THE NECESSITY OF ENTROPY: THE MACROSCOPIC ARGUMENT, THE MICROSCOPIC RESPONSE, AND SOME PRACTICAL CONSEQUENCES

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The Necessity of Entropy: the Macroscopic Argument, the Microscopic Response, and Some Practical Consequences

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Foreword

Students often find thermodynamics baffling. This should not be surprising because it took many years for some of the best scientific minds to work it out. Nor should that arduous history be surprising because thermodynamics links visible phenomena with molecular phenomena, two realms that are more often considered separately. However, the grand ambition of this linkage has been elegantly established and there is nothing convoluted about it.

The primer offered here lays out the foundational logic of thermodynamics in crisp, linear fashion, sidestepping the historical detours and the technical digressions generally included in textbooks. My hope is that this straightforward presentation will provide students with a sturdy scaffold for further exploration of the richness of these ideas and their applications.

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CHAPTER OVERVIEW

Modules

1: Introduction

Entropy is widely understood as a measure of the internal disorder of a system. However, that notion on its own is absurdly vague because, given our modern understanding of the particulate nature of matter, one can imagine many different measures of disorder. In fact, entropy was discerned and defined without reference to any microscopic view of matter, and it is as specific a macroscopic property of a system as the spatial dimensions and the material contents.

At the same time, the existence of entropy as an independent macroscopic property did suggest that the macroscopically observable spatial dimensions and material contents of a system do not tell a complete story, and hinted that matter comprises invisible bits that can be arranged in distinct ways. The question then is what specific account of the microscopic picture corresponds with, and can account for, the macroscopically mandated entropy.

The following two chapters lay out these two developments in their logical sequence: first the macroscopic argument, worked out by Clausius in 1865, and second the microscopic response worked out by Boltzmann in the 1870’s. A final chapter considers the practical significance of the overall framework. Throughout, important material that is tangential to the logic is relegated to appendices. For the present purposes, less is more.

2: The Macroscopic Argument

Definitions

To make the argument we need to agree on some definitions (with notation summarized in Appendix A). We call the part(s) of the world of interest a "system" and everything else its "surroundings". The boundary between the two may be rigid or flexible and distensible, permeable to particles or impermeable, and conducting of heat or insulating. For an "isolated system", the boundary is rigid, impermeable and insulating, so that the system cannot interact in any way with its surroundings. Isolated systems are important for the argument, but other systems are more important in practice.

We will focus on "equilibrium states", i.e., states that prevail after we have waited until no further transfers are occurring within the system or across the boundary. The properties of these states are independent of the path that the system took on its way to equilibrium and we call such properties "state functions". Some state functions, like temperature (T) and pressure (P) are "intensive", i.e., independent of the scale of the system. For example, if system A and system B have the same temperature, then a composite system, AB, comprising A and B as subsystems, also has that temperature. This is in contrast to state functions like energy (E) and volume (V) that are "extensive", i.e., scale with the system. For example, the volume of system AB would be equal to the sum of the volume of A and the volume of B. Of course, the product of an intensive function and an extensive one is extensive (e.g., PV) and the ratio of two extensive functions is intensive (e.g., density).

Conservation of energy

An important observation about energy is that transfers (e.g., between a system and its surroundings) and transformations (e.g., between heat and work) always occur with no overall loss or gain. Given no known exceptions, this conservation of energy is known as The First Law of Thermodynamics (derived from the Greek *therme* for heat and the Greek *dyna* for forces). Taking advantage of the concision and precision of math, we can therefore specify that, for a transfer of energy from the surroundings to the system,

$$\mathit{\Delta} E_{\text{system}} = -\mathit{\Delta} E_{\text{surroundings}} \tag{1}$$

where $\mathit{\Delta}$ is a symbol for change. This being understood, we focus on changes in the energy of the system and drop the subscript in that case.

Reversible energy transfers

As we consider changes, we will want to stay very close to equilibrium, where states are well-defined. This is accomplished by making a series of infinitesimally small changes (denoted by d instead of $\mathit{\Delta}$) and we refer to this as a "reversible path" because infinitesimal steps around equilibrium can be taken in either direction with equal ease.

There are two general ways to increase the energy of a system. One is by doing work on it (w) and the other is by adding heat to it (q). Specifically for the well-defined, reversible path,

$$dE = dw_{\text{rev}} + dq_{\text{rev}} \tag{2}$$

Types of work

There are several forms of work. Even mechanical work comes in three forms. In three dimensions, work can be done on a system by compressing its volume (V) against resistance by the internal pressure (P)

$$dw_{3D} = -PdV \tag{3}$$

where unsubscripted state functions continue to refer to the system. In compression, dV is negative, the work done on the system is positive and its contribution to the energy of the system is positive, $dw_{3D} > 0$. In expansion, the system is expanding against the external pressure (which is the same as the internal pressure on a reversible path hewing close to equilibrium). In this case dV is positive and the system transfers energy to the surroundings, $dw_{3D} < 0$.

Mechanical work can also be done in two dimensions, on stretching the area (A) of a membrane against its surface tension (τ_2), such that

$$dw_{2D} = \tau_2 dA, \tag{4}$$

and in one dimension, on stretching the length (L) of a band against its linear tension (τ_1), such that

$$dw_{1D} = \tau_1 dL \tag{5}$$

Besides mechanical work, there is electrical work and chemical work. Chemical work involves moving moles n_i of chemical i against a chemical potential u_i and, if the chemical i carries a charge q_i per mole, there is also the electrical work of moving that charge against an electric potential ϕ. So for species i,

$$dw_i = (\mu_i + q_i\phi)\, dn_i = \tilde{u}_i dn_i \tag{6}$$

where $\tilde{u}_i = (\mu_i + q_i\phi)$ is known as the electrochemical potential for chemical i.

Since all of these forms of work contribute to dw_{rev} in Equation 2, we have now arrived at

$$dE = -PdV + \tau_2 dA + \tau_1 dL + \sum_{\text{i}} \tilde{u}_i dn_i + dq_{\text{rev}} \tag{7}$$

where the second to last term sums the electrochemical contributions from all chemicals.

Heat capacity

Now let's focus on the heat. Typically, we are interested in three-dimensional systems with fixed contents for which

$$dE = -PdV + dq_{\text{rev}} \tag{8a}$$

or

$$dq_{\text{rev}} = dE + PdV = dH - VdP \tag{8b}$$

where

$$H = E + PV \tag{9}$$

is known as the "enthalpy". (It is another state function because E, P and V are all state functions.) What we observe is that the amount of heat transfer required to change the temperature of the system by a given amount, depends on whether we fix the volume of the system or the pressure. From Equation 8b in the case of fixed volume $(dV = 0)$, we obtain the "constant volume heat capacity"

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{10}$$

and, in the case of fixed pressure $(dP = 0)$, we obtain the "constant pressure heat capacity"

$$C_{\text{P}} = \left(\frac{\partial H}{\partial T}\right)_P \tag{11}$$

The necessity of entropy

Returning to Equation 7, we notice that all the work terms have a consistent structure: each contribution to the change in E, itself an extensive state function, is proportional to the change in one of the other extensive state functions (V, A, L, n_i) multiplied by the "conjugate" (i.e., the conceptually and unit-wise complimentary) one of the intensive state functions $(P, \tau_2, \tau_1, \tilde{u}_i$, respectively). It follows that the heat term, dq_{rev} , should have the same structure. Of course, we have Kelvin temperature (T) as the obvious intensive variable associated with heat and we simply choose the symbol S, and the name "entropy", for its conjugate extensive variable. In these terms, the "fundamental equation" for the energy is

$$dE = -PdV + \tau_2 dA + \tau_1 dL + \sum_{\text{i}} \tilde{u}_i dn_i + TdS \tag{12}$$

This equation summarizes the modes along which energy change can occur, each with an extensive variable expressing the capacity of that mode and intensive variable expressing the resisting force associated with that mode.

About the entropy

What can we say about the entropy mandated by the First Law of Thermodynamics, other than

$$dS = \frac{dq_{\text{rev}}}{T} \tag{13}$$

First, whereas all the other extensive state functions that contribute to the energy represent macroscopically observable features of the system, the entropy does not. Analogical reasoning therefore suggests that it represents a "hidden" or "averaged" feature. Thus, purely classical reasoning about macroscopic variables hints at a complex microscopic structure of matter. With this insight, the distinction between the contributions of heat and work to energy change is seen as a distinction between the random and concerted motions, respectively, of microscopic constituents of the system.

Second, as illustrated by the examples in Appendix B, it has been observed that the entropy of an isolated system always increases until it reaches the maximum possible value at equilibrium. Furthermore, the equilibrium state is a stable state because, if the isolated system were to be perturbed from equilibrium, it would spontaneously return to equilibrium, the highest entropy state. The generalization of these observations to a universal rule is known as "The Second Law of Thermodynamics" and its unidirectional nature is referred to as "Time’s Arrow".

However, we are rarely interested in isolated systems. Most obviously, living organisms are not isolated; they would die if isolated. Less dramatically, simple systems, like ingredients in a kitchen pot and chemicals in a laboratory beaker, are also not isolated. Most commonly, we are interested in three-dimensional systems that are closed (i.e., have fixed contents), have walls that are thermally conducting (so that the temperature is set by the surroundings) and either rigid boundaries (so the volume is fixed) or flexible boundaries (so that the pressure is set by the surroundings). We refer to the former, with constant composition, volume and temperature, as "NVT systems" and the latter, with constant composition, pressure and temperature, as "NPT systems".

Fortunately, as shown in Appendix C, the rule that the entropy of an isolated system always increases to a maximum translates to the progress of other systems to the extrema of other specific state functions, with corresponding stability at equilibrium. For NVT systems, the extremum function is the "Helmholtz free energy"

$$F = E - TS \tag{14}$$

which always decreases to a minimum at equilibrium. As shown in Appendix D, F is also the portion of the energy of any system that is available to do isothermal work on its surroundings. Put another way, TS is the portion of the energy that is not "free" to do isothermal work.

For NPT systems, the extremum function is the "Gibbs free energy"

$$G = E + PV - TS \tag{15}$$

which always decreases to a minimum at equilibrium. This behavior reflects a combination of drives toward giving up energy, giving up volume, and gaining entropy. Notice that the balance between these tendencies depends on pressure and temperature.

- The drive to decrease volume is more important at higher pressures.
- The drive to increase entropy is more important at higher temperatures
- At low pressure and temperature, the drive to decrease energy dominates. This is the realm of ordinary mechanics.

Like F, G is a "free" energy in the sense of being available to do work on its surroundings. As shown in Appendix D, it differs from F in isolating non- pV work and therefore is particularly suited to electrochemical applications.

Finally, the power of multivariable calculus can be brought to bear, as shown in

- Appendix E, interpreting the fundamental equation for each state function, and
- Appendix F, deriving Maxwell’s Relations.

3: The Microscopic Response

Statistics for large numbers

In the previous section, we established that, among the extensive properties of macroscopic systems, there is one, called the entropy, that is not macroscopically observable. Notice that although the development did not depend in any way on any features of the microscopic structure of matter, it did seem to reflect hidden or averaged degrees of freedom within the system. Of course, we now live in a time when the microscopically discrete nature of matter has been deeply characterized and is taken completely for granted. It is clear that very many sets of the positions and velocities of the microscopic constituents of a system can correspond to a single macroscopic state of that system. Considering the very large number of particles involved $\left(\sim 10^{23}\right)$, constructing relationships between the numerous microstates in the microscopic picture and the macroscopic properties is inevitably a statistical enterprise.

Averages for energy and volume

Given the complexity, it helps to start with the energy and the volume, extensive state functions that we have more intuition about. Let's, once again, consider a system A, a system B, and the composite system AB comprising A and B as independent subsystems. It seems reasonable to suppose that the macroscopically observed energy and volume, E and V, of each of these systems will be the average over those of the distinguishable microstates of each system,

$$\begin{aligned} E_A &= \textstyle\sum_{\mathrm{i}} \varepsilon_{\mathrm{i}} p_{\mathrm{i}} & V_A &= \textstyle\sum_{\mathrm{i}} v_{\mathrm{i}} p_{\mathrm{i}} \\ E_B &= \textstyle\sum_{\mathrm{j}} \varepsilon_{\mathrm{j}} p_{\mathrm{j}} & V_B &= \textstyle\sum_{\mathrm{j}} v_{\mathrm{j}} p_{\mathrm{j}} \\ E_{AB} &= \textstyle\sum_{\mathrm{ij}} \varepsilon_{\mathrm{ij}} p_{\mathrm{ij}} & V_{AB} &= \textstyle\sum_{\mathrm{ij}} v_{\mathrm{j}} p_{\mathrm{ij}} \end{aligned} \tag{16}$$

where p_{i} is the probability that the system A is in microstate i with energy ε_{i} and volume v_{i}, p_{j} is the probability that the system B is in microstate j with energy ε_{j} and volume v_{j}, and p_{ij} is the probability that the system AB is in microstate ij (i.e., with subsystem A in state i and subsystem B in state j). As always, energies and volumes are additive,

$$\varepsilon_{\mathrm{ij}} = \varepsilon_{\mathrm{i}} + \varepsilon_{\mathrm{j}} \quad \text{and} \quad v_{\mathrm{ij}} = v_{\mathrm{i}} + v_{\mathrm{j}} \tag{17}$$

and, since the two subsystems are independent of one another,

$$\sum_{\mathrm{ij}} = \sum_{\mathrm{i}} \sum_{\mathrm{j}} \quad \text{and} \quad p_{\mathrm{ij}} = p_{\mathrm{i}} p_{\mathrm{j}} \tag{18}$$

It follows that

$$\begin{aligned} E_{AB} &= \sum_{\mathrm{ij}} \varepsilon_{\mathrm{ij}} p_{\mathrm{ij}} & V_{AB} &= \sum_{\mathrm{ij}} v_{\mathrm{ij}} p_{\mathrm{ij}} \\ &= \sum_{\mathrm{i}} \sum_{\mathrm{j}} \left(\varepsilon_{\mathrm{i}} + \varepsilon_{\mathrm{j}}\right) p_{\mathrm{i}} p_{\mathrm{j}} & &= \sum_{\mathrm{i}} \sum_{\mathrm{j}} \left(v_{\mathrm{i}} + v_{\mathrm{j}}\right) p_{\mathrm{i}} p_{\mathrm{j}} \\ &= \sum_{\mathrm{i}} \sum_{\mathrm{j}} \varepsilon_{\mathrm{i}} p_{\mathrm{i}} p_{\mathrm{j}} + \sum_{\mathrm{i}} \sum_{\mathrm{j}} \varepsilon_{\mathrm{j}} p_{\mathrm{i}} p_{\mathrm{j}} & &= \sum_{\mathrm{i}} \sum_{\mathrm{j}} v_{\mathrm{i}} p_{\mathrm{i}} p_{\mathrm{j}} + \sum_{\mathrm{i}} \sum_{\mathrm{j}} v_{\mathrm{j}} p_{\mathrm{i}} p_{\mathrm{j}} \\ &= \left(\sum_{\mathrm{i}} \varepsilon_{\mathrm{i}} p_{\mathrm{i}}\right) \left(\sum_{\mathrm{j}} p_{\mathrm{j}}\right) + \left(\sum_{\mathrm{i}} p_{\mathrm{i}}\right) \left(\sum_{\mathrm{j}} \varepsilon_{\mathrm{j}} p_{\mathrm{j}}\right) & &= \left(\sum_{\mathrm{i}} v_{\mathrm{i}} p_{\mathrm{i}}\right) \left(\sum_{\mathrm{j}} p_{\mathrm{j}}\right) + \left(\sum_{\mathrm{i}} p_{\mathrm{i}}\right) \left(\sum_{\mathrm{j}} v_{\mathrm{j}} p_{\mathrm{j}}\right) \end{aligned} \tag{19}$$

And, since probabilities sum to 1 (by definition),

$$E_{AB} = \sum_{\mathrm{i}} \varepsilon_{\mathrm{i}} p_{\mathrm{i}} + \sum_{\mathrm{j}} \varepsilon_{\mathrm{j}} p_{\mathrm{j}} = E_A + E_B \qquad V_{AB} = \sum_{\mathrm{i}} v_{\mathrm{i}} p_{\mathrm{i}} + \sum_{\mathrm{j}} v_{\mathrm{j}} p_{\mathrm{j}} = V_A + V_B \tag{20}$$

In other words, our interpretation of the macroscopic values of extensive variables as averages of microscopic ones is self-consistent. This can be generalized to the other macroscopic extensive variables, A, L, Q, N_i and presumably S.

Averages for entropy

An analogous microscopic accounting for S would posit a feature σ of microstates, with the averages

$$\begin{aligned} S_A &= \sum_{\mathrm{i}} \sigma_{\mathrm{i}} p_{\mathrm{i}} \\ S_B &= \sum_{\mathrm{j}} \sigma_{\mathrm{j}} p_{\mathrm{j}} \\ S_{AB} &= \sum_{\mathrm{ij}} \sigma_{\mathrm{ij}} p_{\mathrm{ij}} \end{aligned} \tag{21}$$

The question is what σ should be, given that it must have a value for each microstate that is distinct from those directly related to the macroscopic observables. The remaining possibility is that it is a function of the microstate's probability. But what sort of function would that be?

As the above analysis for E and V shows, for S to be extensive, i.e.,

$$S_{AB} = S_A + S_B \tag{22}$$

it is necessary that

$$\sigma_{\mathrm{ij}}\left(p_{\mathrm{ij}}\right) = \sigma_{\mathrm{i}}\left(p_{\mathrm{i}}\right) + \sigma_{\mathrm{j}}\left(p_{\mathrm{j}}\right) \tag{23}$$

which corresponds to the well-known property of the logarithm,

$$\ln(p_{\mathrm{ij}}) = \ln(p_{\mathrm{i}} p_{\mathrm{j}}) = [\ln(p_{\mathrm{i}}) + \ln(p_{\mathrm{j}})] \tag{24}$$

Since this relationship also holds when multiplied by any constant, we can now posit that

$$\begin{aligned} \sigma_{\mathrm{ij}} &= -k \ln(p_{\mathrm{ij}}) \\ \sigma_{\mathrm{i}} &= -k \ln(p_{\mathrm{i}}) \\ \sigma_{\mathrm{j}} &= -k \ln(p_{\mathrm{j}}) \end{aligned} \tag{25}$$

where k is a yet-to-be-determined constant, and find that, by substitution of Eq.25 into Eq. 21, a proper accounting of the macroscopic entropy S can be had from the averages

$$\begin{aligned} S_A &= -k \sum_{\mathrm{i}} p_{\mathrm{i}} \ln(p_{\mathrm{i}}) \\ S_B &= -k \sum_{\mathrm{j}} p_{\mathrm{j}} \ln(p_{\mathrm{j}}) \\ S_{AB} &= -k \sum_{\mathrm{ij}} p_{\mathrm{ij}} \ln(p_{\mathrm{oj}}) \end{aligned} \tag{26}$$

or, using angle bracket notation for averaging,

$$S = -k \langle \ln(p) \rangle \tag{27}$$

Notice that the values of σ and S are always positive if k is positive, because the probabilities are all ≤ 1. Notice also that $p\ln(p)$ has the peculiar property that it is zero for both $p = 0$ and for $p = 1$, about which more below.

In some simple cases, all the microstates have the same probability. If there are W of them

$$p = 1/W \tag{28}$$

and

$$S = k \ln W \tag{29}$$

This is the expression that appears on Ludwig Boltzmann's grave stone.

The one remaining unknown is the value of the constant k, named after Boltzmann. Once again, we need consistency with macroscopic observations. As shown in Appendix G, this dictates that

$$k = \frac{R}{N_A} \tag{30}$$

where N_A is Avogadro's constant. In other words, Boltzmann's constant k and the gas constant R are the same constant in different units (per particle in k and per mole of particles in R).

Information, order and spread

What more can we say about the entropy from the microscopic vantage point?

As we have seen, S is always positive.

The lower limit, $S = 0$, corresponds to the special situation of certainty that the system exists in just one microstate, in other words that $p = 1$ (so $p\ln(p) = 0$) for one microstate and $p = 0$ (so $p\ln(p) = 0$) for all others.

On the other hand, S has its maximum value in the case of maximum uncertainty where the system is equally likely to be in any microstate, in other words where p is the same for all the microstates. This is the result $S = k\ln W$ for a system with W equally probably states (i.e., Equation 29).

In general, increasing S is associated with decreasing microscopic information or order, and can be imagined as a measure of the "spread" of the system's visits among microstates.

The probabilities

So far, we have seen that understanding the behavior of a system at the microscopic level amounts to enumerating all distinct microstates and determining their probabilities. However, where do the probabilities come from? Specifically, how do the properties of microstates figure into their probabilities of occurring?

Once again, agreement with macroscopic observations is essential. In particular, the probabilities have to comport with the extremum condition that describes equilibrium for each type of system. It is also necessary that the probabilities are normalized (i.e., sum to 1). This sort of constrained optimization is most readily accomplished using the Method of Lagrange Multipliers with the following results for the most common types of systems.

- In an isolated system (i.e., with rigid, insulating and impermeable walls, such that N, V and E are fixed), equilibrium corresponds to the maximum of

$$S = -k\sum_{\mathrm{j}} p_{\mathrm{j}}\ln(p_{\mathrm{j}}) \tag{31}$$

and the corresponding probabilities are all equal to

$$p_{\mathrm{j}} = \frac{1}{Z_{NVE}} \tag{32}$$

where

$$\begin{aligned} Z_{NVE} &= \sum_{\mathrm{k}} 1 = W \\ &= \text{the "multiplicity" (i.e., the number of available microstates)} \end{aligned} \tag{33}$$

normalizes the probabilities (i.e., assures that they sum to 1). Notice that this result followed entirely from the necessary relationship to macroscopic observations. You may come across some presentations of statistical mechanics that avoid this reference to macroscopic observations by citing the equal probabilities of states of the same content, volume and energy as a postulate dubbed "The Principle of Equal A Priori Probabilities". However, it is far more satisfying to derive this result than to assume it.

- For an NVT system (i.e., with thermally conducting, but still rigid and impermeable walls), equilibrium corresponds to the minimum of

$$\begin{aligned} F &= E - TS \\ &= \sum_{\mathrm{j}} \varepsilon_{\mathrm{j}} p_{\mathrm{j}} + kT\sum_{\mathrm{j}} p_{\mathrm{j}}\ln(p_{\mathrm{j}}) \end{aligned} \tag{34}$$

and the corresponding probabilities are equal to

$$p_{\mathrm{j}} = \frac{\exp(-\varepsilon_{\mathrm{j}}/kT)}{Z_{NVT}} \tag{35}$$

where

$$Z_{NVT} = \sum_{\mathrm{k}} \exp(-\varepsilon_{\mathrm{k}}/kT) \tag{36}$$

normalizes the probabilities. In other words, in this non-isolated system, the temperature imposed by the surroundings influences the probability distribution and it does so in a fashion that satisfies the multiplication rule for a system composed of two independent subsystems (see Equation 18). The probability distribution in Equation 35 is known as "the Boltzmann distribution" and it is the basis for the Maxwell-Boltzmann distribution of molecular speeds in a gas.

- For an NPT system (i.e., with thermally conducting and flexible, but still impermeable walls), equilibrium corresponds to the minimum of

$$\begin{aligned} G &= E + PV - TS \\ &= \sum_{\mathrm{j}} \varepsilon_{\mathrm{j}} p_{\mathrm{j}} + \sum_{\mathrm{j}} P v_{\mathrm{j}} p_{\mathrm{j}} + kT \sum_{\mathrm{j}} p_{\mathrm{j}} \ln(p_{\mathrm{j}}) \end{aligned} \tag{37}$$

and the corresponding probabilities are equal to

$$p_{\mathrm{j}} = \frac{\exp(-(\varepsilon_{\mathrm{j}} + P v_{\mathrm{j}})/kT)}{Z_{NPT}} \tag{38}$$

where

$$Z_{NPT} = \sum_{\mathrm{k}} \exp(-(\varepsilon_{\mathrm{k}} + P v_{\mathrm{k}})/kT) \tag{39}$$

normalizes the probabilities. In other words, in this non-isolated system, the probability distribution is influenced by the temperature and pressure imposed by the surroundings, in a fashion that satisfies the multiplication rule for a composite system comprising two independent subsystems (see Equation 18).

The partition function

The symbol Z comes from the German "Zustandssumme" for "sum over states". Of course, the sum varies with the values of the applied conditions and, in this respect, Z is known as the partition function. As for any function of multiple variables, we can take partial derivatives and we find that those with respect to intensive variables provide averages of practical significance. In particular, for the NVT system

$$\frac{\frac{\partial Z_{NVT}}{\partial(1/T)}}{Z_{NVT}} = -E/k \quad \text{or} \quad E = kT^2 \left[\frac{\partial \ln(Z_{NVT})}{\partial(T)}\right] \tag{40}$$

and for the NPT system

$$\frac{\frac{\partial Z_{NPT}}{\partial(1/T)}}{Z_{NPT}} = -(E+PV)/k \quad \text{or} \quad H = kT^2 \left[\frac{\partial \ln(Z_{NPT})}{\partial(T)}\right] \tag{41}$$

and

$$\frac{\frac{\partial Z_{NPT}}{\partial(P)}}{Z_{NPT}} = -V/kT \quad \text{or} \quad V = -kT \left[\frac{\partial \ln(Z_{NPT})}{\partial(P)}\right] \tag{42}$$

From these results, other state functions can be obtained by using the relationships in Appendices E and F.

4: Some Practical Consequences

In the foregoing, we have shown how entropy completes macroscopic thermodynamics and connects it to microscopic statistics. While this is highly satisfying, it is the predictive power of theory that is of practical significance. Working our way backwards through the relationships in the previous two chapters, we see that if we can enumerate the microstates of a system and propose energies and volumes for each of them, then we can calculate the equilibrium probabilities of these states and the averages that correspond to macroscopic properties at equilibrium. Thus, the statistical thermodynamics takes us from a microscopic model to macroscopic predictions, with increasing confidence as models are validated by experiments that test their predictions. Let's consider some examples.

Heat capacities

Quantum mechanics allows us to calculate the energies of molecules. At ordinary temperatures, only the ground electronic state is significantly populated because even the first excitation requires an energy $\gg kT$. However, rotational, vibrational and translational excited states are all populated at ordinary temperatures and it turns out that the spacings in their energy ladders have different characteristic patterns. As a result, the contributions to the constant volume heat capacity are $k/2$ for each translational or rotational mode and k for each vibrational mode. This prediction comports with several interesting experimental observations.

- All molecules have three translational modes (one for each Cartesian coordinate), but linear molecules have one less rotational mode and one more vibrational mode than nonlinear molecules with the same number of atoms. This difference agrees with the experimentally observed differences in gas phase heat capacities of linear vs. non-linear molecules.
- A lattice solid can be viewed as a single very large molecule of N atoms, where N is of the order 10^{23}. Since N atoms have a total of $3\ \mathrm{N}$ degrees of freedom, the three translational and three rotational modes are vastly outnumbered by the $(3N-6) \sim 3N$ vibrational modes. This agrees with the experimentally observed heat capacity of $3k$ per atom for lattice solids.
- Liquid water has the $3k$ per atom heat capacity typical of lattice solids. This attests to the importance of its three-dimensional hydrogen bonding network.
- Excitations are frozen out with decreasing temperature, as expected according to the Boltzmann distribution. First to go are the electronic excitations (already at ordinary temperatures in most cases), then the vibrational excitations (in the infrared range of energies), and then the rotational excitations (in the microwave range of energies). At each of these stages, the corresponding contributions to the constant volume heat capacity also disappear as predicted.

Gas phase chemical equilibria

The reactants and products of a chemical reaction are different arrangements of the same atoms. Using quantum mechanics, we can calculate energies for the electronic, rotational, vibrational and translational states of each, and then use these to determine the temperature and pressure dependence of the relative probabilities of products and reactants. This yields an equilibrium reaction quotient (generally known as the "equilibrium constant"). While the form of the equilibrium constant can be derived from the macroscopic picture of mass action, the value of the equilibrium constant is predicted from the microscopic picture by statistical thermodynamics.

Phase behavior of pure substances

All uncharged molecules attract one another. Even if they have no hydrogen bonding capability and have no permanent dipole moment, they have fluctuating dipole moments due to electron motion. The tendency of these fluctuations to become coordinated in neighboring molecules results in intermolecular attractions, known as "London dispersion forces". As a result, only small molecules (i.e., those with few electrons) occur as gases at ordinary temperatures and pressures. As expected, the phase behavior follows a pattern dictated by trade-offs between energy, volume and entropy. At low temperature, where entropy is unimportant, the lowest energy phase prevails at low pressure and the lowest volume phase prevails at high pressure. Either way, this is a condensed phase. With increasing temperature, higher entropy becomes important and the gas phase eventually prevails. For a given pressure, this transition occurs at the temperature where the free energy of the gas phase dips below that of the condensed phase. Both of these free energies can be calculated from a model of intermolecular attractions in the condensed phase vs. the absence of intermolecular interactions in the gas phase. For transitions between different condensed phases, modeling must consider how the details of molecular packing distinguish the intermolecular attractions in each phase.

Phase behavior of mixtures

Entropy always favors mixing and the energies of intermolecular interactions almost always favor demixing to some extent. The latter is because mixing involves replacing interactions between like neighbors with interactions between unlike neighbors and this often involves losing H-bond interactions or dipole-dipole interactions. As a result,

- Gases are always completely mixed because there are no intermolecular interactions.
- Lattice solids are generally nearly pure, due to packing constraints that optimize intermolecular interactions.
- The tradeoffs between entropy and energy play out primarily in the liquid phase. This is where we most commonly see phase separation. The difference in composition of the coexisting phases increases with the severity of the energy penalty for mixing. However, neither phase will ever be completely pure because the entropy that is sacrificed in removing minor component(s) in either phase gradually diverges.

Polymer swelling and collapse

Entropy favors polymer chains exploring all configurations that their lengths and open space allow. This will be countervailed by energy costs of bending. The balance will be influenced by the nature of the interactions between polymer units and solvent, with swelling in a good solvent (one where hetero interactions are more favorable) and collapse in a bad solvent (one where hetero interactions are less favorable).

Elasticity

Configurational statistics also underlie the ability of polymeric materials to sustain very large deformations in reversible fashion. This can be demonstrated by a simple experiment with an ordinary rubber band. When a weight is suspended from the rubber band, the equilibrium length reflects a compromise between the gravitational potential energy of the weight, which tends to stretch the rubber band, and the configurational entropy of the polymers, which works against the distortion. Accordingly, the rubber band shortens with increasing temperatures, where the influence of entropy is greater.

Thermal expansion

For most materials, higher temperatures lead to expansion because higher volume states are usually higher entropy states. Moreover, the trade-off against energy is such that the thermal expansion is typically greater for materials with weaker bonds. In the unusual cases where thermal expansion is negative, it is a sign of access to bonding arrangements with greater entropy at reduced volume. The most well-known case is that of water from $0^{\circ}\mathrm{C}$ to $4^{\circ}\mathrm{C}$, at 1 atm. The anomalously high density of liquid water near freezing causes bodies of water to freeze from the top down which helps to protect aquatic life through the winter.

Liquid crystals

When molecules are elongated, they spontaneously align above a certain concentration. This would seem to violate the rule that spontaneous change occurs in the direction of increasing entropy. However, a close examination of the statistics shows that this is a case of "entropically-driven order": when elongated particles align at concentrations high enough to get in each other’s way, it is because the gain in their translational freedom (both laterally and longitudinally) exceeds the loss in their orientational freedom.

Hydrophobicity

Liquid water is a very special substance due to its exceptional entropy. Not only are water molecules free to move as in any liquid, but their interactions with one another are highly labile. In roughly tetrahedral fashion, each oxygen can donate up to two hydrogen bonds to neighbors and accept up to two from others. Moreover, the protons can hop-scotch through the network, interconverting donated and accepted H-bonds as they go. Solutes interfere with this network’s very high multiplicity of states. Therefore, the entropy of mixing solute and solvent is not enough for non-polar solutes to dissolve to significant extent in water. On the other hand, for polar solutes, energetically favorable interactions with water can tip the balance to allow greater solubility and, in some cases, even full miscibility.

The surface charge of neat water

Water is amphiprotic and forms both hydroxide, by loss of a proton, and hydronium, by gain of a proton. None of these three species can form as many hydrogen bonds at the surface as in the bulk. However, when a surface water molecule is exchanged with a hydroxide from the bulk, there is a net gain in hydrogen bonding. As a result, hydroxide prefers residence at the surface to residence in the bulk. On the other hand, when a surface molecule is exchanged with a hydronium from the bulk, there is a net loss of hydrogen bonds and hydronium prefers residence in the bulk to residence at the surface. This behavior is manifest in the more than century old observation that the mist formed by shearing the surface of water (e.g., by gravity in water falls or by wind over water bodies) is negatively charged. In effect, mechanical energy is being converted into electrical energy by separation of the negative surface charge from the bulk positive charge. Recently interest in this phenomenon has evolved from simple curiosity to schemes for harvesting the energy stored in water mists.

Chemical kinetics

Given its focus on equilibrium states, it would seem that thermodynamics has nothing to say about dynamics. However, this turns out not to be the case. In particular, statistical thermodynamics can predict the rates of chemical reactions. Just as we can use quantum mechanics to calculate energies for reactants and products, we can also use quantum mechanics to calculate energies for other configurations of the same collection of atoms. The resulting energy landscape maps the energy barrier between the reactants and products. The lowest region on this barrier (analogous to a pass in a mountain range) is called the "transition state" because it has the greatest chance of being populated according to the Boltzmann probability distribution and, consequently, the greatest chance of leading to a crossing from reactant to product. Given occupancy of the transition state, how long does the crossing take? A reasonable estimate is the period of the molecular vibration that corresponds to the shift from the reactant side of the barrier to the product side. The resulting prediction of the reaction rate is the product of the probability that the transition state is occupied and the frequency of the vibration that crosses the barrier.

CHAPTER OVERVIEW

Appendices

A: Notation

- $\mathit{\Delta}$ change
- d, ∂ infinitesimal change
- t time
- Z partition function
- k Boltzmann’s constant
- R the gas constant
- N_A Avogadro’s number

Macroscopic Energies

- E energy
- F Helmholtz free energy
- G Gibbs free energy
- H enthalpy
- w work done on the system
- w' work done by the system
- q heat taken up by the system

Macroscopic Capacities

- A area
- L length
- V volume
- S entropy
- n_i moles of chemical i
- q_i charge per mole of chemical i

Conjugate Forces

- τ_2 surface tension
- τ_1 linear tension
- P pressure
- T Kelvin temperature
- u_i chemical potential of i
- ϕ electric potential
- $\tilde{u}_i$ electrochemical potential of i

Microstate Properties

- ε_j energy of microstate j
- v_j volume of microstate j
- p_j probability of microstate j
- σ_j entropy of microstate j

B: Time’s Arrow

Let’s look at how entropy changes in some simple and familiar systems.

Simple systems

In order to focus on entropy, it helps to consider isolated systems in which all the other extensive variables are fixed by virtue of rigid, impermeable and insulating walls. To then interrogate spontaneous processes in the simplest way, we divide the isolated system into just two subsystems, A and B, each initially at internal equilibrium and consider what happens when the boundary between them is changed to allow transfers.

The convenience of an isolated system is that we know that extensive quantities can only be redistributed between the subsystems:

$$dE = dE_A + dE_B = 0 \qquad \text{i.e., } dE_A = -dE_B \tag{B1}$$

$$dV = dV_\mathrm{A} + dV_\mathrm{B} = 0 \qquad \text{i.e., } dV_\mathrm{A} = -dV_B \tag{B2}$$

What about dS? Rearranging the fundamental equation for the energy (Equation 12) gives

$$dS_\mathrm{A} = \left(\frac{1}{T_\mathrm{A}}\right) dE_\mathrm{A} + \left(\frac{P_\mathrm{A}}{T_\mathrm{A}}\right) dV_\mathrm{A} \tag{B3}$$

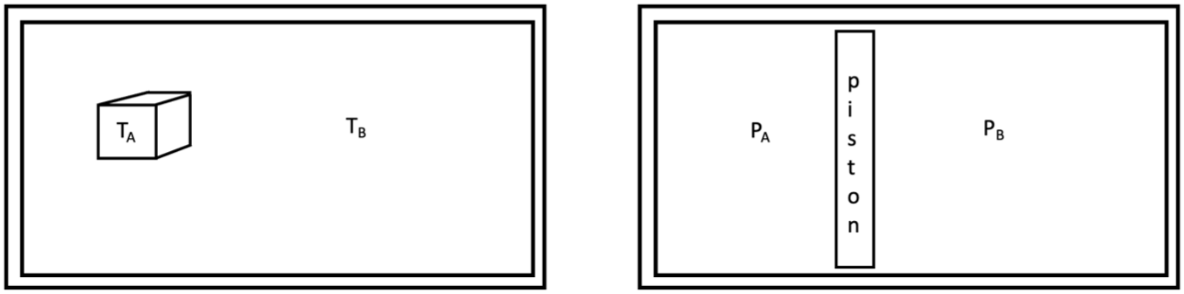
$$dS_\mathrm{B} = \left(\frac{1}{T_\mathrm{B}}\right) dE_\mathrm{B} + \left(\frac{P_\mathrm{B}}{T_\mathrm{B}}\right) dV_\mathrm{B} \tag{B4}$$

Given Equations B1 and B2, we see that the sign of each of the terms in dS_B is opposite that of the corresponding term in dS_A no matter how the energy and volume are redistributed. However, we are interested in the overall change in entropy

$$\begin{aligned} dS &= dS_\mathrm{A} + dS_\mathrm{B} \\ &= \left[\left(\frac{1}{T_\mathrm{A}}\right) - \left(\frac{1}{T_\mathrm{B}}\right)\right] dE_\mathrm{A} + \left[\left(\frac{P_\mathrm{A}}{T_\mathrm{A}}\right) - \left(\frac{P_\mathrm{B}}{T_B}\right)\right] dV_\mathrm{A} \end{aligned} \tag{B5}$$

Familiar systems

The idea is to choose scenarios with which we have ample experience. The figure below shows two such cases. In one, the subsystems are initially at different temperatures, to make use of our experience that energy always moves from hotter to cooler objects. In the other, the subsystems are initially at different pressures, to make use of our experience that a region of lower pressure always gives up volume to a region of higher pressure. The following analyses show that both spontaneous processes are accompanied by an increase in the total entropy of the composite system, with one subsystem gaining more entropy than the other loses until overall equilibrium is achieved. The reader can verify that a similar analysis obtains the same result for a scenario in which the subsystems differ in the electrochemical potential for a constituent.



Two simple and familiar systems. Both are isolated (with their rigid, impermeable and insulating boundaries represented by double lines according to convention). Both have two subsystems that are initially at internal equilibrium. In one case, the two subsystems differ in temperature and the other in pressure.

The *ΔT* system

Suppose that the barrier between subsystems is rigid and impermeable (so $dV_A = 0$), but becomes thermally conducting (so $dE_A \neq 0$). Then

$$dS = \left[\left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right)\right] dE_A \tag{B6}$$

and, specifically, with respect to time, t

$$\frac{dS}{dt} = \left[\left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right)\right] \frac{dE_A}{dt} \tag{B7}$$

We know from experience that

$$\begin{aligned}
&\text{if } T_{\mathrm{A}} = T_{\mathrm{B}}\text{, then } \left(\frac{dE_{\mathrm{A}}}{dt}\right) = 0 \text{ and so } \left(\frac{dS}{dt}\right) = 0 \\
&\text{if } T_{\mathrm{A}} < T_{\mathrm{B}}\text{, i.e., } \left[\left(\frac{1}{T_{\mathrm{A}}}\right) - \left(\frac{1}{T_{\mathrm{B}}}\right)\right] > 0 \text{ then } \left(\frac{dE_{\mathrm{A}}}{dt}\right) > 0 \text{ and so } \left(\frac{dS}{dt}\right) > 0 \\
&\text{if } T_{\mathrm{A}} > T_{\mathrm{B}}\text{, i.e., } \left[\left(\frac{1}{T_{\mathrm{A}}}\right) - \left(\frac{1}{T_{\mathrm{B}}}\right)\right] < 0 \text{ then } \left(\frac{dE_{\mathrm{A}}}{dt}\right) < 0 \text{ and so } \left(\frac{dS}{dt}\right) > 0
\end{aligned}$$

In other words, our experience for this system says that

$$\frac{dS}{dt} > 0 \tag{B8}$$

until the system reaches equilibrium where $T_{\mathrm{A}} = T_{\mathrm{B}}$, $(dE_{\mathrm{A}}/dt) = 0$ and $(dS/dt) = 0$.

Notice that, according to Equation B6,

$$\frac{dS}{dE_{\mathrm{A}}} = \left[\left(\frac{1}{T_{\mathrm{A}}}\right) - \left(\frac{1}{T_{\mathrm{B}}}\right)\right] = 0 \text{ at equilibrium } (T_{\mathrm{A}} = T_{\mathrm{B}}) \tag{B9}$$

and

$$\frac{d^2S}{dE_A^2} = \frac{d\left(\frac{1}{T_A}\right)}{\mathrm{d}E_A} - \frac{d\left(\frac{1}{T_B}\right)}{dE_A} < 0 \text{ for all } dE_A \tag{B10}$$

Therefore, S has a maximum value at equilibrium $(T_A = T_B)$ and no distribution of E between A and B has a higher S.

The ΔP system

Suppose that the barrier between subsystems is a perfect thermal conductor (so that $T_{\mathrm{A}} = T_{\mathrm{B}} = T$) and becomes free to move (so $\mathrm{d}V_A \neq 0$). Then

$$dS = \left[\left(\frac{P_{\mathrm{A}}}{T}\right) - \left(\frac{P_{\mathrm{B}}}{T}\right)\right] dV_{\mathrm{A}} \tag{B11}$$

and specifically, with respect to time

$$\frac{dS}{dt} = \left[\left(\frac{P_{\mathrm{A}}}{T}\right) - \left(\frac{P_{\mathrm{B}}}{T}\right)\right] \frac{dV_A}{dt} \tag{B12}$$

We know from experience that

$$\begin{aligned}
&\text{if } P_{\mathrm{A}} = P_{\mathrm{B}}\text{, then } \left(\frac{dV_{\mathrm{A}}}{dt}\right) = 0 \text{ and so } \left(\frac{dS}{dt}\right) = 0 \\
&\text{if } P_{\mathrm{A}} < P_{\mathrm{B}}\text{, then } \left(\frac{dV_{\mathrm{A}}}{dt}\right) < 0 \text{ and so } \left(\frac{dS}{dt}\right) > 0 \\
&\text{if } P_{\mathrm{A}} > P_{\mathrm{B}}\text{, then } \left(\frac{dV_{\mathrm{A}}}{dt}\right) > 0 \text{ and so } \left(\frac{dS}{dt}\right) > 0
\end{aligned}$$

In other words, our experience for this system says that

$$\frac{dS}{dt} > 0 \tag{B13}$$

until system reaches equilibrium where $P_{\text{A}} = P_{\text{B}}, (dV_{\text{A}}/dt) = 0$ and $(dS/dt) = 0$.

Notice that, according to Equation B11,

$$\frac{dS}{dV_{\text{A}}} = \left[\left(\frac{P_{\text{A}}}{T}\right) - \left(\frac{P_B}{T}\right)\right] = 0 \text{ at equilibrium } (P_A = P_B) \tag{B14}$$

and

$$\frac{d^2 S}{dV_{\text{A}}^2} = \frac{d\left(\frac{P_{\text{A}}}{T}\right)}{dV_{\text{A}}} - \frac{d\left(\frac{P_{\text{B}}}{T}\right)}{dV_{\text{A}}} < 0 \text{ for all } dV_{\text{A}} \tag{B15}$$

Therefore, S has a maximum value at equilibrium $(P_A = P_B)$ and no distribution of V between A and B has a higher S.

Generalizing from the above examples, with no known counter-examples

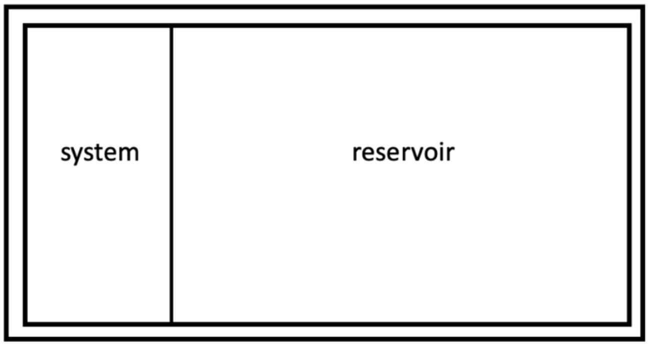
In an isolated system, S increases until it attains its maximum possible value with respect to all available "degrees of freedom".

Notice that, while the entropy of the entire isolated system increases, the entropy of a subsystem can decrease. However, a local decrease in entropy always occurs at the expense of a greater increase in entropy elsewhere. This is especially relevant to biological growth and differentiation.

Notice also that, while the total energy in the system remains constant, one subsystem is initially capable of doing work on the other and finally is not. In other words, in the course of redistributing the energy, its availability to do work has been degraded.

C: Practical Variations of the 2nd Law

Again, we isolate a composite system comprising two compartments. For the present purposes, one compartment is our system of interest and the other is a "reservoir" (as shown in the figure below). The reservoir is an extremely large bath, such that any interaction with the system involves changes in the reservoir that are so tiny by comparison that they are reversible. Two cases are of particular interest. In one, thermal contact allows the reservoir to control the temperature of the system, while the system’s volume and contents are fixed. We call this an **NVT system**. In the other, thermal and mechanical contact allows the reservoir to control the temperature and pressure of the system, while the system’s contents are fixed. We call this an **NPT system**.



An isolated composite system (with its rigid, impermeable and insulating boundaries represented by double lines according to convention) comprising our system of interest in contact with a "reservoir".

NVT systems

NVT conditions are maintained by perfect thermal contact with a reservoir at temperature T^r, so $T = T^r$, and by rigid and impermeable boundaries so $dV, dN_i = 0$. This system’s only degree of freedom is heat exchange between the compartments.

Because the composite system is isolated, we know that

$$0 = d\left(E + E^r\right) \tag{C1}$$

and that

$$0 < \frac{d\left(S + S^r\right)}{dt} \tag{C2}$$

approaching equilibrium and

$$0 = d\left(S + S^r\right) \quad \text{and} \quad 0 > d^2\left(S + S^r\right) \tag{C3}$$

at equilibrium. The key to making use of this information is to realize that, due to its huge size, the changes in the reservoir are reversible and therefore

$$dE^r = T^r dS^r = T dS^r \tag{C4}$$

By replacing dE^r in Equation C1 and then dS^r in Equations C2 and C3, we arrive at

$$0 < \frac{d(S - E/T)}{dt} \tag{C5}$$

approaching equilibrium and

$$0 = d(S - E/T) \quad \text{and} \quad 0 > d^2(S - E/T) \tag{C6}$$

at equilibrium. Since $T > 0$, we can multiply through without a change the direction of the inequalities and obtain

$$0 < \frac{d(TS - E)}{dt} \tag{C7}$$

approaching equilibrium and

$$0 = d(TS - E) \quad \text{and} \quad 0 > d^2(TS - E) \tag{C8}$$

at equilibrium. Thus, for an NVT system, the Helmholtz free energy, $F = E - TS$, decreases with time

$$\frac{dF}{dt} < 0 \tag{C9}$$

until it reaches a minimum

$$dF = 0 \quad \text{and} \quad d^2F > 0 \tag{C10}$$

at equilibrium.

NPT systems

NPT conditions are maintained by perfect thermal and mechanical contact with a reservoir at temperature T^r and pressure P^r, so $T = T^r$ and $P = P^r$, and by impermeable boundaries so $dN_\text{i} = 0$.

Because the composite system is isolated, we know that

$$0 = d\left(E + E^r\right) \tag{C11}$$

$$0 = d\left(V + V^r\right) \tag{C12}$$

as well as that

$$0 < \frac{d(S + S^r)}{dt} \tag{C13}$$

approaching equilibrium and

$$0 = d\left(S + S^r\right) \quad \text{and} \quad 0 > d^2\left(S + S^r\right) \tag{C14}$$

at equilibrium. Again, the key to making use of this information is to realize that, due to its huge size, the changes in the reservoir are reversible and therefore

$$\begin{aligned} dE^r &= -P^r dV^r + T^r dS^r \\ &= +PdV + TdS^r \end{aligned} \tag{C15}$$

Using Equation C12 and the fact that P is constant, we obtain

$$dE^r = d(PV) + TdS^r \tag{C16}$$

By substituting for E^r in Equation C11 and then for S^r in Equations C13 and C14, we arrive at

$$0 < \frac{d(S - (E + PV)/T)}{dt} \tag{C17}$$

approaching equilibrium and

$$0 = d(S - (E + PV)/T) \quad \text{and} \quad 0 > d^2(S - (E + PV)/T) \tag{C18}$$

at equilibrium. Since $T > 0$, we can multiply through without change the direction of inequalities and obtain

$$0 < d(TS - E + PV)/dt \tag{C19}$$

approaching equilibrium and

$$0 = d(TS - E + PV) \quad \text{and} \quad 0 > d^2(TS - E + PV) \tag{C20}$$

at equilibrium. Thus, for an NVT system, the Gibbs free energy, $G = E + PV - TS$, decreases with time

$$\frac{dG}{dt} < 0 \tag{C21}$$

until it reaches a minimum

$$dG = 0 \quad \text{and} \quad d^2G > 0 \tag{C22}$$

at equilibrium.

In summary

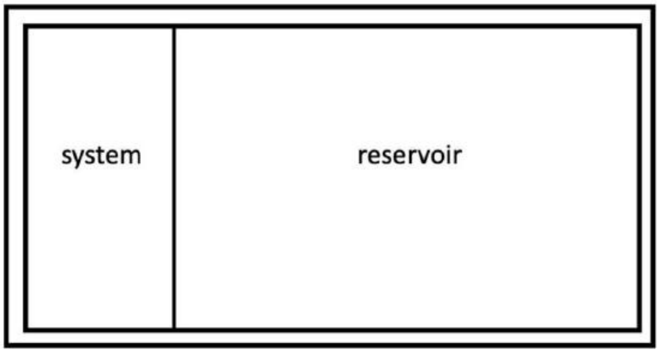
We have found extremum conditions for equilibrium in three types of systems:

System	Constants	2^{nd} Law
isolated	$E, V, \{n_i\}$	$S \uparrow$ to a max
thermal contact only	$T, V, \{n_i\}$	$F \downarrow$ to a min
thermal & mechanical contact only	$T, P, \{n_i\}$	$G \downarrow$ to a min

All equilibrium states are stable, i.e., perturbations and fluctuations regress in return to the extremum condition.

D: Energy Free to Do Work

An interesting question is how the work $\delta w'_{actual}$ that a system actually does on its surroundings differs from the work $\delta w'_{rev}$ that it would do if it operated in infinitesimal steps (i.e., reversibly). As in Appendix C, we consider an isolated composite system, comprising the working system and a large "reservoir". The difference is that we now posit perfect thermal contact ($T = T^r$) and any other contact that allows the system to do work.



An isolated composite system (with its rigid, impermeable and insulating boundaries represented by double lines according to convention) comprising our system of interest in contact with a "reservoir".

Since dE is independent of path

$$dE = \delta q_{\text{rev}} - \delta w'_{\text{rev}} = \delta q_{\text{actual}} - \delta w'_{\text{actual}} \tag{D1}$$

Here δq continues to refers to heat taken up by the system while $\delta w'$ carries a prime to indicate that it refers to work done by the system (hence the negative sign in front of it). Rearranging,

$$\delta w'_{\text{actual}} - \delta w'_{\text{rev}} = \delta q_{\text{actual}} - \delta q_{\text{rev}} \tag{D2}$$

By definition of entropy for each of the compartments,

$$dS = \frac{\delta q_{\text{rev}}}{T} \quad \text{and} \quad dS^r = \frac{-\delta q_{\text{actual}}}{T^r} = \frac{-\delta q_{\text{actual}}}{T} \tag{D3}$$

Rearranging,

$$\delta q_{\text{actual}} - \delta q_{\text{rev}} = -T\left(dS + dS^r\right) \tag{D4}$$

According to the 2$^{\text{nd}}$ Law for the isolated composite system

$$d\left(S + S^r\right) \geq 0 \tag{D5}$$

where the equality applies only at equilibrium. Combining Equations D2, D4, and D5,

$$\delta w'_{\text{actual}} - \delta w'_{\text{rev}} \leq 0 \tag{D6}$$

In other words, the actual path always produces less work than the reversible path (except at equilibrium where there is no distinction). Furthermore,

$$\begin{aligned} \delta \mathrm{w}'_{\text{rev}} &= \delta q_{\text{rev}} - dE \\ &= -\left[dE - T^r dS\right] \\ &= -d(E - TS) \\ &= -dF \end{aligned} \tag{D7}$$

Thus, at a fixed temperature, the maximum work that can be done **by a system on its surroundings** is done in a reversible process (i.e., against max resistance) and equals $-dF$ or the loss of the Helmholtz free energy of the system. In other words, F is a "free energy" in the sense that the change in F is the maximum energy available to do work at a given temperature. It is less than the change E by an amount equal to the change in TS.

When the contact between system and reservoir allows both PV work and other forms of work, we can isolate the latter by subtracting the former and then making use of Equation D7 to arrive at

$$\begin{aligned}\delta \mathrm{w}'_{\text{rev-nonPV}} &= \delta \mathrm{w}'_{\text{rev}} - p^r dV \\ &= -\left[dE + p^r dV - T^r dS\right] \\ &= -d(E + pV - TS) \\ &= -dG\end{aligned} \tag{D8}$$

In other words, at a given temperature and pressure, the maximum non-PV work that the system can do on its surroundings is done in a reversible process and equals $-dG$ or the loss of the Gibbs free energy of the system. This is useful for electrochemical work.

E: Interpreting the Fundamental Equations

The fundamental equation for the variation of a state function $\mathfrak{F}$ expresses the contributions due to changes in its natural independent variables (x, y, z)

$$d\mathfrak{J} = \left(\frac{\partial \mathfrak{F}}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \mathfrak{F}}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \mathfrak{F}}{\partial z}\right)_{x,y} dz$$

The following table summarizes the partial derivatives for the most commonly used state functions.

$\mathfrak{F}$	fundamental equation	natural independent variables	first derivatives
E	$dE = TdS - PdV + \Sigma_i \tilde{\mu}_i dn_i$	$S, V, \{n_\mathrm{i}\}$	$(\partial E/\partial S)_{V,\{n_i\}} = T$ $(\partial E/\partial V)_{S,\{n_i\}} = -P$ $(\partial E/\partial ni)_{S,V,\{n_{j\neq i}\}} = \tilde{\mu}_i$
H	$dH = TdS + VdP + \Sigma_i \tilde{\mu}_i dn_i$	$S, P, \{n_\mathrm{i}\}$	$(\partial H/\partial S)_{P,\{n_i\}} = T$ $(\partial H/\partial P)_{S,\{n_i\}} = V$ $(\partial H/\partial n_i)_{S,P,\{n_{j\neq i}\}} = \tilde{\mu}_i$
F	$dF = -SdT - PdV + \Sigma_i \tilde{\mu}_i dn_i$	$T, V, \{n_\mathrm{i}\}$	$(\partial F/\partial T)_{V,\{n_i\}} = -S$ $(\partial F/\partial V)_{T,\{n_i\}} = -P$ $(\partial F/\partial n_i)_{T,V,\{n_{j\neq i}\}} = \tilde{\mu}_i$
G	$dG = -SdT + VdP + \Sigma_i \tilde{\mu}_i dn_i$	$T, P, \{n_\mathrm{i}\}$	$(\partial G/\partial T)_{P,\{n_i\}} = -S$ $(\partial G/\partial P)_{T,\{n_i\}} = V$ $(\partial G/\partial n_i)_{T,P,\{n_{j\neq i}\}} = \tilde{\mu}_i$

F: Maxwell's Relations

For a well-behaved function, $\mathfrak{F}$, the order of derivatives is permutable

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial \mathfrak{F}}{\partial x}\right)_{y,z}\right]_{x,z} = \left[\frac{\partial}{\partial x}\left(\frac{\partial \mathfrak{F}}{\partial y}\right)_{x,z}\right]_{y,z}$$

Corresponding relationships from the second derivatives of E are

$$\left(\frac{\partial T}{\partial V}\right)_{S,\{n_i\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{n_i\}}$$

$$\left(\frac{\partial \tilde{\mu}_i}{\partial V}\right)_{S,\{n_i\}} = -\left(\frac{\partial P}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}}$$

$$\left(\frac{\partial \tilde{\mu}_i}{\partial S}\right)_{V,\{n_i\}} = \left(\frac{\partial T}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}}$$

$$\left(\frac{\partial \tilde{\mu}_\mathrm{k}}{\partial n_\mathrm{j}}\right)_{S,V,\{n_{i\neq j}\}} = \left(\frac{\partial \tilde{\mu}_\mathrm{j}}{\partial n_\mathrm{k}}\right)_{S,V,\{n_{i\neq k}\}}$$

from the second derivatives of H are

$$\left(\frac{\partial T}{\partial P}\right)_{S,\{n_i\}} = \left(\frac{\partial V}{\partial S}\right)_{P,\{n_i\}}$$

$$\left(\frac{\partial \tilde{\mu}_i}{\partial P}\right)_{S,\{n_i\}} = \left(\frac{\partial V}{\partial n_i}\right)_{S,P,\{n_{j\neq i}\}}$$

$$\left(\frac{\partial \tilde{\mu}_i}{\partial S}\right)_{P,\{n_i\}} = \left(\frac{\partial T}{\partial n_i}\right)_{S,P,\{n_{j\neq 1}\}}$$

$$\left(\frac{\partial \tilde{\mu}_\mathrm{k}}{\partial n_\mathrm{j}}\right)_{S,P,\{n_{i\neq j}\}} = \left(\frac{\partial \tilde{\mu}_\mathrm{j}}{\partial n_\mathrm{k}}\right)_{S,P,\{n_{i\neq k}\}}$$

from the second derivatives of F are

$$-\left(\frac{\partial S}{\partial V}\right)_{T,\{n_i\}} = -\left(\frac{\partial P}{\partial T}\right)_{V,\{n_i\}}$$

$$\left(\frac{\partial \tilde{\mu}_i}{\partial V}\right)_{T,\{n_i\}} = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,\{n_{j\neq i}\}}$$

$$\left(\frac{\partial \tilde{\mu}_i}{\partial T}\right)_{V,\{n_i\}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,V,\{n_{j\neq t}\}}$$

$$\left(\frac{\partial \tilde{\mu}_\mathrm{k}}{\partial n_\mathrm{j}}\right)_{T,V,\{n_{i\neq j}\}} = \left(\frac{\partial \tilde{\mu}_\mathrm{j}}{\partial n_\mathrm{k}}\right)_{T,V\{n_{i\neq k}\}}$$

and from the second derivatives of G are

$$\begin{aligned}
-\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}} &= \left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}} \\
\left(\frac{\partial \tilde{\mu}_i}{\partial P}\right)_{T,\{n_i\}} &= \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j\neq 1}\}} \\
\left(\frac{\partial \tilde{\mu}_i}{\partial T}\right)_{P,\{n_i\}} &= -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,\{n_{j\neq t}\}} \\
\left(\frac{\partial \tilde{\mu}_\mathrm{k}}{\partial n_\mathrm{j}}\right)_{T,P,\{n_{i\neq j}\}} &= \left(\frac{\partial \tilde{\mu}_\mathrm{j}}{\partial n_\mathrm{k}}\right)_{T,P,\{n_{i\neq k}\}}
\end{aligned}$$

E: Boltzmann's Constant

The simplest system for relating microscopic features to macroscopic observations is a dilute gas of N atoms. There are four steps:

a. For this system, the fundamental equation for energy simplifies to

$$dE = -pdV + TdS \tag{G1}$$

b. For this system, the ideal gas law applies, such that

$$P = nRT/V \tag{G2}$$

where $n =$ the number of moles of atoms and $R =$ the gas constant. Therefore

$$-PdV = -\left(\frac{\text{nRT}}{V}\right) dV \quad \text{and} \quad dE = -\left(\frac{\text{nRT}}{V}\right) dV + TdS \tag{G3}$$

c. In this system, the number of ways to place an atom is proportional to the available volume V and, because they don't interact, the number of ways of placing all N atoms is proportional to V^N, i.e.,

$$W = cV^N \tag{G4}$$

where c is a proportionality constant. Therefore,

$$S = k\ln(cV^N) = k[\ln(c) + N\ln(V)] \tag{G5}$$

and, for a volume change dV, the change in entropy is

$$dS = kN\left(\frac{1}{V}\right) dV \tag{G6}$$

Substituting into Equation G3, the change in energy due to a volume change dV is

$$dE = -\left(\frac{\text{nRT}}{V}\right) dV + TkN\left(\frac{1}{V}\right) dV \tag{G7}$$

d. A monatomic gas has only kinetic energy which, according to kinetic theory, is

$$E = \left(\frac{3}{2}\right) PV = \left(\frac{3}{2}\right) nRT \tag{G8}$$

independent of volume. In other words, for any volume change, dV, $dE = 0$.

Thus, from Equation G7,

$$0 = -\left(\frac{nRT}{V}\right) dV + \left(\frac{TkN}{V}\right) dV = (-nR + Nk)\left(\frac{T}{V}\right) dV \tag{G9}$$

This can only hold for all possible volume changes, dV, if

$$(-nR + Nk) = 0, \quad \text{i.e.,} \quad k = \left(\frac{n}{N}\right) R = \frac{R}{N_A} \tag{G10}$$

where N_A is Avogadro's constant. In other words, Boltzmann's constant k and the gas constant R are the same constant in different units (per particle in k and per mole of particles in R).

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