Revista do Professor de Física, v. 5, n. 3, p. 1-28, Brasília, 2021.
Instituto de Física - Universidade de Brasília

Artigo original

Revista do Professor de Física

Ensino de Física

AN *E-DIGRAPH* FOR THE THERMODYNAMIC POTENTIAL ENERGIES

Jornandes Jesús Correia[1]

[1]Universidade Estadual do Sudoeste da Bahia - UESB

DOI: 10.26512/rpf.v5i3.37178

Abstract

This paper aims to present a cubic structure in which the thermodynamic potential energies are directionally distributed (E-digraph) for a single-component system (CALLEN, 1985, p. 168), in order to complement the cubics structures of Pate (1999), Pogliani (2018) and Kocik (2018) and the octahedron of Kerr & Macosko (2011), as well as proposes an alternative model for obtaining the Maxwells Identities, and the Differential Relations of Euler, Gibbs, Gibbs-Duhen and Euler where Legendre Transformations were not used. The six free variables of thermodynamics were linked two by two, in order to facilitate the understanding of the meanings of Thermal, Chemical and Mechanical energy. As future perspectives, this cubic structure will be applied to Massieus Thermodynamic Potentials, by means of a S-digraph, in order to continue the study of these potentials, first introduced in 1869 by François Massieu under the name of fonctions caractéristiques (BALIAN, 2017).

Keywords: *hermodynamic Potentials Energies. Thermodynamic Cube. Teaching of Thermodynamics. E-digraph representation. Open Systems.*

I. Introduction

Thermodynamics is a modern science that emerged around 1824 when Sadi Carnot (1786-1832) published his only book on the performance of thermal machines and presented a principle that later came to be treated as the Second Law of Thermodynamics (BALIAN, 2017).

In the same perspective, the free encyclopedia *Wikipedia*[1] presents another reference that marked the beginning of Thermodynamics:

> In the history of thermodynamics, *On the Equilibrium of Heterogeneous Substances* is a 300-page paper written by american chemical physicist Willard Gibbs. It is one of the founding papers in thermodynamics, along with

---

[1] Available in <https://en.wikipedia.org/wiki/On_the_Equilibrium_of_Heterogeneous_Substances#cite_note-1>. Access at Feb. 02 2021.

> German physicist Hermann von Helmholtzs 1882 paper *Thermodynamik chemischer Vorgänge*. Together they form the foundation of chemical thermodynamics as well as a large part of physical chemistry. Gibbss *Equilibrium* marked the beginning of chemical thermodynamics by integrating chemical, physical, electrical, and electromagnetic phenomena into a coherent system. It introduced concepts such as chemical potential, phase rule, and others, which form the basis for modern physical chemistry. American writer Bill Bryson describes Gibbss *Equilibrium* paper as the *Principia* of thermodynamics. *On the Equilibrium of Heterogeneous Substances*, was originally published in a relatively obscure American journal, the *Transactions of the Connecticut Academy of Arts and Sciences*, in several parts, during the years 1875 to 1878 (although most cite 1876 as the key year). It remained largely unknown until translated into German by Wilhelm Ostwald and into French by Henry Louis Le Châtelier.

Classical Thermodynamics or Equilibrium Thermodynamics, although their postulates were formulated *a priori*,

> is one of the best consolidated areas of Physics. It is synthesized by a well-defined and self-consistent knowledge structure. The essence of the theoretical structure of Classical Thermodynamics lies in a set of natural laws that govern the behavior of macroscopic physical systems. These laws were formulated from generalizations of observations and are, to a large extent, independent of any hypotheses regarding the microscopic nature of matter.
>
> (PÁDUA *et al*, 2008).

Despite this consolidation of this theoretical framework, the universal axiomatic mathematical tooling and the cold mechanistic formalism of Differential Equations that structures the laws and relations of the Phenomenological Equilibrium Thermodynamics (TEP) hinders a conceptual interpretation (KOCIK, 2018) of both Classical Thermodynamics and Quantum Statistics. In order to facilitate the interpretation of thermodynamic equations, Percy Williams Bridgmam (1882-1961) presented in 1914 an extensive method in order to phenomenologically signify the equations, which was simplified by Albert Norman Shaw in 1935 (POGLIANI, 2018). However, this didactic work did not obtain the desired scientific recognition.

Also in this perspective, Josiah Willard Gibbs (1839-1903) activated Constantin Carathéodory (1873-1950) to elaborate an *ab-initio* formulation to the Laws of the Thermodynamics (BRAGA, 2018). Although Carathéodorys work represents phenomena of Nature, it still challenged the significance of the differential relations of Potentials and their association with physical phenomena, contributing to not well accepted by the scientific literature (ARENS, 1963).

Max Born (1882-1970), attempted to present a more logical form more logical to Thermodynamics (GIBBS, 1928, apud KOCIK, 2018), as he understood that Gibbss worldwide accepted treatment until then was not based on fundamental principles. In this perspective, Born presented a square that related four potential energies (the Internal Energy, the Enthalpy, the Free Energy of Helmholtz and the Free Energy of Gibbs) arranged at the edges of that square and its free variables located at the vertices of that same square, connected by diagonal arrows (ZHAO, 2009). Borns initiative marked the beginning of the representation model of the spatial distribution of Thermodynamic Potentials for closed systems and facilitated the visualization of the interdependence of these potentials.

In this paper a model for simple systems is proposed that interrelate the energies of closed systemss thermodynamic potential (Internal Energy, Enthalpy, Helmholtz Free Energy and Gibbs Free Energy) with another four potentials for open systems (Great Potentials). The simple systems...

> ... are macroscopically homogeneous, isotropic, and uncharged, that are large enough so that surface effects can be neglected, and that are not acted on by electric, magnetic, or gravitational fields ...
>
> (CALLEN, 1985, p. 9).

Although the Great Potentials have attracted the attention of researchers, only the Grand Canonical Potential or Landau Potential (), in honor of the Russian physicist Lev Davidovich Landau (1908-1968), it has been discussed prominently in the scientific literature.

Recently, some researchers have rejoined the formulation of thermodynamics through spatial representations, such as the three-dimensional representations of Pate (1999) and Kocik (2018) and the two-dimensional representation of Kerr & Macosko (2011). These models, relaxed for open systems, present their own rules of symmetry to interrelate thermodynamic potentials energies.

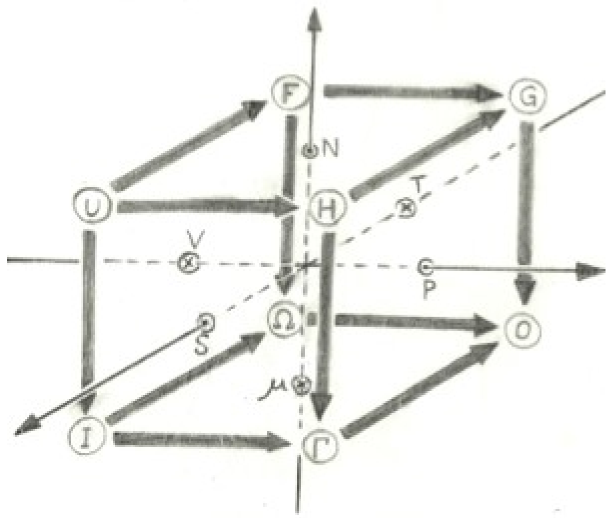
Despite the efforts and contributions of the researchers, thermodynamics potential energies are still superficially addressed by textbooks on the subject, lacking clearer definitions and needing theoretical and phenomenological explanations.

In summary, this article presents a cube-shaped model for the spatial distribution of the thermodynamic potential energies, complementing the cube of Pate (1999) and the octahedron of Kerr Macosko (2011), the cubes Pogliani (2018) and Kocik (2018) aiming to facilitate obtaining the equations that interrelate the Thermodynamic Potential Energies, as well as giving meaning to the Thermodynamic Transformations through the proposition of Arrows Edges and Coordinated Arrows, whose axes will be presented in the next section.

II. The Thermodynamic Cube, the Edge Arrows, the Coordinated Arrows and the Potential Energies of Thermodynamics and the Conjugated Variables

II.1. The Thermodynamic Cube

The cube proposed here proposes to connect, by arrows, the thermodynamic potential energies of, articulating them, as well as presenting a new reference for orthogonal axes.



The Denominations of the Thermodynamic Potential Energies:
F - The Helmholtz Free Energy;
G - The Gibbs Free Energy;
H - The Enthalpy;
U - The Internal Energy;
I - The unnamed Potential;
Ω - The Landaus Great Potential;
Γ - The unnamed Potential;
0 - The Null Potential.

Figure 1: *The Thermodynamic Cube for the Potential Energies*

The orthogonal system of this cube has the same configuration as the Cartesian Orthogonal Reference frame, the difference is that in this reference system each axis contains a pair of conjugated variables, in which one of these free variables is located in the origin (*cross-side*) while the other free variable, conjugated to the first, is located at end (*dot-side*) of that same Coordinate Arrow. Note that, for the same axis, the *cross-side* is parallel to the *dot-side*.

The layout of these variables in this new orthogonal system, based on the figure above, is as follows:

- In the $\vec{TS}$ axis of this Cartesian Framework, the Temperature T is exhibited at the *cross-side* of the cube, while the Entropy S is exhibited at the *dot-side* of the cube;
- In the $\vec{VP}$ axis of this Cartesian Framework, the Volume V is exhibited at the *cross-side* of the cube, while the pressure P is exhibited at the *dot-side* of the cube;
- In the $\vec{\mu N}$ axis of this Cartesian Framework, the Chemical Potential μ is exhibited at the *cross-side* of the cube, while the Number of Particles N is exhibited at the *dot-side* of the cube.

Each of the eight potential thermodynamic energies can be linked to its adjacent potential energy by an edge arrow, by suppressing or adding the transformation energy. This transformation energy is obtained from the product of the two free variables articulated. This cube is shown in Figure 01 as a set of two complete and disconnected graphs. In the graph of energies, the Internal Energy represents the potential source and the Null Potential represents the sinkhole. In the graph of free variables, the vectors $\vec{TS}$, $\vec{VP}$ and $\vec{\mu N}$ intersect at the center of the presented Thermodynamic Cube.

The nest section of this article also proposes the Symmetry Rules that govern the signs in the Thermodynamic Potential Equations of State, which describe a possible evolution of a system, due to the variation of one of the three potential energies, without applying Legendres transformations.

The description of edge arrows and coordinate arrows are presented in the following subsection.

II.2. Edges Arrows

One of the purposes of this article is to propose the replacement of the cube edges of Figure 6.1 (KOCIK, 2018, p. 11) and Figure 4 (PATE, 1999, p. 1113) by arrows that indicate the directions of thermodynamic transformations, in addition to adding arrows representing the energies necessary to these transformations, maintaining the positions of the eight thermodynamic potentials of Pates Cube (1999) and Kociks Magic Cube (2018). The Arrow Edge indicates the transformation of the potential energy from the origin of that Arrow Edge into the potential energy located at the end of that arrow. The equation that describes this process is called the State Equation of the Thermodynamics Potential Energy. The state energies (Mechanical, Thermal and Chemical) can be modeled by the product of two variables conjugated by Coordinated Arrows, whose description can be found in the following section.

II.3. Coordinated Arrows

They are proposed to articulate, two by two, the six Free Variables of the eight potential energies of thermodynamics, through coordinated orthogonal axes. While one of the variables is located at the origin (cross) of one of the Coordinated Arrows, the other variable, combined with the first by that same Arrow, is located at the end (dot) of that same axis. The Chemical, Thermal and Mechanical energies, necessary for the transformation between adjacent thermodynamic potentials, are derived from the product of the two conjugated variables. Therefore, the Coordinated Arrows, which intersect in the center of this cube, are oriented axes that compose the orthogonal frame. It is noteworthy that each of these arrows crosses perpendicularly the center of a pair of parallel faces of this cube.

The *dot* and *cross* notations adopted here were based on the Thermodynamic Cuboctahedron of Fox (1976).

This model aims to facilitate the understanding of the interdependence between thermodynamics potential energies, as well as to establish meanings to thermodynamic transformations, in addition to easy the writing, the memorization and the understanding of logical constructs of the Balance of Thermodynamics Potentials Energies.

Equations presented in this article were addressed by Koenig (1935). However, in that case, the equations are assembled by Characteristics Group, as mentioned below:

> Attention is called to the fact that certain important equations of thermodynamics such as the two Gibbs-Helmholtz equations may be grouped into families, but that a precise definition of such families has hitherto been lacking.
>
> (KOENING, 1935, p. 9)

Koening (1972), in the second part of the article that was published in 1935, again addresses the potential energies of thermodynamics and presents a geometric method for:

> For resolving into families a certain class of thermodynamic equation involving characteristic functions. The extension consists of operations upon a regular octahedron analogous to the upon a square (the thermodynamic square)...

In this paper, it is presented a cube in order to complement the geometric figures covered so far. The cube is presented in the next section.

These State Equations will be presented in the following section.

II.4. The State Equations of the Thermodynamic Potential Energies

This article also proposes to present a simplified model to describe the equations of state of a thermodynamic system. These mathematical relations allow to equate the potential energies associated with the transformations between two thermodynamic states, without the need to use Legendres Transformations. For this, the potential thermodynamic energies are displayed at the vertices of a cube. These energies, obtained by their own symmetry rules, through the use of Arrows Edges and Coordinated Arrows, have the following structure:

$$x_l = x_i \pm x_j x_k \tag{1}$$

This State Equation indicates that a system can evolve from the initial state x_i, exhibited at the origin of the Arrow Edge, to the final state x_l, exhibited at the end of this same arrow. Such evolution is conditioned to the addition or subtraction of the energy from the product $x_j x_k$ (TS, PV or μN). The quantities originating from these products between the intensive quantities (T, P or μ) and the corresponding extensive variable arranged in the same order as the intensive variable (S, V or N), give rise to Transformation Functions established by the Thermodynamics Relations.

The rules for the signs of the equations of state of the thermodynamic potentials will be presented in the following section.

II.5. The Rules of Signs for the Equations of State

In this section, the symmetry rules that will be used to describe the energy of the thermodynamic state of a system, whose mathematical relations is represented by the Equation 1, will be presented.

The First Rule is:

- The sign that precedes the potential energies x_l and x_i is always positive.

The Second Sign Rule is:

- The energy $x_j x_k$ will be preceded by a positive sign if the Coordinate Arrow is in the same direction as the Arrow Edge;

- The energy $x_j x_k$ will be preceded by a negative sign if the Coordinate Arrow is in the opposite direction of the Arrow Edge.

All State Equations involving Thermodynamic Potentials can be obtained from the Equation 1, as can be seen in the following equations:

$$H = U + PV \tag{2}$$

$$0 = \Omega + PV \tag{3}$$

$$G = F + PV \tag{4}$$

$$\Gamma = I + PV \tag{5}$$

$$\Omega = F - \mu N \tag{6}$$

$$I = U - \mu N \tag{7}$$

$$0 = G - \mu N \tag{8}$$

$$\Gamma = U - \mu N \tag{9}$$

$$0 = \Gamma - TS \tag{10}$$

$$\Gamma = I - TS \tag{11}$$

$$G = H - TS \tag{12}$$

$$F = U - TS \tag{13}$$

II.6. The Potential Energies of Thermodynamic and their Free Variables

In this section, we will present a technique for obtaining free variables for a given thermodynamic potential energy.

Each potential energy has a set of three free variables. This trio is composed of each one of the three faces that form the vertex where the potential energy is located. Based on the cube presented here, the relations of the potentials energies and their free variables are as follows:

$$0 = f(T, P, \mu) \tag{14}$$

$$\Gamma = f(S,P,\mu) \tag{15}$$

$$I = f(S,V,\mu) \tag{16}$$

$$\Omega = f(T,V,\mu) \tag{17}$$

$$F = f(T,V,N) \tag{18}$$

$$G = f(T,P,N) \tag{19}$$

$$H = f(S,P,N) \tag{20}$$

$$U = f(S,V,N) \tag{21}$$

The potential energies for closed systems are defined in the following references: Internal Energy (CORREIA & OLIVEIRA, 2018); Enthalpy (CORREIA & OLIVEIRA, 2019); Helmholtz Potential (CORREIA & GUIMARÃES, 2020); and Gibbs Potential (CORREIA & GUIMARÃES, 2021).

The next step is to obtain the equations that describe the variation of the thermodynamic potential energy. These equations are described by the tooling of the differential equations, such as the use of the Legendre Transformations. However, this work aims to present a technique for obtaining these energies, in an alternative way, without using these Transformations.

In the following section, the differential of each of the thermodynamic potential energies will be presented.

II.7. The Exact Differential Equations of the Thermodynamic Potential Energies

The potential $[\phi(x,y,z)]$ variation at each edge of this cube will be described by its exact differential (d), truncated in the first order. The mathematical relation of this transformation is given by:

$$d\phi(x,y,z) = \pm X dx \pm Y dy \pm Z dz \tag{22}$$

Based on the cube in question, we have:

- $\phi(x,y,z)$ is the thermodynamic potential energy located at the corner under analysis;
- x (y or z) is the free variable at the center of the one of the tree squares that forms the vertex of the cube where $\phi(x,y,z)$ is located;

- X (Y or Z) is the free variable located in the center of the parallel side to the side containing x (y or z).

This model of representation of the variation of the thermodynamics potential energies $\phi(x_i, x_j, x_k)$, can be described by means of the exact differential tooling, which is called Gibbs Differential Form.

The derivatives of the potential energies in relation to each of their free variables x_i, x_j ou x_k are described as follows:

$$\left.\frac{\partial[\phi(x_i, x_j, x_k)]}{\partial x_i}\right|_{x_j, x_k} = \pm X \tag{23}$$

$$\left.\frac{\partial[\phi(x_i, x_j, x_k)]}{\partial x_j}\right|_{x_i, x_k} = \pm Y \tag{24}$$

$$\left.\frac{\partial[\phi(x_i, x_j, x_k)]}{\partial x_k}\right|_{x_i, x_j} = \pm Z \tag{25}$$

The positive and negative signs based on the Third Rule, in which:

- The variable X (Y ou Z) will be positive if it is a *cross-side*;
- The variagle X (Y ou Z) will be negative if it is a *dot-side*.

The following differential equations for the thermodynamic potential energies are presented, based on this signal rule.

The differential equation for Internal Energy (U) is

$$dU = TdS + (-P)dV + \mu dN \tag{26}$$

$$dU = TdS - PdV + \mu dN \tag{27}$$

The Equation 27 is named by Differential Form of the Euler Relation of Thermodynamics.

The Differential Equation for Entalpy (H) is

$$dH = +TdS + VdP + \mu dN \tag{28}$$

$$dH = TdS + VdP + \mu dN \tag{29}$$

The Differential Equation for Gibbs Free Energy (G) is

$$dG = +(-SdT) + VdP + \mu dN \tag{30}$$

$$dG = -SdT + VdP + \mu dN \tag{31}$$

The Differential Equation for Helmholtz Free Energy (F) is

$$dF = +(-S)dT + PdV + \mu dN \tag{32}$$

$$dF = -SdT + PdV + \mu dN \tag{33}$$

The Differential Equation for Unnamed Great Potencial (I) is

$$dI = +TdS + (-P)dV + (-N)d\mu \tag{34}$$

$$dI = TdS - PdV - Nd\mu \tag{35}$$

The Differential Equation for Unnamed Great Potencial (Γ) is

$$d\Gamma = +TdS + VdP + (-N)d\mu \tag{36}$$

$$d\Gamma = +TdS + VdP - Nd\mu \tag{37}$$

The Differential Equation for Landau Great Potencial (Γ) is

$$d\Omega = +(-S)dT + (-P)dV + (-N)d\mu \tag{38}$$

$$d\Omega = -SdT - PdV - Nd\mu \tag{39}$$

The Differential Equation for Null Potencial (0) is

$$d0 = +(-S)dT + VdP + (-N)d\mu \tag{40}$$

$$d0 = -SdT + VdP - Nd\mu \tag{41}$$

Since $d0 = 0$, then

$$VdP - SdT - Nd\mu = 0 \tag{42}$$

Relation 42 called Gibbs-Duhen Relation, is the same Equation 3.15 deduced by Callen (CALLEN, 1985, p. 62).

Equations 35 and 37 were named as The Kerr Potential and The Macosko Potential, respectively, according to Figure 3 of the reference Kerr & Macosko (2011, p. 951). However, these denominations have not yet been disseminated by the scientific community.

II.8. The Deduction of Thermodynamics Euler Equation

This differential equation will serve as a basis to obtain the equation equivalent to each of the thermodynamic energies. In order to simplify the deduction of these mathematical relations, lets to consider the potential energy $\phi(x_1, x_2)$ depending only on two variables.

This thermodynamic potential energy $\phi(x_1,x_2)$ will be homogeneous in the first order if (CALLEN, 1985, p. 37).

$$\phi(\lambda x_1,\lambda x_2) = \lambda\phi(x_1,x_2) \tag{43}$$

.

When replacing λx_1 by u_1 and λx_2 by u_2 we will have

$$\phi(\lambda x_1,\lambda x_2) = \phi(u_1,u_2) \tag{44}$$

Deriving $(\lambda x_1,\lambda x_2)$ with respect to λ and using the Chain Rule, we have

$$\frac{\partial[\phi(\lambda x_1,\lambda x_2)]}{\partial\lambda} = \frac{\partial[\phi(\lambda u_1,\lambda u_2)]}{\partial u_1}\frac{\partial u_1}{\partial\lambda} + \frac{\partial[\phi(\lambda u_1,\lambda u_2)]}{\partial u_2}\frac{\partial u_2}{\partial\lambda} \tag{45}$$

But, since $\frac{\partial u_1}{\partial\lambda} = x_1$, $\frac{\partial u_2}{\partial\lambda} = x_2$ and $\frac{\partial[\phi(\lambda x_1,\lambda x_2)]}{\partial\lambda} = \phi(x_1,x_2)$, the expression of the partial derivative of the potential energy $\phi(\lambda x_1,\lambda x_2)$ in relation to λ is represented by the relation

$$\phi(x_1,x_2) = \frac{\partial[\phi(u_1,u_2)]}{\partial u_1}x_1 + \frac{\partial[\phi(u_1,u_2)]}{\partial u_2}x_2 \tag{46}$$

But, since $u_1 = \lambda x_1$ and $u_2 = \lambda x_2$, we have

$$\phi(x_1,x_2) = \frac{\partial[\phi(\lambda x_1,\lambda x_2)]}{\partial(\lambda x_1)}x_1 + \frac{\partial[\phi(\lambda x_1,\lambda x_2)]}{\partial(\lambda x_2)}x_2 \tag{47}$$

And, since $\phi(x_1,x_2)$ is a homogeneous function, we find

$$\phi(x_1,x_2) = \frac{\lambda\partial[\phi(x_1,x_2)]}{\lambda\partial(x_1)}x_1 + \frac{\lambda\partial[\phi(x_1,x_2)]}{\lambda\partial(x_2)}x_2 \tag{48}$$

And, thus,

$$\phi(x_1,x_2) = \frac{\partial[\phi(x_1,x_2)]}{\partial(x_1)}x_1 + \frac{\partial[\phi(x_1,x_2)]}{\partial(x_2)}x_2 \tag{49}$$

With this last equation, each one of the potential thermodynamic energies can be obtained in an alternative way to that using Legendres Transformations. As an example of the application of this method, consider the thermodynamic potential named by Internal Energy (U) with his free variables (S, V and N). Considering $U = f(S,V,N)$, one has:

$$U = \frac{\partial U}{\partial S}S + \frac{\partial U}{\partial V}V + \frac{\partial U}{\partial N}N \tag{50}$$

But, carrying out operations according to the third rule of signs presented above we have

$$\begin{cases} \frac{\partial U}{\partial S} = T \\ \frac{\partial U}{\partial V} = T \\ \frac{\partial U}{\partial N} = -P \end{cases} \tag{51}$$

Thereby

$$U = TS + \mu N - PV \tag{52}$$

Equation 052 is named Thermodynamics Euler Equation (CALLEN, 1985, p. 60) in the representation of the energy, from which we can infer the real meaning of the Internal Energy (U) quantity, as the sum of the Thermal, Chemical and Mechanical Energies of a thermodynamics system.

The differential in the expression of this energy gives rise to another fundamental thermodynamic equation, which will be demonstrated in the following section.

II.9. The Gibbs-Duhens Relation Dedution

Differentiating the Thermodynamics Euler Equation we have

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \tag{53}$$

$$dU = TdS - PdV + \mu dN + (SdT - VdP + Nd\mu) \tag{54}$$

From the Differential Mathematical Relation 27, the portion in parenthesis is identically null. So

$$SdT - VdP + Nd\mu = 0 \tag{55}$$

Note that the Equation 28, Thermodynamics Euler Equation in the differential form, depends on the extensive variables (S, V, N), while the Gibbs-Duhen Relations (Equation 55) depends only on the intensive variables (T, P, μ).

This Euler equation indicates that a variation of the Internal Energy is due only to the variation of the extensive variables.

In the next section we will discuss the definition of the equation for each of the Great Potentials of the Thermodynamics.

III. A DISCUSSION ABOUT THE THERMODYNAMICS GREAT POTENTIALS

The eight potentials of thermodynamics are articulated in the proposed cube. Four of them are the potentials for open systems (Internal Energy, Enthalpy, Helmholtz Free Energy and Gibbs Free Energy).

III.1. The Unnamed Potential Γ

Due to the fact that the Null Potential 0 is identically null, we can obtain, from Equation 10,

$$\Gamma = TS \tag{56}$$

It can be stated that Potential Γ is the thermodynamics Thermal Energy of a system that is initially within the system (CORREIA & GUIMARÃES, 2020) that, when degraded, will no longer be fully available for further Work.

In other words, this potential must be understood as the Thermal Energy that must be extracted from the system by shrinking it down to nothing[2], when the system has only Thermal Energy.

A quantity of Thermal Energy Γ, despite being a potential quantity, can be interpreted by Heat (CORREIA *et al*, 2008) only when this portion TS is in a transfer state due to the temperature difference.

III.2. The Landaus Potential Ω

From Equation 3, it is possible to obtain:

$$\Omega = -PV \tag{57}$$

From this State Equation it can be stated that the potential *Omega* is an energy that, although it is informing within the system in the mathematical format PV (CORREIA & OLIVEIRA, 2019), when the system undergoes a thermodynamic transformation, this amount of energy can be obtained from the System to carry out Work. PV can also be interpreted as the amount of energy that was spent to provide a volume V of the total volume of the Environment that was at pressure P. The negative sign that precedes the product PV, in the Thermodynamics Euler Equation, is due to energy transfer from the System to the Environment. Furthermore, it is the energy in the form of Work on the System, to isolate a volume V from the total volume of the Environment.

The potential mechanical energy *Omega* can be interpreted as Work (CORREIA & JOSÉ, 2011) as long as the PV term is in a transfer status due to the pressure difference.

In other words, the Landau Potential must be understood as Mechanical Energy that must be extracted from the system by shrinking it down to nothing, when the system has only Mechanical Energy.

III.3. The Unnamed Potential I

From the Equation of State 7 or from the Equation 11, the following equation can be obtained for the Anonymous Potential I:

$$I = TS - PV \tag{58}$$

This equation indicates that the thermodynamic potential energy I can be interpreted as the sum of the Thermal and Mechanical Energies that can still be removed from a Thermodynamic System after the removal of Chemical Energy.

---

[2] Available in <https://en.wikipedia.org/wiki/Grand_potential>. Access at Sep. 23 2021.

III.4. The Null Potential 0

O Observe in the figure of cube that the arrows of the transformations (Arrows Edges) converge to this potential. Due to this detail, the terminology evolve from nothing (SÁ MARTINS, 2014), apparently without physical meaning, used by many physicists, takes on logical meaning. A thermodynamic system that is reduced to nothing is due to the extraction of all its energy.

Another curious detail is that, due to the fact that this is null equal to zero, it facilitates the definition of the potential energies adjacent to it, such as the Great Potential of Landau *Omega*, the Great Potential Anonymous *Gamma* and the Potential of Gibbs G.

In the following section, Conservation Principles can be observed based on this cube.

IV. THE PRINCIPLES OF CONSERVATION OF THE THERMODYNAMICS POTENTIAL ENERGY

Making convenient symmetry operations two conservation principles can be presented, which will be presented in the following two sections.

IV.1. The First Principle of Energy Conservation

The sum of two potential energies conjugated by one of the diagonals of either side of the cube is equal to the sum of the potential conjugated by the other diagonal of that same face (KOCIK, 2018, p. 11). From this symmetry rule, the following relations can be obtained:

$$0 + I = \Omega + \Gamma \tag{59}$$

$$\Gamma + U = I + H \tag{60}$$

$$\Gamma + G = 0 + H \tag{61}$$

$$\Omega + U = I + F \tag{62}$$

$$\Omega + G = 0 + F \tag{63}$$

$$G + U = H + F \tag{64}$$

IV.2. The Second Principle of Energy Conservation

The sum of the potential energies at the ends of a main diagonal of the thermodynamic cube is equal to the Internal Energy U (KOCIK, 2018, p. 11). From this rule the following relations are obtained:

$$0 + U = U \tag{65}$$

$$\Gamma + F = U \tag{66}$$

$$\Omega + H = U \tag{67}$$

$$G + I = U \tag{68}$$

Conveniently using the Thermodynamic Cube and the symmetry rules now proposed, the Gibbs Relations and Maxwell Identities can be obtained, without using the Legendre Transformations, as we show in the following sections.

V. Gibbs Relations

Gibbs Relations of Thermodynamics can also be obtained through the Symmetry Rules applied to the Thermodynamic Cube, according to the equation below.

$$\left.\frac{\partial}{\partial x_i}\left[\phi(x_i, x_j, x_k)\right]\right|_{x_j, x_k} = \pm x_l \tag{69}$$

Although these signs rules have already been presented in section 2.4.1.2, they follow the following denominations:

- $\phi(x_i, x_j, x_k)$ is a thermodynamic potential energy located at one of the cube vertices, which depends on the variables x_i,x_j e x_k;
- x_j and x_k, are the free variables kept constant, while the potential $\phi(x_i, x_j, x_k)$ is being derived in relation to the free variable x_i;
- x_l is the free variable located at the center of the side parallel to the side that contains x_i, x_j or x_k.

The following expressions can be obtained from these rules, the set of which is called Gibbs Relations:

$$\left.\frac{\partial U}{\partial V}\right|_{S,N} = \left.\frac{\partial f}{\partial V}\right|_{N,T} = \left.\frac{\partial \Omega}{\partial V}\right|_{T,\mu} = \left.\frac{\partial I}{\partial V}\right|_{S,\mu} = -P \tag{70}$$

$$\left.\frac{\partial 0}{\partial \mu}\right|_{T,P} = \left.\frac{\partial \Omega}{\partial \mu}\right|_{T,V} = \left.\frac{\partial I}{\partial \mu}\right|_{S,V} = \left.\frac{\partial \Gamma}{\partial \mu}\right|_{P,S} = -N \tag{71}$$

$$\left.\frac{\partial G}{\partial T}\right|_{P,N} = \left.\frac{\partial 0}{\partial T}\right|_{P,\mu} = \left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu} = \left.\frac{\partial F}{\partial T}\right|_{V,N} = -S \tag{72}$$

$$\left.\frac{\partial U}{\partial N}\right|_{S,V} = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \left.\frac{\partial G}{\partial N}\right|_{T,P} = \left.\frac{\partial H}{\partial N}\right|_{P,S} = \mu \tag{73}$$

$$\left.\frac{\partial G}{\partial P}\right|_{T,\mu} = \left.\frac{\partial 0}{\partial P}\right|_{T,\mu} = \left.\frac{\partial \Gamma}{\partial P}\right|_{S,\mu} = \left.\frac{\partial H}{\partial P}\right|_{S,N} = V \tag{74}$$

$$\left.\frac{\partial U}{\partial S}\right|_{V,N} = \left.\frac{\partial H}{\partial S}\right|_{P,N} = \left.\frac{\partial \Gamma}{\partial S}\right|_{P,\mu} = \left.\frac{\partial I}{\partial S}\right|_{V,\mu} = T \tag{75}$$

VI. MAXWELLS IDENTITIES

Each of Maxwells Identities, called Maxwells Relations, will be obtained from Schwartzs Theorem and from Gibbs Relations, according to the following equations:

- $$\left.\frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_j}\right)[\phi(x_i,x_j,x_k)]\right|_{x_k} = \left.\frac{\partial}{\partial x_j}\left(\frac{\partial}{\partial x_i}\right)[\phi(x_i,x_j,x_k)]\right|_{x_k} \tag{76}$$
- $$\left.\frac{\partial}{\partial x_j}\left(\frac{\partial}{\partial x_k}\right)[\phi(x_i,x_j,x_k)]\right|_{x_i} = \left.\frac{\partial}{\partial x_k}\left(\frac{\partial}{\partial x_j}\right)[\phi(x_i,x_j,x_k)]\right|_{x_i} \tag{77}$$
- $$\left.\frac{\partial}{\partial x_k}\left(\frac{\partial}{\partial x_i}\right)[\phi(x_i,x_j,x_k)]\right|_{x_j} = \left.\frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_k}\right)[\phi(x_i,x_j,x_k)]\right|_{x_j} \tag{78}$$

Properly applying the Gibbs Relation to each of the eight potential energies, three Maxwells identities are obtained for each of the potential thermodynamic energies. With that, twenty-four Maxwells Relations would be obtained, according to the deductions that follow:

VI.1. The Internal Energy U

$$U = f(S,V,N)$$

(a)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial V}\right)U\right|_{N} = \left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial S}\right)U\right|_{N};$$

$$\left.\frac{\partial U}{\partial V}\right|_N = -P \text{ and } \left.\frac{\partial U}{\partial S}\right|_N = T$$

Then

$$\left.\frac{\partial}{\partial V}(T)\right|_N = -\left.\frac{\partial}{\partial S}(P)\right|_N \tag{79}$$

(b)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial N}\right)U\right|_V = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial S}\right)U\right|_V;$$

$$\left.\frac{\partial U}{\partial N}\right|_V = \mu \text{ and } \left.\frac{\partial U}{\partial S}\right|_V = T$$

Then

$$\left.\frac{\partial}{\partial S}(\mu)\right|_V = -\left.\frac{\partial}{\partial N}(T)\right|_V \tag{80}$$

(c)

$$\left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial N}\right)U\right|_S = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial V}\right)U\right|_S;$$

$$\left.\frac{\partial U}{\partial N}\right|_S = \mu \text{ and } \left.\frac{\partial U}{\partial V}\right|_S = -P$$

Then

$$\left.\frac{\partial}{\partial V}(\mu)\right|_S = -\left.\frac{\partial}{\partial N}(P)\right|_S \tag{81}$$

VI.2. The Helmholtz Potential F

$$F = f(T, V, N).$$

(a)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial V}\right)F\right|_N = \left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial T}\right)F\right|_N;$$

$$\left.\frac{\partial F}{\partial V}\right|_N = -P \text{ and } \left.\frac{\partial F}{\partial T}\right|_N = -S$$

Then

$$\left.\frac{\partial}{\partial T}(P)\right|_N = \left.\frac{\partial}{\partial V}(S)\right|_N \tag{82}$$

(b)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial N}\right)F\right|_V = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial T}\right)F\right|_V;$$

$$\left.\frac{\partial F}{\partial N}\right|_V = \mu \text{ and } \left.\frac{\partial F}{\partial T}\right|_V = -S$$

Then

$$\left.\frac{\partial}{\partial T}(\mu)\right|_V = -\left.\frac{\partial}{\partial N}(S)\right|_V \tag{83}$$

(c)

$$\left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial N}\right)F\right|_T = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial V}\right)F\right|_T;$$

$$\left.\frac{\partial F}{\partial N}\right|_T = \mu \text{ and } \left.\frac{\partial F}{\partial V}\right|_T = -P$$

Then

$$\left.\frac{\partial}{\partial V}(\mu)\right|_T = -\left.\frac{\partial}{\partial N}(P)\right|_T \tag{84}$$

VI.3. The Unnamed Potential I

$$I = f(S, V, \mu).$$

(a)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial V}\right)I\right|_\mu = \left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial S}\right)I\right|_\mu;$$

$$\left.\frac{\partial I}{\partial V}\right|_{\mu} = -P \text{ and } \left.\frac{\partial I}{\partial S}\right|_{\mu} = T$$

Then

$$\left.\frac{\partial}{\partial V}(T)\right|_{\mu} = -\left.\frac{\partial}{\partial S}(P)\right|_{\mu} \tag{85}$$

(b)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial \mu}\right) I\right|_{V} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial S}\right) I\right|_{V};$$

$$\left.\frac{\partial I}{\partial \mu}\right|_{V} = -N \text{ and } \left.\frac{\partial I}{\partial S}\right|_{V} = T$$

Then

$$\left.\frac{\partial}{\partial \mu}(T)\right|_{V} = -\left.\frac{\partial}{\partial S}(N)\right|_{V} \tag{86}$$

(c)

$$\left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial \mu}\right) I\right|_{S} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial V}\right) I\right|_{S};$$

$$\left.\frac{\partial I}{\partial \mu}\right|_{S} = -N \text{ and } \left.\frac{\partial I}{\partial V}\right|_{S} = -P$$

Then

$$\left.\frac{\partial}{\partial V}(N)\right|_{S} = \left.\frac{\partial}{\partial \mu}(P)\right|_{S} \tag{87}$$

VI.4. The Entalpy H

$$H = f(S, P, N).$$

(a)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial P}\right) H\right|_{N} = \left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial S}\right) H\right|_{N};$$

$$\left.\frac{\partial H}{\partial P}\right|_N = V \text{ and } \left.\frac{\partial H}{\partial S}\right|_N = T$$

Then

$$\left.\frac{\partial}{\partial S}(V)\right|_N = \left.\frac{\partial}{\partial P}(T)\right|_N \tag{88}$$

(b)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial N}\right)H\right|_P = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial S}\right)H\right|_P;$$

$$\left.\frac{\partial H}{\partial N}\right|_P = \mu \text{ and } \left.\frac{\partial H}{\partial S}\right|_P = T$$

Then

$$\left.\frac{\partial}{\partial S}(\mu)\right|_P = \left.\frac{\partial}{\partial N}(T)\right|_P \tag{89}$$

(c)

$$\left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial N}\right)H\right|_S = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial P}\right)H\right|_S;$$

$$\left.\frac{\partial H}{\partial N}\right|_S = \mu \text{ and } \left.\frac{\partial H}{\partial P}\right|_S = V$$

Then

$$\left.\frac{\partial}{\partial P}(\mu)\right|_S = \left.\frac{\partial}{\partial N}(V)\right|_S \tag{90}$$

VI.5. The Unnamed Potential Γ

$$\Gamma = f(S,P,\mu).$$

(a)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial P}\right)\Gamma\right|_\mu = \left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial S}\right)\Gamma\right|_\mu;$$

$$\left.\frac{\partial \Gamma}{\partial P}\right|_{\mu} = V \text{ and } \left.\frac{\partial \Gamma}{\partial S}\right|_{\mu} = T$$

Then

$$\left.\frac{\partial}{\partial P}(T)\right|_{\mu} = \left.\frac{\partial}{\partial S}(V)\right|_{\mu} \tag{91}$$

(b)

$$\left.\frac{\partial}{\partial S}\left(\frac{\partial}{\partial \mu}\right)\Gamma\right|_{P} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial S}\right)\Gamma\right|_{P};$$

$$\left.\frac{\partial \Gamma}{\partial \mu}\right|_{P} = -N \text{ and } \left.\frac{\partial \Gamma}{\partial S}\right|_{P} = T$$

Then

$$\left.\frac{\partial}{\partial \mu}(T)\right|_{P} = -\left.\frac{\partial}{\partial S}(N)\right|_{P} \tag{92}$$

(c)

$$\left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial \mu}\right)\Gamma\right|_{S} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial P}\right)\Gamma\right|_{S};$$

$$\left.\frac{\partial \Gamma}{\partial \mu}\right|_{S} = -N \text{ and } \left.\frac{\partial \Gamma}{\partial P}\right|_{S} = V$$

Then

$$\left.\frac{\partial}{\partial \mu}(V)\right|_{S} = -\left.\frac{\partial}{\partial P}(N)\right|_{S} \tag{93}$$

VI.6. The Gibbs Potential G

$$G = f(T,P,N).$$

(a)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial P}\right)G\right|_{N} = \left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial T}\right)G\right|_{N};$$

$$\left.\frac{\partial G}{\partial P}\right|_{N} = V \text{ and } \left.\frac{\partial G}{\partial T}\right|_{N} = -S$$

Then

$$\left.\frac{\partial}{\partial T}(V)\right|_{N} = -\left.\frac{\partial}{\partial P}(S)\right|_{N} \tag{94}$$

(b)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial N}\right)G\right|_{P} = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial T}\right)G\right|_{P};$$

$$\left.\frac{\partial G}{\partial N}\right|_{P} = \mu \text{ and } \left.\frac{\partial G}{\partial T}\right|_{P} = -S$$

Then

$$\left.\frac{\partial}{\partial T}(\mu)\right|_{P} = -\left.\frac{\partial}{\partial N}(S)\right|_{P} \tag{95}$$

(c)

$$\left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial N}\right)G\right|_{T} = \left.\frac{\partial}{\partial N}\left(\frac{\partial}{\partial P}\right)G\right|_{T};$$

$$\left.\frac{\partial G}{\partial N}\right|_{T} = -\mu \text{ and } \left.\frac{\partial G}{\partial P}\right|_{T} = V$$

Then

$$\left.\frac{\partial}{\partial P}(\mu)\right|_{T} = \left.\frac{\partial}{\partial N}(V)\right|_{T} \tag{96}$$

VI.7. The Landau Potential Ω

$$\Omega = f(T, V, \mu).$$

(a)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial V}\right)\Omega\right|_{\mu} = \left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial T}\right)\Omega\right|_{\mu};$$

$$\left.\frac{\partial\Omega}{\partial V}\right|_{\mu} = -P \text{ and } \left.\frac{\partial\Omega}{\partial T}\right|_{\mu} = -S$$

Then

$$\left.\frac{\partial}{\partial V}(S)\right|_{\mu} = \left.\frac{\partial}{\partial T}(P)\right|_{\mu} \tag{97}$$

(b)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial \mu}\right)\Omega\right|_{V} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial T}\right)\Omega\right|_{V};$$

$$\left.\frac{\partial\Omega}{\partial \mu}\right|_{V} = \mu \text{ and } \left.\frac{\partial\Omega}{\partial T}\right|_{V} = -S$$

Then

$$\left.\frac{\partial}{\partial T}(N)\right|_{V} = \left.\frac{\partial}{\partial \mu}(S)\right|_{V} \tag{98}$$

(c)

$$\left.\frac{\partial}{\partial V}\left(\frac{\partial}{\partial \mu}\right)\Omega\right|_{T} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial V}\right)\Omega\right|_{T};$$

$$\left.\frac{\partial\Omega}{\partial \mu}\right|_{T} = -N \text{ and } \left.\frac{\partial\Omega}{\partial V}\right|_{T} = -P.$$

Then

$$\left.\frac{\partial}{\partial V}(N)\right|_{T} = \left.\frac{\partial}{\partial \mu}(P)\right|_{T} \tag{99}$$

VI.8. The Null Potential 0

$$0 = f(T, P, \mu).$$

(a)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial P}\right)0\right|_{\mu} = \left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial T}\right)0\right|_{\mu};$$

$$\left.\frac{\partial 0}{\partial P}\right|_{\mu} = V \text{ and } \left.\frac{\partial 0}{\partial T}\right|_{\mu} = -S$$

Then

$$\left.\frac{\partial}{\partial T}(V)\right|_{\mu} = -\left.\frac{\partial}{\partial P}(S)\right|_{\mu} \tag{100}$$

(b)

$$\left.\frac{\partial}{\partial T}\left(\frac{\partial}{\partial \mu}\right)0\right|_{P} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial T}\right)0\right|_{P};$$

$$\left.\frac{\partial 0}{\partial \mu}\right|_{P} = -N \text{ and } \left.\frac{\partial 0}{\partial T}\right|_{P} = -S$$

Then

$$\left.\frac{\partial}{\partial T}(N)\right|_{P} = \left.\frac{\partial}{\partial \mu}(S)\right|_{P} \tag{101}$$

(c)

$$\left.\frac{\partial}{\partial P}\left(\frac{\partial}{\partial \mu}\right)0\right|_{T} = \left.\frac{\partial}{\partial \mu}\left(\frac{\partial}{\partial P}\right)0\right|_{T};$$

$$\left.\frac{\partial 0}{\partial \mu}\right|_{T} = -N \text{ and } \left.\frac{\partial 0}{\partial P}\right|_{T} = V.$$

Then

$$\left.\frac{\partial}{\partial \mu}(V)\right|_{T} = -\left.\frac{\partial}{\partial P}(N)\right|_{T} \tag{102}$$

The twenty-four expressions above would belong to such Thermodynamics Maxwell Identities. Callen (1985, p. 182-183) claims that there are only twenty-one maxwell relations, because he considers that there are only seven potential energies. But, only twelve of these twenty-four expressions would be enough. However, when regrouping these last twelve remaining equations, there would still duplication of the half of the equations, which would be with inverted derivatives. Thus, six more equations can be neglected so that only six distinct equations remain. Finally, we present Maxwells Identities of Thermodynamics:

$$\left.\frac{\partial}{\partial V}(T)\right|_{N,\mu} = -\left.\frac{\partial}{\partial S}(P)\right|_{N,\mu} \tag{103}$$

$$\left.\frac{\partial}{\partial T}(\mu)\right|_{V,P} = -\left.\frac{\partial}{\partial N}(S)\right|_{V,P} \tag{104}$$

$$\left.\frac{\partial}{\partial S}(\mu)\right|_{V,P} = -\left.\frac{\partial}{\partial N}(T)\right|_{V,P} \tag{105}$$

$$\left.\frac{\partial}{\partial V}(\mu)\right|_{S,T} = -\left.\frac{\partial}{\partial N}(P)\right|_{S,T} \tag{106}$$

$$\left.\frac{\partial}{\partial T}(P)\right|_{N,\mu} = \left.\frac{\partial}{\partial V}(S)\right|_{N,\mu} \tag{107}$$

$$\left.\frac{\partial}{\partial V}(N)\right|_{S,T} = \left.\frac{\partial}{\partial \mu}(P)\right|_{S,T} \tag{108}$$

VII. Discussions

In this paper, we present a new interpretation for Internal Energy U, whose rereading of the Thermodynamics Euler Equation expands the understanding of the energies inherent to a Thermodynamic System that already contains Thermal Energy TS, with positive sign, Chemical Energy μN, also with positive sign and Mechanical Energy PV with a negative sign. The negative sign of this Mechanical Energy is due to the Work done previously on the Environment to insert the system in that Environment.

Although the image of the proposed cube does not explicitly show the causes of the transfer of Thermal, Mechanical or Chemical Energies, these processes, resulting from thermodynamic imbalance, will only occur if there is a difference in temperatures, pressures or chemical potentials of interacting systems. Thus, there will be a change in the values of the quantities TS, PV and μN, in case to occur a thermodynamic transformation. In these situations, the values of T, P and μ cannot be fixed.

Note that the Arrows Edge of the cube diverge from the Internal Energy U and converge to the Null Potential 0. Following this path, always in the same direction, from the Internal Energy, each Arrow Edge represents the extraction of energy from the previous state due to the transformation of the System. After the withdrawal of the three energy terms, the thermodynamic system will end up in its zero internal energy, making logical meaning the jargon reduce a system to nothing (SÁ MARTINS, 2014).

VIII. CONCLUSIONS

Although there is a consolidated algebra that equates the Laws and Relations of Equilibrium Thermodynamics, a Thermodynamic Cube and the Symmetrical Rules proper for obtaining Maxwell Identities, obtaining Euler Differential Relations, abstaining from Gibbs relations, obtaining the Gibbs-Duhen relation and obtaining the Euler relation from thermodynamics of simple systems without the application of Legendre Transformations, aiming to minimize efforts to obtain the matematical expressions of classical thermodynamics, as well as the to facilitate the teaching and learning of the theory of the Great Potentials of Thermodynamics.

In this sense, this *E-Digraph* model proposed here aims to facilitate obtaining the interrelations between free energies and between Thermodynamic Potential Energies for open systems, aiming to give meaning to the Great Potentials of Thermodynamics, since the scientific literature still deals with them very superficially.

It was observed during the elaboration of this article that Thermodynamics for Open Systems is a field that still needs investigation and epistemological analysis, even lacking a more concise elaboration and presentation of the definitions that involve the Great Potentials.

REFERÊNCIAS

ARENS, R. An Axiomatic Basis for Classical Thermodynamics. *Journal of Mathematical Analysis and Applications*. 6, 207-229. 1963. Available in <https://www.sciencedirect.com/science/article/pii/0022247X63900052>. Access at: Jan. 02 2020.

BALIAN, R. François Massieu and the thermodynamic potential. *Comptes Rendus Physique*. 18,526-539. 2017.

BRAGA, J. P. A Formulação *ab-initio* da segunda lei da termodinâmica. Química Nova, 21(4), 1998. Available in <http://www.scielo.br/pdf/qn/v21n4/3200.pdf>. Access at: Jan 02 2020.

CALLEN, H. B. Thermodynamics and a Introduction to Thermoestatistics, Second Edition, *John Wiley and Sons*, New York, 1985.

CORREIA, J.J.; MAGALHÃES, L. D. R.; LIMA, L. S. Obstáculos Epistemológicos e o Conceito de Calor. *Scientibus Série Ciências Físicas* 04: 1-10, 2008. Available in: <http://dfis.uefs.br/sitientibus/vol4/Jornandes-Main-SPSS2008.pdf>. Access at: Nov 10 2019.

CORREIA, J.J; JOSÉ, W. D. O conceito de trabalho de uma força em livros didáticos, In: *IX COLÓQUIO DO MUSEU PEDAGÓGICO* (ISSN 2175-5493), Vitória da Conquista (BA), Anais. Vitória da Conquista. MUSEU PEDAGÓGICO CASA PADRE PALMEIRA. 2011. v. 9, n. 1, p. 727-740, 2011. Available in: <http://periodicos.uesb.br/index.php/cmp/article/viewFile/2663/2330>. Access at: Nov 10. 2019.

CORREIA, J. J.; OLIVEIRA, W. C. A Definição de Energia Interna e o Enunciado da Primeira

Lei da Termodinâmica nos Livros Didáticos. *Revista Binacional Brasil-Argentina*: Diálogo entre as ciências, [S. l.], v. 7, n. 2, p. 184-215, Dez. 2018. ISSN 2316-1205. Available in: <http://periodicos2.uesb.br/index.php/rbba/article/view/4647>. Accesso at: Nov 10 2019.

CORREIA, J. J.; OLIVEIRA, W. C. A definição de Entalpia em Livros Didáticos. *Revista Binacional BrasilArgentina*. v. 8, n. 1, p. 327-363, Mai. 2019. Available at: <https://www.researchgate.net/publication/339276026_A_definicao_de_%27entalpia%27_em_livros_didaticos>. Access at: Jan 13 2021.

CORREIA, J. J; GUIMARÃES, G. F. Definição da energia livre de Gibbs em fontes didáticas. *Caderno de Física da UEFS*, v. 18, n. 2, p. 2502.1-25, Mar. 2020. ISSN 2316-1205. Recovered from: <http://dfisweb.uefs.br/caderno/vol18n2/S5Artigo02_Jornandes_Fontes_Didaticas.pdf>. Access at: Jul. 12 2021.

CORREIA, J. J; GUIMARÃES, G. F. Definição da energia livre de Helmholtz em fontes didáticas. *Revista Binacional Brasil-Argentina*: Diálogo entre as ciências, [S.l.], v. 8, n. 2, p. 141-169, Mar. 2020a. ISSN 2316-1205. Recovered from: <https://periodicos2.uesb.br/index.php/rbba/article/view/7869>. Access at: Jan. 28 2021.

CORREIA, J. J; GUIMARÃES, G. F. A Definição de Potencial Químico em fontes didáticas. *Revista Binacional Brasil-Argentina*: Diálogo entre as ciências, [S.l.], v. 10, n. 1, p. 412-438, Jun. 2021. ISSN 2316-1205. Recovered from: < <https://periodicos2.uesb.br/index.php/rbba/article/view/8003>. Access at: Jun 08 2021.

FOX, R. F. J. Chem. Educ. 53, 7 (1976).

GIBBS, J. W. Collected Works, Vol. I, *Thermodynamics, Longman*, New York, 1928.

KERR, W. C.; MACOSKO, J. C. Thermodynamic Venn diagrams: Sorting out forces, fluxes, and Legendre transforms. American Journal of Physics. 79 (9), 950. 2011. Available in: <https://www.researchgate.net/publication/235736528_Thermodynamic_Venn_diagrams_Sorting_out_forces_fluxes_and_Legendre_transforms>. Access at: Apr 18 2020. DOI: 10.1119/1.3599177.

KOCIK, J.: On Geometry of Pheonomenological Thermodinamics. Jul. 2018. Available in: <https://www.researchgate.net/publication/326586312_On_geometry_of_phenomenological_thermodynamics>. Access at: Dec 25 2019.

KOENIG, F. O. J. *Chem. Phys.* 3, 29 (1935).

KOENIG, F. O. J. *Chem. Phys.* 56, 4556 (1972).

PÁDUA, A. B.; PÁDUA, C; G.; SILVA, J. L. C.; MARTINS, R. S.; POSTALI, F. B.; TIRITAN, L. A. C. Termodinâmica clássica ou termodinâmica do equilíbrio: aspectos conceituais básicos.

Semina: Ciências Exatas e Tecnológicas. v. 29, n. 1, p. 57-84. 2008.

PATE, S. F. The thermodynamic cube: A mnemonic and learning device for students of classical thermodynamics. *American Journal of Physics*. 67, 1111. 1999.

POGLIANI, L. Digraphs, Graphs and Thermodynamics Equations. In: HAGHI, A. K. *et al* (org.) Applied Chemistry and Chemical Engineering, Vol. I Mathematical and Analytical Techniques. *Apple Academic Press*, Canadá, 2018.

SÁ MARTINS, J. S de. Aula 2.5 [Termodinâmica] Processos a pressão constante, calor latente e entalpia. Physics Institute of Universidade Federal Fluminense (UFF). Rio de Janeiro, Brazil. Youtube, *video classes UFF*, 2014. Available in: <https://www.youtube.com/watch?v=2CkJ1iJ3nBI&list=PLJHqUYUf9YoopjoVLiuc1jj3YSiT9yzpl&index=5>. Access in: Jan 25 2019.

ZHAO, J. C. A Minemonic Scheme for Thermodynamic. *Materials Reseach Society Bulletin*. V. 34, February 2009. Available in: <http://web.mit.edu/course/8/8.593/spring10/bk/on_MRS_Thermodynamic_Mnemonic.pdf> Access at: Apr 16 2020.