

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,

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}} \quad (1)$$

where Δ 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 Δ) 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,

$$dE = dw_{\text{rev}} + dq_{\text{rev}} \quad (2)$$

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)

$$dw_{3D} = -PdV \quad (3)$$

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

$$dw_{2D} = \tau_2 dA, \quad (4)$$

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

$$dw_{1D} = \tau_1 dL \quad (5)$$

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 ,

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

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

$$dE = -PdV + \tau_2 dA + \tau_1 dL + \sum_i \tilde{u}_i dn_i + dq_{\text{rev}} \quad (7)$$

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

$$dE = -PdV + dq_{\text{rev}} \quad (8a)$$

or

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

where

$$H = E + PV \quad (9)$$

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"

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

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

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (11)$$

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 , τ_2 , τ_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

$$dE = -PdV + \tau_2 dA + \tau_1 dL + \sum_i \tilde{u}_i dn_i + TdS \quad (12)$$

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

$$dS = \frac{dq_{\text{rev}}}{T} \quad (13)$$

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"

$$F = E - TS \quad (14)$$

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"

$$G = E + PV - TS \quad (15)$$

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.

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