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Review

Chemical Thermodynamics—A Practical Wonderland

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Abstract: Chemical thermodynamics is frequently thought of as being a hard subject and quite abstract. In fact, it is one of the most practical of subjects when you consider that the field of chemical engineering (responsible for endless useful applications) is effectively applied chemical thermodynamics. In this essay, examples of these applications are given, especially with respect to sustainability. The essay first considers the limits of thermodynamics and the constraints put on it in terms of the rigorous definitions of the principal function's energy, entropy, and Gibbs energy.

Keywords: chemical thermodynamics; sustainability; rigorous definitions of functions and effects

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1. Introduction

When we were undergraduate students majoring in chemistry, it was common knowledge among us that physical chemistry was the hardest subject in the curriculum, and that within that, thermodynamics was the most difficult to master. Consider that chemistry is triply difficult to learn since it involves a knowledge of and skill in mathematics (algebra early and calculus later), an ability to handle abstract ideas (the quantum chemistry involved in the electronic structure of the elements, and the entropy function later), as well as memorizing lots of information about chemical reactions and chemical properties. We believe it is unfortunate that modern general chemistry texts include too much information about thermodynamics, especially about the entropy and Gibbs functions (see Battino 1979 [1]). In the next section, RB will discuss the rigor necessary for understanding and utilizing chemical thermodynamics. The discussion in Section 3, by TML, will be concerned with sustainability and the environment, and how these are related to the practicality of chemical thermodynamics.

2. Need for Rigorous Definitions RB

I taught a graduate course in chemical thermodynamics for about 47 years. The texts were various editions of a book by I. M. Klotz (7th Ed. [2]), which I first came across in graduate school. Klotz emphasized the rigor needed in defining thermodynamics terms, and how this could be done operationally (i.e., in terms of experimental operations).

Let us begin with some comments about the scope and limitations of macroscopic thermodynamics. The scope consists of four parts: (1) predicting whether a given transformation will take place spontaneously; (2) predicting the extent (or limit) of the reactions; (3) calculations of the work obtainable from a system; and (4) calculations of energy changes in chemical reactions. The limitations of macroscopic thermodynamics are several-fold (see explanatory comments following):

1. It deals solely on a macroscopic scale with large aggregates of molecules;
2. Time is not a thermodynamic coordinate;
3. Thermodynamics deals with equilibrium conditions;
4. It is not concerned with systems in motion, per se.

Kinetics, the kinetic theory of matter, and statistical thermodynamics are different approaches. Macroscopic thermodynamics does not need the existence of molecules. With respect to item 2, note that benzene (C_6H_6) can exist in the presence of C(gr) and H_2(g), but if these three substances were in *equilibrium* benzene would be unstable, i.e., very small concentrations, with respect to the other two. Moreso, if the allotropic forms of carbon, diamond, and graphite were in equilibrium, there would mostly be graphite.

The following quote by the physicist Eugene Wigner is enlightening: "With thermodynamics, one can calculate almost everything crudely; with kinetic theory, one can calculate fewer things, but more accurately; and with statistical mechanics, one can calculate almost nothing exactly".

Now, let us continue with an examination of the First Law of Thermodynamics (actually, the Second Law was known before the First). The First Law defines the energy *function* (E) in terms of heat (Q) and work *(W) effects*:

$$\mathrm{d}E = \mathrm{D}Q + \mathrm{D}W \tag{1}$$

Please note that we are already making important distinctions in that energy is a *function* and that heat and work are *effects*. In calculus, this distinction is made by using the lowercase d for *exact* differentials, and the uppercase D for *inexact* differentials. The integral of an inexact differential between the initial and final states of a process depends on the *path* between those states. On the other hand, the integral of an exact differential is *independent* of the path between the initial and final states (it depends solely on the difference between those states). The marvel of Equation (1) is that somehow in our universe, the *sum* of two inexact differentials yields an exact differential.

Accordingly, we can define the energy function operationally by describing how to measure heat and work effects. Heat effects can be determined experimentally (operationally) by the use of a Bunsen ice calorimeter. Imagine a very well-insulated container with an opening on top into which a glass tube is fixed. Inside this container are a mixture of ice and water and the system of interest. The water is partly up the glass tube. A reaction occurs in the system in which heat is evolved or absorbed. If heat is evolved, the height of the water in the tubing *decreases* since some ice melts; if heat is absorbed, the height of the water increases since some ice is formed. (Recall that ice has a lower density than liquid water).

Consider two thermally isolated masses of different substances (A at T_2 and B at T_1) that are at different temperatures (next paragraph is on operationally defined thermometers) which are in contact with each other. With $T_2 > T_{1,}$ heat "flows" from the hotter to the colder body until, at equilibrium, both bodies are at the temperature T_3. We then have the following two equations:

$$Q_\mathrm{A} = C_\mathrm{A}(T_3 - T_2) \tag{2}$$

$$Q_\mathrm{B} = C_\mathrm{B}(T_3 - T_1) \tag{3}$$

where

$$Q_\mathrm{A} = -Q_\mathrm{B} \tag{4}$$

The units of heat are joules (J). When heat is absorbed by the system, Q is positive, and it is negative when the system evolves heat. The C term is the *heat capacity* of each substance, and it depends on the characteristics of the substance, is proportional to the mass of the substance, and is a function of temperature. We can also define *heat* as being the name for energy, as it is transferred from one region to another by the thermal processes of conduction (regions in contact), convection (regions connected by a fluid), or radiation (radiant energy). By convention, if a system absorbs heat, the value is positive (+), and if it evolves heat, then Q is negative.

Equations (2) and (3) involve the measurement of temperature. Thus, to operationally define heat effects, we first need to do this for temperature. For this, we need a temperature scale that involves knowing five things:

1. A standard substance (e.g., helium gas);
2. A physical property of the standard substance (such as the volume or pressure for a gas, and the length or electrical resistance of a solid). For a gas, the mass and either the pressure or the volume are held constant;
3. An interpolation formula connecting the physical property to the temperature (linear or exponential or...);
4. A sufficient number of *fixed points*, i.e., those physical states where the temperature is invariant, such as a melting or boiling point at constant pressure, or a triple point like that of water where three phases are in equilibrium;
5. Numerical values are then assigned to the fixed points. (0 °C to the melting point of water and 100 °C to the boiling point, or 273.16 K to the triple point of water).

Once all of these choices are made, a temperature scale has been operationally defined. In practice, the internationally accepted way to do this involves a platinum resistance thermometer in which the electrical resistance of a small coil of pure platinum wire is the preferred device. (Beyond this description, the reader can go to the literature for more information—it suffices here to know that temperature measurement can be defined rigorously and operationally).

Before operationally defining the work effects, it is useful to cite what is commonly called the *Zeroth Law of thermodynamics*: two systems in thermal equilibrium with a third are in thermal equilibrium with each other.

Work is the name for energy transferred by mechanical means, e.g., compression, magnetization, or stirring. Operationally, work is defined as a force times a displacement. Frequently, in thermodynamics, we are concerned only with pressure/volume work or $P\mathrm{d}V$. Denoting the displacement by x, the work by W, and the external force by F' we get:

$$\mathrm{D}W = -F'\mathrm{d}x \tag{5}$$

Since $F' = P'\mathrm{A}$ where A is the area and P' is the external pressure, we get:

$$W = \int_{\mathrm{a}}^{\mathrm{b}} F'dx = \int_{\mathrm{a}}^{\mathrm{b}} P'\mathrm{A}\mathrm{d}x = \int_{\mathrm{a}}^{\mathrm{b}} P'\mathrm{d}V = \int_{\mathrm{a}}^{\mathrm{b}} P\mathrm{d}V \tag{6}$$

where A$\mathrm{d}x$ is the differential of the volume ($\mathrm{d}V$) and we no longer need the prime on the P term. The work effect is defined by an inexact differential, and you always need to specify the path, since the value of the integral between states a and b is dependent on the path. By definition, the value of the work effect is positive (+) if work is done *on* the system, and negative (−) if work is done *by* the system.

The enthalpy function H is defined as $H = E + PV$. In differential form, this is:

$$\mathrm{d}H = \mathrm{D}Q + V\mathrm{d}P \tag{7}$$

The exact differential of the enthalpy function is the sum of one inexact differential for the heat effect Q and the exact differential of $V\mathrm{d}P$. Thus, the integral of $\mathrm{d}H$ between two states is solely a function of those states and independent of the path. For only $P\mathrm{d}V$, the work effects changes occurring in the energy function E are the heat effect for a particular process or reaction at constant volume, and the changes in the enthalpy function are the heat effect for a particular process or reaction at constant pressure.

Since most chemical processes occur at constant pressure (open vessels), the enthalpy function is quite important in knowing and determining the heat effects for these processes. For changes in the enthalpy, for any change at constant pressure, Hess's Law applies. This law states that the heat changes occurring in a given chemical reaction are independent of the path: that is, the thermodynamic function H. This law means that thermochemical equations can be manipulated as ordinary mathematical equations, e.g., added and subtracted. Please note, the enthalpy function is a practical one, but not a fundamental one (it has been defined in terms of the fundamental energy function).

The *Second Law of Thermodynamics* involves the entropy function, S. The Thomson (Lord Kelvin) definition is, "It is impossible by a cyclic process to take heat from a reservoir and convert it to work without, in the same operation, transferring heat from a hot to a cold reservoir". The entropy function is defined as:

$$\mathrm{d}S = \mathrm{D}Q_{\mathrm{rev}}/T \tag{8}$$

We have earlier, operationally defined the heat effect Q and the temperature T. This apparently simple equation incorporates a major constraint: *the heat effect must be determined along a reversible path.* A *reversible process* is a succession of states, each of which is an equilibrium state, in which the temperature and pressure have defined values; such a process is also called a *quasi-static process*. The change in the entropy function is:

$$\Delta S = S_2 - S_1 = \int_1^2 \mathrm{d}S = \int_1^2 (\mathrm{D}Q_{\mathrm{rev}}/T) \tag{9}$$

Note that all natural processes are *irreversible*—this means that in any such process, there is a net increase of the entropy of the universe. As such, all spontaneous processes are not thermodynamically reversible. The definition of the entropy function is such that one must always be aware of the way it is defined, and also know the constraints on determining changes in the entropy for any given process. Consequently, changes in the entropy function can *only* be determined along reversible paths. In practice, reversible paths can be adequately defined or approximated.

There are two practical thermodynamic functions that are based on the entropy function. They are the Gibbs function or Gibbs energy defined as:

$$G = H - TS \text{ or } \mathrm{d}G = \mathrm{d}H - S\mathrm{d}T - T\mathrm{d}S \tag{10}$$

and the Helmholtz function or Helmholtz energy defined as:

$$A = E - TS \text{ or } \mathrm{d}A = \mathrm{d}E - S\mathrm{d}T - T\mathrm{d}S \tag{11}$$

Since both the Gibbs and Helmholtz functions are defined in terms of the entropy function, changes in them *must be along reversible paths*. This constraint on these functions is often overlooked. These definitions are such that changes in the Gibbs energy can be determined in processes that occur at constant pressure, and those in the Helmholtz energy, at constant volume. Again, this makes the Gibbs energy more useful since most chemical processes occur at constant pressure. A practical version of the Gibbs energy can be derived to be:

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = V\mathrm{d}P - S\mathrm{d}T + DW' \tag{12}$$

For reactions occurring at constant pressure and temperature (most common):

$$\mathrm{d}G = \mathrm{D}W' \text{ or } \Delta G = W' \tag{13}$$

That is, this is the *maximum* non-PV work the system can do. ("Maximum" is italicized since the changes in these functions must be evaluated along reversible paths).

In closing this section on the need for rigorous definitions of changes in thermodynamic functions, it is reiterated that, in applying thermodynamics to the real world, one must always be aware of these constraints. The entropy function has been found in politics, economics, sociology, and psychology and is used therein *without any understanding* of the need for reversible paths. The Gibbs energy is frequently found in biological and biochemical publications, again, without an overt acknowledgment that thermodynamics is limited to equilibrium states, and changes in this function must be determined along reversible paths (it is difficult to conceive how this may be known in living systems).

3. Thermodynamics and Sustainability and the Environment (TML)

In linking thermodynamics to sustainability, it is necessary to first define sustainability in terms of conserving matter and energy. In today's world, we are living in a most unsustainable way; depleting our natural resources of minerals (one example involves rare earth metals); fossil fuels; and biota, which includes trees, vegetation, and the fish in the sea. Furthermore, we are adding CO_2 to the atmosphere which is resulting in global climate change, and we are depleting our soil of nutrients through unsustainable farming practices. All of these compromise future generations. In short, we are living a very unsustainable life. (See Ref. [3].)

Sustainability of the environment implies causing little or no damage to the environment, to make it possible for our civilization to continue for a long time. The energy we use at the moment is not sustainable as there is a limit on the amount of coal, oil, and gas in the Earth's crust. Furthermore, the use of fossil fuels results in an increase in the CO_2 level in the atmosphere, which in turn causes an increase in global temperature, which in turn causes climate change. These changes involve changes in weather patterns, increased rainfall in some areas, drought in other areas, and an increase in violent winds, hurricanes, and tornadoes.

To be sustainable, we must not let the resources of our planet change from the equilibrium levels which have sustained the biota on Earth for thousands of years. This, of course, includes the gaseous mix of our atmosphere.

Thermodynamics tells us that, in a closed system (no interchange of matter and energy with the outside world) the inter-conversion of matter into energy, and vice versa always involves an increase of entropy. As a result, in the end, the system runs down. In other words, sustainability is not possible in a closed system when matter and energy are interchanged. *Fortunately*, Earth is not a closed system and energy does enter the system via the Sun.

To maintain a sustainable system on Earth, the incoming energy—the Sun's energy—must be harnessed. We can do this by using solar cells to convert the Sun's energy into electricity, or we can harness the energy from wind to make electricity. The latter is indeed a secondary effect resulting from the Sun's energy. Unfortunately, the efficiency in both these cases (solar cell and wind turbine technologies) is relatively low. The most efficient way of collecting the Sun's energy is via plant material—plants on land and phytoplankton in the seas. Thus, in the end, the sustainability of human life on Earth is dependent on the sustainability of other living systems.

The dilemma facing our civilization is this: how can we best harness the Sun's energy to create a sustainable life on Earth? There are many ways of doing this:

☐ Growing trees and harvesting the wood to make electricity;
☐ By converting CO_2 to O_2, trees replenish $O_{2;}$
☐ Extract chemicals from plants for plastic manufacture, pharmaceutical manufacture, etc.;
☐ Use solar cells;
☐ Use wind energy to generate power;
☐ Develop permaculture;

We have focused largely on creating electricity in a sustainable way by using the Sun's energy. To be sustainable, other issues have to be taken into account and these include recycling, reusing, and reducing.

The central connection between sustainability and thermodynamics is via the entropy function: the first part of this paper concerns the rigorous definitions, understanding, and knowledge of the entropy and Gibbs functions. The necessity for performing calculations along reversible paths is essential for these two functions. For this, an understanding of chemical thermodynamics is critical to understanding the world that we live in, and the ways in which it continues to change.

Beginning students in physical chemistry and graduate students in chemical thermodynamics often think of these subjects as being too theoretical and unconnected with the reality of daily activities. If you are breathing now, and your body temperature is around 37 °C, then there are almost endless thermodynamic processes going on within your body. There are exothermic reactions that maintain your temperature, there are solubilities of gases in various bodily fluids and membranes and cells, and there are many chemical reactions in the digestive and elimination systems. We are, in effect, chemical factories, and much of what transpires can be described and calculated by chemical thermodynamics. The efficiencies of automobile engines and other machines can be calculated. Power plants and engines of all varieties operate via describable heat cycles, and their efficiencies can be calculated. Please be aware, that the practical field of chemical engineering is in effect, applied thermodynamics. Industrial processes, such as the manufacturing of plastics, the refining of petroleum, recycling, sewage treatment, materials based on natural gas, and the food industry all use thermodynamics. Additionally, how these processes function in terms of acquiring materials and their disposal also affects the health of our environment.

Finding ways to sustain our planet and all of its inhabitants (fauna and flora) in a healthy condition benefits from an understanding of how to apply thermodynamics to environmental concerns. Even more important is that our knowledge of the limits of thermodynamics and the rigor needed are essential.

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