

Adiabatic Expansion ($\Delta Q = 0$)

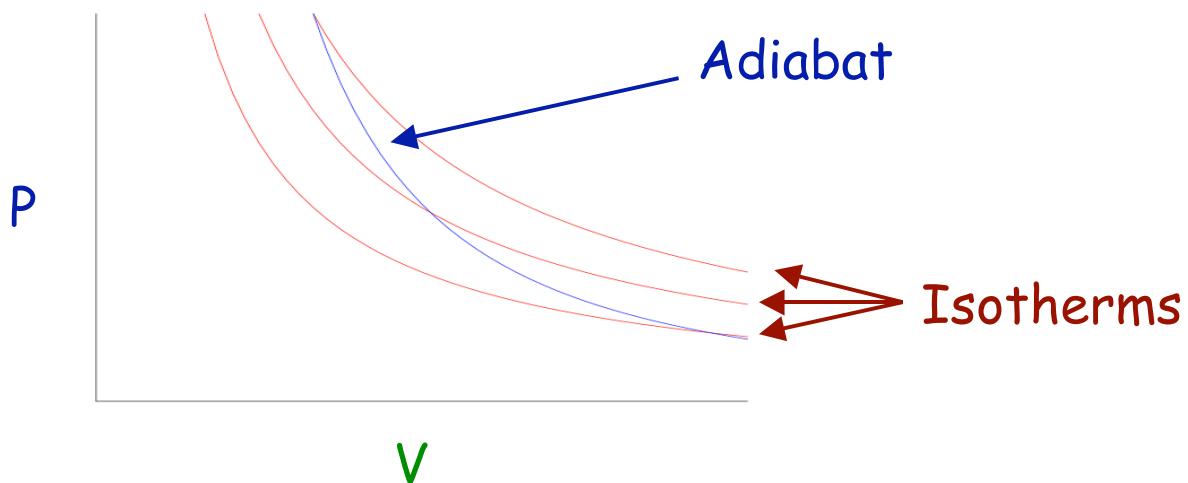
Occurs if:

- 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):

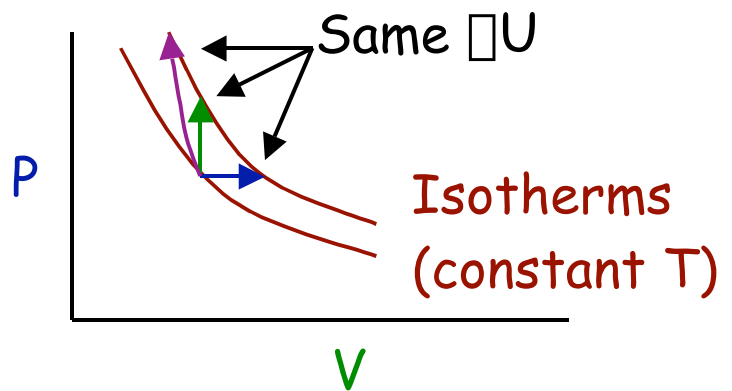
$$V^{\gamma-1} T = \text{constant} \quad (\text{for adiabatic})$$

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

(for adiabatic process)

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

2) U only depends on T :



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

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:

$$\begin{aligned} (dP/P) &= - (C_V + R)/C_V (dV/V) \\ &= - \gamma (dV/V) \end{aligned}$$

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

Integrate both sides:

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

or

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

or

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

QED

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.

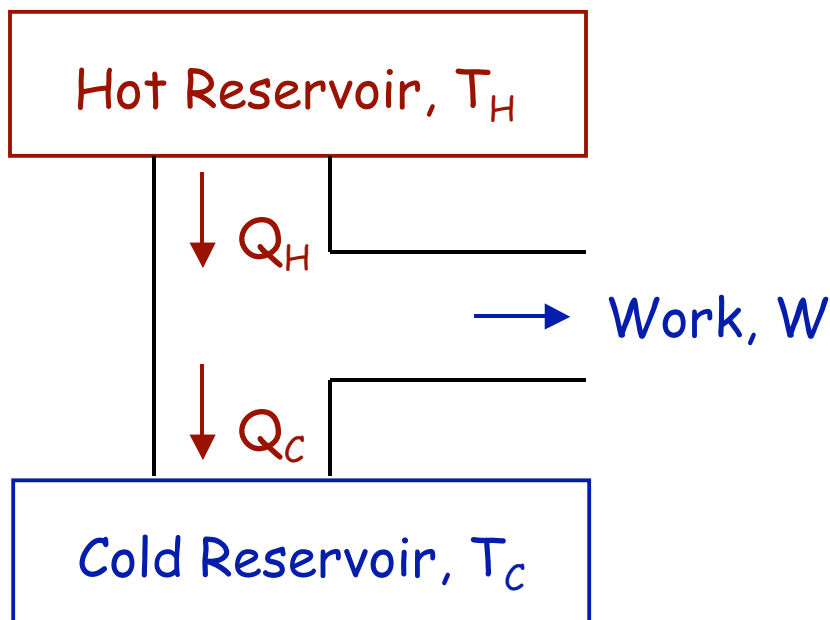
 arrow of time

Why?

2nd Law of Thermodynamics (entropy)

Heat Engines

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



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 cyclic engine $\Delta U = 0$,

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

$$W = Q_H - Q_C$$

Define the Efficiency of the engine:

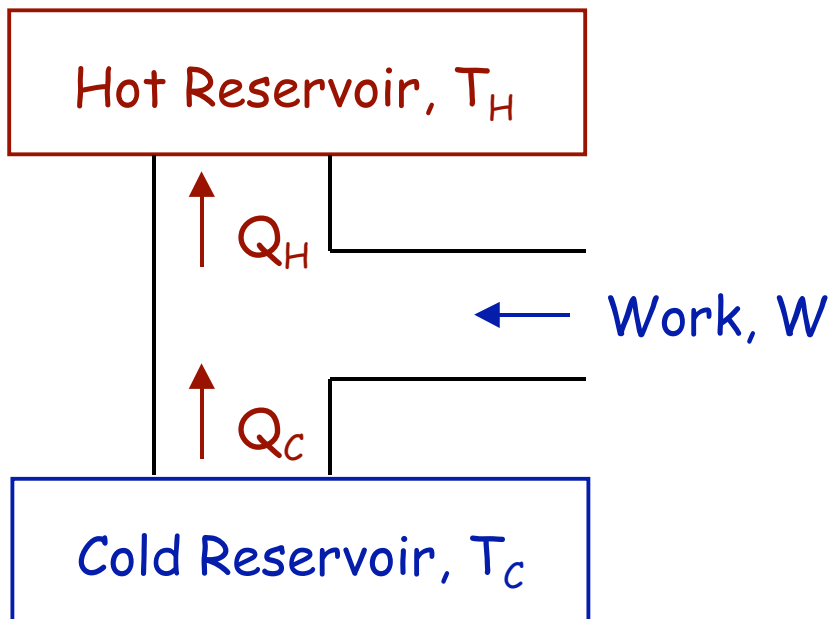
$$\eta = W/Q_H = (Q_H - Q_C)/Q_H = 1 - Q_C/Q_H$$

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.



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.)

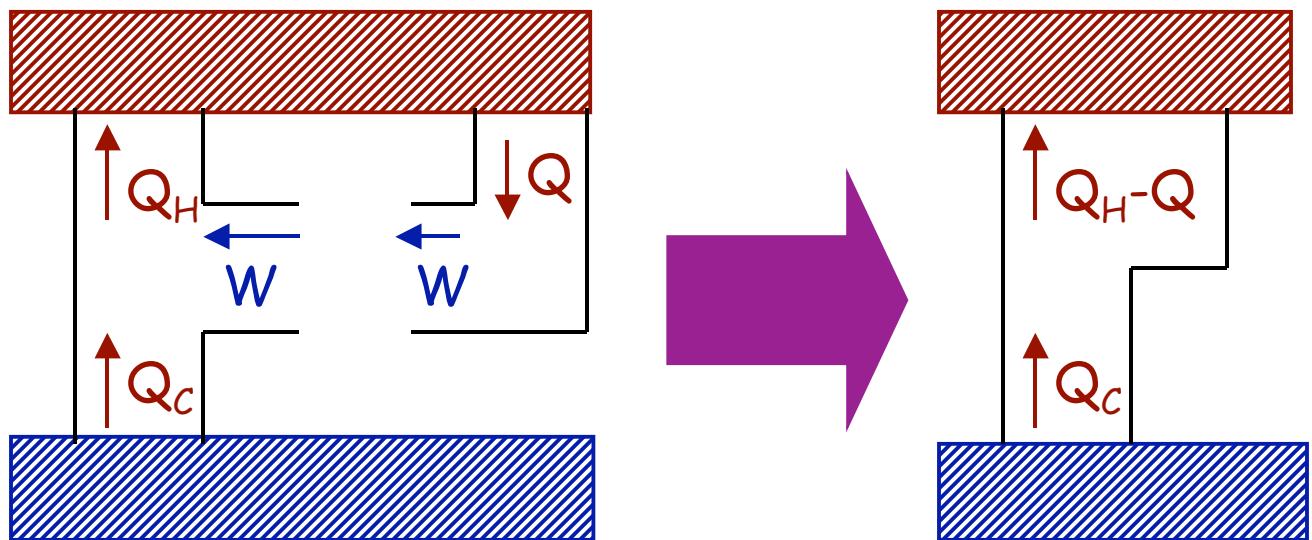
Corollary of the 2nd Law of TD:

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?

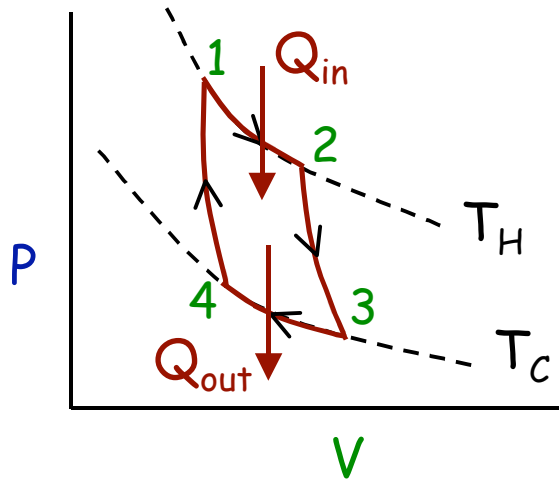
No engine working between 2 heat reservoirs can be more efficient than an ideal engine acting in a Carnot cycle.

(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

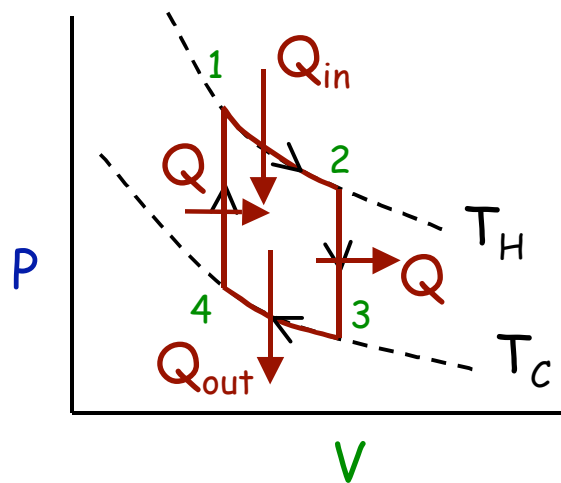


- 1-2: Isothermal (Q_{in} at T_H)
- 2-3: Adiabatic expansion
- 3-4: Isothermal (Q_{out} at T_C)
- 4-1: Adiabatic compression

$$\eta = 1 - T_C/T_H$$

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.

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

Entropy

Consider a reversible process for an ideal gas:

$$\begin{aligned}dQ &= dU + dW = n C_v dT + P dV \\ &= n C_v dT + n R T (dV/V)\end{aligned}$$

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 :

$$dQ/T = n C_v (dT/T) + n R (dV/V)$$

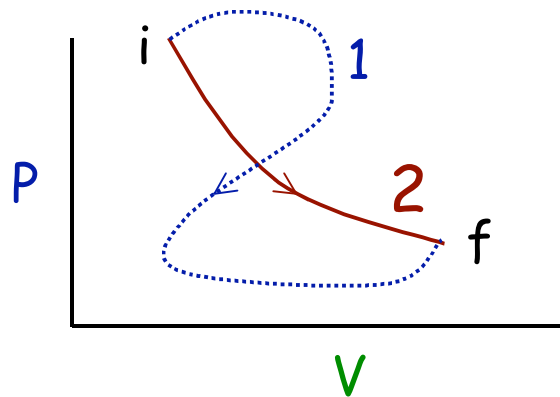
is integrable independent of path.

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

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

(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

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

The entropy change of the reservoir is

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

The net entropy change is

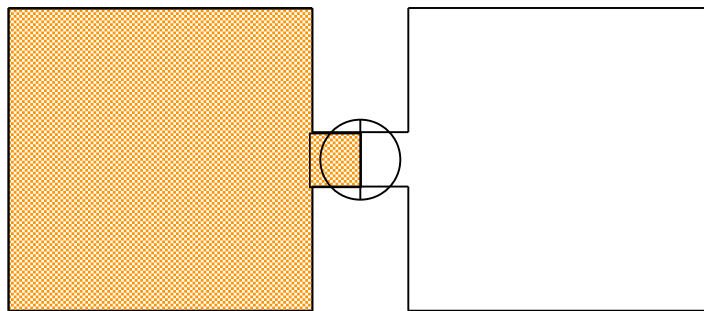
$$\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} = 0.$$

This illustrates a general result:

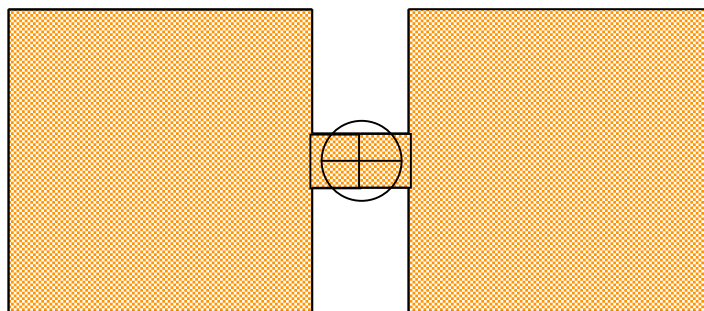
In a reversible process, the entropy change of the universe (system + surroundings) is zero.

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

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

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

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

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

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

and

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

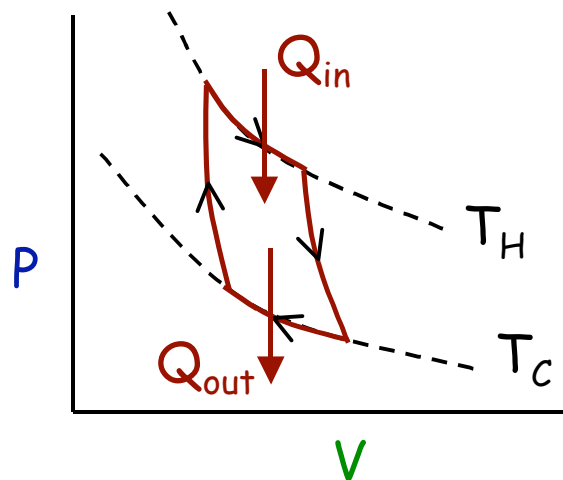
In an irreversible process, the entropy of the universe increases.

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.

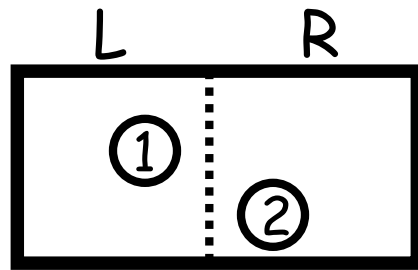
First, two definitions:

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:

	$\frac{N}{1}$	$\frac{W}{2}$	$\frac{M}{2}$
1 1	1	2	2
1 2 1	2	4	3
1 3 3 1	3	8	4
1 4 6 4 1	4	16	5
1 5 10 10 5 1	5	32	6
1 6 15 20 15 6 1	6	64	7
1 7 21 35 35 21 7 1	7	128	8
1 8 28 56 70 56 28 8 1	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:

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

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

"multiplicity"

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.

"Improbable", quantitatively:

For large N , $\sigma/\mu \rightarrow 1/\sqrt{N}$

For $N \sim N_A$, $\sigma/\mu \rightarrow 1.3 \times 10^{-12}$

~ 70% of time within 10^{-10} % of expected

Probability of $< 10^{-99}$ to find more than 2.7×10^{-9} % from expected!

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

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

$$\ln(W_f/W_i) = N \ln(V_f/V_i) = n N_A \ln(V_f/V_i) \quad (1)$$

We have seen for a free expansion that

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

So, using (1) for $\ln(V_f/V_i)$,

$$\Delta S = (R/N_A) \ln(W_f/W_i) = k_B \ln(W_f/W_i)$$

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.