

Introduction of Entropy via the Boltzmann Distribution in Undergraduate Physical Chemistry: A Molecular Approach

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Entropy and the second law of thermodynamics are pivotal topics in undergraduate physical chemistry (1). Traditionally in this course for majors, entropy has been introduced by the Clausius definition thereby emphasizing its macroscopic aspect.

$$dS = \frac{\delta q_{\text{reversible}}}{T} \quad (1)$$

Of the physical chemistry textbooks for majors listed in the Buyers Guide of this *Journal* (2), 13 of 20 use this approach (two books were unavailable to me). In such traditional books, the modern statistical consideration of entropy is separated from its classical definition and is dealt with many chapters later, emphasizing its mathematical basis rather than conceptual connections with eq 1. However, this approach presents a problem to students. Current general and organic chemistry texts emphasize chemistry as a molecular science. Thus, the phenomenological introduction of entropy in physical chemistry, if divorced from molecular behavior, appears to be abstract in its bases. My experience has shown that this strongly contributes to the previously described resentment toward physical chemistry (1) and multiple misconceptions (1a, 3). One of the most serious of these misconceptions is that students often believe that there are two entropies: “thermal” involving heat transfer, and “positional” that manifests itself in gas expansion and mixing.

Relatively few of the textbooks in physical chemistry for majors, 5 out of 18 (4), have used the molecular approach. This usually entails the introduction of entropy based on molecular statistics using the Boltzmann formula,

$$S = k_B \ln W$$

$$\Delta S = k_B \ln \left(\frac{W_{\text{final}}}{W_{\text{initial}}} \right) \quad (2)$$

where W is the number of microstates within the system and k_B is Boltzmann's constant. In most of these texts (4) the prototypical example dealing with the entropy of an ideal gas doubling its volume upon expansion into vacuum precedes a similar illustration treated by the Clausius approach (eq 1). Using eq 2 in calculating the number of possible molecular combinations before and after the expansion is intended to introduce students to a quantitative molecular sense of entropy. However, with this instructional sequence the above-mentioned misconception about “two kinds of entropy” is not removed because this gas expansion to different positions in space is never specifically related to thermal events. In addition, such an initial example using molecules dispersing in space as the statistical introduction of entropy implicitly reinforces the error of “entropy is ‘disorder’,” a misconception that was recently decried by Lambert (5a).

Davies in 1972 published a brilliant textbook that introduces entropy thoroughly based on rigorous statistical calculation of the number of microstates using eq 2 (6). Despite its great examples and fine quantitative approach, this book has one problem: the detailed introduction of statistics is inherently long and challenging.¹

I propose a molecular approach for the introduction of entropy in undergraduate physical chemistry that incorporates the best features of Davies' treatment (based on eq 2 and, thus, focused on energy dispersion²) but meets the needs of present students by bypassing the complexities of statistics. It upgrades the qualitative, intuitive approach of Lambert for general chemistry (5b) to a semiquantitative treatment using the Boltzmann distribution.

Sequence for a Molecular Approach to the Introduction of Entropy

I suggest introducing entropy prior to its phenomenological description with four essential components: (i) A continual emphasis on entropy as a measure of the dispersion of energy among accessible microstates. (ii) A quantum mechanical explanation for the increase of accessible microstates in a box containing molecules when the box is enlarged. (iii) The use of the Boltzmann distribution to explain the increase in accessible microstates caused by either expansion or heating. (iv) Connecting the molecular significance of entropy (eq 2) with eq 1 by illustrating the directionality of the heat transfer from a hot to cold body.

Component 1: Entropy as a Measure of the Energy Dispersal among Accessible Microstates

Baierlein defined a microstate as the state of a system in which the location and momentum of each molecule and atom are specified in great detail (7a). One may call it a particular combination of molecules distributing the given quantity of quantized energy.³ For quantum systems considered in this article where the particle's location is not defined, a simple analogy may be suggested: A microstate is one way of arranging the finite number of similar books (particles) on a certain number of horizontal shelves of different height (quantum levels) in a library; the accessible energy levels are those that can be reached by a librarian depending on how high the shelf is.

Entropy increase involves an increase in the number of accessible microstates among which the energy of a system can be distributed. Thus, there is only one kind of entropy change in a system: the spreading of energy among a changed number of accessible microstates (5b) whether that process may be due to the change of volume, composition, or temperature. The essence of my approach is that the numerical values of W in eq 2 do not have to be calculated; W_{final} and W_{initial} should only be qualitatively compared for assessing the sign of ΔS . Then, only one principle of statistical ther-

modynamics will be used henceforth: greater population of higher quantum levels leads to a greater number of microstates. This principle is based on the Boltzmann distribution, namely, on the fact that there are always fewer particles on the upper energy levels; so the accessibility of higher levels limits the number of microstates.

Component 2: Entropy Change in Ideal Gases Due to Volume Increase: Goals and Background

The pedagogical goals here are dual: first, to reinforce the concept that spontaneous changes (the expansion of a gas into a vacuum, the mixing of different ideal fluids) involve an increase in entropy owing to an increase in the number of accessible microstates, to show thereby that “positional entropy” is dependent on energy dispersion; and, second, to demonstrate a connection between quantum mechanics and the second law of thermodynamics. This approach was used on an elementary level by Lambert (5b), and Atkins and Jones (8).

In quantum mechanics, translational energy is modeled by considering the particle-in-a-box (a one-dimensional box, i.e., a string, is used here for simplification),

$$E = \frac{n^2 h^2}{8ma^2} \quad (3)$$

where m is the mass of the particle, h is the Planck constant, n is an integer (quantum number), and a is the box length. Upon the box expansion (for instance, from a to $2a$), the energy of each quantum level (n) decreases as can be seen in eq 3. This result will hold in three dimensions, making the case directly applicable to gas expansion. Since the total energy of the gas does not change upon expansion into vacuum, the gap between the energy levels narrows. This can be illustrated for the gap between the first and second levels: for a one-dimensional box, $\Delta E_{1-2} = 3h^2/8ma^2$; that is, ΔE_{1-2} decreases upon the increase of parameter a . I suggest taking this qualitative example one step further by considering the increase of accessible microstates after expansion semi-quantitatively, by using the Boltzmann distribution.

Component 3: The Boltzmann Distribution and the Increase of the Number of Microstates upon Expansion and upon Heating

Many physical chemistry textbooks use a very convincing and yet simple example in introducing the Boltzmann distribution with 10^3 – 10^4 particles of a hypothetical chemical whose molecule has just two energy levels, 0 and ϵ ($\epsilon = \Delta E_{1-2}$ in the previous section). I personally like the development in Noggle (9). According to the Boltzmann distribution law, the relative populations, N_i , of these two levels are expressed as follows:

$$\frac{N_1}{N_1 + N_2} = \frac{e^{-0}}{e^{-0} + e^{\frac{-\epsilon}{k_B T}}} = \frac{1}{1 + e^{\frac{-\epsilon}{k_B T}}} \quad (4a)$$

$$\frac{N_2}{N_1 + N_2} = \frac{e^{\frac{-\epsilon}{k_B T}}}{e^{-0} + e^{\frac{-\epsilon}{k_B T}}} = \frac{e^{\frac{-\epsilon}{k_B T}}}{1 + e^{\frac{-\epsilon}{k_B T}}} \quad (4b)$$

I suggest using this formula for illustration of the increase in the number of accessible microstates upon both expansion and heating. For expansion, the temperature is constant but, as shown above, the value of ϵ (energy gap, ΔE) declines. Thus, based on eq 4a, the denominator increases, that is, the population of the lowest energy level declines and some molecules are promoted to the second energy level. As noted in Component 1, this leads to an increase in the number of their combinations, that is, microstates. This result applies not only to movement of a gas into a vacuum, but to expansion of all types of ideal fluids—precisely to mixing of different gases, superficially to the mixing of ideal miscible liquids.

As far as heating is concerned, a simple algebraic analysis of eq 4 shows that at a low temperature approaching absolute zero all particles must stay on the lowest energy level ($W = 1$ and, thus, $S = 0$), whereas at an infinitely high temperature the particle distribution between the two energy levels becomes equal (1/2 vs. 1/2, see the values of N_2 fractions in Table 1). Therefore, an increase of temperature clearly makes higher energy levels accessible to more particles—an overall increase in accessible microstates—implying that the system's entropy increases (eq 2).

To make this qualitative illustration more tangible, one needs to compare the fractions of N_2 at different temperatures. This can be done numerically (Table 1). An analytical solution can be obtained for the population ratio of two energy levels, $(N_2/N_1)_T$. By dividing eq 4b by eq 4a, many books show that N_2/N_1 is equal to $e^{\epsilon/k_B T}$ (6, 9).⁴ I suggest using this to evaluate the population of the second energy level (and, thus, the number of microstates) by considering the ratio of these factors at two different temperatures:

$$\begin{aligned} \frac{\left(\frac{N_2}{N_1}\right)_{T_2}}{\left(\frac{N_2}{N_1}\right)_{T_1}} &= \frac{e^{\frac{-\epsilon}{k_B T_2}}}{e^{\frac{-\epsilon}{k_B T_1}}} = \exp\left[\frac{-\epsilon}{k_B}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \\ &= \exp\frac{\epsilon(T_2 - T_1)}{k_B T_2 T_1} \end{aligned} \quad (5)$$

Based on eq 5, the ratio of relative populations is greater than unity if $T_2 > T_1$, that is, heating increases the entropy of the system.

Component 4: Connection to the Laws of Thermodynamics

Just as important, I suggest that the same example (based on eq 5) immediately demonstrates the connection between eqs 1 and 2. The presence of temperature in the denominator of entropy-defining eq 1 can be illustrated as follows. Imagine a situation when two otherwise identical systems, one at a high temperature and the other at a low temperature, are given a small increment of heat (thermal energy transfer) resulting in a 1 °C increase of temperature. Note that the product $T_1 T_2$ is present in the denominator of the exponent in eq 5. Therefore, the change in N_2/N_1 is merely infinitesimal upon a heat transfer at very high temperatures. Conversely, the smaller the value of T_1 , the greater the increase in the population of higher energy levels upon even a

Table 1. Relative Population of the Highest of the Two Energy Levels at Varied Temperatures

T_{cold}/K	T_{hot}/K	$T_{\text{final}}/\text{K}$	$N_2/(N_1 + N_2)$	$N_2(T_{\text{final}})/N_2(T_{\text{cold}})$	$N_2(T_{\text{hot}})/N_2(T_{\text{final}})$
1	—	—	4×10^{-44}	—	—
—	3	—	3×10^{-15}	—	—
—	—	2	2×10^{-22}	5×10^{21}	1.5×10^7
10	—	—	4.5×10^{-5}	—	—
—	30	—	0.034	—	—
—	—	20	0.0067	1.5×10^2	5.1
100	—	—	0.2689	—	—
—	300	—	0.4174	—	—
—	—	200	0.3775	1.404	1.106
1000	—	—	0.4750	—	—
—	3000	—	0.4917	—	—
—	—	2000	0.4875	1.026	1.009

NOTE: Based on eq 4b and $\epsilon/k_B = 100$ K. T_{cold} and T_{hot} are the temperatures of two connecting otherwise identical systems. T_{final} is the final, average temperature upon the completion of the heat transfer.

small increase of temperature. Examples of calculations of N_2 fractions at both low and high temperatures are shown in Table 1. In a sense, heat transfer to a very cold body is similar to gas expansion into vacuum because the system ends up with many more accessible microstates.

As qualitatively demonstrated by Atkins and de Paula (10), showing the favorability of the heat transfer to a colder body is tantamount to demonstrating the impossibility of the heat transfer from a cold to hot body, thus leading to one of the formulations of the second law of thermodynamics. A short calculation can be performed to provide a more tangible illustration of this principle. In Table 1, the relative population of the second, highest energy level (N_2) is calculated based on eq 4b and the ratio $\epsilon/k_B = 100$ K [this value, corresponding to the rotation of light molecules, was suggested by Noggle (9)]. Now, consider allowing the heat transfer between the otherwise identical systems at $T_{\text{cold}} = 1, 10, 100$, and 1000 K and $T_{\text{hot}} = 3, 30, 300$, and 3000 K, respectively. The resulting temperatures, T_{final} , will be the mean values of T_{cold} and T_{hot} : 2, 20, 200, and 2000 K. Now, we can verify whether equalizing the temperatures via the heat transfer is, indeed, favorable. The last two columns in Table 1 show that the value of N_2 and, thus, the number of microstates will increase significantly upon warming the colder body. The magnitude of this favorable change is always greater than that of the corresponding decrease of N_2 upon cooling the hotter body, the effect being more pronounced at lower temperatures. This is true for any T_{cold} and T_{hot} . Therefore, whenever the final temperature is different from the average of T_{cold} and T_{hot} , there is a driving force for reaching the thermal equilibrium by equalizing the temperatures.

Parenthetically, eq 4 also illustrates the third law (the system is uniform and, thus, has only one macrostate, $S = \ln 1 = 0$ at $T = 0$ K). Equation 5 demonstrates that $T_1 = 0$ K is not attainable.

Implementation

Obviously, this way of introducing entropy in physical chemistry requires some prior background but it need not be the extensive treatment of quantum and statistical mechanics that will come later in the course. Specifically, the idea of the particle-in-a-box (or on a line) model and the Boltzmann distribution should be presented simply (as outlined here) prior to introducing thermodynamics. A facile derivation of the Boltzmann distribution based on eq 2 without using the variation methods is available (11). The energy levels for the particle-in-a-box can be derived without the mathematical complexities of quantum mechanics as it is done by Barrow (12).

Summary

Using simple examples based on the Boltzmann distribution, entropy can be introduced consistently on a molecular basis by emphasizing energy distribution among the accessible microstates. Students are strengthened in their understanding of chemistry as a molecular science. Then they can remain focused in the ensuing phenomenological consideration of thermodynamics because it has been given a molecular foundation for its concrete and well-defined goal of calculating entropy using the experimental measurable values of work, heat, and temperature.

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Notes

1. One of the few schools that maintain the legacy of this approach, St. Olaf College (MN), allocates one entire semester to this statistical treatment of thermodynamics (13).

2. The words “distribution”, “dispersion”, “dispersal”, “spreading out” are also applicable as long as they do not bear a connotation of energy being lost.

3. Leff’s metaphor of an “energy storage mode” (7b) can be used.

4. Recently, Novak suggested an alternative approach for deriving the second law using the Boltzmann distribution (14). His method is based on the $N_2/N_1 = e^{-\epsilon/k_B T}$ relation, which is solved for T and then differentiated to yield dT as a function of $d\epsilon$ and dN . The essence of his original treatment is bypassing eq 2 whereas I make this equation a centerpiece of my algebra-based treatment: thus, these two methods complement one another. Novak’s consideration of mechanical work, isochoric heating, and heat engines appears especially suited to thermodynamics classes involving engineering students.

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