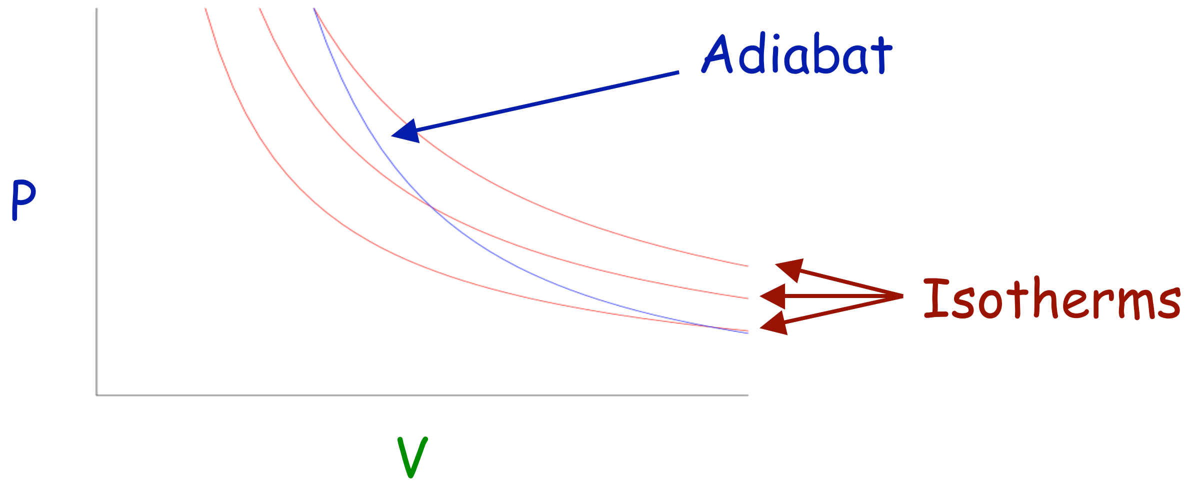
Adiabatic Expansion ($\Delta Q = 0$)

Occurs if:
- change is made sufficiently quickly
- and/or with good thermal isolation.

Governing formula:

$$PV^{\gamma} = \text{constant}$$

where $\gamma = C_P/C_V$



Because PV/T is constant (ideal gas):

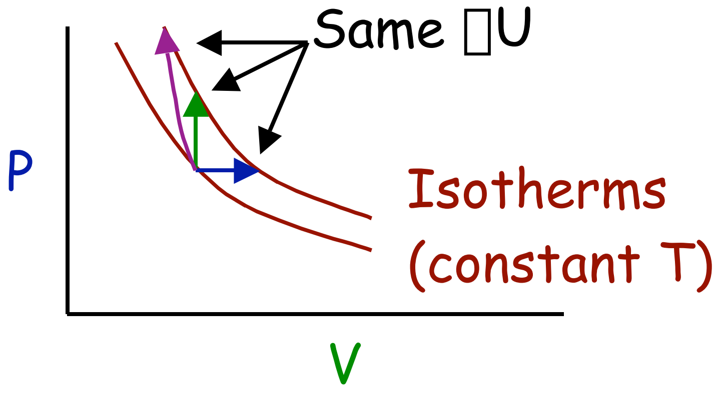
$$V^{\gamma-1}T = \text{constant} \qquad \text{(for adiabatic)}$$

Proof of $PV^{\square}$=constant

(for adiabatic process)

1) Adiabatic: $dQ = 0 = dU + dW$
$$= dU + PdV$$

2) U only depends on T:



$dU = n\,C_V\,dT$ (derived for constant volume, but true in general)

3) Ideal gas: $T = PV/(nR)$
$$dT = [(dP)V + P(dV)]/(nR)$$

Plug into 2): $dU = (C_V/R)[VdP + PdV]$

Plug into 1): $0 = (C_V/R)[VdP + PdV] + PdV$

Rearrange:

$$(dP/P) = -\,(C_V+R)/C_V\,(dV/V)$$
$$= -\,\square\,(dV/V)$$

where $\square = (C_V+R)/C_V = C_P/C_V$

Integrate both sides:

$$\ln(P) = -\,\square\,\ln(V) + \text{constant}$$

or

$$\ln(PV^{\square}) = \text{constant}$$

or

$$PV^{\square} = \text{constant}$$

<u>QED</u>

Irreversible Processes

Examples:

- Block sliding on table comes to rest due to friction: KE converted to heat.
- Heat flows from hot object to cold object.
- Air flows into an evacuated chamber.

Reverse process allowed by energy conservation, yet it does not occur.

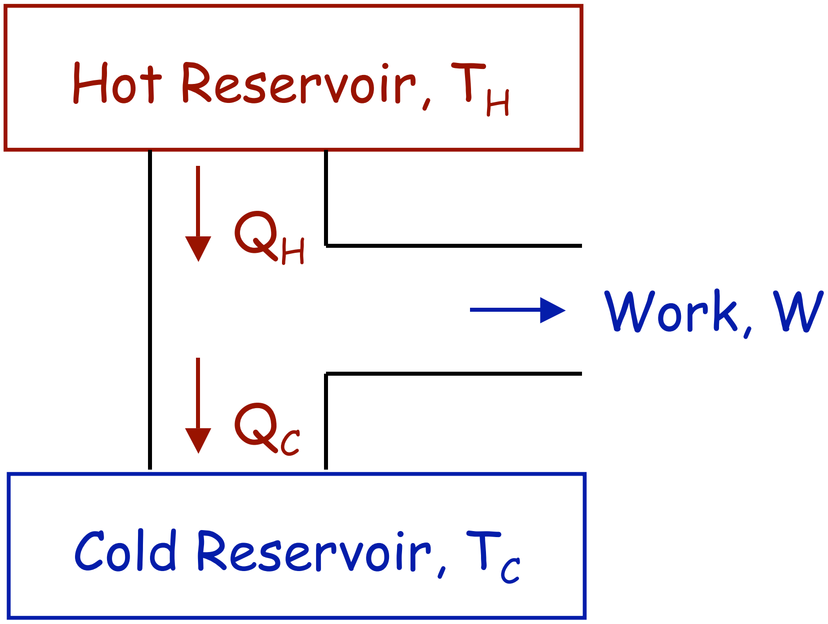
→ arrow of time

Why?

2nd Law of Thermodynamics (entropy)

Heat Engines

Heat engine: a cyclic device designed to convert heat into work.



Hot Reservoir, T_H

Q_H

Work, W

Q_C

Cold Reservoir, T_C

2nd Law of TD (Kelvin form):

It is impossible for a cyclic process to remove thermal energy from a system at a single temperature and convert it to mechanical work without changing the system or surroundings in some other way.

For a cycling engine $\square U = 0$,

So work done is equal to
heat in minus heat out:

$$W = Q_H - Q_C$$

Define the Efficiency of the engine:

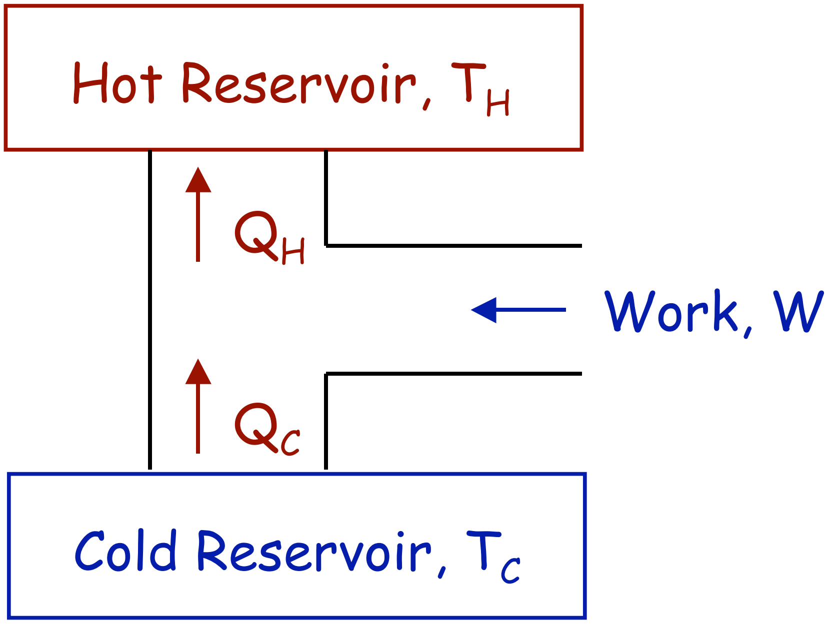
$$\square = W/Q_H = (Q_H - Q_C)/Q_H = 1 - Q_C/Q_H$$

Corollary of the 2nd Law of TD:

> It is impossible to make a heat engine whose efficiency is 100%.

Refrigerators

Refrigerator: a cyclic device which uses work to transfer heat from a cold reservoir to hot reservoir.



Hot Reservoir, T_H

Q_H

Work, W

Q_C

Cold Reservoir, T_C

2nd Law of TD (Clausius form):

It is impossible for a cyclic process to have no other effect than to transfer thermal energy from a cold object to a hot object.

A measure of refrigerator performance is the ratio:

$$K = Q_C / W$$

"Coefficient of performance"
(The larger the better.)

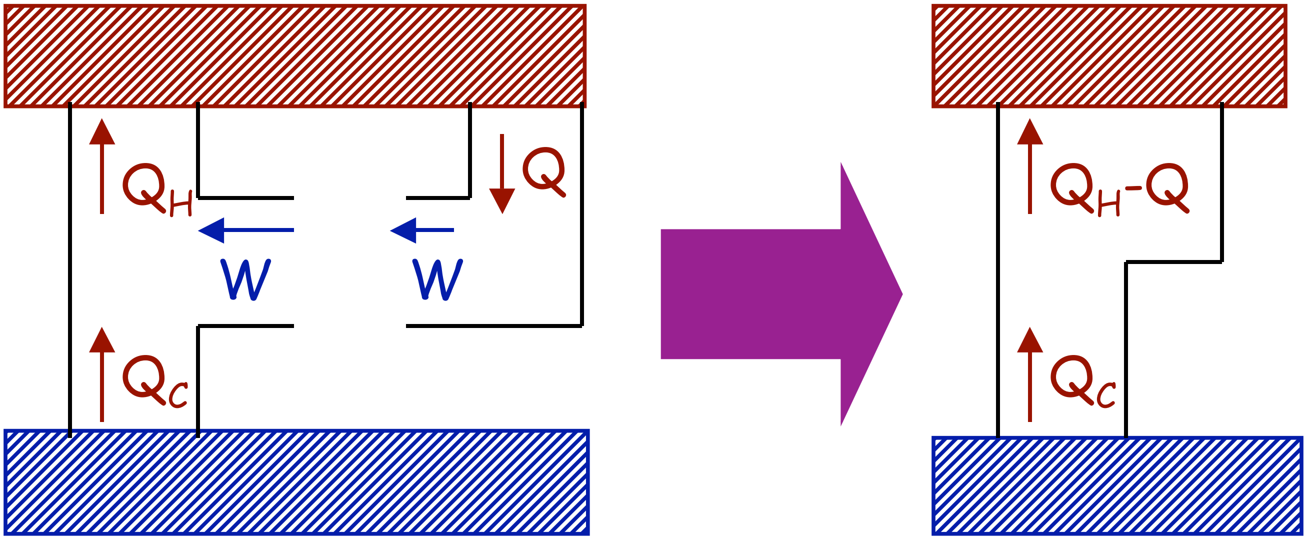
Corollary of the 2nd Law of TD:

It is impossible for the coefficient of performance to be infinite.

Equivalence of Kelvin and Clausius Statements

For example:

You could combine an ordinary refrigerator with a perfect engine (impossible)...



to obtain a perfect refrigerator (also impossible).

The Carnot Engine

2nd Law of TD says:
100% efficient Heat Engine is impossible.

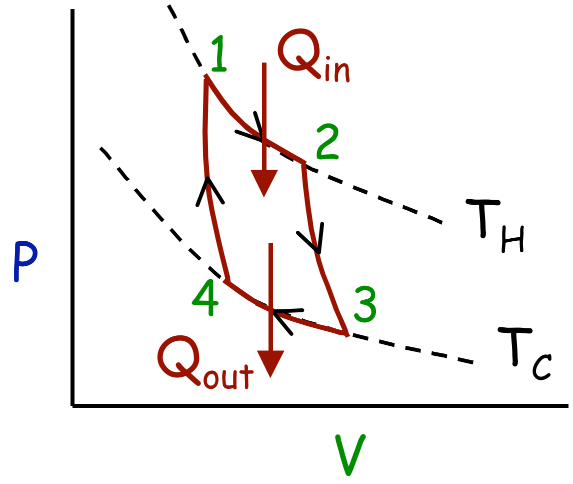
What is the maximum possible efficiency?

No engine working between 2 heat reservoirs can be more efficient than an ideal engine acting in a Carnot cycle.
(Sadi Carnot, 1824)

Properties of the Carnot cycle:

1. It is reversible: no friction or other dissipative forces.
2. Heat conduction only occurs isothermally at the temperatures of the two reservoirs.

Derivation of Carnot Efficiency

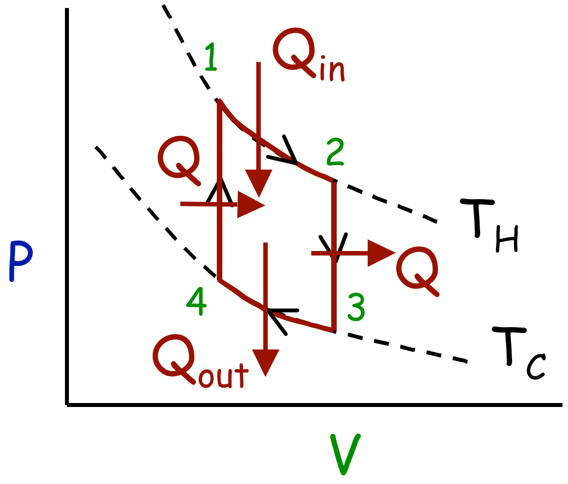


1-2: Isothermal (Q_{in} at T_H)
2-3: Adiabatic expansion
3-4: Isothermal (Q_{out} at T_C)
4-1: Adiabatic compression

$$\boxed{\square = 1 - T_C/T_H}$$

The Stirling Engine

Invented by Robert Stirling in 1816.
Its operating cycle is:



The two temperature-changing steps are performed at constant volume; A heat transfer occurs at these steps also.

$$\eta_{Stirling} < \eta_{Carnot}$$

Entropy

Consider a reversible process for an ideal gas:

$$dQ = dU + dW = n\,C_V\,dT + P\,dV$$

$$= n\,C_V\,dT + n\,R\,T\,(dV/V)$$

We cannot write a general integral of this, because dW (and therefore dQ) depends on the functional form of $T(V)$ (i.e. the path). However, if we divide by T:

$$dQ/T = n\,C_V\,(dT/T) + n\,R\,(dV/V)$$

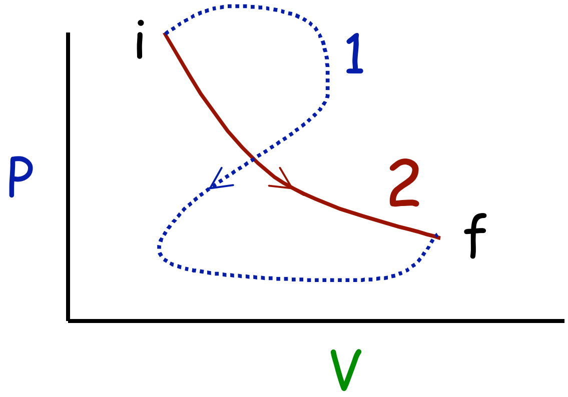
is integrable independent of path.

This suggests a new state function, Entropy, defined by:

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

(Valid for any system)

In general, the process may be too complicated to do the integral (particularly if irreversible process):



However, because entropy is a state function, we can choose any convenient path between i and f to integrate.

For an ideal gas:

$$\Delta S = n\, C_V \ln(T_f/T_i) + n\, R \ln(V_f/V_i)$$

This only depends on the initial state (V_i,T_i) and final state (V_f,T_f), but not the path.

Isothermal Expansion: $T_f = T_i$, $V_f > V_i$

The amount of heat which leaves the reservoir and enters the gas is

$$Q = n R T \ln(V_f/V_i).$$

The entropy change of the gas is

$$\Delta S_{gas} = + Q/T = n R \ln(V_f/V_i).$$

The entropy change of the reservoir is

$$\Delta S_{reservoir} = - Q/T.$$

The net entropy change is

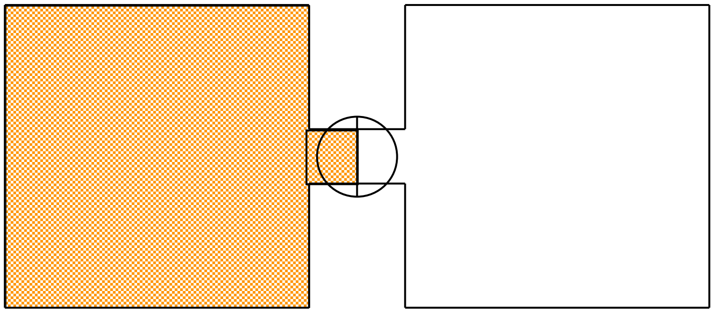
$$\Delta S_{universe} = \Delta S_{gas} + \Delta S_{reservoir} = 0.$$

This illustrates a general result:

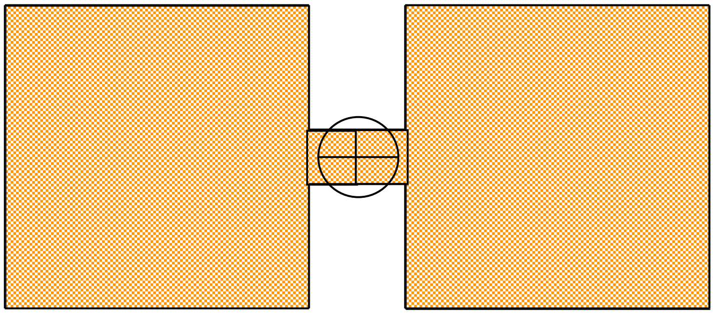
In a reversible process, the entropy change of the universe (system + surroundings) is zero.

Adiabatic Free Expansion of an Ideal Gas

Two containers connected by stopcock. They are thermally insulated so no heat can flow in or out.



Initial: One container is evacuated. Gas is in volume V_i at temperature T_i.



Final: Stopcock opened, gas rushes into second chamber. Gas does no work (nothing to push against) and there is no heat transfer. So internal energy does not change. Final volume $V_f > V_i$ at temperature $T_f = T_i$.

Because there is no heat transfer, you might think $\Delta S = 0$. WRONG! This is an irreversible process. We can't integrate

$$\int \frac{dQ}{T} \quad .$$

But entropy is a state function, and we do know the initial and final conditions for the Free Expansion. They are exactly the same as for an Isothermal Expansion. So

$$\Delta S_{gas} = n\,R\,\ln(V_f/V_i).$$

just as for an isothermal expansion. However, since it is thermally isolated from its surroundings,

$$\Delta S_{surround} = 0$$

and

$$\Delta S_{universe} = \Delta S_{gas} + \Delta S_{surround} = n\,R\,\ln(V_f/V_i) > 0.$$

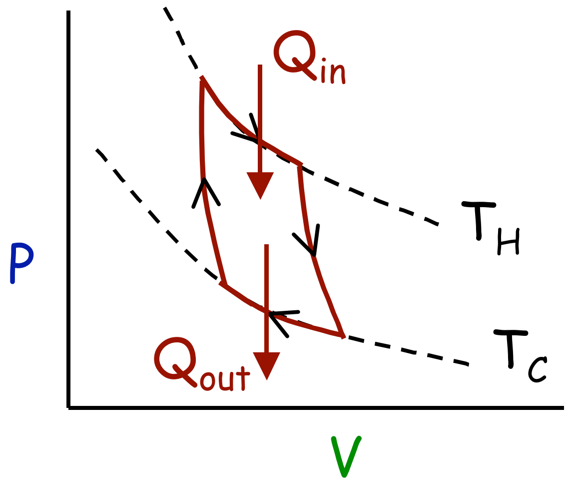
In an irreversible process, the entropy of the universe increases.

Entropy and Heat Engines

For a reversible cycle:

$$\Delta S = \oint \frac{dQ}{T}$$

This implies that dQ cannot be strictly positive. There must also be heat released in the cycle.



Carnot cycle: $(Q_{in}/T_H) + (-Q_{out}/T_C) = 0.$

2nd Law of TD (Entropy form):
$\Delta S_{universe} \geq 0.$
(greater-than sign for irreversible processes, and equals sign for reversible processes)

Entropy and Probability

(A statistical view)

Entropy ~ a measure of the disorder of a system.

A state of high order = low probability
A state of low order = high probability

In an irreversible process, the universe moves from a state of low probability to a state of higher probability.

We will illustrate the concepts by considering the free expansion of a gas from volume V_i to volume V_f.

The gas always expands to fill the available space. It never spontaneously compresses itself back into the original volume.

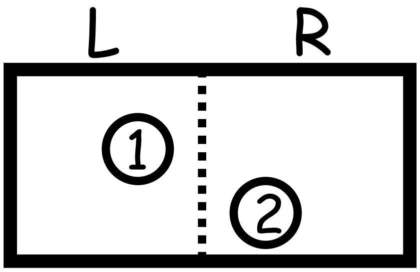
First, two definitions:

Microstate: a description of a system that specifies the properties (position and/or momentum, etc.) of each individual particle.

Macrostate: a more generalized description of the system; it can be in terms of macroscopic quantities, such as P and V, or it can be in terms of the number of particles whose properties fall within a given range.

In general, each macrostate contains a large number of microstates.

An example: Imagine a gas consisting of just 2 molecules. We want to consider whether the molecules are in the left or right half of the container.



There are 3 macrostates: both molecules on the left, both on the right, and one on each side.

There are 4 microstates:
LL, RR, LR, RL.

How about 3 molecules? Now we have:

LLL, (LLR, LRL, RLL), (LRR, RLR, RRL), RRR

↑ ↑ ↑ ↑

(all L) (2 L, 1 R) (2 R, 1 L) (all R)

i.e. 8 microstates, 4 macrostates

How about 4 molecules? Now there are 16 microstates and 5 macrostates

(all L) (3L, 1R) (2L, 2R) (1L, 3R) (all R)

↑ ↑ ↑ ↑ ↑

1 4 6 4 1

number of microstates

In general:

1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 $\boxed{15}$ 20 15 6 1
1 7 21 35 35 21 7 1
1 8 28 56 70 56 28 8 1

N	W	M
1	2	2
2	4	3
3	8	4
4	16	5
5	32	6
6	64	7
7	128	8
8	256	9
	$\uparrow$ 2^N	$\uparrow$ $N+1$

This table was generated using the formula for # of permutations for picking n items from N total:

$$W_{N,n} = \frac{N!}{N!\,(N-n)!}$$

"multiplicity"

i.e. $W_{6,2} = \dfrac{6!}{2!\,4!} = 15$

Fundamental Assumption of Statistical Mechanics: All microstates are equally probable.

Thus, we can calculate the likelihood of finding a given arrangement of molecules in the container.

E.g. for 10 molecules:

Conclusion: Events such as the spontaneous compression of a gas (or spontaneous conduction of heat from a cold body to a hot body) are not impossible, but they are so improbable that they never occur.

We can relate the # of microstates W of a system to its entropy S by considering the probability of a gas to spontaneously compress itself into a smaller volume.

If the original volume is V_i, then the probability of finding N molecules in a smaller volume V_f is

$$\text{Probability} = W_f/W_i = (V_f/V_i)^N$$

- $\ln(W_f/W_i) = N \ln(V_f/V_i) = n\, N_A \ln(V_f/V_i)$

We have seen for a free expansion that

$$\square S = n\, R \ln(V_f/V_i)\ ,$$

so

$$\square S = (R/N_A) \ln(W_f/W_i) = k \ln(W_f/W_i)$$

or

$$S_f - S_i = k \ln(W_f) - k \ln(W_i)$$

Thus, we arrive at an equation, first deduced by Ludwig Boltzmann, relating the entropy of a system to the number of microstates:

$$S = k \ln(W)$$

He was so pleased with this relation that he asked for it to be engraved on his tombstone.