Entropy Is Simple — If We Avoid The Briar Patches!

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Introduction

The second law of thermodynamics is a powerful aid to help us understand why the world works as it does — why hot pans cool down, why our bodies stay warm even in the cold, why gasoline makes engines run. It is the ultimate basis of chemical industries that have kept the world from starvation for the past half century (fertilizer manufacture using nitrogen from the air) and kept us healthy and less in pain in that time (via processes for life-saving and pain-relieving pharmaceuticals).

Entropy also is simple to describe and explain qualitatively. (Entropy in quantitative thermodynamics is more difficult and often complex.) However, to begin our qualitative approach we must avoid the briar patches involving the second law and entropy that have been planted all over acres of book pages and Web sites.

For those who prefer conclusions before explanations:

The second law of thermodynamics says that energy of all kinds in our material world disperses or spreads out if it is not hindered from doing so. Entropy is the quantitative measure of that kind of spontaneous process: how much energy has flowed from being localized to becoming more widely spread out (at a specific temperature).

This article will use many everyday examples to illustrate those conclusions and briefly relate them to atomic and molecular behavior.

Briar Patch #1. Writers who are not scientists, and joking mathematicians

Unfortunately, the ideas of entropy and the second law have been almost hopelessly muddled by well-meaning but scientifically naïve philosophers and writers of both fiction and non-fiction. Search engines have correctly called a popular website on entropy "puzzling". Its author is an architect, not a scientist. The only best-selling book on entropy ever published, filled with errors leading to absurd statements, was written by a person with degrees in economics and in international affairs but no scientific background.

An additional source of confusion to anyone outside of chemistry or physics is due to brilliant but thoughtless mathematicians. They decided that it would be amusing to name a very important new mathematical function communication "entropy" because "no one knows what [thermodynamic] entropy really is, so in a debate you will always have the advantage". (That quote is of John von Neumann speaking to Claude Shannon (*Sci. Am.* **1971** , *225* , 180.) For the past half-century this has turned out to be a cruel practical joke imposed on generations of scientists and non-scientists because many authors have completely mixed up information "entropy" and thermodynamic entropy. They are *not* the same! From the 1860s until now, in physics and chemistry (the two sciences originating and most extensively using the concept) entropy has applied **only** to situations involving energy flow that can be measured as "heat" change, as is indicated by the two-word description, thermodynamic ("heat action or flow") entropy. Only thermodynamic entropy will be dealt with in this article.

Whenever information "entropy" is discussed — especially when it is in the same article as thermodynamic entropy — that mathematical "entropy" should be in quotes to clearly distinguish it from entropy, i.e., thermodynamic entropy.

Scientific Note (for chemists, physicists, mathematicians): Thermodynamic entropy change consists of two factors. Entropy change is enabled in chemistry by the motional energy of molecules (or from bond energy change in a chemical reaction) but thermodynamic entropy is only actualized if the process itself (expansion, heating, mixing, reaction) makes available a larger number of microstates, a maximal Boltzmann probability at the specific temperature. (Information "entropy" consists only of the latter factor of probability. The 'sigma entropy' of physics that equals S/k_B has only ln W, unrelated to energy of any sort.)

Briar Patch #2. "Isolated systems"

In articles and Web pages introducing entropy to non-scientists, the most unnecessary of all misleading emphases that appears in them is an extended discussion of physicists' "isolated systems". These theoretical systems are not only useless to a beginner but what happens in them can profoundly confuse anyone trying to understand entropy and the second law in the real world. We humans live in an open system of earth, sun, and outer space. We encounter the second law and entropy within that open system. Therefore, the energy-entropy relationships that are useful for us to examine are in that real system.

Briar Patch #3. "Entropy is disorder" (Entropy is NOT disorder!)

This confusion about disorder and entropy comes from an 1898 statement by a brilliant theoretical physicist whose mathematical contributions to thermodynamics and entropy are still totally valid. However, his attempt to interpret entropy in simple language was incorrect because only after his death in 1906 came an understanding of molecular behavior. Order/disorder became increasingly obsolete to apply to entropy and the second law when the existence of quantized energy levels in physics and chemistry was generally accepted after the mid-1920s.

Although order/disorder is still present in some elementary chemistry texts as a gimmick for guessing about entropy changes (and useful to experts in some areas of thermodynamics), it is both misleading and an anachronism for beginners in chemistry. It has been deleted from most first-year university chemistry textbooks in the US.. In the humanities and popular literature, the repeated use of entropy in connection with "disorder" (in the multitude of its different common meanings) has caused enormous intellectual harm. Entropy has been thereby dissociated from the quintessential connection with its atomic/molecular energetic foundation. The result is that a nineteenth century error about entropy's meaning has been generally and mistakenly applied to disorderly parties, dysfunctional personal lives, and even disruptions in international events. This may make pages of metaphor but it is totally unrelated to thermodynamic entropy in physico-chemical science that actually does impact our lives. It is as ridiculous as talking about how Einstein's relativity theory can be applied to a person's undesirable relatives in Chicago.

The second law of thermodynamics

A warning about scientifically improper verbiage in the following sections: For convenience the word "heat" is sometimes used in the erroneous sense of a "something", a substance in an object. (See a full explanation in the Appendix.)

The second law of thermodynamics — what a forbidding group of words! However, any fear of the phrase or what lies behind it disappears when we realize that we already know the second law well from our everyday experience. We just haven't recognized that such varied happenings as the following are all examples of the second law: hot pans cool; water spontaneously flows down Niagara Falls; the air in our tires will blow out to the atmosphere if the tire walls are punctured; when gasoline is mixed with air in a car's cylinders, it explodes if a spark is introduced; a speeding car that hits a brick wall doesn't passively stop. There is a loud crash as the car's metal is bent and plastic and glass broken and the bricks (slightly warmed) fly all over area. Cream put in coffee doesn’t stay by itself but instead spreads throughout the coffee. How are all these different events described by just one law, especially a law with a complicated name?

In a hot metal pan the atoms are very rapidly vibrating (because heat has been spread out in the pan from a hotter flame). These atoms will disperse the energy of their vigorous but restricted movement to any less rapidly moving molecules — to those in a cool counter top or the more freely but less vigorously moving nitrogen and oxygen molecules in the air of a cool room. Molecules of water atop Niagara Falls have relatively great potential energy; they disperse it if they fall far down to the river below. Molecules in the air that is confined to the small volume of a car tire will immediately flow out to the larger volume of the outside air, spreading out their energy more widely in the atmosphere if the tire is punctured or the tread separates from the walls.

Molecules of gasoline with oxygen (in air) have greater energy in the internal bonds that hold their atoms together than do the carbon dioxide and water that are formed when gasoline reacts with oxygen. Therefore, gas and oxygen spontaneously *tend* to react and make carbon dioxide and water because then energy would be dispersed to the surroundings in the process. However, just as air in a tire is physically blocked or'hindered' from spreading out the energy of its molecules more widely in the larger volume of the atmosphere by the strong tire walls and tread, gasoline and air are chemically blocked from immediately dispersing their energy by a barrier called an *activation energy*. (See Appendix for details.) Thus, gasoline and the oxygen of air can remain in contact with one another unchanged for years and centuries. However, given a spark to overcome the activation energy that is hindering their reaction, gasoline and oxygen will violently react to spread out large quantities of heat that results from a transformation of part of their high-energy bonds as the lower-energy bonds of carbon dioxide and of water are formed.

In the example of the speeding car, all of the molecules of its plastics and its atoms of glass and metal have great kinetic energy in the direction that it is racing. For it to come to a stop, that kinetic energy must be dispersed somehow, somewhere. If a brick wall stops it, the great amount of kinetic energy in the car is changed into sound, kinetic energy of bricks flying after being torn from the wall, warmth of the bricks, and broken warmer bits of plastic, glass and twisted metal — a very widespread spreading out of the energy previously all concentrated in the moving car.

Finally, and seemingly totally unrelatable to the preceding examples, is the case of cream spontaneously mixing with coffee (even it were unstirred and convection currents prevented). This is a prototype of all spontaneous mixing of fluids and dissolving (although dissolving of solids in liquids has factors in addition to simple mixing).

All of the minute particles, the atoms or molecules in these examples, are in constant violent random motion. (Oxygen molecules in our air, on average, are moving about a thousand miles an hour at ordinary temperatures, but changing from 0 to almost 3000 miles an hour as they crash into other molecules after moving about 15 millionths of an inch. In solids, the particles 'dance in place' (vibrate) with energies dependent on temperature.) All energetic atoms and molecules will spread out their motional energy if they are given an opportunity to do so — in a larger volume, to other molecules not moving as rapidly (i.e., at a lower temperature).. The second law of thermodynamics merely summarizes the fact of such molecular motional energy dispersing if it is not hindered from doing so. Far more extensive than those several examples: **All spontaneous happenings in the material world** (those that continue without outside help, except perhaps for an initial start) **are examples of the second law because they involve energy dispersing**. Energy that is in the rapidly moving, ceaselessly colliding minute particles of matter (including that which is made more available by chemical reactions such as gasoline with oxygen, that contain higher-energy bonds within them than their possible products) will diffuse, disperse, spread out if there is some way for that to occur without hindrance.

The second law of thermodynamics is so much a part of our everyday experience that it is adequately summarized in the simple examples we have seen, the three archetypes being:

"hot pans cool down", the case of an immediate dispersal of energy,

because they tend to disperse the energy of their fast moving particles [that we commonly call heat] in their metal or glass containers to anything they contact, such as the cooler room air [slower moving molecules that then increase their speed somewhat],

or "gasoline explodes", the case of a hindered dispersal of energy from a chemical reaction,
because it tends to react with the oxygen in air, but does so **only if** the mixture is ignited, i.e. given a little extra energy from a spark or tiny flame. Then, the gasoline and oxygen can spread out some of the energy in their bonds (chemical bonds hold atoms together in molecules) in forming carbon dioxide and water that have lesser energy in their bonds. The *difference in energy* is dispersed to *all* the molecules in the gaseous vapor (left-over oxygen, nitrogen, carbon dioxide, H_2O, CO, etc.). This makes them move extremely fast (characteristic of the

molecules/atoms in anything that is very hot) and the pressure in a confined space immediately increases. Such a high pressure in the small cylinder volume, `further spreads out the energy of the hot molecules (second law again) by pushing the car's pistons down forcefully so that the piston rods disperse their kinetic energy by turning the crankshaft.etc., etc.

"tires blow out" and "cream mixes in coffee" , the case of substances spreading out their energy in space without any change in that original energy

because these seemingly disparate examples involve no change in the temperature or change in their initial energy. (Actually, this is an idealization because real air does cool down on expansion.) Scientifically, these spontaneous events are in the same category — expansion of a gas like air involves volume increase (a spreading out of the original energy in a larger space), mixing involves a separation of molecules of one type from its kind (a sort of dispersal of the initial energy because all the molecules of the same kind are no longer adjacent to one another.)

The sense of “if not hindered” in the foregoing cannot be overemphasized. It is omission of this idea of ‘hindrance’ or ‘obstruction,momentarily or for a long time’ that leads most non-scientists astray in their reading or writing about the second law. So much stress is usually placed on the immediacy and the inevitability of dire effects of the second law (and its supposed complexity) that it can be made to seem unduly threatening to almost every aspect of our lives.

The second law of thermodynamics is by no means an instantaneously obeyed edict. It accurately predicts the *probability* of the dispersal of energy that is localized or "concentrated" in a group of molecules or atoms — and that can result in undesirable events ranging from serious accidents to disastrous forest fires or to our ultimate death. In this sense, the second law is our "baddest bad". However, the law is completely silent about how long it may take for its predictions to be fulfilled.

What is entropy? How is it related to the second law?

Entropy is simply a quantitative measure of what the second law of thermodynamics describes: the dispersal of energy in a process in our material world. Entropy is not a complicated concept qualitatively. Most certainly, entropy is not disorder nor a measure of chaos — even though it is thus erroneously defined in dictionaries or pre-2002 sources.

Because entropy is an index of the second law's predictions about energy, the short word entropy is often used interchangeably for the cumbersome phrase, "the second law of thermodynamics". A concise summary of entropy's nature is: **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). You see now how hot pans cooling and chemical reactions belong to the 'how much' category where energy is being transferred. Coffee in cream and gas expansion and perfume in air are 'how widely' processes where the initial energy of the molecules stay the same but the volume occupied by the molecules increases. Energy's dispersal can be easily seen by anyone in hundreds of common occurrences like the few we have presented here because the second law isn't some exotic or abstract mathematical theory. The second law is really just a summary of ordinary human experience. The details of how energy spreads out or disperses in such everyday practical events can be elegantly correlated with the probable behavior of atoms and molecules.

Our greatest good, the second law of thermodynamics

The second law is a constant threat to us. Our bodies are made up of tens of thousands of chemical substances ("compounds") that are essential to our functioning. However, the oxygen in our atmosphere that we need to live also tends to destroy almost every one of those essential biochemical compounds. Why? Oxygen plus any of our essential organic compounds have a total higher energy content than the oxidized compounds of carbon dioxide and water (CO_2 and H_2O) that would be formed from them. Thus, if the second law were not somehow obstructed, almost all the substances in our bodies would immediately react with oxygen in the air so that some of the bond-energy in those essential substances would spread out as heat. Concentrated or localized energy to diffused or dispersed energy — that's the pattern in nature that the second law sums up.

This is exactly similar to gasoline and oxygen having higher energy in their bonds than do their products, carbon dioxide and water. However, a superficial reason that we could never spontaneously oxidize ("combust") as rapidly as does gasoline in oxygen is the large amount of water throughout our cells restraining such a process. (Wood in the trunks of living trees burns (oxidizes) slowly and with difficulty because it is both solid and wet — in contrast to faster burning leaves and branches with less moisture and more surface area.) Nevertheless, even if our whole body didn't quickly oxidize, we might have a sufficient number of cells in us, say a hundredth of a percent of our total of critical cells to our life continuance, that could randomly oxidize and follow the second law in dispersing their concentrated energy. That could be enough to cause serious dysfunction and death.

Fortunately, there is a profound reason that our cells and their chemical constituents resist the threat of the second law (i.e., that they "must" react with oxygen because then they would follow the law by dispersing their energy.) The reason is the existence of activation energies, an innate obstacle to the second law of thermodynamics in chemical reactions. We have seen it present in our oft-used illustration of gasoline and oxygen: no reaction occurs until a spark or flame is first injected in the mixture to give a little energy "push" to start it. This is typical of almost all reactions of oxygen with the biochemicals within us.. Thus, even though the second law is a fundamental threat to our lives in our atmosphere that contains oxygen, the second law is equally fundamentally obstructed. by *activation energies* from causing our oxidation and death. (See the Appendix or http://secondlaw.oxy.edu/three.html for details about activation energies.

http://shakespeare2ndlaw.oxy.edu site describes the importance of activation energies to our lives.)

At the same time that we realize the second law of thermodynamics to be a constant threat, we should also see that it is our "greatest good": What if the direction of energy flow was **not** always from concentrated to dispersed? What if the process was often erratic or precisely 50-50 — with energy flowing in reverse from dispersed to concentrated half the time? No organism could live in such an erratic universe. As organisms, we are basically energy-processing machines. To maintain the multitude of different 'automatic' biochemical processes in our body that require energy to force substances 'up an energy hill' to have more concentrated energy within them, we must continually have energy supplied to us from outside ourselves in the form of oxygen and food. It is the always-dependable direction of spontaneous energy dispersion from that oxidation of food that makes possible the total range of our energy-demanding activities that constitute our very lives themselves.

This oxidation process occurs in astoundingly complex ways and in many steps (so any energy that is spread out as heat is slowly and moderately released, unlike the seemingly instant "one-step" explosive dispersal of energy when gasoline reacts with oxygen). Furthermore, any heat that is dispersed in our bodies is not wasted because it keeps our bodies warm to function optimally even in a cold environment. Some of the energy flowing downhill from food oxidation is captured by "coupled reactions" so that a medium energy substance, ADP, is raised in energy to become a greater energy-containing substance like ATP. ATP is in every cell in our bodies to disperse energy for a multitude of different reactions while it becomes ADP and then is regenerated by a coupled reaction. Of course, the storage of ATP is contrary to the predictions of the second law, but we know how it 'beats' the second law: :The energy within the bonds of those ATP molecules and similar varieties is kept from being dispersed by activation energy barriers until, of course unknown to us, our cells need it for some action. ATP and similar energy-storage sources are what give us the instant conscious choice of using our arm muscles for work or our eye muscles for looking in a particular direction — or our brain for thought. Many of our ~30,000 chemical substances and the complex cells from which they are made must continually be destroyed and the residues excreted as new ones are synthesized. (For one example, there are about 250 million hemoglobin molecules in each red blood cell. Every hemoglobin has four iron atoms that are responsible for capturing oxygen in our lungs, transporting it to all the cells of our bodies and releasing it there to produce energy via an oxidation process. A person of average weight synthesizes approximately 500 *trillion* molecules of iron-containing hemoglobin *per second* in the bone marrow. The same number of hemoglobin molecules are destroyed each second and then excreted as part of fecal matter giving it the color of one form of iron oxide (rust.) There cannot be minutes in which oxygen is *not* supplied to the energy-requiring cells of the heart or pumped to the energy-requiring brain: we die from a heart attack if adequate oxygen isn't given to its cells and the brain will either be permanently damaged or, if too many minutes elapse without oxygen for energy dispersal and ATP synthesis, death results.. The second law — or better, the energy flow predicted by the second law — is essential to all life.

(A few additional details are in http://secondlaw.oxy.edu/five.html) Thousands of times a day in our normal activities (and untold trillions times trillions of times in the biochemistry of our bodies), we unknowingly use the second law's directionality of energy flow to our great advantage.

In our open system of earth and sun and outer space we have the enormous privilege of taking advantage of the second law for human benefit, as does nature for maintenance of its high-energy-content ecology on the earth. We do this by *diverting* part of the energy to our purposes as it is *dispersing* when a spontaneous process follows the second law. The preeminent example is our use of combustion or oxidation in our machines.. Combustion is the spontaneous reaction of carbon-containing substances like wood, coal, gas or oil with oxygen — after the reaction has been initiated with a flame or spark. Because it is spontaneous according to the second law, in addition to the new lower-energy chemical compounds formed (mainly carbon dioxide and water), oxidation dissipates a great deal of energy in the form of heat (that is actually very rapidly moving molecules of the carbon dioxide + water + air) and some light. Then comes the payoff: our **use** of the second law for our human goals. Today, it is not just diverting some of that dissipating energy from the burning wood of a campfire in a cave for warming ourselves and cooking our food as has been done for millennia, but diverting the energy flow of fossil fuel to our activities that make engines and machines which function to transform our material world.

Obviously, if we think of being grateful for natural phenomena such as the glory of the warm sun each day and the benefit of rain on fertile soil, we should be grateful indeed for the second law. How could we overvalue the enormous diversion of energy that we are able to achieve from the dispersal of energy that the second law favors when we burn fossil fuels? Coal, and especially petroleum-sourced fuel in cars, planes, trucks, earth-movers, trains, ships and electrical power plants are the life-blood, arms, and legs and support of the nervous system of modern society. Of course, we are not able to divert more than a portion of the energy obtained from combustion for our use. Some of any energy dispersion continues immediately on its way to complete dissipation in the environment and ultimate loss to outer space. Most energy not "dammed" by synthesis of new higher energy long-lived compounds (as in photosynthesis) but just used in moving cars or similar temporary functions is merely dispersed later than the waste heat lost from the tailpipe following the initial explosion of the fuel. The second law is often delayed but it is never violated.

Equally obviously, our truly greatest gratitude for the second law should be for the continued dispersal of the sun's energy that long ago aided the various life-forms that ultimately formed fossil fuels like petroleum and coal — the same solar energy-dispersing-process that makes possible plant and human life today. Of the enormous amount of solar energy dispersed to outer space, just one-billionth of it strikes the tiny volume of the earth. About 30% of this is immediately reflected and dispersed to outer space and 70% is temporarily absorbed by clouds and the earth's surface. Only about 0.02% of the one-billionth of the sun's energy coming to the earth is captured for photosynthesis. (These figures set in context the irrationality of writers who say, in essence, that the universe is moving toward "a flowering of increased life and complex organization [of plants and animates]". Such flowering, though all-important to us, is ultramicroscopic so far as the universe is concerned.)

Obstruction of the second law

Energy dispersal can be delayed for microseconds to millennia or eons by barriers that are described in chemistry texts or http://secondlaw.oxy.edu/three.html or are obvious. Objects that are high above ground level have potential energy. The second law predicts that they tend to disperse that energy by falling to ground level. Obviously, mountains do not rapidly carry out this prediction of the second law. The topmost stone peaks just as all the supporting stone of a mountain are held in place by firm chemical bonds joining the silicon and oxygen and calcium and magnesium and other atoms in place. (Moreover, these bonds not at all affected by oxygen — unlike those of gasoline — because they are already in a low-energy fully-oxidized state.) Thus, no change occurs in high mountain stone until external energy sources such as extremely violent windstorms or many freezing and thawing cycles first physically break or crack rock portions and pieces of the mountain so that they can disperse their potential energy by falling to lower levels. The second law can indeed be blocked for millions of years in some substances and some arrangements of them.

We humans devise all sorts of methods for obstructing or "damming" the second law for considerable periods of time. A mundane example: We paint iron to prevent it from rusting. Painting is effective in this way not because of any sophisticated chemistry but simply because it keeps the oxygen away from iron so reaction can't occur. (Rust, iron oxide, tends to form from iron metal and oxygen gas because, as in most spontaneous chemical reactions, the reactants, iron and oxygen, have larger internal energies than the product, iron oxide. Concentrated energy to less concentrated energy as per the second law.) Chrome plating of steel is a method of hindering the second law by interfering with the oxidation of steel. A Thermos bottle for hot or cold liquids (just like a very different insulating container made of that white Styrofoam) is a simple example of obstructing the rapid dissipation of heat that is predicted by the second law. (The Thermos bottle's vacuum between its two walls does not have many air molecules that can carry energy from the hot liquid to the cooler atmosphere — or from the warmer atmosphere to cold liquids inside. Styrofoam's poor transmission of energy similarly obstructs what the second law predicts — the spreading out of energy.)

Some systems spread out their energy rapidly, e.g., the thermal energy in hot objects to a cooler room. Most however, fortunately, do so very slowly. As has been pointed out – too frequently (!) but it is a vital point that is little known to those not in chemistry about the action of the second law — - some systems and forms of energy, such as the energy contained within chemical bonds, remain "dammed" and cannot disperse their energy in a chemical reaction until an extra energy, an activation energy, is given them to start the process. The energy within cellulose and other chemical substances in trees, surrounded by the oxygen in air, remains unchanged for years or centuries, but in a short while hot flames can start the release of that energy in the form of heat and carbon dioxide and water – and the amount of energy released can be enough to spread a forest fire. (Smoke and much of the ash are the result of incomplete oxidation of the chemicals in trees.)

The sun will take a total of around 5,000,000,000 years to release the nuclear energy in its hydrogen that is fusing to form helium. Some people see this a cause for despair even from the vantage point of our 12,000 year old civilization. Others are not perturbed.

Briar Patch #4. Mixed-up things (papers on a desk, clothes in a bedroom)

In a natural spontaneous "energy-spreading-out" process, visible objects from pebbles to papers to pyramid stones can be moved to random locations if the magnitude and type of energy being dispersed impacts the objects to affect them. A common mistake in interpreting entropy change is to state that there is an entropy increase in the objects when things that we define as being in "orderly" arrangements are pushed around to random or "disorderly" arrangements. This is incorrect. It is looking at the passive half of the picture, the objects, instead of the energy that is pushing things around and becoming spread out in the process! Entropy change has to do with *energy* spreading out, not with pretty patterns. No entropy change occurs in objects if their *energy* is not altered after the move, thus, no increase in *entropy* is caused in them if no *energy* has been dispersed from them or to them. The messy room of a student may not appear to be a neat pattern but it does not represent any increase in entropy in the objects compared to an originally neat room. The only energy change that has occurred is in the energy dispersed in the student's muscles during the tossing or dropping of things here or there, not in the objects themselves.

Shuffled cards, a classic erroneous example of entropy increase, become "disorderly" because of the energy being dispersed in the muscles of the shuffler whose ATP is used to move the cards (along with the production of a slight amount of heat). The cards themselves don't undergo any change in entropy because no dispersal of energy occurs within them. An overly-extended discussion of this error is in http://secondlaw.oxy.edu/six.html and succeeding pages. A more scholarly analysis is in http://www.jce.divched.org/Journal/Issues/1999/Oct/abs1385.html

The earth benefits from the second law — using energy spreading out from the sun

In nature, the sun's radiant energy disperses as it strikes water molecules in the ocean and causes them to move more rapidly, i.e., the water becomes warmer and evaporates more readily. In this process of dissipating the sun's energy, untold tons of water are raised in the air, creating clouds as some of the water molecules spread out part of their energy to the cooler upper atmosphere. When the sun's energy is dispersed in striking the earth's surface and heating it, some of it is shadowed by clouds. The uneven warming of land and water causes variable columns of warm air rising and increases random air motion. The results are winds that further diffuse the original energy of the massive air movement. Water in the air, that was in the form of clouds, cools radically as it starts to flow over high mountains or encounters cold air and precipitates as rain, adding to lakes and creating stream sources at high elevations. Of course, this gives potential energy to such streams because they are far above sea level. Water flowing from heights dissipates its potential energy (if it is not dammed, and the second law thus obstructed) by flowing downward, cutting ravines and, with uplift of the earth (caused by the dispersal of energy deep beneath the surface), forming small, as well as grand, canyons.

We take advantage of water movement in rivers (dispersing their potential energy as they flow down toward sea level) to turn turbines connected to electrical generators that produce electrical power for us (further diffusing the potential energy of the flowing water). Winds dissipating their energy in turning windmills attached to generators also produce some electrical power. These are a few of the actions by which nature, in following the second law, provides us with fresh water, with variable breezes, with snow-capped mountains, and with higher-than-sea-level water that drives our turbines and generates electricity.

Occasionally and coincidentally, movements of wind and warm moisture from a tropical ocean can cause a concentration of energy to form a hurricane. (Hurricanes are no more a violation of the second law than a car with a cranky engine that happens to sputter its way uphill and dies, so with no brakes it then becomes a missile speeding backward down hill and into a house.. More heat in the rising moisture from thewarm ocean surface has been fed into the incipient circling vague wind pattern and by chance the weak Coriolis force from the earth's rotation aids the circling a bit and more moisture is sucked up. Thus, a huge vortex begins and sweeps more warm moisture into it.. Of course, the observer of a destructive hurricane cannot sense the basic contributions of solar energy nor the complex energy dissipation from warm ocean surface to cooler upper air that coincidentally formed it.) The "death" of a hurricane is a more obvious example of the second law in action: Unless this kind of ocean-originated storm is continuously fed thermal energy from warm waters to maintain its high-energy existence, a hurricane spreads out its energy and dies down. The second law always is a valid tendency and — in dynamic cases like this - demonstrates that tendency in a relatively short time rather than years or eons.

Photosynthesis, another example of the coupling of energy dispersal with diversion of part of that energy flow to yield a new, more concentrated energy state

In general the photosynthetic process uses second law dispersal of the sun's energy similarly to what we humans do with fossil fuels. We take the energy that is in the chemical bonds of the fuel and oxygen to make engines accomplish what we want — at the expense of spreading out some of the chemical energy in the fuels and oxygen as waste heat and carbon dioxide plus water to the atmosphere. Plants take some wavelengths of the sun's dispersing energy (plus carbon dioxide from the air and water from the air or earth) and make new chemical compounds in the plant that are more complex and more energy-containing than the original carbon dioxide and water. (Meanwhile oxygen is released and that most of that solar energy striking the plant is spread out to the surroundings as heat).

Subsequently those new active chemical substances in the plant, in breathtakingly complicated processes form carbohydrates, some amino acids, fatty acids and thousands of other compounds by a myriad of other reactions — but also dissipate some energy in all of these secondary syntheses as heat. Overall in the plant, the "downhill" process of energy being dispersed from the sun is diverted and then coupled with an "uphill" process of concentrating energy in new plant substances but there is no violation of the second law: only about 30% of the downhill solar energy has been captured to synthesize new substances in the primary process of photosynthesis. *The net overall dispersion, "loss", of energy (70%) is still greater than the concentration, "gain", of energy (30%).*

(The overall energy pattern is similar to our driving a car uphill. This may seem to be contrary to the second law for a moment because we have "created" great potential energy by ending with a heavy car at the top of a hill. However, calculations quickly show that far **more** energy has been dispersed from changing the chemical bonds in the gasoline and oxygen to carbon dioxide, water and heat (to make the pistons, gears, and wheels move) than the potential energy that the car acquires by being at the top of the hill. In the huge number of processes more complex than driving a car up a hill, photosynthesis uses or diverts only some of the downhill second-law energy flow to create the "uphill" substances and supply the energy for the growing plant to continue to function.

It is accurate to say that we **use** or **take advantage of** the second law by diverting energy from its "downward" (dispersing) flow to run engines that aid our transportation across the earth and into space, to change the earth's topography for our pleasure and for our increased safety (dikes, levees, water diversion), to make useful things from skis to skyscrapers, or simply to rearrange small and massive objects to please our sense of beauty or order. However, neither we nor nature's photosynthesis ever are actually **defeating** the second law. Energy spontaneously disperses if it is not obstructed — or **diverted** by us or by nature from doing so.

What happened to entropy?

Where was entropy in all the preceding discussion of our, and of nature's, involvement with the second law? We were surveying many aspects of the dispersal of energy, the fundamental process predicted by the second law. Entropy is the quantitative measure of that process. In talking about the second law, we have been speaking generally, qualitatively. Any example of a spontaneous physical or chemical change (other than a gravitational potential energy change) involves an increase in entropy so in each of those many preceding spontaneous cases there was entropy increase. (That itself is a qualitative sentence, of course. The quantitative calculation of the amount of entropy change is sometimes far from easy.)

A common error in informal discussions of entropy involves the entropy changes in photosynthesis. This has just been analyzed in terms of the second law and energy. The following is a recapitulation in terms of entropy.

Because complex and highly-energetic compounds (compared to the starting materials of carbon dioxide and water) are formed in photosynthesis, the conclusion is often drawn that there is a *decrease* in entropy in the process. This is looking at only half of the participants in the reaction — the atoms from carbon dioxide and water that have been reorganized. But it is energy change/dispersal in the whole system of both the plant *and its surroundings* that determines entropy change! (Here is where the "isolated system" viewpoint of Briar Patch #2 is often misleading. Photosynthesis in a plant does *not* consist of a isolated system of the plant alone.) We cannot omit considering what has happened to the sunlight that is dispersing energy and driving all the enormous changes in the plant leaves.

As we have seen, experiments and calculations indicate that the maximum efficiency of photosynthesis in most plants is in the 30% range. This means that, of the sunlight that strikes the plant, 70% is dispersed to the environment (an entropy increase in slightly heating the leaf and the atmosphere), while 30% is absorbed by the plant in the initial steps of photosynthesis of new complex "high-energy" substances (entropy decreased in the plant). Of course, this is less than the 100% increase in entropy that occurs when the sunlight simply strikes a patch of sand (and merely warms it and the air and re-radiates back to space) instead of striking the leaf.

Nevertheless, photosynthesis is still a net increase in entropy and **not** a decrease in entropy for the overall process that includes both plant and incident sunlight as has often been stated in print.

The second law is an accurate description of how the world works. It was derived from common human experience and has been verified in innumerable cases, including photosynthesis, by exact scientific observation.

Entropy increase without <u>energy</u> increase

Many everyday examples of entropy increase involve a simple energy increase in a particular 'system' (a part of the totality of 'system plus surroundings').. This energy increase is usually evident from a rise in temperature (caused by more rapidly moving molecules) in the system after some occurrence than before, e.g., when a pan or water in the pan is warmed or when a room is warmed, their entropy increases. Additional energy has been dispersed in them from some outside source, the 'surroundings'. The outside source is often combustion, the chemical reaction of petroleum products — natural gas or fuel oil — with oxygen to yield the lesser energetic carbon dioxide and water plus heat. The energy dispersed *from* the chemical bonds of gas or oil and oxygen is dispersed *to*the slower moving molecules of the pan, the water, or the air of the room. If an energy increase occurs inside a system, there must be an entropy increase in it. More energy has been dispersed within the system and this is what entropy measures.

Thus, we can analyze many simple situations in terms of energy and entropy. Why does ice melt in a warm room? A first approximation is easy. The faster moving ("hotter") molecules in the room can disperse their energy by making the slower moving ("colder") molecules in the ice speed up. This would be a following of the second law and therefore it should be a spontaneous process involving an increase in entropy in the ice as it melts to form water. A more sophisticated view includes the fact that liquid water can have many more ways of spreading out their energy than ice — water 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 crystalline ice. Therefore, if water more effectively disperses energy than ice, when they are together at a temperature just a tiny amount above the equilibrium temperature, liquid water will be favored because it better disperses the energy available in the system than does ice.

The wise observer will ask "Doesn't the warm room *decrease* in *its* entropy when its molecules have to slow a little bit as a result of transferring some of their energy to the slower ones in ice and to the more varied-moving ones in water?" The answer is yes, the room does decrease in entropy but final state of the room PLUS that of the warmed and melted ice results in a net entropy increase. To evaluate an entropy change properly, one must always examine both the system and its surroundings.[The following is a quick summary for those with some prior knowledge of entropy: Recall that entropy is q/T and therefore, with the lower T in ice than in the room, the amount of entropy increase in the ice is greater than q/T decrease in the higher temperature room. A general conclusion: any transfer of energy due to T difference results in a net entropy increase *in the totality of system plus surroundings*.])

The same wise observer could have asked a similar question at the beginning of this article when hot pans cooling in room air were mentioned. The pan decreases in entropy, but the total entropy change in pan + room is a net increase in entropy. Higher temperature systems/surroundings decrease *less* in entropy than lower temperature systems/surroundings increase in entropy.

Conversely, why do snowflakes form when moisture (water) is in air that is colder than water's freezing temperature? If energy can readily spread out, it will. That is the second law! Therefore, if something is warmer than something else and the two are in contact, the warmer will spread or dissipate some of its energy to the colder. This is why the water will disperse its energy to the colder air and then the water's temperature will drop to freezing and the water will begin to form crystals of ice that we recognize as snowflakes. (Water molecules in air form snowflakes, ice, in hexagonal patterns because the energies in that shape of crystal are lowest — a greater amount of energy will be dispersed as per the second law if those hexagonal patterns are formed rather than other possible forms.)

Some seemingly more complex evaluations of energy and entropy are involved even in mundane situations encountered daily. However, with a few hints we can arrive at general answers for all such events.

1. Why do gases mix spontaneously? The same basic question is expressed in "Why could you quickly smell perfume that is released in one corner of a large room in the far corner even if the room air could be 'absolutely perfectly' still?" (There is NO change in energy in the process and yet it is spontaneous. Where is any energy dispersal here that the second law says is characteristic of all spontaneous happenings?)

2. Why do liquids mix spontaneously? Same question, "Why does cream mix with coffee at the same temperature?" (NO change in energy. Where is any kind of energy dispersal?!)

3. Why would perfume vapor or oxygen or nitrogen or helium spontaneously and instantly flow into an evacuated chamber? (NO change in energy. Where's the second law here?)

The quick, easy and correct qualitative answer is that these examples of mixing or volume expansion are simply illustrations of what happens when fast moving, randomly colliding molecules do when they are given the opportunity of *spreading out their energy in a greater space*.

[The following is considerably more detail than any casual reader need be concerned with. It is a somewhat more sophisticated examination of the scientific background of energy dispersal in volume expansion and mixing, although it is lower level than the ultimate statement of the second law presented in the "Box" near the start of this article that includes microstates.]

To understand these cases we must be told about how energy levels are involved in the behavior of energetic molecules. (Figures 1 and 2 in http://2ndlaw.oxy.edu/entropy.html .) There is a broad range of speed and kinds of motion in any group of molecules that is above absolute zero. Molecules move (translate), tumble around (rotate) and vibrate (atoms in the molecules act as though they were connected with springs, stretching back and forth, or wig-wagging). All of these motions increase as energy content increases (indicated by the temperature). Each type of motion is associated with specific energy levels ranging from lower to higher energy content. For more precise understanding, the dispersal of energy, that we have treated rather non-scientifically as just spreading out to other molecules, etc., must be interpreted in terms of energetic molecules being in or "occupying" particular energy levels or groups of levels. These levels are discrete, i.e., molecules cannot be in any in-between energy state. Energy is "quantized" and treating their energy relationships is part of quantum mechanics.

The more energy levels that can be occupied by energetic molecules, the more widely energy can be dispersed and the greater is the entropy. But in the many cases we have talked about, additional energy levels could only be occupied if the system were heated so the slower molecules would be speeded and there would be many more fast moving molecules to occupy the accessible higher levels. However, this is not the only way that additional energy levels can be made available.

When molecules are allowed to expand into a larger volume (in three-dimensional space) , quantum mechanics shows that an interesting change in possible energy levels takes place: the energy levels become closer together. (Technically, we must say that the density of occupy able levels in any selected energy *range* is greater.) This means effectively that molecules, if allowed to occupy a larger volume even **without any increase in their energy**, can spread out to occupy many more energy levels. This means greater dispersal of energy and an increase in entropy simply by there being a greater three-dimensional volume in which the molecules can move. (Further, because any change in which entropy increases is a spontaneous change. It happens without any outside aid, energy input, etc.)

How does that apply to (1), perfume in a room? It spontaneously mixes with the gases in the large room **because its energy is redistributed among more energy levels** than in the small vapor space of the bottle. This is the same as having greater energy dispersal = an increase in entropy = spontaneity.

And (2), cream in coffee? (Or any other kinds of liquids mixing?) Same as above. Because the motional energy in the molecules of the substances in cream can be more spread out between the molecules in the coffee, the energy of the cream, or of any liquid mixing with another, is redistributed among **more energy levels** in the mixture than alone by itself = greater energy dispersal = increase in entropy = spontaneous mixing.

(3) A gas spontaneously rushing in to a space that was a vacuum? Same explanation as (1) above. Increase in volume = more energy levels available for a substance with the same energy as in a smaller volume = redistribution of energy among more energy levels = increased energy dispersal = increase in entropy = spontaneous process.

In this example of a gas being "allowed" to go into an evacuated bottle, box, or chamber, our feelings are that this should not only be spontaneous (happen by itself) but instantaneous (happen very fast). But feelings aren't reliable. Science demands reasons (and, as we are aware, the second law makes predictions only about the spontaneity of events, not about their rates or speed of their taking place). Fortunately, there is now a firm theoretical basis for our practical gut feeling that "of course a gas would automatically fill a vacuum!". Quantum mechanics provides unquestionable calculations that are the reasonable basis, not just for a gas expanding into a vacuum, but for all the results of the second law presented in this article. In science, that's even better than feeling.

Peroration

We have seen a number of examples of the importance of the second law of thermodynamics in correlating, if not explaining, why or how many kinds of events happen. There are at least 30 different authoritative statements of the second law published by prominent physicists and chemists over the past 130 years. None aids in understanding the general thrust of the law better than "The second law of thermodynamics says that energy of all kinds in our material world spontaneously disperses or spreads out if it is not hindered from doing so."" Its quantitative codicil is "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). Entropy really is simple, qualitatively!

Appendix

Heat

Unlike in most common parlance, in science the word "heat" does not mean a substance or thing or commodity. Strictly speaking therefore, it is not possible to have heat in an object because heat is not a bunch or some more dignified unit of a kind of energy. Heat is the name for a **process of energy transfer** from a body at a higher temperature to one that is at a lower temperature. In molecular terms heat is the transfer of energy via chaotic/random molecular motion — more rapidly moving molecules striking less rapidly moving molecules and increasing the speed of the slower.

"This room is full of heat" is wrong scientifically (and admittedly improbable in conversation). "The room is hot" is a correct feeling and statement. "I heated the room" is correct because it implies a process of energy transfer.

However, it is often distressingly cumbersome to be precise either in science or conversation and so "heat" is often used outside of thermodynamics (and in many texts) as though it were a substance — knowing that it isn't! "The heat from my gas burner was used to…" may be technically incorrect but it is clear communication. It is certainly preferable to "The thermal motion of the products of oxidation of the methane with oxygen (resulting from the energy evolved because the bond energies of carbon dioxide and water are so much less than the reactants) was partially transferred to…". :-)

Activation Energy

The cause of "activation energy" lies in the nature of chemical bonds and how bond strengths influence whether or not a chemical reaction occurs. Therefore, we need to talk about bonds in chemistry first.

Chemical bonds are the forces that hold atoms together in a molecule. In a diagram of a hydrogen molecule, H-H, the dash represents the bond between the two atoms that firmly holds them in a unit. Most bonds between atoms in molecules are quite strong; it usually takes a great deal of energy to *break* them. (Conversely, when bonds are *formed*between individual atoms to yield a molecule, much energy is usually evolved.) The bonds in water, H2O or in more detail H-O-H (that should have an angle of 105° between the H-O and the O-H), keep water from breaking into individual atoms not only at its boiling point of 212°F but even far above 2000°F where the energy in the water molecules would be very great. (They would not only be moving rapidly, but vibrating in stretching the length of the bonds between the O and the H atoms.)

In a chemical reaction, say of hydrogen with oxygen to produce water (H-H and O-O yielding H-O-H), the bonds between hydrogen atoms in two molecules and that between oxygen atoms must be broken and new bonds between hydrogen and oxygen must be formed to yield two molecules of water. But the process cannot be stepwise in that order — that all the bonds must be broken before new ones are formed - because it usually takes a great deal of energy to break a chemical bond. To break all or many bonds in a reaction mixture before any new ones can form would require an enormous amount of external energy to be supplied.

This is why most reactions require a relatively small energy "push" to start. For example, a spark has to be introduced into a mixture of hydrogen and oxygen before the reaction begins to form water, but then immediately it becomes an explosion. Why this strange combination of molecular recalcitrance followed by fantastically rapid reaction? Breaking the old bonds (requiring energy) normally must occur slightly **before** the formation of new ones (evolving energy). Thus, even though water has lower energy in its bonds than hydrogen molecules plus oxygen molecules in theirs so that a large amount of energy is evolved overall when a reaction occurs, none of that energy can be released without an initial "push" to aid the break of a few hydrogen and oxygen bonds just before they form a few water molecules. Once that "push" occurs, the energy evolved as the water is formed feeds back to make many of the unreacted hydrogen and oxygen molecules move far more rapidly and collide forcefully so they react to evolve more energy and so on and on.

The initial"push" described in the preceding paragraph is what chemists call an **activation energy**. Most spontaneous reactions require this initial input of an amount of energy, activation energy, to aid the first few molecules to react so they feed back their evolved energy to serve as activation energy for succeeding molecules to repeat the cycle. (See http://shakespeare2ndlaw.oxy.edu for diagrams of activation energies, E_{ACT}, that is designated properly as E_a in texts and scientific publications.)

It is this "minor" detail of chemical reactions, the activation energy, that obstructs the instant carrying out of second law predictions and thus protects our bodily biochemicals and our degradable artifacts from instant oxidation and other deleterious reactions