COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
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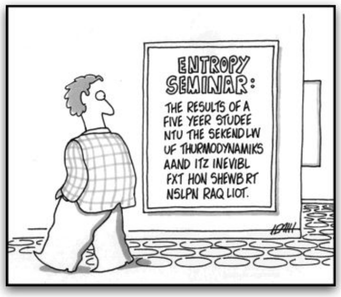
Lecture 7.

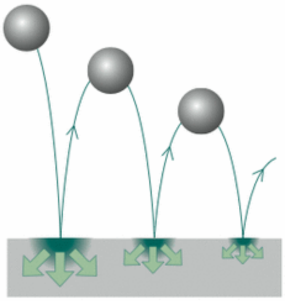
Entropy and the second law of thermodynamics.

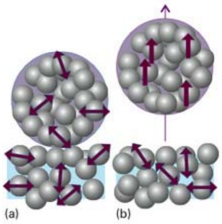


Recommended Reading

Entropy/Second law Thermodynamics

- http://en.wikipedia.org/wiki/Entropy
- http://2ndlaw.oxy.edu/index.html. This site is particularly good.
- Chemistry and chemical reactivity, Kotz, Treichel, Townsend, 7th edition, Chapter 19, pp.860-886. (Entropy, Gibbs energy)
- Chemistry^3, Chapter 15, Entropy and Free Energy, pp.703-741





A rationale for the second law of thermodynamics

The first law of thermodynamics states that the energy of the universe is constant: energy is conserved. This says nothing about the spontaneity of physical and chemical transformations.
The first law gives us no clue what processes will actually occur and which will not. The universe (an isolated system) would be a very boring place ($q = 0$, $w = 0$, $\Delta U = 0$) with only the first law of thermodynamics in operation.

The universe is not boring: Stars are born and die, planets are created and hurl around stars, life evolves amongst all this turmoil.

There exists an intrinsic difference between past and future, an arrow of time. There exists a readily identifiable natural direction with respect to physical and chemical change.

How can this be understood?

Spontaneous processes and entropy

Kotz, Ch.19, pp.862-868.
Discussion on energy dispersal
Very good.

A process is said to be spontaneous if it occurs without outside intervention.
Spontaneous processes may be fast or slow.
Thermodynamics can tell us the direction in which a process will occur but can say nothing about the speed or the rate of the process. The latter is the domain of chemical kinetics.
There appears to be a natural direction for all physical and chemical processes.

- A ball rolls down a hill but never spontaneously rolls back up a hill.
- Steel rusts spontaneously if exposed to air and moisture. The iron oxide in rust never spontaneously changes back to iron metal and oxygen gas.
- A gas fills its container uniformly. It never spontaneously collects at one end of the container.
- Heat flow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.
- Wood burns spontaneously in an exothermic reaction to form CO_2 and H_2O, but wood is never formed when CO_2 and H_2O are heated together.
- At temperatures below 0°C water spontaneously freezes and at temperatures above 0°C ice spontaneously melts.

The First Law of thermodynamics led to the introduction of the internal energy, *U*.
The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant.

The law that is used to identify the signpost of spontaneous change, the Second Law of thermodynamics, may also be expressed in terms of another state function, the **entropy**, *S*.

We shall see that the entropy (which is a measure of the energy dispersed in a process) lets us assess whether one state is accessible from another by a spontaneous change.

The First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify the *spontaneous changes* among those permissible changes.

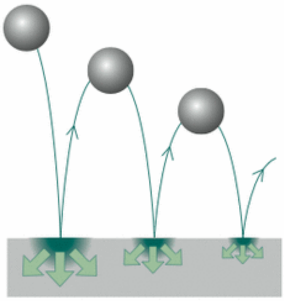
Atkins, de Paula PChem 8e OUP 2008
Ebook.
http://ebooks.bfwpub.com/pchemoup.php

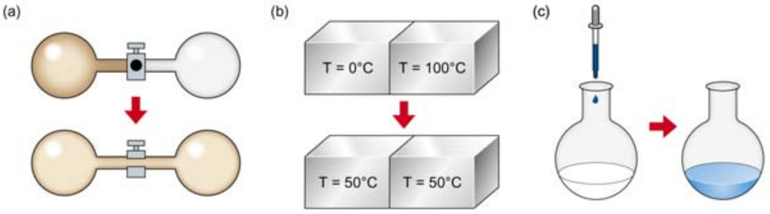
Spontaneity & Reversibility

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

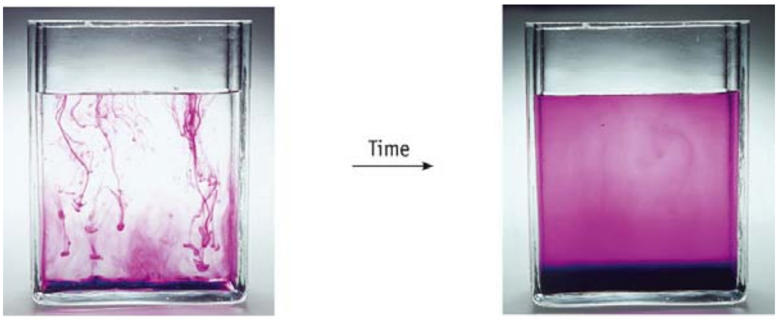


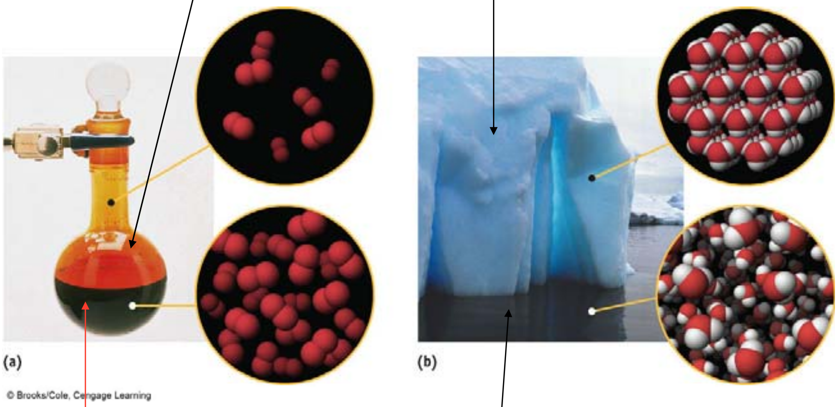


When the tap is opened, the gas expands into the empty bulb

A hot block and a cold block in contact—the temperatures become equal

The ink diffuses through the solution





$S^0(Br_2(vap) = 245.47\ JK^{-1}mol^{-1}$

ice

$S^0(Br_2(liq) = 152.2\ JK^{-1}mol^{-1}$

water

Kotz, p.869

What principle can be used to understand and explain all these diverse observations?
Early on in thermodynamics it was suggested that exothermicity might provide the key to understanding the direction of spontaneous change.
This is not correct however since, for example the melting of ice which occurs spontaneously at temperatures above 0°C is an endothermic process.

The characteristic common to all spontaneously occurring processes is an increase in a property called **entropy** (S). Entropy is a state function.
This idea form the basis of the Second Law of Thermodynamics.
The change in the entropy of the universe for a given process is a measure of the driving force behind that process.

In simple terms the second law of thermodynamics says that energy of all kinds in the material world disperses or spreads out if it is not hindered from doing so.
In a spontaneous process energy goes from being more concentrated to being more dispersed.
Entropy change measures the dispersal of energy: how much energy is spread out in a particular process or how widely spread out it becomes at a specific temperature.

Second law of Thermodynamics

The second law of thermodynamics states that a spontaneous process is one that results in an increase in the entropy of the universe, $\Delta S_{universe} > 0$, which corresponds to energy being dispersed in the process.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

See the following excellent account authored by Frank Lambert.

http://entropysite.oxy.edu/students_approach.html

His website is at: http://entropysite.oxy.edu/.

See also: Chemistry^3 pp.704-707 where disorder and entropy are related.

The Wikipedia site is also useful.
http://en.wikipedia.org/wiki/Entropy.

These is a considerable quantity of dross on the web purporting to define and discuss the entropy concept!

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

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

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

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

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

Entropy measures the spontaneous dispersal of energy :
How much energy is spread out in a process,
or how widely spread out it becomes – at a specific temperature.

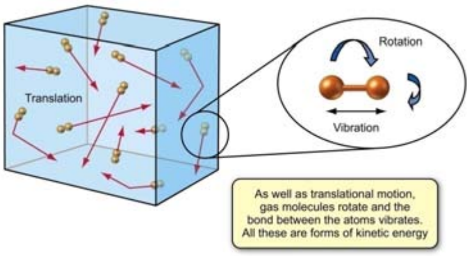
Mathematically we can define entropy as follows : entropy change = energy dispersed/temperature. In chemistry the energy that entropy measures as dispersing is 'motional energy', the translational, vibrational and rotational energy of molecules, and the enthalpy change associated with phase changes.

Energy transferred as heat
Under reversible conditions.

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

$$\Delta S_{system} = \frac{\Delta H_{phase\,change}}{T}$$

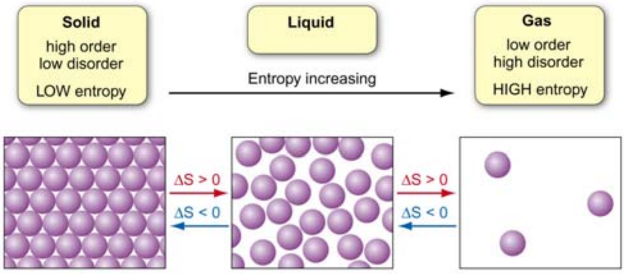
Entropy units : J mol^{-1} K^{-1}



Note that adding heat energy reversibly means that it is added very slowly so that at any stage the temperature difference between the system and the surroundings is infinitesimally small and so is always close to thermal equilibrium.

Entropy changes during phase transformation.

Read Chemistry^3 worked Example 15.2 p.710.



We can readily calculate ΔS during a phase change – fusion (melting), vaporization, sublimation. These processes occur reversibly and at constant pressure and so we assign $q_{rev} = \Delta H$.

Vaporization
Liquid/vapour
transition

$$\Delta_{vap}S = S_{vap} - S_{liq}$$
$$q_{rev} = \Delta_{vap}H$$
$$\Delta_{vap}S^0 = \frac{\Delta_{vap}H^0}{T_b}$$

Fusion
Liquid/solid
transition

$$\Delta_{fus}S = S_{liquid} - S_{solid}$$
$$q_{rev} = \Delta_{fus}H$$
$$\Delta_{fus}S^0 = \frac{\Delta_{fus}H}{T_m}$$

Entropy change at standard pressure (p = 1 bar).

T_b, T_m refer to boiling point and melting point temperatures respectively.

Temperature variation of system entropy.

See worked example 15.3 Chemistry^3, p.711-712.

The entropy of a system increases as the temperature is increased, but by how much?
If $S(T_1)$ denotes the entropy of 1 mol of substance at a temp. T_1 then the entropy of that substance at a temperature T_2 assumed greater than T_1 is given by the following expression.

$$S(T_2) = S(T_1) + C_{P,m}\ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = S(T_2) - S(T_1) = C_{P,m}\ln\left(\frac{T_2}{T_1}\right)$$

Derivation (following Chemistry^3 box 15.1 p.711)

We need to express the definition of entropy in terms of the differential $d'q_{rev}$, and also recall the definition of the latter.

$$dS = \frac{d'q_{rev}}{T}$$

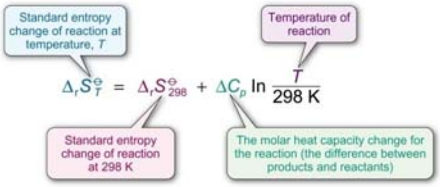
$$d'q_{rev} = C_{P,m}dT$$

We now integrate to obtain the necessary result.

$$dS = \frac{C_{P,m}dT}{T}$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{C_{P,m}dT}{T} = C_{P,m}\int_{T_1}^{T_2}\frac{dT}{T}$$

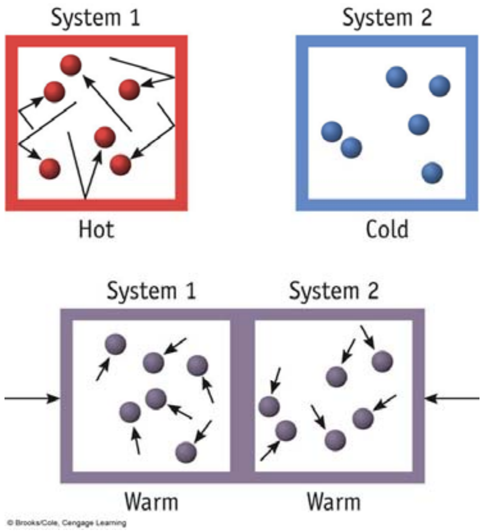
$$\Delta S = S(T_2) - S(T_1) = C_{P,m}\ln\left(\frac{T_2}{T_1}\right)$$



Entropy : a microscopic representation.

See Kotz, section 19.3 pp. 864-868

Entropy is a measure of the extent of energy dispersal At a given temperature.
In all spontaneous physical and chemical processes energy changes from being localized or concentrated in a system to becoming dispersed or spread out in a system and its surroundings.
Why however does energy dispersal occur?
To answer this we need to resort to the microscopic scale and look at quantized energy levels.
This type of approach leads to the realm of <u>molecular</u> or <u>statistical thermodynamics</u>.



Spontaneous process tends towards the equilibrium state.

What entropy is not and what it is.

Entropy is not disorder. Entropy is not a measure of disorder or chaos. Entropy is not a driving force.
The diffusion, dissipation or dispersion of energy in a final state as compared with an initial state is the driving force in chemistry.
Entropy is the index of that dispersal within a system and between the system and its surroundings.
In short entropy change measures energy's dispersion at a stated temperature.
Energy dispersal is not limited to thermal energy transfer between system and surroundings ('how much' situation).
It also includes redistribution of the same amount of energy in a system ('how far' situation) such as when a gas is allowed to expand adiabatically ($q = 0$) into a vacuum container resulting in the total energy being redistributed over a larger final total volume.

Entropy measures the dispersal of energy among molecules in microstates. An entropy increase in a system involves energy dispersal among more microstates in the system's final state than in its initial state.

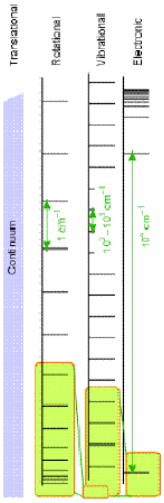
Reference: R.M.Hanson, S. Green, Introduction to Molecular Thermodynamics, University Science Books, 2008.

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)

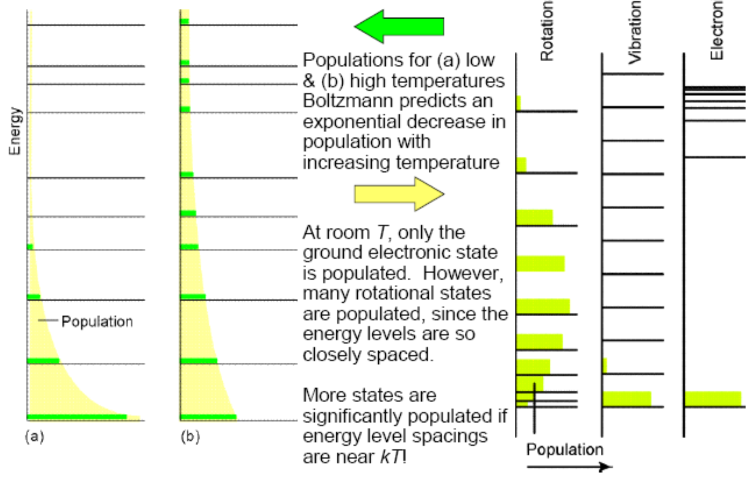
At temperatures > 0, molecules are distributed over available energy levels according to the **Boltzmann Distribution**, which gives the ratio of particles in each energy state:

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

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

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

Aside: Boltzmann Distributions

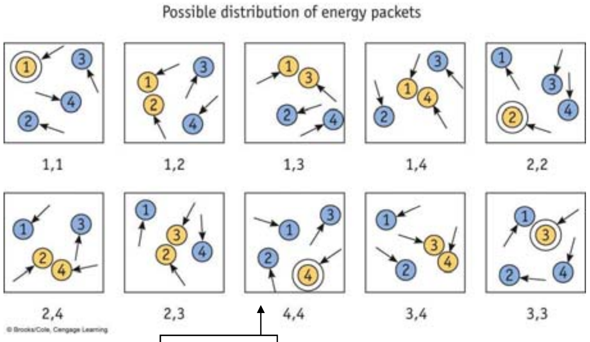


Populations for (a) low & (b) high temperatures Boltzmann predicts an exponential decrease in population with increasing temperature

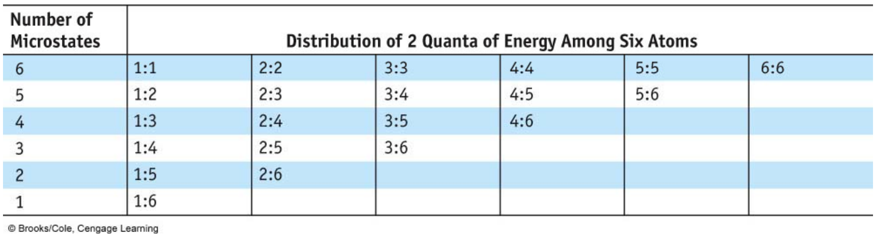
At room T, only the ground electronic state is populated. However, many rotational states are populated, since the energy levels are so closely spaced.

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

Possible ways of distributing two packets of energy between four atoms.
Initially one atom has 2 quanta and three with zero quanta.
There are 10 different ways (10 <u>microstates</u>) to distribute this quantity of energy

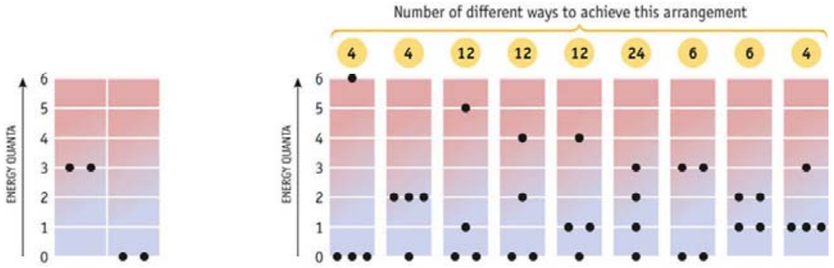


Microstate



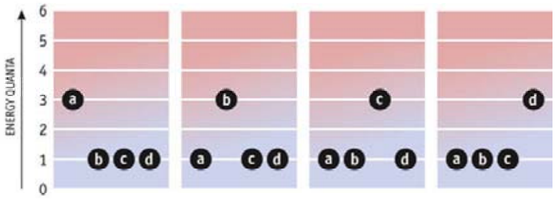
Number of Microstates	Distribution of 2 Quanta of Energy Among Six Atoms					
6	1:1	2:2	3:3	4:4	5:5	6:6
5	1:2	2:3	3:4	4:5	5:6	
4	1:3	2:4	3:5	4:6		
3	1:4	2:5	3:6			
2	1:5	2:6				
1	1:6					

21 ways (21 microstates) to distribute 2 quanta of energy among 6 atoms.



(a) Initially, four particles are separated from each other. Two particles each have 3 quanta of energy, and the other two have none. A total of 6 quanta of energy will be distributed once the particles interact.

(b) Once the particles begin to interact, there are nine ways to distribute the 6 available quanta. Each of these arrangements will have multiple ways of distributing the energy among the four atoms. Part (c) shows how the arrangement on the right can be achieved four ways.



(c) There are four different ways to have four particles (a, b, c, and d) such that one particle has 3 quanta of energy and the other three each have 1 quantum of energy.

A total of 84 microstates is possible.

Fig. 19-6, p. 866

Entropy in the context of Molecular Thermodynamics.

Entropy measures the dispersal of energy among molecules in microstates.
An entropy increase in a system involves energy dispersal among more microstates in the system's final state than in its initial state.

$$S = k_B \ln W$$

$$\begin{aligned}\Delta S &= S_{final} - S_{initial} \\ &= k_B\left\{\ln W_{final} - \ln W_{initial}\right\} \\ &= k_B \ln\left(\frac{W_{final}}{W_{initial}}\right)\end{aligned}$$

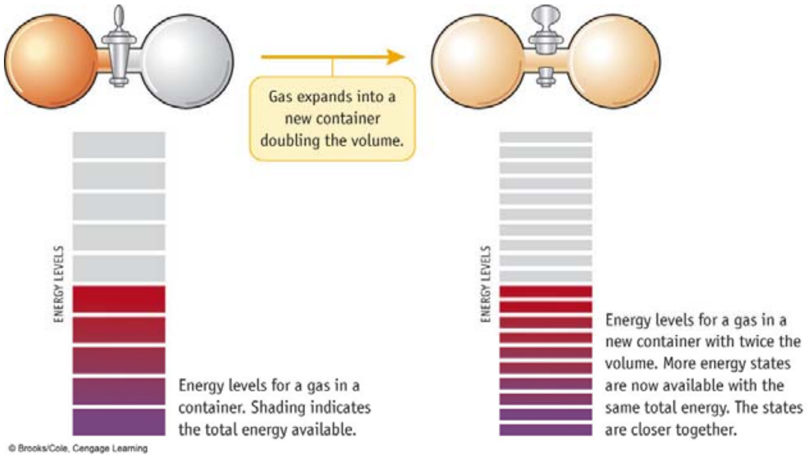
W = number of accessible Microstates
k_B = Boltzmann constant
= 1.38×10^{-23} J K^{-1}

Microstates with greatest energy dispersion are most probable.

Reference: R.M.Hanson, S. Green, Introduction to Molecular Thermodynamics, University Science Books, 2008.

Isothermal expansion of Ideal gas

$$\Delta S = nR \ln\left\{\frac{V_{final}}{V_{initial}}\right\}$$



Energy levels for a gas in a container. Shading indicates the total energy available.

Energy levels for a gas in a new container with twice the volume. More energy states are now available with the same total energy. The states are closer together.

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At a given temp T the volume V is proportional to the total number of microstates.

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