CHAPTER 9
A SEARCH FOR CONCEPTUAL CLOSURE

9.1 SCIENCE AND THERMODYNAMICS

Having previously noted its strangeness and Bridgman's discomfort with its human scent, it should be added that thermodynamics is more applied and goal-oriented than most of science. This has been its character since its very beginnings deeply rooted in the study of heat engines and is attested to by the fact that the vast majority of its practitioners are engineers interested in obtaining practical results.

As an illustration of its applied nature, consider one of its major achievements, the simplification of calculations involving chemical equilibrium and heat effects due to chemical reactions. This is accomplished through the concepts of standard state and formation reaction which allow the real process to be replaced by a contrived computational path, with hypothetical states, that contains a single step to which all chemical effects and only chemical effects are assigned. The result of this is the tables of heats and free energies of formation that are so useful to chemical engineers in making process calculations — an outstanding example of data reduction! Here it is obvious that thermodynamics is goal-directed and being employed to ends that science would surely consider to be mundane and pragmatic, or even economic.

Thermodynamics does provide a framework for viewing certain phenomena, however, it is a framework that is usually not particularly insightful and one that the practitioner has to learn to use. To say, for example, that a phase change occurs because the free energy change is negative or that phase equilibrium obtains when fugacities are equal is extremely useful to one who possesses the necessary experimental information and wishes to make a quantitative calculation, but it provides little insight into the mechanism of the phenomena other than a "feel" that an experienced practitioner may eventually develop. As an example, consider the thermodynamic explanation of freezing point depression. Here equilibrium exists between pure solid and a liquid solution and the equating of fugacities can be written functionally as

$$f_i^S(\ T\ )= f_i^L(\ T, x\ )$$

The addition of solute to the solution increases the mol fraction x and thereby decreases the liquid-phase fugacity, f^L. As the fugacity of the pure solid, f^S, depends only on temperature, the temperature must decrease in order that the decrease in liquid-phase fugacity be matched by that of the solid phase. Because thermodynamics supplies relationships that allow quantitative determination of these fugacity changes, one is able to determine exactly the depression of the freezing point corresponding to any solution concentration. However, one could hardly say that this thermodynamic approach is particularly insightful in terms of what are considered to be fundamental quantities of scientific description: the masses and motions of molecules and the forces between them. Instead, thermodynamics offers a calculation method based on precise relationships involving the fugacity which is nothing more than a properly defined function — a useful thermodynamic artifact with no intrinsic value.

While there is no question that thermodynamics is a part of science, it differs in that while science seeks the ultimate explanation of phenomena, thermodynamics is content to deal with phenomena in a way that is reliable and productive but not necessarily insightful.   Science is considered to be the disinterested pursuit of knowledge and understanding; thermodynamics is a useful and reliable tool for the exploitation of available knowledge. There is no better illustration of this difference in approach and objectives than the *ad hoc* adjustments required to bring the quantum statistical mechanical entropy into agreement with the thermodynamic entropy. The final result is a quantum statistical mechanical entropy expressed in logical or human-scented terms.

9.2 ENTROPY'S HUMAN SCENT

Chapters 2 through 7 describe various attempts to employ quantum statistical mechanics to gain insight into the meaning of entropy. Invariably, the result has been that the quantum statistical mechanical entropy can not be expressed solely in physical terms but requires terms that are logical or human scented. This is entirely appropriate when we recall that the thermodynamic entropy is defined in terms of a heat effect in a reversible process — a process

requiring the assistance of a human agent. Thus, it can be said that quantum statistical mechanics has successfully portrayed entropy and captured its human scent.

9.2.1 Chapter 2. In Sec. 2.1 the approach of quantum statistical mechanics was delineated and used to derive expressions for internal energy, temperature, and entropy. In Sec. 2.2 these expressions were examined in an inquiry into their ability to provide insights into the physical significance of these thermodynamic functions. No insight into the physical significance of internal energy or temperature was discovered, but the familiar relationship

$$S = k \ln \Omega$$

suggested that a microscopic, physical interpretation of entropy might be possible. This equation is the basis for the putative identification of entropy with disorder despite the fact that disorder is an imprecise, non-objective concept that can not always be relied upon in explaining entropy changes. The reason for this interpretative shortcoming is found in the nature of the term Ω which is the number of quantum states available to the assembly of particles. This is not a physical quantity such as mass, position, and velocity, but is a parameter that has been devised in order that systems so complex as to defy detailed description can be modeled. It is not something that could possibly be observed, but is a mental construct, or logical term, redolent of a human mind.

In Sec. 2.3 an ideal gas was subjected to a "naive" application of the methods of quantum statistical mechanics which produced the correct results for the internal energy and equation of state but yielded an expression for entropy that was correct in some aspects, but predicted an entropy change for the mixing of the same gas. This defect was corrected by introducing the concept of indistinguishability of the gas particles which directs our attention not to the physical system being described but rather to the mind that is describing it.

9.2.2 Chapter 3. While every system so far treated by quantum statistical mechanics does show a vanishing entropy as the absolute zero of temperature is approached, this condition is always seen in terms of accessible quantum states and only seems to offer insight in physical terms for the case of a crystalline solid. Here the physical picture is that there is only one possible arrangement of particles on the crystal lattice and therefore Ω is unity and S is zero. This, of

course, strengthens the view of entropy as a measure of disorder and tempts one to regard entropy as an intrinsic physical property of matter. This picture of zero entropy as perfect order in a physical(spatial) sense, however, is marred by the fact that liquids and gases also exhibit zero entropies as absolute zero temperature is approached. Again, Ω can not be reliably identified with physical quantities.

<u>9.2.3 Chapters 4 and 5.</u> There has long been an association of entropy with information about the microscopic state of a system. It seems to have begun with Maxwell and his conjecture that a sentient, but extremely small, being with acute senses(a demon) might be able to circumvent the second law by using microscopic information to sort hot molecules from cold ones. The development of communication theory with its unfortunately misnamed, but similarly expressed "entropy" obviously did much to reinforce this view.

The entropy-as-information argument is developed from the relationship

$$S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1}$$

where $S_2 > S_1$ requires $\Omega_2 > \Omega_1$ and a spontaneous change is interpreted as an increased number of available quantum states for the system. The argument proceeds by stating that an increase in Ω amounts to a decrease in an observer's microscopic knowledge of the system because there is more uncertainty regarding the quantum state of the system when an increased number of quantum states is available to it. This leads to an extremely subjective view of entropy because instead of an objective quantity depending only on the macroscopic state of the system, the argument asserts that it depends on someone's knowledge of the microscopic system. Further, this knowledge that entropy is said to depend on, Ω, does not refer to the system but to our description of the system. It is an artificial quantity that can be identified with information only within the restricted confines of a model; in physical terms such as positions and velocities, the amount of information remains constant regardless of changes in the value of Ω.

While there is no formal association of information with entropy, again we see that attempted microscopic descriptions and interpretations of entropy always require logical or non-physical terms.

9.2.4 Chapter 6.   With his H-theorem, Boltzmann applied the methods of classical statistical mechanics to describe a system of non-interacting particles (an ideal gas).   He obtained the result that the quantity *H* monotonically decreases with time and at equilibrium becomes equal to the negative of the statistical mechanical entropy.   Thus, it appeared that he had obtained the result that the entropy of an isolated system never decreases.   This result, however, was quite controversial and raised the obvious question: *How is it that the equations of classical mechanics which are symmetrical in time can give rise to an expression for the entropy which is asymmetric in time?*   It is now generally agreed that the answer to this question is that Boltzmann's assumption of molecular chaos amounted to the specification of a Markovian system and Markovian systems always exhibit time asymmetry.   Boltzmann was forced by the extreme complexity of the problem to use the molecular chaos assumption, but in doing so he unknowingly imported time asymmetry into the otherwise time-symmetric theory.   We are forced to conclude that this effort to derive the second law of thermodynamics from classical mechanics failed and did not enlighten us as to the source of irreversibility.   Again, entropy seems to have resisted our attempt to express or interpret it in physical microscopic terms.

9.2.5 Chapter 7. The Gibbs mixing paradox provides an excellent illustration of the need for an *ad hoc* adjustment of quantum statistical mechanical entropy in order to correctly represent the behavior of thermodynamic entropy. In Chap. 7 it was suggested that the concept of indistinguishability of particles was necessary because the mixing (or unmixing) process is viewed in economic or utilitarian terms where $T_0 \Delta S$ is the minimum work of separation.   The naive approach resulted in the same entropy of mixing regardless of whether the gases were the same or dissimilar.   This result is unacceptable because we have no need to unmix(or separate) when the gases are identical and therefore need expend no work.   Hence, practical considerations dictate that ΔS be zero then the gases are the same and this can only be obtained when we consider particles to be indistinguishable.   Again, the human element finds its way into our microscopic representation of entropy as the indistinguishability of particles reminds us that there is an observer who is unable to keep track of things.

9.2.6 Commentary. If entropy is an intrinsic property of matter it should be expressible in terms of physical quantities.   Instead, we find that quantum statistical mechanical renderings of entropy are characterized by the existence of

logical terms that remind us of the presence of a human mind that is describing or modeling the system. It would seem that it is only possible to describe entropy, a function with a human scent, by including human or logical terms in the description. Thus, quantum statistical mechanics consistently tells us that entropy is not an intrinsic property of matter but rather a function whose definition is such that it can not be expressed in terms of purely physical properties such as position, mass, and motion.   The *ad hoc* adjustments necessary to bring the quantum statistical mechanical entropy into agreement with thermodynamic entropy arise from a mismatch between the classical thermodynamic perspective which is utilitarian(or economic) and the quantum statistical mechanical perspective which is idealized.

9.3 REALMS OF PERFECTION

The differences between the thermodynamic approach and the approach of modern science as employed by quantum statistical mechanics are illustrated in Table 9-1 where the two basic models are compared. While it is often stated that the results of thermodynamics do not depend on the validity of models, in Table 9-1 the term model refers to the rubric of thermodynamics itself and the view of Nature or stance toward Nature implied by this rubric. For thermodynamics the particulars of this model must be inferred from its rubric while for science in general the converse procedure of deducing results from a well-defined model is applied.

9.3.1 The Thermodynamic Model. The reversible process never occurs in Nature and is an idealization that would require human assistance for its execution. This unnatural idealization owes its existence to the human desire to obtain the maximum return from the utilization of physical processes. This is a view of perfection in a temporal and economic sense; its scope is specific and its stance is practical. The emphasis is on HOW TO accomplish a given task. The reversible process carries a strong human scent and because the entropy is defined in terms of a reversible heat effect, it also is human scented. Additionally, an entropy change can only be calculated by means of a reversible path devised by a human mind. Entropy could not exist independently of the human mind.

9.3.2 The Model of Science. In contrast to the thermodynamic model, the model employed by quantum statistical mechanics — molecules in motion — is totally

independent of the presence of a human mind. Here, molecules are continually on the move, colliding with each other and the containing walls, never flagging, never wearing out, and never requiring any adjustment or assistance from the human quarter. It is believed that all physical phenomena can be explained in terms of this model and, indeed, it has been extremely successful. Its one notable failure, as we have seen in Sec. 2.3, is in its naive application to entropy. Because entropy is closely associated with the human mind, it is not surprising that it can not be described solely in terms of molecules and their motions but requires quantities such as Ω which is a logical construct and not a physical attribute of the system. The incongruities surrounding entropy should not be blamed on either classical thermodynamics or quantum statistical mechanics but on the mismatch of their underlying models.

9.4 ARE THE LAWS OF THERMODYNAMICS STATISTICAL?

In the popular press one often sees the statement that the laws of thermodynamics are statistical and that processes that show a negative entropy change — e.g., the spontaneous occurrence of a temperature gradient in a body previously at a uniform temperature — are not prohibited but rather have a very, very small probability of occurrence. They could occur but no one has lived long enough to have observed their occurrence. One often wonders why this distinction is made because the witnessing and reporting of such an event would fall into the category of UFO reports. While this question has no practical ramifications, it is nevertheless of philosophical interest. To state that the laws of thermodynamics are statistical is tantamount to stating that quantum statistical mechanics subsumes thermodynamics.

Of the two laws of thermodynamics only the second has evoked claims of statistical grounding. The first law serves to define energy which is a basic concept of science. Energy is always conserved regardless of the size of the system; no one ever states that energy conservation is a statistical concept. The fact that quantum statistical mechanics arises from our most basic conception of matter and has been successfully applied to the calculation of thermodynamic properties provides a strong argument for the proposition that it subsumes thermodynamics. Additionally, the fact that the concepts and methods of quantum statistical mechanics have also been successfully applied to

calculations for non-equilibrium processes and yield very good estimates of the transport coefficients increases our confidence in its efficacy. No one could dispute the statement that quantum statistical mechanics is obviously more general and more basic than thermodynamics. Yet, because quantum statistical mechanics and thermodynamics are based on different and irreconcilable models of reality, one can not say that the former subsumes the latter. Moreover, the claim that the second law is statistical or that quantum statistical mechanics subsumes thermodynamics should not be taken seriously until Blotzmann's project of reconciliation outlined in Chap. 6 has been accomplished; the origin of irreversibility has not been identified.

9.5 THE ESSENCE OF ENTROPY

The first law describes Nature as it actually is although the distinction between heat and work may be considered artificial or anthropomorphic. The second law, or rather entropy, the function derived from it, does not describe Nature as it is but rather an idealized version of Nature. This applies not only to direct applications of the second law, but to applications of the concept of equilibrium which derives from the entropy. While it would be desirable to be able to describe the actual workings of Nature, nevertheless, it is still quite useful to make calculations concerning this idealized, but approachable, condition. And it is only in this context that an unambiguous interpretation of entropy can be found: the total entropy change measures the lost work when a process falls short of this idealized condition. Entropy reminds us that something we value has been lost — work. Carried into the microscopic realm, the putative view is that order or information, each an anthropomorphic quantity, is the lost valued commodity.

The anthropomorphic nature, or in Bridgman's words the unblushing economic tinge, of thermodynamics should not be unexpected if we believe that Nature answers questions in a context shaped by the questioner. When asked a question concerning the efficiency of a heat engine, a obvious man-made system, the reply is in terms of entropy, a quantity that can not be cleansed of its human tinge or economic taint. E.F. Schumacher has speculated on the nature of

economics that might have developed in a Buddhist society[1] — Buddhist economics.   A similar speculation regarding thermodynamics would be interesting. Could thermodynamics have developed only in a capitalistic society? Could it have developed in a Buddhist or classical Greek society? How would these societies have framed their questions to Nature?

The usefulness of entropy derives from the fact that it is a state function, however, this alone should not be taken as evidence that entropy is an intrinsic property of matter. There are many possible state functions that could be formulated from the thermodynamic variables *U, S, T, P,* and *V* subject to the condition of dimensional consistency, but few would argue that state functions such as *U-PV* or *U+TS* are intrinsic properties of matter. An intrinsic property of matter would be totally objective with no subjective component; it should be expressible in terms of things which are believed to exist independently of the human mind. Although we have seen that both the thermodynamic and quantum statistical mechanical entropy suggest the presence of the human mind, this does not mean that entropy is a totally subjective quantity. It is objective enough that we can agree upon its definition and usage which, after all, is all that is required by thermodynamics.

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 does not seem possible.

---

[1] E.F. Schumacher, *Small is Beautiful*, Harper and Row, New York, 1973.

Table 9-1. REALMS OF PERFECTION

MODEL PROPERTIES	THE MODEL OF	
	THERMODYNAMICS	MODERN SCIENCE
Central Concept	reversible process	molecular motion
Bounds	human scale	ultra small
Scope	temporal	universal
Control	human agent	inaccessible
Perspective	specific/practical	universal/mechanistic
Orientation	how to?	how?