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.

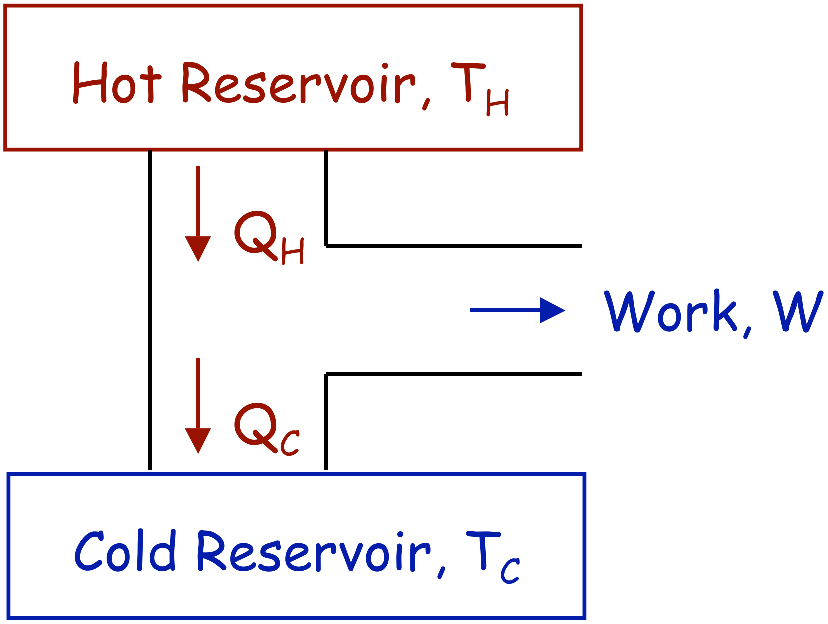
➡ arrow of time

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 cyclic engine $\square U = 0$,

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

$$W = Q_H - Q_C$$

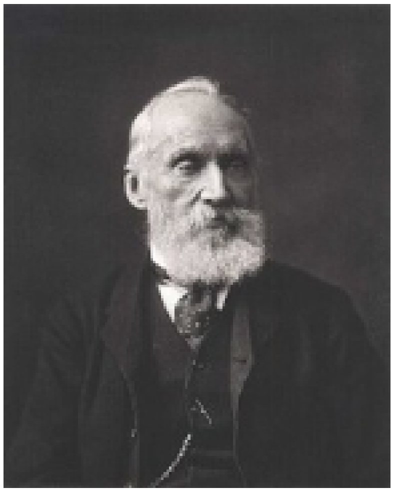
Define the Efficiency of the engine:

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

Corollary of the 2nd Law of TD:

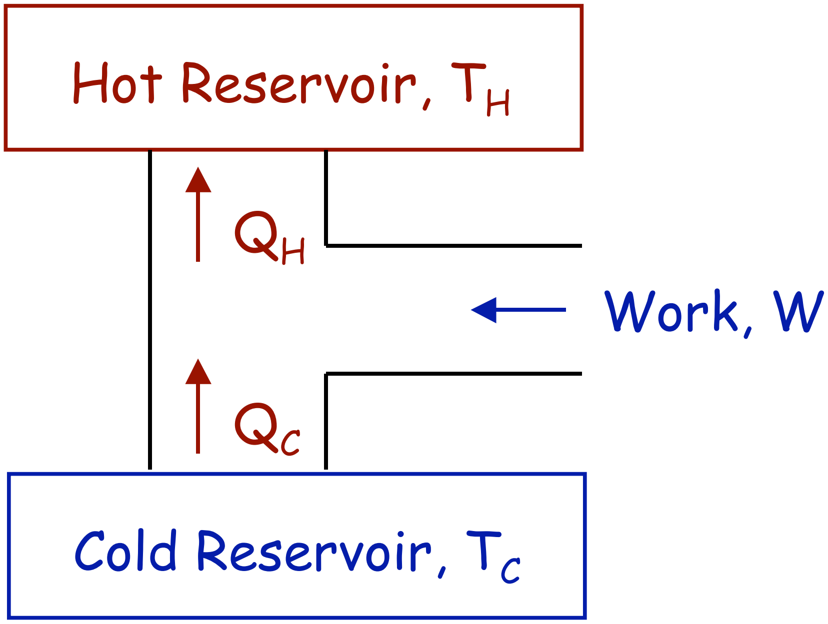
It is impossible to make a heat engine whose efficiency is 100%.

Lord Kelvin



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:

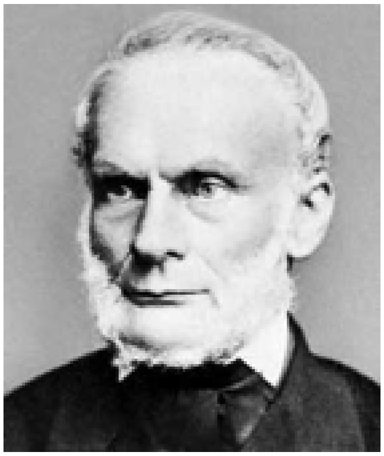
$$K = Q_C / W$$

"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.

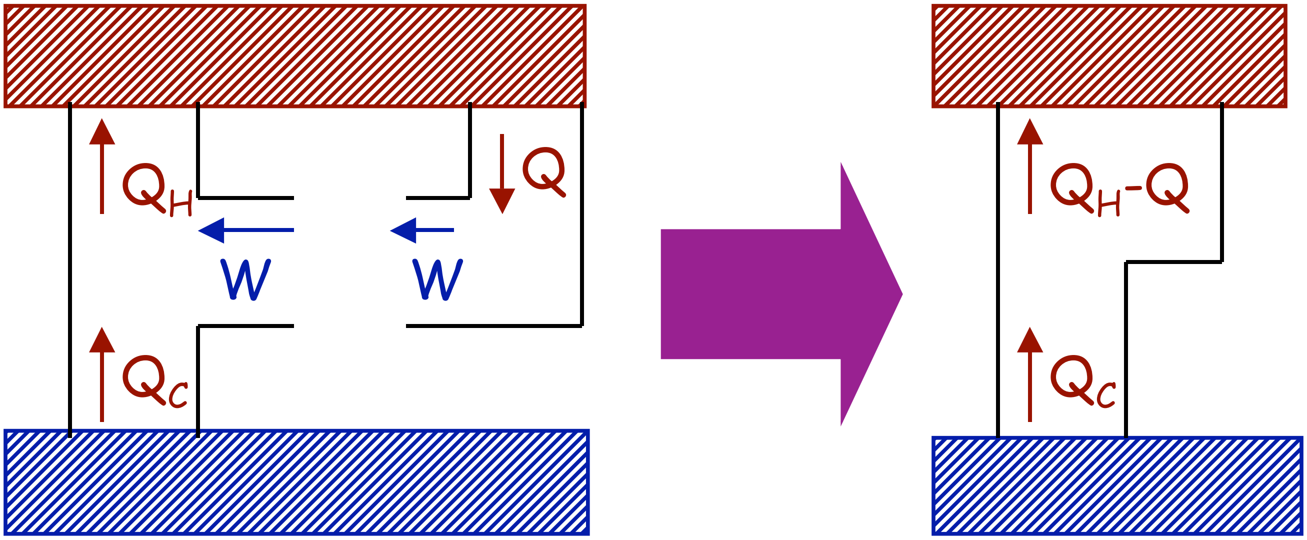
Rudolf Clausius



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?

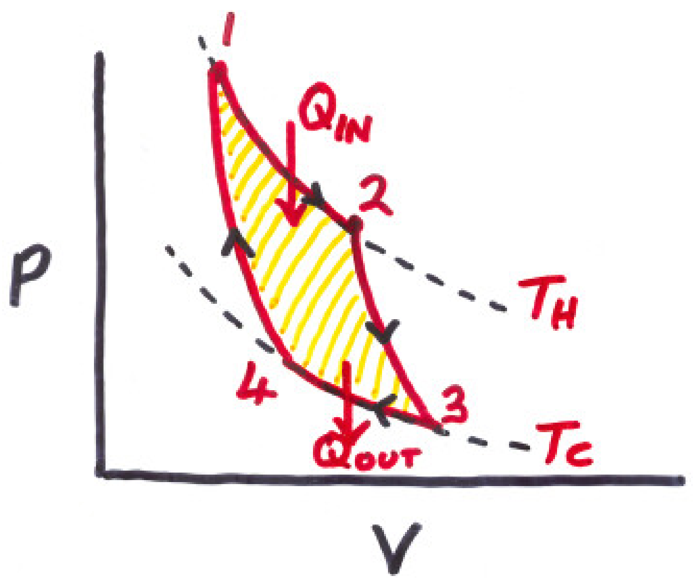
No engine working between 2 heat reservoirs can be more efficient than an ideal engine acting in a Carnot cycle.
(Sadi Carnot, 1824)

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.

Sadi Carnot

THE CARNOT CYCLE CONSISTS OF 4 REVERSIBLE STEPS.



1→2 ISOTHERMAL ABSORPTION OF HEAT FROM A HOT RESERVOIR

2→3 ADIABATIC EXPANSION TO A LOWER TEMPERATURE

3→4 ISOTHERMAL EXHAUSTION OF HEAT TO A COLD RESERVOIR

4→1 ADIABATIC COMPRESSION BACK TO THE ORIGINAL STATE

THE NET WORK DONE IN THE CYCLE IS GIVEN BY THE SHADED AREA.

THE EFFICIENCY OF THIS CYCLE IS

$$\varepsilon = 1 - \frac{Q_{OUT}}{Q_{IN}} \Rightarrow 1 - \frac{T_C}{T_H}$$

derived in the following page and by FGT on page 583

HEAT ABSORBED IN THE ISOTHERMAL EXPANSION $(\Delta U = 0)$
= THE WORK DONE BY THE GAS

$$Q_{IN} = W = \int_1^2 P\,dV = \int_1^2 \frac{nRT_H}{V}\,dV = nRT_H \ln \frac{V_2}{V_1}$$

SIMILARLY, THE HEAT EXHAUSTED IN GOING FROM 3 TO 4 IS

$$Q_{OUT} = nRT_C \ln \frac{V_3}{V_4}$$

$$\therefore \frac{Q_{OUT}}{Q_{IN}} = \frac{T_C}{T_H} \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$$

WE CAN RELATE V_2 AND V_3 BECAUSE IT IS AN ADIABATIC EXPANSION

$$TV^{\gamma-1} = \text{CONSTANT}$$

$$\therefore T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1} \qquad \ldots\ldots (2)$$

SIMILARLY, $T_H V_1^{\gamma-1} = T_C V_4^{\gamma-1}$ $\ldots\ldots (1)$

DIVIDING (2) BY (1) =>

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

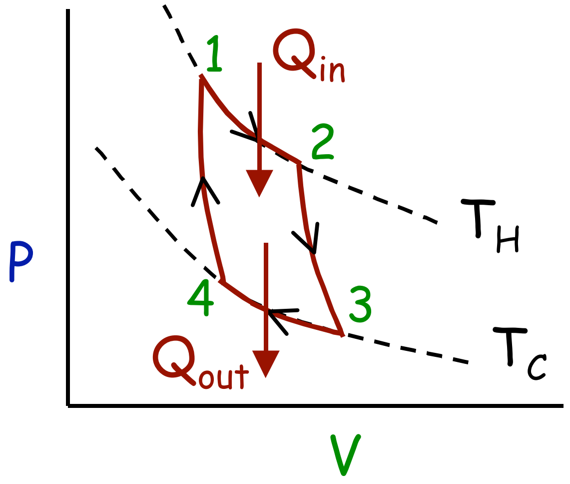
$$\therefore \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\therefore \quad \frac{Q_{OUT}}{Q_{IN}} = \frac{T_C}{T_H}$$

∴ THE CARNOT EFFICIENCY IS

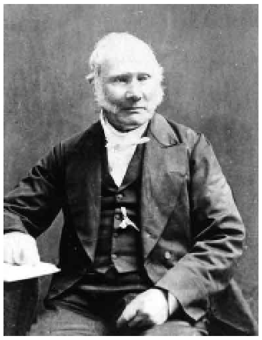
$$\varepsilon_c = 1 - \frac{T_c}{T_H}$$

Derivation of Carnot Efficiency



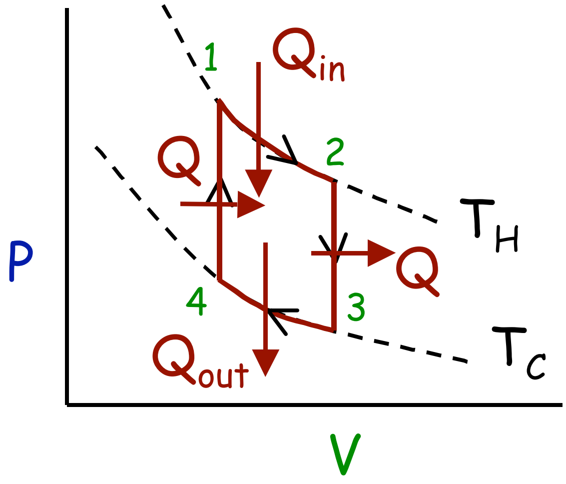
1-2: Isothermal (Q_{in} at T_H)
2-3: Adiabatic expansion
3-4: Isothermal (Q_{out} at T_C)
4-1: Adiabatic compression

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



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.

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

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:

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

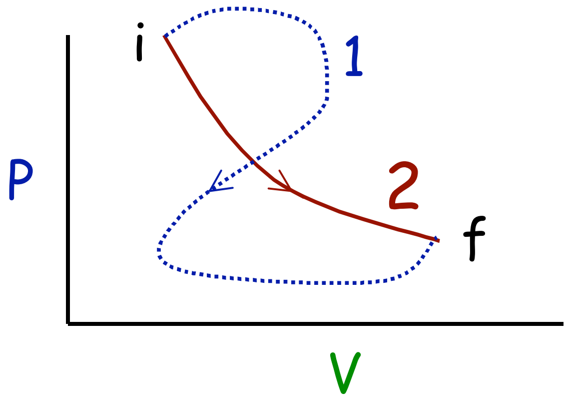
is integrable independent of path.

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

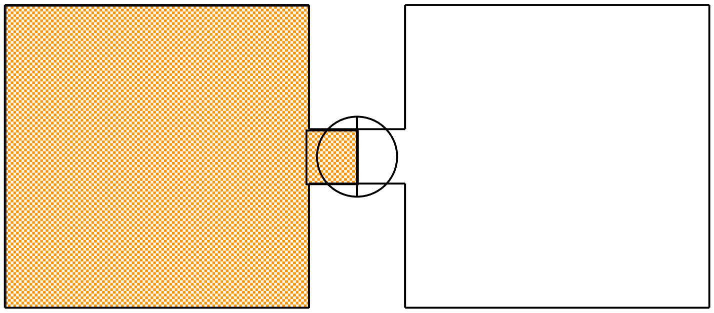
$$\Delta S_{universe} = \Delta S_{gas} + \Delta S_{reservoir} = 0.$$

This illustrates a general result:

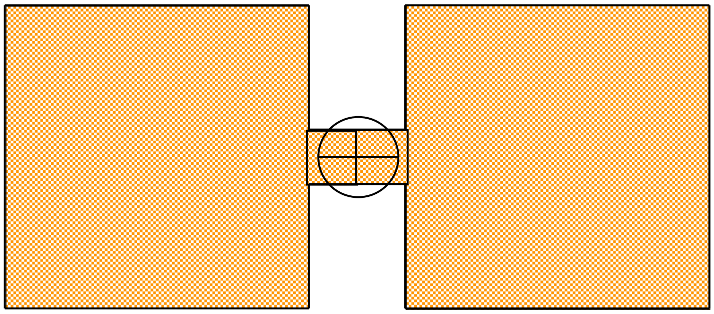
In a reversible process, the entropy change of the universe (system + surroundings) is zero.

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

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

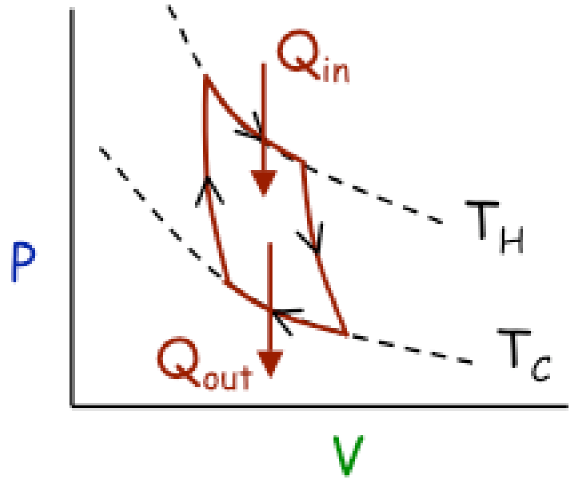
In an irreversible process, the entropy of the universe increases.

Entropy and Heat Engines

For a reversible cycle:

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

$\Delta S=0$ implies that dQ cannot be strictly positive. There must also be heat released in the cycle.



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

$$\Longrightarrow \quad \Delta S = 0$$

2nd Law of TD (Entropy form):

$$\Delta S_{universe} \geq 0.$$

> for irreversible
= for reversible

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.

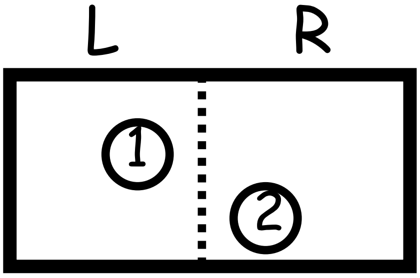
First, two definitions:

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 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
	↑	↑
	2^N	$N+1$

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

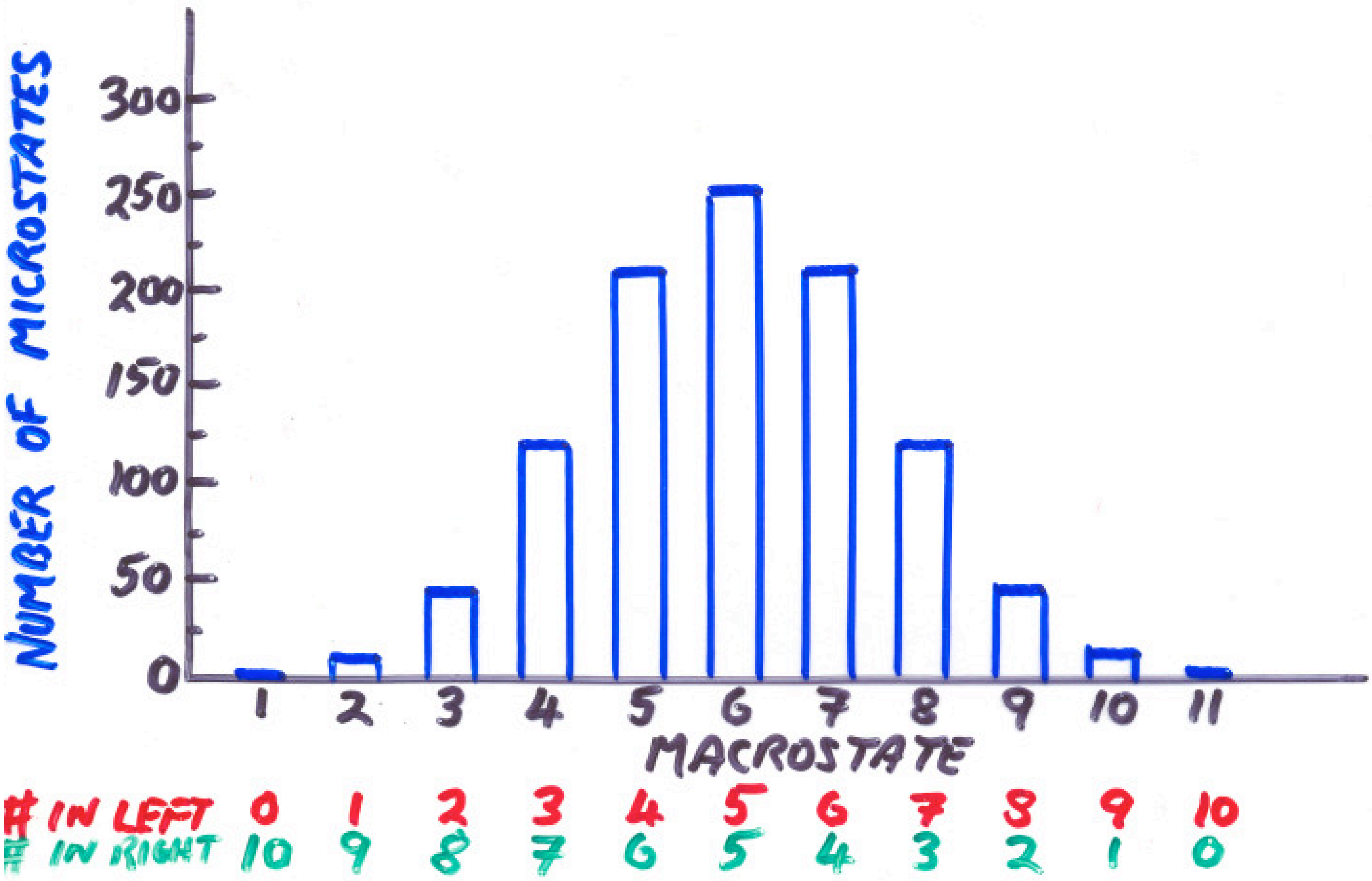
$$W_{N,n} = \frac{N!}{N!\,(N-n)!} \qquad \text{i.e. } W_{6,2} = \frac{6!}{2!\,4!} = 15$$

"multiplicity"

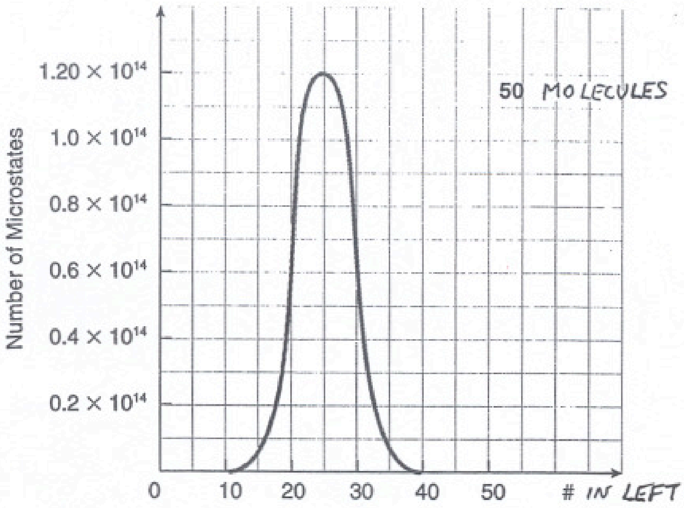
Fundamental Assumption of Statistical Mechanics: All microstates are equally probable.

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

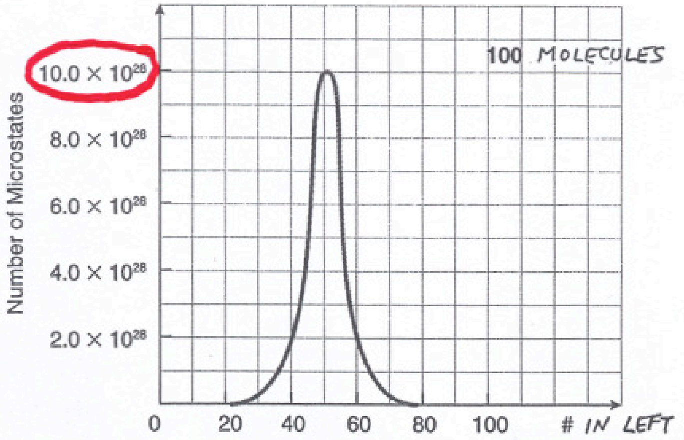
E.g. for 10 molecules:



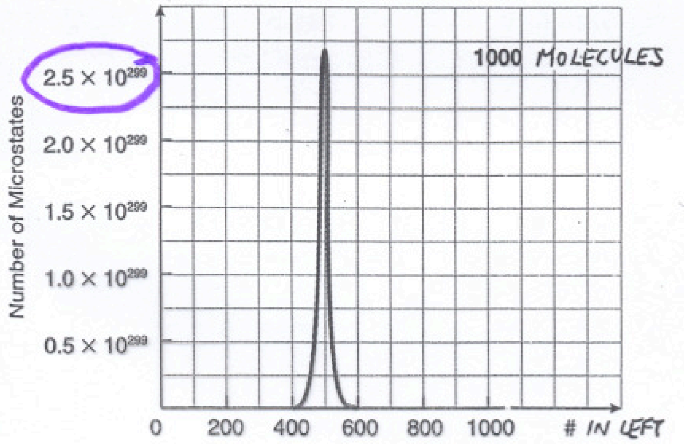
WE FIND THAT, AS N INCREASES, THE NUMBER OF MICROSTATES CORRESPONDING TO THE CENTRAL PEAK INCREASES RAPIDLY.



AND THE WIDTH OF THE DISTRIBUTION SHRINKS.



THE TEXT POINTS OUT THAT, COUNTING THESE STATES AT A RATE OF 1 EVERY NANOSECOND, IT WOULD TAKE YOU 3E12 YEARS (ABOUT 750 TIMES THE AGE OF THE UNIVERSE)!!



!!!!

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, $\sigma/\mu \dashrightarrow 1/\sqrt{N}$

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

~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

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

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

so

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

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.