

THE ESSENCE OF ENTROPY

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WHO AMONG US, the initiated, has never paused in the midst of a second-law problem to ask, "Is there really such a thing as entropy?" As an unabashed admission of such waverings of faith, this essay attempts to answer the question. It is an examination of paradoxes and putative interpretations of entropy in search of its essence.

THE QUANTUM-STATISTICAL VIEW

Quantization of energy is the salient feature that distinguishes quantum mechanics from classical mechanics. Because a large number of quantum states are available to a single molecule and an enormous number of molecules are present, the number of quantum states accessible to a system of thermodynamic interest is an astronomically large number. In addition to this, the quantum state of the system is continually changing as a result of the motion and collisions of the molecules. It now becomes obvious that to calculate the thermodynamic properties of such a system, some type of statistical averaging process must be used. Fortunately, the extremely large size of the statistical population insures the success of such an averaging procedure and permits certain convenient simplifications in the attendant mathematics.

The average value of any thermodynamic property, X , is calculated in the following manner

$$\bar{X} = \sum P_i X_i \quad (1)$$

where P_i is the probability that the system is in the i^{th} quantum state, and X_i is the value of the property when the system occupies the i^{th} quantum state. In

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assigning probabilities to quantum states the following rules are followed:

- 1) Quantum states of equal energy have equal probabilities.
- 2) The statistical weight of a quantum state depends upon the energy of that state and is proportional to $\exp(-E/kT)$.

The probability of finding the system in the i^{th} quantum state with energy E_i is

$$P_i = \frac{\exp(-E_i/kT)}{\sum \exp(-E_i/kT)} \quad (2)$$

The summation in the denominator is taken over all quantum states and is a normalizing factor needed to make the sum of the probabilities of all states equal to unity. This sum will be denoted by Z and is referred to as the partition function.

$$Z = \sum \exp(-E_i/kT) \quad (3)$$

The partition function provides the bridge between statistical mechanics and thermodynamics, for it can be shown that the thermodynamic properties are related in a fairly simple manner to the partition function. The function A' is defined by

$$A' = -kT \ln Z \quad (4)$$

and it can be shown that this function has the properties of the Helmholtz Free Energy.

The statistical entropy can be calculated from Eq. 4 via the thermodynamic relation

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

In terms of the partition function this becomes

$$S = k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (5)$$

which after some manipulation can be written in terms of probabilities

$$S = -k \sum P_i \ln P_i \quad (6)$$

In an isolated system the internal energy is invariant and all quantum states have the same energy level. Thus, our probability rules require that all quantum states be equally probable and

$$P_i = \frac{1}{\Omega}$$

where Ω is the total number of quantum states accessible to the system. When this probability is substituted into Eq. 6, the statistical entropy of an isolated system becomes

$$S = k \ln \Omega \quad (7)$$

For a spontaneous change occurring in an isolated system we write

$$S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1} \quad (8)$$

and note that the required condition $S_2 > S_1$ dictates $\Omega_2 > \Omega_1$. This means that the more-stable state is characterized by a larger number of accessible quantum states or a greater number of microscopic configurations (each a quantum state contributing to the number Ω) constituting the macroscopic, or thermodynamic, state.

ENTROPY AS DISORDER

Thermodynamics requires the existence of a function we call entropy and provides the means of calculating its changes as well as the framework within which it can be advantageously employed. While this is sufficient for any application of thermodynamics, we are nevertheless uncomfortable with abstractions and prefer to attach physical significance to the quantities we deal with. Yet, when the physical representation is strained and leads to ambiguous or erroneous interpretation, the effort is counterproductive. This can often be the case with entropy, especially when it is identified with disorder.

From a molecular viewpoint, the association of

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positive entropy changes with an increase in disorder seems quite reasonable for phase changes and mixing. For other processes the association is less obvious and for at least one process (the adiabatic crystallization of a subcooled liquid) it fails completely. Unfortunately, order and disorder are not precise objective terms, but carry considerable subjective bias. For example, on consulting a thesaurus one finds many synonyms for order, including regularity, symmetry, harmony, and uniformity. Conceivably, the absence of gradients or differences in potential could be thought to characterize an ordered state. Thus, one who held this view would never realize that these are the conditions of an equilibrium state when told that equilibrium, or a state of maximum entropy, is identified by a maximum of disorder.

In interpreting Eq. 8 it must be remembered that the subscripts 1 and 2 refer to equilibrium states. The accepted microscopic model of an equilibrium state entails complete randomness with regard to molecular motion—chaos or maximum disorder. It therefore seems inappropriate to regard $\Omega_2 > \Omega_1$ as representing an increase in disorder when each state represents maximum disorder. All we can say is that Ω measures the complexity of our microscopic description of a system, and an increase in Ω can be visualized as a spreading of the system over accessible quantum states. The system moves in the direction of more possibilities.

This is not a physically satisfying representation; it is not based on the virtual observables of our microscopic model (*e.g.*, positions and velocities). Its significance is found on a level removed from these in terms of something which can exist only in the mind—the number of quantum states. This concept comes into being only when we move further into the mental realm and begin to translate the physical into the mathematical description. Rudolf Carnap [1] seems to have had this in mind when he stated that the statistical concept of entropy is a logical instead of a physical concept.

THE GIBBS MIXING PARADOX

In 1875 Willard Gibbs published his landmark paper "On the Equilibrium of Heterogeneous Sub-

stances." In this paper he determined the properties of an ideal gas mixture and found the entropy change on mixing to be

$$\Delta S = -R \sum y_i \ln y_i \quad (9)$$

He had firmly established the validity of this expression but Gibbs was not comfortable with the result, and his deliberations over this result have come to be known as the Gibbs Mixing Paradox.

According to Eq. 9, the entropy change on mixing equimolar quantities of two gases is

$$\Delta S = R \ln 2$$

a result that is seen to be independent of the nature of the gases. Gibbs was concerned about the "degree of dissimilarity" between the two gases which could be visualized being made as close to zero as possible. As long as there is some dissimilarity, the entropy of mixing is $R \ln 2$, but when the "degree of dissimilarity" becomes zero (mixing the same gas), the entropy change is zero. Thus, the entropy of mixing depends not on the "degree of dissimilarity," but only on whether any dissimilarity exists. It is this "either-or" situation which constitutes the Gibbs Mixing Paradox. As we have seen, the paradox arises out of classical thermodynamics and does not require a statistical or molecular kinetic context. Several attempts have been made to resolve the paradox with the help of either statistical mechanics, quantum mechanics, or information theory. All have been evaluated by Denbigh and Denbigh [2] and were found wanting.

The usual mixing process is carried out with no recovery of work, and because the heat of mixing is zero, there is no exchange of heat with the surroundings. In fact, there is no external change to indicate that the process has occurred. An ordinary mixing of the same gas could not be distinguished experimentally from the mixing of different gases, although an entropy change occurs in the latter case and not the former. Thus, while Eq. 9 was determined in an indirect, but rigorous, thermodynamic manner, we have seen that the entropy of mixing exhibits curious behavior, and further, we have no means of experimental verification.

Insight into the curious behavior of entropy can be found by considering distinguishable spatial configurations. This can be illustrated with the lattice model of solutions [3]. Here one interprets Ω_1 and Ω_2 in Eq. 8 as the number of spatial arrangements or lattice configurations before and after mixing. Before mixing there is but one configuration, and Ω_1 is unity. After mixing the number of configurations is

$$\Omega_2 = \frac{(N_A + N_B)!}{N_A! N_B!}$$

With these values of Ω_1 and Ω_2 Eq. 8 can be reduced to Eq. 9. Although the lattice model is more appropriate to liquids, we note that Eq. 9 also gives the entropy of mixing in an ideal liquid solution, and thus we may expect that the entropy of mixing gases arises from similar configurational considerations. There are more distinguishable spatial arrangements available, hence a larger number of quantum states available, to a mixture than to a pure gas. The only factor determining the entropy of mixing is the distinguishability of the particles of portion A from the particles of portion B. A reason for this will be proposed later.

THE GIBBS INDISTINGUISHABILITY PARADOX

Eq. 5 may be used to calculate the entropy of an ideal gas once the partition function has been formulated. The only type of energy possessed by a monatomic ideal gas is kinetic energy and because the energy levels, E_i 's, are extremely close together, E can be closely approximated as a continuum, and the summation in Eq. 3 can be replaced by an integral. Omitting the particulars of the calculation, the partition function can be obtained straightforwardly and is

$$Z = V^N \left(\frac{2\pi k}{h^2} mT \right)^{3N/2} \quad (10)$$

The entropy may be obtained by the substitution of Eq. 10 into Eq. 5

$$S = kN \left(\ln V + \frac{3}{2} \ln \left(\frac{2\pi k m T}{h^2} \right) + \frac{3}{2} \right) \quad (11)$$

Entropy is an extensive property, but, unfortunately, not according to Eq. 11. For the simple operation of combining two $\frac{1}{2}$ -mol quantities of the same gas, this equation yields

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

We have already seen that this is the entropy of mixing different gases, but we know that there is no entropy change on mixing the same gas. This problem is sometimes identified as the Gibbs paradox although it is really a special case of the mixing paradox [4].

The problem was resolved by Gibbs in 1902 by the ad hoc correction of dividing the partition function of Eq. 10 by $N!$ —the number of permutations involving N distinguishable entities. This results in the following expression for the entropy

$$S = kN \left(\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi k m T}{h^2} \right) + \frac{5}{2} \right) \quad (12)$$

Eq. 12 satisfies the condition that the entropy be an extensive property. It has become known as the Sackur-Tetrode equation and has been verified experimentally.

Today, in the quantum age of physics, it is customary to specify whether or not the constituent particles of a system are distinguishable. However, in the classical age of Gibbs' day, the particles of an ideal monatomic gas were assumed independent with their motion described by classical mechanics. While there was certainly an impossible computational difficulty in providing the exact description prescribed by the equations of classical mechanics, there was no doubt that in principle, particles could be traced and thus retained their identity. While still holding to the principle of the distinguishability of particles, Gibbs justified the adventitious insertion of $N!$ into Eq. 10 by saying that the interchange of like particles should be of no statistical consequence.

It is interesting to note that the ad hoc adjustment is unnecessary in the case of the internal energy. Combination of Eqs. 4 and 5 shows that the internal energy is

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (13)$$

Regardless of whether the partition function of Eq. 10 is divided by $N!$, the result is the same and correctly shows that U is linear in N . Thus, of the two basic thermodynamic properties, only the entropy requires an adjustment of classical thought by introducing the concept of indistinguishable particles.

Again, it appears that in order to deal successfully with entropy it is necessary to go a step beyond a description of the system in terms of virtual observables. Instead of a model involving physical quantities, we have included factors such as distinguishability which arise from our mathematical treatment and exist only in the mind of the model maker. The focus has been shifted from the system to our representation of the system—again, a move from the physical to the logical realm.

ENTROPY, INFORMATION, AND SUBJECTIVITY

A major tenet of the philosophical underpinning of science is the concept of objective observation—an observer independent of the observed object. An unquestioning acceptance of this concept had prevailed until recent developments in modern physics suggested that it may not be applicable at the sub-

atomic level. Specifically, Bohr's concept of complementarity and Heisenberg's uncertainty principle recognize that the behavior of a system cannot be properly described until the presence of observing instruments is accounted for. This implies that the observer is part of the system and has encouraged in some quarters the advancement of a subjective philosophic view [5].

The concept of objective observation has been challenged only in the sub-atomic realm; it is still firmly entrenched outside this realm, and is unquestioned when dealing with systems of thermodynamic interest. Nevertheless, there exists a tendency to take a subjective viewpoint in regard to entropy when interpreted microscopically from the perspective of information. Recently, Denbigh and Denbigh [2] have convincingly shown that no formal relation exists between thermodynamic entropy, a physical quantity, and a term labeled entropy that arises from information theory and is a logical quantity [6]. However, because the entropy-information association considerably predates information theory [7], it will probably remain well-ingrained despite the Denbighs' efforts.

The putative view interprets the condition $\Omega_2 > \Omega_1$ corresponding to an increase in entropy as an observer's loss of information about the microscopic state of the system. Accordingly, one reasons that there are more possibilities in state 2 and therefore the increase in Ω implies more uncertainty or a loss of information. This view presents two difficulties. First, because Ω is not a virtual observable quantity, it is doubtful that an observer could have access to this type of information. The information associated with Ω concerns not the system, but our description of the system. Second, it is unreasonable to believe that ΔS , a thermodynamic property change which depends on objectively determined macrostates, could also depend on microscopic information gained or lost by an observer.

In an effort to blunt the last criticism, Jaynes [8] has suggested the following carefully worded definition of information.

The entropy of a thermodynamic system is a measure of the degree of ignorance of a person whose sole knowledge about its microstate consists of the values of the macroscopic quantities X_i which define its thermodynamic state. This is a completely "objective" quantity, in the sense that it is a function only of the X_i , and does not depend on anybody's personality. There is then no reason why it cannot be measured in the laboratory.

Here, one wonders what type of knowledge of the

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microstate is lacking. Virtual observables such as position and velocity would be subject to continual fluctuation, and hence an instantaneous determination of these would be of no practical value. The identification of quantum states and the knowledge of their corresponding probabilities would be of obvious value, but these, as we have also shown with Ω , are not virtual observables but rather are mental constructs which allow us to model the system. It would appear then that this unpossessed knowledge of the microstate is either unusable or is an artifact of the microscopic model we have constructed to represent the macrostate of the system. We surmise that Jaynes is speaking of useful microscopic knowledge, but must note that there is a double dose of subjectivity here. First, we have introduced quantities such as Ω which are mental constructs that relate to our description of the system rather than to the system itself. Second, we now say that the macroscopic behavior of the system, as reflected in the value of the entropy, is dependent on the extent of our knowledge of these model parameters.

Let us test Jaynes' interpretation through the use of Eq. 8 that relates the statistical entropy change to Ω_2/Ω_1 . It would seem that a definite informational value could be assigned to the knowledge of Ω regardless of its numerical value. We are not asking which microstate the system is presently in, which would have informational value dependent on the numerical value of Ω , but rather how many microstates are possible. We are dealing with a model parameter, Ω , and therefore the knowledge embodied in its determination should be constant and independent of the macrostate of the system. If this is so, then there is no change in knowledge of microstates between any two macrostates and the informational entropy change is always zero. We reach the same conclusion by noting that the number of position coordinates and velocity components is always $6N$ regardless of the macroscopic state of the system—a constant amount of microscopic knowledge. Thus, the concept of entropy as a measure of microscopic information is inconsistent as well as extremely subjective.

THE ESSENCE OF ENTROPY

The interpretation of entropy in terms of information leads to an extreme subjective position and must

be rejected. On the other hand, it must be confessed that entropy is more subjective, or less objective, than other properties of matter. This is because the existence of a human mind must be assumed before an entropy change for a macroscopic system can be evaluated or, as we have already seen, a microscopic interpretation can be appreciated. In the case of the evaluation of an entropy change, it is first necessary to devise a reversible path and then perform the calculation from the definition

$$\Delta S = \int \frac{dQ_{rev}}{T}$$

This is not an act of rote calculation but is rather a process of mental creation.

While entropy seems the most subjective property, the whole field of thermodynamics is uncomfortably redolent of human intent. The requirement of subscripts on its partial derivatives reminds us that the system is being constrained, or manipulated. Many of its variables lack easy physical correspondence and only seldom is a thermodynamic variable evaluated except as a means of calculating some more "practical" quantity. In fact, it has been suggested that its various applications can be integrated into a coherent whole only by recognizing thermodynamics to be "a means of extending our experimentally gained knowledge of a system or as a framework for viewing and correlating the behavior of the system" [9]. Clearly, the emphasis is on utility. Having arisen from efforts to exploit rather than to observe nature, the laws of thermodynamics cannot be completely cleansed of their earthy taint and are often embarrassing to the scientist for their lack of intellectual purity. Uneasiness with this anthropomorphic quality of thermodynamics has been confessed by P. W. Bridgman, one of its foremost thinkers [10]:

It must be admitted, I think, that the laws of thermodynamics have a different feel from most of the other laws of the physicist. There is something more palpably verbal about them—they smell more of their human origin. The guiding motif is strange to most of physics: namely, a capitalizing of the universal failure of human beings to construct perpetual motion machines of either the first or the second kind. Why should we expect nature to be interested either positively or negatively in the purposes of human beings, particularly purposes of such an unblushingly economic tinge?

Modern science begins with experience, which is by nature local and transitory, and by ratiocination arrives at laws that are considered universal and timeless. These laws usually connect quantities which are not directly related to our sensory experience, even to the extent of being only mental constructs that are often contrary to common sense. (Recall Newton's uneasiness over the need for a gravitational force which acts at a distance.) Thus, the formulations of science are considered to be in the realm of the pure intellect. In recognizing this, Sir Arthur Eddington has referred to the enterprise of science as "mind-stuff" and has expanded this theme most eloquently [11]:

We have found that where science has progressed the farthest, the mind has but regained from nature that which the mind put into nature. We have found a strange footprint on the shores of the unknown. We have devised profound theories, one after another, to account for its origin. At last, we have succeeded in reconstructing the creature that made the footprint. And Lo! it is our own.

Paraphrasing Eddington with the incorporation of Bridgman's thought, we could say that in the case of thermodynamics, that which the mind has regained from nature reflects the economic, or human, quality of the input.

Entropy's human scent can be traced to its derivation. Essential to both the conventional Carnot-cycle proof and the mathematically more elegant Caratheodory proof [12] is the concept of a reversible process. Seldom is this even an approximation of reality. It is a concept understandable only to economic man desiring to reap the most from his attempted taming of nature and can not be considered scientifically objective. Yet, only in this context can an unambiguous interpretation of entropy be found: the total entropy change measures the lost work when a process falls short of this human-scented, value-laden standard. Something on which we have placed value has been lost. This carries over into the microscopic view where the valued commodity is either order or information.

The mixing paradox exposes the incongruity of the value-laden macroscopic view and a naive microscopic view of entropy. The microscopic description of an ideal gas in purely physical terms leads to Eq. 11 and to the conclusion that the process of mixing the same gas is no different from the mixing of different gases. It is the economic or utilitarian aspect of the situation, the work of separation, that discriminates between the processes and forces the inclusion of $N!$ into the microscopic description. The reversal of the mixing

process requires separational work when the gases are different. However, we have neither the need nor the ability to exactly reverse the mixing of portions of the same gas and therefore need expend no separational work. Because the minimum work of separation is $T\Delta S$ for ideal gas mixtures, there must therefore be no entropy change on mixing the same gas. The microscopic description is brought into conformance with the macroscopic situation by requiring indistinguishability of particles. Thus, a utilitarian consideration, human in origin, requires the insertion of a logical (or human-scented) term into the microscopic model.

In failing to examine nature in a disinterested or completely objective manner, we have obtained a quantity, the entropy, which is not completely objective and which can be understood only by an appeal to the human mind. We can only conclude that entropy is neither completely subjective nor completely objective. Its existence can be publicly agreed upon and its consistent use has great utility, but its existence does not seem to be independent of the human mind. It may not be an intrinsic property of matter, but rather an objectively defined quantity which, for our convenience, we may treat as a property. Born of the unnatural union of wish and reality, entropy is objective enough to be useful in dealing with the physical world, but subjective enough that a purely physical interpretation lies beyond our grasp.

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