NOTES ON ENTROPY

THERMODYNAMICS

Three laws lead to a vast array of relationships between measurable properties.

This construct is one of the great achievements of the human intellect. It is even useful.

In thermodynamics:

NO MICROSCOPIC MODELS and NO MOLECULES.

The Three Laws:

$$dE = dQ - dW$$ First Law

$$dS \geq \frac{dQ}{T}$$ Second Law

$$S(B) - S(A) \geq \int_A^B \frac{dQ}{T}$$

Clausius: There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir.

$$S(T) = \int_0^T \frac{dQ}{T} = \int_0^T \frac{C(T)}{T}\, dT$$ Third Law

The entropy of a system at absolute zero is a universal constant, which may be taken to be zero.

Obviously, entropy and the Second Law have to do solely with *heat flow and temperature*.

The Carnot cycle, heat pumps, steam engines, etc., are often used to develop the concept of S as a state function.

The thermodynamic temperature scale follows from the Second Law. Note that $dS/dE = 1/T$, for a system at thermodynamic equilibrium.

PHYSICAL PICTURE, OR LACK THEREOF, FOR THE THERMODYNAMIC ENTROPY

One has an intuitive or early-learned feeling for many of the functions and variables found in thermodynamics: e.g., E, Q, W, P, V.

We do not have this for the entropy.

Entropy is a thermodynamic variable, to be distinguished from mechanical variables such as E, P, V, etc.

One cannot make a simple measurement of the entropy or of entropy change, as one can for other principal variables.

The entropy can be evaluated for a substance by use of the Second and Third Laws, i.e., integration of the heat capacity, determined by calorimetry, with respect to $\log T$, from near absolute zero to temperature T, taking into account the entropy of any phase transitions.

Although important, this analysis does not help develop a physical picture of the entropy.

Entropy change is commonly evaluated for a process as:

$$\Delta S = \frac{\Delta H}{T} - \frac{\Delta G}{T}$$

This relationship shows that the entropy is that part of the energy that is unavailable for doing work. If the path between equilibrium states is not reversible, then ΔS contains also a contribution from the irreversibility. In both senses, S is a measure of our ignorance about the system.

Again, these statements, although important, do not help one develop a gut-level understanding of entropy.

INFERENCE FROM MEASUREMENT OF THE ENTROPY OR ENTROPY CHANGE

To the extent that one wants a set of thermodynamic measurements to allow inference about the nature of a process at the microscopic level, definitions of the thermodynamic entropy are particularly unsatisfying.

Note that by assumption, thermodynamics *does not allow* inference about microscopic properties. Thermodynamics is model independent.

Nevertheless, scientists do insist upon making inferences. Sometimes, with justification, in which cases typically through use of extra-thermodynamic information: structure; analogy with a more completely analyzed system; etc.

Statements based upon measurement of the energy (ΔH) are often sensible. E.g., if the heat of ionization is measured for a protein process and found to be near zero, after correction for buffer ionization, etc., then a conclusion that a carboxylic side-chain group was titrated is not unreasonable.

Free energy measurements seem to show plausible patterns that help in understanding equilibria and even reaction rates, e.g., the linear free-energy relationships of physical organic chemistry. In this connection, a free energy change measures work done by or on the system in an isothermal reversible process.

So what should one do with a value or set of values of ΔS?

Good advice, is to do nothing with them.

The obvious problem for interpretation of ΔS is, as we have seen, thermodynamics does not give a physical picture for S that leads to simple interpretation in terms of a microscopic model.

Thus one relies on statistical mechanics for an understanding of S, which is taken to be that S measures disorder and ΔS measures changes in order.

This is not incorrect.

But, one must carefully define what one means by order, to be sure it fits the requirement of the statistical-physical definition of the entropy.

Not often is this done well.

Thus we give the advice, that one, when faced with an overwhelming desire to interpret values of ΔS, should restrain these base impulses, shut down the computer, and go for a beer.

STATISTICAL MECHANICAL DEFINITION OF THE ENTROPY

Statistical mechanics is based upon a set of mechanical laws, classical (Newtonian) or quantum, a fundamental hypothesis of equal *a priori* probabilities (and random phases), and a formalism for statistical averaging.

Like thermodynamics, it is a towering achievement of human intellect.

Unlike thermodynamics, the development of which was driven by the need to understand steam engines, statistical mechanics arose as the intellectual (curiosity-driven) product of two minds, Boltzmann's and Gibbs', working essentially independently in the latter part of the 19th century.

Also unlike thermodynamics, statistical mechanics is absolutely model-based. Atoms and molecules and their motions are at its heart.

Connection between the statistical-mechanical model and thermodynamics is made by finding statistical-mechanical functions that are equivalent to a particular thermodynamic variable.

For example, the thermodynamic energy E is identified, not unreasonably, as the expectation value for the statistical mechanical energy.

The definition of S is somewhat less intuitive. In classical theory, the normalized probability density $\rho(\Gamma)$ will be *very* sharply peaked in some region of the phase space Γ. We define $\Delta\Gamma$ as the volume of phase space about the maximum ρ_{max} such that $\rho_{\text{max}} \cdot \Delta\Gamma = 1$. $\Delta\Gamma$ is a measure of the spread of the probability density about the maximum.

We identify the entropy, within an additive constant, as

$$S = k \log \Delta\Gamma \tag{1}$$

which can be shown equivalent to

$$S = -k < \log \rho > \tag{2}$$

$$= -k \int_{\Gamma} d\Gamma \ \rho \log \rho \tag{3}$$

Similarly, for quantum systems, where $\Delta\Gamma$ corresponds to the number of quantum states in the interval of energy corresponding to the mean energy fluctuation of the system about the most probable value,

$$S = -k \ Tr \hat{\rho} \log \hat{\rho} \tag{4}$$

The entropy also may be written as an explicit average over quantum states

$$S = -k \sum_i P_i \log P_i \tag{5}$$

where for the canonical ensemble

$$P_i = \frac{e^{-E_i/kT}}{Q}$$

with the partition function

$$Q = \sum_i e^{-E_i/kT}$$

where the E_i are the energy eigenvalues of the quantum states of the system. Any particular member of the ensemble will be characterized by one of the energies, E_i, with the probability $e^{-E_i/kT}$.

We obtain the necrological inscription of Boltzmann

$$S = k \log W \tag{6}$$

where W is the number of accessible quantum states of the system ($\Delta\Gamma$), by evaluation of eq. (5) for the microcanonical ensemble, which has equal probabilities P_i.

For molecules such as CO_2, CH_4, etc., that can be studied as ideal gasses, the statistical-mechanical entropy can be calculated with Eq. 5 and experimental values of the vibrational energies E_i, determined from IR and Raman spectroscopic measurements (normal mode frequencies). These spectroscopic values agree with and can be more accurate than thermodynamic values from calorimetric determinations of the heat capacity.

IMPLICATIONS OF THE STATISTICAL MECHANICAL DEFINITION OF THE ENTROPY

Eq. 1 and Eq. 6, respectively, relate the entropy to the volume of phase space and the number of quantum states accessible to the system (of significant probability for the system).

In its relation to the spread of the probability density, the entropy is a measure of the imprecision of our knowledge of the system.

Presumably Eq. 1 and Eq. 6 are why some people interpret increase in the thermodynamic entropy as increase in disorder for a system. Why others choose to identify entropy with randomness is less clear.

The entropy is associated with reduced complexity in the description of a system.

At the microscopic level, a system is described classically in great and unknowable detail by $6N$ variables (coordinates and momenta for the N particles comprising the system). Statistical averaging, over the ensemble or over time, produces a description with the vastly smaller number of variables of classical thermodynamics. The loss of detail in the description appears in the entropy, i.e., the entropy is a measure of the imprecision of our knowledge of the system - of our ignorance about its microscopic behavior.

Entropy is a statistical quantity.

Some variables, such as the mechanical variables $E, P, \text{and} V$, are defined for a particular arrangement of particles (a particular member of an ensemble, a particular time along a trajectory). *Average* (expectation) values of E, etc., are defined by statistical averaging over the ensemble.

The variable S, in contrast, is defined *only* for the ensemble, as a statistically averaged quantity.

The special and difficult character of the variables F and S derives from their dependence on the logarithm of the partition function, $\log Q$. In contrast, mechanical variables such as *E* have expectation values that are simple weighted averages. This difference has implications for understanding the response of *F* or *S* to change in system conditions. It also explains the difficulty of evaulating *F* or *S*, compared with *E*, from molecular dynamic simulations. The following paragraphs are an attempt to clarify these statements.

From Eq. 5, inserting the canonical ensemble expression for P_i,

$$S = \frac{1}{T}\sum_i E_i e^{-E_i/kT} / Q + k\log Q \tag{7}$$

Agreement with the classical thermodynamic expression

$$S = \frac{E}{T} - \frac{F}{T} \tag{8}$$

is found for

$$E = \sum_i E_i e^{-E_i/kT} / Q \tag{9}$$

and

$$F = -kT\log Q \tag{10}$$

The partition function *Q* is the normalization factor for the probability density in the averaging for E (Eq. 9). With Eq. 10, we can write *Q* as a function of *F*, and with Eq. 9,

$$E = \sum_i E_i e^{(F - E_i)/kT} \tag{11}$$

Also, from Eq. 9 and the definition of *Q*,

$$E = -\frac{k}{Q}\frac{\partial Q}{\partial 1/T} = kT^2\frac{\partial \log Q}{\partial T} \tag{12}$$

Eq. 9-12 show that *F* and *E* are qualitatively different types of average quantities. The expectation value for the mechanical variable *E* is a simple Boltzmann-weighted average (Eq. 9). *F* is not a simple average (Eq. 10); rather, it is the logarithm of the sum of the weighting factors used in the averaging for the energy *E*. Eq. 11 shows that *F* is a normalizing factor, equivalent to *Q*. *E* depends on the *shape* of the function $\log Q$ (the temperature derivative, Eq. 12), and not explicitly on $\log Q$, as does *F*. Change in the weights $e^{E_i/kt}$ affects both numerator and denominator terms of Eq. 9, leading through compensation to a reduced effect on the expectation value *E*. Change in the weights affects the free energy *F* without compensation (Eq. 10).

Clearly, change in a system variable can affect F or S differently than E. For example, if in response to some small change in a system variable, a hindered rotation becomes free (e.g., 180^o flip of an aromatic ring), the partition function would be increased (for flip of an aromatic ring, Q would be doubled, with $-kT\log 2$ change in F) with essentially no change in the expectation value for E.

Molecular dynamics simulations sample preferentially states with high probability, according to the Boltzmann weighting $e^{E_i/kt}$. Thus a relative short simulation can give a trajectory average close to the true ensemble average for the energy, provided states not sampled, and having significant but small weights, are distributed sufficiently randomly about the maximum term so as to compensate. However, such unsampled states result in uncompensated reduction of the value of the sum Q, and evaluation of F from an MD trajectory by use of Eq. 10 is difficult. Values of ΔF can be obtained by thermodynamic integration, a relatively complex procedure.

COMMENT BY TOLMAN (1955)
R. C. Tolman, "The Principles of Statistical Mechanics", p560ff, Oxford (1955). [The first edition was published in 1938.]

131. Remarks on the statistical explanation of thermodynamics.

We may now conclude this present chapter by making a few remarks concerning the nature of the explanation which the methods of statistical mechanics have provided for the principles of thermodynamics.

The fundamental idea in this explanation lies in regarding the thermodynamic behaviour of a single system of interest as equivalent to the mechanical behaviour which would be exhibited on the average by a suitably chosen ensemble of systems of similar structure. [Rest of paragraph deleted.]

In carrying out the implications of this fundamental idea, we have found it necessary to correlate the thermodynamic variables ordinarily used to specify the condition of a thermodynamic system with mechanical quantities applying to the corresponding representative ensemble. In the case of the external coordinates describing a thermodynamic system, we have found it possible -- paying due regard to the new requirements imposed by the quantum mechanics -- to give all the systems in the ensemble the same values for their external coordinates as those of the system to be represented. In the case of purely mechanical quantities, such as the energy or external forces exhibited by a thermodynamic system, we have found it possible to make a correlation with the average values of these quantities in the representative ensemble. Here it may be remarked that the mean proves the most desirable average to take, and that inevitable quantum mechanical as well as deliberate experimental limitations on the accuracy of our observational information may play a role in the necessity for representing such quantities by their mean values. *In the case of the essentially thermodynamic variables, entropy and temperature, considerable investigation was necessary to validate the choice of statistical correlates.* [Italics added.]

In the case of entropy, except for a constant factor needed to allow for choice of units, it was found satisfactory to correlate this thermodynamic quantity with the negative of the quantity $\overline{\overline{H}}$ for the ensemble used to represent the system of interest.

$$S \text{ <--> } -k\,\overline{\overline{H}} = -k \sum_n P_n \log P_n \qquad (131.1)$$

[Equation moved from below to this place in text.]

Several remarks may be made in this connexion.

In the first place, it is to be noted, as has been emphasized in connexion with our derivation of the *H*-theorem, that the ensemble which we choose to represent a mechanical system of interest is determined by the observations we have made on the condition of that system. Thus also the value of $\overline{\overline{H}}$ will be determined by the nature of our knowledge of the condition of the system. Since the value of $\overline{\overline{H}}$ is lower the less exactly the quantum mechanical state of the system is specified, this provides the reason for the statement sometimes made that the entropy of a system is a measure of the degree of our ignorance as to its condition. From a precise point of view, however, it seems more clarifying to emphasize that the entropy can be regarded as a quantity which is thermodynamically defined with the help of its relation to heat and temperature given by

$$\Delta S \geq \int \frac{\delta Q}{T} \tag{130.1}$$

[eq. 130.1, Second Law of thermodynamics, moved to this place in text],

and statistically interpreted with the help of the analogous relation

$$-\Delta\overline{\overline{H}} \geq \int \frac{\delta\overline{\overline{Q}}}{\theta} \tag{130.4}$$

[eq. 130.4 moved to this place in text]

between the mechanical quantities $\overline{\overline{H}}$, $\overline{\overline{Q}}$ and θ.

[Two paragraphs deleted.]

As a final point concerning the correlation between the entropy S and the statistical mechanical quantity $\overline{\overline{H}}$, as given by (131.1), it is of interest to consider the special case of a system which we regard as being with *equal* probability in one or another of a group of W eigenstates between which we do not distinguish on the basis of our macroscopic measurements. It will be seen that the relation (131.1) would then assume the form

$$S \longleftrightarrow k \log W \tag{131.2}$$

This has the form of the relation between entropy and probability considered by Boltzmann and Planck, and the quantity W is sometimes spoken of as the *thermodynamic probability*. It is evident, however, that (131.2) *is best regarded merely as a special case of the generally satisfactory and understandable expression for the entropy given by (131.1).* [Italics added.]

We may now turn to the correlation of the temperature T with .....

TEXTS: TREATMENT OF ENTROPY AND DISORDER

From Biochemistry texts:

Lehninger, "Principles of Biochemistry", 3rd edition, 2000:
(page 72) "The randomness of the components of a chemical system is expressed as entropy, *S*."

Garrett and Grisham, "Biochemistry", 2nd edition, 1999:
(page 60) "... concept of entropy, which is a measure of disorder and randomness in the system (or the surroundings)."

Voet, Voet and Pratt, "Fundamentals of Biochemistry", 1999:
(page 15) "The degree of randomness of a system is indicated by its entropy..."

Examples from Chemistry and Physics texts can be summarized as:

Statistical Physics texts do not relate entropy to disorder.

Chemistry texts are cautious if they do this.

EXAMPLES OF INTERPRETATIONS OF ENTROPY CHANGE

Crystals

Helix-coil transition

Nonpolar solutes in aqueous solution

Cells and organisms

WEB REFERENCES:

"Entropy" gets 532,000 Web hits (on 4/6/02; 145000 hits last year) on Google; for amusement, try "entropy" and Google Images (7,830 hits; 4/6/02); for information, try "entropy" and Google Groups (232,000 hits, 4/6/02); but for good, basically sensible links, try "entropy" and Google Directory (633 hits, 4/6/02).

Perhaps for starters try one of the following:

- Entropy on the World Wide Web
  - http://www.math.psu.edu/gunesch/entropy.html
- ENTROPY and the Second Law of Thermodynamics!
  - http://www.2ndlaw.com/
- Principia Cybernetica Web, Entropy and the Laws of Thermodynamics
  - http://pespmc1.vub.ac.be/ENTRTHER.HTML
- Note on Entropy, Disorder and Disorganization
  - http://www.endeav.org/evolut/text/denbig1/denbig1e.htm

Other definitions of entropy, besides thermodynamic and statistical.

Wacky stuff.