
The Second Law: The Concepts

Chapter 4 of Atkins: The Second Law: The Concepts

Sections 4.1 and 4.2, both 6th & 7th editions

Sections 3.1 and 3.2, 8th and 9th editions

Direction of Spontaneous Change

Dispersal of Energy

Entropy

Thermodynamic definition

Entropy as a State Function

Thermodynamic Temperature (skip)

The Clausius Inequality

First vs. Second Law

First Law of Thermodynamics:

The energy of the universe is constant - energy is conserved

- This law tells us nothing about the **spontaneity** of physical and chemical transformations

Consider the formation of water:



Using the first law, it is easy to calculate ΔU and ΔH associated with this spontaneous reaction - we can also calculate ΔU and ΔH for the reverse reaction, which we know does not occur **spontaneously** (thankfully!!)

What about gases? We know that gases expand spontaneously to fill a container - we know that the opposite does not happen - *unless some sort of work is done to bring about this reverse change*

Neither the sign nor the magnitude of ΔU and ΔH tell us which way the reaction will go - however, we can get this information from the **Second Law of Thermodynamics**

First vs. Second Law

The first law gives us no clue what processes will actually occur and which ones will not. For that matter, why does anything ever happen at all? The universe is an isolated system after all. There is no change in internal energy. There is no heat transferred in or out and no work is done on or by the system as a whole. $q=0$; $w=0$; $\Delta U=0$.

Without only the first law, and without the second law:

The universe is a boring place

Yet, the universe is not a boring place:

- Stars come into existence and blow up into oblivion
- Planets are created and hurl around stars
- Life evolves amid all of this turmoil on these planets

Why? What is driving all of this?

These processes do not lead to a lower energy for the universe as a whole. So what is going on?

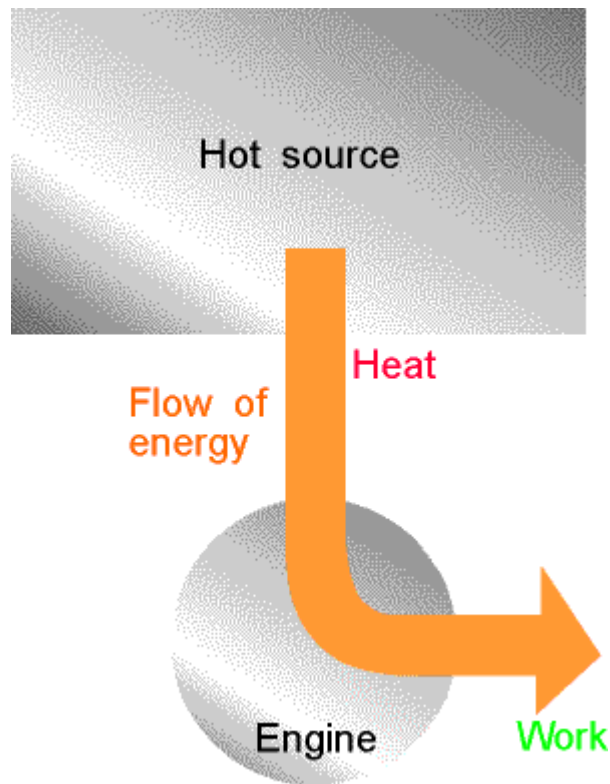
Statements of the Second Law

Elements in a closed system tend to seek their most probable distribution; in a closed system entropy always increases.

1. **Clausius** (1822-1888) It is impossible that, at the end of a cycle of changes, heat has been transferred from a colder to a hotter body without at the same time converting a certain amount of work into heat.
2. **Lord Kelvin** (1824-1907) In a cycle of processes, it is impossible to transfer heat from a heat reservoir and convert it all into work, without at the same time transferring a certain amount of heat from a hotter to a colder body.
3. **Ludwig Boltzmann** (1844-1906) For an adiabatically enclosed system, the entropy can never decrease. Therefore, a high level of organization is very improbable.
4. **Max Planck** (1858-1947) A perpetual motion machine of the second kind is impossible.
5. **Caratheodory** (1885-1955) Arbitrarily near to any given state there exist states which cannot be reached by means of adiabatic processes.

The Second Law of Thermodynamics*

The second law of thermodynamics can be stated in a number of equivalent ways; an early statement of the law from Lord Kelvin says: *No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work*



All heat engines have a source of heat and a **cold sink**, into which some heat is always discarded and not converted into work

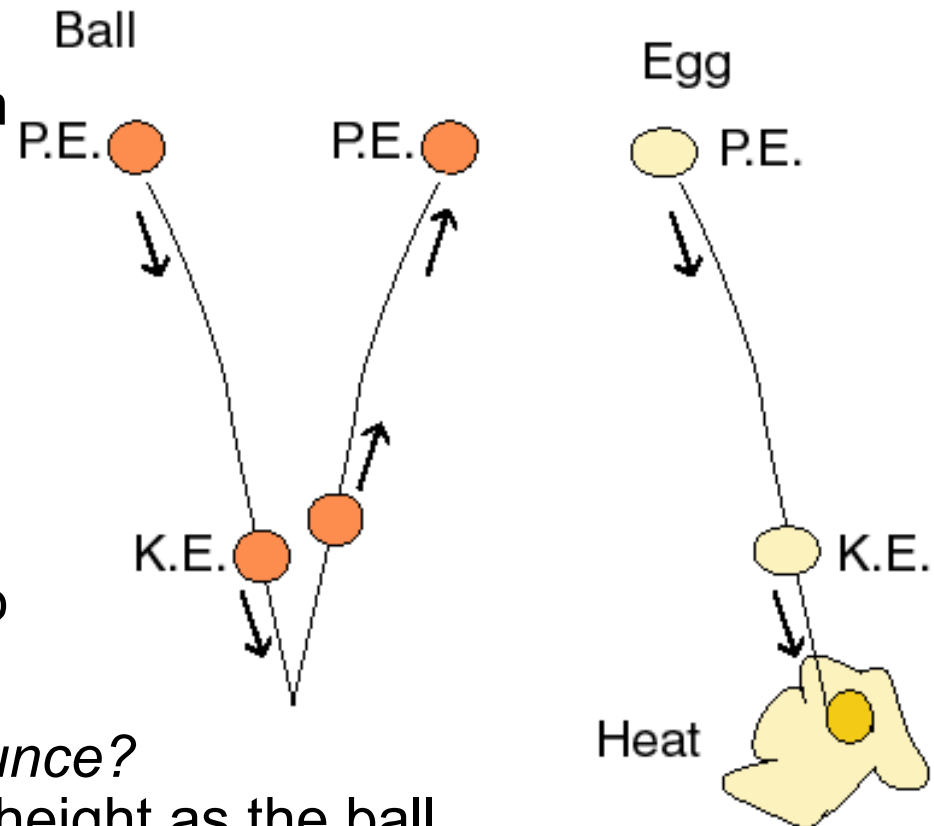
The engine on the left violates the second law - this is equivalent to a ball initially at rest on a heated surface starting to bounce (i.e., heat absorbed from this surface is converted into orderly work) - this has not been observed

What determines how physical and chemical processes proceed spontaneously? Energy? Tendency towards minimum energy? It is none of these, as we shall see...

Simple Processes

Process 1: *First Law fulfilled*

- A perfectly elastic ball in a vacuum is dropped from some height with an initial potential energy.
- When it strikes the ground, all energy is converted into kinetic energy
- The ball bounces back to the original height, where all of the kinetic energy is converted back to the original potential energy



Process 2: *Why doesn't the egg bounce?*

- An egg is dropped from the same height as the ball
- Initial and final states are not the same - seem to have lost energy!
- First Law: we cannot lose energy - where did it go?
 - Converted into random molecular motion and heat
 - We wound up with a more disorganized form of matter

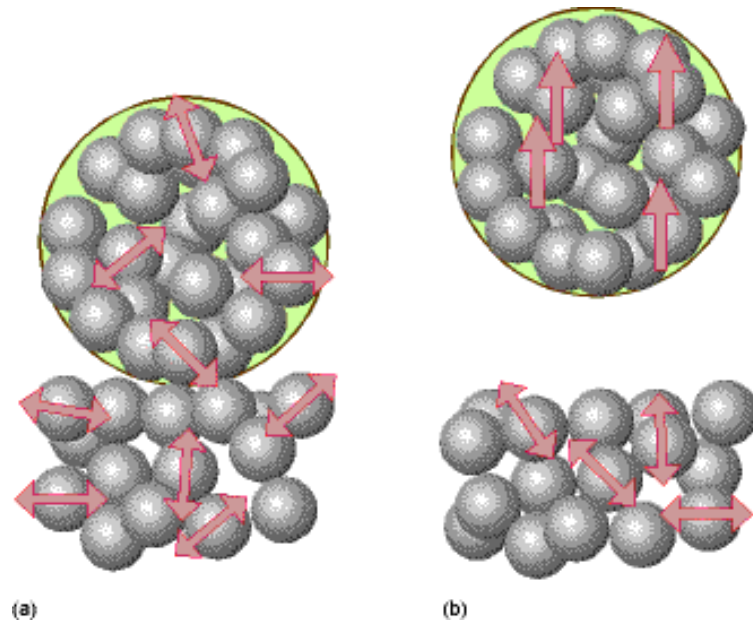
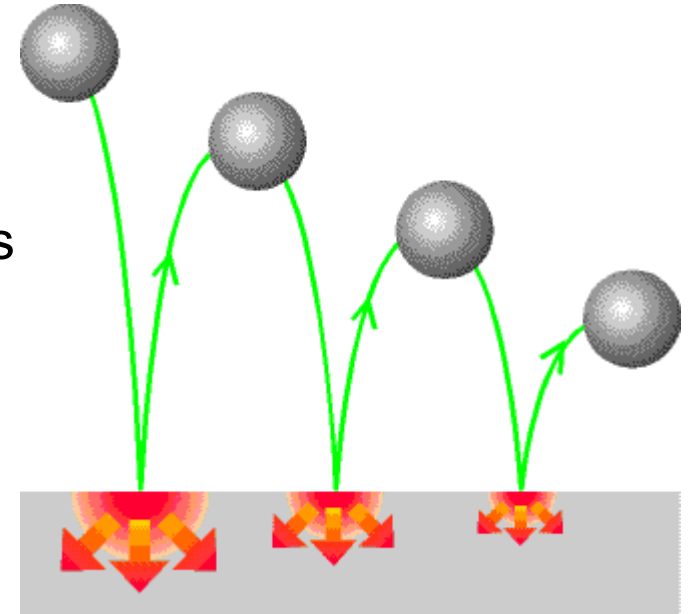
The universe tends to more random disorganized states

Dispersal of Energy*

Spontaneous changes are accompanied by dispersal of energy into a more disordered form

Bouncing ball:

- Ball does not return to original height, as energy is redistributed to molecules in the floor and ball as heat - inelastic energy losses
- Ball eventually comes to rest, losing all energy into thermal motion of atoms in the floor - the reverse process will never occur!



Heated floor and ball:

- Molecules and atoms in the floor (and ball) undergo thermal (random) motion
- In order for the ball to spontaneously bounce, it would require a **spontaneous localization of motion**, to create an upwards motion of all of the atoms - a **virtually impossible process****

****Boltzmann paradox: could happen!**

*happy

Irony of the Second Law: Entropy

The universe tends towards more random, disorganized states.

This is a rather loose statement of the second law of thermodynamics and our way of quantitating the disorder and randomized motion in one state versus another is a **state function** called **entropy**:

Increasing entropy means increasing disorder and randomized motion.

Melodramatic viewpoint: Every star that burns, every planet whose orbit is slowly decaying, every breath you take and calorie you metabolize brings the universe closer and closer to the point when the entropy is maximized, organized movement of any kind ceases, and nothing ever happens again. There is no escape. No matter how magnificent life in the universe becomes or how advanced, the slow increase in entropy cannot be stopped - the universe will eventually die.

Irony of the second law:

Without the second law, nothing would ever happen at all. With it, the universe is doomed. Darn.

General Thoughts on Second Law

Signpost for spontaneous change:

Direction of change that leads to general chaotic dispersal of total energy of an isolated system

- Ball will bounce and come to rest
- Gas spontaneously expands, does not spontaneously contract
- Object does not suddenly become warmer than its surroundings for no reason at all - random vibration of atoms will not suddenly lead to an excess of thermal motion (and therefore heating) - however, the object does spontaneously release energy into the surroundings as thermal motion (consequence of chaos...)

Puzzling thought:

The fall into disorder can result in highly **order** substances such as crystals, proteins, life!!, etc: *organized structures and patterns can emerge as energy and matter disperse (i.e., the entropy increases)*

The meaning of life: to increase entropy in the universe

Check out: <http://www.secondlaw.com> and <http://www.2ndlaw.com>

Spontaneity & Reversibility

Spontaneous:

It has little to do with an impromptu gesture, a witty saying or impulsive shopping. It means a process that results in a change from one state to another in an **irreversible way**. *Anything that happens in the universe that results in an irreversible change in state is spontaneous.*

Reversible Change (Not Spontaneous):

Truly reversible processes do not happen in reality, because in a truly reversible process all forces would be perfectly balanced and there would be no driving force for the system to move. By moving things very slowly always keeping forces in near perfect balance, we can approximate reversible processes to whatever degree we like. For example, during reversible expansion of a gas, we keep the pressures essentially the same on the inside and the outside - if this was strictly true, the gas would not have any driving force to expand and nothing would ever happen. However, we can make it as close to true as we like by making the imbalance as small as we want.

Irreversible Change (Spontaneous): All processes that really happen are irreversible; forces driving process are substantially out of balance

Second Law and Entropy

The law used to identify spontaneous change, and can be quantified in terms of a *state function* known as **entropy**, S

First Law

Uses internal energy, U , to identify **permissible** changes

Second Law

Uses entropy, S , to identify the spontaneous (irreversible) changes among the permissible changes

The entropy of an isolated system increases in the course of spontaneous change

$$\Delta S_{\text{total}} > 0$$

where S_{tot} is the total entropy of a system and its surroundings.

$$\text{i.e., } \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

Entropy is a measure of molecular disorder in a system, letting us assess whether one state is accessible from another via spontaneous change

Thermodynamic Definition of Entropy*

An infinitesimal change in entropy is dS , and this can occur as a result of a chemical or physical process. The thermodynamic definition of entropy:

$$dS = \frac{dq_{\text{rev}}}{T}$$

infinitesimal change

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$$

measurable change

If we perform some process along a reversible path, then the entropy produced should be proportional to the amount of heat produced (or consumed) and inversely proportional to the temperature

*Measurable entropy difference between two states, ΔS : find a reversible path, calculate heat supplied **at each stage of the path** divided by temperature at which heat is supplied*

Why is this? The change in the extent to which energy is dispersed in a random disorderly manner depends on the amount of energy transferred as **heat** (creates *random “thermal” motion*). **Work** is not accompanied by increase in random motion, but rather, implies *uniform motion*, and is therefore not accompanied by changes in entropy.

*bouncing - 2ndlaws

Entropy Example: Isothermal Expansion*

Consider **reversible isothermal expansion** of a perfect gas ($pV = nRT$)

$$p = p_{\text{ex}}$$

$$\Delta T = 0$$

$$\Delta V = V_f - V_i \quad \therefore w < 0$$

In an isothermal expansion, $\Delta U = 0$, so $q = -w$

Since T is constant:

$$\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

We know the work of this type of expansion, so

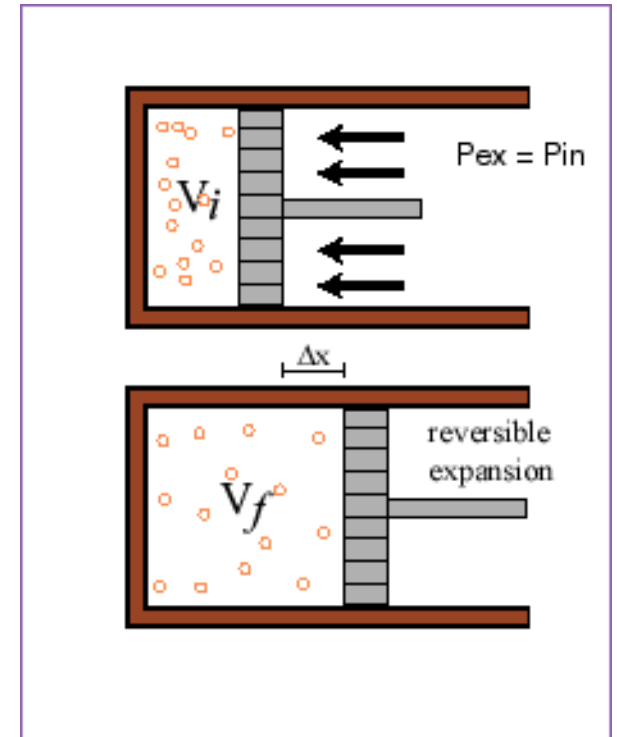
$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \left(\frac{V_f}{V_i} \right)$$

Thus, it follows that

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right)$$

Simple probability: molecules will randomly occupy the space that is available to them - **tendency of system to explore all available states**

*aside: $S = k \ln W$



Surroundings

Surroundings are treated in a manner similar to the system, except that surroundings are so large that we consider them to be **isothermal** and (generally) at **constant pressure**. Thus, $q_{\text{sur}} = \Delta H_{\text{sur}}$ (recall, $\Delta H = q_p$)

Therefore, heat transferred to the surroundings is equal to a state function and is independent of the path that the heat used to get out into the surroundings: it has been transferred by a reversible path.

Another view: **the surroundings are generally assumed not to change state when something happens in the system**, thus transfer of heat to and from the surroundings is effectively reversible (since there is no change of state, we cannot say that the change was irreversible):

$$dS_{\text{sur}} = \frac{dq_{\text{sur,rev}}}{T_{\text{sur}}} = \frac{dq_{\text{sur}}}{T_{\text{sur}}}$$

Since the surroundings are isothermal:

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}}$$

So for any adiabatic change ($q_{\text{sur}} = 0$):

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

Entropy as a State Function

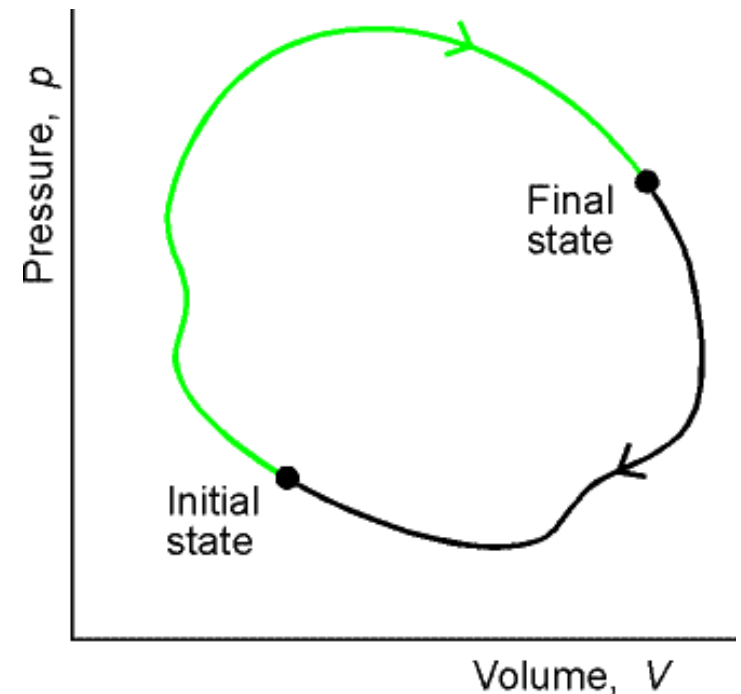
In order to prove that entropy is a state function, the integral of dS must be independent of path:

$$\oint \frac{dq_{\text{rev}}}{T} = 0$$

where \oint means integration about a closed path.

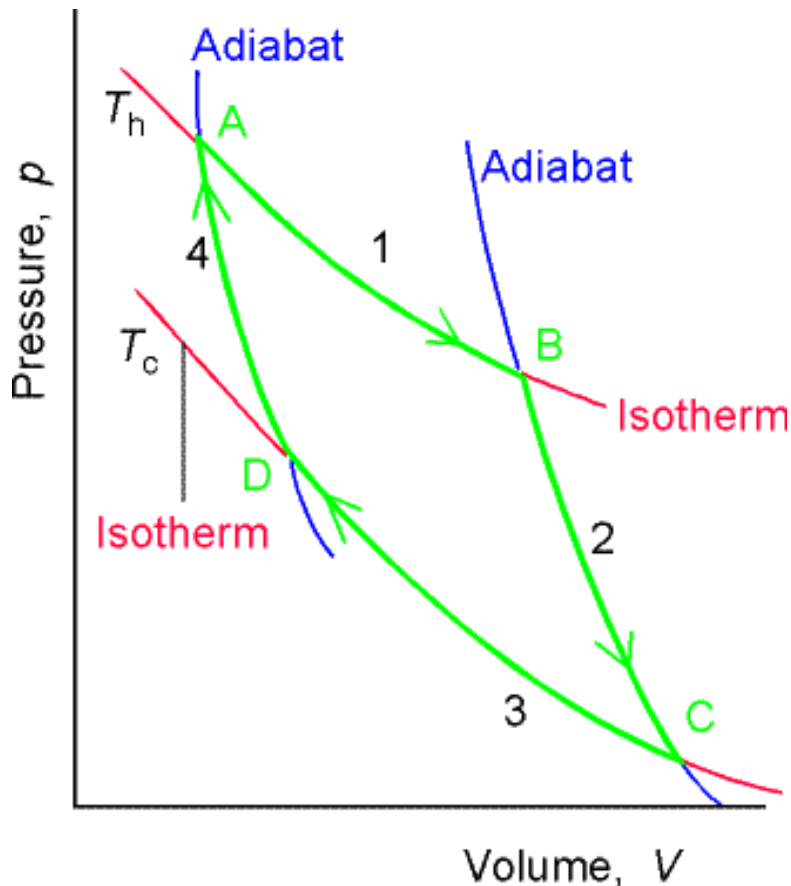
If the integration of the above equation above an arbitrary cycle (cyclic system) is zero, this will show that the entropy of the system in the initial and final states is the same, regardless of the path taken.

In a **thermodynamic cycle**, the overall change in a state function is zero, and is independent of path.



Carnot Cycle

The **Carnot cycle**, named after Sadi Carnot, has four reversible stages



1. Reversible isothermal expansion from A to B at T_h , $\Delta S = q_h/T_h$, q_h is heat supplied from a hot source, and is positive
2. Reversible adiabatic expansion from B to C, no heat leaves system ($\Delta S = 0$), temperature falls from T_h to T_c , where T_c is the temperature of the cold sink
3. Reversible isothermal compression from C to D, $\Delta S = q_c/T_c$, q_c is heat released into a cold sink, and is negative
4. Reversible adiabatic compression from D to A, no heat enters the system ($\Delta S = 0$), temperature rises from T_c to T_h

Total entropy change
in Carnot cycle:

$$\oint dS$$

$$= \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

This is zero
since:

$$\frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

$\Delta S = 0$ for Carnot Cycle

Recall for reversible isothermal expansion of a perfect gas

$$q_h = nRT_h \ln \left(\frac{V_B}{V_A} \right) \quad q_c = nRT_c \ln \left(\frac{V_D}{V_C} \right)$$

and for reversible adiabatic processes

$$V_A T_h^c = V_D T_c^c \quad V_C T_c^c = V_B T_h^c$$

Multiplying the expressions together:

$$V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c$$

and simplifying:

$$\frac{V_A}{V_B} = \frac{V_D}{V_C}$$

we get:

$$q_c = nRT_c \ln \left(\frac{V_A}{V_B} \right)$$

therefore:

$$\frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

Recall:

$$V_f T_f^c = V_i T_i^c \quad c = \frac{C_{V,m}}{R}$$

Efficiency

The same calculation just completed for gases applies to all types of materials and systems. We define the **efficiency**, ε , of a heat engine:

$$\varepsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h}$$

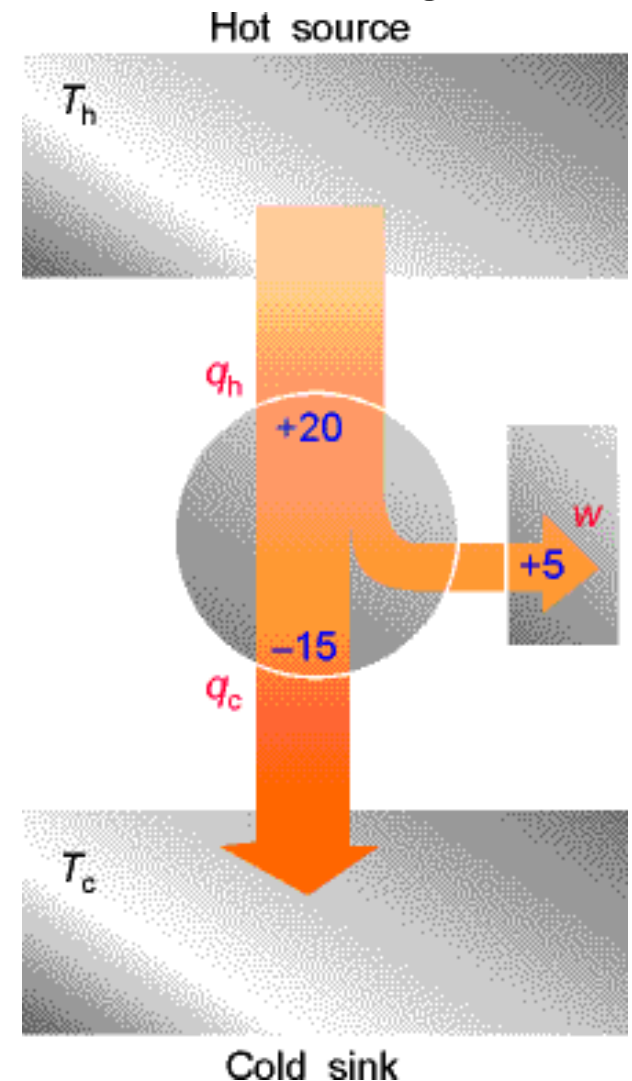
The greater the work output from a given supply of heat, the greater the efficiency of the engine

Work performed by the engine is the difference between heat supplied from the heat source and returned to the cold sink:

$$\varepsilon = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

Since $q_c < 0$,

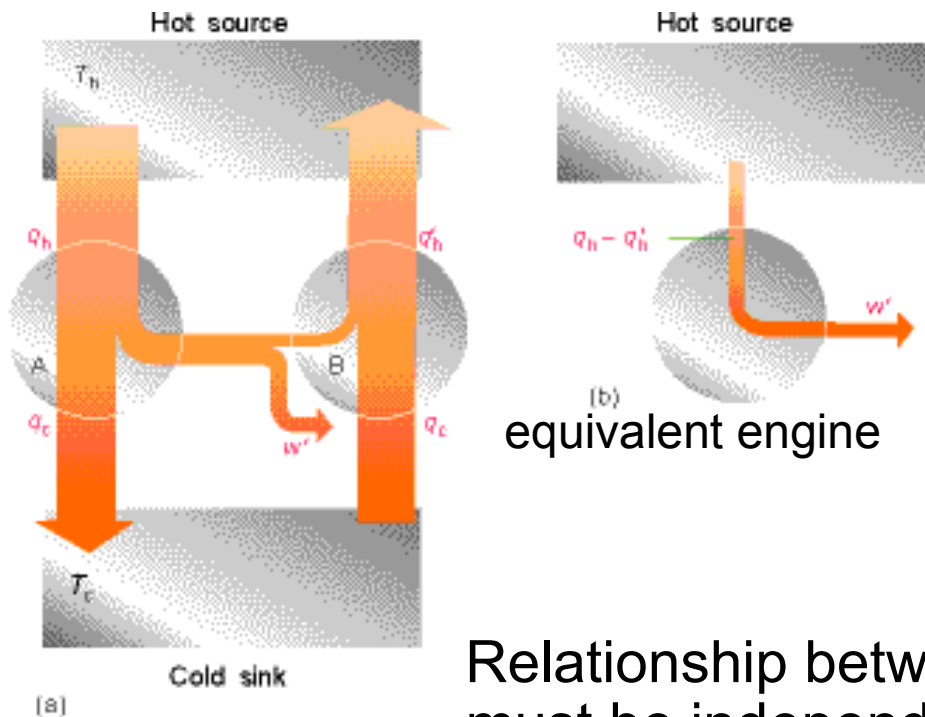
$$\varepsilon_{\text{rev}} = 1 - \frac{T_c}{T_h}$$



Carnot Cycles and Engines

Second Law: all reversible engines have the same efficiency regardless of construction - Two engines A and B, assume A more efficient than B, coupled together using the same reservoirs

A: takes heat q_h , releases heat q_c , B: takes heat q_c releases q_h'
Since A more efficient than B, not all work A produces is needed for this process, and difference can be used to do work



Net result: cold reservoir stays the same, hot reservoir loses energy, and work has been produced.
Problem: heat (disordered thermal motion) has been converted directly into work (ordered molecular motion) without the need for a cold sink - assumption that reversible engines A and B can have different efficiencies is false!

Relationship between heat transfers and temperatures must be independent of working materials

Carnot Cycles: S is a State Function*

Any reversible cycle can be thought of as a collection of Carnot cycles - this approximation becomes exact as cycles become infinitesimal

Entropy change around an individual cycle is zero
Sum of entropy changes over all cycles is zero

In interior, entropy change along any path is cancelled by the entropy change along the path of shared with its neighbour

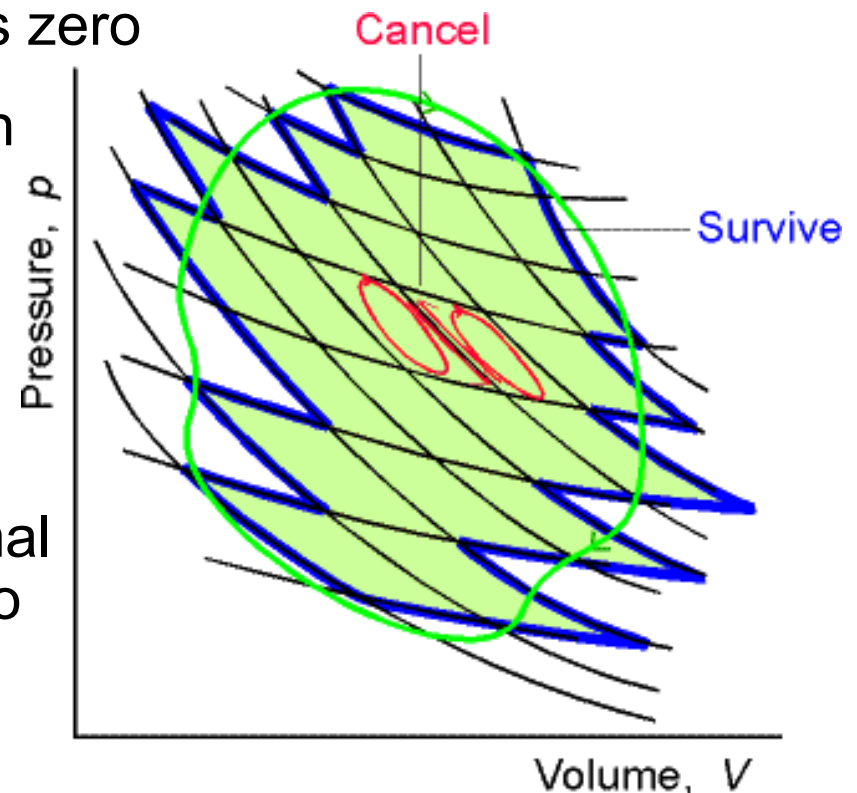
Thus, all entropy changes cancel except those along the perimeter of the entire cycle - but the sum of the paths along of the perimeter, if the paths are infinitesimal in size, match the overall cycle exactly, so

$$\sum_{\text{all}} \frac{q_{\text{rev}}}{T} = \sum_{\text{perimeter}} \frac{q_{\text{rev}}}{T} = 0$$

$$\oint \frac{dq_{\text{rev}}}{T} = 0$$

dS is an exact differential and therefore S is a state function

*Carnot engine



Rudolf Clausius

Rudolf Julius Emanuel Clausius (January 2, 1822 – August 24, 1888), was a German physicist and mathematician, and was one of the founders of thermodynamics. His most important paper, on the mechanical theory of heat, published in 1850, first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of entropy. He discovered the fact that entropy can never decrease in a physical process and can only remain constant in a reversible process, a result which became known as the Second Law of Thermodynamics



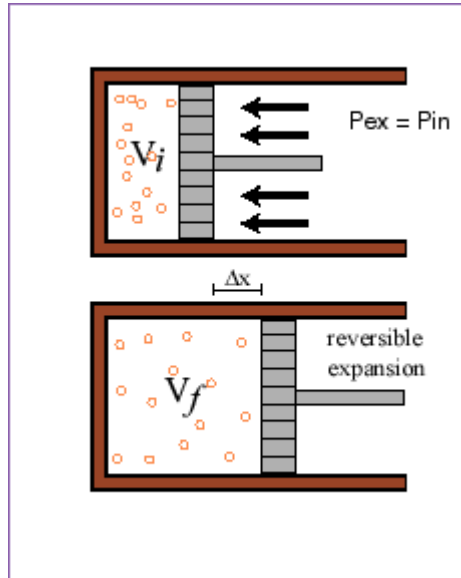
Clausius graduated from the University of Berlin in 1844, and got his doctorate from the University of Halle in 1848. He then taught in Berlin, Zürich, Würzburg, and Bonn.

In 1870 Clausius organized an ambulance corps in the Franco-Prussian War. He was wounded in battle, leaving him with a lasting disability. He was awarded the Iron Cross for his services. His wife, Adelheid Rimpham, died in childbirth in 1875, leaving him to raise their six children. He continued to teach, but had less time for research thereafter. A crater on the Moon has been named in honor of this founding father of thermodynamics.

The Clausius Inequality

Isothermal expansion of a perfect gas:

$$w_{\text{isothermal,rev}} = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

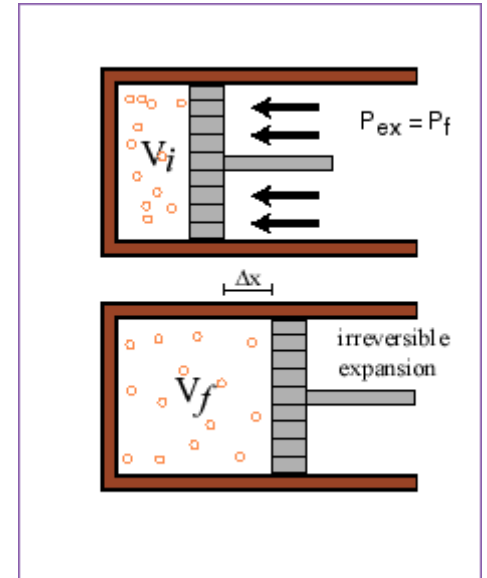


$$w_{\text{isothermal,irrev}}$$

$$= -p_f \Delta V$$

$$= -\frac{nRT}{V_f} \Delta V$$

$$= -nRT \frac{\Delta V}{V_f}$$



- Take $V_f = 2V_i$, $w_{\text{irrev}} = -(0.5)nRT$, and $w_{\text{rev}} = -(0.693)nRT$ (more work done on surroundings by reversible expansion)
- Since isothermal expansion, $\Delta U = \Delta H$, and $q = -w$
- This means that $q_{\text{rev}} > q_{\text{irrev}}$
- S_{sys} is state function, independent of path, $\Delta S_{\text{sys}} = q_{\text{rev}}/T = (0.693)nR$
- S_{sur} depends on amount of heat transferred:
 $\Delta S_{\text{sur, rev}} = -(0.693)nR$, $\Delta S_{\text{sur, irrev}} = -(0.5)nR$

The Clausius Inequality, 2

- In the reversible case, $\Delta S_{\text{tot, rev}} = 0$, since the entropy change of system and surroundings will have opposite signs
- In the irreversible case, $\Delta S_{\text{tot, irrev}} = 0.193nR$

This is a general result: *all irreversible reactions are spontaneous and have a total entropy change which is greater than zero*

For system in mechanical and thermal contact with surroundings, at some temperature, T , there may not be mechanical equilibrium. Any change in state has entropy changes dS_{sys} (system) & dS_{sur} (surroundings). The process may be irreversible, total entropy will increase

$$dS_{\text{sys}} + dS_{\text{sur}} \geq 0, \quad \text{or} \quad dS_{\text{sys}} \geq -dS_{\text{sur}}$$

Since $\Delta S_{\text{sur}} = q_{\text{sur}}/T_{\text{sur}}$, $dS_{\text{sur}} = -dq/T$, where dq is the heat provided to the system during the process, and $dq_{\text{sur}} = -dq$). Then for any change

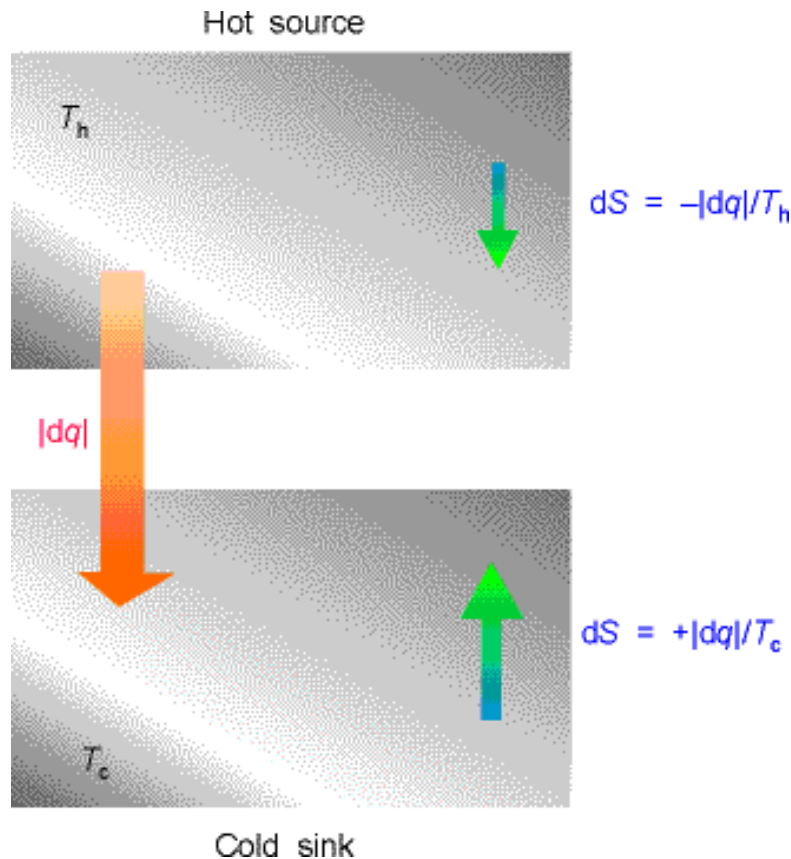
$$dS_{\text{sys}} \geq \frac{dq}{T}$$

$$dS_{\text{sys}} \geq 0 \quad (\text{system isolated from surroundings})$$

The Clausius Inequality, 3

This is our signpost of spontaneous change: in an isolated system the entropy of the system alone cannot decrease due to spontaneous change

Example 1: Irreversible adiabatic change, $dq = 0$, and $\therefore dS \geq 0$
 Entropy of system increases, entropy of surroundings stays constant (since no heat transfer has occurred), $dS_{\text{tot}} \geq 0$



Example 2: Irreversible isothermal expansion of perfect gas: $dq = -dw$
 If into a vacuum, $w = q = 0$, so $dS \geq 0$, $dS_{\text{sur}} = 0$ and $dS_{\text{tot}} \geq 0$

Example 3: Spontaneous cooling

$$dS = \frac{|dq|}{T_c} - \frac{|dq|}{T_h} = |dq| \left(\frac{1}{T_c} - \frac{1}{T_h} \right)$$

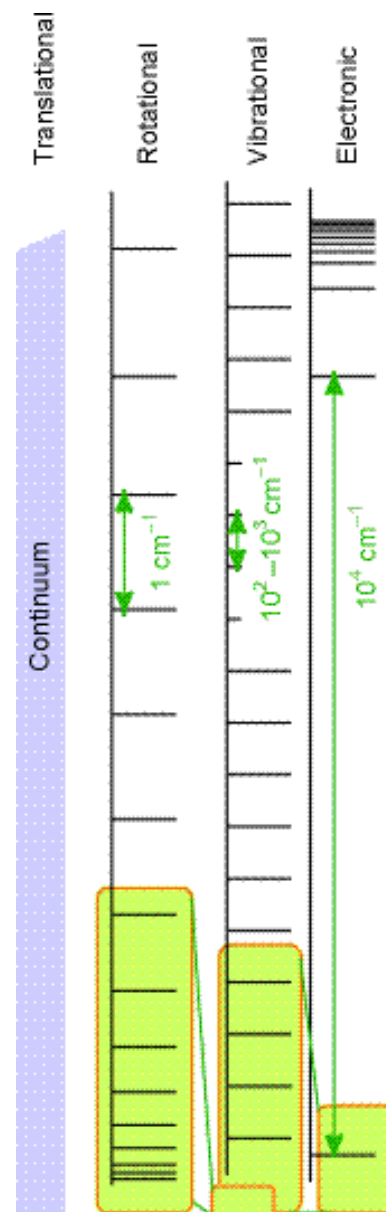
$dS > 0$, since $T_h > T_c$, so cooling is spontaneous - if two temperatures are equal, $dS_{\text{tot}} = 0$

Aside: Energy Quantization

At the start of this century, there were certain physical anomalies which could not be explained using **Newtonian (Classical) Mechanics** - at the atomic level matter behaves differently

A new set of mechanics, developed by Einstein, Schroedinger and others, demonstrated both experimentally and theoretically that at the atomic and molecular levels, the energy of particles is not a **continuum**, but rather, is **quantized: Quantum Mechanics**

Translational motion of molecules in macroscopic containers can be treated in many cases by *classical mechanics*, but rotation, vibration and motion of electrons (electronic transitions) have **quantized energy levels**



Aside: Populations of States

Molecules and atoms at a single temperature will individually be in one energy state in one instant, and another completely different energy state in another, due to collisions, etc. We cannot track the energy of an individual molecule: but, we can however monitor the populations of the various energy states quite easily (i.e., watch the behaviour of collections or ensembles of molecules)

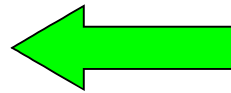
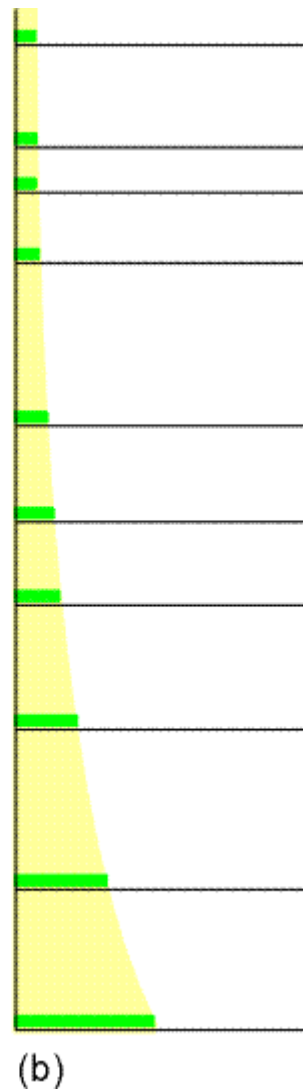
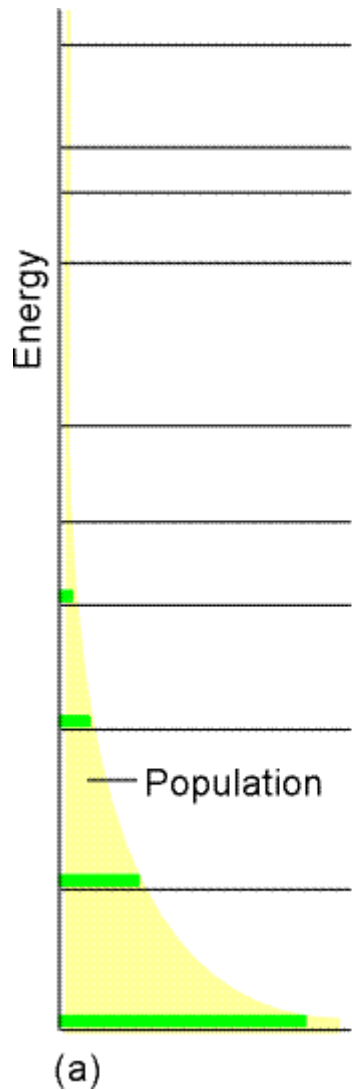
At temperatures > 0 , molecules are distributed over available energy levels according to the **Boltzmann Distribution**, which gives the ratio of particles in each energy state:

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/kT}$$

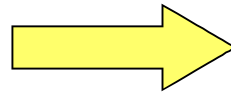
At the lowest temperature $T = 0$, only the lowest energy state is occupied. At infinite temperature, all states are equally occupied.

Degenerate states: States which have the same energy
These will be **equally populated!**

Aside: Boltzmann Distributions

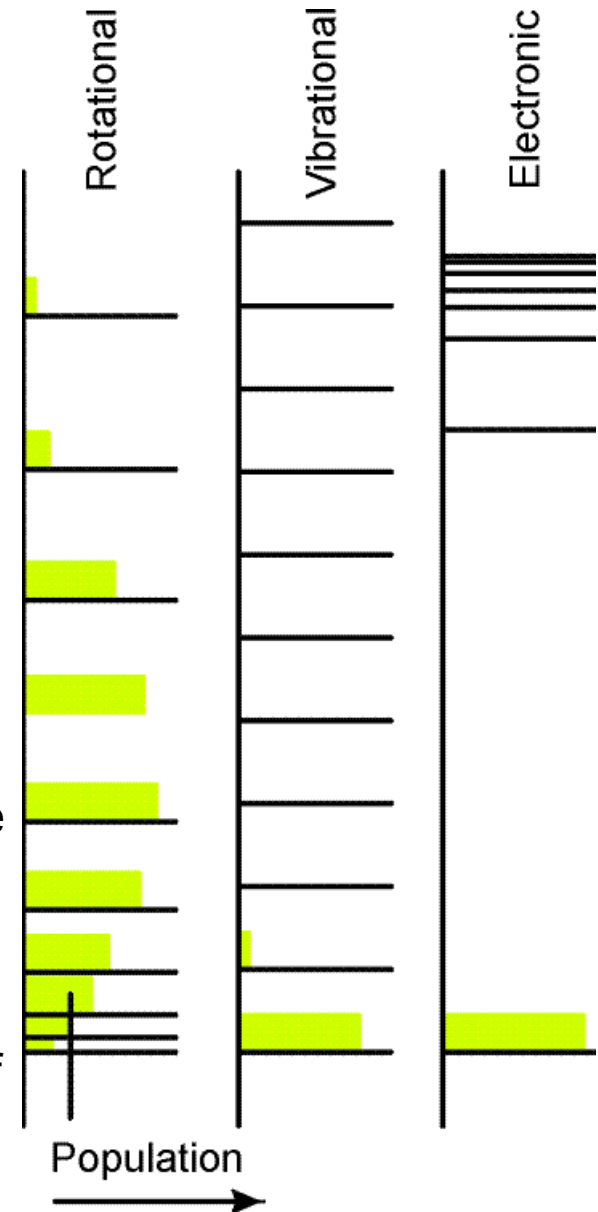


Populations for (a) low & (b) high temperatures Boltzmann predicts an exponential decrease in population with increasing temperature



At room T , only the ground electronic state is populated. However, many rotational states are populated, since the energy levels are so closely spaced.

More states are significantly populated if energy level spacings are near kT !



Aside: Boltzmann's Entropy

Ludwig Boltzmann (1844-1906) was an Austrian mathematician and physicist who was most famous for his creation of **statistical mechanics**, which connects the properties and behaviour of collections or **ensembles** of atoms and molecules with the large scale properties and behaviour of the substances of which they were the building blocks.

Entropy is a measure of disorder in a system, where **disorder** is defined formally as *the number of different microstates a system can be in, given that the system has fixed composition, volume, energy, pressure and temperature*. By "microscopic states", we mean the exact states of each of the molecules making up the system.

$$S = k \ln W \quad \text{or} \quad W = e^{S/k}$$

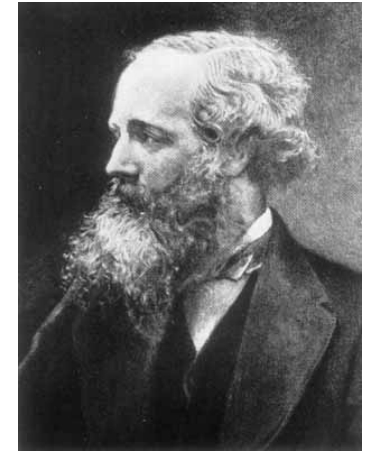
where W is defined as the number of total possible microstates or the number of total ways the constituents of the system can combine. Thus, the more microstates or combination pathways there are, the higher the entropy.

Boltzmann has also be called a "grandfather" to quantum theory, since modern stat mech connects classical mechanics and quantum mechanics

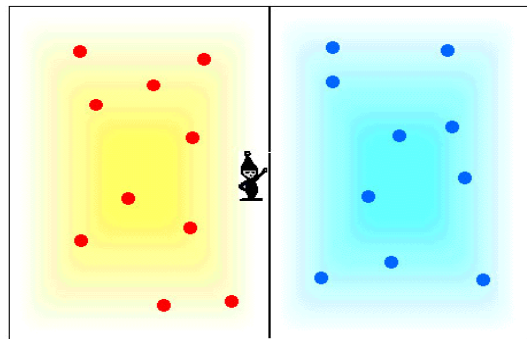
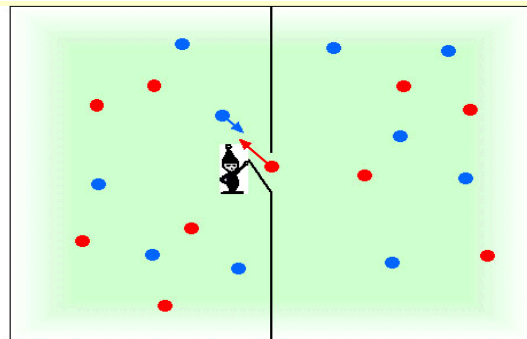


Aside: Maxwell's Demon

James Clerk Maxwell (1831-1879) was a Scottish mathematician and physicist who published physical and mathematical theories of the electromagnetic field, published as "A Treatise on Electricity and Magnetism (1873)", which included the formulas today known as the **Maxwell equations**.



With Clausius, he developed the kinetic theory of gases. In "Illustrations of the Dynamical Theory of Gases" (1860), he described the velocity distribution of molecules. His studies of kinetic theory led him to propose the Maxwell's demon paradox in a 1867 letter to Tait.



Maxwell's demon (termed a "finite being" by Maxwell) is a tiny hypothetical creature that can see individual molecules. The demon can make heat flow from a cold body to a hot one by opening a door whenever a molecule with above average kinetic energy approaches from the cold body, or below average kinetic energy approaches from the hot body, then quickly closing it. This process appears to violate the second law of thermodynamics, but was used by Maxwell to show that the second law of thermodynamics is a statistical law describing the properties of a large number of particles.

Why? Because the acts of observation and information necessarily requires changes in entropy (**information theory** - entropy is the lack of information about a system!).