

Notice: entropysite.com is now <http://entropysite.oxy.edu>. Please update your links and bookmarks.

Entropy is not “disorder”

Entropy change measures the dispersal of energy (at a specific temperature), i.e. q_{rev}/T

An introduction for instructors

Energy of any type disperses from being localized to becoming spread out*, if it is not constrained.

This is the ultimate basis of all statements about the second law of thermodynamics and about all spontaneous physical or chemical processes.

* Energy dispersal; energy becoming spread out. In simple physico-chemical processes such as ideal gas expansion into a vacuum, “spread out” describes the literal movement of energetic molecules throughout a greater volume than they occupied before the process. The final result is that their initial, comparatively localized, motional energy has become more dispersed in that final greater volume. . Such a spontaneous volume change is fundamentally related to macro entropy change by determining the reversible work ($=-q$) to compress the gas to its initial volume, $RT \ln (V_2/V_1)$ with the result being $\Delta S = R \ln (V_2/V_1)$. On a molecular thermodynamic basis, gas expansion into a vacuum would be described in terms of microstates by the Boltzmann equation via:

$$\begin{aligned}\Delta S &= k_B \ln W_2/W_1 \\ &= k_B \ln [(V_2/V_1)^N] \\ &= k_B N \ln V_2/V_1 \\ &= R \ln V_2/V_1.\end{aligned}$$

Thus, the amount of the spontaneous dispersion of molecules' energy in three-dimensional space is related to molecular thermodynamics, to a larger number of microstates, and measured by changes in entropy.

IMPORTANT NOTE: The initial statement above (about the movement of molecules into a larger volume as solely due to their motional energy) is only valid as a description of entropy change to high school students or non-scientists when there will not be any further discussion of entropy. Such a statement “smuggles in entropy change” wrote Norman C. Craig. I interpret this to be ‘smuggling’ because thermodynamic entropy change is not simply a matter of random molecular movement, but consists of two factors, not one. Entropy change is certainly *enabled* in chemistry by the motional energy of molecules (that can be increased by bond energy change in chemical reactions) but thermodynamic entropy is only *actualized* if the process itself (expansion, heating, mixing) makes accessible a larger

number of microstates, a maximal Boltzmann probability at the specific temperature. [Information 'entropy' only has the latter factor of probability (as does the 'sigma entropy' of physics, $\sigma = S/k_B$) This clearly distinguishes both from thermodynamic entropy.]

Thus, to describe the cause of spontaneous events to less able or even to many students, I see no harm in "smuggling in entropy" as appearing to be simply a result of the nature of kinetic molecular behavior: Molecules spread out or disperse in three-dimensional space IF they are provided with a greater volume (and are separated from like molecules in a mixture). However, in speaking to capable students, the instructor should decide how much to share with them. We ourselves, of course, must always be aware that thermodynamic entropy involves the two factors of (1), motional energy and (2), calculation that indicates how much that energy can be dispersed (probability; the number of accessible microstates) under the conditions of the process. Each is necessary; neither is sufficient alone.

- In the case of gas expansion both macro and molecular thermodynamic *calculation* procedures can appear to be partly misleading to students and instructors so far as *what is happening* in the system in regard to motional energy dispersal. In macro thermodynamics, the restoration of the initial state certainly does result in calculating - q, the amount of energy dispersed. However, volume appears to be the only variable — as it is, but only because it is the indication of how greatly molecular motional energy *has been dispersed*! Then, similarly, in molecular thermodynamics via statistical mechanics using a cell model (where one molecule occupies one cell), the only factor that changes is V, dependent on the number of additional unoccupied cells. However, each accessible cell represents not only a volume of space but a microstate containing a molecule with motional energy.. Therefore, although the final calculation appears to represent only V increase due to additional spatial “positions”, this is a misleading “smuggling in entropy change”. The essential enabling factor in thermodynamic entropy, molecular motional energy, is present (and should be mentioned to students) because it was explicitly in each accessible cell counted by the combinatorics of statistical mechanics.

- A microstate of a thermodynamic system is a state containing the total energy of the system in *one* of an extremely large number of accessible arrangements of the energy of each of its particles at one instant. The constant redistribution of that energy among the particles leads successively to other accessible arrangements. If the entropy of a system increases in some process or reaction, that means that there are more accessible microstates for that macro state. More microstates mean that there are more chances for the system's total energy to be in a different microstate at any time — in contrast to its lesser chances when fewer microstates are accessible (a relatively greater localization). That is the meaning in molecular thermodynamics of energy becoming “more spread out or dispersed”. (Energy becoming more “spread out” or “dispersed” does *not* mean something like “smeared over many microstates”, an impossibility. The expressions refer only to *an increased number of accessible microstates in any one of which, at one instant, the total energy of the system might be*. This increased number of microstates is the fundamental reason that the qualitative view of spontaneous “energy dispersal” is applicable to all types of spontaneous chemical processes — to three-dimensional space occupancy, to energy transfer to a cooler system, to formation of a mixture, or to a complex chemical reaction.)

A useful approach to microstates for students is [here](#).

Entropy change is measured by the dispersal of energy: how *much* is spread out in a process, or how *widely* dispersed it becomes — always at a specific temperature.

"energy" in entropy considerations refers to the motional energy of molecules, and (if applicable) any phase change, and (in chemical reactions) bond energies in a system.

"dispersal of energy" in *macro* thermodynamics occurs in two ways:

(1) "how *much*" involves heat transfer, usually ΔH , to or from system and thus from or to its surroundings;
(2) "how *widely*" means spreading out the initial energy of a system in some manner, e.g., in gas expansion into a vacuum or mixing of ideal gases, the system's volume increases and thereby the initial energy of any component is simply more dispersed in that larger three-dimensional volume without any change in motional or other energies. In chemical reactions, ΔG is the function that must be used to evaluate the net energy dispersal in the universe of system and surroundings. In macro thermodynamics, both spontaneous and non-spontaneous processes are ultimately measured by their relationship to $\Delta S = q_{\text{rev}}/T$, where q is the energy that is dispersible/dispersed.

In *molecular* thermodynamics, all changes in the internal energy in a system or its surroundings (either ΔH increase or decrease in a system, or any type of more widely spreading its unchanged enthalpy) cause a change in the number of microstates and thus an increase or decrease in entropy. (A microstate is described above and also in detail at <http://entropysite.oxy.edu/microstate/index.html>.) An entropy change that is measured by macro methods is related to W , the number of microstates, by $\Delta S = k_B \ln W_{\text{final}}/W_{\text{initial}}$ where k_B is the Boltzmann constant.

"motional energy", its meaning.

In my writing for students, I sensed that many beginners are 'symbol challenged' from dealing with the many 'deltas' of ΔH , ΔE , ΔU , $P\Delta V$, ΔT (with ΔS and ΔG now coming). Thus, I have used "motional energy" (that is due to molecular motion) to make less abstract the ΔH involved in entropy change. Certainly, any instructor can transmit to all levels of students the idea of energy *dispersal* in entropy by "Molecules are astoundingly energetic particles. They average over a thousand mph (near room temperature) in gases and liquids (and vibrating *extremely* rapidly in solids) — colliding violently — and thus ceaselessly changing their speeds, individual energy states and direction of movement. They're instantly ready to bounce into any larger volume, if they aren't kept in a crystal by the attraction of other particles — or, if a gas, obstructed by a container (or a stopcock!) or if a liquid, kept from moving elsewhere by the container." "Motional energy" has dynamic connotations to better students that are implicit in H or ΔH but may be too abstract to most beginners. In chemistry, it is the kinetic energy of particles that in most simple processes *enables* a system's energy in changing from localized to becoming more dispersed or spread out.

The other common source of change is in a chemical reaction where the enthalpies of formation of the reactants are less than those of products that can be formed from them. In general terms, as an exothermic reaction is occurring, the $-\Delta H$ of the process is first spread among the products, increasing their motional energy, and then dispersed to the surroundings as the motion of the products decreases to the temperature of the original system. In an endothermic reaction, the required thermal energy is supplied to the system from (even slightly) hotter surroundings. There is a fundamental difference between the overall process of energy transfer in an endothermic reaction and simple contact of a hotter system with one that is cooler. (See the following section that treats such spontaneous heat transfer, i.e., phase change.) In an

endothermic reaction, the large quantities of energy, equal to the ΔH of the reaction, flow spontaneously from the surroundings because the temperature of the system does *not* rise to that of the surroundings until "completion" of the reaction. ("Completion" is in quotes because, of course, the final state may consist of an equilibrium mixture of the products and reactants rather than pure products.) The cause of the continued flow is the greater net dispersal of energy that occurs in the system during the process than the decreased dispersion in the surroundings, i.e., many more ways (microstates) that are accessible for the system's energy.

"phase change energy"

"Phase change energy" is a potential energy change in a system. Therefore, it is not as easily described to students as motional energy and, of course, is not pertinent to all entropy discussions, i.e., not to those in which no phase change has occurred from 0 K to the temperature being considered, or in the process at hand. However, the phrase encompasses the important process of transforming "motional energy" to potential energy. In a fusion or vaporization phase change occurring at a temperature minutely above the equilibrium temperature for such a change, ΔH from energetic molecules in the surroundings (molecular motion in the surroundings) causes the reversible breaking of intermolecular bonds and/or bond reorganization in the system. This influx of energy from the surroundings, in molecular thermodynamics terms, enormously increases W_{Final} , the number of accessible microstates for the system. Furthermore in fusion, because of bond cleavage the original total vibrational ("motional") energy of the molecules in the crystal is transferred to the translational movement of molecules in the liquid. The liquid-phase molecules rapidly break their bonds with adjacent molecules and can move a minute distance while making new bonds with other molecules. This motion, though slight, is far greater than the prior "dancing at a point" in the crystal. In vaporization, the thousand-fold increase in volume that becomes possible when intermolecular bonds in the liquid are broken results in an immense increase in accessible microstates — closer energy levels in greater volume leading to far larger numbers of those accessible microstates. (Of course, this can be presented to lower level students as simply "the energy of the liquid at the boiling point becoming more spread out in the larger volume".)

"always at a specific temperature"

"always at a specific temperature" means inclusion of T in any quantitative treatment of entropy change, fundamentally as $Dq(\text{rev})/T$. It is 'silent' in isothermal processes such as ideal gas expansion, but active as a denominator in phase change, and when temperature changes in a chemical process.

(1) In "how much" irreversible processes such as heating a system, where the reversible entropy change is

measured by incremental steps: $\Delta S = C_p \int d \ln T$ and the energy, $q(\text{rev})$, that is dispersed reversibly stepwise to the system from the surroundings (or the converse), is $C_p dT$.

(2) In "how widely dispersed" irreversible processes such as gas expansion into a vacuum, the reversible re-compression of the gas is $\Delta S = -q(\text{rev})/T = R \ln [V_2/V_1]$ and the "wider dispersal" of the energy in the original expansion is $RT \ln [V_2/V_1]$; similarly, for fluids that mix to result in a combined volume, V_2 , so that each component's internal energy that was originally confined in a volume of V_A or V_B , becomes more widely dispersed: $\Delta S = R \ln [V_2/V_{A \text{ or } B}]$, and the "wider dispersal" of the component's energy is $RT \ln [V_2/V_{A \text{ or } B}]$.

(3) In "how much AND how widely" reversible processes such as phase change: $\Delta S = q(\text{rev})/T$ where $q(\text{rev})$ is ΔH , the energy dispersed to or from the system. Phase change is not an increase in the motional energy of the system. It is an increase in the system's *potential energy* because the heat transfer breaks intermolecular bonds — that will reform and release the latent potential energy if the temperature falls below the phase change equilibrium temperature. However, that bond-breaking also increases the number

of locations accessible to molecules by allowing the vibrational energy of the crystal to be allocated to translation over greater distances in three dimensions. Thus, the description of "wider dispersal" of the original internal energy content by phase change is apropos. ("How much and how widely" also is an essential view of Chemical Reactions, as is developed in detail at the end of this presentation.)

As discussed before, with this terminology — and knowingly "smuggling in entropy" — entropy change in gas expansion, for example, can be readily described to lower level classes simply as "What would energetic, fast moving, continually colliding molecules of a gas do if they were in a glass bulb and they were allowed to get into a bigger volume? Just sit at the opening and stay in the bulb? Or spontaneously spread out their thousand mile an hour motional energy all over that new larger volume? Of course they'd zoom into a bigger space! That kind of spontaneous movement by molecules, "spreading out their energy" (although involving no change in temperature in ideal gases) is what we call an entropy increase."

[As mentioned in the [IMPORTANT NOTE](#) in the box at the start of this web page, probability and probability distributions are the very important second factor in entropy change but for most students, this is a topic that can be saved until physical chemistry.]

To middle level students, the standard approach of describing gas expansion into a vacuum can be used: Though there is no q or ΔH change in the process, a spontaneous event has occurred and thereby the innate "motional energy" of the energetic molecules has become dispersed because the process has given it space into which it can expand (the qualitative substitute for the probability factor of entropy increase). Then, the ΔS in that spontaneous process can be shown to be the negative of the reversible compression to the original volume when calculated as $\Delta S = q/T = R \ln [V_2/V_1]$.

To the higher level students, the macro view of entropy change in gas expansion caused by energetic molecules spreading out their energy in a larger volume can be better related to molecular thermodynamics: That "motional energy" is "dispersed" in the sense, first, of a larger number of microstates for the larger volume as shown by the Boltzmann entropy equation, $\Delta S = k \ln [W_2/W_1] = k \ln [V_2/V_1]^N = R \ln [V_2/V_1]$. (Each fast-moving molecule can be thought of as occupying a tiny cell of volume V_1 . Then, if the volume of the system increases by the addition of an empty cell (doubling the volume available), the energy of that molecule can be in two volumes (or, grossly speaking has been spread out in the larger volume of $2V_1$, even though this fact/emphasis has traditionally been hidden by the concept of "positional" entropy). But there are N molecules in a molar system, so the $[W_2/W_1]$ in the Boltzmann equation becomes $[2V_1/V_1]^N$. Then, of course, the total system energy after the expansion has the chance of being in any one of the greater number of microstates at one instant than with fewer microstates before the expansion. (As an alternate and more visual quantum mechanical approach using energy levels for the total unchanged molecular energy, the relationship of a particle in a 'one-dimensional box' to the more closely spaced ("denser") energy levels in larger and larger boxes can be developed. Thus, the additional accessible energy levels in larger boxes can be described as leading to a great increase in the number of microstates for the system, an increase in W_2 — i.e., an increase in entropy with increased volume.)

The meaning of 'microstates' (described near the start of this page and discussed in details [here](#)) can be briefly introduced as follows:

If a Figure of the changes in speed distribution in a gas with temperature has appeared in the text (or can be drawn/projected for a class), it is easy to show students qualitatively that heating a system causes its energy to be far more dispersed. The

curves for the speeds in a hot gas are obviously broader, less centered around fewer speeds, and thus both speeds and kinetic/motional energies ($= mv^2/2$) are more spread out than in a cooler gas. The original molecules have greater and more different energies than before heating from simple considerations of kinetic molecular theory. For a more advanced class, that increase in energy due to heat input and the resulting change in the Figure can be said to result in a greater number of microstates, W_2 for the hotter system. Therefore, there are more accessible microstates in any one of which the system might be at any instant — the molecular meaning of greater dispersal of the total energy (the original energy of the system plus the added ΔH_{input}) entropysite.oxy.edu contains an alternative verbal introduction to microstates [here](#).

Thermal energy always spontaneously flows from a hotter system (or subsystem) to cooler surroundings (or subsystem), and conversely.

Such "hotter to cooler" spontaneous transfers of energy are due to the nature of energy to become more dispersed — if it is not constrained.

A simple proof of the foregoing for beginning students could involve a hot metal bar touching a bar that is just barely cooler. Designate q for the thermal energy/"motional energy" in the solid metal (actually 'vibrational energy, of course, in the metal) that could be transferred between the bars under these nearly reversible conditions, with T (bold type) for the temperature of the hotter bar, and T for the temperature of the slightly cooler. Therefore, because T is larger than T , q/T is smaller than q/T . If $-q/T$ is transferred from the hotter bar to the barely cooler bar, the cooler would be given q/T . But q/T is larger than $-q/T$, so the cooler bar has increased in entropy more than the hot bar has decreased. Since the conditions are near reversibility (and the same entropy increase would be found to be true at a larger temperature difference, via $C_p \int dT/T$), it can be generalized: Energy transfer from hot to cold systems results in an increase in entropy. Then, because $\Delta S = k_B \ln W_{\text{Final}}/W_{\text{Initial}}$, the number of *accessible* microstates in the cooler bar must have increased more than the number in the warmer bar decreased. The energy, q , hasn't changed but it is more dispersed in the cooler bar because there are more *accessible* microstates for the cooler bar in any one of which it (added to the original enthalpy of the system) might be at one instant. Thus, the entropy increase that we see in a spontaneous change is caused by increased energy dispersal.

A note on the global view of entropy change

Deciding the direction of spontaneous change often involves considering a system and its surroundings as a "universe". (This preceding case of two bars of metal could be seen as such.) As a result, the global view (system plus surroundings) of entropy change means examining the system and surroundings together to find the net result of energy transfer, whether energy overall has become more spread out and less localized. A difference in temperature between a system and its surroundings is a prime case: Because energy always becomes more dispersed in the cooler of the two than it was in the warmer, such a transfer of energy is always spontaneous and the net result is a greater entropy in the universe of system and surroundings. Entropy always increases in the universe as a result of a spontaneous process — one of the ancient expressions of the second law that is gibberish to the average person and a major reason for stating it in the simpler terms of 'dispersal of energy': "Energy of all types changes from being localized to becoming dispersed or spread out, if it is not hindered."

Standard State Entropies, S° in Tables .

(An S^0 value is actually not "entropy", of course. It is an entropy *change* in a substance because S^0 is the result of the substance being heated from 0 K to 298 K, a process that involved an incremental dispersal of energy to the substance from the surroundings.)

My early writing about the S^0 of a substance described it poorly.* It should have been " S^0 is an index, relative to other substances, of the ΔH energy that has been reversibly dispersed (at small temperature increments) to it from the surroundings to raise its temperature from 0 K to 298 K".

*The word "at" in my original statement about S^0 can be seriously misunderstood, i.e., "a measure of the energy that can be dispersed within the substance at T". The reversible energy transfer from the surroundings to a substance that was carried out over the range of 0 K - 298 K can never be thought to be **effected** at the single temperature T of 298 K. That 298 K is the end of a long process from 0 K, not the temperature **at which** any thermal energy was transferred!

In considering S^0 in terms of the amount of energy that has been dispersed to a substance from its surroundings in the 0-298 K process, it is best to use a word like "indicator" or "index" that less connotes "exact numerical value" than does "measure" even though "measure" can have a general and not a precise meaning. Thus, for example, that the S^0 of water is 69.9 joules/K-mol, in no way means that 69.9 joules have been spread out/dispersed to a mole of water to heat it from 0 K and change its phase from ice XI to ice 1H and then that ice to water! (Many many thousands of joules were involved in that process.) To determine an entropy change (under reversible conditions) over a temperature range from 0 K is very complex when the heat capacity is radically changing, as described here:

Finding the entropy change in a substance from very low temperatures up to 298 K is difficult, and not only because of experimental problems at low temperatures. The major problem is caused by the drastically varying heat capacity of substances at low temperatures. In the calculations of entropy change with temperature via the usual equation of $\Delta S = C_p \int dT/T$ over a very wide range of temperatures above 250 K, the C_p can be considered a constant with an error of only a few percent. In contrast, from 15 K to 298 K, C_p values vary enormously — from <10 J/Kmol at 15 K to 75.3 J/Kmol for water at 298 K (and 139 J/Kmol for sulfuric acid, with 217 J/Kmol for glycerol at 298 K). Therefore, the usual equation cannot be used. Instead, a point by point plot of precise C_p/T values vs. T is made and the area under the curve to 298 K is measured (equaling the results of integration of an equation with a variable C_p , $\int C_p/T dT$). Then, to this number (that is the result of "motional energy" transfer, but is a complex function of T) is added the $\Delta H/T$ of any phase change (including transitions from one crystalline form to another). In addition, any 'residual entropy', determined from spectroscopic data, must also be added. Thus, the final S^0 is a cumulation of the reversible/stepwise incremental entropy values from 0 to 298 K, a sum of the increase in motional energy plus any phase change energy.

The resultant summation in S^0 , e.g. 69.9 joules/Kmol for water, of course is **not** equivalent to the simple equation, $\Delta S = q_{\text{reversible}} / T$, or to any easy calculation of the amount of energy that has been dispersed in the substance. (To repeat, S^0 is the result of a large number of reversible processes from 0 K to 298 K, but itself not a reversible function **at** 298 K.) However, any value of an S^0 , e.g., 69.9 joules/K mol, **is** a useful index, even though it may be much less than a hundredth or so of the energy

dispersed from the surroundings to a mol of substance from 0 K. It is extremely helpful to view it as a roughly *relative quantity of energy that must be distributed in different substances/systems for them to exist at 298 K*. In fact, this considering of entropy in relative terms of energy content or energy dispersal to a substance is a better intuitive basis than entropy itself for the ordinary use of S° in general chemistry texts — namely, generalizing to link types of molecules with their entropy values:

monatomic gases vs. polyatomic, congeneric elements of increasing atomic weight, solids vs. similar solids in terms of the strength of their bonds (K vs. Ca, KCl vs CaCl_2), liquids vs. gases of the same substance, diamond vs. graphite vs. metals vs. iodine, similar organic compounds (or different types) of increasing molecular weight, compounds vs. the hydrated compound etc., etc.

That same fundamental difference, i.e., in the energy needed for substances to exist at T, is implicit when general chemistry texts use entropy increases to predict favorable conditions for reaction. (An increase in S° of products compared to reactants is commonly taken to mean an entropy increase in the system - a favoring of the reaction as it is written. Basically, we see that conclusion is *due to* the opportunity for greater dispersal of energy in the products for their stable existence in the specified state at a particular temperature.):

when a solid changes to a liquid, when a liquid changes to a gas; when a mole of reactant forms two or more moles of product – most general when the products are gases, when the concentration of products compared to reactants (measured by Q) is far less than at the equilibrium (measured by the equilibrium constant, K).

Of course, these rough predictions about the outcomes of chemical reactions are superseded by the precise criterion for dispersible energy in both surroundings and system, ΔG , and that for overall entropy increase, $\Delta G/T$. This will be discussed in detail later in connection with chemical reactions.

The Mixing of Ideal Liquids and of a Solute with a Solvent

Mixing of gases results in an increase in their volume and a greater density of molecular motional energy levels — resulting in a large increase in the number of accessible microstates for the final mixture. The same phenomena obviously cannot apply to ideal liquids in which there is quite variable volume increase when they are mixed. However, as has been said, "The 'entropy of mixing' might better be called the 'entropy of dilution'". By this one could mean that the molecules of either constituent in the mixture become to some degree separated from one another and thus their energy levels become closer together by an amount determined by the amount of the other constituent that is added. It is not harmful to students that this approximate view be presented to them. Certainly, it is preferable to telling them that mixing is a different sort of entropy, "configurational" or "positional" entropy. The actual situation that is briefly stated below (and described in detail at <http://entropysite.oxy.edu/#calpoly>) is too complex for any but a few superior students, but it is essential to understanding entropy.

In general chemistry texts, configurational entropy is called 'positional entropy' and is contrasted to the classic entropy of Clausius that is then called 'thermal entropy'. The definition of Clausius of 'thermal energy'/T is fundamental; positional entropy is derivative in that its conclusions can be derived from thermal entropy concepts and procedures, but the reverse is *not* possible. Most important is the fact that positional entropy in texts — as is configurational entropy in statistical mechanics — usually is treated as though the number of the positions of molecules in space determine the entropy of the system. This is a valid probability calculation via combinatorics — and the second factor in thermodynamic entropy, but traditionally this process has been totally silent about any consideration of molecular energies of the individual components that formed the solution. This is misleading. Those molecular energies have not

changed from their initial values, of course, but their molecules (and their individual energies) have become literally more dispersed, less localized in the final mixture. Any count of 'positions in space' or of 'cells' in statistical mechanics implicitly includes the fact that molecules being counted are particles with energy and so each cell is a microstate. Thermodynamic entropy increase always involves an increase in energy dispersal at a specific temperature no matter how the essential second factor of probability in thermodynamic entropy is calculated or determined.

Colligative properties: The Effects of Entropy Change in a Solution.

The fundamental basis for colligative effects is that a solvent in a solution has a higher entropy than the pure solvent. Obviously, the increase in entropy of the solvent is proportional to the number of molecules of solute that may be added to it.

Freezing of a liquid is a spontaneous process at any temperature that is infinitesimally below the temperature at which a liquid and its solid and their surroundings are in thermal equilibrium. There, because the surroundings of the liquid are barely cold enough to reduce the liquid's molecular motion appropriately, intermolecular bonds can form to yield a solid because the latent potential enthalpy of fusion (stored in the liquid, measured as entropy) can reversibly be dispersed to the surroundings.

However, the solvent in a solution has higher entropy than pure solvent and this state of more dispersed motional energy does not permit intermolecular bonds to form at the usual freezing temperature. (Traditionally stated: The solvent's "escaping tendency" from a solution to form a solid is less than from the pure solvent itself.) The solvent in a solution cannot freeze until its greater energy dispersal is decreased — visually, conceptually, the molecules in motion are too spread out; molec thermodynamically, there are too many microstates in any one of which the total energy of the system might be — and so somehow the motion of the molecules should be decreased. This can easily be done by cooling the solution, i.e. by lowering the temperature of the surroundings. Then, because liquid water at 273 K, as well as dilute solutions, have about twice the heat capacity (that is actually an "energy per degree" or "specific entropy") of ice or air a little cooling of the solution decreases the motional energy of its molecules faster than the vibrational energy of the ice decreases. As a result, at a degree or two below the normal freezing point, an aqueous solution has had its entropy reduced enough to be in equilibrium with its surroundings and thus able to release the latent potential energy of bond formation reversibly and form ice.

Similarly, the solution will have a higher boiling point than the pure solvent because solvent molecules, with their lesser escaping tendency, require a higher temperature to raise their vapor pressure to reach an equilibrium with the pressure of the surroundings.

Likewise, molecules of solvent on one side of a semi-permeable membrane that has a solution on the other side will preferentially go through the membrane to the solution. This occurs not solely for obvious reasons of kinetics (although there is some preponderance of solvent molecules at the membrane interface on the pure solvent side). The overriding effect is due to the far greater tendency of the solvent molecules to spread out their energy by leaving the pure solvent and going to the solution on the other side of the membrane.

Chemical Reactions — "how much" and "how widely" energy is dispersed.

The Gibbs "free energy" equation: $\Delta G = \Delta H - T\Delta S$, an All-Entropy Equation State.

Undoubtedly, the first-year chemistry texts that directly state the Gibbs equation as

$\Delta G = \Delta H - T \Delta S$, without its derivation involving the entropy of the universe, do so in order to save valuable page space. However, such an omission seriously weakens students' understanding that the "free

energy" of Gibbs is more closely related to entropy than it is to energy. This quality of being a very different variety of energy is seen most clearly if it is derived as the result of a chemical reaction as is shown in some superior texts, and developed below.

If there are no other events in the universe at a particular moment that a spontaneous chemical reaction occurs in a system, the changes in entropy are: $\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$. However, the internal energy evolved from changes in bond energy, $-\Delta H$, in a spontaneous reaction in the system passes to the surroundings. This $-\Delta H_{\text{system}}$, divided by T , is $\Delta S_{\text{surroundings}}$. Inserting this result (of $-(\Delta H/T)_{\text{system}} = \Delta S_{\text{surroundings}}$) in the original equation results in $\Delta S_{\text{universe}} = -(\Delta H/T)_{\text{system}} + \Delta S_{\text{system}}$. But, the only increase in entropy that occurred in the universe initially was the dispersal of differences in bond energies as a result of a spontaneous chemical reaction in the system. To that dispersed, evolved bond energy (that therefore has a negative sign), we can arbitrarily assign any symbol we wish, say $-\Delta G$ in honor of Gibbs, which, divided by T becomes $(-\Delta G/T)_{\text{system}}$. Inserted in the original equation as a replacement for $\Delta S_{\text{universe}}$ (because it represents the total change in entropy in the universe at that instant): $-(\Delta G/T)_{\text{system}} = -(\Delta H/T)_{\text{system}} + \Delta S_{\text{system}}$. Finally, multiplying the whole by $-T$, we obtain the familiar Gibbs equation, $\Delta G = \Delta H - T\Delta S$, all terms referring to what happened or could happen in the system.

The "free energy, $-\Delta G$, is not a true energy in the sense that it is not conserved as energy must be. Explicitly ascribed in the derivation of the preceding paragraph (or implicitly in similar derivations), $-\Delta G$ is plainly the quantity of energy that can be dispersed to the universe, the kind of entity always associated with entropy increase, and not simply energy in one of its many forms. Therefore, it is not difficult to see that ΔG is indeed not a true energy. Instead, as dispersible energy, when divided by T , $\Delta G/T$ is an entropy function — the total entropy change associated with a reaction, not simply the entropy change in a reaction, i.e., $S_{\text{products}} - S_{\text{reactants}}$, that is the ΔS_{system} . This is why ΔG has enormous power and generality of application, from prediction of the direction of a chemical reaction, to prediction of the maximum useful work that can be obtained from it. The Planck function, $-\Delta G/T$, is superior in characterizing the temperature dependence of the spontaneity of chemical reactions. These advantages are the result of the strength of the whole concept of entropy itself and the relation of ΔG to it, not a result of ΔG being some novel variant of energy.

Relationship of ΔG° to ΔG for Non-standard Conditions

Far more important practically than the foregoing use of standard states in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ — because therein all constituents are assumed to be confined to the unreal world of 1M or 1 bar concentrations — is a modification of that equation that can include differences in realistic concentrations of the reactants and products. Many texts present the result, $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient after only a brief discussion of a reaction attaining an equilibrium state. (A notable exception is the careful development in General Chemistry, 8th edition, by Petrucci, Harwood, and Herring.)

Even though this equation may not be developed in detail in a text or a class, it certainly should be better explained to students than it is in most texts. The inclusion of $RT \ln Q$ so that the equation becomes $\Delta G = \Delta G^\circ + RT \ln Q$ involves practical concentrations, but *why* does it "work"? And, if the more detailed equation is shown $\Delta G = \Delta H^\circ - (T\Delta S^\circ - RT \ln Q)$, why is that $RT \ln Q$ associated with the entropy part of the equation — how can $RT \ln Q$ be a change in *entropy*?

Many good general chemistry texts have a preliminary development of entropy changes that occur in dissolving ionic solids in water. Some mention entropy increase when gases or liquids mix. (Chemistry, 2nd edition, by Moore, Stanitski, and Jurs is unique in its thorough treatment of this topic from the first mention of reactions in gases.) A simple explanation of the $RT \ln Q$ "problem" would start with stating

that mixtures of fluids (gases or liquids) have an increased entropy than the pure gas or liquid because the energy of each component is spread out in the final larger volume for gases and the greater number of 'cells' for liquids. Therefore, a mixture of some amount(s) of reactants with some amount(s) of products has a higher entropy than any single pure product or mixture of products. But a mixture of products and reactants that is an *equilibrium* mixture as a result of a spontaneous change would have the largest entropy value of any possible combination — by the very definition of equilibrium. An equilibrium is a stable unchanging ratio of components because that ratio is the maximal entropy for the particular system.

From the foregoing, it should be clear not only why $RT \ln Q$ is part of a 'realistic' treatment of the Gibbs energy equation, but also that as Q changes toward K , the equilibrium constant, during the course of a reaction, and ends at K . A professor in Minnesota (who modestly wishes to be unnamed) has written that "when a stoichiometric amount of reactants is turned into products, $\Delta S_{\text{universe}} = R \ln K/Q$ ". I don't know if this is common elsewhere in the literature, but I believe it to be unusually significant - entropy maximization in spontaneous events as complex as chemical reactions can be expressed concisely. Spontaneous energy dispersal, the causal factor for entropy increase, is as fundamental to the Gibbs energy equation as it is in all energy-related chemical behavior.

entropy.lambert@gmail.com

Last revised and updated: November 2005

[back to entropysite](#)

Copyright © 2008 [Frank Lambert](#), Ph.D. All rights reserved.