

- *Нови подходи* •
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## A MODERN VIEW OF ENTROPY

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**Abstract.** Entropy may be the most feared topic in beginning university chemistry – by students because of its complexity, by instructors because students fail to understand its basic principles. Although in advanced areas entropy change can indeed be extremely complex and subtle, this is not the case in the first course. Historically, experts in thermodynamics have not aided beginners by providing an introduction to the subject in simple terms. Entropy is *not* ‘disorder’ nor does it have anything to do with ‘mixed-up things’ like disorderly desks or shuffled cards. This article in simple, step-wise fashion details how instructors can begin with ordinary physical and chemical events whose spontaneity can be seen to be due to energy dispersing or spreading out. Then this can be generalized to “energy of all types changes from being localized to becoming dispersed if it is not hindered from doing so. The overall process is an increase in thermodynamic entropy”. Thus, the focus is on seeing the dispersal of molecular motional energy that instructors can readily apply to all the common examples of beginning chemistry – including new insight to the meaning of  $S_{298}^0$  and a quick introduction to mixing (usually omitted in the first course) that explains all colligative effects.

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### **The Problem**

A majority of students in beginning chemistry, and perhaps a like number of their instructors who are not experts in physical chemistry or thermodynamics, would say that entropy is their most disliked topic. I admit that this is my conclusion only from informal conversations over many years, rather than from scientific data. However, regardless of the precise numbers of such students and professors in the past, this article is written so that this kind of unfortunate antipathy toward entropy and the

second law need not be continued. No concept pervades chemistry more profoundly or is more essential to our overall understanding of the whole subject. No concept is more relevant to the events in the physical world that we and our students encounter daily. The second law originated from human experience with thermal energy, not from abstract theory.

### **The Cause of the Problem**

The basic ideas surrounding entropy – obvious to those who were specialists in thermodynamics – have not been interpreted in simple fashion for educators. The result is that entropy has been poorly presented to students for the last century. Clausius’ fundamental equation of  $q_{\text{rev}}/T$  does not appear complex (although it is the only *quotient* in the list of thermodynamic quantities of  $P$ ,  $V$ ,  $T$ , and  $E$ ). However, its wide acceptance in the latter part of the nineteenth century coupled with the brilliant quantitative work of Boltzmann led to a strange situation for educators. Scientists in the developing fields of thermodynamics and statistical mechanics were so focused on their quantitative research – and admittedly, the knowledge of the nature of real molecules was so sparse then – that they did not adequately explain the *meaning* of their work to those outside their field. The most unfortunate event was the pronouncement of Boltzmann in his influential lectures and their subsequent 1898 publication, in essence, “entropy is disorder”.

He is not to be blamed for this error. This statement was made before he could do modern calculations (never using the famous equation carved on his tombstone), or know about molecular energy levels (prior to quantum mechanics), or have a  $W_0$  for his probabilities (prior to the third law). Boltzmann spoke innocently, as best he could with the knowledge of that day [1]. However, the many competent thermodynamicists of the twentieth century continued their focus on exploring the quantitative complexities and relationships of the subject with little effort to explain the meaning of basic thermodynamics to the rest of us. It is time that educators hear straightforward, understandable statements about what entropy really is or is not.

### **The Solution: A Focus on What Is Responsible For Entropy Change**

The definition, “entropy is disorder”, used in all US first-year college and university textbooks prior to 2002, has been deleted from 15 of 16 new editions or new texts published since 2002 [2]. Entropy is *not* ‘disorder’ [3] nor is entropy change a change from order to disorder. (Messy papers on a desk or shuffled cards are totally irrelevant to thermodynamic entropy).<sup>1</sup>

All substances above ca. 1 K are incomprehensibly disorderly in the arrangements of their molecular energy (with numbers of microstates greater than  $10^{26,000,000,000,000,000,000}$ ) [1] and thus there is never ‘order’ in any real system so far as energy distributions are concerned. Yet, energy and energy distributions are what entropy change ( $\Delta S$ ) is all about: Consider Clausius’

$$\Delta S = [q_{\text{rev}} = \text{thermal energy} = \text{'heat'}] \text{ divided by } T.$$

Then, examine the molecular thermodynamics of the modern interpretation of Boltzmann.:  $\Delta S = k_{\text{b}} \ln W/W_0 = k_{\text{b}} \ln W$ , where  $W$  is the number of microstates available for the system at its temperature; a microstate being one arrangement (of all the motional energies of the molecules, i.e., of the quantum states) in which the total energy of the system might be at one instant [4, 5].

If we focus on what *happens* to the energy that Clausius uses in his equation, rather than just solving the equation (and treat Boltzmann's equation and his microstates similarly), suddenly the mystery and complexity of entropy as presented and used in the beginning course all vanishes. Consider this most basic process: When thermal energy is transferred from a warm flask of gas to a very slightly cooler flask (separated from the warm flask only by a thin metal membrane), what is actually occurring on a molecular scale? The faster moving molecules (on average) in the warmer flask that hit the membrane transfer some of their energy to it and the atoms in it vibrate just a bit faster. Then some of the molecules that are moving slightly slower (on average) in the cooler flask hit the warmed membrane and move a bit faster. The process continues until both flasks and the membrane are at exactly the same temperature. What has happened? Energy – **the greater average motional energy of the molecules** – in the warmer flask has been dispersed or spread out to the motional energy of the molecules in the slightly cooler flask. What could be more obvious? But do we not almost always concentrate on the calculation of the  $q/T$  in the process, and overlook the fact that the fundamental *nature* of that event on molecular scale and what entropy change *measures* on a macroscale, is **a spontaneous dispersal of energy from a warmer source to a cooler receiver?**

A second classic example (that made me despair of ever understanding entropy when I was a student of 18) was that of a gas spontaneously expanding isothermally into an evacuated chamber. But then the professor told us that there was no change in ' $q$ ' involved. Therefore, we did not have a ' $q$ ' to insert in the equation, yet because the process was spontaneous, the entropy had increased! Why were we not also told that the significant *event* that occurred was the initial motional *energy* of the gas, the motions of its molecules, in one chamber had **spontaneously become dispersed or spread out** over the entire volume of the two chambers? (Instead, of course, we were shown how to reversibly compress the gas to its original volume and that the work of that process,  $-RT \ln V_2/V_1$ , was equivalent to the  $-q$  of spontaneous expansion so we could proceed with our calculation of the entropy change.) But why was not the *nature* of the event of spontaneous expansion underscored as an example of the **dispersal of the initial motional energy of the molecules so that its energy became spread throughout a greater volume?**

### A Modern View of the Second Law

If the energy in the motion of molecules is essential to understand entropy in

chemistry, what is the place of energy in a modern statement of the second law? A definition that fits both with our experience and with fundamental science is “Energy of all types changes from being localized to becoming dispersed or spread out, if it is not hindered from doing so. The overall process is measured by the increase in thermodynamic entropy.”<sup>2</sup>

### **The Dispersal of Energy in Simple Examples of Entropy Change**

It is easy to show students how the modern view of the second law describes what is happening in spontaneous events around us, i.e., those processes that result in entropy increase.

“A hot pan spontaneously disperses some of its energy to the cooler air of a room. (That means that the faster vibrating iron atoms in the pan transfer some of their motional energy to the slower moving nitrogen and oxygen molecules that strike the pan.)

Conversely, even a cool room would disperse a portion of its energy to colder ice cubes placed in it. (Again, the molecules in the air that are moving faster, on average, spread out some of their energy to the water molecules that are vibrating in the ice.)

When a container of nitroglycerine is merely dropped on a concrete floor, the nitroglycerine can change into other substances explosively. This occurs because its activation energy for decomposition is exceeded due to the mechanical blow, and the nitroglycerine’s bonds break to form gaseous products wherein some of its bond energy is spread out in enormously increasing the vigorous motions of those product molecules.

At a high pressure in a car tire, the compressed air tends to blow out because then that localized energy of the air molecules can be far more spread out among the air molecules in the lower pressure normal atmosphere.

Batteries, small or large, “lose their charge” (i.e., spontaneously react to decrease the amount of the reactants) and thereby disperse their chemical potential energy in heat if even a slightly conductive path is present between the two poles. .

Hydrogen and oxygen in a closed chamber will remain unaltered for years and probably for millennia, despite their larger combined bond energies compared to water. However, if a spark is introduced, they will react explosively — a phenomenon characteristic of rapid reactions in which a portion of the reactants’ bond energies disperses in causing a very great increase in the product molecules’ motion (and high pressure in a small volume) that ultimately becomes spread out in molecular motional energy in the surroundings” (adapted from [6]).

Are those descriptions complex or difficult to understand? They are what is happening in terms of energy – the energy of molecular motion or, in two cases, bond energy – in five chemical and physical events. Why have textbooks continued to tell students that these or similar processes show “increased entropy production” or

“creating entropy” rather than directly stating what is responsible for entropy change so that it is readily connected to common experience or common chemical behavior by the student?

### A Modern View of Entropy Change

To the question that innumerable students have asked, “What is entropy, **really**?” a clear answer is now “Entropy measures the dispersal of energy: How *much* energy is spread out in a process, or how *widely* spread out it becomes – at a specific temperature.”

“How much”, of course, means the input of energy to a system as in the usual examples used in the beginning course: phase change or heating a system. “How widely” includes those processes in which the initial energy in a system is unchanged but it becomes more spread out: expansion of an ideal gas or mixing of all types – ideal gases or liquids or solutes in liquids. The combination of both “how much” and “how widely” applies to a wide variety of chemical reactions in which not only are bonds broken in reactants and formed in products but the products have more molecules or undergo phase change or become mixed with reactants.

There is not space in this brief introduction to a modern view of the second law and entropy to discuss all of the aspects of its applicability. However, most US first-year chemistry texts now use the approach [2] and several online articles give additional information [7-10].

### Two Areas in Which the Focus on Energy Dispersal Gives New Understanding

#### 1. The meaning of standard molar entropy values

When seen in their relation to the *energy* content of a substance, standard molar entropy values,  $S_{298}^0$ , give useful insight that is absent when – as is usual – those J/K values are treated as merely abstract numbers to be added or subtracted in determining a  $\Delta S_{\text{reaction}}^0$ . A  $S_{298}^0$  value for a substance is the number of joules of energy/ $T$  transferred incrementally (reversibly, from the surroundings at each  $T$ ) to a mole of substance from 0 K to 298 K. Thus, this number is a rough indicator or approximate index (**not** the joules dispersed at 298 K, **nor** the total joules dispersed from 0 K to 298 K!) of the relative amount of energy **that the substance must have to be exist stably at 298 K**. This is *why*  $S_{298}^0$  values illuminate e.g., the difference in rigidity of bonding: the more rigid bonds of diamond (2.4 J/K) vs. the looser interatomic bonds in graphite (5.7 J/K), as well as the host of other comparisons of monatomic gases vs. polyatomic, or congeneric elements of increasing atomic weight, or organic substances of increasing molecular weight (and increasing demand for energy to be stored in their internal rotational modes). Of course, the energy of phase change that is essential to cause such a change at some temperature between 0 K and 298 K is reflected in the  $S_{298}^0$  of solids vs. liquids and liquids vs. gases.

Yes,  $S_{298}^0$  values are the actual entropy content of substances at 298 K, but students can have a far better sense that these are not just abstract numbers for a difficult concept, if they are told that the numbers are *related to* the actual amount of energy as heat that was given to each substance so that it could exist at 298 K.

## **2. A Rapid Introduction to Entropy Change in Mixing; The Importance of the Entropy Change in Mixing**

Because the time allotted for thermodynamics in the beginning course is so extremely limited, the topic of entropy change in mixtures cannot be treated in any detail and often is omitted. However, if the course has its focus on energy dispersal in presenting entropy and spontaneity, as emphasized in this article, only a few sentences are needed to help students see how the entropy of mixtures clarifies their understanding of all colligative effects.

When two liquids are mixed, or a solid solute is added to a solvent, no matter how small or how large a volume change occurs, the motional energy of the molecules of each component has become more dispersed in the resulting solution.<sup>3</sup> This means that the entropy of each component has increased. Then, because the solvent in any solution has its motional energy more dispersed, its molecules less tend to leave that solution compared to solvent molecules in pure solvent. (In some texts this is called “a reduction in escaping tendency”.)

If a solution is heated to the normal boiling point of a solvent, it is clear that the solvent molecules would not escape to the vapor phase in the same quantities as from pure solvent at that temperature, i.e., not in sufficient quantities to equal the atmospheric pressure. That is why the temperature of solutions must be raised above the normal boiling point of the solvent to cause boiling.

Similarly, when a solution is cooled to the normal freezing point of the solvent, the energy of the solvent molecules is so dispersed that they do not readily arrange themselves so that a solid could form as it does in the pure solvent. The temperature of the solution must be lowered below the normal freezing point before the lesser energy of the solvent molecules compensates for their greater dispersion and, moving more slowly, they can escape the solution to form solid.

Osmosis is a process that involves a semi-permeable membrane (that allows only solvent molecules to pass through it) between a solution and some pure solvent. Only the pure solvent will pass through the membrane to the solution, and not the reverse, because the molecules of the solvent have their motional energy more dispersed if they are in the solution – their entropy will increase, the sign of a spontaneous process. Movement in the opposite direction, from solution to solvent, would mean a non-spontaneous decrease in spreading out of motional energy.

### **Summary**

Over the past century, experts in thermodynamics have not well supported non-

specialists so that instructors could explain the meaning of the second law and of entropy in simple terms. The second law that can be simply stated and is based on fundamental thermodynamics is “Energy of all types changes from being localized to becoming dispersed or spread out, if it is not hindered from doing so. The overall process is measured by the increase in thermodynamic entropy.”

Entropy is not ‘disorder’ and entropy change is not ‘from order to disorder’. Entropy measures the dispersal of energy: how much energy is spread out in a process, or how widely spread out it becomes – at a specific temperature. In chemistry the energy that entropy measures is ‘motional energy’, the translational, vibrational and rotational energy of molecules and, if applicable, phase change energy. (Bond energy is only involved when chemical reactions occur.)

Beyond the many topics in beginning thermodynamics that the above viewpoint simplifies, a new insight is realizing that  $S^{\circ}_{298}$  values are rough relative indices of the amount of energy that a substance must have to exist in its normal form at 298 K. More important, three or four sentences are all that are needed to show beginners why there is an entropy change in mixing a solute and a solvent – the key to understanding all colligative effects.

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### Notes

1. Nearly all US general chemistry textbooks prior to 2000 had an illustration or a description of a disorderly desk, or messy student room, or shuffled cards as an *example* (a minority of texts said “an analogy”) of an increase in entropy. This is absurd. Macro objects do not undergo any thermodynamic change of state by simply being rearranged in space as was established in a 1999 article [11]. Due to that article, no US college/university chemistry text published since 2004 has such a misleading illustration.

2. The more complete statement is “Energy of all type changes from being localized to becoming dispersed or spread out, if it is not hindered from doing so. The overall process is an increase in thermodynamic entropy, **enabled** in chemistry by the motional energy of molecules or the energy from bond energy change and **actualized** because the process makes available a larger number of microstates, a maximal probability.

The two factors, energy and probability, are both necessary for thermodynamic entropy change but neither is sufficient alone. In sharp contrast, information ‘entropy’ and ‘sigma entropy’ of physics ( $\sigma = S/k_B$ ) depend only on the one factor of probability,  $\ln W$ .”

This complete statement is more than should be shared with beginning students! However, in this article I have diligently tried to imply that motional energy *dispersal* is the most obvious sign of a process of entropy change, but not that motional energy per se is the whole of entropy change: Although for simplicity, I do not explicitly talk about the second factor of probability, of providing access to additional microstates, *this factor is included by the process itself* when we talk about energy *dispersal*. (This is true whether it be a *possible* increase in volume or energy as heat *becoming available* to the system or a solvent that *can dissolve* a solute.) Kinetic molecular energy in and of itself does not imply an entropy increase if a gas is presented with a larger volume; it is the probability of additional microstates in that larger volume that together with the enabling motional energy makes entropy change possible.

Textbooks that emphasize “positional entropy” or “configurational entropy” for gas expansion or for mixing and say nothing about the motional energy (unchanged in total amount, but dispersed in greater space) are essentially calculating only the second factor of probability and confusing the student by not mentioning the necessary enabling factor of motional energy [12].

3. The amount of the entropy change, the equations, need not be mentioned in the beginning course. They are developed via statistical mechanics and have been called ‘configurational entropy’ because the procedure depends of dividing a liquid into ‘cells’, often identified with “positions” or “locations”. However, each cell represents a microstate that in thermodynamic entropy must contain the entire energy of the whole macrosystem. The combinatorial count of those cells results in the well-known equations for mixing. (See [12].)

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## ЕНТРОПИЯТА ОТ СЪВРЕМЕННА ГЛЕДНА ТОЧКА

**Резюме.** Повечето от студентите, а навярно и повечето от техните преподаватели, които не са специалисти по физикохимия и термодинамика, казват, че вторият принцип на термодинамиката и ентропията не са между любимите им теми. Навярно в основата на това е злополучното твърдение на Болцман от 1998 г., че „ентропията е безпорядък“. **Ентропията не е безпорядък, нито пък промяната на ентропията означава преход от ред към безпорядък.** Всички вещества при температура над 1 К вече са в състояние на безпорядък с брой на микросъстоянията по-голям от  $10^{26\,000\,000\,000\,000\,000\,000}$  [1], така че в реалните системи да се говори за някакъв ред, изглежда лишено от смисъл. Още по-неуместно е да се „обяснява“ ентропията с примери на хаотично разпръснати материални обекти, например карти за игра или разхвърляни листа върху писмена маса.

Тази статия съдържа подробен анализ и препоръки как трябва да се тълкува ентропията от съвременна гледна точка. Дори читателят да не се съгласи с всичко, което предлага авторът, статията съдържа богата храна за размисъл и ценни методични указания. Усилията му да въведе в обръщение защитаваните от него представи дават резултат — в повечето от новите издания на американските учебници по обща химия твърдението „ентропията е безпорядък“ вече не може да се намери.



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