Thermodynamics and Entropy

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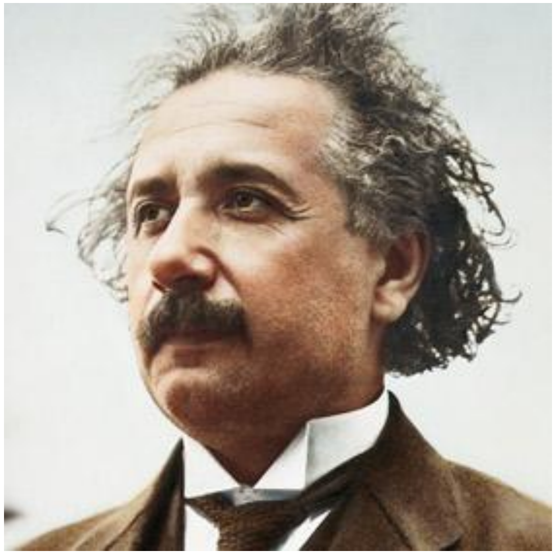
"Classical thermodynamics is the only theory of universal content which I am convinced will never be overthrown." – Albert Einstein



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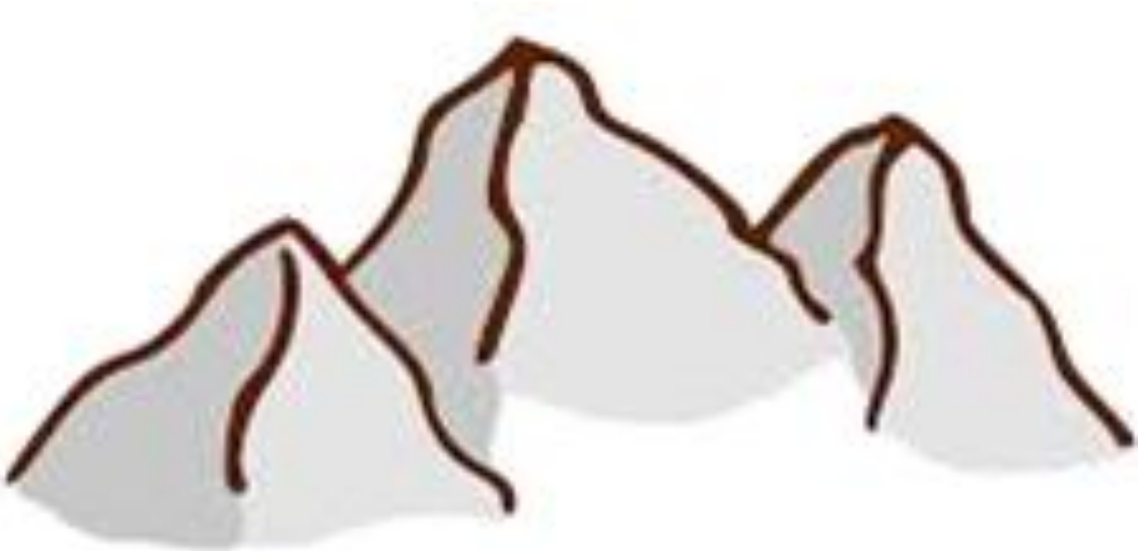
Another state function is the volume, V. This depends only on the number of moles, the pressure, and the temperature of the system through the equation of state, $V=V(n,P,T)$.

State Functions

A state function is like the altitude of a point on earth. It has the same value, regardless of how you get there.



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A good example is the total energy of a system, E(n,P,T).

Just as the elevation change in going from point A to point B only depends on those points, not the path taken, the change in energy of a system, ΔE, only depends on the initial and final points:

$\Delta E = E(\text{final}) - E(\text{initial})$

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You can change the energy of a system in two ways:

By transferring heat (q) to the system

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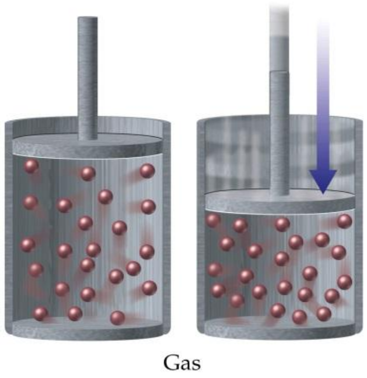

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In general chemistry, the most common form of work done on a system is pressure-volume work:

$$w = -\int_{V_1}^{V_2} P\, dV$$

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Note: q and w are not state functions. They depend on how the system is taken from one state to another.

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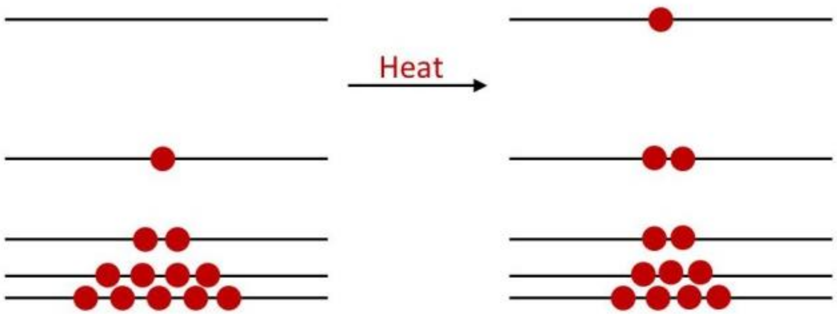
Heat and Work

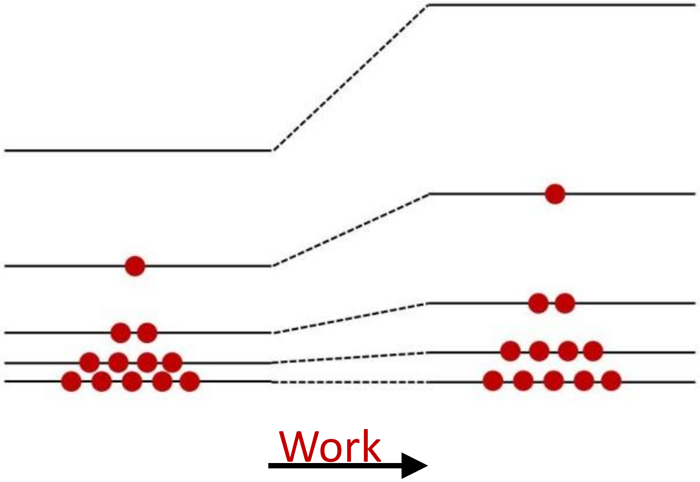
In terms of their definitions at a microscopic level, heat and work are different:

When heat is transferred to a system, the distribution of molecules in the different quantum states is changed:



Heat is added to the system

When work is done on a system, the energy levels themselves change:



Work is done on the system

In either case, the energy of the system goes up.

Enthalpy

The enthalpy, H, is another state function defined as

$$H \equiv E + PV$$

This is a useful state function because when the only sort of work involved is pressure-volume work.

$$\Delta H \quad = \quad \Delta E + \Delta(PV) \quad = \quad q + w + \Delta(PV) \quad = \quad q - \int_{V_1}^{V_2} P\, dV + \Delta(PV)$$

If the change in state occurs at constant pressure:

$$\Delta H \quad = \quad q - P\int_{V_1}^{V_2} dV + P\Delta V \quad = \quad q - P\Delta V + P\Delta V \quad = \quad q$$

The enthalpy change equals the heat absorbed in a process that occurs at constant pressure. Since most chemistry experiments are done at atmospheric pressure,

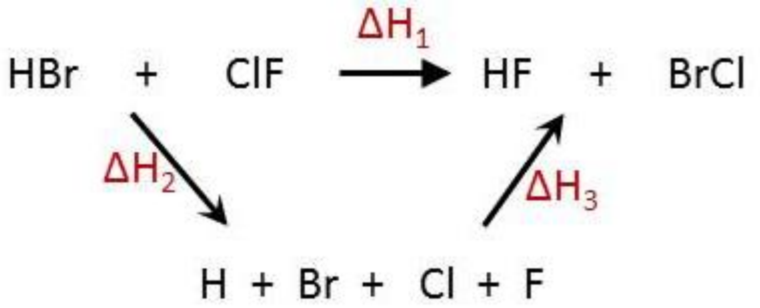
$$\Delta H \quad = \quad q_P$$

This is why ΔH values are commonly called "heat of reaction", "heat of vaporization", "heat of formation", "heat of fusion", etc. They are precisely the heat absorbed by the system, when the reaction is conducted at constant pressure.

Enthalpy as a State Function

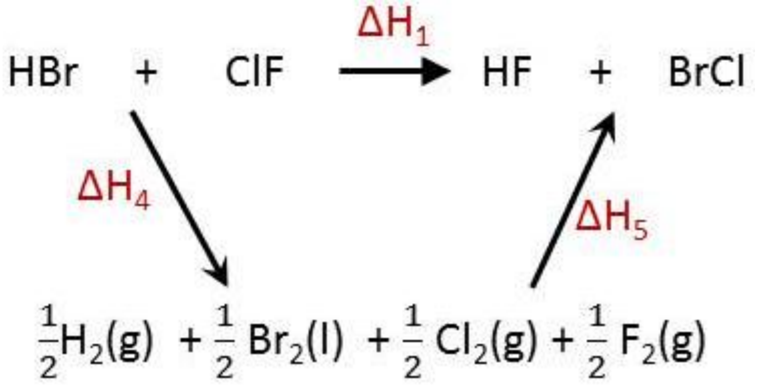
Because enthalpy is a state function, you get the same value for ΔH, no matter what path you take from reactants to products.

For example, you can take the reactants apart to atoms and then reassemble them to make the products:



$\Delta H_1 = \Delta H_2 + \Delta H_3$
$= D(HBr) + D(ClF) - D(HF) - D(BrCl)$
= bond energies of reactants
- bond energies of products

Or, you can take the reactants to their elements and then recombine them to form the products:



$\Delta H_1 = \Delta H_4 + \Delta H_5$
$= -\Delta H_f(HBr) - \Delta H_f(ClF)$
$+\Delta H_f(HF) + \Delta H_f(BrCl)$
= heat of formation of products
- heat of formation of reactants

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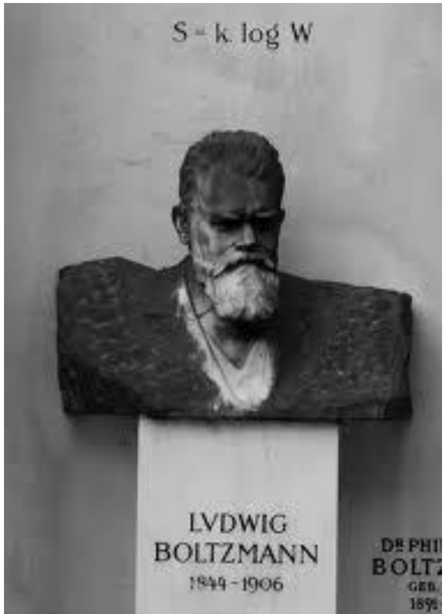

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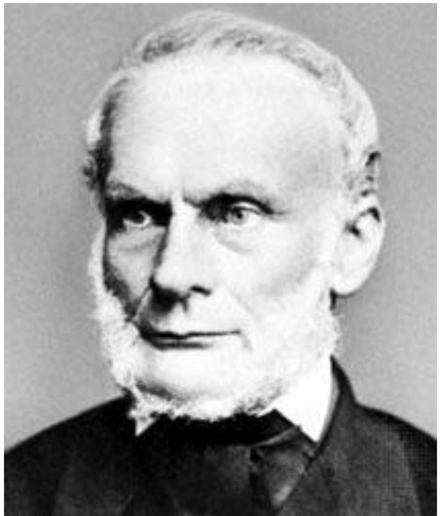

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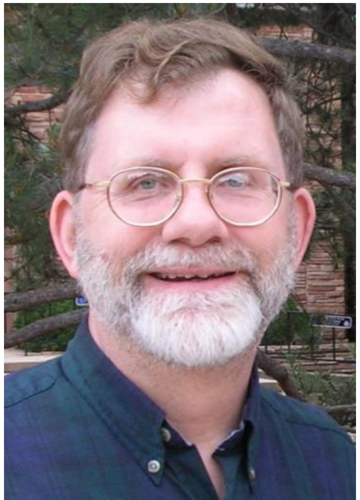

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All are true statements (though some are more precise or useful than others).

$S = k\,\ell n\,W$

In Boltzmann's formula, W is the number of ways the system can be arranged, consistent with the specified thermodynamic state of the system. It is NOT work, which is symbolized by a lower case w.

Then, ΔS will be given by ΔS = S(state 2) – S(state 1)

$$= k\,\ell n\,W(\text{state 2}) - k\,\ell n\,W(\text{state 1})$$

$$= k\,\ell n\,\frac{w(\text{state 2})}{w(\text{state 1})}$$

$$= k\,\ell n\,\frac{W_2}{W_1}$$

Here, k is appropriately called Boltzmann's constant and is given by

$$k = 1.3806 \times 10^{-23}\ \text{J}\cdot\text{K}^{-1}$$

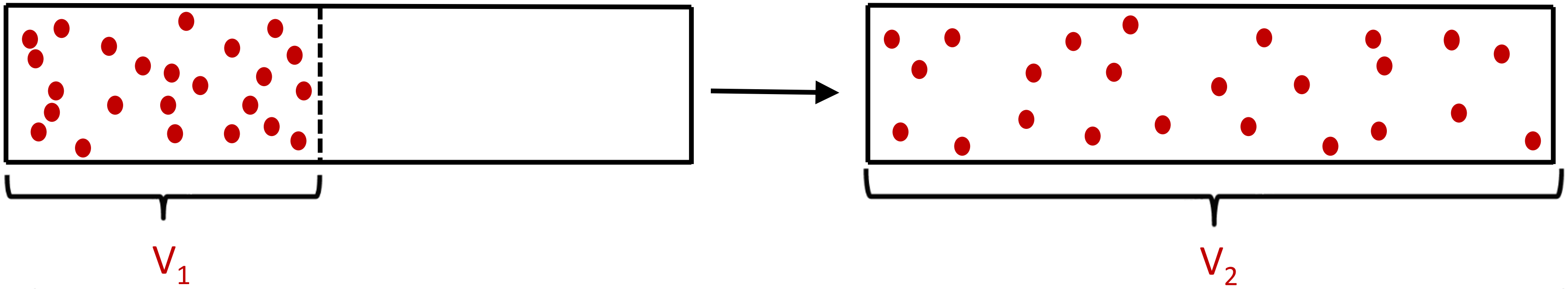
Boltzmann's constant, k, is just the gas constant, R, from the ideal gas law PV=nRT, expressed per molecule instead of per mole, so $k=R/N_A$, where N_A is Avogadro's number.

$$R = 0.08206\ \text{L-atm-mol}^{-1}\text{-K}^{-1}$$

or $$R = 8.314\ \text{J-mol}^{-1}\text{-K}^{-1}$$

$\Delta S = k\,\ell n\,\frac{W_2}{W_1}$: An example

Imagine a gas expanding from a volume V_1 into a volume V_2 at a constant temperature, T. [This is called an isothermal expansion.]



If each molecule has a volume v, then the volume V_1 can be divided into small volumes of size v, and the first molecule can be in any of the (V_1/v) small volumes. It can be in any of (V_1/v) places. This gives (V_1/v) ways of placing the molecule.

Ignoring the fact that the second molecule can't be in the same place as the first, it also have (V_1/v) places where it could be. This gives $(V_1/v)^2$ ways of placing the 2 molecules.

If we have N molecules, then the total number of ways of arranging them in the (V_1/v) small volumes is given by $(V_1/v)^N$. Therefore, $W_1=(V_1/v)^N$. Similarly, $W_2=(V_2/v)^N$.

Therefore, for an isothermal expansion of an ideal gas,

$$\Delta S = k\,\ell n\,\frac{W_2}{W_1} = k\,\ell n\,\frac{(V_2/v)^N}{(V_1/v)^N} = k\,\ell n\left(\frac{V_2}{V_1}\right)^N = Nk\,\ell n\left(\frac{V_2}{V_1}\right).$$

$\Delta S = \int_1^2 \frac{dq_{reversible}}{T}$ [Clausius]

If we reversibly expand a gas from volume V_1 into V_2 at a constant temperature, T, this means that we must supply an external pressure that is always infinitesimally less than the internal pressure of the gas. Then,

$$\Delta E = q + w = q_{reversible} + w = q_{reversible} - \int_{V_1}^{V_2} P\, dV$$

Because the gas is considered ideal, PV=nRT, and P = nRT/V. Therefore,

$$\Delta E = q_{reversible} - \int_{V_1}^{V_2} \frac{nRT}{V}\, dV = q_{reversible} - nRT \int_{V_1}^{V_2} \frac{dV}{V} = q_{reversible} - nRT\ell n\left(\frac{V_2}{V_1}\right)$$

$$\Delta E = q_{reversible} - nRT\ell n\left(\frac{V_2}{V_1}\right).$$

But the internal energy of an ideal gas depends only on T. An isothermal process cannot change the internal energy, so ΔE = 0.

This implies that $q_{reversible} = nRT\ell n\left(\frac{V_2}{V_1}\right)$

For an isothermal process, according to Clausius,

$$\Delta S = \frac{1}{T}\int_1^2 dq_{reversible} = \frac{q_{reversible}}{T} = \frac{1}{T} nRT\ell n\left(\frac{V_2}{V_1}\right) = nR\ \ell n\left(\frac{V_2}{V_1}\right).$$

So for the expansion of gas from V_1 to V_2, Clausius finds a change in entropy of $\Delta S = nR\ \ell n\left(\frac{V_2}{V_1}\right)$. This is exactly what Boltzmann's definition gave!

A question for you:

A very crude estimate for the entropy of vaporization of a liquid is to treat the liquid as a highly compressed ideal gas, then calculate the entropy change for expanding the gas to its volume at 1 atm pressure.

At its boiling point (100°C = 373.15K) , 1 mole of water occupies 0.01878 L; 1 mole of H_2O vapor at this temperature occupies 30.61 L from the ideal gas law.

If we treat the liquid water as a highly compressed ideal gas, then

$$\Delta S = nR\,\ell n\left(\frac{V_2}{V_1}\right) = 1\text{ mol} \times 8.315\,\frac{\text{J}}{\text{mol}\cdot\text{K}} \times \ell n\left(\frac{30.61\text{ L}}{0.01878\text{ L}}\right)$$

$$\boxed{\Delta S = 61.49\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}$$

YOUR QUESTION: Because this is an approximate treatment that considers liquid water to be a highly compressed ideal gas, will the value given above overestimate, or underestimate ΔS(vap)? Or will this estimate be exactly correct?

The accepted value is ΔS(vap) = 118.89 J/mol-K. What does this tell you about the relative amount of disorder in liquid water vs. highly compressed ideal gas water?

Isothermal Expansion of an Ideal Gas

The increase in entropy is caused by an increase in the number of states (ways of arranging the atoms or molecules) consistent with the thermodynamic state. The states of the individual atoms or molecules are often called microstates, so an increase in entropy is associated with an increase in the number of microstates available for the system.

The system is more "disordered" after the expansion, because you have lost information about where the molecules are located. Before the expansion, you knew for sure that the molecules were in the region designated as V_1, but now you know they could be there, or in the additional space. An increase in entropy is therefore associated with a loss of information about the system.

In this case, the increase in entropy is related to the dispersal of matter into a larger space.

A gas expands to fill the available volume, because that increases its entropy.

What about dispersal of energy?

Suppose we have two sets of molecules, both containing 1000 molecules. In set A, 6 molecules are in an excited state. In set B, none are. What will happen when the two sets are placed in thermal contact, so they can exchange energy?

Before thermal contact:

Set A	Set B
6 excited state 994 ground state	0 excited state 1000 ground state

After thermal contact:

Set A	Set B
6-n excited state 994+n ground state	n excited state 1000-n ground state

What is the change in entropy? What will happen, physically?

Dispersal of energy

Before thermal contact: State 1

6 excited state
994 ground state

Set A

0 excited state
1000 ground state

Set B

$W_{A1} = \frac{1000!}{6!\,994!} = 1.368 \times 10^{15}$

$W_{B1} = \frac{1000!}{0!\,1000!} = 1$

$W_1 = W_A \times W_B = 1.368 \times 10^{15}$

That's a LOT of microstates, but much smaller than a real system.

After thermal contact: State 2

6-n excited state
994+n ground state

Set A

n excited state
1000-n ground state

Set B

$W_{A2} = \frac{1000!}{(6-n)!(994+n)!}$

$W_{B2} = \frac{1000!}{n!(1000-n)!}$

$W_2 = \frac{(1000!)^2}{n!(1000-n)!(6-n)!(994+n)!}$

What is the most probable outcome?

Total number of microstates

Before thermal contact: $W_1 = 1.368 \times 10^{15}$ microstates

6 excited state
994 ground state

Set A

0 excited state
1000 ground state

Set B

After thermal contact: W_2

6-n excited state
994+n ground state

Set A

n excited state
1000-n ground state

Set B

$$\Delta S = k\,\ell n\,\frac{W_2}{W_1}$$

For n = 0 we get $W_2 = 1.368 \times 10^{15}$ microstates — $\Delta S = 0$
For n = 1 we get $W_2 = 8.249 \times 10^{15}$ microstates — $\Delta S = 1.80\,k$
For n = 2 we get $W_2 = 20.68 \times 10^{15}$ microstates — $\Delta S = 2.72\,k$
For n = 3 we get $W_2 = 27.61 \times 10^{15}$ microstates — $\Delta S = 3.00\,k$
For n = 4 we get $W_2 = 20.68 \times 10^{15}$ microstates — $\Delta S = 2.72\,k$
For n = 5 we get $W_2 = 8.249 \times 10^{15}$ microstates — $\Delta S = 1.80\,k$
For n = 6 we get $W_2 = 1.368 \times 10^{15}$ microstates — $\Delta S = 0$

The greatest entropy increase corresponds to the two systems reaching the same T.

Entropy increases when:

- Matter disperses through a system

  Examples: A gas filling a volume
  Two liquids or gases mix
  A solute dissolves in a solvent
- The range of possible locations of particles in the system increases

  Examples: A solid is melted to form a liquid
  A protein or polymer “melts” from a more rigid structure into a random coil structure
- Energy disperses through the system

  Examples: Two materials at different temperatures come to thermal equilibrium, and reach the same temperature.
- A system is heated to a higher temperature

In all cases, the system becomes more disordered in the sense that the thermodynamic state is consistent with a larger number of microscopic states.

The Second Law of Thermodynamics

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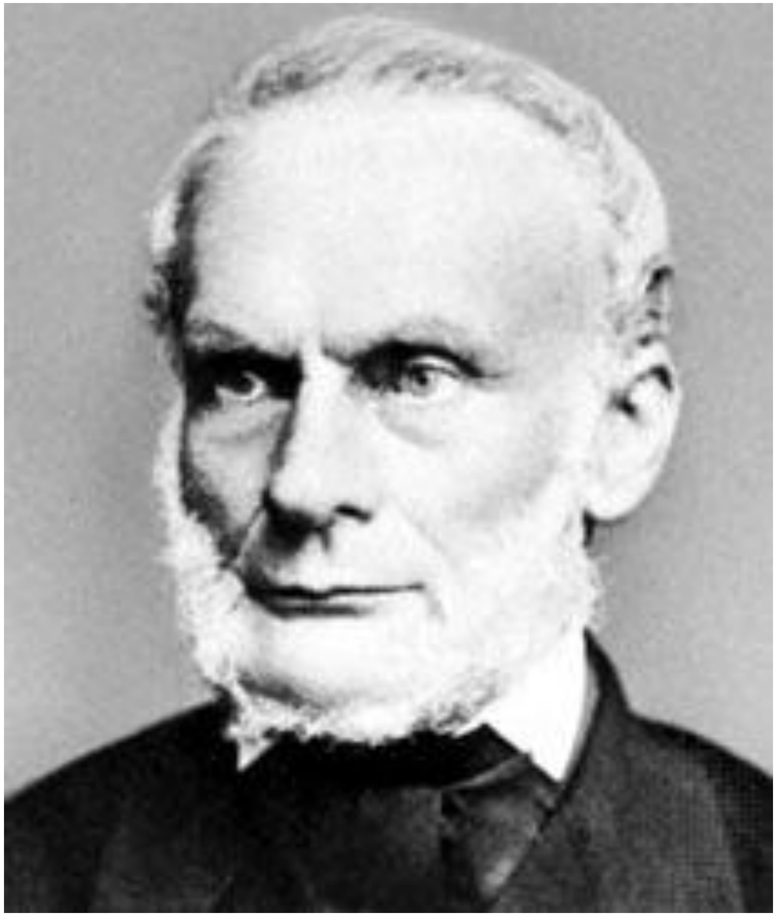

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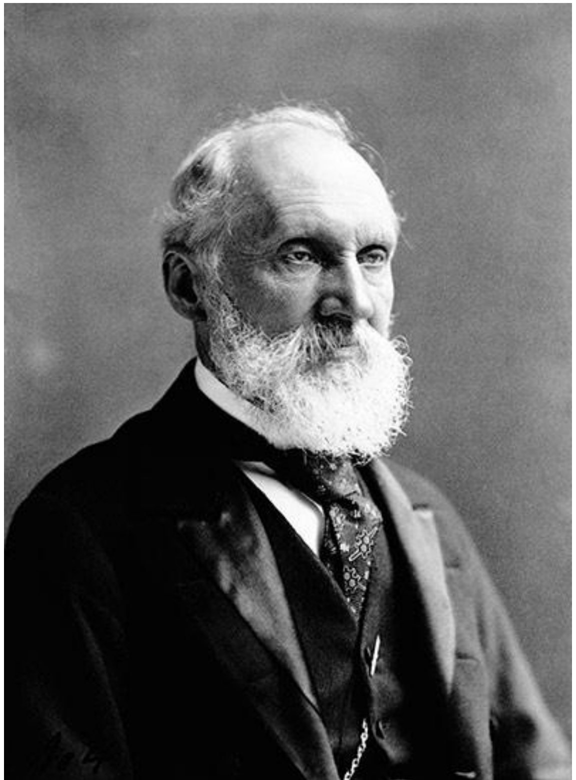

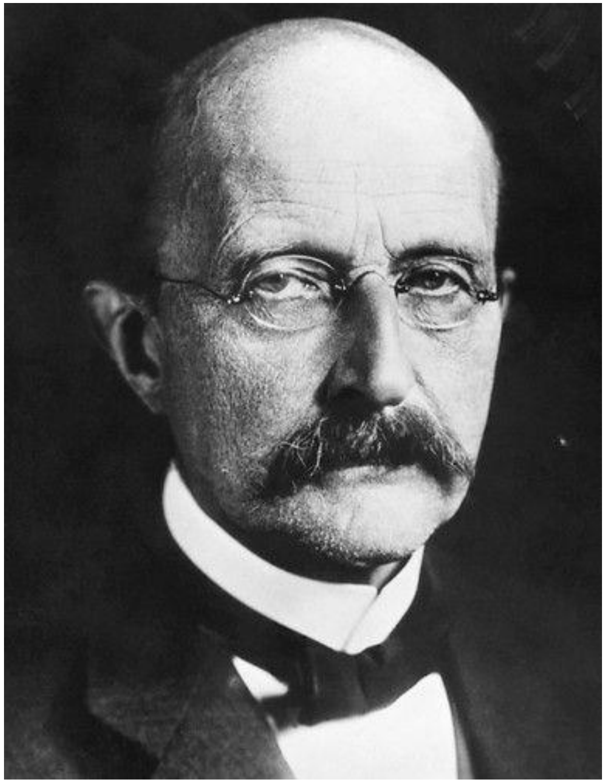

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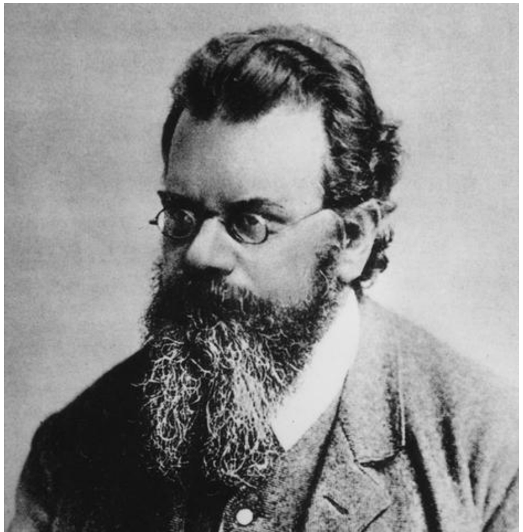
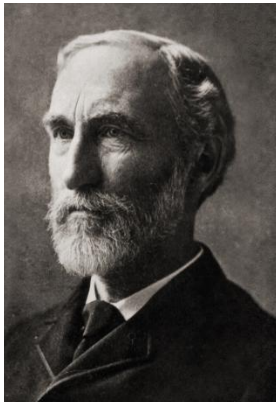
In an isolated system, the thermodynamic state that maximizes the number of microscopic states, W, is the equilibrium state. [Boltzmann]



The Second Law of Thermodynamics

Gibbs Free Energy, G



Another state function is the Gibbs free energy, defined as:

$$G \equiv H - TS$$

With this definition, we get $\Delta G = \Delta H - \Delta(TS)$

or $\Delta G = \Delta H - T\Delta S$

for processes occurring at a fixed temperature.

For processes occurring at a fixed temperature and pressure, $\Delta H = q_P$, so then

$$\Delta G = q_P - T\Delta S.$$

The heat transferred to the system is q_P, so the heat transferred to the surroundings is $-q_P$. The surroundings are everything except the system, so the transfer of any finite amount of heat is so minor that it may be considered a reversible process (as far as the surroundings are concerned). Therefore,

$$\Delta S_{surr} = -q_P/T$$

Solving $\Delta G = q_P - T\Delta S$ for ΔS, which is really ΔS_{system}, we get:

$$\Delta S_{system} = -\Delta G/T + q_P/T$$

Therefore,

$$\Delta S_{universe} = \Delta S_{surr} + \Delta S_{system} = -q_P/T - \Delta G/T + q_P/T = -\Delta G/T$$

But according to the second law, $\Delta S_{universe} \geq 0$ in any spontaneous, allowed process.
Therefore, $-\Delta G/T \geq 0$ or $\Delta G \leq 0$ in any spontaneous process.

For spontaneous processes that occur at constant T and P, ΔG must be negative.

The Third Law of Thermodynamics

The third law of thermodynamics is absolutely trivial if we use Boltzmann's definition of entropy.

The third law says:

The entropy of a perfect crystal at absolute zero is zero.

Using Boltzmann's definition of entropy, S = k $\ell n\ W,$ it is obvious that in a perfect crystal, all the molecules are oriented in the same way, so there is only one way of arranging them – therefore only one microstate.

$$\mathrm{S} = \mathrm{k}\ \ell n\ W\ = k\ \ell n\ 1 = 0$$

Likewise, at absolute zero, all of the molecules must be in their ground state, so there is only one way the excitations can be arranged.

$$\mathrm{Again, S} = \mathrm{k}\ \ell n\ W\ = k\ \ell n\ 1 = 0$$

Things to Think About
(or to discuss with your students)

1. When the molecules in a liquid (like water, for example) freeze, they become more ordered, so their entropy decreases. Why doesn't this contradict the second law of thermodynamics?

2. Imagine that you have 20 coins in a shoebox, all "heads" side up. Use Boltzmann's definition to calculate the change in entropy when the box is shaken and a random arrangement of "heads" vs. "tails" is obtained. Get your students to plot the probability of getting N coins "heads" up, as a function of N.

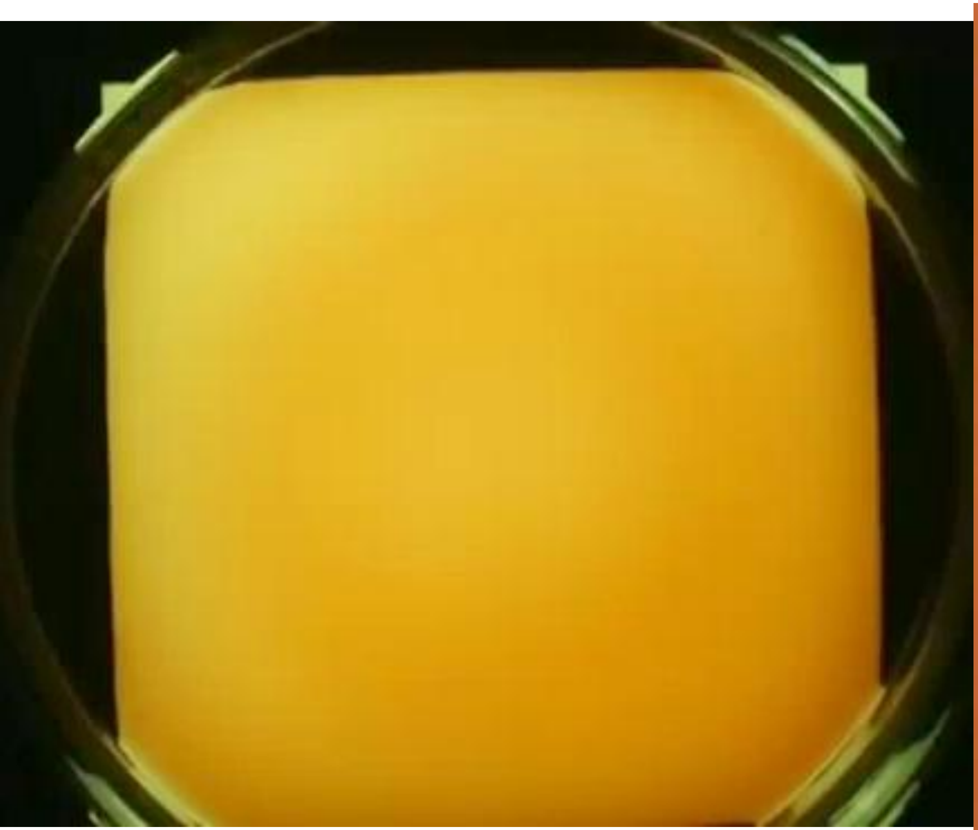
3. When a seed sprouts and grows into a tree, the tree takes in carbon dioxide from the air and minerals from the soil and forms a highly ordered structure. This corresponds to a decrease in entropy. Why doesn't this contradict the second law of thermodynamics?

Things to Think About
(or to discuss with your students)

4. When an object is exposed to a heat source on one side and a colder object on another, heat is taken in from one side and given off on the other. The dissipation of the heat can lead to the formation of interesting structures in the material substance, called dissipative structures. The structures formed decrease entropy, but the transport of heat causes an overall increase in entropy.

Things to Think About
(or to discuss with your students)

4. More dissipative structures, with chemical reactions added:



Things to Think About
(or to discuss with your students)

4. Dissipative structures in nature: