Entropy: The Effects of Distinguishability

J.N. Spencer
Department of Chemistry
Franklin & Marshall College
Lancaster, PA 17604
J_Spencer@acad.fandm.edu

John P. Lowe
Department of Chemistry
The Pennsylvania State University
University Park, PA 16802
JL3@psu.edu

Abstract

   The effects of distinguishability on entropy changes are important but often unrecognized except in obvious situations such as Gibbs' paradox. Distinguishability effects are explored, and a new term, "cohort," is defined and used to provide a clearer understanding of the factors that contribute to entropy changes. Although entropy change is independent of choice of path, the explanation for the entropy change does depend on the process selected to get from the initial to the final state. Certain processes for which nothing appears to happen are shown to involve a subtle cancellation of factors at the microscopic level. Entropy of mixing is demonstrated to be a misleading term. The role of distinguishability in the entropy change produced in the mixing of liquids is discussed.

Entropy: The Effects of Distinguishability

J.N. Spencer
Department of Chemistry
Franklin & Marshall College
Lancaster, PA 17604
J_Spencer@acad.fandm.edu

John P. Lowe
Department of Chemistry
The Pennsylvania State University
University Park, PA 16802
JL3@psu.edu

Young Thermo Teacher: Good Morning Professor. This is my first year of teaching physical chemistry, and I hope that you might share with me some of the insights you have gained from teaching courses in thermodynamics over your long career.

Old Thermo Teacher: Ah yes, thermodynamics, that most subtle of subjects. I've been teaching it for 35 years, and each year I become aware of new ways to understand its relationships and better ways to try to explain them.

YTT: Several years ago, while still an undergraduate, I had a helpful discussion with one of my instructors about entropy (1). Now that I am teaching a physical chemistry course myself, I am encountering some types of entropy problems that seem to fall outside of the models he and I discussed.

OTT: Can you give me a specific example?

YTT: Well, suppose we have a pure optical isomer of a gas in a rigid container and we insert a catalyst that permits interconversion of this isomer and its enantiomer. After sufficient time, it seems to me, we'd find a 50-50 mixture of the two isomers at the same temperature.

OTT: Yes, that seems correct. We should expect equilibrium to be achieved when the rate of conversion from the *l* to the *d* form equals the rate of the reverse process, and, for a thermoneutral process like this one, that should happen when we have equal quantities of the two forms. What does that mean about entropy?

YTT: Well, because the change is spontaneous, the entropy of the universe must increase. If the process occurs at constant temperature and pressure, I would expect that no energy flows into or out of the surroundings, so it must be that the entropy of the system has increased.

OTT: I agree. So where is the problem?

YTT: I can't find a way to rationalize this entropy change for my students in terms of the model that my instructor and I were discussing. You see, we discussed two limiting extremes for entropy-affecting processes. One extreme was exemplified by heating an ideal monatomic gas at constant volume, and the other was by allowing an ideal gas to expand isothermally into a vacuum. In this example of optical isomers, neither the temperature nor the volume is changing.

OTT: Aha, I see your problem. I think that I can help you with this. When you were discussing these things with your instructor, did you have a simple model system to illustrate your thinking?

YTT: Yes. We talked about 10 molecules in a one-dimensional box, each capable of having translational energies of 0, 3, 8, or 15 units.

OTT: Shouldn't it be 1, 4, 9, and 16 units?

YTT: The mental computations are easier if we redefine the zero point to be the lowest allowed energy. Anyway, we saw quite easily that the number of distinguishable ways to apportion energy among the molecules increases if we either add energy without changing the possible translational energies, which is equivalent to heating at constant volume, or if we keep the same amount of energy but cause the allowed translational energies to get closer together, which is

3

equivalent to increasing the volume of the gas isothermally.

OTT: And neither of these things is happening in the case of the optical isomers.

YTT: Exactly. But entropy is a measure of the number of distinguishable ways the energy can be apportioned, and because the entropy must have increased in this spontaneous, isolated process, I seem to be missing something.

OTT: Let's go back to the simple model of ten molecules. How many distinguishable arrangements did you find when the total energy available for apportionment is three units?

YTT: One molecule has three units and the other nine have zero. That's the only possibility. We decided that there was no way to say which molecule it is that has three units because the molecules are all the same, so there is only one distinguishable arrangement.

OTT: Right. So far so good. Now, how would you analyze the situation if you had five *l* molecules and five *d* molecules?

YTT: Hmmm. It could be that an *l* molecule has three units of energy, but it could also be that a *d* molecule has three units of energy. That's two distinguishable arrangements. Gad! How could I have missed that?

OTT: So how does the entropy of this mixed pair of molecules compare to that of a pure enantiomer?

YTT: It's greater, and it has nothing to do with any sort of change of total energy or any change in translational energies.

OTT: What about vibrational and rotational levels?

YTT: Well, molecules capable of optical isomerism would certainly possess such levels, but I would expect them to be identical in the two isomers because they have identical bonds and moments of inertia.

OTT: So what does this example show you?

YTT: That there are *three* factors that affect entropy change: the total energy available, change in the energy levels available for storing that energy, and change in the extent to which molecules are distinguishable.

OTT: Now you have the ideas you need to explain some of the situations that have confused you.

YTT: Yes, I see now that my previous discussion was restricted to pure systems, and so the molecules were all indistinguishable. With mixtures we get this new factor of distinguishability.

OTT: There is a lot of confusion about this factor. I think it will help if we consider a few simple cases. First, though, we should identify the ways in which molecules can be distinguishable.

YTT: For a gas, the obvious way is if the species are different, like ^{3}He vs. ^{4}He, which have different masses and therefore differently spaced translational energy levels, or H_2O vs. CH_4, which differ in mass and internal (electronic, vibrational, and rotational) energy levels.

OTT: Yes, that's what one thinks of first. But we've just discussed a more subtle case.

YTT: Ah yes! The case of optical isomers, where mass and internal energy modes are the same.

OTT: Another important case is that where molecules occupy separate volumes. Even if they are otherwise identical, we can still distinguish between a molecule in box 1 and one in box 2.

YTT: Now that's interesting. I'll bet it comes into the question of entropy of mixing.

OTT: It does indeed, as we will soon see.

YTT: OK, are we ready to proceed?

OTT: Almost. I think it will help if we choose a word that we can use to identify a group of indistinguishable molecules. I suggest the term "cohort," because it suggests a group of identical molecules, all within the same volume.

YTT: Why not "system"? That's already used.

OTT: Yes, but it's often used in a different way. A container of air can be called a system, but it contains molecules of different kinds that can be distinguished. There is a cohort of O_2, another of N_2, etc.

YTT: I get it.

OTT: Let's begin by revisiting the optical isomer case you brought up earlier. Using the simple model of ten molecules in a one-dimensional box, we've seen that the conversion from pure *d* isomer to a racemic mixture increases the number of distinguishable microstates, W, and hence the entropy, $S = k \ln W$. Do you recall an equation that would enable you to actually calculate ΔS?

YTT: Well, one way I could do it would be to slice the box of pure *d* isomers in half with a nonpermeable barrier, and replace one half with a half-box of pure *l* isomers. That should not affect the entropy. Then I can remove the barrier to let them mix. Here, let me put Figure 1 on your board.

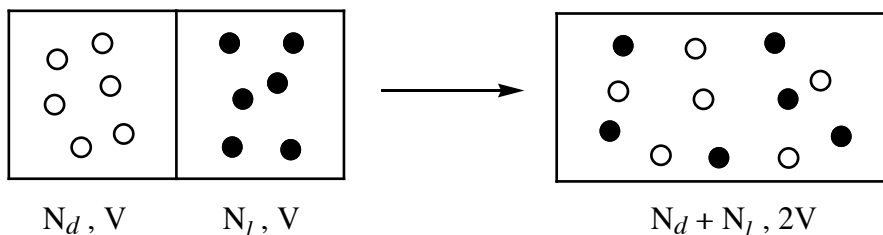N_d , V N_l , V $N_d + N_l$, 2V

Figure 1. A partition is removed from between two compartments of equal volume, each containing the same number of indistinguishable particles. $\Delta S > 0$.

OTT: Not exactly what I had in mind, but fine. What would that give you?

YTT: Well, I could use the entropy of mixing relationship derivable from classical thermodynamics

$$\Delta S = -k(N_A + N_B)(X_A \ln X_A + X_B \ln X_B) \qquad (1)$$

where the N's are numbers of molecules, k is Boltzmann's constant, and the X's are mole

fractions. If I start with 2N molecules of *d* isomer, I'll end up with N molecules of each isomer

and, because $X_A = X_B = 1/2$,

$$\Delta S = 2Nk\ln 2$$

OTT: Very good. Now, *why* has the entropy increased?

YTT: Because we have allowed separated volumes of two different isomers to mix.

OTT: True, but can you break it down into the three factors we recognized earlier?

YTT: Let's see. Clearly we are not adding or removing energy, so the total energy to be

allocated to molecular energy levels is unchanged. Volume effect? Yes, I guess, because the

half-box of *d* isomer has expanded to twice that volume, and ditto for the *l* isomer.

OTT: What entropy change results from that volume change?

YTT: Classically, for the A particles the entropy change for an expansion at constant

temperature is:

$$\Delta S_A = n_A R \ln \frac{V_f}{V_i}$$

and similarly for the B particles, where I have used n_A for the number of moles of A and f and i

for final and initial states. Then the entropy change for A and B together is

$$\Delta S = n_A R \ln \frac{V_f}{V_i} + n_B R \ln \frac{V_f}{V_i}$$

$$= N_A k \ln \frac{V_f}{V_i} + N_B k \ln \frac{V_f}{V_i} \qquad (2)$$

and, if $N_A = N_B = N$

$$\Delta S = 2Nk\ln V_f/V_i = 2Nk\ln 2.$$

Hey, that's enough to account for the whole thing!

OTT: What about the effect of distinguishability?

YTT: Well, two separated half-boxes constitute distinguishable groups, or two cohorts. Actually, these two cohorts are also distinguishable because one set is *d* and the other is *l*. That makes *two* reasons for there being two cohorts.

OTT: OK. Now, what about after they mix?

YTT: They are all in one volume but they remain distinguishable by virtue of their isomerism. So there are still two cohorts, but now for only one reason.

OTT: So what effect does the distinguishability factor have on ΔS?

YTT: None. There has been no change in the number of distinguishable molecules.

OTT: Very good. You have shown that bringing a container of *l* isomer up to a container of *d* isomer and allowing them to mix gives an increase in entropy that results from expansion of each gas into a larger volume. Period. How do you feel about that?

YTT: I'm uneasy. For one thing, I feel that something is strange about this mixing calculation. It is evidently the case that ΔS comes from the expansion of each gas, but that they are expanding *into each other* doesn't enter the calculation in any obvious way. I mean, how is the fact that the two gases are mixing taken into account?

OTT: Good point. We'll return to it later. Anything else?

YTT: Yes. This calculation seems to indicate that distinguishability factors make no contribution to ΔS, but when we first looked at the racemization process, distinguishability was the *only* factor that contributed to ΔS.

OTT: Very good. I see that you retain your ability to recognize when you don't understand something. That's crucial in science. Now, can you figure out why the explanation of ΔS has apparently changed?

YTT: It's pretty easy to see that the explanation based on volume change comes because I postulated bringing the isomers together in half-volumes and letting them mix while expanding to a larger volume. Earlier, though, we described the racemization as resulting from a reaction in a fixed volume.

OTT: Exactly. Now that you see that, you should be able to rationalize the two explanations for ΔS.

YTT: The original case of racemization occurs at constant volume and proceeds from one cohort to two. The route I chose in order to calculate ΔS kept the number of cohorts fixed at two but included expansion from half-volumes.

OTT: An important lesson here is that there are often several possible routes to choose from in calculating an entropy change, and the apparent explanation for the entropy change will depend on the route chosen. You asked why the entropy increases in the catalyzed racemization at constant volume; the answer is that it results from an increase in particle distinguishability.

YTT: It would be nice to be able to calculate ΔS directly from the distinguishability factor.

OTT: You can do that. In fact, that's what I was hinting at a minute ago when I asked if you knew the equation that allows you to calculate ΔS. Do you recall the statistical thermodynamic relation for the entropy of an ideal gas composed of N indistinguishable atoms? Let me remind you of it.

$$S(m, T, V, N) = 3/2 \, Nk \; + \; k\ln \frac{V^N}{\Lambda^{3N} N!} \qquad (3)$$

where N is the number of particles, V is volume and $\Lambda^3 = h^3/(2\pi mkT)^{3/2}$. The N! term accounts for the indistinguishability of the molecules in a pure gas. By using this formula, you can calculate the effect on S of changing the number of cohorts in your sample.

YTT: Can you run through the racemization process with this?

OTT: Sure. The key feature requires us to recognize explicitly that a system having several cohorts requires a *sum* of expressions like that in eq 3, one for each cohort. So, for the racemization process $2N_d \longrightarrow N_d + N_l$, $\Delta S = S(\text{final}) - S(\text{initial}) = 2S(m,T,V,N) - S(m,T,V,2N)$.

$$\Delta S = 2\left[\frac{3}{2}Nk + k\ln\frac{V^N}{\Lambda^{3N}N!}\right] - \left[\frac{3}{2}(2Nk) + k\ln\frac{V^{2N}}{\Lambda^{6N}(2N)!}\right] = k\ln\frac{(2N!)}{(N!)^2}$$

If we use Stirling's approximation that $\ln N! = N\ln N - N$ for large N, we obtain

$$\Delta S = 2Nk\ln 2 .$$

This shows us that the entropy increases by 2Nk ln2 when, at constant volume and temperature, a single cohort of 2N particles turns into two cohorts of N particles each.

YTT: OK, I see now how this works. And this formula, when applied to the alternative route where half-boxes are mixed, would generate the 2Nk ln2 value from the volume change.

OTT: Right. The formula is always the same, but the T, V, and N factors change with choice of route and show what the explanation for ΔS is for each choice. It is important to notice the effect of changing the number of cohorts. If the only change is that different cohorts somehow combine into one cohort, the number of *distinguishable* ways to store energy decreases, and hence the entropy decreases. This process is called "assimilation" by Ben-Naim (2).

YTT: Using that term, I guess we would say that the entropy increase accompanying

racemization at constant volume is due to deassimilation. But how useful is this terminology? Most processes also involve changes in V or T.

OTT: Ah, but entropy effects from changes in distinguishability still contribute, even when other things are going on. In general, increasing the number of cohorts, or deassimilation, contributes positively to the overall entropy change for a process. The entropy effects of factors you were talking about with your instructor years ago—total energy to be distributed and the energy levels and degeneracies among which that energy is to be distributed in distinguishable ways—are sometimes lumped together under the term "thermal entropy." You have now recognized that there is another factor, distinguishability, that is different from the other two and that must be accounted for separately. For now, let's just continue calling it the distinguishability factor.

YTT: I think I'm seeing things much more clearly now. But I'm still not happy with the entropy of mixing. The statistical thermodynamic formulas you've presented seem to lack any term to correspond to the presence or absence of other molecules in a gas mixture.

OTT: Let's turn to that issue. And let's begin by considering a box of volume 2V, containing 2N identical non-interacting atoms of mass m and temperature T. An impermeable partition divides the box in half, with N atoms in each chamber. What happens to the entropy of this system if the partition is removed as shown in Figure 2?

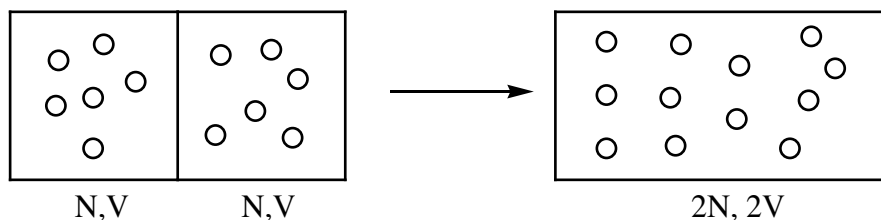N,V   N,V   2N, 2V

Figure 2. A partition is removed from between two compartments of equal volume, each

containing the same number of identical particles. $\Delta S = 0$.

YTT: My gut reaction is that nothing happens to it. I would expect the entropy of two one-liter containers of helium at STP to equal that of the same total amount of helium at STP in a two-liter container. Isn't that what we mean when we say that entropy is an extensive property?

OTT: Right. But *why* is ΔS equal to zero? Is it because all three types of contribution we have been discussing are zero?

YTT: Let's see. No energy is added or removed, so that has no effect. Volume? It doubles, so $\Delta S = 2Nk \ln 2$ from this factor. Distinguishability? When we remove the partition, we go from two cohorts to one. Assimilation occurs. The contribution from that is $-2kN \ln 2$, giving a total ΔS of zero. Remarkable! It seems like nothing happens, but really two things happen with effects that cancel.

OTT: Excellent. In fact, it is not possible to provide a rationale for this process, known as Gibbs' paradox, unless indistinguishability is taken into account.[1] Recall that you sliced the box of *d* isomers in half in your earlier calculation of ΔS for the racemization process with no concern that such a process might change the entropy. In fact, it doesn't. But you can now appreciate that such a process of division is a bit richer in conceptual content than you realized.

YTT: I would be chagrined if I weren't so delighted at seeing it now. But this latter process isn't really the mixing process I am concerned about. The two gases being "mixed" are the same.

OTT: But now you are ready for the crowning touch. Repeat the analysis for the case where the gases in the separate chambers are different. Let's say one is helium and the other is neon—a situation exactly as pictured in Figure 1.

YTT: OK. This is just like the previous calculation, where one gas was a *d* isomer and the other was the *l* isomer. We've already seen that ΔS equals $2Nk \ln 2$, called the entropy of mixing.

Again, total energy is unchanged. Again, the volume accessible for each gas doubles, allowing translational energy levels to get closer together and yielding a translational entropy contribution of 2Nk ln2. The number of cohorts is initally two—and it remains two, so no entropy contribution comes from the distinguishability factor. So ΔS = 2Nk ln2 because of the volume effect. This is the same conclusion we saw earlier. I'm still not happy.

OTT: But now you can compare the case where the two chambers contain helium with the case where one contains helium and the other contains neon.

YTT: The difference is easy to see. With only helium, there is a decrease in the number of cohorts, and that cancels the effect of expansion. With helium and neon, the effect of expansion is not canceled because there is no effect from a distinguishability change. We continue to have two cohorts.

OTT: So what does this tell you about entropy of mixing?

YTT: It seems to me to be a misleading term. It had me thinking that gases somehow "like to mix," when they actually just "like to expand." I guess this makes more sense though, since ideal gas A will expand to fill a larger volume without "knowing" whether some other ideal gas B is already there. I mean, we sometimes explicitly postulate ideal gases to be point masses with zero probability of encountering each other.

OTT: But let's check this. If you are right, then what would ΔS be if a liter of helium and a separate liter of neon are combined into a single one-liter vessel, all at the same temperature, as illustrated in Figure 3?

13
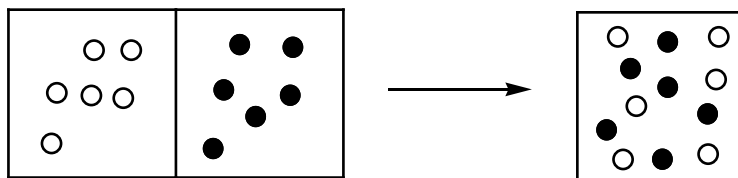
N_A,V N_B, V′ N_A,N_B, V

Figure 3. Compartments containing the same number of indistinguishable particles (but a different kind in each compartment) and having the same volume are collapsed into one another. $\Delta S = 0$

YTT: Well, if I'm right, there will be no volume effect, no distinguishability effect, and no total energy effect, and ΔS should be zero. Let me go back to Figure 1. We've already traced the combining of V with V′ to give 2V. (I'm using V′ to indicate that it is separated from V.) For this process, $\Delta S = 2kN \ln2$. Now we'll isothermally and reversibly compress the doubled volume as shown in Figure 3. In this case, $\Delta S = -2kN \ln2$. So overall, $\Delta S = 0$.

OTT: Right. Clearly the entropy for these gases is indifferent as to whether they cohabit the same container of volume V or each inhabits one of two separate containers of volume V. We can symbolize this conclusion as follows:

$$S(m_1,T,V,N_1) + S(m_2,T,\,V′,N_2)\ = S(m_1,T,V,N_1) + S(m_2,T,V,N_2) \qquad (4)$$

where V and V′ are separated volumes of equal size. Because the *values* of V and V′ and N_1 and N_2 are the same, the equality is obvious (3).

YTT: This is really helping me sort out my thinking. I'm not sure how much of this I can divulge to my physical chemistry class, but it certainly clears up some of my own uncertainties.

OTT: You are right in seeing that your own level of understanding can help you make intelligent choices of how to handle your classes. Certainly, entropy of mixing is a good example of this. The term is widely used and is quite misleading when applied to gases, where it is first encountered by students. But this might present an opportunity to deepen your students' understanding of entropy.

YTT: I'm not sure I follow you.

OTT: Well, if we go back to the racemization example, we've already seen how to calculate the change in entropy from a route involving spontaneous mixing. You could point out to your students that this is one way to evaluate the entropy change for the catalyzed racemization process. Then you could challenge them to think of a *reversible* route for this process for which they could calculate the entropy change from the heat transferred divided by the absolute temperature.

YTT: I like that. It would reinforce the notion that the entropy change for any process can ultimately be linked to q/T for any reversible path between the same states. It would be a challenge for them to find a reversible path for the racemization process, but I could throw in a hint [2].

OTT: Yes. And even if you don't go into the concept of cohorts and all that, this allows you to make the point that "distinguishability" simply means that some physical difference exists that allows us to imagine a reversible mixing process. In fact, the entropy of mixing, eq 1, represents the effects of molecular distinguishability (4).

YTT: I notice that the entropy of mixing for the process of Figure 1 obeys the standard classical eq 1 while that for the process of Figure 3 does not. But the latter process does not proceed at constant pressure. Of course! What the standard classical formula yields should really be called "the entropy of mixing *at constant pressure*." When I say it that way, I can see how the need for the presence of the "other" gas can be rationalized. It's there to maintain the correct pressure in the additional volume into which the first gas is going to expand.

OTT: And the other gas flows into the first volume to replace the portion of the first gas that flows out, helping to keep the pressure constant there too. So the presence of two gases is

necessary for keeping the pressure constant, but the entropy change is completely explainable by the *expansion* process, and the mixing is a *consequence* of the expansions.

YTT: Maybe this is the definition I should use in class: The entropy of mixing is the entropy increase due to expansion of initially separated, distinguishable gases or liquids into each other's volumes at constant pressure and temperature.

OTT: Good. I see you have included liquids, which is correct. We should talk more about liquids later, though, since students will view them as being different from gases.

YTT: It is interesting to see that the mixing of different gases at constant *volume* and temperature gives an entropy change of zero.

OTT: That's an excellent observation. It would helpful to point out this contrast in the classroom.

YTT: Let me see if I can imagine another system to which these ideas might apply. If we carry out an isothermal, constant volume transformation on an ideal gas, the translational energy levels' spacings remain unchanged and the total energy present is unchanged. So, for the process of combining two separated volumes of a single gas, shown in Figure 4, we might naively expect ΔS to be zero.
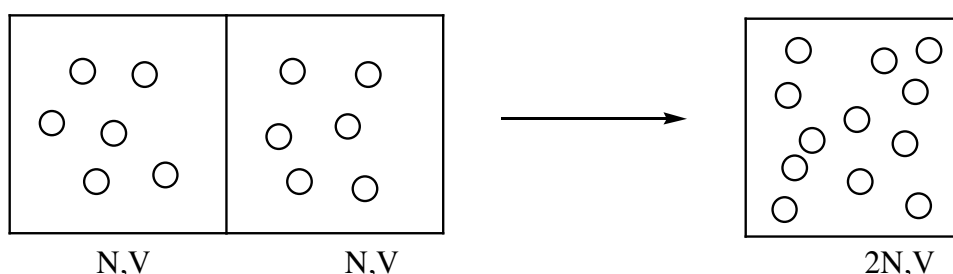

Figure 4. Compartments containing the same number of identical particles and having the same volume are collapsed into one another. $\Delta S < 0$.

But, because two cohorts have collapsed into one, ΔS is less than 0. In fact, it's $-Nk\ln 2$. And we

16

know this is right because this is simply an isothermal compression of an ideal gas to half its initial volume.

OTT: Before we go any further, can you summarize how the factors behave for the five types of situations we've discussed so far?

YTT: The total energy remains the same for all five of these changes.[3] The racemization process takes place at constant volume ($\Delta S = 0$), and the system goes from one cohort to two ($\Delta S > 0$). Entropy increases. The "mixing" of two samples of an identical gas doubles the volume ($\Delta S > 0$), and the system goes from two cohorts to one ($\Delta S < 0$). Entropy is unchanged. The mixing of two different gases doubles the volume ($\Delta S > 0$), and the number of cohorts remains unchanged ($\Delta S = 0$). Entropy increases. The mixing of two different gases with compression to the same final volume ($\Delta S = 0$) has no effect on the number of cohorts ($\Delta S = 0$). Entropy is unchanged. The "mixing" of two identical gases with compression to the same final volume ($\Delta S = 0$) reduces the number of cohorts ($\Delta S < 0$). Entropy decreases.

OTT: I think you have a good understanding of gases. However, when we come to solids, liquids, or surfaces, a new feature enters the picture.

YTT: Ah yes.   I would suppose that chemisorbed molecules could be distinguishable.

OTT: It's probably best to start with a simpler system. Let's begin with a volume V containing N molecules of a pure gas. How many cohorts?

YTT: Just one.

OTT: I put in a partition. Cohorts and entropy?

YTT: Two cohorts, increasing the entropy, and the volume is halved, decreasing the entropy, so over all the entropy is unchanged.

OTT: In goes another partition, perpendicular to the first, making four subchambers. So now

17

we have....?

YTT: Four cohorts, still the same entropy.

OTT: Let's say I keep doing this, ultimately arriving at N equal volumes, v = V/N. Let's also say that, with the help of Maxwell's demon, I manage to get exactly one molecule of gas in each of these volumes. I now have....?

YTT: N cohorts, and the same entropy—I think. I'm not sure though. Maxwell's demon is sometimes used to perturb normal entropic proceedings.

OTT: True enough. But when you think of the way the volume factor affects entropy in a way that just counters changes in number of cohorts, it seems that you must have it right. In fact, what if we reverse the argument and *begin* with N little volumes, v = V/N, with one molecule in each cell? We then *remove* partitions, and....

YTT: ...the entropy remains unchanged as the effects of increasing volumes and decreasing number of cohorts cancel.

OTT: This is the *cell model* for a gas, and we'll return to it in a moment. But first, let's suppose that we transform this picture so that it describes a pure liquid.

YTT: A liquid? Oh, you mean by making the little volumes so tiny that each is filled up by a single molecule?

OTT: Right. In this model we imagine that a molecule is confined by a cage of other molecules. The cage molecules contain the central molecule for a time that is long compared to the time it takes to move across the cage so we can consider the molecule to be constrained to move within a cell (4). We can view a pure liquid as consisting of N molecules, each in its own tiny volume, v, and each belonging to its own cohort of one. What will happen to the entropy of this liquid if you divide it in two with a partition?

YTT: Well, the total volume V is divided into two half-volumes, but I guess that really doesn't matter because the translational energy levels depend on v, and that's unchanged.

OTT: Right. And the number of cohorts?

YTT: Still N, because each molecule is still in its own little cell. So ΔS is zero, just as we would expect.

OTT: Good. Notice how different this is from the gas case, where you found ΔS is zero for partitioning because of cancellation of volume and distinguishability effects. For a liquid, these effects are both equal to zero.

YTT: Interesting. The cell viewpoint is making a fundamental change in the way we attribute contributions to ΔS.

OTT: Now let's consider a solution made by mixing this liquid A with a second liquid B, both at the same temperature. To keep it as simple as possible, we'll assume the molecules of A and B to be of the same size and also that all of the interactions between A and B are the same as A with A or B with B.

YTT: OK. That means that there will be no changes in thermal entropy or enthalpy due to intermolecular interactions as these liquids mix. This is an ideal solution.

OTT: Right. Now, what about cohorts?

YTT: No change there either.

OTT: So what is the entropy change?

YTT: Zero, it appears. But that can't be right. These two liquids should mix spontaneously. The equation for entropy of mixing that we apply to gases should apply to liquids too.

OTT: You see the problem: The three factors we've used to understand entropy changes of gases don't reveal an explanation for the entropy increase accompanying mixing liquids. Can

you see what's missing?

YTT: Well, the difference between the before and after situations is that, before, the A and B molecules are in different macroscopic volumes V_A and V_B, and after, are scattered throughout $V=V_A+V_B$. Because there are no changes that affect entropy in translational or internal energy levels due to mixing, there must be some change in the number of distinguishable ways to count microstates.....Oh, I think I see where it is. Because the tiny cells in the liquid mixture are in distinguishable spatial locations, we can distinguish between an arrangement for which a particular cell contains a molecule of A and one in which it contains B.

OTT: Very good! Describe how you now visualize the unmixed and mixed situations.

YTT: OK. Before mixing, liquid A is in volume V_A with entropy S_A. There are N_A cells, each of volume V_A/N_A, each containing one A molecule. Each A molecule is a cohort of one. Ditto for B. $S_{thermal} = S_A + S_B$. Now, they mix. Each A molecule remains in a cell of identical dimensions, and the intercell interactions are as before because we are assuming ideality. This continues to give $S_{thermal} = S_A + S_B$. But the location of such a cell is no longer restricted to the volume V_A. It can be anywhere in V_A+V_B. The same applies for B. Where before mixing we had no choice as to which cells had an A or a B molecule, we now have a huge choice. In fact, there are $(N_A+N_B)!/N_A!N_B!$ distinguishable arrangements.

OTT: Excellent! You've analyzed it beautifully. It's particularly interesting to observe that you've treated the particles as all *distinguishable* in saying there are N_A+N_B cohorts--one per cell--but then you've treated all the A or B molecules as being *indistinguishable* when dividing

by $N_A!N_B!$ in counting distinguishable arrangements. Were you aware of doing that?

YTT: No, I wasn't. It does seem inconsistent, and yet…. well, the A molecules certainly *are* indistinguishable for the process of placing them into cells. But once they are *in* a cell, then they can be distinguished from A molecules in *other* cells—because the *cells* are distinguishable. Wow! This really gets subtle.

OTT: What would be the effect on the entropy of the increased number of distinguishable arrangements?

YTT: Because that's the only change, we can identify ΔS with $k \ln[(N_A+N_B)!/N_A!N_B!]$.

OTT: Yes, and that leads to $\Delta S=-k(N_A+N_B)(X_A \ln X_A+X_B \ln X_B)$, where X_A is the mole fraction of A. It is just our good old entropy of mixing equation.

YTT: How about that! You know, I feel that the term "mixing" is more appropriate for this process. With gases, "mixing" at constant pressure occurs due to expansions into larger volumes that happen to contain other molecules. Here, however, the increase in the number of ways to place A in cells really does come about as a result of B's presence, because that's what increases the total liquid volume and the total number of cells.

OTT: Maybe you're being too hasty. A *and* B molecules have to be present in *both* cases. In the case of liquids, that yields more cells. And with gases...

YTT: ...they provide the additional volume for each other. I guess you're right. From the classical vantage, these processes are equivalent. But our microscopic picture is sure different.

OTT: Yes indeed. The entropy contribution due to this additional type of distinguishability is sometimes referred to as "configurational entropy." I think you can see why. The term seeks to convey the idea that the increase in the number of distinguishable ways to distribute the energy

results from the increase in the number of ways a system can be set up, or configured, when placing molecules into cells at particular sites. Each configuration can distribute energy in its own variety of ways, and the grand total of ways comes from adding up the results of all the configurations.

YTT: And in the present case we contrived, by assuming ideality, to make every configuration possess the same "variety of ways," so we could simply multiply by the number of configurations.

OTT: Quite right. I want to emphasize that the distinguishablity factor is entering in a new way now. In our example of gases, we focused on the effects of changing the total volume and/or the number of cohorts. Mixing two liquids, however, does not change the cell volume v or the number of cohorts. If the two liquids are the same liquid, the net effect on entropy is zero. If they are different liquids, an additional kind of distinguishability comes in and gives us the configurational entropy. This effect is still one of distinguishability, but not because of changing number of cohorts. It is because of distinguishable *spatial arrangements*. Because presenting each species with more choice of site is akin to allowing it to "spread out" or "expand," this configurational entropy term feels analogous to gas expansion into a vacuum, or into another gas. Even the mathematics is the same as entropy of mixing of gases.

YTT: You're right. It feels analogous to gas expansion, but the underlying model is physically different. The gas picture takes account of the change in total volume, V, and doesn't need to consider configurations. The liquid picture keeps a constant volume, v, for a molecule's "cage," but has to bring in the configurational concept in order to account for distinguishable cage locations. Both pictures correspond to identical entropies of mixing, though, so it's inevitable that there will be confusion.

22

OTT: Yes. The cell model for gases that are under ideal conditions artificially constrains the molecules into imagined volumes that are much smaller than the actual volume in which they move. That means that the translational energy levels will be too far apart, so the calculated thermal entropy will be too small. But the configurational entropy that results from using this physically unrealistic model compensates.

YTT: But I've certainly seen the cell model used for gases. If we consider real gases at normal pressures, the mean free path for the molecules is far smaller than the container dimensions. That seems to be an in-between physical situation.

OTT: Good point. Fortunately, the model used to choose the equation with which to calculate the entropy turns out not to matter insofar as affecting the value of ΔS_{mixing}. We get the same result whether we use the classical mixing formula, the statistical thermodynamic formula using full volume, or the statistical thermodynamic formula using cell volumes. The classical formula gives us a number, but no explanation. As for the statistical formulas, we are at liberty to use either choice for any phase, but the apparent *explanation* for the entropy increase depends on which model is selected.

YTT: It seems to me that the pedagogically preferable choice is to use the full-volume model for describing ideal gases and the cell model for liquids. That seems more in line with the actual physical situation. If we try to apply a full volume concept to the mixing of two identical liquids we are back to a variant of the Gibbs' paradox. Because the full volume of the mixture is available, the translational entropies are affected and we are once again required to deal with distinguishability by recognizing that the number of cohorts is changing, bringing the total entropy change back to zero. As for discussing real gases or critical fluids at intermediate

pressures, I guess I would opt for a cell model wherein the cell size bears some relation to the physical situation. I'd use the simple classical formula, though, to calculate actual values of ΔS_{mixing} at constant pressure and temperature.

OTT: I agree. It is truly fortunate that we can get the numerical value without having to worry about getting the detailed physical picture figured out. However, when teaching a course, I prefer *describing* the situation in physical terms that are appropriate, and that means avoiding configurational entropy in cases where ideal gases are mixed, and including it in cases where we are considering liquids, solids, or real gases at pressures where their mean free paths are less than the full volume.

YTT: I begin to understand why there is so much confusion and disagreement about this aspect of entropy. The testable, numerical aspect is model-neutral, and the conceptual aspect is a matter of taste.

OTT: Exactly right. And I think we have to anticipate that our taste may not be universally shared. Anyway, let's proceed. How do you now see the ways that entropy can be affected?

YTT: Change in total energy, changes in the energy levels available to the molecules, and changes in distinguishability. Distinguishability is determined by differences in the molecules themselves, or by differences in their locations. We can account for these by counting cohorts or configurations.

OTT: I think the approach we have been taking, following the situation from one or two cohorts in one or two macroscopic volumes all the way down to a cellular model, where each molecule is in its own cohort, allows us to see how changes in distinguishability and changes in volume offset each other, and reveals how the volume contribution to entropy at one extreme is linked to

the configurational entropy at the other.

YTT: And it shows how the extensive property of entropy is maintained all the way. What fascinating stuff! My students might be able to understand some of this, but, even if they don't, it certainly helps me see what's taking place in these processes. Thank you for taking the time to guide me through all this.

OTT: It's been a pleasure. Perhaps someday you'll be able to pass the favor along to the next generation of teachers.

Acknowledgment

Notes

1. It is sometimes claimed that Gibbs' paradox arises only from the statistical thermodynamic point of view. However, the fact that "mixing" two volumes of neon yields no entropy change whereas mixing a volume of neon with a volume of helium leads to an entropy increase can be explained at the classical level only by the incorporation of distinguishability in some way. Discussions relevant to this matter appear in references 4-6.

2. One possible way: 1. Divide a sample of one enantiomer in two, and separate the two half-samples. $\Delta S = 0$. 2. Replace one of the half-samples with an equal amount of the other enantiomer at the same T and P. Because each enantiomer has the same entropy, $\Delta S = 0$. 3. Place the two half-samples together, separated by a barrier made by the heads of two pistons in contact. One piston is permeable only to one enantiomer and the other piston is permeable only to the other enantiomer. $\Delta S = 0$. 4. Move one piston in an isothermal, reversible expansion through the enantiomer to which it is permeable. This allows the other enantiomer

to fill the container. Repeat the operation for the other piston. Now the enantiomers are fully

mixed. The heat absorbed in the isothermal, reversible expansions, divided by T, gives ΔS >

0. It is relevant to note that the "concept of a semipermeable membrane requires the

existence of some feature distinguishing the molecules of the mixture"(4, p. 558).

3. Work and heat are zero for the first three processes. For the last two processes they are

   nonzero, but they cancel.

Literature Cited

1. Lowe, J.P. *J. Chem. Educ*. **1988**, *65*, 403-406.

2. Ben-Naim, A. *Statistical Thermodynamics for Chemists and Biochemists*, Plenum: New

    York, 1992; Chapter 2.

3. Levine, I.M. *Physical Chemistry*, 5th ed.; McGraw-Hill: New York, 2002; pp 88-90.

4. Berry, S.R., Rice, S.A., Ross, J. *Matter in Equilibrium*; 2nd ed.; John Wiley and Sons, Inc.:

    New York, 2002; p 558; p733.

5. Silbey, R.J., Alberty, R.A., *Physical Chemistry*, 3rd ed.; John Wiley and Sons, Inc.: New

    York, 2001; p 90.

6. Zemansky, M.W. *Heat and Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1951; p 383.

N_d , V N_l , V $N_d + N_l$, 2V

N,V N,V   2N, 2V

N_A,V N_B, V′ N_A,N_B, V
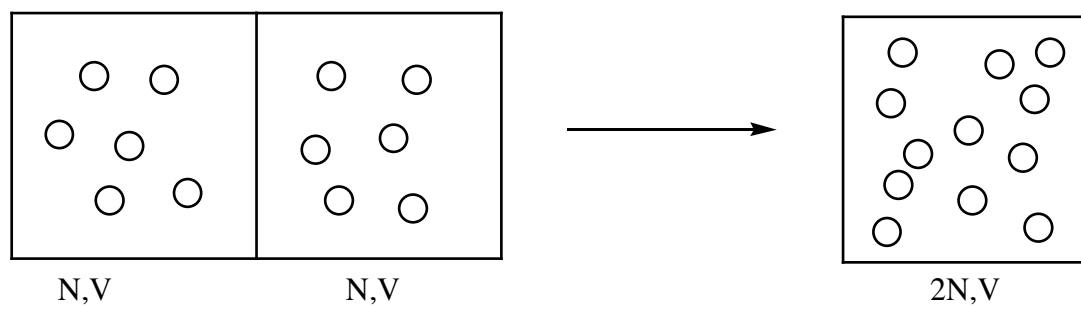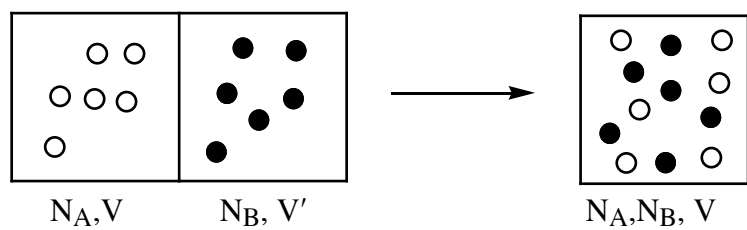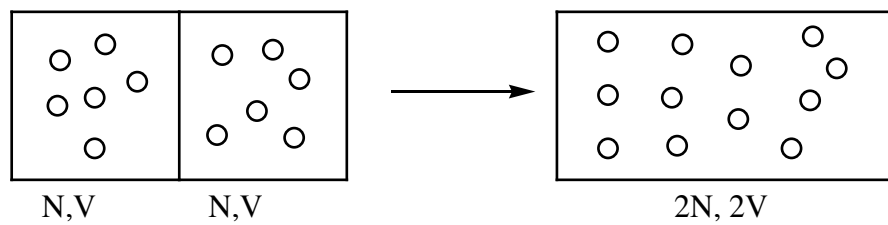
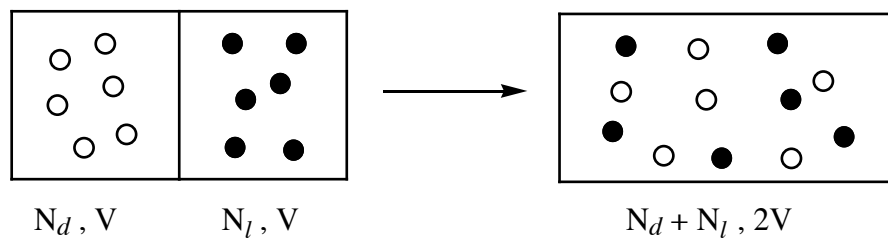N,V N,V   2N,V

Figure 1. A partition is removed from between two compartments of equal volume, each containing the same number of indistinguishable particles. $\Delta S > 0$.

Figure 2. A partition is removed from between two compartments of equal volume, each containing the same number of identical particles. $\Delta S = 0$.

Figure 3. Compartments containing the same number of indistinguishable particles (but a different kind in each compartment) and having the same volume are collapsed into one another. $\Delta S = 0$

Figure 4. Compartments containing the same number of identical particles and having the same volume are collapsed into one another. $\Delta S < 0$.