

## MDAG.com Internet Case Study 65

### Thermodynamics - Not Designed for Minesite Components and Their Drainages

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#### Abstract

Based on the excellent work of Barbour (2020b), the reviews of thermodynamics, its history and development, and its application to chemistry show that thermodynamics cannot be reliably applied to minesite components and their drainages. The original authors and researchers back to the 1800's specify conditions that confirm this, including J. Willard Gibbs who developed chemical thermodynamics. The requirements for closed systems (“isolated boxes”), for the validity of entropy and the Second Law of Thermodynamics, and for infinitesimal changes in temperature and pressure, also confirm this. Barbour (2020b) states,

*“[N]othing remotely like thermodynamic systems exist in natural form in the universe. They can be realized in a good approximation for a long time in a laboratory, but in the pure form they exist only on paper and in the brains of theoreticians.”*

Thus, the usage of thermodynamics and chemical equilibrium is inherently unreliable in the forward modelling of minesite drainages with stock programs like PHREEQE and MINTEQ. Similarly invalid is the invocation of one-sided “equilibrium” by programs like Goldsim that lower any supersaturated aqueous concentrations but do not raise undersaturated concentrations.

There is no doubt that drainages at full-scale minesites often attain some type of equilibrium, but this is not necessarily close to thermodynamic equilibrium. More reasonable and accurate site-specific approaches recognize factors like: site-specific solubilities and meta-stabilities, scale emergence, self-organization, other forms of energy that affect aqueous concentrations, electrohydrodynamics, non-equilibrium thermodynamics at least on a microscopic scale, and the many wavelengths of periodicity that affect aqueous concentrations synergistically and/or antagonistically.

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## 1. Introduction

Quantum physics and the fundamental nature of elapsing time are not usually important to minesite drainages and their chemistries. In this MDAG case study, they are, but in an indirect way.

Dr. Julian Barbour recently published a book entitled *The Janus Point - A New Theory of Time* (Barbour, 2020a). It includes an intriguing argument that the passage of time, particularly as implied by the Second Law of Thermodynamics, may not be an intrinsic characteristic of the Universe.

Dr. Barbour has explained that *The Janus Point* included a detailed history of thermodynamics. However, the book's editor had much of that history removed, about 100 pages. This inspired Dr. Barbour to compile the deleted information into a free 96-page PDF download called *The History of Thermodynamics* (Barbour 2020b). In my opinion, this should be required reading for anyone using thermodynamics.

One lesson learned from *The History of Thermodynamics* is that thermo (heat-driven) dynamics (movement) was originally developed for the specific purpose of closed-system heat-driven mechanical work like steam engines. Gibbs (1875 - 1878) extended thermodynamics to chemistry leading to chemical equilibrium. Without good justification, thermodynamics was applied to the Universe as a whole and, by extension, to portions of the Universe like minesite components. This is summarized below in Chapter 3.

This MDAG case study summarizes Barbour (2020b) and the notes of caution from Gibbs (1875-1878) to show thermodynamics cannot apply reliably to minesite components and their drainages. The fact that thermodynamics has been applied regularly to minesite drainages is mostly testimony to (1) other options that could better explain geochemical processes receiving less attention and (2) chemical equilibrium performs relatively well as long as not taken literally and as accurate. Chapter 4 lists some alternatives and extensions to thermodynamics.

## 2. The Laws of Thermodynamics

To show that thermodynamics does not apply to minesite components and their drainages, a good starting point is a review of the Laws of Thermodynamics. Wikipedia (2021a) is used for this, because it gives relatively simple and alternative versions of each Law.

First Law:

*“The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic systems. In general, the law of conservation of energy states that the total energy of **an isolated system** [MDAG emphasis] is constant; energy can be transformed from one form to another, but can be neither created nor destroyed . . . [I]t is not possible to construct a machine which will perpetually output work without an equal amount of energy input to that machine. Or more briefly, a perpetual motion machine of the first kind is impossible.”*

Second Law:

*“The second law of thermodynamics indicates the irreversibility of natural processes, and, in many cases, the tendency of natural processes to lead towards spatial homogeneity of matter and energy, and especially of temperature. It can be formulated in a variety of interesting and important ways. One of the simplest is the Clausius statement, that heat does not spontaneously pass from a colder to a hotter body . . . According to the second law, in a reversible heat transfer, an element of heat transferred,  $dQ$ , is the product of the temperature ( $T$ ), both of the system and of the sources or destination of the heat, with the increment ( $dS$ ) of the system’s conjugate variable, its entropy ( $S$ ):  $\delta Q = T dS$ ”*

Third Law:

*“The third law of thermodynamics can be stated as: A system’s entropy approaches a constant value as its temperature approaches absolute zero. At zero temperature the system must be in the state with the minimum thermal energy (the ground state).”*

### 3. The Basis of Thermodynamics

#### 3.1 Introduction

As a weak substitute to repeating Barbour (2020b) in its entirety, this section will briefly summarize some major points in the history of thermodynamics. Please understand that “thermodynamics” primarily describes the physical movement and the work produced by heat, and vice versa. It is a long story, spanning much more than a century, showing how “heat-driven movement” evolved to define chemical reactions and aqueous equilibrium.

Although the word was first used in 1849, Barbour (2020b) traces the start of thermodynamics back to the mid-1700's to:

*“a strange observation made by Joseph Black (1728-1799). A professor at Edinburgh who discovered magnesium and advised whisky distillers, he happened during his work to leave two buckets of water in a room. The first contained ice and water, the second only water. The water temperature in both buckets was at the freezing point. When he came back a few hours later, the first bucket contained less ice and correspondingly more water but, to Black's surprise, it was still at the freezing point. The water in the second bucket was noticeably warmer. Only when all the ice had melted did the water in the first bucket begin to get warmer.”*

This led to the definition of “caloric” as an invisible and indestructible “heat fluid” that flows from one body to another. This definition was eventually shown to be seriously inaccurate in some ways.

In the early 1800's, Sadi Carnot focussed on work done by mechanical machines like steam engines using heat, as published in his *Reflections on the Motive Power of Fire* (translated to English in 1824). Carnot emphasized that, for steam engines to work, some heat must be transferred from a hotter body to a colder body. This observation later led others to some fundamental laws for motion caused by heat, thus becoming thermodynamics (see Chapter 2 above).

#### 3.2 The Requirement of Infinitesimal Temperature Changes

It is worth emphasizing here that the laws of thermodynamics apply only when temperature differences between two bodies are “infinitesimal”. This requirement can be traced back to a statement by Carnot that for maximum work using the Ideal Gas Law in a finite period:

*“the bodies employed to realize the motive power of heat there should not occur any change of temperature which may not be due to a change of volume.”*

However, this is not realistic. If a temperature difference caused by any change other than volume is larger than “infinitesimal”, then some transferred heat is involved raising the cooler temperature rather than in work (see Figure 1 and the related discussion in Barbour, 2020b, for more detail). Barbour (2020b) adds, “it is very important that the ideal process is perfectly reversible”. Similarly, the definition of a typical thermodynamic system by Nobel Laureate Enrico Fermi is:

*“confined ideal gas whose pressure  $P$ , volume  $V$  and temperature  $T$  can be changed from without in infinitesimal reversible transformations through a succession of equilibrium states.”*

As a result, the Laws of Thermodynamics do not apply when a temperature change is more than infinitesimal. This situation can be expected spatially and temporally in minesite components and their drainages which are open to short-term climatic and weather variations.

### 3.3 The Second Law and Its Various Meanings

Even under ideal conditions, the return of a system to its original condition after doing work can not be achieved unless additional heat (or work) is used to get it there. That observation led to “entropy”, which is basically heat (now sometimes generalized to “energy”) that is “lost” or “consumed” and does no work.

This is attributed to Rudolf Clausius in the mid-1850's (Barbour, 2020b), who also wrote that heat can never pass from a colder body to a warmer body without some other change occurring at the same time. This in turn led to the Second Law of Thermodynamics (see Chapter 2), which can be stated in many ways, more or less ambiguous, and still open to some debate and redefinition (e.g., Section 2.1 of Morin, 2020a).

Simplistically, the Second Law is mathematically expressed as:  $dS = \delta Q / T$ , where  $T$  is absolute temperature in Kelvin (see also the Third Law in Chapter 2). Therefore, any spontaneous transfer of heat ( $\delta Q$ ) from a higher-temperature body (higher  $T$ ) connected to a lower-temperature body (lower  $T$ ) mathematically forces  $dS$  to be positive. Barbour (2020b) points out:

*“The key concept of entropy can be defined for thermodynamic systems in large part because they can be **confined and controlled** [MDAG emphasis]. Who can do that for the universe? ... [N]othing remotely like thermodynamic systems exist in natural form in the universe. They can be realized in a good approximation for a long time in a laboratory, but in the pure form they exist only on paper and in the brains of theoreticians.”*

In the 1850's, based on the then-current understanding of the Universe being formed recently, some physicists concluded that the Laws of Thermodynamics applied to the entire Universe. As a result, geological principles like uniformitarianism came under attack. After all, the Second Law says that (1) all heat that can perform work is eventually lost, (2) there is ongoing dissipation in energy, and (3) eventually the Universe and everything in it will suffer a “heat death” (the combination of the Second and Third Law).

As Barbour (2020b) puts it:

*“For several decades a battle raged between, on the one hand, the geologists and supporters of evolution and, on the other, the physicists. It pitted two ‘bulldogs’ against each other: Thomas Huxley on Darwin’s side and Peter Guthrie Tait, who argued very dogmatically for the line taken by Thomson. Of course, all Thomson’s arguments about the [misunderstood] nature and [vastly underestimated] age of the sun and earth were hopelessly premature.”*

While such attacks on geology and evolution by thermodynamics were eventually put down, the belief that the Laws apply to the Universe was not and persists to this day (discussed further in Chapter 4 below).

### 3.4 Thermodynamics is Applicable to Closed, Isolated “Boxes”

Barbour (2020a and 2020b) often refer to thermodynamics as applying to a closed or confined or isolated rigid box, with gas molecules bouncing off the walls to create “pressure”. Recent information on the expansion rate of the Universe (not available in the 1800's) indicates the “box” of the Universe can be expanding faster than particles can reliably continue to collide with the walls to create and maintain a “pressure”.

This was foreshadowed by J. Willard Gibbs (Section 3.5 below) in 1902 (*Elementary Principles in Statistical Mechanics*). Gibbs pointed out that a thermodynamic system cannot be allowed to (1) spread out in an infinite space or (2) have velocities that can grow faster than a certain rate. These carry similar implications as the requirement of a rigid box for the Universe, where thermodynamics would not apply because “[o]nly if confined can it be carried through a sequence of equilibrium states.” Thus, thermodynamics would not apply to the Universe for yet another reason.

Therefore, as illustrated above, thermodynamics does not apply to an unconfined open system, through which mass (such as air and water) can enter and leave. In turn, thermodynamics does not apply to the Universe as a whole or even to minesite components and their drainages, although some still believe this (see Chapter 5). Minesite components and their drainages are not closed and isolated “boxes”.

### 3.5 J. Willard Gibbs and Chemical Thermodynamics

Gibbs (1875-1878) adapted thermodynamics to chemistry to create chemical thermodynamics and to define chemical equilibrium (Wikipedia, 2021b).

Today, the characterization and interpretation of minesite drainage, its aqueous chemistry, and ML-ARD rely heavily on chemical thermodynamics and its derived chemical equilibrium. This includes common geochemical models such as PHREEQC and MINTEQ.

However, the third page (p. 110, Part 1) of Gibbs (1875-1878) says:

*“In the first place, all variations in the state of the system which involve the transportation of any matter through any finite distance are of course to be excluded from consideration, although they may be capable of expression by infinitesimal variations of quantities which perfectly determine the state of the system.”*

Gibbs is saying, as the first step, that any system with significant matter passing through it, like minesite components are known to experience, is excluded from chemical thermodynamics.

Gibbs (1875-1878) continues,

*“For example, if the system contains two masses of the same substance, not in contact, nor connected by other masses consisting of or containing the same substance or its components, an infinitesimal increase of the one mass with an equal decrease of the other is not to be considered as a possible variation in the state of the system.”*

Thus, even with infinitesimal changes required by thermodynamics (see Section 3.2 above which rules out minesite components), chemical thermodynamics would not apply to a system with two masses of the same substance unless they are connected or connected by masses of the same substance. Minesite components are rarely composed of “the same substance” throughout, such as a single mineral with no air or water. A simple example would be a waste-rock pile with water draining through and away in two separate directions.

Gibbs’ name is best known in aqueous chemistry for Gibbs Free Energy (Wikipedia, 2021c) which leads to parameters such as equilibrium constants and solubility constants.

*“In thermodynamics, the Gibbs free energy (or Gibbs energy) is a thermodynamic potential that can be used to calculate the maximum reversible work that may be performed by a thermodynamic system **at a constant temperature and pressure** [MDAG emphasis].”*

Of course, variations are allowed and valid if they are infinitesimal (Section 3.2). However, minesite components are open systems that are exposed to significant variations in temperature and pressure that can occur quickly.

Therefore, even Gibbs work on which chemical thermodynamics and equilibrium shows that thermodynamics should not be applied to minesite components and their drainages.



## 4. Conclusion

Based on the excellent work of Barbour (2020b), the reviews of thermodynamics, its history and development, and its application to chemistry show that thermodynamics cannot be reliably applied to minesite components and their drainages. The original authors and researchers back to the 1800's specify conditions that confirm this, including J. Willard Gibbs who developed chemical thermodynamics. The requirements for closed systems (“isolated boxes”), for the validity of entropy and the Second Law of Thermodynamics, and for infinitesimal changes in temperature and pressure also confirm this. Gibbs (1875-1878), in his roughly 350-page tome, *On the Equilibrium of Heterogeneous Substances*, was clear at the start that “*all variations in the state of the system which involve the transportation of any matter through any finite distance are of course to be excluded from consideration [by thermodynamics]. . . .*”

The most egregious abuse of thermodynamics applied to minesite drainage is the application of published thermodynamic databases, such as in PHREEQC and MINTEQA2, in forward modelling of a specific site without site-specific adjustments. Many publications and reports can be found doing this. It implies thermodynamics is applicable as-is around the world. This MDAG Case Study 65 shows why this attitude has existed since the mid-1800's and why it is so wrong.

The second most egregious abuse of thermodynamics applied to minesite drainage is using “equilibrium” to lower aqueous concentrations when supersaturated, but not raising aqueous concentrations when undersaturated. In fact, this violates the basic concept of equilibrium. Models like Goldsim include this corrupted “equilibrium” option.

There is no doubt that drainages at full-scale minesites often attain some type of equilibrium (e.g., Morin and Hutt, 1997, 2001; Morin et al., 2001 and 2012). However, this is not necessarily close to thermodynamic equilibrium. More reasonable and accurate site-specific approaches recognize factors like:

- site-specific solubilities and meta-stabilities (e.g., Morin and Hutt, 1997, 2000, 2001),
- scale emergence (Morin, 2019),
- self-organization (Morin, 2016 and 2018),
- other forms of energy that affect aqueous concentrations (Equation 2-2 and Section 2.1 in Morin 2020a),
- electrohydrodynamics (Section 5.2 of Morin, 2020b),
- non-equilibrium thermodynamics at least on a microscopic scale (Wikipedia, 2021d), and
- the many wavelengths of periodicity that affect aqueous concentrations synergistically and/or antagonistically (Morin, 2016 and 2018).

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