Give Them Money: The Boltzmann Game, a Classroom or Laboratory Activity Modeling Entropy Changes and the Distribution of Energy in Chemical Systems

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Recently in this *Journal (1–10)* and on the CHEMED-L listserv *(11)* there has been a lively discussion of the meaning of "entropy" and, in particular, how characterizing it as "disorder" is not helpful. Attempts have been made to characterize entropy qualitatively as the "spreading and sharing of energy" *(12)* or the "dispersal of energy" *(5)*. However, one of the essential characteristics of entropy often missing in these discussions is its simple relationship to probability. While there are many classroom activities that have been described that model equilibrium and Le Châtelier's principle *(13–17),* and these, too, can all be conceptualized in terms of probability *(18),* what seems to be lacking are simple *quantitative* activities that students can participate in that effectively convey the essential probabilistic nature of entropy. We describe just such an activity, then discuss why it works and suggest variations that might be used to illustrate additional points.

Figure 1. A group of 36 students playing the Boltzmann game.

The Boltzmann Game

Depending upon your teaching style, you may wish to precede this activity with a discussion of energy or not. We have done it both ways to good effect.

1. Have students clear an area of the classroom of desks. (Alternatively, find a space outside the classroom, such as a lobby or cafeteria, where other students, teachers, and administrators can see what fun you are having in chemistry.)
2. Pair up students. If there is an odd number of students, ask for a volunteer to be the "scientist for the day" and record the data. Otherwise, you will need to collect the data yourself. A simple form that can be used is available in the Supplemental Material.W Alternatively, you can participate yourself or find an innocent bystander to achieve an even number of players.
3. Give each student one dollar. We have used real money, board-game money, or, more recently, "Boltzmann Bucks" (see the Supplemental MaterialW). Feel free to use your creativity here.
4. Ask students to stand in two concentric circles as shown in Figure 1, facing their partner. If you stand in the middle of the circle, the inner ring of students will have their back to you, and the students in the outer ring will be facing both you and their partner.
5. Explain the rules of the game: "In this game you will be exchanging both money and partners. It will go fast, so listen carefully. Does everyone know how to play "rock–paper–scissors"?[1] [Ensure that this is the case.] "Students have different ways of playing rock–paper–scissors. We all have to agree to do it the same way: Count 'one, two, three, GO' and only on GO reveal your rock, paper, or scissors." [Some students have learned to reveal on THREE; use your judgment regarding what will work best with your group. Have students practice a bit, and observe that everyone is clear about how to play rock–paper–scissors.] "OK, after you play rock–paper–scissors there will be either a winner and a loser, or there will be a tie. It is very important that you understand that if there is a tie, that's OK. DO NOT PLAY ROCK–PAPER–SCISSORS AGAIN to break the tie. If there is a tie, just relax. If there is a loser, and the loser has money, then the loser must give the winner EXACTLY ONE DOLLAR. Never exchange more than one dollar." [Have students try that, only PRETENDING to exchange money.] "So if there is a tie or the loser doesn't have any money, there's nothing more to do. After playing rock–paper–scissors once and maybe exchanging money, you will go to the next partner. The way we are going to do this is by having everyone in the INNER ring all at the same time (on my signal) move to the right one position. Everyone in the outer ring should stay where they are. Just the students in the inner ring should move. The signal will be the word NEXT. Let's try that." [Say "Next!" and see that students all know their right from their left. Say "Next!" a few more

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times.] “OK, that’s the game. As soon as you get a new partner, play rock–paper–scissors with them and exchange a dollar if necessary. Remember, no tie breaking. Just play rock–paper–scissors ONCE with your new partner. Questions?” [Students often ask, “What if neither of us has any money?” Tell them to play anyway, just for fun.]

6. At this point it is a good idea to get them to make a few predictions. Is this a fair game? What do you expect to happen? What do you think your chances are of walking away with a dollar? Two dollars? Three?
7. Start the game. Some groups will catch on very fast, and after a few rounds you won’t even have to say “Next!” Other groups may not listen as well, and you will have to stop the game and reorganize because somehow the inner ring got out of sync. This is no real problem, but it does slow down the game a bit if it happens.
8. Periodically stop the action, perhaps after five or six games, and ask for a show of hands to find out how many students have no money, have EXACTLY one dollar, EXACTLY two dollars, etc. Record these data for the ensuing discussion in the classroom on a sheet of transparency film, on the board, or on a sheet of paper if you have the means to project it later.
9. You can continue as long as time permits. We have generally collected data five or six times, involving 20–30 exchanges of partners and games of rock–paper–scissors. Admittedly, as the instructor you will know what you are looking for, and it is not a bad idea to prolong the game a bit if you do not see in the data what you need for the discussion. (See below.)

Observations

College Level

A total of 213 students working in 8 laboratory sections of approximately 20–30 students each played the game as part of their first laboratory experiment of the second semester. (See the Supplementary Material$^{\text{W}}$ for details of this experiment.) Data from one of the sections, which were typical, are shown in Table 1. From start to finish the game took about 30 minutes.

What becomes immediately obvious during the game is that a lot of students end up without any money and only a very few students ever end up with more than \$3. The actual “most probable distribution” of money among the students is based on a geometric progression: Roughly half the students will have no money at any given time, one quarter will have \$1, one eighth \$2, one sixteenth \$3, and so forth. Of course, this is only the “most probable” distribution. There will be some “fluctuation”, and *which* students have money and which have none (corresponding to different *microstates*) will change constantly.

High School Level

Four honors chemistry classes of high school students (primarily juniors) with limited thermodynamic experience were introduced to the idea of entropy in terms of energy through the game. Prior to the game the only way entropy had been discussed was in terms of disorder. To begin with, each student was given \$1, but after a few preliminary rounds, a “burst of energy” gave each student another dollar. Results were recorded periodically throughout the game. Representative data recorded for one of the four sections are shown in Table 2.

After about 35 minutes the playing was stopped, and without any discussion the students were asked to address any one of the following:

1. What does energy have to do with probability?
2. Why isn’t the most probable distribution one where everyone has the same quantity of money?
3. Explain what happens when a system gains energy.

The results of the game and the answers to these questions lead to some interesting insights, and we feel the experience

Table 1. Data for 24 Students Carrying Out the Exercise

Cash/\$	Number of Students				Most Probable Distribution
	Round 1	Round 2	Round 3	Round 4	
7	0	0	1	0	0
6	0	1	0	0	0
5	1	0	0	1	0
4	0	2	0	1	1
3	1	1	1	1	2
2	4	0	5	3	4
1	8	7	4	6	6
0	10	13	13	12	11
Total Number of Ways (W)	1.77E11	9.88E9	3.46E10	3.00E11	4.50E11
Relative Probability (Prel)	0.39	0.02	0.08	0.67	1.00

Note: Students each started with \$1 and were interrupted four times to record the number of players with specific quantities of money. The most probable distribution is shown at the right. The total number of ways is shown below the data. While there is significant fluctuation, all of the observed distributions are relatively probable and are fairly similar to the most probable (Boltzmann) distribution. Preliminary rounds involving \$1 each are not shown. These data suffer from deficiencies discussed in the text.

Table 2. Data for 24 Students Who Started with \$2

Cash/\$	Number of Students			Most Probable Distribution
	Round 1	Round 2	Round 3	
8	1	0	0	0
7	0	0	0	1
6	0	0	1	1
5	0	0	2	1
4	3	1	4	2
3	2	2	3	3
2	4	1	3	4
1	4	7	4	5
0	7	11	7	7

Note: Preliminary rounds involving \$1 each are not shown. These data suffer from deficiencies discussed in the text.

was a success. There were many responses that showed that understanding had been gained, especially considering the fact that students did not have the opportunity to discuss the game prior to writing their responses.

The first question had quite a few insightful responses. In general, students seemed to grasp the concept that energy is exchanged randomly. For example, one student wrote: "Probability comes into play with energy because there is a chance that you will gain or lose your energy, and there is a chance of both for every molecule that's floating around other ones just like in the game. You could gain, lose, or simply stay the same."

The second question seemed to be the one most thoroughly understood by students. Many students realized that there is only one possible configuration in which each student has $1, but there are thousands of other possible configurations. They also noticed that after the first turn, half the students already have no money. Two sample student responses include:

> [It can't be the most probable distribution] because each student can have the same quantity of money only one way. There are many other ways to have the money distributed.
>
> Because there are many more ways to have it so many students do not have any money than for each student to have one dollar. Probability is greater for uneven distribution.

The students seemed to struggle with the third question more than the others. However, some students were able to notice that the distribution changed when more energy was added part way through the game. For example, one student wrote: "It seemed that when a system gained energy there was more of a distribution. The average went up and the number of students with zero decreased."

Limitations of the Game

Two limitations of the game noted particularly at the high school level included (i) student understanding of vocabulary and (ii) improper reporting. Because this was part of an introduction to thermodynamics, some students were confused by the vocabulary used. One example is the term *system* as used in question 3. Instead of thinking of the system as all the students together, some thought that they as individuals were a system. Thus, we recommend that it be made clear that the system is represented by the whole group of students, not just a single student.

Another limitation that was an issue at the high school level but not the college level was improper reporting. This took two forms, as revealed by a close look at the data in Table 2. First, not all students raised their hands to be counted when asked to do so. Thus, there are fewer than 24 students reporting in rounds 1 and 2. In addition, it turned out that a few students in this particular class pocketed the money (even though it was fake!) as the game went on. If they lost to someone, they would pretend that they did not have any money to give. As can be seen in Table 2, this greatly affected the results. Round 2 shows direct evidence of student cheating, as there are far too many students reporting $0. Round 3 shows results after they had been caught and began to play fairly (although even here there was some misreporting). Notice that when they played fair the results closely matched what would be expected for the most probable distribution.

Theory behind the Game

The Boltzmann game models the distribution of energy in real chemical systems. In particular, this game simulates the harmonic oscillator model of vibrational excitation. At any given point in time some molecules have more energy than others. Energy is quantized and is constantly being exchanged among the molecules of a system. Interestingly, it is just as probable, when a high-energy molecule meets a low-energy molecule, for the high-energy molecule to take on a quantum of energy as to give one up. This may be counterintuitive for anyone who thinks of energy exchange in terms of billiards, but that's the way it is in the quantum world.

Microstates and Distributions

At any given moment the energy in a system is "distributed" among the molecules in one distinct way. We call each of these distinct ways a *microstate*, and one of the basic tenets of statistical mechanics is that in real chemical systems, each microstate has equal probability. As collisions occur and energy is traded, new microstates arise. The description of a microstate involves recording exactly how much energy each and every molecule has. We do not do that in this game. Instead, we just record *distributions* of energy.

For example, if we have 24 students who were initially given $24, we might record that at a certain time 10 students have $0, 8 have $1, 4 have $2, 1 has $3, and 1 has $5. There are many ways that this distribution can arise. (George or Mary or Kyomi, etc., could have the $5, and if George has the $5, then Mary or José might have $3, etc.) Each of those distinct ways is a microstate of the system.

It is not terribly hard to calculate the number of ways, W, this particular distribution of money can be made. A simple approach is to multiply how many ways there are for 10 of 24 students to have $0 each, by how many ways there are for 8 of the remaining 14 students to have $1 each, by how many ways there are for 4 of the remaining 6 students to have $2 each, and so on. Mathematically what we need to use is the mathematics of *combinations*. This involves the use of factorials,

$$\begin{aligned} W &= C_{10}^{24} \times C_{8}^{14} \times C_{4}^{6} \times C_{1}^{2} \times C_{1}^{1} \\ &= \frac{24!}{10!\,14!} \times \frac{14!}{8!\,6!} \times \frac{6!}{4!\,2!} \times \frac{2!}{1!\,1!} \times 1 \\ &= \frac{24!}{10!\,8!\,4!\,1!\,1!} \end{aligned}$$

where C_p^n stands for "the combination of n things taken p at a time." In this case, $W = 176{,}689{,}553{,}040$. We would say that the distribution "10 students have $0, 8 have $1, 4 have $2, 1 has $3, and 1 has $5" involves 176,689,553,040 possible microstates. Understanding the relationship between microstates and distributions is key to understanding entropy at the molecular level. In general, if we know how many students have each quantity of money, we can calculate the number of ways this can happen as,

$$W = \frac{N_{\text{total}}!}{N_{\$0}!\, N_{\$1}!\, N_{\$2}!\, N_{\$3}!\, N_{\$4}! \ldots} \qquad (1)$$

where N_i is the number of students in group i.

Entropy and Probability

The calculation of the number of microstates associated with a given distribution of energy in a system gets out of hand pretty quickly. There are a lot of ways energy can be distributed among a set of molecules! For this reason (and others), it might be reasonable to have a working definition of *entropy, S,* involving the logarithm of W,

$$S = k \ln W = k \ln \frac{N_{\text{total}}!}{N_{\$0}!\, N_{\$1}!\, N_{\$2}!\, N_{\$3}!\, N_{\$4}! \ldots} \qquad (2)$$

where now k is a constant. (The *Boltzmann* constant, k, is 1.381×10^{-23} J/K; in this case, $S = 3.6 \times 10^{-22}$ J/K.)

Thus, a very simple definition of entropy is "a measure of the number of ways energy can be distributed in a molecular system." But this definition is actually of no particular value as it stands. The importance of W, like all probability measures, is not particularly valuable until it is considered in comparison to the W associated with some other possibility. How much *more* probable is X than Y? Herein lies the beauty of logarithms. Consider the *difference* in entropy, ΔS, between two possible distributions:

$$\Delta S = S_2 - S_1 = k \ln W_2 - k \ln W_1 = k \ln \frac{W_2}{W_1} \qquad (3)$$

Here we employ the fact that $\ln x - \ln y = \ln(x/y)$. What is interesting about this is that W_2/W_1 is very significant. Some distributions of energy in a system are more probable than others. W_2/W_1 is the relative probability of "distribution 2" as compared to "distribution 1". If there are 10 ways energy can be distributed in distribution 1 and 60 ways it can be distributed in distribution 2, then, based on the idea that one way is just as probable as any other way, we would say that distribution 2 is 60/10 = 6 times more probable than distribution 1. Thus, differences in entropy measure the relative probability of one distribution of energy in a system arising as compared to another. It is a simple matter to argue that the distribution with the highest entropy is the "most probable distribution". We call that most probable distribution the *Boltzmann* distribution.

Thus, entropy is intimately related to probability. If we have two situations *that are in constant flux*, and we want to know their relative entropy ($S_2 - S_1$), we simply have to know the probability of each. If one is twenty times as probable as the other, their difference in entropy, ΔS, is $k \ln 20$.

What the Boltzmann game demonstrates is that when energy goes into a molecular system, it gets distributed randomly. There is a constant and continual redistribution of the energy, and, not surprisingly, some distributions are more probable than others. What becomes immediately clear from this exercise is that although each microstate is equally probable, some identifiable distributions of energy are more probable than others. Indeed, students need no convincing that the probability of one of them ending up with all the money is just phenomenally low. What we ultimately observe is based on probability and probability alone. While we cannot *guarantee* in a strict sense of the word that at no time during the game one student will be found to have all the money, we can calculate the probability of that *relative to the most probable distribution* and quickly come to the conclusion that that outcome would be extraordinarily unlikely. (There are only N_{total} ways of doing that.) Interestingly, even more unlikely would be the observation of everyone having exactly \$1. (There is only one way to do that.)

Thus, entropy is seen as a measure of "the number of ways a state can have the same overall distribution of energy", and differences of entropy are measures of the "*relative probability* of two possible distributions". It is easy to show that the most probable state (the one with the largest number of ways) will have the highest entropy.

Fluctuation and Population Size

Equally obvious is that there will be fluctuation. The process is random, and no one can predict exactly what will happen. Occasionally someone in a group of 24 students will end up with \$6 or more. But do not expect it to last long! Students will often report, "Oh, I was doing so well, and then…!" Hey, that is too bad! One microstate is just as probable as another. Better luck next time.

Less obvious is the effect of sample size on fluctuations. In this case, it might be best to rely upon computer modeling. Programs and Web pages exist that can be used to quickly demonstrate the effect of increased sample size, even involving tens of thousands of energy-exchanging particles.[2] Using empirical discovery instead of proof, students quickly observe that as the sample size increases, the quantity of fluctuation decreases. Extrapolating to typical chemical systems involving mole quantities of molecules, it is an easy sell that fluctuations become insignificant. We can focus on the most probable distribution of energy in a system—the Boltzmann distribution.

Extension of the Game

The Surroundings

What the Boltzmann game as described does not model is the fact that a chemical system is rarely isolated from its surroundings. But that, too, perhaps could be modeled. What if we simply define the outer ring of students to be the surroundings? What will happen if we start with all the money in the hands of the outer ring? Will a Boltzmann distribution arise overall? Will it arise both in the system and the surroundings? Will it be the same distribution? Try it and find out! (You might need more that 30 students to get this to work.)

Essentially what we are describing now is a game that models situations where the system is hotter or colder than the surroundings. More money given to the outer ring quickly gets "dispersed" into the inner ring, and vice versa. Again, there will be fluctuation. What makes this game fun is the uncertainty of the outcome. But, again, with larger numbers of "players" such as we typically involve in real chemical reactions comes statistical certainty.

The Effect of Temperature

Going back to the original game where all students are part of the system, and the system is isolated, it is easy to demonstrate that if more money is introduced, it is more likely that someone will end up with more money and less likely for someone to end up with nothing. But with that extra money come more possible distributions of it. The entropy of a system increases when heat is added.

The Effect of Energy-Level Separation

What if the same quantity of money is distributed, but now 12 \$2 bills are given out instead of 24 \$1 bills? It should not be hard to predict that more students will leave the game empty-handed. (The most probable distribution would be 16 students with \$0, 5 with \$2, 2 with \$4, and 1 with \$6. The lesson is, Increased energy-level separation leads to more particles in the ground state for a given quantity of energy. This leads to a larger $N_{\$0}!$ in eq 2 and a correspondingly smaller thermodynamic probability W (only 123,559,128 ways this time, less than 1/1000 the number as when using \$1 bills). Thus, increasing the energy-level separation while keeping the total quantity of energy the same leads to a decrease in entropy.

At least for diatomic molecules, altering the energy-level separation in the harmonic oscillator vibrational model ($\Delta\varepsilon_{\mathrm{vib}}$) amounts to changing either the force constant of a bond (k_{f}) or the reduced mass of the vibrating atoms (μ),

$$\Delta\varepsilon_{\mathrm{vib}} = \frac{h}{2\pi}\sqrt{\frac{k_{\mathrm{f}}}{\mu}}$$

where h is Planck's constant. Thus, at a given temperature (that is, with a given quantity of total energy), the entropy due to vibration is less for systems with stronger bonds or lighter atoms. A comparison of the vibrational systems in H_2, HCl, and Cl_2 are given in Figure 2. Dichlorine, with its large reduced mass, has the closest-spaced energy levels; H_2, with the smallest reduced mass of any molecule, has the furthest-spaced levels. For comparison, the standard molar entropies (1 bar) at 298 Kelvin of H_2, HCl, and Cl_2 are 130.680 J/K, 186.9 J/K, and 223.08 J/K, respectively *(19).*

Further Explorations

There are any number of explorations that could be made using the Boltzmann game. Energetic vibrations can lead to chemical reactions. What if there were some students in reserve who could only swap into the game with students who already had some *minimum* of some number of dollars? Would this model endothermic chemical reactions? What if, given a certain quantity of energy, some students were required to leave the game. Would there be a rate constant for this irreversible "reaction"? What would be the effect of temperature on this rate constant? We leave it to the reader to consider other ways this exercise can be used to model entropy and the ways energy can be distributed in the context of chemical reactions (and write to us to tell us how those modifications worked in class).

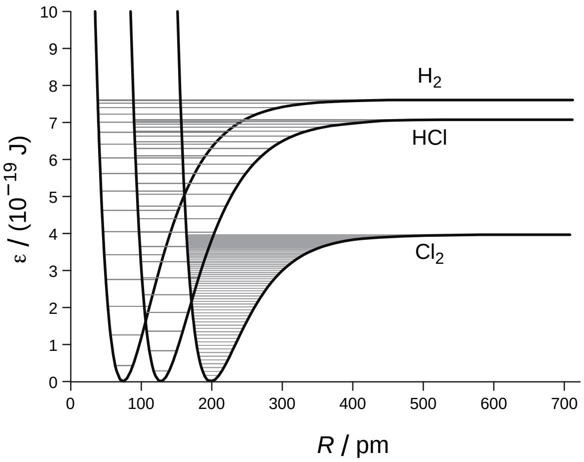

Figure 2. Vibrational energy levels for H_2, HCl, and Cl_2 drawn to scale based on the Morse potential. The Boltzmann game approximates energy exchange among molecules near the bottom of these potential wells using the harmonic oscillator model. Horizontal lines indicate relative minimum and maximum extent of bond stretching in each mode. H_2 has the lowest standard molar entropy; Cl_2 has the highest.

Extension to Translational-Energy Models and Chemical Reactions

The Boltzmann game primarily focuses on vibrational-energy exchange in simple chemical systems involving no chemical reactions. This is just a starting point. The natural question is, "Could we extend these ideas to translation, and thus to relate to chemical reaction?" The extension of the Boltzmann game to translational energy requires some imagination. For one thing, translational-energy levels are not evenly spaced the way the levels are (approximately) in vibration. That is to say, there is no single currency being exchanged. Furthermore, translational-energy levels are so closely spaced, no two particles *ever* have the same energy. But if we allow simply for the idea that "translational-energy levels are more closely spaced than vibrational levels" then, in our context, this amounts to changing the denomination from \$1 bills to, perhaps, quarters. Having 96 tokens in play rather than 24 will obviously change the situation, resulting in far more possibilities and, as a result, a much higher entropy.[3] Not surprisingly, the entropy due to translation (in gases, at least) far exceeds the entropy due to vibration.

A full extension to chemical reactions requires an understanding of how entropy changes when particles themselves (along with their energy) are dispersed within a given volume. The lesson here is that the entropy change for the expansion of an ideal gas, $\Delta S = nR\ln(V_2/V_1)$, can be explained in terms of the effect of volume on the translational-energy level separations in a system. At least for ideal gases, increasing the volume can be shown to be equivalent to decreasing the separation of translational-energy levels, resulting in an increase in entropy *(20).* This increase in entropy explains why gases spontaneously expand into a vacuum and mix with each other.

Recognizing the relationship between molar entropy and molar volume (as measured by concentration or partial pressure) is central to a full understanding of the driving force associated with chemical reactions. In fact, this relationship forms the theoretical basis for the concept of a reaction quotient (and, with that, the equilibrium constant), since for a chemical reaction we have,

$$\Delta_\mathrm{r}G = \Delta_\mathrm{r}H - T\Delta_\mathrm{r}S$$

where

$$\Delta_\mathrm{r}S = \Delta_\mathrm{r}S^\circ - R\ln Q \tag{4}$$

The essence of ΔS as being a measure of the relative probability of two possible outcomes is the key linking feature between the concept of "energy distribution" described here and "particle distribution" or "positional entropy" as described in some general chemistry texts. To this end, we note that the "entropy of mixing" of a number of particles, N_total, of different types (A, B, C, etc.) can be expressed in terms of probability as

$$\Delta S_\mathrm{mix} = k\ln\frac{N_\mathrm{total}\,!}{N_\mathrm{A}!\,N_\mathrm{B}!\,N_\mathrm{C}!\,\ldots} \tag{5}$$

It is the derivative of this quantity along the reaction coordinate that becomes the "$-R\ln Q$" term in eq 4.[4] In short, the calculation for the entropy change upon distribution of energy among particles (eq 2) is precisely the same as the calculation for the increase in entropy due to the mixing of particles among other particles (eq 5).

Thus, an energy-based introduction to entropy such as we propose here can serve just as well, if not better, than one involving "positional entropy" arguments in explaining the origin of the reaction quotient. The two analyses are equivalent.

"Spreading Out" or "Distribution" of Energy?

The Boltzmann game can serve as a basis for discussing what is popularly referred to as the "dispersal" or "spreading" of energy "among the available microstates" of a system. Clearly the use of the common words *dispersal* and *spreading* may be prone to misinterpretation. We generally avoid these terms and instead let the activity speak for itself. However, these terms are showing up in textbooks, and it would be wise to understand what they might mean in this context. For example, as the activity shows, the system is always only in one microstate at any given time. So it is not quite correct to say that energy is being "spread out" among the microstates. [If all the money is given to one student, then that energy will be observed to spatially "spread out" over the group, but that is a different use of the term to which some authors *(12)* but not others *(5)* have adhered.]

Understanding the role probability plays in the concept of an "available microstate" is essential. After just a few minutes with this activity it becomes obvious that even though there are billions of possible ways —individual microstates— in which the system might be found, only an extremely small fraction of these "available microstates" are ever actualized, and still within minutes something very close to a Boltzmann distribution arises. This is because the counting of microstates is simply a way of measuring probabilities. Energy does not really "spread out" among these "available microstates." Rather, energy is *distributed randomly among the particles*, and the system simply shifts from one microstate to another as that energy is dynamically traded. The vast majority of microstates "available" to a system are never explored. In fact, given a mole of molecules, while the number of available microstates is unimaginably large, on the order of 10^{N_Av}, the fraction of "available" microstates actually explored during any real timeframe is unimaginably small, on the order of 10^{-N_Av}. So the concept of energy "spreading" throughout these nonrealized microstates may be difficult for students to imagine.

The microstates that are explored fall into sets that are identifiable as *distributions*, and although each microstate has the same probability of being found (on an infinite time scale), distributions characterized by more microstates are more probable (on a infinite or a real time scale). So, for example, it is obvious from the activity that while one student *could* get all \$24, and there are clearly 24 ways this could happen, it just is not going to happen, because there are billions of ways that other identifiable outcomes—other distributions—could arise. Alternatively, if one student starts with all \$24, the chances of that situation lasting or ever happening again is incredibly small. It is the same with energy. The spatial spreading of energy that is observed as the "flow of heat from hot to cold" is simply the system+surroundings achieving the most probable distribution of that energy. The probability of the reverse happening can be calculated; it is just inconceivably small.

An interesting discovery that students make while playing the Boltzmann game is that, while one might say that energy is "shared" among the particles, it is not shared *evenly* the way one might naturally associate with this word. Indeed, the universal observation from this experiment is that starting with what seems like a "fair distribution" of money, about half of the participants will be found penniless at any given time.

A final characteristic of the distribution of energy that is not particularly obvious from thinking of energy as spreading involves fluctuation. Although fluctuation is not directly observable at equilibrium for typically large systems involving moles of particles, the Boltzmann game clearly demonstrates the dynamic nature of energy distribution, including fluctuation. It can be argued, in fact, that fluctuation is what makes chemical reactions possible. That is, all chemical reactions can be thought of simply as the natural fluctuation of system+surroundings making its way from microstate to microstate, from generally less probable distributions to generally more probable distributions, until, in the end, "equilibrium" is achieved, and we observe the most probable (Boltzmann) distribution. At equilibrium, the dynamic fluctuation-filled activity continues; we just do not see any further changes. Thus, probabilistic fluctuations can be seen as the essence of both equilibrium and chemical reactions.

Conclusions

A modern understanding of entropy cannot be had without focusing on energy and the way it is distributed in chemical systems. The described exercise is intended to get students thinking along these lines. Microstates and distributions, once demonstrated, need not be mysterious concepts. All we are doing is counting, after all! We have found in our experience both at the high school and at the college level that students welcome the chance to apply their limited but sufficient knowledge of chance and probability to chemistry, and even seasoned teachers have expressed amazement that it can be done so simply.

Overall, both students and teachers at the college and high school levels found this to be a fun experience, a welcome change from "typical" laboratory experiments. At the high school level, students reported enjoying seeing how probability could be applied to chemistry—something they had never thought of before. (High school students at Eastview typically study probability in their sophomore-level mathematics class.)

The extent to which this experience is followed up with discussions relating to the Boltzmann distribution, how energy is stored in real chemical systems (electronic, vibrational, rotational, and translational-energy modes), the role of the surroundings, enthalpy, free energy, and so forth will vary depending upon the level of the course. What is central, though, is the understanding that, ultimately, a modern view of chemistry can be based on probability.

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Notes

1. In the popular childhood game "rock–paper–scissors," two players face off, each with one hand extended palm up and one in a partially raised fist. Together, the two count out loud, "One… two… three… GO!" On each of *one*, *two*, and *three*, each player strikes his or her own palm with their fist. On *GO!*, each player strikes their palm with one of three hand formations: palm down (paper), index and middle finger extended (scissors), or closed fist (rock). Comparison of hand formations decides the winner: paper "covers" rock, scissors "cuts" paper, and rock "breaks" scissors. If the two formations are the same, there is a tie. In our implementation a tie is left as is so as not to slow down the game for other players.

2. The Microsoft Windows program, Boltz.exe, written in Visual Basic 6.0, which models this game, can be found at *http://www.stolaf.edu/depts/chemistry/imt/pc*. Also at that site is Wintropy.exe, a simulation of energy distribution in evenly-spaced energy-level systems. See also *http://www.stolaf.edu/depts/chemistry/imt/concept* and associated Web-based tools at *http://www.stolaf.edu/depts/chemistry/imt/js* (all Web sites accessed Jan 2006).

3. With 24 students, there are 1.22×10^{22} ways of distributing 96 tokens, but only 1.61×10^{13} ways of distributing 24 tokens.

4. Given the definition of entropy of mixing in terms of total number of moles, n, and mole fractions of the mixing components, x, *(10)*

$$\Delta S_{\text{mix}} = -nR\left(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}} + x_{\text{C}} \ln x_{\text{C}} + \ldots\right) \qquad (6)$$

it is an interesting application of logarithms and Stirling's approximation (that is, $\ln N! \approx N \ln N - N$) to derive,

$$\Delta S_{\text{mix}} = k \ln \frac{N_{\text{total}}!}{N_{\text{A}}!\, N_{\text{B}}!\, N_{\text{C}}! \,\ldots} \qquad (7)$$

where N_i is the number of molecules in group i, not moles. In the context of chemical reactions, for example, we might have

$$2\text{A(g)} + \text{B(g)} \longrightarrow \text{C(g)}$$

where A, B, and C are all ideal gases. Consider reacting 2 moles of pure A with 1 mole of pure B, each at 1 bar pressure and in separate compartments. We "carry out" the reaction in an imaginary way where A and B remain in separate compartments, and C that is produced is in a separate compartment as well, all still at 1 bar pressure. (The total volume will decrease.) At some point during the reaction we imagine removing the walls between the compartments and letting the gases mix. (Really this is just the independent expansion of gases into a "vacuum".) At the halfway point in the reaction, for example, we would have 1 mole of A, ½ mole of B, and ½ mole of C present, and we calculate from eq 6

$$\begin{aligned}\Delta S_{\text{mix}} &= -(2\ \text{mol})R \times \\ &\quad \left[\left(\frac{1}{2}\right)\ln\left(\frac{1}{2}\right) + \left(\frac{1}{4}\right)\ln\left(\frac{1}{4}\right) + \left(\frac{1}{4}\right)\ln\left(\frac{1}{4}\right)\right] \\ &= 17.29\,\frac{\text{J}}{\text{K}}\end{aligned}$$

Using the Boltzmann formulation (eq 7) we get the same value:

$$\begin{aligned}\Delta S_{\text{mix}} &= \left(1.38066 \times 10^{-23}\,\frac{\text{J}}{\text{K}}\right) \times \\ &\quad \ln \frac{\left(1.2044 \times 10^{24}\right)!}{\left(6.022 \times 10^{23}\right)!\,\left(3.011 \times 10^{23}\right)!\,\left(3.011 \times 10^{23}\right)!} \\ &= 17.29\,\frac{\text{J}}{\text{K}}\end{aligned}$$

In addition, if we define the reaction extent parameter ξ, going from 0 to 1, we can write that $N_{\text{A}} = 2N_{\text{Av}}(1 - \xi)$, $N_{\text{B}} = N_{\text{Av}}(1 - \xi)$, $N_{\text{C}} = N_{\text{Av}}(\xi)$, and $N_{\text{total}} = N_{\text{Av}}(3 - 2\xi)$, where N_{Av} is Avogadro's number. Differentiating eq 7 with respect to x and using the trick that $\mathrm{d}(\ln u!)/\mathrm{d}x \approx (\ln u)(\mathrm{d}u/\mathrm{d}x)$ gives

$$\begin{aligned}\frac{\mathrm{d}(\Delta S_{\text{mix}})}{\mathrm{d}\xi} &= N_{\text{Av}}k\left(-2\ln N_{\text{total}} + 2\ln N_{\text{A}} + \ln N_{\text{B}} - \ln N_{\text{C}}\right)\\ &= -R\ln\frac{{N_{\text{total}}}^2 N_{\text{C}}}{{N_{\text{A}}}^2 N_{\text{B}}} = -R\ln\frac{\left(\dfrac{N_{\text{C}}}{N_{\text{total}}}\right)}{\left(\dfrac{N_{\text{A}}}{N_{\text{total}}}\right)^2\left(\dfrac{N_{\text{B}}}{N_{\text{total}}}\right)}\\ &= -R\ln\frac{x_{\text{C}}}{{x_{\text{A}}}^2 x_{\text{B}}}\end{aligned}$$

Since the overall pressure throughout the reaction is kept at 1 bar, mole fraction is the same as partial pressure in this case, and we can write

$$\frac{\mathrm{d}(\Delta S_{\text{mix}})}{\mathrm{d}\xi} = -R\ln\frac{P_{\text{C}}}{{P_{\text{A}}}^2 P_{\text{B}}} = -R\ln Q \qquad (8)$$

$^{\mathrm{W}}$Supplemental Material

Student version (exp1s04.wpd and exp1s04.pdf), instructor notes, including the suggested form for collecting data (labinstructions.doc), Boltzmann bucks (boltzdollars.doc and boltzdollars.pdf), Morse potential data for H_2, HCl, and Cl_2 (morse.xls), and Visual Basic programs boltz.exe and wintropy.exe are available in this issue of *JCE Online*.

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