Configurational Entropy Revisited

Frank L. Lambert
Department of Chemistry, Occidental College, Los Angeles, CA 90041; *flambert@att.net*

Entropy change is categorized in some prominent general chemistry textbooks as being either positional (configurational) or thermal. Positional entropy focuses on the number of positions in space that can be occupied by the molecules of a system. Then, to the extent that more positions exist after a process than before, the greater is the entropy increase in the system.

Configurational (positional) entropy has a distinguished history. Developed from classical statistical mechanics, it was the basis of Pauling's 1935 determination of the residual entropy in ice *(1),* Bent's brilliantly simple development of the entropy of mixing in 1965 *(2),* and more recently, such publications as Craig's use of the cell model in presenting entropy change in mixing *(3).* There is no question about the correct values obtained from such calculations via configurational entropy change, the facile steps in the procedure, or its being the only practical method for calculating entropy change in some complex areas of thermodynamics.

However, positional entropy as presented in several widely-used and influential general chemistry texts has two serious conceptual flaws in introducing beginners to entropy change.[1] When positional entropy is emphasized, it strongly implies that matter can spread out without any involvement of the energy associated with its mobile molecules. Equally misleading, the undue focus on the difference between "energy-unrelated" positional entropy change and thermal entropy change discounts the shared aspects of their fundamental relationship. One text states (and several others agree substantially), "[there are] two basic types of spontaneous physical process: 1. Matter tends to become dispersed. 2. Energy tends to become dispersed."[1] With "1" as positional entropy and "2" as thermal entropy, there are a number of questions for students both within the thermodynamics chapters and at the chapter ends. Unfortunately, this reinforces the idea of discriminating between "types of entropy" rather than focusing on the common foundation of entropy increase, energy spreading out.

A fundamental problem engendered by general chemistry texts employing positional entropy (and in others not emphasizing that expression) is that gas expansion or fluid mixing is due to "the driving force[2] of probability", as one textbook states. Certainly probability, in the sense of a spatially broader and thus of a probably greater *distribution for the motional energy of each constituent's molecules*, is an essential consideration in mixing or expansion, but this is not the interpretation of probability given in texts employing positional entropy.[3]

The Source of the Problem

I once wrote "…violently energetic, speeding gas molecules will spontaneously move into an evacuated chamber or mix with another gas…summarized as increases in entropy" *(4).* Craig corrected me, "…in saying that, you are 'smuggling in' entropy. Movement of molecules does not *cause* an entropy increase even though [it] *enables* an entropy increase" [italics in original] *(5).*

Craig is right. An increase in thermodynamic entropy is *enabled* in chemistry by the motional energy of molecules (that, in chemical reactions, can arise from the energy released from a bond energy change). However, entropy increase is only *actualized* if the process makes available a larger number of arrangements for the system's energy,[3] a final state that involves the most probable distribution for that energy under the new final conditions.[4] This can be seen in terms of removal of a constraint. For example, a stopcock is opened to an evacuated flask allowing a gas to expand in volume, a partition separating hydrogen and helium is slid aside and the gases mix, or ideal liquids are given the opportunity to mix.

The definition of entropy arose as $dS = Dq_{\mathrm{rev}}/T$ because the major concern of Clausius' day was a heating or cooling process of energy transfer that involved system and surroundings. Of course, that original definition is still the fundamental expression for evaluating entropy change. However, then, spontaneous physicochemical processes involving only the isolated system, mixing or gas expansion, wherein no energy change within the system occurred, could only be evaluated by considering a return path that involved a reversible entropy change in order to satisfy $dS = Dq_{\mathrm{rev}}/T$. The statistical mechanics of Boltzmann and Gibbs and later thermodynamicists focused on molecular interpretations of entropy change. Their development of statistical procedures for treating spontaneous mixing and gas expansion resulted in excellent predictions that apparently were dependent solely on three-dimensional location change (leading to volume or mole fraction change) and have been called configurational entropy change. Unfortunately, nowhere in the descriptions of those statistical methods were there overt statements that any increase in possible locations implicitly also described the increase in *the possible number of ways that the original motional energy of a system could maximally be distributed* within the new constraints of that system. Therefore, statistical mechanics, or an exclusive focus on probability considerations in entropy change, *smuggle-in entropy change by ignoring its enablement by molecular motional energy.* That the initial quantity of molecular motion is unchanged is often mentioned in statistically describing mixing and gas expansion. That either kind of process would be impossible without energetically mobile particles is rarely emphasized. But, presenting these processes to students solely as changes in locations rather than a greater spatial dispersal of their molecules' unchanged motional energy improperly separates configurational entropy from thermal entropy.

In summary, configurational entropy techniques of counting the probabilities of positions of particles in space in a process in which the system's energy does not change can accurately measure that entropy change. However, that actually is "smuggling-in" entropy by dealing only with actualization of the process, the probability of energy dispersal over space (and over time, owing to an increased number of accessible microstates).[3] For general chemistry students, positional entropy not only obscures the essential enabling factor of motional energy that makes any new probabilities accessible, but needlessly sets up two entropies, positional and thermal.

Positional entropy successfully deals with volume expansion and mixing but it cannot treat the transfer of energy, “heat”, between systems and surroundings as required by the expression $dS = Dq_{rev}/T$. In contrast, thermal entropy can quantitatively describe all changes in entropy. Its success in doing so is described next. This unification makes it possible and desirable to discard positional entropy in general chemistry instruction.

The Relationship between Configurational and Thermal Entropy

Two recent articles in this *Journal* strongly support the argument that configurational entropy change is readily understood and calculable not just as locations of particles in space, but in terms of the greater distribution of the energy of a system. Hanson’s Boltzmann game for students is an excellent analogy to a system of energetic molecules *(6).* It begins with students paired in two concentric circles, each having the same quantum unit of “money energy”. The key to the game’s success is that a transfer of the “money energy” cannot occur before one student of a pair wins a fast game of probability, “rock–paper–scissors” *(6a).* The students then become analogous to colliding molecules by their physically *transferring* their quanta if they lose. Thus each “collision” results in transferring “energy” *probabilistically* and continues as the inner ring moves one position. The distribution of “quanta” among the students in a remarkably short time begins to fit a probabilistic model of energy distribution for a system of molecular harmonic oscillators.

This can be shown by calculating the entropy change of the students’ “money energy” system via the Boltzmann entropy equation of $\Delta S = k_B \ln(W/W_0)$, where W is the combinatorial number of ways the students’ “money energy” has become distributed and W_0 is 1, the start of the game. The analogy to a system of energetic, colliding molecules is close: the overall energy of the system has not changed but the probability of the distribution for that energy has greatly increased.

In a later section, Hanson proves that the standard “ΔS_{mix}” (that comes from statistical mechanics of the *locations of particles*, a configurational entropy change) *(6b)* is equivalent to his *energy-based* introduction to entropy change in explaining the origin of the reaction quotient, “$-R\ln Q$”, in the relationship of “$\Delta_r S = \Delta_r S° - R\ln Q$” *(6c).* Configurational entropy increase is thereby shown to be equivalent to an increasingly broad distribution of the initial energy in a system.

In another article, Kozliak’s more fundamental examination of the relation of the Boltzmann energy distribution to configurational entropy change led him to solve what had been a problem in thermodynamic entropy, the residual entropy in crystals *(7).* Residual entropy is the quantity of entropy remaining at temperatures approaching 0 K in the crystals of non-symmetric molecules like CO, N_2O, $FClO_3$, and H_2O that have relatively weak intermolecular forces. It has always been treated as a clear indication of an entropy effect that could only be ascribed to the arrangement of molecules in space. The importance of his work for general chemistry processes goes far beyond this phenomenon of residual entropy. Kozliak shows thermodynamically why configurational entropy yields correct values for entropy change in the simple processes to which general chemistry texts apply it.

In his analysis Kozliak uses the fact that the two different arrangements in crystalline CO, the aligned CO CO CO CO CO and the unaligned CO OC CO CO OC, have different Boltzmann energies with the unaligned being higher. Below the freezing point of CO, the unaligned CO molecules cannot rotate readily (due to an activation energy unavailable at that low temperature) to form a perfectly aligned crystal: their arrangement is “frozen-in”. By use of the Boltzmann distribution and its combinatorial calculations leading to W in $S = k_B \ln W$, the entropy is $R\ln 2$.[5] But this is exactly the same result from a similar combinatorial calculation for two different sets of *positions* in crystalline CO—and this is a *positional entropy* conclusion calculated completely parallel to the way used for volume expansion of a gas.

The important reason for the values coinciding is that the energy difference between the aligned and nonaligned states of CO is very small, just as the energy difference between energy levels of a gas are extremely small. When this is the case, any entropy calculations of a change such as gas expansion or mixing will yield the same result by counting a change in positions as by counting the number of possible distributions for energy.[3] Kozliak’s work, therefore, shows the theoretical basis for Hanson’s statements as well for the qualitative conceptual presentations in this article.

The Implications for General Chemistry Instruction

The fact that thermal entropy (measuring changes in energy distributions) yields the same results as positional entropy (measuring numbers of positions in space) means that there is no reason that positional entropy with its usual lengthy or superficial support via probability need be presented to students in general chemistry. (There is equally no reason why professionals may not continue to use configurational entropy if it fits their preference,)

Beginning students—overloaded with new material as they are and increasingly “concrete minded” rather than enjoying abstractions—should not be presented with positional entropy in general chemistry. A preferred method of describing entropy increase in gas expansion, fluid mixing, of ideal nonvolatile solutes dissolving in solvents (leading to colligative effects) can simply be “violently energetic, five times faster than NASCAR molecules that are constantly colliding ***will*** spontaneously occupy more space—if they are allowed to.” Isn’t this “smuggling-in” entropy? It certainly is, but illustrated dynamically for each case, stated and restated dramatically, it is a *first* step to understanding entropy change, one that can be readily presented to all students. Only after this concept of the meaning of energy dispersal as a measure of entropy increase, and perhaps only to honor students and those going on to physical chemistry, should the second essential *actualizing* factor involving probability be developed.

Conclusion

Configurational entropy has been and will continue to be a useful tool in some complex areas of thermodynamics. However, it is time that configurational or positional entropy is abandoned in general chemistry instruction. It is unnecessary as a separate "type" of entropy. It distracts students from an emphasis on the nature of entropy increase as a measure of the greater dispersal of energy in a system (or system plus surroundings). Positional entropy is seriously misleading when it implies a dispersal of matter with no kinetic molecular enablement.

Spontaneous gas expansion, fluid mixing, and ideal solute dissolving can be adequately described qualitatively to all students as simply an expected result: the spreading out of violently colliding, energetic molecules in a greater volume. This is the same simplified presentation possible for thermal entropy: heating, and all similar energy transfer means that the energy of the hotter surroundings becomes more spread out to the final combination of once-cooler system and once-hotter surroundings. The molecular energy has become more dispersed in a larger volume. Even though such simplification would be a great aid—and perhaps the only goal for "concrete-minded" students, it is also a seamless first step for honor students and those going on to physical chemistry. Their completion of an understanding of entropy change is readily "actualized", second, by their being led to see that the "normal spreading out of molecular motional energy" whether thermal or volume-wise is favored by the greater accessibility of more energy levels, and third, by the probability of a much larger number of microstates[3] in the final state.

There are two requisites for thermodynamic entropy change. An increase in thermodynamic entropy is *enabled* in chemistry by the motional energy of molecules (that, in chemical reactions, can arise from the energy released from a bond energy change). However, entropy increase is only *actualized* if the process makes available a larger number of arrangements for the system's energy,[3] that is, a final state that involves the most probable distribution of that energy under the new constraints.[4]

Acknowledgments

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Notes

1. Singling out individual authors could appear invidious. Thus, citations to specific texts or quotations are not listed.

2. "Driving force" is a phrase that is "empty of useful meaning in chemistry" because it implies Newtonian determinism whereas "entropy is an expression of probabilities" *(8).*

3. By "an arrangement for a system's energy" is meant a quantized *microstate*. At any instant, the energy of a system that is due to the motions of its molecules is arranged or distributed among them in only one way. At the next instant, one collision or many collisions of molecules changes the arrangement into a different distribution of that motional energy and the system is in another microstate. The larger the number of possible microstates *for* a system, the greater is the probability that the system may change from the one in which it is to another at the next moment. In this sense—of more chances for a system to have a different arrangement of its motional energy in the next instant—the energy of the system is less localized and thus, potentially, more dispersed over normal time periods. (Leff calls this a "*temporal* spreading of the system's energy among microstates—an invisible dance (to us) over different microstates" *(9).* Therefore, when a larger number of microstates is *possible* for a system after a process than initially, as calculated from $\Delta S = k_B \ln(W_{\text{Final}}/W_{\text{Initial}})$, the energy of the system has become temporally more dispersed and this final state is more probable.)

4. The two requisites, energy and probability, are both necessary for thermodynamic entropy change but *neither is sufficient alone.* In sharp contrast, information "entropy" is alone sufficient for its mathematical goals, depending only on $-k\Sigma p_i \log p_i$, where k is an arbitrary constant that is not required to involve energy.

5. The predicted value of $R\ln 2$ is equal to 5.76 J/(K mol). The difference found between the theoretical and experimental values is 4.6 J/(K mol).

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