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# Entropy: Conceptual Disorder

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*Student:* Good morning, professor. I have a few questions about entropy. Would this be a good time to discuss them with you?

*Professor:* By all means! Come in, come in. Entropy is one of my favorite subjects.

*S:* I would have guessed that from your enthusiasm in lecture. I have been trying to understand what entropy *really is*, and every time I think I have it nailed down, another example comes along that doesn't seem to fit my understanding.

*P:* (Laughing) That's entropy, all right. I've thought about it, off and on, for years, and I'm *still* adjusting my understanding. I'll never forget how inscrutable entropy seemed when I first encountered it in my college physical chemistry class 30 years ago. Of course, these days physical chemistry students like you have usually encountered entropy in an earlier general chemistry course and perhaps even in high school. Even newspapers talk about entropy these days. It has developed some cult value.

*S:* Yes. I did learn about it as a freshman. It seemed clearer *then* than it does *now*! In fact, I looked back at the discussion in my general chemistry text just yesterday to try to help me with the discussion in my p-chem text, and I just don't understand how these two discussions relate to each other.

*P:* Can you give me an example of the kind of difficulty you are having?

*S:* O.K. My freshman text describes entropy as a measure of randomness, or disorder, in a system. That seems clear enough. It gives examples, too, of spontaneous processes that involve increasing disorder—like a gas expanding into a vacuum, or my room getting messy, or rivers getting polluted. But now we're solving problems where entropy changes don't seem to go along with this picture.

*P:* What sort of problem are you thinking of?

*S:* Well, suppose we have a mole of neon gas in a 20-liter container at 300 K and we heat it at constant volume to 400 K. The entropy of the gas increases, right?

*P:* That's right.

*S:* But it seems to me that the positions of the atoms are just as random at 300 K as at 400 K. I mean, aren't they *completely randomly distributed* in both cases?

*P:* You are absolutely right! What you are seeing here is a limitation in the definition of entropy as it appears in your freshman text. There is really more to entropy than positional disorder or randomness, and the heating of neon at constant volume is an excellent example.

*S:* Is the freshman-text explanation wrong, then?

*P:* Well, it's certainly incomplete. Oversimplified to the point of being misleading, I would say. In many cases, though, it leads to the correct prediction.

*S:* But not always?

*P:* No, not always.

*S:* How am I able to tell when it's right? And what do I use when it isn't correct?

*P:* Let's begin with your second question. Since we know that positional randomness cannot explain the entropy increase that comes with heating neon at constant volume, we know there must be another sort of explanation for that case. Have you any idea what it might be?

*S:* Not really. I know how to *calculate*  $\Delta S$  using the integrated value of energy absorbed divided by absolute temperature, but that doesn't give me a picture analogous to randomness.

*P:* Yet you do know something about what is happening to the atoms as the neon is heated.

*S:* Oh yes. They increase their average kinetic energy by flying about with greater average speed.

*P:* What you are going to see next semester is that entropy is related to the number of ways in which a system can exist. However, when we count "ways" a system can exist, we count the number of ways the total energy of the system can be divided up among the molecules.

*S:* I guess I don't see what you're saying. How would it work with our neon example?

*P:* Let's simplify the argument by discussing the situation for a *truly* ideal gas. Neon will condense to a liquid and freeze to a solid at sufficiently low temperatures, which would complicate our discussion.

*S:* Fine.

*P:* We imagine our gas to be contained in a rigid container. A molecule can travel in any direction in the container, but, once again to keep the argument as simple as possible, I'm going to focus on motion in one direction only, say the  $x$  direction.

*S:* That's like a particle in a one-dimensional box.

*P:* Where did you learn that?

*S:* In freshman chemistry.

*P:* (Is nothing sacred!) Well, in that case you already know that the energies allowed for this particle are discrete, quantized values depending on a quantum number.

*S:* Right. From fitting de Broglie waves into the box.

*P:* Just so. Well, let's imagine that our ideal gas molecules can have some lowest  $x$  translational value.

S: Zero?

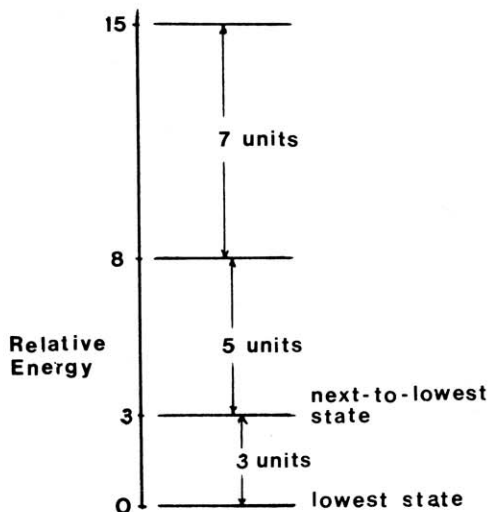
P: Well, not really. They still move about in the box, even at absolute zero. It's one of the peculiarities of quantum mechanics which (thank goodness!) has not yet been put into freshman texts. But, for our convenience, we can define our energy scale so that this lowest allowed energy is zero.

S: So, when our ideal gas is at zero kelvins, all the molecules have this "zero" energy?

P: Right. Now, on this scale, the next energy state that a given molecule can have has three units of energy.

S: Three? If we are defining our own scale, why not make it one?

P: Because that would create fractions when I put in the next states: The state *above* the one we just identified is five units higher, and the next one is seven units higher still. (Goes to board.)



P: Now a mole of gas is a tremendous number of molecules. In order to allow you to follow the argument more easily, I'm going to reduce the number to 10 molecules.

S: I think I'm with you so far: 10 molecules in a one-dimensional box capable of having translational energies of 0, 3, 8, or 15 units.

P: Right. Now, as I mentioned, we are really concerned with the number of ways this system can exist. Let's start with the simplest case—the system at absolute zero. How many ways can it exist?

S: You mean, how many ways can I distribute zero energy among these 10 molecules?

P: Yes.

S: It seems like there's only one way—keep every molecule at  $E = 0$ .

P: That's right. What if I had allowed you more energy? Say, I permit the system to accept between 0 and 2 units of energy.

S: Hmm. I don't see any way for the system to accept 1 or 2 units of energy because of the way we've quantized the energies. I guess there is still only one way—every molecule has zero energy.

P: That's right. Now suppose we "heat" the gas by providing 3 to 5 units of energy. In how many ways can the system exist now?

S: Let's see. . . . There is no way for the system to accommodate 4 or 5 units, but 3 units of the added energy can go to one molecule. . . .

P: Right. . . .

S: But any one of the 10 molecules can have the energy, so it seems like there are 10 ways to place the energy.

P: That certainly *seems* reasonable. But there is a hitch. Is there any way for you to tell *which* molecule has the energy at any particular instant?

S: I guess not. Since the molecules are identical I can't tell them apart. I can't even think of what terms I could use to tell you which one has the energy. I mean, how could you interpret it if I said molecule number 7 has it?

P: I couldn't. The best you can do is to say that one of the molecules has all the energy.

S: That sounds like only *one* way, then.

P: Correct.

S: So we've heated the gas but achieved no increase in the number of ways it can exist?

P: Right. But we are working at a microscopic level. Let's keep adding energy. Let's say that between 6 and 8 units of energy has been added. In how many ways can the gas exist now?

S: One possibility is that 8 units of energy is possessed by one molecule. Another is that one molecule has 3 units and another also has 3 units. Two ways?

P: Good. Now try with 15 to 17 units.

S: One molecule could have 15 units. Two molecules could have 8 units. Or one could have 8 units, and three could have 3 units. Or five molecules could have 3 units. That's all I can think of—four ways.

P: You can see what is happening. As more energy is supplied, the number of ways the gas molecules can absorb it increases. Also, the average kinetic energy of the molecules increases, which is the same thing as saying that the temperature rises.

S: And because the number of ways increases the entropy increases?

P: Yes. Entropy is proportional to the logarithm of the number of ways a system can exist. I should warn you that we've skipped over certain subtleties of temperature and energy that are handled through the concept of ensembles. But the primary point comes through—the more energy that's available, the larger the number of ways a system has to store it up. That's why heating a system always increases its entropy.

S: This approach doesn't seem to have anything to do with randomness of position.

P: It doesn't. It can't, because, as you pointed out at the beginning, neon gas is no more randomly distributed *spatially* at one temperature than at another. Some general chemistry texts try to include the notion of randomness of *energy* distribution along with spatial randomness, but I don't think this is done very successfully in most cases.

S: I think I understand how it works with neon gas now, but I guess I'm unclear about how positional randomness enters at all. Are you claiming that positional randomness *never* enters into entropy values?

P: No, that would be too strong. It is true that we rarely consider positional randomness explicitly when we *calculate* a system's entropy. We deal almost 100% with considerations of energy storage. But it often happens that the factors that lead to a larger number of ways to store energy and hence a larger entropy *also* lead to greater positional randomness. Since we can more easily follow positional randomness in our mind's eye, the tendency is to use that as our qualitative rule of thumb: increasing positional randomness goes with increasing entropy. For example, suppose we were to decrease the size of the box containing our 10 neon atoms. What effect would that have on the (one-dimensional) allowed energies?

S: Let's see. I think that the allowed energy levels rise and get farther apart as the box gets smaller. That's because we have to use shorter de Broglie wavelengths to make them fit in the box.

P: Excellent! Now let's suppose that we have decreased the size so that the allowed energies are doubled to 6 units, 16 units, etc. Whereas before you found that 15 to 17 units could be stored in four ways, now it can be stored in . . . ?

S: Only one way, with one molecule having 16 units. For the same amount of energy, the smaller box has less entropy.

P: Right. Now you got that from considering energies. How does it work with positions?

S: The smaller box allows for less positional randomness, so that argument also gives me less entropy for the small box.

P: You see how it works? If an ideal gas is allowed to expand into a vacuum, it will do so spontaneously. The energy approach sees this as being due to the fact that the larger volume after expansion causes translational energy levels to be closer together, which in turn permits more ways for the energy to be stored, hence greater entropy. The positional randomness approach sees it as allowing more positional randomness, hence greater entropy. The latter view is easier to manage and pedagogically more popular at the introductory level. But it is not always reliable, as the neon example shows.

S: I think I am catching on now. The way these ideas come together is fascinating.

P: Even more interesting, I think, are cases where the system is changing *character* rather than simply changing its volume.

S: You mean a chemical reaction?

P: Possibly. Or even a phase change, like ice melting.

S: I find the positional randomness approach here very easy to follow, with ice being ordered and water being disordered.

P: Yes, indeed. Virtually every chemist I know thinks about it that way. But if you were trying to *calculate* the entropy change for this process, you would do it in terms of energy levels and number of ways of storing energy, without explicit consideration of positional probabilities.

S: I'm afraid I don't see how that approach will lead to an entropy increase for the melting of ice. I mean, I'm sure it *does*, but I don't see *why* it does.

P: It does seem complicated. But there is an easy way to get at the crux of the matter. When ice melts, constraints on molecular motion are released. Where the molecules could only vibrate in ice, they can rotate in the liquid. Energy levels for vibration and rotation are quantized, but those for vibration are spaced much farther apart than those for rotation. So liquid water has more closely spaced energy levels than ice, hence more ways to store the energy and greater entropy.

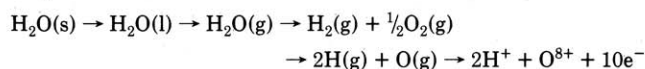
S: When the water evaporates, is the same sort of explanation appropriate?

P: Yes, except now the bouncing about of molecules in liquid (which we can call vibration or translation in a tiny box) becomes replaced by translation in a much larger volume. The resulting translational levels are *very* close together, so once again we get an entropy increase. Of course, we also get increased positional randomness.

S: Is the positional randomness approach pretty reliable for such processes?

P: Yes. Breaking the bonds that confine molecules or atoms causes the number of vibrational modes to decrease and the number of rotational or translational modes to increase, and this increases the number of low-lying energy levels and the entropy. It also increases positional ran-

domness. Entropy increases for each step in the following process:



We have gone from a system with no translational motion to one having only translational motion.

S: I understand what you're saying, but now I'm puzzled by another thing. If entropy increases in spontaneous processes, why doesn't ice spontaneously turn into separated nuclei and electrons as indicated in your process?

P: Good question. The answer is that it *does* if given the choice. But it doesn't have the choice unless we provide enough energy for the bonds to be broken. At extremely high temperatures, where the system can choose among being in the form of H and O atoms flying about or in the form of H<sub>2</sub> and O<sub>2</sub> gas, or in the other forms, like ice, I can guarantee that it won't be ice! It will be an equilibrium between, H, O, H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O(g). The hotter we make it, the more it will be in the form of H and O, and at extremely high temperatures it will become a plasma of ions and electrons.

S: Of course. I should have seen that. There's another question that arises from one of the freshman texts I've looked at. It has to do with diamond and graphite. This book said that diamond has a more ordered structure than graphite, so diamond's entropy is lower. I'm not sure I would have been able to tell that diamond is more ordered. Both structures look pretty regular to me.

P: I would encourage you to consider a career in science. You have that rare gift of knowing when you don't understand something. The fact is you *can't* call diamond more ordered than graphite. Any perfect crystal is perfect.

S: Does diamond have a smaller entropy than graphite?

P: Yes, at any finite temperature. At zero kelvins they both have but one mode of existence, so both have zero entropy. This textbook error is a good example of the slipperiness of the positional randomness argument. The author knows that graphite has the larger entropy (say at room temperature) so he is led to conclude that the graphite crystal is less ordered than the diamond crystal, which doesn't make sense.

S: But why *does* graphite have greater entropy than diamond at room temperature?

P: What kinds of motions are the carbon atoms undergoing?

S: They're both solids, so the atoms are vibrating.

P: Are they vibrating in identical circumstances?

S: I guess not, because the bonding is different. In diamond, each carbon has four carbons bonded to it in a tetrahedral arrangement. In graphite, it's like a lot of sheets made of fused benzene rings.

P: Very good. That's why diamond is so hard. Every atom is strongly bound in place. Graphite is much softer because the sheets are more weakly held together. Strong bonds are associated with more widely spaced energy levels (like smaller boxes), so diamond has vibrational levels more widely separated than graphite. So . . .

S: So graphite has more ways to store a given amount of energy, hence higher entropy.

P: Exactly. Sometimes the argument is made that, because graphite has weaker bonds, the atoms vibrate over larger distances, so positional randomness is greater in graphite than diamond. This is true, but seems to me to be stretching the argument. It is even true at zero kelvins, where the entropies are equal, so it seems misleading.

S: You've shown me one system, neon, where entropy increase is accompanied by no increase in positional randomness, and several where there is an accompanying

- increase in positional randomness. Does it ever happen that a spontaneous process is accompanied by a net *decrease* in positional randomness for the system and its surroundings?
- P:* I can see a way to concoct an example.
- S:* How would you do it?
- P:* I would use our rigid container of neon as a heat sink. Let's make it very cold: Say it's at 200 kelvins and has conductive walls. It is isolated from everything except for a film of water applied to a wall. Spontaneously, the water freezes and forms crystals of ice, which represents a decrease in positional randomness. The heat of fusion flows into the neon, *increasing its entropy, but not changing its positional randomness*. The net result is a spontaneous process and a decrease in positional randomness.
- S:* That seems like a real blow to the claim that positional randomness must increase for a spontaneous process.
- P:* Yes, it's a nice counterexample.
- S:* You've helped me a lot. I think I have a better understanding of how positional randomness relates to entropy.
- P:* How would you sum it up?
- S:* Let's see . . . entropy is really a measure of the number of ways energy can be stored by a system. . . .
- P:* Yes, good. . . .
- S:* . . . And if there are more energy levels available for storing the energy, there are more ways to store it.
- P:* Excellent. And how does this relate to *positional randomness*?
- S:* Most of the processes that we visualize as giving greater positional randomness, like a gas expanding, or a solid melting, also give more available energy levels.
- P:* You understand this well. Now can you tell me why the neon gas you brought up at the beginning has an entropy increase when you heat it at constant volume?
- S:* Hmmm . . . Nothing is happening to the energy levels. . . . Aha! In this case we are simply adding more energy, so naturally we find more and more ways to store it among the existing levels.
- P:* Excellent! You see that there are two extremes involved in this entropy business—addition of energy to a fixed system with unchanging energy levels, and shifting the energy levels of a changing system in the presence of a fixed amount of energy.
- S:* And mixtures of these extremes.
- P:* Yes. And the trouble with the positional randomness argument is that it really only deals with the second extreme—the changing system with its shifting levels. That's why you were puzzled by the neon example. It is of the other kind.
- S:* I see now that *positional order* is only part of the story.
- P:* Yes, indeed. In fact, one can argue that the overzealous identification of entropy with positional order has led to some scientific mischief.
- S:* What are you referring to?
- P:* Some people have claimed that formation of the first replicating molecules—primordial DNA—could not have occurred through natural processes because it would involve a spontaneous increase in order, violating the second law.
- S:* Oh, yes—that's an argument I have heard before. So you're saying that this is an error because they are focusing only on the positional randomness aspect?
- P:* Exactly. It is like the formation of a snowflake in moist air. Let's see if you can analyze that apparently miraculous process. What happens when the snowflake forms?
- S:* Well, material order increases, so I'd expect an entropy decrease from that.
- P:* How about the ways of distributing energy?
- S:* Since we're forming a solid, we're restricting molecular motion. Oh yes, as you said earlier, we are losing rotational modes and gaining vibrations. In fact, since we start in the gas phase, I guess we lose translational motions too.
- P:* Excellent. And as we saw earlier, the vibrational energies are farther apart, so we don't have as many ways to store the energy.
- S:* Right. So the entropy decreases in this analysis too. But snowflakes *do* form spontaneously. Let's see. . . . It's because they release heat of fusion!
- P:* Yes. What happens to it?
- S:* It goes into the cold air, and heating the air causes *its* entropy to go up.
- P:* Now you have it. If the surrounding air is cold enough, the entropy increase there is greater than the entropy decrease in forming the snowflake, and the process occurs spontaneously.
- S:* My problem at first was that I was only thinking about the snowflake.
- P:* That's the danger. Whenever we observe a spontaneous process that creates positional order, we should be alert for the increase in ways of storing energy that accompanies it. Often this concomitant process is the easily overlooked flow of heat from a warmer to a colder object: *Nature dazzles us with magic tricks done by ordering matter with her right hand while with her hidden left hand she unobtrusively transfers heat.*
- S:* Wow! That sounds pretty classy.
- P:* I've been waiting for a chance to use it.
- S:* I guess my problem has been that the arguments based on positional randomness didn't allow me to treat heat flow.
- P:* Yes, aggravated by the fact that positional randomness, while often a convenient way to predict whether the number of ways to store energy will increase or decrease, actually *avoids* explicit consideration of energy. This avoidance of what *really controls* entropy has allowed authors to slip unsuspectingly into examples like messy rooms and scattered trash, which have very little to do with entropy as it is defined and used in the physical sciences.
- S:* Thank you for your time, professor. If I have any more questions, may I visit again?
- P:* By all means. I've enjoyed our discussion.