What Is Entropy, REALLY?

Entropy measures the spontaneous dispersal of energy: how *much* energy is spread out in a process, or how *widely* spread out it becomes — at a specific temperature. (Sometimes, it's a simple equation, Entropy change = "energy dispersed"/T, or $q_{reversible}$/T , as in phase changes like melting or vaporization where $\Delta S = \Delta H_{fusion}$ /T or $\Delta H_{vaporization}$ /T, respectively.)

> (In chemistry the energy that entropy measures as dispersing is "motional energy", the translational and vibrational and rotational energy of molecules [Figure 1 of http://www.2ndlaw.com/entropy.html] and the ΔH of phase change energy — both motional or phase change energy being designated either as "q" or ΔH in many equations. "Bond energy", the potential energy associated with chemical bonds that we talked about in the iron oxidation example, is only measured by the potential energy of bond formation that we talked about in the iron oxidation example, is only measured by entropy change in connection with a chemical reaction in $\Delta G = \Delta H - T \Delta S$

Is that description of an entropy change complicated? Entropy is a sophisticated kind of "before and after" yardstick — measuring how MUCH energy is spread out/T as a result of a process, or how WIDELY spread out is the energy after something happens than before (at a constant temperature). Maybe entropy seems confusing and abstract when the first entropy equation is thrown at you in your text, about a change in entropy in a reversible process: $\Delta S = q_{rev}$ / T. Let's look at it by using a "how MUCH" practical example: ice spontaneously melting in a warm room. (Phase change ΔS, an increase in entropy)

Phase Change — a "how much" energy is dispersed example

From your experience — remember, that's the basis of the second law — what direction do you think the energy of molecules would go — from those faster moving air molecules in the warm room to the slower moving water molecules in the cold ice ... or would the slower moving molecules in the ice give up some of their energy to the warm air? Sure. From the hotter to the colder! Always. [If you need a math proof, it is given in the middle of www.secondlaw.com/six.html] The greater motional energy of the warmer air molecules spreads out some energy to the cold ice and this breaks (or alters) intermolecular hydrogen bonds between the water molecules in the ice. Liquid water

forms at the tiniest temperature above the melting point of 0°C (273 K) and, reversibly, solid ice forms at the tiniest temperature below 0°C.

As the warmer air molecules transfer some of their motional energy to be dispersed in the ice, it breaks many hydrogen bonds in the ice. This allows the molecules to move with the same amount of energy that they had when just "dancing in place" in the ice but now form new bonds with other water molecules, and actually move a little bit, but that's a lot compared to being in one place in a solid. (Their speed is not increased, and thus the resulting liquid's total motional energy is unchanged, and the temperature doesn't rise above 273 K when ice melts to water.) Even though there is an increase only in the potential energy of the liquid water at 273 K compared to ice, no longer are all the molecules held in the very rigid framework of ice. They still are hydrogen bonded in the liquid but constantly move through space by forming new bonds after breaking others.

How MUCH energy is dispersed in melting ice, breaking those original H-bonds and allowing the molecules to move relatively freely? The enthalpy of fusion, ΔH_{fusion}, of course! That's why your text says the entropy increase in melting is $\Delta S = q_{rev}/T = \Delta H/T$.

Standard Entropy — a "how much" energy is dispersed example

Then, many texts go on to talk about "standard entropies", S^o_{298}, of all kinds of elements and compounds. Actually, "standard entropies" should be called "standard entropy *changes*" for substances. This is because the entropy values of S^o_{298} that are listed in Tables come from the total amount of energy (q_{rev}) that has had to be reversibly spread out (at each incremental fraction of temperature, i.e., q_{rev}/T) in any substance as it was very slowly heated up from 0 K to 298 K – a big *change* from 0 entropy at 0 K to S^o at 298 K.

Texts usually urge you to look at S^o_{298} values to see the differences between the standard entropies of different types of molecules – monatomic gases vs. polyatomic, gases vs liquids of the same element, graphite vs. diamond vs. metals vs iodine. However, some texts fail to tell you that these S^o_{298} numbers show a rough *comparative* amount of motional energy (plus any phase change energy given to the substance from 0 K) that each particular substance must have to exist at 298 K — substances that are capable of more free motion need to have more energy spread out in them or they just could not *be* at 298 K.

Specifically, monatomic gases don't require any energy to rotate, but polyatomic gases do — and the more different kinds of turning and wiggling in large molecules, the greater the energy required and the larger is the S^o value. Graphite has a relatively 'loose' structure, a less

rigidly bonded solid than diamond; therefore, graphite requires more energy for the normal slight movement in its crystals than does diamond with its lesser possible movement. Iodine molecules are much less strongly bound by intermolecular attractions to other I_2 molecules that are metal atoms kept in place in their 'sea' of electrons; thus iodine has a higher S^o value because it requires more energy for its molecules to vibrate a bit at 298 K than do 'held in place' iron or copper or gold atoms.

Volume Increase: Gas expansion, gases mixing, liquids mixing — "how widely" examples

Most texts show before and after illustrations of a gas spontaneously expanding into an evacuated bulb. When that happens, there's no energy change, no temperature change. Thus, the total motional energy of the initial gas in one bulb is spread out to be half that amount of energy (and half the molecules of gas) in in each of the two bulbs finally. WHY should a gas behave this way?

Your text may use that kind of illustration and then talk about calculating the probability of the gas all being in one bulb versus being in two — with little red dots for energetically colliding molecules and tables for calculations. (But those texts don't emphasize the energy of those little molecules that are racing around and hitting each other!) If your text does that kind of calculation, go along with it; memorize it; you're going to have it on an exam. But "probabilities" are just half the reason for the gas expanding; they are the math for the *results* (that would not have occurred if *motionally energetic molecules* hadn't been part of the system. Marbles or dice or playing cards don't move to other places no matter what their probability arrangement might be!!).

YOU know the simplified explanation for a gas to move into an evacuated bulb—the second law of thermodynamics — as does any energy, the motional energy of the molecules (translation and rotation) *spreads out as widely as it can*, if it is not hindered. (It certainly wasn't hindered from spreading out just as soon as that stopcock between the two bulbs was opened!) More fundamentally, if there are particles with motional energy AND there is an increased space that probability shows could be occupied, those particles *will* spread out widely and the entropy of the gas will increase. Wider energy dispersal = entropy increase.

How to calculate the entropy increase in the spontaneous expansion process is not obvious, because (1) there isn't any change in the energy of the gas that expands (q = 0), (2) even if there was a change in energy, you couldn 't use the simple equation with q_{rev}/T

because it is an *irreversible* process unlike the reversible melting of ice at 273 K! It isn't a "how much energy is dispersed" situation, it's a question of "how *more widely spread out* in two bulbs" is the gas than it was in one. (Of course, from the definition of entropy as a spontaneous increase in energy dispersal, there is an entropy increase in the expansion because the energy of the gas has obviously spread out more.) In your text probably this entropy increase is calculated from the energy required to reversibly compress the gas back to the volume of one bulb, i.e., RT ln (V_2/V_1) and thus $\Delta S = R \ln (V_2/V_1)$

Gases spontaneously mix — a "how widely" energy is dispersed example;

   If you put two different gases in that same two-bulb apparatus we talked about just now — but both at the same atmospheric pressure — when you opened the stopcock, they would slowly spontaneously mix. Why? Just the second law, of course!

      The molecules of each gas are rapidly moving and colliding; they have "motional energy". So, as the second law predicts, the motional energy in those molecules will cause them to spread out if it is not hindered. Sure enough, when you open the stopcock, you are letting the motional energy of each gas spread out more widely into the larger volume of two bulbs rather than staying in one. Is the probability that there are more *positions* in two bulbs for the molecules than there are in one important? Yes. Even though our simple predictions based on energy dispersal always works, technically and fundamentally, entropy change requires *both* the presence of molecules that have motional energy *and also* calculations that show that it is more probable for such particles to be in two rather than one volume.

Liquids spontaneously mix (if they are like each other) — a "how widely" example

   When liquid water and alcohol are added to one another, they spontaneously mix — as do any 'like' (similar to each other in chemical structure) liquids. This is true regardless of volume change because the mere presence of two substances in the same total volume involves a dispersal of the energy of each in that whole mixture — and increased dispersal and greater entropy change as the relative quantities of each liquid in the mixture increases toward a 50:50 mole ratio. This is one of several cases in which the simple view of energy becoming more dispersed when substances are mixed works — i.e.,

predicts the correct result of spontaneity and of entropy increase. However, the fundamental calculations are relatively complex and involve statistical mechanics in which the solution is considered to be in many 'cells' with each cell a different combination of molecules in the ratio of the quantities of the two liquids present. The equation for the entropy increase in the mixture uses the relative molar quantities of liquids that were mixed.

A small amount of solute is added to a solvent — a "how widely" example

When even a small amount of solid solute is added to a solvent, just as in the mixtures of liquids above, the motional energy of the individual solvent molecules (and the solute molecules) in the new solution is each more separated from its own type of molecule than before, and thus each individual molecule's energy is more spread out or dispersed. The entropy of the solvent and the solute each increases in the solution. (The more fundamental reasoning and resulting equations from statistical mechanics are the same as described above for liquid mixtures.) If we realize that a solvent's energy is more dispersed in a solution than when it is a pure solvent, we can see why a solvent in a solution should be increased in entropy compared to its entropy as a pure solvent. Then also, it is obvous that the entropy will be larger depending on how many molecules of solute are added to the solvent. That increased entropy of the solvent in a solution is the cause of the "colligative effects" that we study: (1) osmotic pressure, (2) boiling point elevation, and (3) freezing point depression.

Now, if the solvent tends to stay in a solution (because its energy is more dispersed there), rather than being with only with its own kind of molecules in pure solvent, it will stay in that solution if it has a 'choice'! That means (1) if there is a membrane placed between a pure solvent and a solution containing it (and that membrane allows solvent molecules from pure solvent to go through it from the other side but not the solute molecules), pure solvent will go through the membrane to get to the solution because its energy is more spread out there. That's 'osmosis', a very important phenomenon in biochemistry; (2) solvent molecules in a solution will not leave that solution to become vapor molecules in the atmosphere above a solution as readily as at the normal boiling point of the pure solvent; a higher temperature will be necessary to cause enough molecules to leave the solution to be in equilibrium with the atmospheric pressure and 'boil'; (3) solvent molecules in a solution will not be in equilibrium with the solid phase (composed of pure solvent molecules) at the normal freezing point; a

lower temperature is necessary to reduce the motional energy of the solvent molecules so that they can make intermolecular bonds to form a solid; i.e., be in equilibrium with their molecules in the solid phase), All of these colligative effects increase as the amount of solute in the solvent is increased because the entropy (i.e., energy dispersal) of the solvent increases in the solution with a greater concentration of solute.

Heating a substance — a "how much" energy is dispersed example

Textbooks that do not use calculus omit this example, but it can easily be described qualitatively because we know the basic idea — energy spontaneously spreads out if it is not hindered. Motional energy from hot surroundings is spontaneously spread out in cooler systems/substances, never the other way around. The entropy of the cooler system always increases more as it is heated than the hot surroundings decrease in entropy. (Calculations are available at http://www.entropysite.com/entropy_isnot_disorder.html#m3)

Chemical reactions — "how much" and "how widely" energy is dispersed

Spontaneous exothermic reactions are usually due to the chemical bonds in the reactants being relatively weaker than the bonds in the products. (What you actually calculate in the ΔH change of a reaction is the enthalpy ["heat"] of formation of products minus the enthalpy of formation of reactants. Enthalpies of formation are closely related to bond strengths/energies) That "how much" energy difference of ΔH in a chemical reaction is spread out as old bonds are being broken and new ones formed by the product molecules (and any unreacted molecules of reactant) in moving much more rapidly than the reactant molecules did at the original T. Then, this motional energy of the products is dispersed to the surroundings and the temperature of the system returns to T.

Now, consider the entropy change in a reaction. It is the reactant's motional energy (plus any phase change energy in them) that determines the value/magnitude of the entropy state of each reactant at T. Then, because the entropy values of possible products at T are usually different than those of the reactants, the ΔS in the reaction is easily calculated from $\Delta S_{products} - \Delta S_{reactants}$. That difference is a combination of "how much" and "how widely" is energy dispersed in the reaction process — whether heat is evolved or absorbed and whether the volume changes or more mixtures are formed. (Thus, the ΔS change alone can be responsible for a spontaneous reaction even

though most often it either simply adds to or subtracts from the usually larger ΔH change.)

> Both kinds of energy difference (i.e., "how much" and "how widely") are combined in the ΔS change you calculate, but often you can estimate whether the ΔS change in a reaction is greater or lesser simply by estimating the " how widely" factor of energy spreading out in the products as compared to the reactants. This is the scientific reason for the textbook 'rules' of entropy increase in reactions: (1) if more molecules are produced, this involves "how widely" (motional energy is more widely spread out if there are more molecules among which it is dispersed); (2) if a phase change from a solid to a liquid occurs (a phase change involves "how much", an increase in potential energy from that in solids to liquids, and "how widely", less restricted locations in space in a liquid allow energy to be more spread out); (3) if a gas is produced from a solid or liquid (as stated in (2), the process involves a phase change in which both "how much" and "how widely" energy is more dispersed.)

Spontaneous endothermic reactions are due to the greater motional energy in the hotter surroundings that can be transferred to reactants in a system. As you know from the Gibbs equation, $\Delta G = \Delta H - T\Delta S$, a high temperature makes the $T\Delta S$ function dominate. Thus, entropy change is causal in endothermic reactions.

In the Gibbs equation, $\Delta G = \Delta H - T\Delta S$, each term describes an aspect of the *energy that is dispersed* because of a chemical reaction occurring in a system:

ΔG is the total energy that is spread out in the universe (<u>system plus surroundings</u>) due to the reaction that has taken place in the system.

ΔH is the energy from the reaction that is dispersed <u>from</u> the system <u>to</u> the surroundings.

$T\Delta S$ is the energy that is dispersed in the system – in the products of the reaction as compared to the reactants.

If each term is divided by T, the Gibbs can be seen as an "all entropy" equation.

The Gibbs "works" because it corresponds to the second law as we would state it, "Energy spontaneously disperses, if it is not hindered. When it does so, entropy increases in the combination of system plus surroundings."

This is what the conventional statement means when it says more succinctly but more obscurely, "The entropy of the universe increases during any spontaneous process."

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