THE GIBBS PARADOX†

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Abstract: We point out that an early work of J. Willard Gibbs (1875) contains a correct analysis of the "Gibbs Paradox" about entropy of mixing, free of any elements of mystery and directly connected to experimental facts. However, it appears that this has been lost for 100 years, due to some obscurities in Gibbs' style of writing and his failure to include this explanation in his later *Statistical Mechanics*. This "new" understanding is not only of historical and pedagogical interest; it gives both classical and quantum statistical mechanics a different status than that presented in our textbooks, with implications for current research.

CONTENTS

† In *Maximum Entropy and Bayesian Methods*, C. R. Smith, G. J. Erickson, & P. O. Neudorfer, Editors, Kluwer Academic Publishers, Dordrecht, Holland (1992); pp. 1–22.

1. Introduction

J. Willard Gibbs' *Statistical Mechanics* appeared in 1902. Recently, in the course of writing a textbook on the subject, the present writer undertook to read his monumental earlier work on *Heterogeneous Equilibrium* (1875–78). The original purpose was only to ensure the historical accuracy of certain background remarks; but this was superseded quickly by the much more important unearthing of deep insights into current technical problems.

Some important facts about thermodynamics have not been understood by others to this day, nearly as well as Gibbs understood them over 100 years ago. Other aspects of this "new" development have been reported elsewhere (Jaynes 1986, 1988, 1989). In the present note we consider the "Gibbs Paradox" about entropy of mixing and the logically inseparable topics of reversibility and the extensive property of entropy.

For 80 years it has seemed natural that, to find what Gibbs had to say about this, one should turn to his *Statistical Mechanics*. For 60 years, textbooks and teachers (including, regrettably, the present writer) have impressed upon students how remarkable it was that Gibbs, already in 1902, had been able to hit upon this paradox which foretold – and had its resolution only in – quantum theory with its lore about indistinguishable particles, Bose and Fermi statistics, etc.

It was therefore a shock to discover that in the first Section of his earlier work (which must have been written by mid–1874 at the latest), Gibbs displays a full understanding of this problem, and disposes of it without a trace of that confusion over the "meaning of entropy" or "operational distinguishability of particles" on which later writers have stumbled. He goes straight to the heart of the matter as a simple technical detail, easily understood as soon as one has grasped the full meanings of the words "state" and "reversible" as they are used in thermodynamics. In short, quantum theory did not resolve any paradox, because there was no paradox.

Why did Gibbs fail to give this explanation in his *Statistical Mechanics*? We are inclined to see in this further support for our contention (Jaynes, 1967) that this work was never finished. In reading Gibbs, it is important to distinguish between early and late Gibbs. His *Heterogeneous Equilibrium* of 1875–78 is the work of a man at the absolute peak of his intellectual powers; no logical subtlety escapes him and we can find no statement that appears technically incorrect today. In contrast, his *Statistical Mechanics* of 1902 is the work of an old man in rapidly failing health, with only one more year to live. Inevitably, some arguments are left imperfect and incomplete toward the end of the work.

In particular, Gibbs failed to point out that an "integration constant" was not an arbitrary constant, but an arbitrary function. But this has, as we shall see, nontrivial physical consequences. What is remarkable is not that Gibbs should have failed to stress a fine mathematical point in almost the last words he wrote; but that for 80 years thereafter all textbook writers (except possibly Pauli) failed to see it.

Today, the universally taught conventional wisdom holds that "Classical mechanics failed to yield an entropy function that was extensive, and so statistical mechanics based on classical theory gives qualitatively wrong predictions of vapor pressures and equilibrium constants, which was cleared up only by quantum theory in which the interchange of identical particles is not a real event". We argue that, on the contrary, phenomenological thermodynamics, classical statistics, and quantum statistics are all in just the same logical position with regard to extensivity of entropy; they are silent on the issue, neither requiring it nor forbidding it.

Indeed, in the phenomenological theory Clausius defined entropy by the integral of dQ/T over a reversible path; but in that path the size of a system was not varied, therefore the dependence of entropy on size was not defined. This was perceived by Pauli (1973), who proceeded to give the correct functional equation analysis of the necessary conditions for extensivity. But if this is required already in the phenomenological theory, the same analysis is required *a fortiori* in both classical and quantum statistical mechanics. As a matter of elementary logic, no theory can determine the dependence of entropy on the size N of a system unless it makes some statement about a process where N changes.

In Section 2 below we recall the familiar statement of the mixing paradox, and Sec. 3 presents the explanation from Gibbs' *Heterogeneous Equilibrium* in more modern language. Sec. 4 discusses some implications of this, while Sections 5 and 6 illustrate the points by a concrete scenario. Sec. 7 then recalls the Pauli analysis and Sec. 8 reexamines the relevant parts of Gibbs' *Statistical Mechanics* to show how the mixing paradox disappears, and the issue of extensivity of entropy is cleared up, when the aforementioned minor oversight is corrected by a Pauli type analysis. The final result is that entropy is just as much, and just as little, extensive in classical statistics as in quantum statistics. The concluding Sec. 9 points out the relevance of this for current research.

2. The Problem

We repeat the familiar story, already told hundreds of times; but with a new ending. There are n_1 moles of an ideal gas of type 1, n_2 of another noninteracting type 2, confined in two volumes V_1, V_2 and separated by a diaphragm. Choosing $V_1/V_2 = n_1/n_2$, we may have them initially at the same temperature $T_1 = T_2$ and pressure $P_1 = P_2 = n_1RT/V_1$. The diaphragm is then removed, allowing the gases to diffuse through each other. Eventually we reach a new equilibrium state with $n = n_1 + n_2$ moles of a gas mixture, occupying the total volume $V = V_1 + V_2$ with uniform composition, the temperature, pressure and total energy remaining unchanged.

If the gases are different, the entropy change due to the diffusion is, by standard thermodynamics,

$$\Delta S = S_{final} - S_{initial} = nR\log V - (n_1R\log V_1 + n_2R\log V_2)$$

or,

$$\Delta S = -nR[f\log f + (1-f)\log(1-f)] \tag{1}$$

where $f = n_1/n = V_1/V$ is the mole fraction of component 1. Gibbs [his Eq. (297)] considers particularly the case $f = 1/2$, whereupon

$$\Delta S = nR\,\log 2.$$

What strikes Gibbs at once is that this is independent of the nature of the gases, "... except that the gases which are mixed must be of different kinds. If we should bring into contact two masses of the same kind of gas, they would also mix, but there would be no increase of entropy." He then proceeds to explain this difference, in a very cogent way that has been lost for 100 years. But to understand it, we must first surmount a difficulty that Gibbs imposes on his readers.

Usually, Gibbs' prose style conveys his meaning in a sufficiently clear way, using no more than twice as many words as Poincaré or Einstein would have used to say the same thing. But occasionally he delivers a sentence with a ponderous unintelligibility that seems to challenge us to make sense out of it. Unfortunately, one of these appears at a crucial point of his argument; and this may explain why the argument has been lost for 100 years. Here is that sentence:

> "*Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have once been mixed.*"

The decipherment of this into plain English required much effort, sustained only by faith in Gibbs; but eventually there was the reward of knowing how Champollion felt when he realized that he had mastered the Rosetta stone. Suddenly, *everything made sense*; when put back into the surrounding context there appeared an argument so clear and simple that it seemed astonishing that it has not been rediscovered independently dozens of times. Yet a library search has failed to locate any trace of this understanding in any modern work on thermodynamics or statistical mechanics.

We proceed to our rendering of that explanation, which is about half direct quotation from Gibbs, but with considerable editing, rearrangement, and exegesis. For this reason we call it "the explanation" rather than "Gibbs' explanation". We do not believe that we deviate in any way from Gibbs' intentions, which must be judged partly from other sections of his work; in any event, his original words are readily available for comparison. However, our purpose is not to clarify history, but to explain the technical situation as it appears today in the light of this clarification from history; therefore we carry the explanatory remarks slightly beyond what was actually stated by Gibbs, to take note of the additional contributions of Boltzmann, Planck, and Einstein.

3. The Explanation

When unlike gases mix under the conditions described above, there is an entropy increase $\Delta S = nR\log 2$ independent of the nature of the gases. When the gases are identical they still mix, but there is no entropy increase. But we must bear in mind the following.

When we say that two unlike gases mix and the entropy increases, we mean that the gases could be separated again and brought back to their original states by means that would leave changes in external bodies. These external changes might consist, for example, in the lowering of a weight, or a transfer of heat from a hot body to a cold one.

But by the "original state" we do not mean that every molecule has been returned to its original position, but only a state which is indistinguishable from the original one in the macroscopic properties that we are observing. For this we require only that a molecule originally in V_1 returns to V_1. In other words, we mean that we can recover the original *thermodynamic state*, defined for example by specifying only the chemical composition, total energy, volume, and number of moles of a gas; and nothing else. It is to the states of a system thus incompletely defined that the propositions of thermodynamics relate.

But when we say that two identical gases mix without change of entropy, we do not mean that the molecules originally in V_1 can be returned to V_1 without external change. The assertion of thermodynamics is that when the net entropy change is zero, then the original *thermodynamic state* can be recovered without external change. Indeed, we have only to reinsert the diaphragm; since all the observed macroscopic properties of the mixed and unmixed gases are identical, there has been no change in the thermodynamic state. It follows that there can be no change in the entropy or in any other thermodynamic function.

Trying to interpret the phenomenon as a discontinuous change in the physical nature of the gases (*i. e.,* in the behavior of their microstates) when they become exactly the same, misses the point. The principles of thermodynamics refer not to any properties of the hypothesized microstates, but to the observed properties of macrostates; there is no thought of restoring the original microstate. We might put it thus: when the gases become exactly the same, the discontinuity is in what you and I mean by the words "restore" and "reversible".

But if such considerations explain why mixtures of like and unlike gases are on a different footing, they do not reduce the significance of the fact that the entropy change with unlike gases is independent of the nature of the gases. We may, without doing violence to the general principles of thermodynamics, imagine other gases than those presently known, and there does not appear to be any limit to the resemblance which there might be between two of them; but ΔS would be independent of it.

We may even imagine two gases which are absolutely identical in all properties which come into play while they exist as gases in the diffusion cell, but which differ in their behavior in some other environment. In their mixing an increase of entropy would take place, although the process, dynamically considered, might be absolutely identical in its minutest details (even the precise path of each atom) with another process which might take place without any increase of entropy. In such respects, entropy stands strongly contrasted with energy.

A thermodynamic state is defined by specifying a small number of macroscopic quantities such as pressure, volume, temperature, magnetization, stress, etc. – denote them by $\{X_1, X_2, \ldots, X_n\}$ – which are observed and/or controlled by the experimenter; n is seldom greater than 4. We may contrast this with the physical state, or microstate, in which we imagine that the positions and velocities of all the individual atoms (perhaps 10^{24} of them) are specified.

All thermodynamic functions – in particular, the entropy – are by definition and construction properties of the thermodynamic state; $S = S(X_1, X_2, \ldots, X_n)$. A thermodynamic variable may or may not be also a property of the microstate. We consider the total mass and total energy to be "physically real" properties of the microstate; but the above considerations show that entropy cannot be.

To emphasize this, note that a "thermodynamic state" denoted by $X \equiv \{X_1 \ldots X_n\}$ defines a large class $C(X)$ of microstates compatible with X. Boltzmann, Planck, and Einstein showed that we may interpret the entropy of a macrostate as $S(X) = k \log W(C)$, where $W(C)$ is the phase volume occupied by all the microstates in the chosen reference class C. From this formula, a large mass of correct results may be explained and deduced in a neat, natural way (Jaynes, 1988). In particular, one has a simple explanation of the reason for the second law as an immediate consequence of Liouville's theorem, and a generalization of the second law to nonequilibrium conditions, which has useful applications in biology (Jaynes, 1989).

This has some interesting implications, not generally recognized. The thermodynamic entropy $S(X)$ is, by definition and construction, a property not of any one microstate, but of a certain reference class $C(X)$ of microstates; it is a measure of the size of that reference class. Then if two different microstates are in C, we would ascribe the same entropy to systems in those microstates. But it is also possible that two experimenters assign different entropies S, S' to what is in fact the same microstate (in the sense of the same position and velocity of every atom) without either being in error. That is, they are contemplating a different set of possible macroscopic observations on the same system, embedding that microstate in two different reference classes C, C'.

Two important conclusions follow from this. In the first place, it is necessary to decide at the outset of a problem which macroscopic variables or degrees of freedom we shall measure and/or control; and within the context of the thermodynamic system thus defined, entropy will be some function $S(X_1, \ldots, X_n)$ of whatever variables we have chosen. We can expect this to obey the second law $TdS \geq dQ$ only as long as all experimental manipulations are confined to that chosen set. If someone, unknown to us, were to vary a macrovariable X_{n+1} outside that set, he could produce what would appear to us as a violation of the second law, since our entropy function $S(X_1, \ldots, X_n)$ might decrease spontaneously, while his $S(X_1, \ldots, X_n, X_{n+1})$ increases. [We demonstrate this explicitly below].

Secondly, even within that chosen set, deviations from the second law are at least conceivable. Let us return to the mixing of identical gases. From the fact that they mix without change of entropy, we must not conclude that they can be separated again without external change. On the contrary, the "separation" of identical gases is entirely impossible *with or without external change.* If "identical" means anything, it means that there is no way that an "unmixing" apparatus could determine whether a molecule came originally from V_1 or V_2, short of having followed its entire trajectory.

It follows *a fortiori* that there is no way we could accomplish this separation reproducibly by manipulation of any macrovariables $\{X_i\}$. Nevertheless it might happen without any intervention on our part that in the course of their motion the molecules which came from V_1 all return to it at some later time. Such an event is not impossible; we consider it only improbable.

Now a separation that Nature can accomplish already in the case of identical molecules, she can surely accomplish at least as easily for unlike ones. The spontaneous separation of mixed unlike gases is just as possible as that of like ones. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.

4. Discussion

The last sentence above is the famous one which Boltzmann quoted twenty years later in his reply to Zermelo's *Wiederkehreinwand* and took as the motto for the second (1898) volume of his *Vorlesungen über Gastheorie.* Note the superiority of Gibbs' reasoning. There is none of the irrelevancy about whether the interchange of identical particles is or is not a "real physical event", which has troubled so many later writers – including even Schrödinger. As we see, the strong contrast between the "physical" nature of energy and the "anthropomorphic" nature of entropy, was well understood by Gibbs before 1875.

Nevertheless, we still see attempts to "explain irreversibility" by searching for some entropy function that is supposed to be a property of the microstate, making the second law a theorem of dynamics, a consequence of the equations of motion. Such attempts, dating back to Boltzmann's paper of 1866, have never succeeded and never ceased. But they are quite unnecessary; for the second law that Clausius gave us was not a statement about any property of microstates. The difference in ΔS on mixing of like and unlike gases can seem paradoxical only to one who supposes, erroneously, that entropy is a property of the microstate.

The important constructive point that emerges from this is that thermodynamics has a greater flexibility in useful applications than is generally recognized. The experimenter is at liberty to choose his macrovariables as he wishes; whenever he chooses a set within which there are experimentally reproducible connections like an equation of state, the entropy appropriate to the chosen set will satisfy a second law that correctly accounts for the macroscopic observations that the experimenter can make by manipulating the macrovariables *within his set*.

We may draw two conclusions about the range of validity of the second law. In the first place, if entropy can depend on the particular way you or I decide to define our thermodynamic states, then obviously, the statement that entropy tends to increase but not decrease can remain valid only as long as, having made our choice of macrovariables, we stick to that choice.

Indeed, as soon as we have Boltzmann's $S = k \log W$, the reason for the second law is seen immediately as a proposition of macroscopic phenomenology, true "almost always" simply from considerations of phase volume. Two thermodynamic states of slightly different entropy $S_1 - S_2 = 10^{-6}/393$ cal/deg, corresponding to one microcalorie at room temperature, exhibit a phase volume ratio

$$W_1/W_2 = \exp[(S_1 - S_2)/k] = \exp[10^{16}]. \tag{2}$$

Macrostates of higher entropy are sometimes said to 'occupy' overwhelmingly greater phase volumes; put more accurately, macrostates of higher entropy may be *realized* by an overwhelmingly greater number, or range, of microstates. Because of this, not only all reproducible changes between equilibrium thermodynamic states, but the overwhelming majority of all the macrostate changes that could possibly occur – equilibrium or nonequilibrium – are to ones of higher entropy, simply because there are overwhelmingly more microstates to go to, by factors like (2). We do not see why any more than this is needed to understand the second law as a fact of macroscopic phenomenology.

However, the argument just given showing how entropy depends, not on the microstate, but on human choice of the reference class in which it is to be embedded, may appear so abstract that it leaves the reader in doubt as to whether we are describing real, concrete facts or only a particular philosophy of interpretation, without physical consequences.

This is so particularly when we recall that after the aforementioned paper of 1866, Boltzmann spent the remaining 40 years of his life in inner turmoil and outward controversy over the second law, repeatedly changing his position. The details are recounted by Klein (1973). In the end this degenerated into nit–picking arguments over the exact conditions under which his H–function did or did not decrease. But none of this was ever settled or related to the real experimental facts about the second law – which make no reference to any velocity distribution! It behooves us to be sure that we are not following a similar course.

Fortunately, the concrete reality and direct experimental relevance of Gibbs' arguments is easily shown. The actual calculation following is probably the most common one found in elementary textbooks, but the full conditions of its validity have never, to the best of our knowledge, been recognized. The scenario in which we set it is only slightly fanciful; the discovery of isotopes was very nearly a realization of it. As examination of several textbooks shows, that discovery prompted a great deal of confusion over whether entropy of mixing of isotopes should or should not be included in thermodynamics.

5. The Gas Mixing Scenario Revisited.

Presumably, nobody doubts today that the measurable macroscopic properties of argon (i.e. equation of state, heat capacity, vapor pressure, heat of vaporization, etc.) are described correctly by conventional thermodynamics which ascribes zero entropy change to the mixing of two samples of argon at the same temperature and pressure. But suppose that, unknown to us today, there are two different kinds of argon, $A1$ and $A2$, identical in all respects except that $A2$ is soluble in Whifnium, while $A1$ is not (Whifnium is one of the rare superkalic elements; in fact, it is so rare that it has not yet been discovered).

Until the discovery of Whifnium in the next Century, we shall have no way of preparing argon with controllably different proportions of $A1$ and $A2$. And even if, by rare chance, we should happen to get pure $A1$ in volume $V1$, and pure $A2$ in $V2$, we would have no way of knowing this, or of detecting any difference in the resulting diffusion process. Thus all the thermodynamic measurements we can actually make today are accounted for correctly by ascribing zero entropy of mixing to argon.

Now the scene shifts to the next Century, when Whifnium is readily available to experimenters. What could happen before only by rare chance, we can now bring about by design. We may, at will, prepare bottles of pure $A1$ and pure $A2$. Starting our mixing experiment with $n_1 = fn$ moles of $A1$ in the volume $V_1 = fV$, and $n_2 = (1-f)n$ moles of $A2$ in $V_2 = (1-f)V$, the resulting actual diffusion may be identical in every detail, down to the precise path of each atom, with one that could have happened by rare chance before the discovery of Whifnium; but because of our greater knowledge we shall now ascribe to that diffusion an entropy increase ΔS given by Eq (1), which we write as:

$$\Delta S = \Delta S_1 + \Delta S_2 \tag{3}$$

where

$$\Delta S_1 = -nRf \, \log f \tag{4a}$$

$$\Delta S_2 = -nR(1-f) \, \log(1-f) \tag{4b}$$

But if this entropy increase is more than just a figment of our imagination, it ought to have observable consequences, such as a change in the useful work that we can extract from the process.

There is a school of thought which militantly rejects all attempts to point out the close relation between entropy and information, claiming that such considerations have nothing to do with energy; or even that they would make entropy "subjective" and it could therefore could have nothing to do with experimental facts at all. We would observe, however, that the number of fish that you can catch is an "objective experimental fact"; yet it depends on how much "subjective" information you have about the behavior of fish.

If one is to condemn things that depend on human information, on the grounds that they are "subjective", it seems to us that one must condemn all science and all education; for in those fields, human information is all we have. We should rather condemn this misuse of the terms "subjective" and "objective", which are descriptive adjectives, not epithets. Science does indeed seek to describe what is "objectively real"; but our hypotheses about that will have no testable consequences unless it can also describe what human observers can see and know. It seems to us that this lesson should have been learned rather well from relativity theory.

The amount of useful work that we can extract from any system depends – obviously and necessarily – on how much "subjective" information we have about its microstate, because that tells us which interactions will extract energy and which will not; this is not a paradox, but a platitude. If the entropy we ascribe to a macrostate did not represent some kind of human information about the underlying microstates, it could not perform its thermodynamic function of determining the amount of work that can be extracted reproducibly from that macrostate.

But if this is not obvious, it is easily demonstrated in our present scenario. The diffusion will still take place without any change of temperature, pressure, or internal energy; but because of our greater information we shall now associate it with a free energy decrease $\Delta F = -T\Delta S$. Then, according to the principles of thermodynamics, if instead of allowing the uncontrolled irreversible mixing we could carry out the same change of state reversibly and isothermally, we should be able to obtain from it the work

$$W = -\Delta F = T\Delta S. \tag{5}$$

Let us place beside the diaphragm a movable piston of Whifnium. When the diaphragm is removed, the $A2$ will then diffuse through this piston until its partial pressure is the same on both sides, after which we move the piston slowly (to maintain equal $A2$ pressure and to allow heat to flow in to maintain constant temperature), in the direction of increasing V_1. From this expansion of $A1$ we shall obtain the work

$$W_1 = \int_{V_1}^{V} P_1 dV = n_1 RT \log(V/V_1)$$

or from (4a),

$$W_1 = T\Delta S_1 \tag{6}$$

The term ΔS_1 in the entropy of mixing therefore indicates the work obtainable from reversible isothermal expansion of component $A1$ into the full volume $V = V_1 + V_2$. But the initial diffusion of $A2$ still represents an irreversible entropy increase ΔS_2 from which we obtain no work.

Spurred by this partial success, the other superkalic element Whafnium is discovered, which has the opposite property that it is permeable to $A1$ but not to $A2$. Then we can make an apparatus with two superkalic pistons; the Whifnium moves to the right, giving the work $W_1 = T\Delta S_1$, while the Whafnium moves to the left, yielding $W_2 = T\Delta S_2$. We have succeeded in extracting just the work $W = T\Delta S$ predicted by thermodynamics. The entropy of mixing does indeed represent human information; *just the information needed to predict the work available from the mixing.*

In this scenario, our greater knowledge resulting from the discovery of the superkalic elements leads us to assign a different entropy change to what may be in fact the identical physical process, down to the exact path of each atom. But there is nothing "unphysical" about this, since that greater knowledge corresponds exactly to – because it is due to – our greater capabilities of control over the physical process. Possession of a superkalic piston gives us the ability to control a new thermodynamic degree of freedom X_{n+1}, the position of the piston. It would be astonishing if this new technical capability did not enable us to extract more useful work from the system.

This scenario has illustrated the aforementioned greater versatility of thermodynamics – the wider range of useful applications – that we get from recognizing the strong contrast between the natures of entropy and energy, that Gibbs pointed out so long ago.

To emphasize this, note that even after the discovery of superkalic elements, we still have the option not to use them and stick to the old macrovariables $\{X_1 \ldots X_n\}$ of the 20'th Century. Then we may still ascribe zero entropy of mixing to the interdiffusion of $A1$ and $A2$, and we shall predict correctly, just as was done in the 20'th Century, all the thermodynamic measurements that we can make on Argon without using the new technology. Both before and after discovery of the superkalic elements, the rules of thermodynamics are valid and correctly describe the measurements that it is possible to make by manipulating the macrovariables *within the set that we have chosen to use.*

This useful versatility – a direct result of, and illustration of, the "anthropomorphic" nature of entropy – would not be apparent to, and perhaps not believed by, someone who thought that entropy was, like energy, a physical property of the microstate.

6. Second Law Trickery.

Our scenario has verified another statement made above; a person who knows about this new degree of freedom and manipulates it, can play tricks on one who does not know about it, and make him think that he is seeing a violation of the second law. Suppose there are two observers, one of whom does not know about $A1$, $A2$, and superkalic elements and one who does, and we present them with two experiments.

In experiment 1, mixing of a volume V_1 of $A1$ and V_2 of $A2$ takes place spontaneously, without superkalic pistons, from an initial thermodynamic state X_i to a final one X_f without any change of temperature, pressure, or internal energy and without doing any work; so it causes no heat flow between the diffusion cell and a surrounding heat bath of temperature T. To both observers, the initial and final states of the heat bath are the same, and to the ignorant observer this is also true of the argon; nothing happens at all.

In experiment 2 we insert the superkalic pistons and perform the same mixing reversibly, starting from the same initial state X_i. Again, the final state X_f of the argon has the same temperature, pressure, and internal energy as does X_i. But now work W is done, and so heat $Q = W$ flows into the diffusion cell from the heat bath. Its existence and magnitude could be verified by calorimetry. Therefore, for both observers, the initial and final states of the heat bath are now different. To the ignorant observer, an amount of heat Q has been extracted from the heat bath and converted entirely into work: $W = Q$, while the total entropy of the system and heat bath has decreased spontaneously by $\Delta S = -Q/T$, in flagrant violation of the second law!

To the informed observer, there has been no violation of the second law in either experiment. In experiment 1 there is an irreversible increase of entropy of the argon, with its concomitant loss of free energy; in experiment 2, the increase in entropy of the argon is exactly compensated by the decrease in entropy of the heat bath. For him, since there has been no change in total entropy, the entire process of experiment 2 is reversible. Indeed, he has only to move the pistons back slowly to their original positions. In this he must give back the work W, whereupon the argon is returned to its original unmixed condition and the heat Q is returned to the heat bath.

Both of these observers can in turn be tricked into thinking that they see a violation of the second law by a third one, still better informed, who knows that $A2$ is actually composed of two components $A2a$ and $A2b$ and there is a subkalic element Whoofnium – and so on *ad infinitum.*

A physical system always has more macroscopic degrees of freedom beyond what we control or observe, and by manipulating them a trickster can always make us see an apparent violation of the second law.

Therefore the correct statement of the second law is not that an entropy decrease is impossible in principle, or even improbable; rather that it *cannot be achieved reproducibly by manipulating the macrovariables* $\{X_1, \ldots, X_n\}$ *that we have chosen to define our macrostate.* Any attempt to write a stronger law than this will put one at the mercy of a trickster, who can produce a violation of it.

But recognizing this should increase rather than decrease our confidence in the future of the second law, because it means that if an experimenter ever sees an apparent violation, then instead of issuing a sensational announcement, it will be more prudent to search for that unobserved degree of freedom. That is, the connection of entropy with information works both ways; seeing an apparent decrease of entropy signifies ignorance of what were the relevant macrovariables.

7. The Pauli Analysis

Consider now the phenomenological theory. The Clausius definition of entropy determines the difference of entropy of two thermodynamic states of a closed system (no particles enter or leave) that can be connected by a reversible path:

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} \tag{7}$$

Many are surprised when we claim that this is not necessarily extensive; the first reaction is: "Surely, two bricks have twice the heat capacity of one brick; so how could the Clausius entropy possibly not be extensive?" To see how, note that the entropy *difference* is indeed proportional to the number N of molecules whenever the heat capacity is proportional to N and the pressure depends only on V/N; but that is not necessarily true, and when it is true it is far from making the entropy itself extensive.

For example, let us evaluate this for the traditional ideal monoatomic gas of N molecules and consider the independent thermodynamic macrovariables to be (T, V, N). This has an equation of state $PV = NkT$ and heat capacity $C_v = (3/2)\,Nk$, where k is Boltzmann's constant. From this all elementary textbooks find, using the thermodynamic relations $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ and $T(\partial S/\partial T)_V = C_v$:

$$\begin{aligned} S(T_2, V_2, N) - S(T_1, V_1, N) &= \int_1^2 \left[\left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \right] \\ &= Nk \log \frac{V_2}{V_1} + \frac{3}{2}\, Nk \log \frac{T_2}{T_1} \end{aligned} \tag{8}$$

It is evident that this is satisfied by any entropy function of the form

$$S(T, V, N) = k \left[N \log V + \frac{3}{2} N \log T \right] + kf(N) \tag{9}$$

where $f(N)$ is not an arbitrary constant, but an arbitrary function. The point is that in the reversible path (7) we varied only T and V; consequently the definition (7) determines only the dependence of S on T and V. Indeed, if N varied on our reversible path, then (7) would not be correct (an extra 'entropy of convection' term $\int \mu dN/T$ would be needed).

Pauli (1973) noticed this incompleteness of (7) and saw that if we wish entropy to be extensive, then that is logically an additional condition, that we must impose separately. The extra condition is that entropy should satisfy the scaling law

$$S(T, qV, qN) = qS(T, V, N), \qquad 0 < q < \infty \tag{10}$$

Then, substituting (9) into (10), we find that $f(N)$ must satisfy the functional equation

$$f(qN) = qf(N) - qN \log q \tag{11}$$

Differentiating with respect to q and setting $q = 1$ yields a differential equation $Nf'(N) = f(N) - N$, whose general solution is

$$f(N) = Nf(1) - N \log N\,. \tag{12}$$

[alternatively, just set $N = 1$ in (11) and we see the general solution]. Thus the most general extensive entropy function for this gas has the form

$$S(T, V, N) = Nk \left[\log \frac{V}{N} + \frac{3}{2} \log T + f(1)\right]\,. \tag{13}$$

It contains one arbitrary constant, $f(1)$, which is essentially the chemical constant. This is not determined by either the Clausius definition (7) or the condition of extensivity (10); however, one more fact about it can be inferred from (13). Writing $f(1) = \log(Ck^{3/2})$, we have

$$S(T, V, N) = Nk \log \left[\frac{CV(kT)^{3/2}}{N}\right]\,. \tag{14}$$

The quantity in the square brackets must be dimensionless, so C must have the physical dimensions of $(volume)^{-1}(energy)^{-3/2} = (mass)^{3/2}(action)^{-3}$. Thus on dimensional grounds we can rewrite (13) as

$$S(T, V, N) = Nk \left\{\log \frac{V}{N} + \frac{3}{2} \log \left[\frac{mkT}{\zeta^2}\right]\right\}\,. \tag{15}$$

where m is the molecular mass and ζ is an undetermined quantity of the dimensions of action. It might appear that this is the limit of what can be said about the entropy function from phenomenological considerations; however, there may be further cogent arguments that have escaped our attention.

8. Would Gibbs Have Accepted It?

Note that the Pauli analysis *has not demonstrated from the principles of physics that entropy actually should be extensive*; it has only indicated the form our equations must take if it is. But this leaves open two possibilities:

(1) All this is a tempest in a teapot; the Clausius definition indicates that only entropy differences are physically meaningful, so we are free to define the arbitrary additive terms in any way we please. This is the view that was taught to the writer, as a student many years ago.

(2) The variation of entropy with N is not arbitrary; it is a substantive matter with experimental consequences. Therefore *the Clausius definition of entropy is logically*

> *incomplete*, and it needs to be supplemented either by experimental evidence or further theoretical considerations.

The original thermodynamics of Clausius considered only closed systems, and was consistent with conclusion (1). Textbooks for physicists have been astonishingly slow to move beyond it; that of Callen (1960) is almost the only one that recognizes the more complete and fundamental nature of Gibbs' work.

In the thermodynamics of Gibbs, the variation of entropy with N is just the issue that is involved in the prediction of vapor pressures, equilibrium constants, or any conditions of equilibrium with respect to exchange of particles. His invention of the chemical potential μ has, according to all the evidence of physical chemistry, solved the problem of equilibrium with respect to exchange of particles, leading us to conclusion (2); chemical thermodynamics could not exist without it.

Gibbs could predict the final equilibrium state of a heterogeneous system as the one with maximum total entropy subject to fixed total values of energy, mole numbers, and other conserved quantities. All of the results of his *Heterogeneous Equilibrium* follow from this variational principle. He showed that by a mathematical (Legendre) transformation this could be stated equally well as minimum Gibbs free energy subject to fixed temperature and chemical potentials, which form physical chemists have generally found more convenient (however, it is also less general; in extensions to nonequilibrium phenomena there is no temperature or Gibbs free energy, and one must return to the original maximum entropy principle, from which many more physical predictions may be derived).

This preference for one form of the variational principle over the other is largely a matter of our conditioning from previous training. For example, from our mechanical experience it seems intuitively obvious that a liquid sphere has a lower energy than any other shape with the same entropy; yet to most of us it seems far from obvious that the sphere has higher entropy than any other shape with the same energy.

It is interesting to note how the various classical textbooks deal with the question of extensivity; and then how Gibbs dealt with it. Planck (1926, p. 92), Epstein (1937; p. 136) and Zemansky (1943; p. 311) do not give the scaling law (10), but simply write entropy as extensive from the start, apparently considering this too obvious to be in need of any discussion. Callen (1960; p. 26) does write the scaling law, but does not derive it from anything or derive anything from it; thereafter he proceeds to write entropy as extensive without further discussion.

In other words, all of these works simply *assume* entropy to be extensive without investigating the question whether that extensivity follows from, or is even consistent with, the Clausius definition of entropy. More recent textbooks tend to be even more careless in the logic; the only exception known to us is that of Pauli. But let us note how much is lost thereby:

(a) The question of extensivity cannot have any universally valid answer; for there are systems, for example some spin systems and systems with electric charge or gravitational forces, for which the scaling law (10) does not hold because of long–range interactions; yet the Clausius definition of entropy is still valid as long as N is held constant. Such systems cannot be treated at all by a formalism that starts by assuming extensivity.

(b) This reminds us that for any system extensivity of entropy is, strictly speaking, only an approximation which can hold only to the extent that the range of molecular forces is small compared to the dimensions of the system. Indeed, for virtually all systems small deviations from exact extensivity are observable in the laboratory; the experimentalist calls them "surface effects" and we note that Gibbs' *Heterogeneous Equilibrium* gives beautiful treatments of surface tension and electrocapillarity, all following from his single variational principle.

Obviously, then, Gibbs did not assume extensivity as a general property, as did the others noted above. But of course, Gibbs was in agreement with them, that entropy is very nearly extensive for most single homogeneous systems of macroscopic size. But he is careful in saying this, adding the qualification "- - - , for many substances at least, - - -". Then he gives such relations as $G = \sum \mu_i n_i$ which hold in the cases where entropy can be considered extensive to sufficient accuracy.

But Gibbs never does give an explicit discussion of the circumstances in which entropy is or is not extensive! He appears at first glance to evade the issue by the device of talking only about the total entropy of a heterogeneous system, not the entropies of its separate parts. Movement of particles from one part to another is disposed of by the observation that, if it is reversible, then the total entropy is unchanged; and that is all he needs in order to discuss all his phenomena, including surface effects, fully.

But on further meditation we realize that Gibbs did not evade any issue; rather, his far deeper understanding enabled him to see that there was no issue. He had perceived that, when two systems interact, *only the entropy of the whole is meaningful.* Today we would say that the interaction induces correlations in their states which makes the entropy of the whole less than the sum of entropies of the parts; and it is the entropy of the whole that contains full thermodynamic information. This reminds us of Gibbs' famous remark, made in a supposedly (but perhaps not really) different context: "The whole is simpler than the sum of its parts." How could Gibbs have perceived this long before the days of quantum theory?

This is one more example where Gibbs had more to say than his contemporaries could absorb from his writings; over 100 years later, we still have a great deal to learn by studying how Gibbs manages to do things. For him, entropy is not a local property of the subsystems; it is a "global" property like the Lagrangian of a mechanical system; *i.e.* it presides over the whole and determines, by its variational properties, all the conditions of equilibrium – just as the Lagrangian presides over all of mechanics and determines, by its variational properties, all the equations of motion.

Up to this point we have been careful to consider only the phenomenology and experimental facts of thermodynamics, in order to make their independent logical status clear. Most discussions of these matters mix up the statistical and phenomenological aspects from the start, in a way that we think generates and perpetuates confusion. In particular, this has obscured the fact that the fundamental operational definitions of such terms as equilibrium, temperature, and entropy – and the statements of the first and second laws – involve only the macrovariables observed in the laboratory. They make no reference to microstates, much less to any velocity distributions, probability distributions, or correlations. As Helmholtz and Planck stressed, this much of the field has a validity and usefulness quite independent of whether atoms and microstates exist.

9. Gibbs' Statistical Mechanics

Now we turn to the final work of Gibbs, which appeared 27 years after his *Heterogeneous Equilibrium*, and examine the parts of it which are relevant to these issues. We expect that a statistical theory might supplement the phenomenology in two ways. Firstly, if our present microstate theory is correct, we would get a deeper interpretation of the basic reason for the phenomenology, and a better understanding of its range of validity; if it is not correct, we might find contradictions that would provide clues to a better theory. Secondly, the theoretical explanation would predict generalizations; the range of possible nonequilibrium conditions is many orders of magnitude greater than that of equilibrium conditions, so if new reproducible connections exist they would be almost impossible to find without the guidance of a theory that tells the experimenter where to look.

It is generally supposed that Gibbs coined the term "Statistical Mechanics" for the title of this book. But in reading Gibbs' *Heterogeneous Equilibrium* we slowly developed a feeling, from the above handling of entropy and other incidents in it, that his thermodynamic formalism corresponds so closely to that of Statistical Mechanics – in particular, the grand canonical ensemble – that he must have known the main results of the latter already while writing the former.

This suspicion was confirmed in part by the discovery that the term "Statistical Mechanics" appears already in an Abstract of his dated 1884, of a paper read at a meeting but which, to the best of our knowledge, was never published and is lost. The abstract states that he will be concerned with Liouville's theorem and its applications to astronomy and thermodynamics; presumably, the latter is what appears in the first three Chapters of his *Statistical Mechanics*, 18 years later.

It seems likely, then, that Gibbs found the main results of his *Statistical Mechanics* very early; perhaps even as early as his attending Liouville's lectures in 1867. But he delayed finishing the book for many years, probably because of mysteries concerning specific heats that he kept hoping to resolve, but could not before the days of quantum mechanics; his remarks in the preface indicate how much this bothered him. The parts that seemed unsatisfactory would have been left unwritten in final form until the last possible moment; and those parts would be the ones where we are most likely to find small errors or incomplete statements.

Gibbs' concern about specific heats is no longer an issue for us today, but we want to understand why classical statistical mechanics appeared (at least to readers of the book) to fail badly in the matter of extensivity of entropy. He introduces the canonical ensemble in Chapter IV, as a probability density $P(p_1 \ldots q_n)$ in phase space, and writes (his Eq. 90; hereafter denoted by SM.90, etc.):

$$\eta = \frac{\psi - \epsilon}{\Theta} = \log P \qquad (SM.90)$$

where $\epsilon = \epsilon(p_1 \ldots q_n)$ is the Hamiltonian (same as the total energy, since he considers only conservative forces), Θ is the "modulus" of the distribution, and ψ is a normalization constant chosen so that $\int P dp_1, \ldots, dq_n = 1$. He notes that Θ has properties analogous to those of temperature, and strengthens the analogy by introducing externally variable coordinates a_1, a_2 with the meaning of volume, strain tensor components, height in a gravitational field, etc. with their conjugate forces $A_i = -\partial\epsilon/\partial a_i$. On an infinitesimal change (*i.e.*, comparing two slightly different canonical distributions) he finds the identity

$$d\overline{\epsilon} = -\Theta d\overline{\eta} - \sum \overline{A}_i \, da_i \qquad (SM.114)$$

where the bars denote canonical ensemble averages. He notes that this is identical in form with a thermodynamic equation if we neglect the bars and consider $(-\overline{\eta})$ as the analog of entropy, which he denotes, incredibly, by η.

Here Gibbs anticipates – and even surpasses – the confusion caused 46 years later when Claude Shannon used H for what Boltzmann had called $(-H)$. In addition, the prospective reader is warned that from p. 44 on, Gibbs uses the same symbol η to denote both the "index of probability" as in (SM.90), and the thermodynamic entropy, as in (SM.116); his meaning can be judged only from the context. In the following we deviate from Gibbs' notation by using Clausius' symbol S for thermodynamic entropy.

Note that Gibbs, writing before the introduction of Boltzmann's constant k, uses Θ, with the dimensions of energy, for what we should today call kT; consequently his thermodynamic analog of entropy is what we should today call S/k, and is dimensionless.*

* In this respect Gibbs' notation is really neater formally – and more cogent physically – than ours; for Boltzmann's constant is only a correction factor necessitated by our custom of measuring temperature in arbitrary units derived from the properties of water. A really fundamental system of units would have $k \equiv 1$ by definition.

The thermodynamic equation analogous to (SM.114) is then

$$d\epsilon = T dS - \sum A_i \, da_i \tag{SM.116}$$

Now Gibbs notes that in the thermodynamic equation, the entropy S "is a quantity which is only defined by the equation itself, and incompletely defined in that the equation only determines its differential, and the constant of integration is arbitrary. On the other hand, the $\overline{\eta}$ in the statistical equation has been completely defined." Then interpreting $(-\overline{\eta})$ as entropy leads to the familiar conclusion, stressed by later writers, that entropy is not extensive in classical statistical mechanics.

Right here, we suggest, two fine points were missed, but the Pauli analysis conditions us to recognize them at once. The first is that normalization requires that P has the physical dimensions $(\text{action})^{-n}$, while the argument of a logarithm should be dimensionless. To obtain a truly dimensionless $\overline{\eta}$, we should rewrite (SM.90) as $\eta = \log(\xi^n P)$ where ξ is some quantity of the dimensions of action. This point has, of course, been noted before many times.

The second fine point is more serious and does not seem to have been noted before, even by Pauli; the question whether $-\overline{\eta}$ is the proper statistical analog of thermodynamic entropy cannot be answered merely by examination of (SM.114). Let us denote by σ the correct (dimensionless) statistical analog of entropy that Gibbs was seeking. The trouble is again that in (SM.114) we are varying only ϵ and the a_i; consequently it determines only how σ varies with ϵ and the a_i. As in (9), from Gibbs' (SM.114) we can infer only that the correct statistical analog of entropy must have the form

$$\sigma = -\overline{\eta} + g(N), \tag{16}$$

where $N = n/3$ denotes as before the number of particles. Again, the "constant of integration" is not an arbitrary constant, but an arbitrary function $g(N)$. Clearly, no definite "statistical analog" of entropy has been defined until the function $g(N)$ is specified.

However, in defense of Gibbs, we should note that at this point he is not discussing extensivity of entropy at all, and so he could reply that he is considering only fixed values of N, and so is in fact concerned only with an arbitrary constant. Thus one can argue whether it was Gibbs or his readers who missed this fine point (it is only 160 pages later, in the final two paragraphs of the book, that Gibbs turns at last to the question of extensivity).

In any event, a point that has been missed for so long deserves to be stressed. For 60 years, all scientists have been taught that in the issue of extensivity of entropy we have a fundamental failure, not just of classical statistics, but of classical *mechanics*, and a triumph of quantum mechanics. The present writer was caught in this error just as badly as anybody else, throughout most of his teaching career. But now it is clear that the trouble was not in any failure of classical mechanics, but in our own failure to perceive all the freedom that Gibbs' (SM.114) allows. If we wish entropy to be extensive in classical statistical mechanics, we have only to choose $g(N)$ accordingly, *as was necessary already in the phenomenological theory.* But curiously, nobody seems to have noticed, much less complained, that Clausius' definition $S \equiv \int dQ/T$ also failed in the matter of extensivity.

But exactly the same argument will apply in quantum statistical mechanics; in making the connection between the canonical ensemble and the phenomenological relations, if we follow Gibbs and use the Clausius definition of entropy as our sole guide in identifying the statistical analog of entropy, it will also allow an arbitrary additive function $h(N)$ and so it will not require entropy to be extensive any more than does classical theory. Therefore the whole question of in what way – or indeed, whether – classical mechanics failed in comparison with quantum mechanics in the matter of entropy, now seems to be re–opened.

Recognizing this, it is not surprising that entropy has been a matter of unceasing confusion and controversy from the day Clausius discovered it. Different people, looking at different aspects of it, continue to see different things because there is still unfinished business in the *fundamental definition of entropy*, in both the phenomenological and statistical theories.

In the case of the canonical ensemble, the oversight about extensivity is easily corrected, in a way exactly parallel to that indicated by Pauli. In the classical case, considering a gas defined by the thermodynamic variables $A_1 = p =$ pressure, $a_1 = V =$ volume, Gibbs' statistical analog equation (SM.114) may be written

$$d\overline{\epsilon} = -\Theta d\overline{\eta} - \overline{p} dV \tag{17}$$

The statistical analog of entropy must have the form (16); and if we want it to be extensive, it must also satisfy the scaling law (10). Now from the canonical ensemble for an ideal gas, with phase space probability density

$$P = \frac{1}{(2\pi m\Theta)^{3N/2} V^N} \exp\left[-\sum \frac{p_i^2}{2m\Theta}\right] \tag{18}$$

(which we note is dimensionally correct and normalized, although it does not contain Planck's constant), we have from the dimensionally corrected (SM.90),

$$-\overline{\eta} = N \log V + \frac{3N}{2}\left[\log(2\pi m\Theta) + 1\right] - 3N \log \xi \tag{19}$$

Then, substituting (19) and (16) into (10), we find that $g(N)$ must satisfy the same functional equation (11), with the same solution (13). The Gibbs statistical analog of entropy (16) is now

$$\sigma = N\left[\log \frac{V}{N} + \frac{3}{2}\log \frac{2\pi m\Theta}{\xi^2} + \frac{3}{2} + g(1)\right]. \tag{20}$$

The extensive property (9) now holds, and the constants $g(1)$ and ξ combine to form essentially the chemical constant. This is not determined by the above arguments, just as it was not determined in the phenomenological arguments.

Therefore it might appear that the shortcoming of classical statistical mechanics was not any failure to yield an extensive entropy function, but only its failure to determine the numerical value of the chemical constant. But even this criticism is not justified at present; the mere fact that it is believed to involve Planck's constant is not conclusive, since e and c are classical quantities and Planck's constant is only a numerical multiple of e^2/c. We see no reason why the particular number 137.036 should be forbidden to appear in a classical calculation. Since the problem has not been looked at in this way before, and nobody has tried to determine that constant from classical physics, we see no grounds for confident claims either that it can or cannot be done.

But the apparent involvement of e and c suggests, as Gibbs himself noted in the preface to his *Statistical Mechanics*, that electromagnetic considerations may be important even in the thermodynamics of electrically neutral systems. Of course, from our modern knowledge of the electromagnetic structure of atoms, the origin of the van der Waals forces, *etc.*, such a conclusion is in no way surprising. Electromagnetic radiation is surely one of the mechanisms by which thermal equilibrium is maintained in any system whose molecules have dipole or quadrupole moments, rotational/vibrational spectrum lines, *etc.* and no system is in true thermal equilibrium until it is bathed in black–body radiation of the same temperature.

At this point the reader may wonder: Why do we not turn to the grand canonical ensemble, in which all possible values of N are represented simultaneously? Would this enable us to determine by physical principles how entropy varies with N? Unfortunately, it cannot do so as long as we try to set up entropy in statistical mechanics by finding a mere *analogy* with the Clausius definition of entropy, $S = \int dQ/T$. For the Clausius definition was itself logically incomplete in just this respect; the information needed is not in it.

The Pauli correction was an important step in the direction of getting "the bulk of things" right pragmatically; but it ignores the small deviations from extensivity that are essential for treatment of some effects; and in any event it is not a fundamental theoretical principle. A truly general and quantitatively accurate definition of entropy must appeal to a deeper principle which is hardly recognized in the current literature, although we think that a cogent special case of it is contained in some early work of Boltzmann, Einstein, and Planck.

10. Summary and Unfinished Business.

We have shown here that the Clausius definition of entropy was incomplete already in the phenomenological theory; therefore it was inadequate to determine the proper analog of entropy in the statistical theory. The phenomenological theory, classical statistical mechanics, and quantum statistical mechanics, were all silent on the question of extensivity of entropy *as long as one tried to identify the theoretical entropy merely by analogy with the Clausius empirical definition.* The Pauli type analysis is a partial corrective, which applies equally well and is equally necessary in all three cases, if we wish entropy to be extensive.

It is curious that Gibbs, who surely recognized the incompleteness of Clausius' definition, did not undertake to give a better one in his *Heterogeneous Equilibrium*; he merely proceeded to use entropy in processes where N changes and never tried to interpret it in such terms as phase volume, as Boltzmann, Planck, and Einstein did later. In view of Gibbs' performance in other matters, we cannot suppose that this was a mere oversight or failure to understand the logic. More likely, it indicates some further deep insight on his part about the difficulty of such a definition.

A consequence of the above observations is that the question whether quantum theory really gave an extensive entropy function and determined the value of the chemical constant, also needs to be re–examined. Before a quantum theory analog of entropy has been defined, one must consider processes in which N changes. If we merely apply the scaling law as we did above, the quantum analog of entropy will have the form (20) in which ξ is set equal to Planck's constant; but a new arbitrary constant $\alpha \equiv f_q(1)$ is introduced that has not been considered heretofore in quantum statistics. If we continue to define entropy by the Clausius definition (7), quantum statistics does not determine α.

This suggests that, contrary to common belief, the value of the chemical constant is not determined by quantum statistics as currently taught, any better than it was by classical theory. It seems to be a fact of phenomenology that quantum statistics with $\alpha = 0$ accounts fairly well for a number of measurements; but it gives no theoretical reason why α should be zero. The Nernst Third Law of Thermodynamics does not answer this question; we are concerned rather with the experimental accuracy of such relations as the Sackur–Tetrode formula for vapor pressure. Experimental vapor pressures enable us to determine the difference $\alpha_{gas} - \alpha_{liquid}$. Therefore we wonder how good is the experimental evidence that α is not needed, and for how many substances we have such evidence.

For some 60 years this has not seemed an issue because one thought that it was all settled in favor of quantum theory; any small discrepancies were ascribed to experimental difficulties and held to be without significance. Now it appears that the issue is reopened; it may turn out that α is really zero for all systems; or it may be that giving it nonzero values may improve the accuracy of our predictions. In either case, further theoretical work will be needed before we can claim to understand entropy.

There is a conceivable simple resolution of this. Let us conjecture that the present common teaching is correct; *i.e.*, that new precise experiments will confirm that present quantum statistics does, after all give the correct chemical constants for all systems. If this conjecture proves to be wrong, then some of the following speculations will be wrong also.

We should not really expect that a phenomenological theory, based necessarily on a finite number of observations that happened to feasible in the time of Clausius – or in our time – could provide a full definition of entropy in the greatest possible generality. The question is not an empirical one, but a conceptual one; and only a definite theoretical principle, that rises above all temporary empirical limitations, can answer it. In other words, it is a mistake to try to define entropy in statistical mechanics merely by analogy with the phenomenological theory. The only truly fundamental definition of entropy must be provided directly by the statistical theory itself; and comparison with observed phenomenology takes place only afterward.

This is how relativity theory was constituted: empirical results like the Michelson–Morley experiment might well suggest the principle of relativity; but the deduction of the theory from this principle was made without appeal to experiment. After the theory was developed, one could test its predictions on such matters as abberation, time dilatation, and the orbits of fast charged particles.

The answer is rather clear; for both Clausius and Gibbs the theoretical principles that were missing did not lie in quantum theory (that was only a quantitative detail). The fundamental principles were the principles of probability theory itself; how does one set up a probability distribution over microstates – classical or quantum – that represents correctly our information about a macrostate? If that information includes all the conditions needed in the laboratory to determine a reproducible result – equilibrium or nonequilibrium – then the theory should be able to predict that result.

We suggest that the answer is the following. For any system the entropy is a property of the macrostate (more precisely, it is a function of the macrovariables that we use to define the macrostate), and it is defined by a variational property: it is the upper bound of $-k\,\mathrm{Tr}(\rho\,\log\rho)$ over all density matrices that agree with those macrovariables. This will agree with the Clausius and Pauli prescriptions in those cases where they were valid; but it automatically provides the extra terms that Gibbs needed to analyze surface effects, if we apply it to the finite sized systems that actually exist in the laboratory.

When thermodynamic entropy is defined by this variational property, the long confusion about order and disorder (which still clutters up our textbooks) is replaced by a remarkable simplicity and generality. The conventional Second Law follows *a fortiori*: since entropy is defined as a constrained maximum, whenever a constraint is removed, the entropy will tend to increase, thus paralleling in our mathematics what is observed in the laboratory. But it provides generalizations far beyond that, to many nonequilibrium phenomena not yet analyzed by any theory.

And, just as the variational formalism of Gibbs' *Heterogeneous Equilibrium* could be used to derive useful rules of thumb like the Gibbs phase rule, which were easier to apply than the full formalism, so this generalization leads to simple rules of thumb like the phase volume interpretation $S = k\log W$ of Boltzmann, Einstein, and Planck, which are not limited to equilibrium conditions and can be applied directly for very simple applications like the calculation of muscle efficiency in biology (Jaynes, 1989).

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