



AN EMERGENCE TO THERMODYNAMICS AND IT'S POTENTIAL APPLICATIONS

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ABSTRACT

The laws of thermodynamics represent a magnificent mathematical expression of some experimentally observed natural truths. The energy conservation concept enables the calculation of process energy needs. The concept of increasing entropy (and the ensuing free-energy minimization) enables forecasts of how far those processes can progress.

KEYWORDS: *thermodynamics, energy conservation, entropy*

INTRODUCTION

Pyrometallurgy includes extreme temperatures and the application of energy to materials by its definition. As a result, one of the most essential aspects of the topic is the study of thermodynamics.

What specifically is thermodynamics?

Thermodynamics is a compilation of valuable quantitative relationships between variables, each of which can be measured separately. Although thermodynamics provides no information about the microscopic reason for macroscopic changes, it is helpful in that it can be used to measure many unknowns. Some quantities are simpler to quantify than others, which makes thermodynamics advantageous.

The thermodynamic principles are an efficient mathematical illustration of some experimentally found natural truths. The energy conservation concept enables the calculation of process energy needs. The concept of rising entropy (and the ensuing free-energy minimization) enables forecasts of how far those processes can progress.

Thermodynamics deals with very vague variables and derives conclusions using mathematical relationships. It is similar to mathematics, which, according to Bertrand Russell, is a realm where you never know a) what you're talking about, or b) whether what you're saying is accurate. However, thermodynamics is regarded as a reliable source of knowledge about the actual world because it has previously delivered. The fact that it works is its conclusive reason.

When words in thermodynamics are not correctly defined, confusion can easily occur. In this topic, there is no space for imprecise wording.

Heat or Energy

The words "heat flows," "heat is a form of energy," "heat is energy in transit," "heat is energy at an equilibrium" "heat is the process," and "heat is the mechanism by which energy is transferred" are found in many texts on thermodynamics. Work is 'being done' or is 'being converted into heat'. Heat and labor, these "two illegitimate troublemakers," as Barrow¹ put it, don't offer a sound foundation on which to construct thermodynamics.

Work and heat seem to move between the environment and the machine we work with. They do not belong to the system we are working with or to any other system. It is not appropriate to combine the quantities q and w (to be described later) with real characteristics like energy and heat capacity.

Energy has a clear definition, unlike heat and labor. Its roots can be found in the concepts of kinetic and potential energy in basic mechanical systems. Experiments like Joule's "mechanical equivalent of heat" allow us to broaden the meaning and include thermal energy in the idea. Then, shifts in the energy of a chemical system of any intricacy can be handled using the concept of energy conservation.

However, there is an application for the activity words "heating" and "doing work". They can be used to show that a change in the temperature or mechanical environment occurs at the same time as the system's energy changes.

Our devotion to "heat," according to Barrow¹, is a result of the caloric theory that was popular in the 18th and 19th centuries. According to that hypothesis, a substance known as "caloric" manifests itself as heat. When the temperature shifted, this material entered and exited things. Heat was not one of the elements of the material universe, according to research by Mayer, Thompson, and Joule that demonstrated caloric could be produced or destroyed. The so-called "caloric period" was over. By utilizing "heat," we keep our ties to the tales of the past. It is time to abandon this odd holdover and proceed to develop thermodynamics solely based on 'energy.'

STATE FUNCTIONS

Quantities with state functions have values that only rely on their current state, not on how they came there. An illustration of this is height above mean sea level. As long as one can determine the altitude at the location, one does not need to be aware of the route taken to get there. Obviously, the route taken and the method of conveyance have a significant impact on the distance traveled or the amount of work involved in the voyage.

It is feasible to use a hypothetical route to reach the target when calculating state functions without the result changing. While paths (used for the convenience of calculations) are mathematical abstractions, processes (which happen typically as a succession of non-equilibrium phases) are physical abstractions. Fortunately, Gibbs free energy (G), entropy (S), and enthalpy (H) are all state variables.

Enthalpy, entropy, and Gibbs free energy (of a specific substance) all functionally rely on factors like temperature and pressure, as demonstrated by all excellent primers to thermodynamics. These thermodynamic functions are easily transformable mathematically into terms of other factors, such as volume, for example. However, for pyrometallurgists, temperature and pressure are the state factors of greatest concern.

$$H = H(T, P) \quad [1]$$

$$S = S(T, P) \quad [2]$$

$$G = G(T, P) \quad [3]$$

For the time being, it is acknowledged that the functions H , S , and G are well-defined and have known values that are either present or measurable.

The relationship between the quantifiable characteristics P , V , and T is calculated using an equation of state (such as $PV = nRT$ for an ideal gas).

Most pyrometallurgist-focused processes can be imagined as running at constant pressure or temperature (isothermal). (isobaric). Less frequently encountered is the condition of uniform volume (also known as isometric or isochore).

The energy needed for any steady-state flow process is basically the difference in enthalpy between the products and reactants plus the quantity of energy lost to the environment, as will be demonstrated in the following section. If the enthalpies of all the chemical species are computed relative to the same reference state, namely that of the elements in their standard states at 25°C and 1 atm, it is simple to figure the change in enthalpy over the course of the process. By using the elemental reference state, it is possible to determine the difference in enthalpy without taking into consideration any potential chemical processes. (If there are no interactions, it is acceptable to use compounds as the basis; however, the above-mentioned foundation is simple to recall and is always relevant. As a result, it is highly advised.) The values of the three important thermodynamic functions—enthalpy, entropy, and Gibbs free energy—can be determined without reference to any particular chemical route because they are all state functions.

In general, temperature, pressure, and makeup all affect a molecular species' partial molal enthalpy. In most instances, the influence of makeup on the enthalpies of individual components is negligible, and in any case, there is very little information on the enthalpy variation with composition. Therefore, it is common practice to disregard the impacts of composition on enthalpy, which is equal to treating the process streams (at least for this purpose) as ideal solutions. (i.e. the enthalpy of mixing is taken to be zero). The reliance of enthalpy on pressure is minimal, with the exception of gases under great pressure. (If deemed important, the effect could be allowed for by the use of equations of state, or reduced property correlations.) The enthalpy is frequently thought to be entirely dependent on temperature in the area of high-temperature chemistry. The sum of the enthalpies of all the chemical species in a stream is considered to represent the overall enthalpy of the stream. Regarding every molecular type*:

$$H = \Delta H_{f298}^{\circ} + \int_{298}^{T1} C_{P1} dT + L_{T1} + \int_{T1}^T C_{P2} dT \quad [4]$$

$$S = S_{298}^{\circ} + \int_{298}^{T1} \frac{C_{P1}}{T} dT + \frac{L_{T1}}{T} + \int_{T1}^T \frac{C_{P2}}{T} dT \quad [5]$$

where:

H	=	enthalpy of chemical species relative to elements in their standard states at 25°C and 1 atm (J / mol)
ΔH_{f298}°	=	standard enthalpy of formation of the species at 298K (J/mol)
$T1$	=	phase transition temperature (K)
$C_P(T)$	=	$a + bT + cT^{-2} + dT^2$ (J/mol/K) (subscripts 1 and 2 refer to different phases)
T	=	temperature (K)
L_{T1}	=	latent energy of phase transformation (J/mol)
S	=	absolute entropy of chemical species relative to elements in their
		standard states at 25°C and 1 atm (J/mol/K)
S_{298}°	=	standard entropy of the species at 298K (J/mol/K)

Also:

$$G = H - TS \quad [6]$$

Where,

G = Gibbs free energy of chemical species with respect to elements in their ground states at 25 °C and 1 atm (J/mol)

It should be noted that formulae [4] and [5] can be readily expanded to account for situations where multiple phase transitions take place.

Enthalpy and entropy can be determined computationally simply by carrying out a single summation for each instance. The first terms of formulae [4] for enthalpy and [5] for entropy can be mixed as integration constants in order to accomplish this. The same equations can be applied in this manner, with various constant values being appropriate for various temperature ranges. The temperature of a phase transition at one atmosphere of pressure is frequently the higher temperature of each range, but this is not always the case. For instance, the temperature at which the data on gases are terminated depends on the range of the actual observations. Additionally, to obtain an improved correspondence to the data, the temperature range for a specific phase can be randomly split in situations where it is challenging to properly describe the C_P term with a four-term expression (for example). Now, the following formulae hold:

$$H = \Delta H_{f,298}^{\circ} + \int_{298}^T C_P dT \quad [7]$$

$$S = S_{298}^{\circ} + \int_{298}^T \frac{C_P}{T} dT \quad [8]$$

$$C_P(T) = a + bT + cT^{-2} + dT^2 \quad [9]$$

The numbers a , b , c , and d are peculiar to the phase (or temperature range) that is the subject of equations [7], [8], and [9], respectively. Keep in mind that " $\Delta H_{f,298}^{\circ}$ " and " S_{298}° " can be regarded as the standard formation entropy and enthalpy of the phase in its metastable condition at 298K, respectively. It is essential to ascertain the accurate values of the constants relevant to that specific temperature range in order to compute the enthalpy and entropy of a specific compound at a given temperature. The software chooses by default the thermodynamic parameters of the species' most stable phase at the given temperature.

For further clarification, " $\Delta H_{f,298}^{\circ}$ " refers to the standard isothermal enthalpy change for the formation process from the most stable stages of the elements at 25 °C and 1 std atm. " S_{298}° " stands for the phase's absolute (or Third Law) entropy at 25°C and 1 atmosphere. When there are multiple data sets for a particular phase, " $\Delta H_{f,298}^{\circ}$ " and " S_{298}° " allude to the characteristics that would be reported at 25 °C and 1 atmosphere if the C_P function acted similarly to how it does in the given temperature range. It should not be unexpected that some unstable phases at 25°C may have negative "absolute entropy" since we are only working with practical integration constants.

The fictitious entropy factors serve only to simplify the calculation of the real entropy at higher temps where the relevant phase is stable.

It is frequently essential to consider rocks as a mixture of chemical species because thermodynamic statistics for minerals as such are not always easily accessible. For most elements, this is simple.

PRINCIPLE OF ENERGY CONSERVATION (FIRST LAW)

Sometimes, the conservation formulae for matter in general can be quite challenging. Thankfully, these can frequently be made simpler. The First Law of Thermodynamics does not reflect a universal energy balance, but rather the internal energy balance for a substance with very specific constitutive characteristics, most notably the lack of irreversible energy transfer. The First Law of Thermodynamics basically states that an isolated system, or one that doesn't share matter or energy with its environment, has a fixed amount of energy.

The principal of energy conservation says that for non-nuclear processes, the sum of the modifications to the comprehensive properties kinetic energy (E_k), potential energy (E_p), and internal energy (U) equals the aggregate of the energy transfer modes q (defined as the thermal transfer of energy) and w (defined as the mechanical transfer of energy).

$$\Delta E_k + \Delta E_p + \Delta U = q + w \quad [10]$$

All constant-matter systems in general and stable flow processes in particular can be described by this equation.

It is possible to create a general equation that links the change in enthalpy to the sum of the thermal transfer of energy and the so-called shaft work, w_s , and the change in the product of the pressure, P , and volume, V , as shown in equation [11] by assuming mechanical equilibrium for the entering and exiting regions of a hypothetical volume. Equation [12] uses one of the basic thermodynamic relationships to link the change in internal energy, U , to the change in enthalpy, H .

$$w = w_s + \Delta PV \quad [11]$$

$$\Delta H = \Delta U + \Delta PV \quad [12]$$

Therefore,

$$\Delta E_k + \Delta E_p + \Delta H = q + w_s \quad [13]$$

The differences in kinetic and potential energy are, however, typically much smaller for the chemical processes of concern than the changes in H . As a result, equation [13] can be made simpler as shown below.

$$\Delta H = q + w_s \quad [14]$$

Using this equation, we can determine the quantity of energy that is transferred to or from any activity by comparing the enthalpy before and after. Since enthalpy, H , is a state function, neither the process itself nor the hypothetical route taken during the process has any bearing on its value. Only temperature and pressure affect enthalpy. However, the pressure dependence is typically negligible and disregarded at normal pressures.

When $H > 0$, a process is said to be endothermic, and when $H < 0$, it is exothermic.

PRINCIPLE OF INCREASING ENTROPY (SECOND LAW)

C.P. Snow² once proposed the second law of thermodynamics as a measure of scientific reading for the humanist, and said it was 'about the scientific equal of: Have you read a book of Shakespeare's?'. However, the majority of individuals in the scholarly community also have many misunderstandings about the idea of entropy.

Investigating the "meanings" of thermodynamic measures like enthalpy or entropy is enticing but ultimately pointless. Nothing about the functions of thermodynamics that is subatomic or molecule is revealed.

It is generally accepted that entropy assesses how chaotic, unpredictable, or "mixed-up" a system is. In reality, thermodynamics states that the entropy change that takes place when a solitary entity moves voluntarily toward balance is always positive. By using statistical mechanics techniques, it is possible to directly correlate the rise in the isolated body's access to distinct eigenstates with the entropy growth in such a system. Only three very special cases—mixtures of perfect gases, mixtures of isotopes, or crystals at temperatures close to absolute zero—can be simply related to the purely geometrical or spatial mixed-upness, and none of these are typically studied in the typical chemical laboratory, let alone in high-temperature furnaces. In all other circumstances, even for changes in isolated entities, the entropy change is not amenable to a straightforward quasi-geometrical explanation.

The problem is worse than this, though, because chemists frequently act not only as though entropy increases in isolated bodies were a measure of disorder, but also as though this were true of entropy changes at constant temperature and pressure, which are conditions that are very different from isolation and under which the majority of chemical reactions are actually carried out. Even if the entropy change were a measure of disorder in a solitary entity, the Gibbs free-energy function rather than the entropy would serve as the equivalent measure in an isothermal and isobaric experiment.

Entropy misunderstandings have contributed to some widely held myths, including the idea that the cosmos is supposedly dying from heat. By pointing out some of the fallacies that underpin this notion, McGlashan³ rather persuasively disproves it. The line of reasoning goes something like this. The entropy of the universe is increased by every activity that truly occurs in it. Entropy growth indicates a rise in chaos. So disorder is the universe's final destiny. We might conclude that the universe would ultimately achieve a state of full equilibrium if thermodynamics could be demonstrated (but how?), and if the universe were known to be a limited and solitary entity. However, there is no evidence from science to support the idea that the cosmos is a contained, isolated entity. Even if it were true, there is no reason to believe that the world can be modeled using the actual science of thermodynamics.

It is possible to forecast how far those processes will go using the rising entropy principle (and the ensuing free-energy minimization).

The concept of free energy ($G = H - TS$) was developed by Willard Gibbs as a measure for showing the unidirectionality of random change because the concept of entropy is of limited direct use for open systems. Systems will modify themselves to produce a minimal amount of renewable energy.

The Gibbs free energy method is the primary way that the Second Law is used in pyrometallurgy to forecast whether and how much a reaction will occur under specific circumstances. Spontaneous reactions move forward in a manner that reduces the system's total free energy.

SIMPLE REACTION EQUILIBRIUM CALCULATIONS

When a system is in homeostasis, it displays a collection of constant characteristics that don't change over time or space. This ostensibly calm condition is dynamic and sustained by a delicate equilibrium between opposing reactions. A closed system is said to be in balance when the total Gibbs free energy is minimum with regard to all potential changes at the specified temperature and pressure.

ΔG^0_r is a numerical value that describes a specific response and is solely dependent on the temperature at which the system is maintained. All free energies of formation are computed at the system temperature, and ΔG^0_r is defined as the combination of the stoichiometric coefficients and the free energies of formation of the products of a reaction minus that of the reactants.

By definition:

$$K = \exp(\Delta G^0_r/RT) \quad [15]$$

According to Harris⁴, there is only one equilibrium constant, K , that is directly linked to ΔG^0_r for any particular chemical process. (the free energy of reaction). Since it is not a constant at all but rather a consequence (only) of temperature, the phrase "equilibrium constant" is somewhat misleading.

One advantageous repercussion of the unidirectionality of change principle is that K can be linked to the ratio of the activities of the products elevated to their stoichiometric power to those of the reactants. Activity is the ratio of fugacity to the baseline fugacity. (Almost always taken to be 1 atm. or 101.325 kPa). We can write: " $A + 2B = 3C$ " for the reaction:

$$K = \frac{a_C^3}{a_A \cdot a_B^2} \quad [16]$$

CONCLUSION

Some empirically found truths of nature are elegantly mathematically expressed by the laws of thermodynamics. Calculations of the energy needs for processes are possible thanks to the energy conservation concept. It is possible to forecast how far those processes will go using the rising entropy principle (and the ensuing free-energy minimization).

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