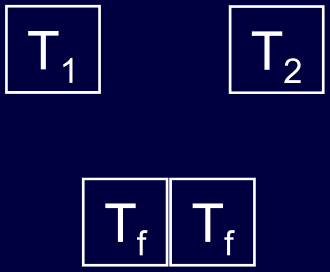
***For a solid, $C = C_V = C_p$, to good approximation, since $\Delta V \approx 0$.**

# Solution

Two blocks, each with heat capacity* $C = 1$ J/K are initially at different temperatures, $T_1 = 250$ K, $T_2 = 350$ K. They are then placed into contact, and eventually reach a final temperature of 300 K. (Why?) What can you say about the total change in entropy $\Delta S_{tot}$?



$T_1 = 250$K

$T_2 = 350$K

$T_f = 300$ K

Two masses each with heat capacity $C = 1$J/K*

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ $\boxed{\text{c) } \Delta S_{tot} > 0}$

This is an irreversible process, so there must be a net increase in entropy.
Let's calculate $\Delta S$:

$$\begin{aligned}\Delta S_{tot} &= C\ln\left(\frac{T_f}{T_1}\right) + C\ln\left(\frac{T_f}{T_2}\right)\\ &= C\ln\left(\frac{300}{250}\right) + C\ln\left(\frac{300}{350}\right)\\ &= C\ln\left(\frac{300^2}{250\times 350}\right) = (0.028)C = 0.028\text{ J/K}\end{aligned}$$

The positive term is slightly bigger than the negative term.

*For a solid, $C = C_V = C_p$, to good approximation, because $\Delta V \approx 0$.

# A Review of Some Thermodynamic Processes of an Ideal Gas

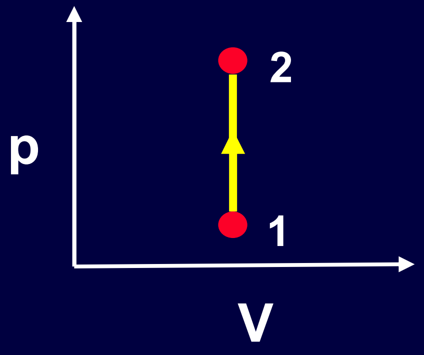
We will assume ideal gases in our treatment of heat engines, because that simplifies the calculations.

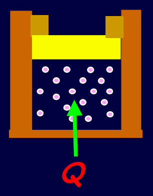
Isochoric (constant volume)

$$W_{by} = \int p\,dV = 0$$

$$\Delta U = \alpha Nk\Delta T = \alpha V\Delta p$$

$$Q = \Delta U$$





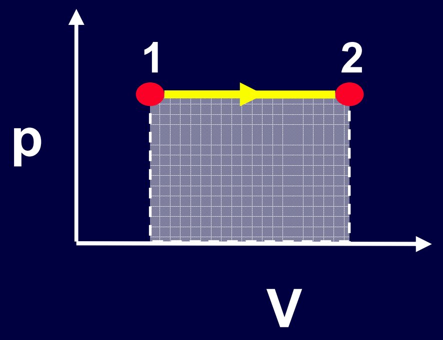
Temperature changes

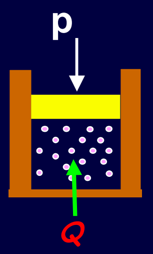
Isobaric (constant pressure)

$$W_{by} = \int p\,dV = p\Delta V$$

$$\Delta U = \alpha Nk\Delta T = \alpha p\Delta V$$

$$Q = \Delta U + W_{by} = (\alpha + 1)\,p\Delta V$$





Temperature and volume change

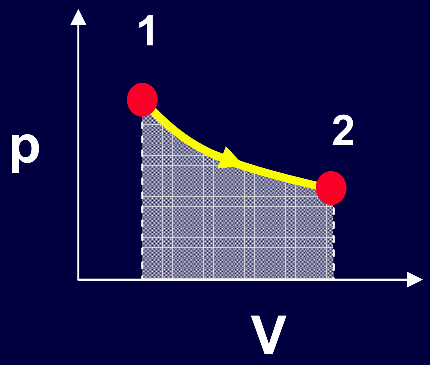
# Review (2)

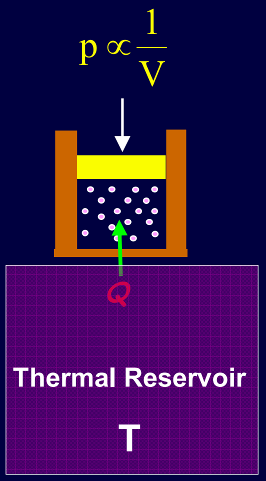
## Isothermal (constant temperature)

$$W_{by} = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} \frac{NkT}{V}\,dV = NkT\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U = 0$$

$$Q = W_{by}$$





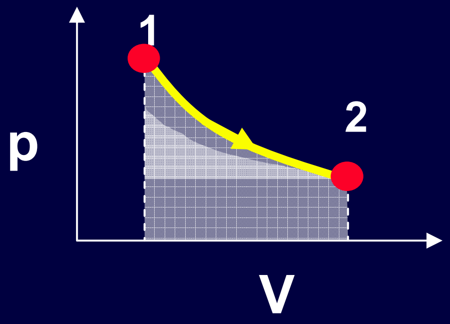
Volume and pressure change

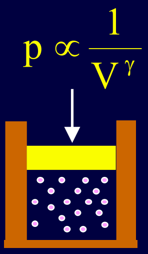
## Adiabatic (no heat flow)

$$W_{by} = -\Delta U$$

$$\Delta U = \alpha Nk\left(T_2 - T_1\right) = \alpha\left(p_2V_2 - p_1V_1\right)$$

$$Q = 0$$



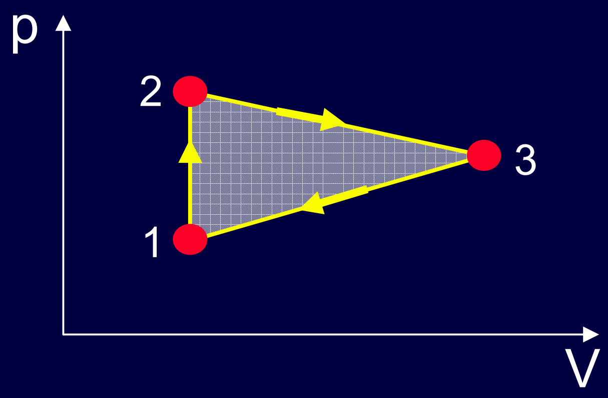


Volume, pressure and temperature change

# Closed Thermodynamic Cycles

Closed cycles will form the basis of our heat engine discussion.

A closed cycle is one in which the system returns to the initial state. (same *p*, *V*, and *T*) For example:



- U is a state function. Therefore: $\Delta U = 0$
- The net work is the enclosed area. $W = \oint p dV \neq 0$
- Energy is conserved ($1^{st}$ Law): $Q = W \neq 0$

This is the reason that neither W nor Q is a state function. It makes no sense to talk about a state having a certain amount of W.

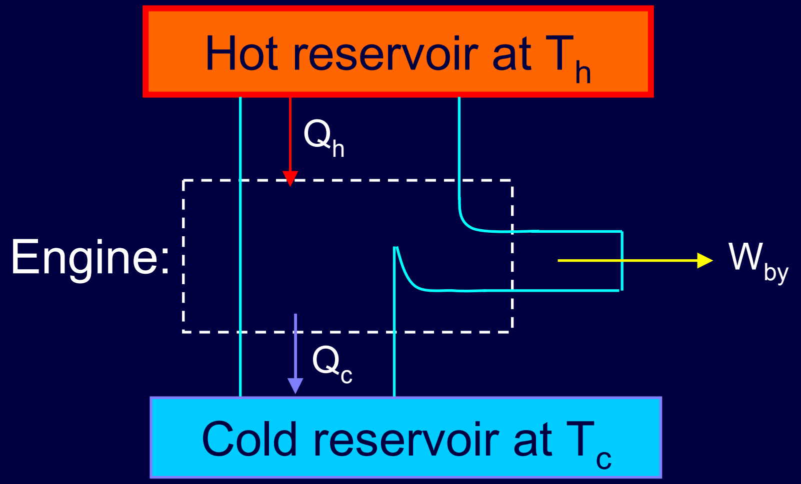
Though of course we could use *any* curves to make a closed cycle, here we will consider isochoric, isobaric, isothermal, and adiabatic processes.

# Introduction to Heat Engines

One of the primary applications of thermodynamics is to Turn heat into work.

The standard heat engine works on a cyclic process:

1) extract heat from a hot reservoir,
2) perform work, using some of the extracted heat,
3) dump unused heat into a cold reservoir (often the environment).
4) repeat over and over.   We represent this process with a diagram:



Hot reservoir at $T_h$

$Q_h$

Engine:

$W_{by}$

$Q_c$

Cold reservoir at $T_c$

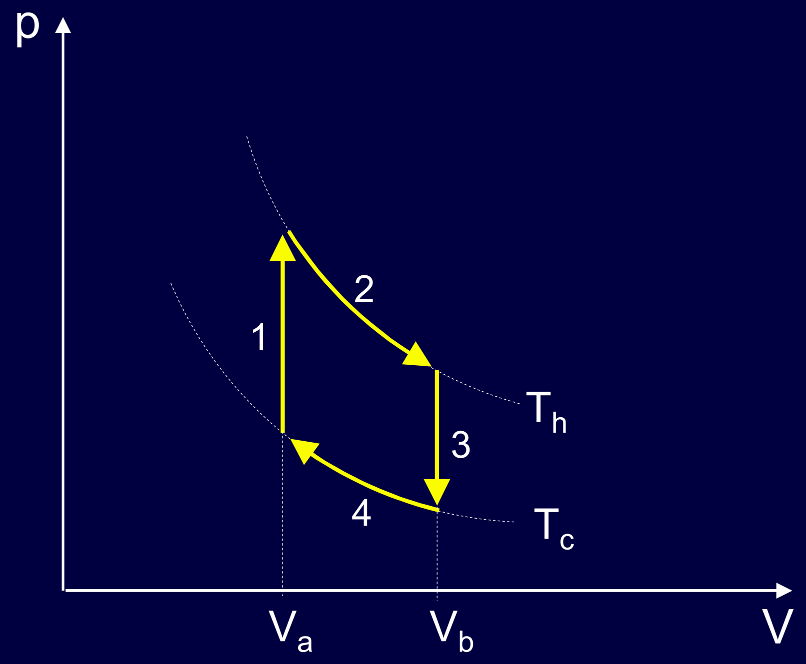
A “reservoir” is a large body whose temperature doesn’t change when it absorbs or gives up heat

For heat engines we will define $Q_h$ , $Q_c$ , and $W_{by}$ as positive.

Energy is conserved: $Q_h = Q_c + W_{by}$

# A Simple Heat Engine:

## the Stirling Cycle

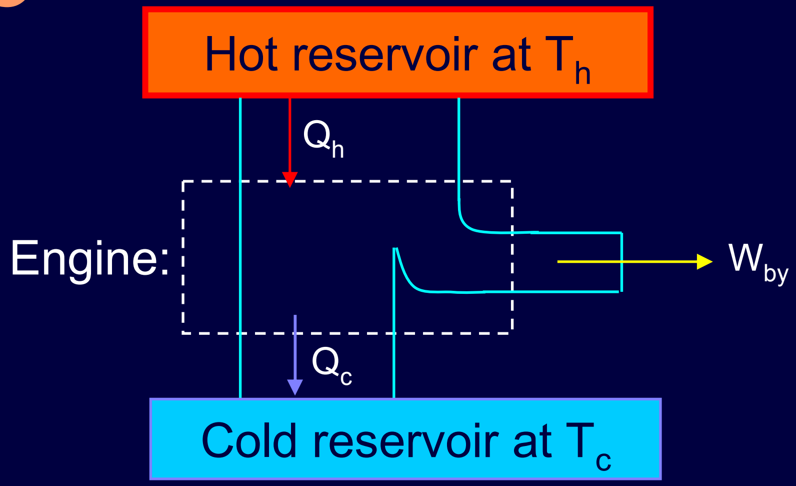


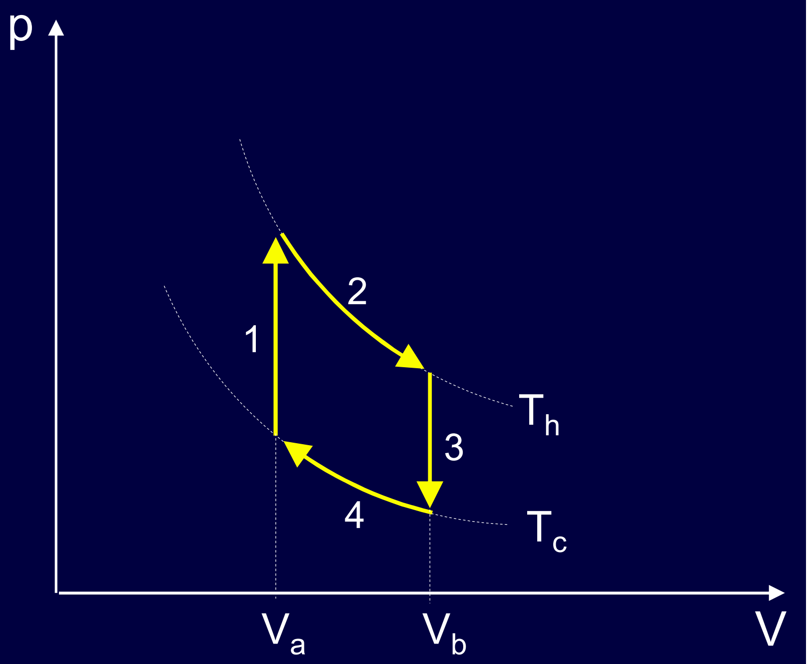
Two reservoirs: $T_h$ and $T_c$.
Four processes: Two isotherms and two isochors
The net work during one cycle: The area of the “parallelogram”.

# Act 3

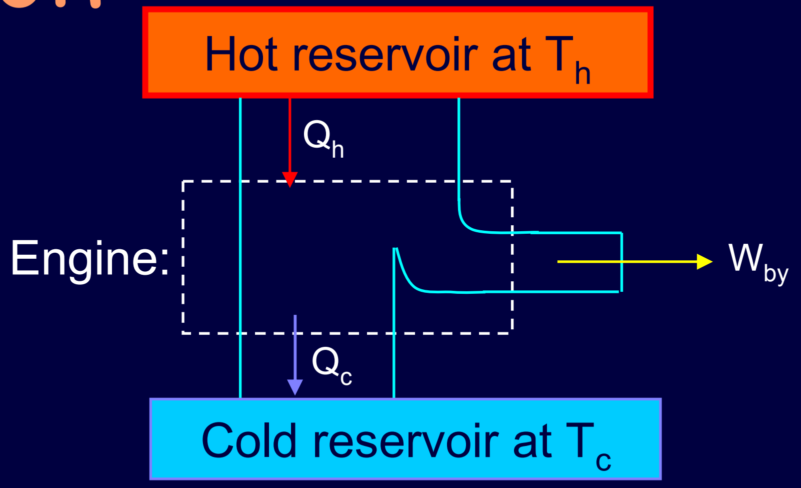
Which processes in a Stirling cycle correspond to $Q_h$ in the heat flow diagram?

a) 1
b) 2
c) 1 and 2
d) 3
e) 3 and 4





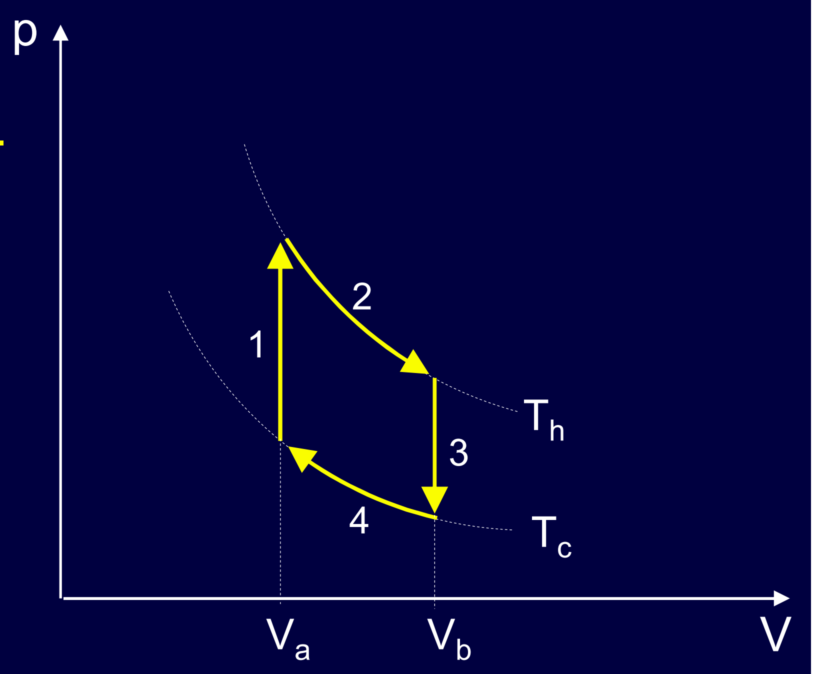
# Solution



Which processes in a Stirling cycle correspond to $Q_h$ in the heat flow diagram?

a) 1
b) 2
[✓ c) 1 and 2]
d) 3
e) 3 and 4

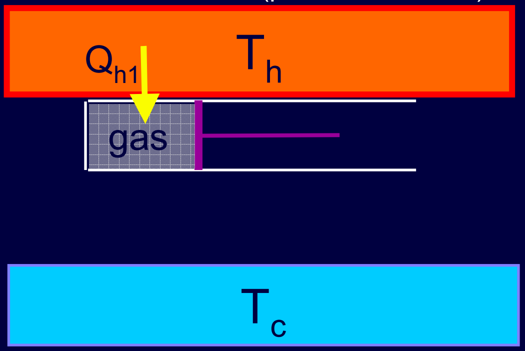
Process 1 is obvious, since we're heating the gas. In the isothermal expansion (process 2), although the temperature is kept constant we still have to put heat in to do the work from the expansion.



# The Stirling Cycle (2)

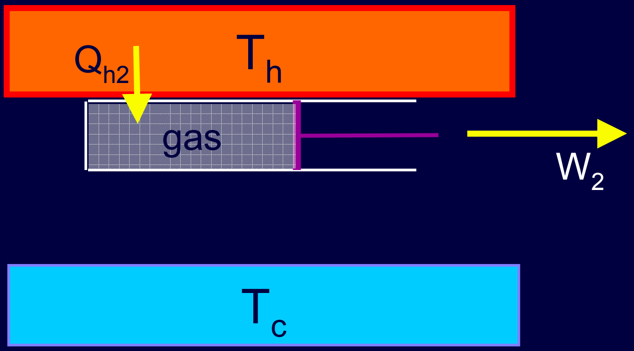
## 1) Isochoric

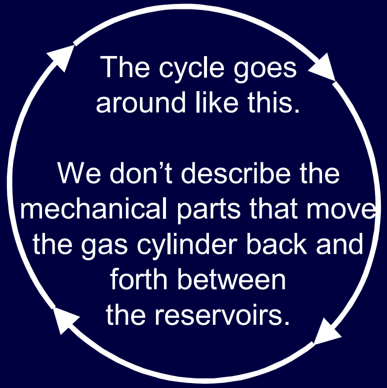
Gas temperature increases
at constant volume (piston can't move)



## 2) Isothermal

Gas expands at constant $T_h$



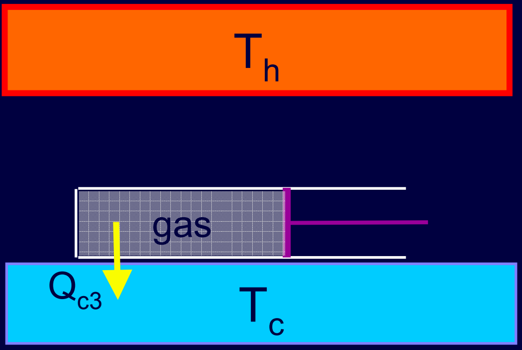


The cycle goes
around like this.

We don't describe the
mechanical parts that move
the gas cylinder back and
forth between
the reservoirs.

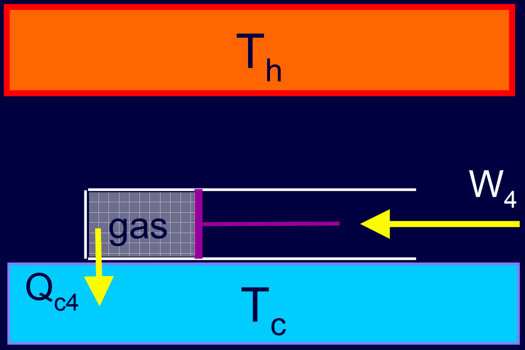
## 3) Isochoric

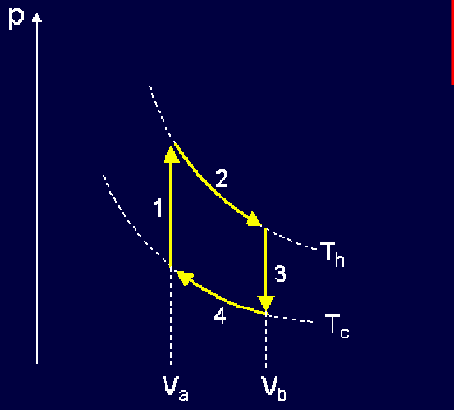
Gas temperature decreases
at constant volume (piston can't move)



## 4) Isothermal

Gas is compressed at constant $T_c$





# How Does this Engine Do Work?

Look at the two isothermal processes (2 and 4) on the previous slide
Process 2: expanding gas does $W_2$ on the piston, as it expands from $V_a$ to $V_b$.
Process 4: contracting gas is done $W_4$ by the piston, as it contracts from $V_b$ to $V_a$.
If $W_2 > W_4$, the net work is positive.
This is true, because the contracting gas is colder (⇒lower pressure).

During one cycle:

- The hot reservoir has lost some energy ($Q_h=Q_{h1}+Q_{h2}$).
- The cold reservoir has gained some energy ($Q_c=Q_{c3}+Q_{c4}$).
- The engine (the gas cylinder) has neither gained nor lost energy.

The energy to do work comes from the hot reservoir, not from the engine itself.

The net work done by the engine is:

$$\boxed{W_{by} = W_2 - W_4 = Q_h - Q_c = Q_{h2} - Q_{c4}}$$

Not all of the energy taken from the hot reservoir becomes useful work.
Some is lost into the cold reservoir. We would like to make $Q_c$ as small as possible.

# Heat Engine Efficiency

We pay for the heat input, $Q_H$, so:

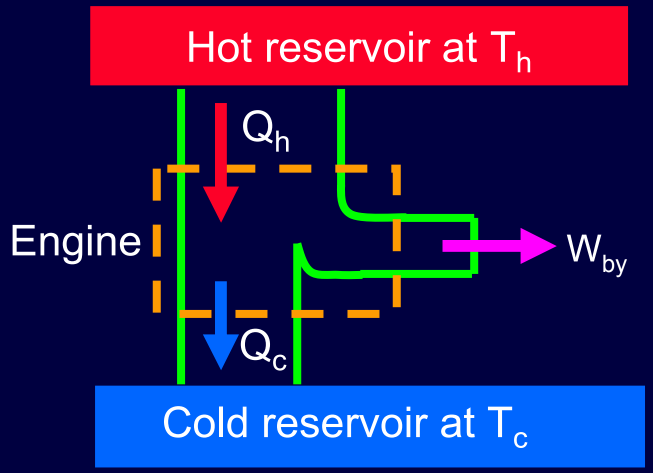
Define the efficiency

$$\varepsilon \equiv \frac{\text{work done by the engine}}{\text{heat extracted from reservoir}} = \frac{\text{results}}{\text{cost}}$$

$$\boxed{\varepsilon \equiv \frac{W_{by}}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}}$$

Valid for all heat engines.
(Conservation of energy)

Cartoon picture of a heat engine:



Hot reservoir at $T_h$

$Q_h$

Engine

$W_{by}$

$Q_c$

Cold reservoir at $T_c$

Remember:

We define $Q_h$ and $Q_c$ as *positive*.
The arrows define direction of flow.

What's the best we can do?

The Second Law will tell us.

# The 2nd Law Sets the Maximum Efficiency (1)

$$\boxed{\Delta S_{tot} \geq 0}$$

How to calculate $\Delta S_{tot}$?

Over one cycle:

$$\Delta S_{tot} = \underset{= 0}{\cancel{\Delta S_{engine}}} + \Delta S_{hot} + \Delta S_{cold}$$

Remember:

From the definition of T

$Q_h$ is the heat taken from the hot reservoir, so $\Delta S_{hot} = -Q_h/T_h$.

$Q_c$ is the heat added to the cold reservoir, so $\Delta S_{cold} = +Q_c/T_c$.

$$\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0$$

2nd Law

$$\Rightarrow \boxed{\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}}$$

$Q_c$ cannot be zero.
Some energy is always lost.

# The 2nd Law Sets the Maximum Efficiency (2)

$$efficiency = \varepsilon \equiv \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$$ from the 2nd Law

$$\Rightarrow \boxed{\varepsilon \leq 1 - \frac{T_C}{T_H}}$$

**This is a universal law !!** (equivalent to the 2nd law)

It is valid for any procedure that converts thermal energy into work.
We did not assume any special properties (*e.g.*, ideal gas)
of the material in the derivation.

The maximum possible efficiency, $\varepsilon_{Carnot} = 1 - T_c/T_h$, is called the Carnot efficiency.
The statement that heat engines have a maximum efficiency was the first
expression of the 2nd law, by Sadi Carnot in 1824.

# How Efficient Can an Engine be?

Consider an engine that uses steam ($T_h$ = 100° C) as the hot reservoir and ice ($T_c$ = 0° C) as the cold reservoir. How efficient can this engine be?

The Carnot efficiency is $\varepsilon_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{273\text{ K}}{373\text{ K}} = 0.27$

Therefore, an engine that operates between these two temperatures can, at best, turn only 27% of the steam's heat energy into useful work.

Question: How might we design an engine that has higher efficiency?

Answer: By increasing $T_h$. (That's more practical than lowering $T_c$.)

Electrical power plants and race cars obtain better performance by operating at a much higher $T_h$.

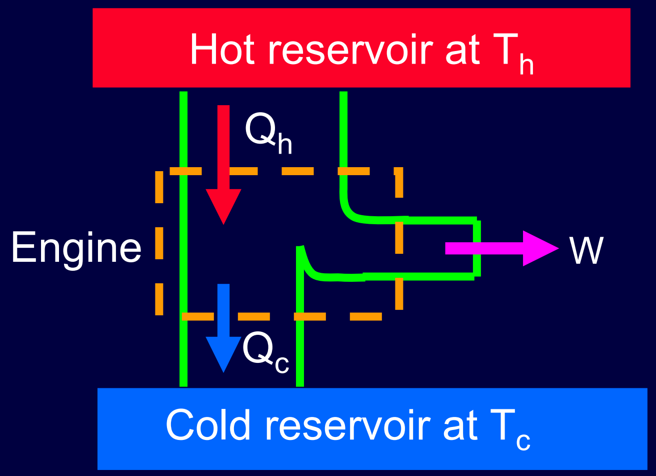
# When Is $\varepsilon$ Less than $\varepsilon_{Carnot}$?

We can write the efficiency loss in terms of the change of total entropy:

$$\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = -\frac{Q_H}{T_H} + \frac{Q_H - W}{T_C}$$

$$\Rightarrow W = Q_H\left(1-\frac{T_C}{T_H}\right) - T_C\Delta S_{tot}$$

$$\varepsilon \equiv \frac{W}{Q_H} = \underset{\varepsilon_{Carnot}}{\left(1-\frac{T_C}{T_H}\right)} - \frac{T_C\Delta S_{tot}}{Q_H}$$



Lesson: Avoid irreversible processes.
(ones that increase $S_{tot}$).

- direct heat flow from hot to cold
- free expansion (far from equilibrium)
- sliding friction

# Next Time

Carnot Engines

Refrigerators

Heat Pumps