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THEORETICAL ARGUMENTS ON EXERGY METHOD AND NON-EQUILIBRIUM IN NUCLEAR PROCESSES

Argomentazioni teoriche sul metodo exergetico e non equilibrio nei processi nucleari

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ABSTRACT

The present Ph.D. thesis aims at discussing theoretical aspects and arguments concerning thermodynamic methods and applications to fission and fusion nuclear plants. All parts of the thesis are rooted in the ground of the scientific literature, and all outcomes and conclusions corroborate the conceptual building with no disprove of any foundations constituting the framework accepted and shared by the whole scientific community. Though, clarifications, extensions, generalizations and applications of concepts and definitions represent primary outcomes deemed by the author beneficial for a rational and systematic perspective of Physics and Thermodynamics in the research and applications to technological and industrial developments. This abstract attempt to summarize state-of-the-art and references, methods, achievements, original results, future perspectives and is followed by an index breaking down all sections to enable an overview on the way the thesis is organized.

The mechanical aspect of the entropy-exergy relationship, together with the thermal aspect usually considered, represents the outset of the research and one of the central topics. This very aspect leads to a formulation of physical exergy and chemical exergy based on both useful work and useful heat, or useful work and useful mass, representing first outcomes based on the concept of available energy of a thermodynamic system interacting with a reservoir. By virtue of the entropy-exergy relationship, this approach suggests that a mechanical entropy contribution can be defined, in addition to the already used thermal entropy contribution, for work interaction due to pressure and volume variations. The mechanical entropy is related to energy transfer through work interaction, and it is complementary to the thermal entropy that accounts energy transfer by means of heat interaction. Then, the logical sequence to get mechanical exergy expression to evaluate useful work withdrawn from available energy is demonstrated. Based on mechanical exergy expression, the mechanical entropy set forth is deduced in a general form valid for any process. Finally, the formulation of physical exergy is proposed that summarizes the contribution of either heat or work interactions and related thermal exergy as well as mechanical exergy that both result as the outcome from the available energy of the composite of the system interacting with a reservoir. This formulation contains an additional term that takes into account the volume and, consequently, the pressure that allow to evaluate exergy with respect to the reservoir characterized by constant pressure other than constant temperature. The basis and related conclusions of this paper are not in contrast with principles and theoretical framework of thermodynamics and highlight a more extended approach to exergy definitions already reported in literature that remain the reference ground of present analysis.

The literature reports that equality of temperature, equality of potential and equality of pressure between a system and a reservoir are necessary conditions for the stable equilibrium of the system-reservoir composite or, in the opposite and equivalent logical inference, that stable equilibrium is a sufficient condition for equality. A novelty of the present study is to prove that equality of temperature, potential and pressure is also a sufficient condition for stable equilibrium, in addition to necessity, implying that stable equilibrium is a condition also necessary, in addition to sufficiency, for equality. A subsequent implication is that the proof of the sufficiency of equality (or the necessity of stable equilibrium) is attained by means of the generalization of the entropy

property, derived from the generalization of exergy property, which is used to demonstrate that stable equilibrium is a logical consequence of equality of generalized potential. This proof is underpinned by the Second Law statement and the Maximum-Entropy Principle based on the generalized entropy which depends on temperature, potential and pressure of the reservoir. The conclusion, based on these two novel concepts, consists of the theorem of necessity and sufficiency of stable equilibrium for equality of generalized potentials within a composite constituted by a system and a reservoir.

Among all statements of Second Law, the existence and uniqueness of stable equilibrium, for each given value of energy content and composition of constituents of any system, has been adopted to define thermodynamic entropy by means of the impossibility of Perpetual Motion Machine of the Second Kind (PMM2) which is a consequence of the Second Law. Equality of temperature, chemical potential and pressure in many-particle systems are proved to be necessary conditions for the stable equilibrium. The proofs assume the stable equilibrium and derive, through the Highest-Entropy Principle, equality of temperature, chemical potential and pressure as a consequence. In this regard, a first novelty of the present research is to demonstrate that equality is also a sufficient condition, in addition to necessity, for stable equilibrium implying that stable equilibrium is a condition also necessary, in addition to sufficiency, for equality of temperature potential and pressure addressed to as generalized potential. The second novelty is that the proof of sufficiency of equality, or necessity of stable equilibrium, is achieved by means of a generalization of entropy property, derived from a generalized definition of exergy, both being state and additive properties accounting for heat, mass and work interactions of the system underpinning the definition of Highest-Generalized-Entropy Principle adopted in the proof.

To complement the physical meaning and the reasons behind the need of a generalized definition of thermodynamic entropy, it is proposed a logical relation of its formulation on the base of Gibbs equation expressing the First Law. Moreover, a step forward is the extension of the canonical Equation of State in the perspective of thermal and chemical aspect of microscopic configurations of a system related to inter-particle kinetic energy and inter-particle potential energy determining macroscopic parameters. As a consequence, a generalized State Equation is formulated accounting for thermal, chemical and mechanical thermodynamic potentials characterizing any system in any state.

As far as the Non-Equilibrium Thermodynamic is concerned, the present research aims at discussing the hierarchical structure of so-called mesoscopic systems configuration. In this regard, thermodynamic and informational aspects of entropy concept are highlighted to propose a unitary perspective of its definitions as an inherent property of any system in any state, both physical and informational. The dualism and the relation between physical nature of information and the informational content of physical states of matter and phenomena play a fundamental role in the description of multi-scale systems characterized by hierarchical configurations. A method is proposed to generalize thermodynamic and informational entropy property and characterize the hierarchical structure of its canonical definition at macroscopic and microscopic levels of a system described in the domain of classical and quantum physics. The conceptual schema is based on dualisms and symmetries inherent to the geometric and kinematic configurations and interactions occurring in many-particle and few-particle thermodynamic systems. The hierarchical configuration of particles and sub-particles,

representing the constitutive elements of physical systems, breaks down into levels characterized by particle masses subdivision, implying positions and velocities degrees of freedom multiplication. This hierarchy accommodates the allocation of phenomena and processes from higher to lower levels in the respect of the equipartition theorem of energy. However, the opposite and reversible process, from lower to higher level, is impossible by virtue of the Second Law, expressed as impossibility of Perpetual Motion Machine of the Second Kind (PMM2) remaining valid at all hierarchical levels, and the non-existence of Maxwell's demon. Based on the generalized definition of entropy property, the hierarchical structure of entropy contribution and production balance, determined by degrees of freedom and constraints of systems configuration, is established. Moreover, as a consequence of the Second Law, the non-equipartition theorem of entropy is enunciated, which would be complementary to the equipartition theorem of energy derived from the First Law.

A section is specifically dedicated to specialize Second Law analyses to characterize balances of properties, and efficiencies of processes, occurring in elemental fission and fusion nuclear reactions. The conceptual schema is underpinned by the paradigm of microscopic few-particle systems and the inter-particle kinetic energy and binding potential energy determined by interactions among atomic nuclei and subatomic particles in non-equilibrium states along irreversible phenomena. The definition here proposed for thermodynamic entropy calculation is based on energy and exergy both being measurable properties by means of those values calculated from particles mass defect and used to directly derive entropy balances along nuclear processes occurring in operating industrial plants.

Finally, it is proposed a preliminary exergy analysis of EU DEMO pulsed fusion power plant considering the Primary Heat Transfer Systems, the Intermediate Heat Transfer System (IHTS) including the Energy Storage System (ESS) as a first option to ensure the continuity of electric power released to the grid. A second option here considered is a methane fired auxiliary boiler replacing the ESS. The Power Conversion System (PCS) performance is evaluated as well in the overall balance. The performance analysis is based on the exergy method to correctly assess the amount of exergy destruction determined by irreversible phenomena along the whole cyclic process. The pulse and dwell phases of the reactor operation are evaluated considering the state of the art of the ESS adopting molten salts alternate heating and storage in a hot tank followed by a cooling and recovery of molten salt in a cold tank to ensure the continuity of power release to the electrical grid. An alternative plant configuration is evaluated on the basis of an auxiliary boiler replacing the ESS with a 10% of the power produced by the reactor during pulse mode.

The conclusive summary of main achievements and original outcomes is followed by proposals of future developments in different fields of theoretical and applied research and technology. These themes represent an outlook on the opportunities and initiatives originating from the passionate dedication effort spent along the here ended Doctorate.

MAIN ACHIEVEMENTS AND ORIGINAL OUTCOMES

- Definition of generalized thermodynamic exergy and thermodynamic entropy properties;
- Theorem of necessity and sufficiency of stable equilibrium and Highest-Generalized-Entropy principle for stable equilibrium and non-equilibrium
- Perspective of the State Equation extended to both thermal aspect and chemical aspect; relationship of State Equation with generalized thermodynamic entropy property; analysis of Gibbs equation incoherence and demonstration of units of measure equivalence; generalization of ideal state equation taking into account kinetic and potential energy due to inter-particle kinematic and geometric configurations;
- Hierarchical structure of thermodynamic entropy defined for mesoscopic systems: non-equipartition theorem on entropy, complementary to the equipartition theorem of energy for microscopic systems;
- Fission and fusion elemental reactions second law analyses based on exergy method: thermodynamic and informational aspect accounted for in nuclear physics;
- Simplified exergy balances and efficiencies calculations of ABWR and AP1000 fission nuclear reactors considering nuclear core and conventional plant;
- Preliminary exergy analysis of EU DEMO pulsed fusion reactor with molten salts energy storage system and auxiliary boiler configurations.

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1. INTRODUCTION

The area of interest of the present doctoral dissertation is twofold. On the one side, conceptual and theoretical aspects and arguments are discussed with the intent of arguing on basic fundamentals of Thermodynamics and extending the standpoint and definitions to achieve a more general perspective.

Thermodynamic foundations, laws, principles and theorems represent a conceptual framework still under development. The body of Thermodynamics as a domain of Physics in its broader sense is reported in pioneering and seminal textbooks authored by the most outstanding and distinguished Scientists who have paved the path of scientific researches and developments in all fields of Engineering and Living Sciences [1.1-1.9]. Among all authoritative textbooks in the literature, the ones mentioned as References of the present thesis are those addressed to in the publications representing the present status and progress of the theme treated in the present research. The intent is here to provide a set of references of the conceptual framework constituting the foundations of thermodynamic methods and analyses. Nevertheless, the most recent progresses in this framework represent a useful tool to investigate the design criteria of nuclear plants thus representing a ground where the literature is less focusing.

On the other side, the present research is oriented to industrial applications concerning fission and fusion nuclear reactions and plants design and technology: the reason behind the selection of this topic is to investigate the methodology that could be beneficial for industry along the design of nuclear plants. Nuclear technology considered in the research is that at the basis of III+ generation of ABWR and AP1000 fission reactors as well as EU DEMO fusion technologies today undergoing a strong development momentum looking forward operational application in next future.

1.1. Premise

Thermodynamics occupies a large and significant part of Physics and represents the utmost general framework of theories, methods and applications. Thermodynamics generality, in its foundations, laws, principles, theorems, properties and processes, is so general that it could be considered as the closest discipline to philosophical and epistemological vision of science and, for this very reason, it constitutes a powerful tool of knowledge. To argue this statement, mention can be made to the fact that, since early appearance of the fundamental laws of conservation and evolution during mid eighteenth century, the building of theories and methods have been ever confirmed and corroborated by further theoretical researches and developments as well as experiments and industrial applications. No disprove of any statement have been backed up so far with logical and mathematical robust and coherent demonstrations.

This unavoidable premise is posited to clarify that, the present dissertation, moves on the solid ground of thermodynamics as it is today described in the literature and no attempts of disproving its conceptual framework based on those foundations are moving the author. Nevertheless, under its very generality and validity in all contexts of non-living and living sciences, extensions of definitions and applications to complex systems has been pursued along the research studies to propose an original and innovative standpoint and the utilization to those areas overarching applications in nuclear industry.

1.2. Purpose and Significance

The purpose of the present doctoral thesis is to report researches carried out to envisage and develop an overarching perspective aimed at assessing, comparing and optimizing the performance of different nuclear plant design configurations accounting for the whole life cycle including nuclear fuel production and treatment. The research is rooted on the scientific literature produced since ever in all Physics areas somehow correlated to Thermodynamics and is articulated through the following parts: i) theoretical foundations, ii) methodological procedure, iii) industrial design and application. The phases i) and ii) are described in the following sections 2,3,4 and the phase iii) is developed in the remaining sections of the present thesis.

Results and conclusions proposed in this thesis move in two directions. The first direction moves to outline novelties in the definitions of thermodynamic properties implied in Second Law analyses. The second direction provides a more detailed analysis starting from elemental fission and fusion nuclear reactions to be accounted for in the overall design of nuclear plants.

1.3. Reference Literature and State of the Art

Fundamentals of Thermodynamics are the legacy of scientists such as Max Planck [1.1] in the twentieth century. Last decades, from last to present century, have been progressing in the evolution of Equilibrium and Non-Equilibrium Thermodynamics pioneered by Keenan [1.2], Hatsopoulos, Gyftopoulos and Beretta at the Massachusetts Institute of Technology (MIT) in Boston [1.9], by von Spakovsky at Virginia Tech, by Gaggioli at Milwaukee University and by Sciubba at Sapienza Università. These mentioned authors have been building up a rationale and rigorous body of formalisms and definitions, theorems, lemma and proofs demonstrating the overarching completeness and unitary coherence of the whole conceptual architecture of thermodynamics.

The Unified Quantum Theory of Mechanics and Thermodynamics, authored by Hatsopoulos and Gyftopoulos, constitute the cornerstone of the whole complete and consistent conceptual architecture of fundamental in Classical and Quantum Thermodynamics that has been consolidated so far, without any logical, mathematical or experimental disproving rationale.

In 1961 Tribus first conceived the idea of availability that was redefined as available energy (non-additive) exergy (additive), a property adopted to establish the exergy method extensively developed and described by Kotas, Tsatsaronis, Szargut, Moran, Sciubba, Wall.

The importance and influence of Thermodynamics as an area of Physics can be ascribed to its great generality and the extension to all other scientific Disciplines. Since it appears in the first half of nineteenth century, its fundamentals and laws have been affecting the conception of theories in Physics, Chemistry, Biology and, more recently, in Information sciences. Even more surprisingly, Thermodynamics has been impacting the discussion within science philosophy and in particular epistemology because if observes nature at the ultimate essence of its elementary mechanisms on the one side and the emergence of complex phenomena on the other side. Therefore, it is worth placing Thermodynamics in a central role of an architecture of science disciplines mutually influencing each other as described in the following Figure 1.1 depicting the framework of all Disciplines involved in Physics and Epistemology. Complexity, and complex thought, represent the paradigm conceived and elaborated by Edgar Morin [1.23-1.26] spreading through non-living [1.23] and living [1.24] portions of the universe. One of the outcomes of complex thought is the dialectic and mutual logical inference of reductionism, as a consequence of deterministic mechanicism, and holism, as a consequence of probabilistic organicism. On the opposite edge of science knowledge, the Quantum Physics deals with the ultimate nature of elementary particle behaving through the wave-particle duality expressed while interacting with an observer. Surprisingly, the more fundamental level of description of physical objects, the more complex conceptual paradigm is needed to achieve the essence of the “physis”. Interestingly, the set of mathematical disciplines is adequate to this complexity. In fact, Quantum Physics relies, or is itself consisting of, four areas of Mathematics: Linear Algebra, Complex Analysis, Functional Analysis and Statistics. All these mathematic bodies are embedded in Quantum Physics and the border separating the logical-mathematical language from the physical reality essence is subtle. Hence, the methodological research paradigm in its entirety should be rooted in the ground of Logics, Epistemology, Mathematics and the Theory of Theories which provides the guideline to identify the perimeter and the set of foundations and theorems constituting the body of a theory.

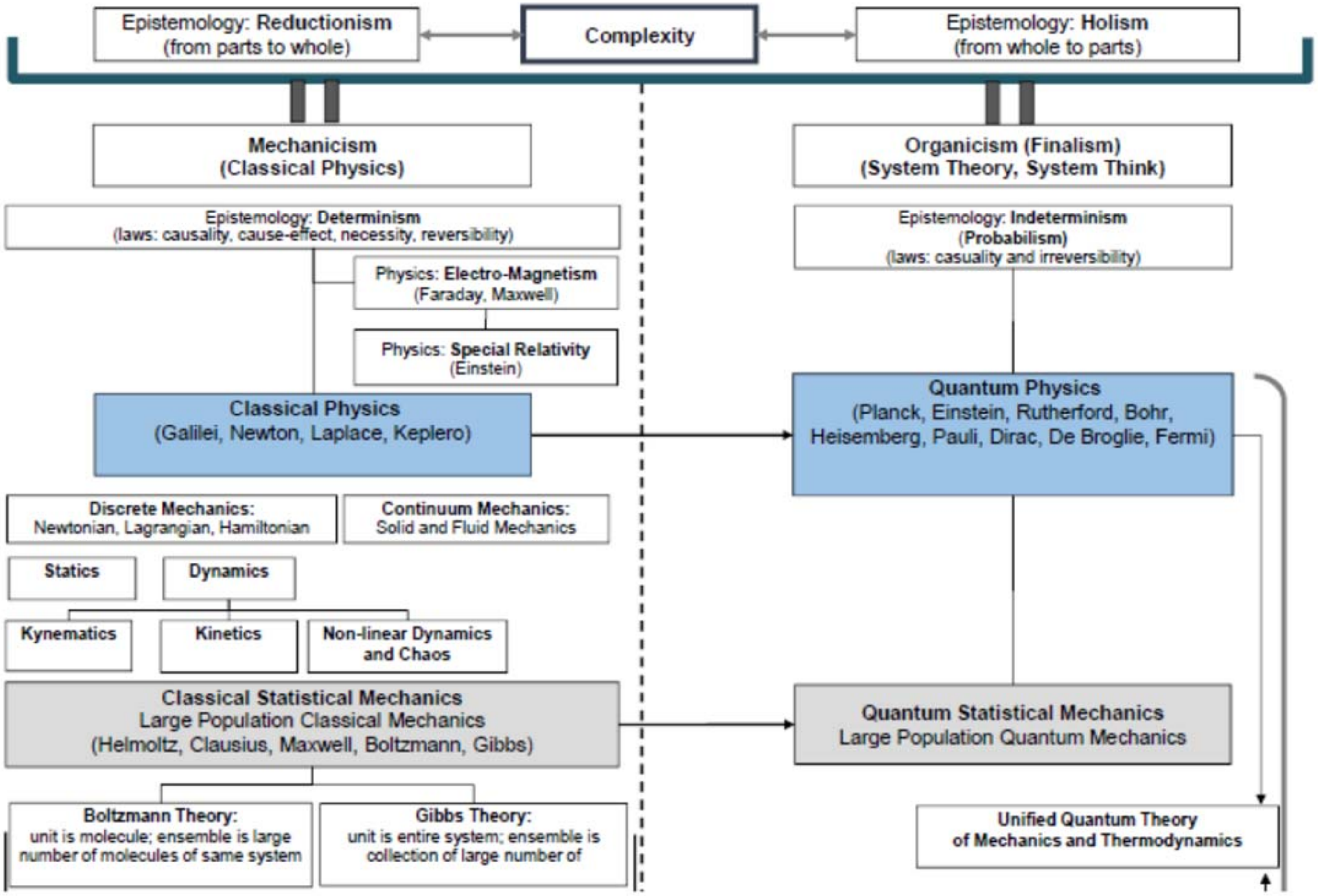


Figure 1.1a – Physics Disciplines Framework

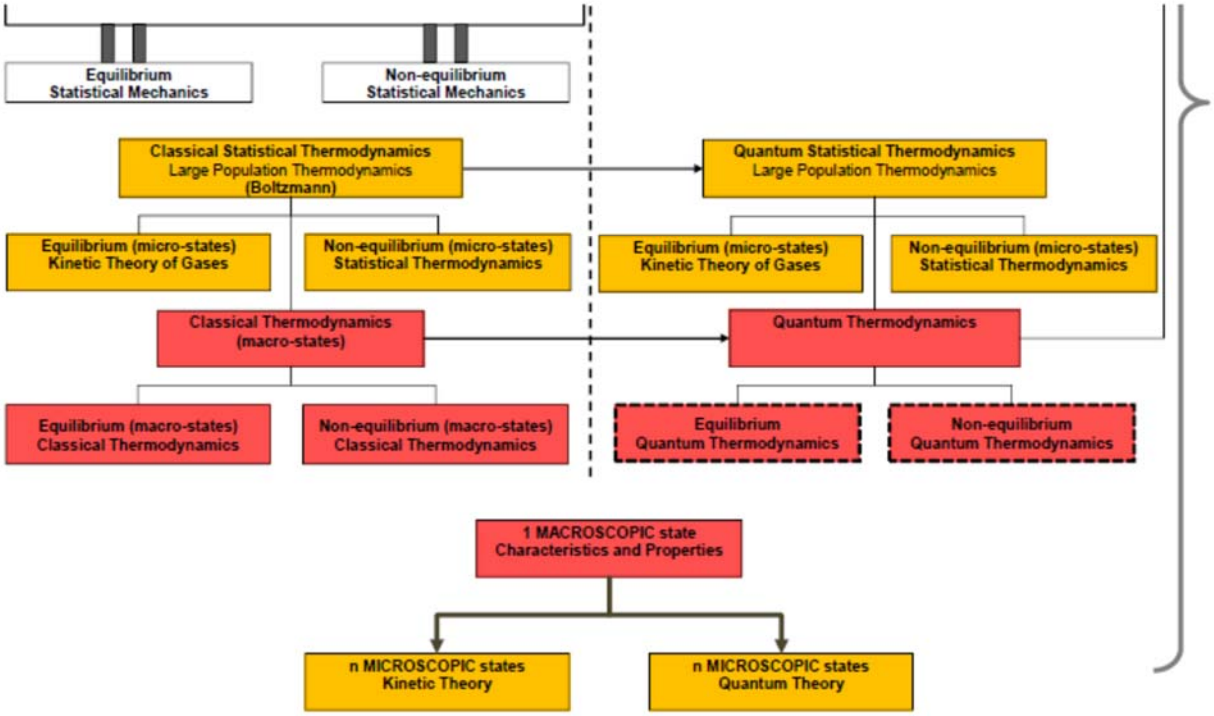


Figure 1.1b – Physics Disciplines Framework

Although thermodynamic analyses have been, since ever, based on Fist Law and energy quantity, from theoretical and practical standpoint exergy property allows the complete and consistent evaluation of systems performance and optimization since both reversible and irreversible phenomena are isolated and evaluated. Indeed, energy can be neither created nor destroyed while, during real processes, exergy is destroyed and the capability of the system to cause change is reduced as well.

The canonical definition of exergy is maximum theoretical net useful work obtained along processes determined by the mutual interaction between a system and the external reference system or reservoir up to the thermodynamic stable equilibrium state of the system-reservoir composite. In this definition, the term "theoretical" addresses to ideal systems and processes, and the term "net" means the result from system-to-reservoir and or reservoir-to-system interactions at the end of the process.

1.4. Methodological Paradigm

As far as the methodological paradigm here adopted is concerned, it is worth mentioning the masterpiece of Edgar Morin entitled "La Methode" (in original French language). This cornerstone masterpiece in the epistemology literature is a paramount view of the complex thought and the complexity of systems in nature. One of the most outstanding and fruitful paradigms devised and described by Morin is the logical relationship and dialectic recursive sequence "*order-disorder-organization*" representing one of the fundamental schemas adopted in Non-Equilibrium Thermodynamics. The historical outset is counted in the textbooks of Prigogine who first rationalized the creative capability of nature in generating organized structures within systems undergoing far-from-equilibrium dissipative processes induced by large driving forces and thermodynamic potential differences. These first notes underline how Thermodynamics, among all other disciplines of Physics, is intimately and strictly connected to epistemology and induce philosophical reasoning beyond the engineering and practical usefulness of its methodologies and operative procedures and analytical and numerical calculations.

A mention of Logics and Proof Theory is deemed worthy since most common definitions are hereafter quoted to facilitate the reader in understanding the procedures and demonstrations reported in the references addressed to:

- **Law**: a statement of an order or relation of phenomena that so far as is known is invariable under the given conditions;
- **Principle**: logical premise or existence reason of real fact;
- **Assumption**: a statement that is accepted as true or as certain to happen, without proof;
- **Axiom**: proposition accepted with no proof, assumed among principles of a deductive theory;
- **Postulate**: primitive proposition of a theory, assumed with no proof;
- **Theorem**: a statement that has been proven on the basis of previously established statements, such as other theorems, and generally accepted statements, such as axioms; a theorem is a logical consequence of the axioms; the proof of a mathematical theorem is a logical argument for the theorem statement given in accord with the rules of a deductive system;
- **Corollary**: enunciation or theorem that can be derived from a proved statement and normally has an extension and importance that is less with respect to the enunciation from which it is derived;
- **Lemma**: assertion or premise to demonstrate a different proposition;
- **Proof**: logical sequence, in the domain of Proof Theory, demonstrating the rationale to achieve the correctness, completeness, and consistency of a statement (the thesis of a theorem), related to, and inferred from, assumptions, axioms or postulates (hypothesis of a theorem).

The Proof Theory is here mentioned to highlight that one of the most used logical procedures is the demonstration by the "Reductio Ad Absurdum" used to prove a theorem by means of the falsification of the thesis negation. This procedure is adopted to prove both necessity and sufficiency of a hypothesis for an enunciated theorem.

The methodological paradigm here referred to, is articulated in the dialectic sequence "*inductive analysis and deductive synthesis*" constituting a double and bi-directional logical inference commonly adopted in scientific investigation and research. This is the very reason for providing the framework of disciplines where specific concepts, assumptions, axioms, and postulates are followed by particular cases and thought or real experiments to identify a proper discipline or context.

Two main parts compose this thesis: the first one is primarily theoretical and methodological, while the second part focuses on non-equilibrium fission and fusion nuclear processes and the analysis of nuclear reactor and conventional plant in industrial applications.

1.5. Main Objectives

Purpose of the present research is twofold: i) on the one side the theoretical-methodological aspect is aimed at demonstrating original aspects and additional properties based on the presents state of the art of thermodynamics foundations currently adopted in plants and components design; ii) on the other side to provide specific applications to nuclear technology and plant configuration of fission and fusion technology representing present and future enhancing progress.

Despite the bias of the present research centered on mechanical engineering and physics of inert non-living systems, the attempt is to outline and propose research directions in the domain of complex and biological systems and life phenomena governed by those thermodynamic thought paradigms. This objective is underpinned by the absolute generality of Thermodynamics that can be adopted as a powerful epistemological method to investigate complex epi-phenomenological processes emerging from the complexity of physical systems through a unified reductionistic and holistic overarching and unitary perspective. The statement "the whole which is in the part which in turn is in the whole" is a representation of this dialectics that can be considered the ultimate logical syllogism of everything.

2. EXERGY METHOD

Theoretical arguments, aspects and implications of Thermodynamics and the exergy method represent the central part of the present research. As anticipated in the Introduction, all Disciplines of Physics are somehow involved and correlated each other. This vast extension of the domain of knowledge requires the identification of a perimeter and foundations of these Disciplines to properly correlate the most significant aspects looking forward to the objectives of the research. To do so, the advantage of starting with the exergy method is twofold. Firstly, the exergy property offers a method for Second Law analyses of any process including those pertaining to nuclear and sub-nuclear particles and reactions. Secondly, the extension of its applicability derives from accounting of aspects that are less treated in the literature and may represent a novelty to corroborate the rigorous and practical applicability of this method in all physics and engineering industrial applications. The advantages of exergy property, and the method based on this property, are the following:

- it is a non-conservative, extensive and additive state property;
- it is a measurable physical quantity;
- it allows to assess irreversibilities and dissipative phenomena along any process in any system;
- it is an indicator of the “thermodynamic quality” of the energy available in a given equilibrium or non-equilibrium state characterizing any system.

The exergy analysis is a part of the Second Law analysis underpinned by the entropy-exergy relationship, and it can be considered as complementary to the First Law analysis, and vice versa. Indeed, the First Law analysis accounts for energy transformations and transfers while the Second Law analysis focuses on energy conversions and interactions. Both analyses provide a complete and rigorous method to design and optimize performances of component and any plant configuration as a whole. Nevertheless, the earned value got by applying the exergy method is to more rigorously characterize and categorize, in terms of “thermodynamic quality”, different forms of energy, energy streams and interactions, even in ideal conditions, to optimize the configuration and performance of components and plants. This type of assessment will become clear along forthcoming sections of the present thesis.

As far as the conceptual origin and the definition, the exergy property directly derives from the concept of availability function or available energy first devised and applied by J.W.Gibbs in seminal and since ever mentioned publications [2.1,2.2]. These terms have been rephrased in the term exergy directly addressing to the mechanical aspect of available energy representing the portion, of the whole energy content of a system, that can be withdrawn as available work along processes where a mutual interaction between the system and an external reference environment, or reservoir, occurs. The literature reports treatises elaborating Gibbs conceptual foundations and demonstrating the characteristics and applicability of exergy as a state, additive and non-conservative property [2.3-2.6].

The above-mentioned relationship is used to start with defining exergy and the method adopting this quantity in this section 2., and then deducing entropy using the formulation extensively adopted in next section 3. of this research.

2.1. Physical Models of Systems

Physical models of systems are the internal system, constituted by a set of chemical constituents r, a set of parameters β, and physical particles undergoing processes, and the external reference system assumed behaving as a reservoir.
The system consisting of the moving parts interacting with the internal system or external system composing a machine or any other device can be defined as the “useful system” that, in turn, can be specialized into motor system or operator system where requested.

According to the terminology and definitions adopted by Gyftopoulos and Beretta [1.9], the internal system (or system), denoted by the symbol A, may be large or small, even at molecular level. Such a system can experience states of equilibrium and non-equilibrium; the external reference system, denoted by the symbol R behaves as a reservoir at constant temperature, potential and pressure, experiences stable equilibrium states only and is in mutual stable equilibrium with a replica of the reservoir itself [1.9].

Models adopted rely on the concept of many-particle or few-particle systems which are considered to fully comply with the terminology in the most recent literature. Two main systems mutually interacting are considered namely, the internal system undergoing thermodynamic processes, the external “useful” system, and the external “reference” system accurately defined to behave as a reservoir.

The internal system can be may-particle or few-particle with the following characteristics and properties described in the following sections. It worth noticing that in terms of Classical Thermodynamics, a system assumes the properties of a thermodynamic system when the number of particles is equal or higher three. This limit is established by the “Three-Body Theorem” conceived by Henri Poincaré who demonstrated that equations governing the motion of three particles are approximated by series that are diverging.

2.1.1. Internal Many-Particle Systems

The internal system A is constituted is considered a many-particle system, that is, constituted by a number of particles such that pressure is determined by both velocity and frequency of particles collisions against the external system represented by a cylinder-piston device. This model implies that the velocity is associated to the kinetic energy of particles and, in this case, the specific volume determines the frequency of collisions corresponding to the number of collisions per unit of time. Lennard-Jones potential accounts for repulsive and attractive interactions occurring at an increasing distance among particles. Besides, the position is associated with the potential energy and, in this case, the specific volume determines the intensity of interactions corresponding to the distance among particles.

Assumptions and physical model of nuclear reactions occurring in the core of nuclear plants consider the typical many-particle systems representing fuel and all particles involved in nuclear reactions.
All characteristics of the system and phenomena occurring within it are assumed as real then considering all interactions among particles.

2.1.2. Internal Few-Particle Systems

As far as the internal system is concerned, it can be constituted by few particles as can be thought at microscopic and quantum level. The few-particle perspective becomes applicable in nuclear physics, in quantum physics and in those discrete systems where Classical Thermodynamics requires a proper adaptation and suitable assumption and models. Typical examples of few-particle systems are nuclei and neutrons interacting in fission and fusion nuclear reactions; another notable example is the case of a particle-in-a-box used to resolve parameters of the wavefunction in quantum physics. Nanotechnologies and nanosystems represent a domain where few-particle modeling is needed for a proper description of mechanisms and processes.

2.1.3. External Systems

External systems are mainly of two types: the useful system and the reference system. The useful system is intended as any device using or releasing interactions to the internal system.

2.1.3.1. Useful Systems

The term useful system is referred to the external system that uses the interaction coming from the internal system as a consequence of occurring processes. A typical example is the weight device that allows the displacement of a mass in the gravitational, or a charge in an electromagnetic field, along a weight process or an electro-magnetic process [1.9]. The weight process represents a device with measurable parameters suitable to be adopted in experiments and as an interacting system in theoretical descriptions. A cylinder-piston or a turbo-machinery are other examples encountered in current practical applications.

2.1.3.2. Reference System or Reservoir

The reference system behaves as a reservoir here identified with the symbol R, according to the definition of Gyftopoulos and Beretta [1.9]. Specific definitions adopt the symbology in conformity with the literature authored by Hatsopoulos, Gyftopoulos and Beretta. The reference system can be external or can be a subsystem displaying the same properties of a reservoir characterized in the macroscopic domain. The reservoir is an open system exchanging energy, entropy, amounts of constituents and volume while experiencing stable equilibrium states only. The reservoir R is in mutual stable equilibrium with a duplicate of itself, behaves ideally at a permanent stable equilibrium while interacting with the internal system with no variations of characteristic parameters and thermodynamic states along whatever process.

The properties associated to and characterizing a reservoir may be obtained by means of a system constituted by a mass larger than the system (and ideally infinitely large). As an alternative, a pure finite-mass substance in a fixed region of space at the triple-point state behaves at constant temperature considering that heat interactions with the system occur with no changes in volume [2.18]. Nevertheless, the triple point ensures that pressure is constantly provided that the reservoir is adiabatic and able to change its volume as work interactions with the system occur while the two systems are in mutual neutral equilibrium [2.18]. The system A is characterized by its states of equilibrium or non-equilibrium determined by the equality or non-equality of temperature, chemical potential (also referred to as potential), and pressure.

2.1.3.3. Reservoir as Auxiliary System

A caveat is here needed to clarify the most recent studies and the criticisms to the use of the reservoir. The role of the reservoir is essential in the definition of exergy property; however, it has been proved to be auxiliary only in the definition of entropy property that has been derived from energy and exergy [1.9]. Indeed, this fact is the direct consequence of the inherent nature of entropy property such as mass, energy, momentum, and not depending on statistical or information states of the system. This conclusion has been derived for many-particle systems, however, studies are underway to achieve the same conclusion for few-particle systems. Moreover, the attempt is to prove the definition of exergy for equilibrium and non-equilibrium states with no use of external auxiliary thermal reservoir. The first treatise of this alternative, and more general approach was pioneered by Gaggioli in 1998 [2.4] who clarifies that the available energy is non-additive while the exergy is additive and balances can be calculated in design applications.

2.1.4. Stable-Equilibrium Reversible and Non-Equilibrium Irreversible Contributions

All phenomena within a system can be considered as the result of contribution due to reversibility and irreversibility along whatever process occurs.

As regard equilibrium and non-equilibrium, reversibility is a particular case of irreversibility and both should be always treated as a whole. The section 4. is specially dedicated to the Non-Equilibrium Thermodynamics and theories accounting for equilibrium and non-equilibrium states and processes.

2.2. Adiabatic Availability and Available Energy

The term “available energy” was first devised and clarified by J.W. Gibbs in his seminal treatise entitled “On the Equilibrium of Heterogeneous Substances” and in other publications [2.1,2.2].

Gaggioli defines the non-homogeneity of portions of constituents within an isolated system as “available energy” being non-additive property. The corresponding non-additive property is defined by Gyftopoulos and Beretta as “adiabatic availability” (with a constant amount of constituents and parameters) and “generalized adiabatic availability” (with a variable amount of constituents and parameters), indicated with the symbol Ψ .

The non-homogeneity of density within a system interacting with an external reference system, or reservoir R , constitutes the rationale of two definitions: the available energy (with constant amount of constituents and parameters) and “generalized available energy” (with variable amount of constituents and parameters), denoted by the symbol Ω, in the sense of Gyftopoulos and Beretta, or the exergy in the sense of Gaggioli. Both, available energy and exergy are additive properties since their definition is referred to an external reservoir or an internal reference stable equilibrium state that makes the system itself behaving as a reservoir. In this regard, Gaggioli [2.4] has proved that exergy can be formulated with respect to an internal reference stable equilibrium state (or "thermostatic" state). On the other side, though in a convergent pathway towards a coherent vision, Gyftopoulos and Beretta have proved that there is no need of an external reservoir to define entropy that, for this very reason, becomes an inherent property of any system in any state. Consequently, exergy can be proved as a corollary; however, it does depend on the reservoir because it is the result of the capability of withdrawing the "availability" from the composite system-reservoir.

The adiabatic availability can also be defined as "non-interaction availability" or "isolated availability" since no interaction occurs with any external system.

As established and proved by Gaggioli [2.4-2.6], work is not better than heat from a thermodynamic point of view. A more general statement, considering all interactions in closed and open systems, can be as follows: work interaction is not better than heat interaction or work interaction is not better than mass interaction. These statements account for interactions equivalence and inter-convertibility heat-work and work-heat or mass-work and work-mass. This concept is valid for thermodynamic work as well as mechanical work and electrical-magnetic work as proved by Gaggioli [2.5,2.6] for locomotive and hydraulic pump-turbine devices. The relationship between thermal and mechanical aspect and chemical and mechanical aspect represents the rationale behind dualism and symmetry as a paradigm to envisage thermodynamic concepts, principles and properties framework.

2.3. Definitions of Exergy Components

As far as the concept and definition is concerned, exergy is a non-conservative, extensive and additive thermodynamic state property, as entropy is, from which it can be derived and with which it is correlated by means of an entropy-exergy relationship. Consequently, in case of irreversible processes, the exergy depends on the process undergone by the system between two different thermodynamic states. As anticipated in the Introduction the canonical definition of exergy is termed as: maximum theoretical net useful work obtained along processes determined by the mutual interaction between a system and the external reference system or reservoir up to the thermodynamic stable equilibrium state of the system-reservoir composite.

The canonical definition of exergy is the following:

"Exergy is the maximum theoretical net useful work available in a system A *and withdrawable along a reversible interaction process from the initial state to the stable equilibrium state between the system and the external reference system, or reservoir* R *, behaving at permanent stable equilibrium state"*.

This definition implicitly assumes that a portion of the useful work is lost because it is not released to the ueful external system being released to the non-useful external system, namely the reservoir R. Therefore, a complementary definition would state that exergy is the minimum theoretical net useful work, associated to the minimum heat, reversibly released to R and hence not available to the useful external system.

From an opposite perspective, considering an inverse interaction process of the composite AR , the definition of exergy addresses to an opposite process starting from an initial stable equilibrium state to a different non-equilibrium state of AR . To this regard, among all definitions of exergy reported in the literature, the following one focuses on the non-available energy released to R :

”*Exergy is the minimum work that must be given to an isolated system at equilibrium to force it to a non-equilibrium state, or the maximum work obtainable from an isolated non-equilibrium system, and it is a state function. Instead of isolated systems out of equilibrium, exergy usually refers to a system in internal equilibrium in the presence of another much larger system: the environment; in this case, exergy is a state function of the combination of system and environment*”.

This twofold way to describe and define exergy reflects two different properties of a system and its “availability” to release work interaction to the useful external system. A step forward in the direction of an extension of exergy definition to heat and mass interactions will imply a generalization of the concept of exergy that will be discussed in the following sections of the present chapter. Indeed, the concepts of equivalence and interconvertibility between heat and work pointed out by Gaggioli [2.4-2.6], and, according to the here proposed extension, between mass and work, implies that “work is not better than heat” and, extending to chemical processes, work is not better than mass. These statements constitute the rationale to consider exergy as a property suitable to evaluate the thermodynamic content of mechanical internal energy and the work interactions along the transfer process to the external system. Hence, the maximum theoretical net useful heat, or the maximum theoretical net useful mass, resulting from the capability of internal mechanical energy of A to be withdrawn, become measurable effects to evaluate mechanical energy and work interactions in terms of Second Law. Consequently, the entropy-exergy relationship becomes the logical rationale to associate a mechanical entropy as an additive component, in addition to thermal entropy and mechanical entropy associated to thermal energy and chemical energy respectively. This logical rationale is an anticipation of the arguments treated in the following sections of the present thesis.

Concerning the terminology, it is worth noticing that Gyftopoulos and Beretta attribute the characteristic of non-additivity to the “adiabatic availability” while the “available energy” is instead additive and the term “exergy” is used in case the reservoir is represented by the environment at standard conditions.

The following terminology is hereafter summarized to provide a clear prospect and distinction among definitions reported in the literature, and will account for:

- Adiabatic Availability: non-additive according to Gyftopoulos and Beretta [1.9]
- Available Energy: non-additive according to Gaggioli [2.4]); additive according to Gyftopoulos and Beretta [1.9]
- Exergy: additive according to Gaggioli [2.4] and additive according to Gyftopoulos and Beretta [1.9]

From here on, and in compliance to the majority of papers and textbooks on these topics, the term exergy will be adopted to identify the "additive available energy" and the term "exergy" itself, represented by the symbol $"ex"$ (standing for specific exergy) or $"EX"$ (standing for exergy), will be used in lieu of the term "available energy" represented by the symbol $"\Omega"$. Thus, the denomination of "exergy" in Gaggioli literature will be preferred to "available energy" in Hatsopoulos-Gyftopoulos-Beretta literature and will be adopted unless differently clarified.

2.3.1. Thermal and Mechanical Aspect of Entropy-Exergy Relationship

The behavior of the exergy property is characterized by additivity because it is defined considering an external reference system or an internal part of the system itself that behaves as a reservoir [1.9,2.4]. Exergy is derived from the generalized available energy that is a consequence of the concept of generalized adiabatic availability when the system interacts with a reservoir [1.9].

2.3.2. Thermal Exergy

The definitions of available energy and exergy are based on the mutual stable equilibrium of a system A with a reservoir R at constant temperature T_R and account for work interaction by means of a weight process. This definition implies that, if stated in these terms, thermal exergy expresses the theoretical maximum net useful work $\left(W_{10}^{AR\rightarrow}\right)^{MAX}$ connecting two states 0 and 1 obtained by means of a weight process resulting from the available energy released along a process between variable temperatures T of the system A, and a constant temperature T_R and constant pressure P_R of the reservoir R. For a non-cyclic process, the expression of thermal exergy, in finite terms, adopting the symbols used by Gyftopoulos and Beretta [1.9] is the following:

$$EX^{T} = \left(W_{10}^{AR\rightarrow}\right)_{HEAT}^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)_{HEAT}^{MAX}$$
$$= \left(U_1^T - U_0^T\right) - T_R \cdot \left(S_1^T - S_0^T\right) + P_R \cdot \left(V_1 - V_0\right) \tag{2.1}$$

In differential terms:

$$dEX^{T} = \left(\delta W^{AR\rightarrow}\right)^{MAX} = \left(d\Omega^{R}\right)^{MAX} = dU^{T} - T_R dS^{T} + P_R dV$$

Although referred to a non-cyclic process, the above expression remains valid for, and is applicable to, any non-cyclic and cyclic process with the same physical meaning.

2.3.3. Thermal Entropy Derived from Thermal Exergy

Based on the entropy-exergy relationship, the definition of entropy is derived from the difference between energy and available energy, times a constant factor depending on the reservoir [1.9] and is here defined as thermal entropy S^T by virtue of the considerations that it is obtained from the very thermal exergy of the system A:

$$S_1^T - S_0^T = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^T \tag{2.2}$$

These equations, reported in the addressed literature, constitute the outset of the present study underpinned by the consideration that equality of temperature is a necessary condition that is not sufficient to prove that a system is in stable equilibrium with the reservoir. Indeed, even though two interacting systems are in thermal stable equilibrium determined by the equality of temperatures of the composite AR, the two systems may experience non-equilibrium states due to the non-null difference between chemical potentials or pressures. The equality of chemical potential and pressure between system and reservoir should therefore constitute the set of additional necessary conditions to ensure the stable equilibrium so that the equality of the complete set of "generalized potentials" constitutes a necessary and sufficient condition for mutual stable equilibrium in compliance with the Second Law as worded by Gyftopoulos and Beretta [1.9]. The solution to this issue is treated and demonstrated in the following section 3. As a consequence of the procedure adopted for its definition, entropy is an additive property that can be generalized to include the contribution of additional components fulfilling to the conditions of equality of chemical potential and pressure ensuring the mutual stable equilibrium of the composite system-reservoir.

An intuitive approach to the rationale here adopted to define entropy may be explained considering that internal energy is characterized by a "hybridization" of ordered and disordered (due to the distribution of molecule' position and velocity of system's particles) energy status. Entropy may be regarded as the measure of the amount of disordered energy – released to the reservoir – resulting from the difference of hybrid energy – ordered and disordered – and available energy – ordered energy – transferred, as useful interaction, to the external system. The Figure 2.1 depicts this approach.

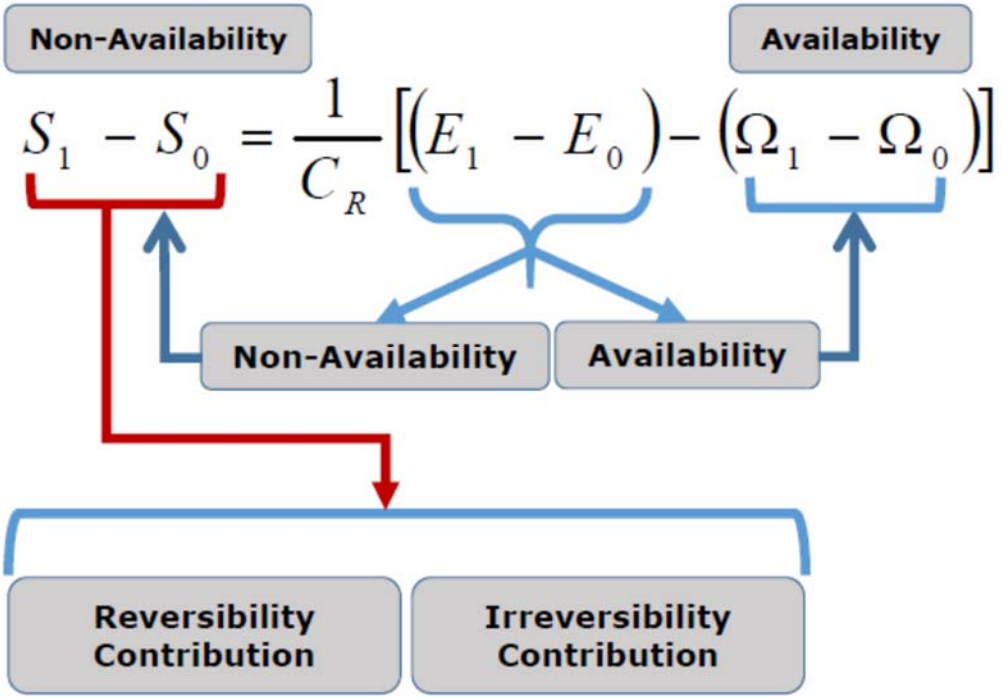


Figure 2.1 – Availability and Non-Availability

This separation between availability and non-availability is valid for processes occurring in isolated systems and in closed or open systems experiencing irreversible processes.

The common expression of thermal entropy is the one depending on temperature and volume: $S^T(T,V) = C_V ln\frac{T}{T_R} + \bar{R}ln\frac{V}{V_R}$, or the one depending on temperature and pressure: $S^T(T,V) = C_P ln\frac{T}{T_R} - \bar{R}ln\frac{P}{P_R}$. It is worth noticing that these expressions have two terms in the right side, the first of which depends on the temperature constituting the thermodynamic potential (or intensive property) determining the thermal internal energy of the system.

2.3.4. Chemical and Mechanical Aspect of Entropy-Exergy Relationship

The chemical potential is generated by electromagnetic interactions among atoms and molecules of a system and constitutes the internal potential energy as a component of the generalized internal energy and is defined as a form of distribution of energy among all elemental particles constituting the system, as kinetic energy with respect to thermal internal energy [1.10].

The maximum theoretical net useful work, according to the canonical definition of exergy related to a reversible (internally and externally) chemical reaction process, is expressed by the Gibbs function so that $W_{REV}^{NET} = -\Delta G$.

The Van't Hoff equilibrium open system at constant temperature and constant pressure is a suitable device for reproducing a typical chemical reaction where A, B are reactants and C, D are products [2.7]:

$$n_A A + n_B B \leftrightarrow n_C C + n_D D \Rightarrow \quad -\frac{\Delta G_0}{\overline{R} T_0} = \ln K_P = \ln \frac{x_i}{x_i^R} \tag{2.3}$$

is adopted to express maximum work taking into account the internal mechanism of chemical reaction by means of the expression depending on the equilibrium constant K_P of the reaction. In the above relation x_i is the molar fraction of the $i-th$ constituent of a system and x_i^R is the molar fraction of the same constituent in the reference environment or chemical reservoir R^C. The chemical equilibrium constant K_P, appearing in the above equation (2.3), expresses the dynamical equilibrium at which the chemical reaction occurs in both directions (forth from reactants to products and back from products to reactants) at the same permanent (chemical) stable equilibrium of the isolated system. The physical interpretation of that constant has a corresponding analogy in the "thermostatic temperature" of the isolated system at the end of the transitory process leading the mutual interacting portions of the system to the (thermal) stable equilibrium state.

The Gibbs relation, obtained from mass and internal energy balance, is as follows:

$$dU = T \cdot dS - P \cdot dV + \sum_i \mu_i \, dn_i = \left(\frac{\partial U}{\partial S} \right)_{V,n} dS - \left(\frac{\partial U}{\partial V} \right)_{S,n} dV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{V,S,n} dn_i \tag{2.4}$$

where $\mu_i = \left(\frac{\partial U}{\partial n} \right)_{V,S,n}$ represents the chemical potential of the $i-th$ constituent.

The following definitions are stated for chemical exergy in finite terms adopting the symbols and meaning already introduced for the thermal exergy: $EX^C = \left(W_{10}^{AR\rightarrow} \right)_{MASS}^{MAX} = \left(\Omega_1^R - \Omega_0^R \right)_{MASS}^{MAX}$, and in infinitesimal terms: $dEX^C = \left(\delta W^{AR\rightarrow} \right)_{MASS}^{MAX} = \left(d\Omega^R \right)_{MASS}^{MAX}$. The subscript "MASS" corresponds to the subscript "HEAT" and specifies the origin of exergy and its nature.

2.3.5. Chemical Exergy

The chemical exergy is defined by Kotas [2.7] as "the maximum work obtainable from a substance when it is brought from the environmental state to the dead state by means of processes involving interaction only with the environment." In this definition, the environment consists of the chemical reservoir that can be characterized according to the definition proposed by Gyftopoulos and Beretta [1.9] as a "reservoir with variable amounts of constituents and experiencing stable equilibrium states only." The whole chemical and physical process are modeled by a schema subdivided into two typical steps: the initial molecular system form's rearrangement (molecular structure) and the final molecular system's dimensional change (geometry-kinematics or pressure and temperature). The two representative processes are: chemical reaction open system (such as combustion, oxidation, reduction) and physical operation open system (such as mixing, separation, distillation); the two processes in series provide an expression of maximum theoretical net useful work withdrawn from the system at constant temperature along these reversible processes.

Following equations governing the isothermal-isobaric process and considering the State Equation per mole $PV=\overline{R}T_R$ [2.1], the work interaction of the $i-th$ constituent of a substance from its restricted reservoir state, denoted as RR, to the reference environment reservoir state R is related to the constituent potential energy transfer along the process between RR and R :

$$W_i = \int_{\mu_{i,R}}^{\mu_{i,RR}} d\mu_i = \int_{P_{i,R}}^{P_{i,RR}} VdP = \overline{R}T_R \int_{P_{i,R}}^{P_{i,RR}} \frac{dP_i}{P_i} = \overline{R}T_R \int_{P_{i,R}}^{P_{i,RR}} d\ln P_i \tag{2.5}$$

Then: $$\mu_{i,RR} - \mu_{i,R} = \overline{R}T_R \ln\left(\frac{P_{i,RR}}{P_{i,R}}\right) \tag{2.6}$$

where $\overline{R}$ is the universal gas constant, $P_{i,RR}$ and $P_{i,R}$ are the partial pressures of the substance i at the restricted reference state and at the environmental reference state respectively. Considering that $x_{i,RR}$ and $x_{i,R}$ are the molar fractions of the substance i at the restricted reference state and at the environmental reference state at pressure P_R , then:

$$\mu_i^{RR} - \mu_i^R = \overline{R}T_R \ln\left(\frac{x_{i,RR}P_R}{x_{i,R}P_R}\right) = \overline{R}T_R \ln\left(\frac{x_{i,RR}}{x_{i,R}}\right) \tag{2.7}$$

Mass interaction is characteristic of chemical energy transfer and it is moved by the difference of chemical potential between the system and the chemical reservoir. For this reason, the procedure to achieve the expression of chemical exergy reported by Moran and Sciubba [2.8], with n_i representing the number of moles of the $i-th$ constituent and μ_i representing the chemical potential of the $i-th$ constituent, is the one based on the total work interaction of an open bulk-flow system confined by a control volume:

$$EX^C = \sum_{i=1}^{n} n_i\left(\mu_i^{RR} - \mu_i^R\right) = \sum_{i=1}^{n} n_i\mu_i^{RR}\left(1 - \frac{\mu_i^R}{\mu_i^{RR}}\right) = M_{REV}\left(1 - \frac{\mu_i^R}{\mu_i^{RR}}\right) \tag{2.8}$$

In the above formulation of chemical exergy, the chemical potential of each and every constituent can be obtained considering that the chemical potential is expressed by the Gibbs function here after reported [1.14]:

$$\mu_i^R = \overline{g}_i \left(T_{RR}, P_{RR}\right) + \overline{R}T_{RR} \ln x_i^R \quad \text{and}$$

$$\mu_i^{RR} = \overline{g}_i \left(T_{RR}, P_{RR}\right) + \overline{R}T_{RR} \ln x_i^{RR} \tag{2.9}$$

where $\overline{g}_i$ is the molar Gibbs function of the pure constituent i and x_i is the molar fraction of the $i-th$ constituent in the compound. The meaning of μ_i^{RR} is the chemical potential of the $i-th$ constituent related to its thermodynamic state (restricted) and μ_i^R in the reference reservoir R represented by the environment.

The substitution of the two expression of chemical potential in the formulation of chemical exergy gives that, for a substance composed by r constituents each one with an amount of moles n_i, the chemical exergy formulation becomes:

$$\overline{EX}^C = \sum_{i=1}^{n} \left(W_{10}^{AR\rightarrow}\right)_i^{MAX} = \overline{R}T_R \sum_{i=1}^{r} n_i \ln \frac{x_i^{RR}}{x_i^R} \tag{2.10}$$

Considering one mole of the overall substance and subsequent molar fractions of constituents, then the molar specific chemical exergy $\overline{ex}^C$ is obtained:

$$\overline{ex}^C = \overline{\left(W_{10}^{AR\rightarrow}\right)_{MASS}^{MAX}} = \sum_{i=1}^{n} x_i \left(\mu_i^{RR} - \mu_i^R\right) = \overline{R}T_R \sum_{i=1}^{n} x_{i,R} \ln\left(\frac{x_{i,RR}}{x_{i,R}}\right) \tag{2.11}$$

representing the chemical exergy per mole of the mixture of i constituents.

The above expressions are obtained assuming that constituents of initial reacting and product substances also exist among those substances constituting the external reference environment R. Though this is not always the case, but those reaction substances can be formed by means of substances already available in the environment. In this case, the reaction of formation has to be included in the overall definition of chemical exergy relating to a substance. To do so, and to define the method to achieve a general definition of chemical exergy a typical reaction for hydrocarbons formation is considered based on common substances such as carbon dioxide and water largely present in the environment:

$$aCO_2 + \frac{b}{2}H_2O \leftrightarrow C_aH_b + \left(a + \frac{b}{4}\right)O_2 \tag{2.12}$$

Also in this case, the equilibrium reaction equation has to account for chemical potentials of species within the environment, again denoted with the superscript RR, is:

$$a\mu_{CO_2}^{RR}+\frac{b}{2}\mu_{H_2O}^{RR}=\mu_{C_aH_b}^{RR}+\left(a+\frac{b}{4}\right)\mu_{O_2}^{RR} \tag{2.13}$$

where $\mu_{CO_2}^{RR}$, $\mu_{H_2O}^{RR}$, $\mu_{C_aH_b}^{RR}$, $\mu_{O_2}^{RR}$ specifically denote the chemical potential of each substance in the same reference reservoir state of the reacting hydrocarbon, for example, the standard conditions of $25°C$ and $1BarA$. Solving the above relation for $\mu_{C_aH_b}^{RR}$:

$$\mu_{C_aH_b}^{RR}=a\mu_{CO_2}^{RR}+\frac{b}{2}\mu_{H_2O}^{RR}-\left(a+\frac{b}{4}\right)\mu_{O_2}^{RR} \tag{2.14}$$

used in all cases in which compounds, such as hydrocarbons C_aH_b, are not present in the reference environment.

Inserting this expression of $\mu_{C_aH_b}^{RR}$ in the definition of chemical exergy $EX^C=\sum_i^n n_i\left(\mu_i^R-\mu_i^{RR}\right)$ with unitary hydrocarbon's number of moles, $n_i=n_{C_aH_b}=1$ above stated and considering $1mol$, the specific molar chemical exergy is:

$$\overline{ex}_{C_aH_b}^{C}=\mu_{C_aH_b}^{R}-\mu_{C_aH_b}^{RR}=\mu_{C_aH_b}^{R}-\left[a\mu_{CO_2}^{RR}+\frac{b}{2}\mu_{H_2O}^{RR}-\left(a+\frac{b}{4}\right)\mu_{O_2}^{RR}\right] \tag{2.15}$$

The chemical potential $\mu_{C_aH_b}^{R}$ of the hydrocarbon is equal to its molar Gibbs function $G=U-TS+PV=H+PV$, hence, using the expressions $\mu_i^R=\overline{g}_i\left(T_{RR},P_{RR}\right)+\overline{R}T_{RR}\ln x_i^R$ and $\mu_i^{RR}=\overline{g}_i\left(T_{RR},P_{RR}\right)+\overline{R}T_{RR}\ln x_i^{RR}$ the following is obtained:

$$\overline{ex}_{C_aH_b}^{C}$$

$$=\left[\overline{g}_{C_aH_b}+\left(a+\frac{b}{4}\right)\overline{g}_{O_2}-a\overline{g}_{CO_2}-\frac{b}{2}\overline{g}_{H_2O}\right]_{T_{RR},P_{RR}}$$

$$+ \overline{R}T_{RR} \ln\left[\frac{\left(x_{O_2}^{RR}\right)^{a+b/4}}{\left(x_{CO_2}^{RR}\right)^{a}\left(x_{H_2O}^{RR}\right)^{b/2}}\right] \tag{2.16}$$

The formulation of chemical exergy above obtained is specifically evidencing chemical parameters of substances given in the restricted reference system and in the reference environment. Nevertheless, an equation of chemical exergy should also be similar, and corresponding to the form of thermal exergy thus leading to the following definition:

$$EX^{C} = \left(W_{10}^{AR\rightarrow}\right)_{MASS}^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)_{MASS}^{MAX}$$

$$= \left(U_1^C - U_0^C\right) - \mu_R \cdot \left(S_1^C - S_0^C\right) + P_R \cdot \left(V_1 - V_0\right) \tag{2.16a}$$

In differential terms:

$$dEX^{C} = \left(\delta W^{AR\rightarrow}\right)_{MASS}^{MAX} = \left(d\Omega^R\right)_{MASS}^{MAX} = dU^C - \mu_R dS^C + P_R dV \tag{2.16b}$$

In this case too, the caveat underlined for thermal exergy remains valid for chemical exergy: even though established for non-cyclic processes, the above expression applies to both non-cyclic and cyclic process with the same physical meaning.

2.3.6. Chemical Entropy Derived from Chemical Exergy

The equality of total potentials is accounted for as an additional necessary condition of mutual stable equilibrium between the system and the reservoir other than the equality of temperature [1.1]. This implies a definition of chemical entropy derived from chemical exergy and chemical energy in line with the methodology previously adopted for thermal properties.

If the concept of generalized available energy is now again considered, the formulation of chemical exergy should be translated into the following expression:

$$EX^{C} = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)^{C} \tag{2.17}$$

where the superscript “C” stands for “Chemical reservoir” since the composite of system and reservoir undergoes a “mass interaction”.

Now that chemical exergy is defined, and considering that entropy is an additive property, the expression used for entropy associated with heat interaction can be extended to chemical potential depending on mass interaction:

$$\left(S_1 - S_0\right)^C = \frac{1}{\mu_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^C \tag{2.18}$$

The above one constitutes the expression of the chemical entropy derived from chemical available energy based on the equality of chemical potential which constitutes a necessary condition for mutual stable equilibrium between the system and the chemical reservoir. If the chemical available energy is replaced by the chemical exergy then the above expression becomes:

$$\left(S_1 - S_0\right)^C = \frac{1}{\mu_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^C \tag{2.19}$$

Since entropy is an inherent property of all systems [2.1-2.10], chemical entropy would be characterized by the chemical potential of all atoms and sub-molecules that constitute all compounds and determine the supra-molecular architecture and configurations of all molecular systems. The dimensions and shapes of molecular structures play, in this perspective, a fundamental role in determining the minimum entropy level that ensures the stability of matter and its capability to react with other co-reactants, as well as to undergo endogenous or exogenous processes.

The definition of chemical exergy EX^C can be stated as follows:

$$EX^C = \left(U_1^C - U_0^C\right) - \mu_R\left(S_1^C - S_0^C\right) \tag{2.20}$$

If a combustion reaction is considered, an elementary quantity of mass is given for a chemical compound such as, for example, methane. This amount of mass enters a combustion chamber containing oxygen at a temperature and pressure suitable to enable the combustion chemical reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

On the left-hand side of the reaction equation there are the high-chemical-potential reactants: $\mu_{CH_4} + 2\mu_{O_2}$.

On the right-hand side there are the low-chemical-potential products: $\mu_{CO_2} + 2\mu_{H_2O}$.

This partition of potential among the particles in the combustion chamber is similar to the partition of temperature as described by the partition function in Classical Statistical Mechanics at stable equilibrium state of the whole system. Then, Maxwell's normal distribution function q, reflected in the Boltzmann molecular partition function, corresponds to the reaction equilibrium constant K_P characterizing any chemical reaction equilibrium. In turn, the reaction equilibrium constant specifies the fraction of reactants undergoing transmutation into products and defines the partition of chemical potential at assigned thermodynamic conditions. This constant would correspond to the partition of molecules among all accessible states at certain given thermodynamic conditions.

That said, two cases of transformation process are possible:

1) Bound potential energy is transformed into kinetic energy from which a) transfer to heat interaction or b) transfer to work interaction
2) Bound potential energy is transformed into repulsion potential energy (Lennard-Jones potential) so that a) transfer to mass interaction or b) transfer to work interaction

Processes a), b) can occur simultaneously or independently.

In this case, the expression of chemical entropy can be replicated from the one of thermal entropy replacing thermal properties with chemical properties. Then, the expression depending on chemical potential and volume is: $S^C(\mu, V) = C_V ln \frac{\mu}{\mu_R} + \bar{R} ln \frac{V}{V_R}$; and the one depending on chemical potential and pressure becomes: $S^C(\mu, V) = C_P ln \frac{\mu}{\mu_R} - \bar{R} ln \frac{P}{P_R}$. The same remark is here highlighted that these expressions have two terms in the right side, the first of which depends on the chemical potential constituting the thermodynamic potential (or intensive property) determining the chemical internal energy of the system. In both thermal and chemical cases, the second term of the right hand side of the expression will be clarified and physically explained in the following section here after.

2.3.7. Mechanical Exergy Related to Mechanical Entropy

The origin and the definition of mechanical entropy property, as well as mechanical entropy-exergy relationship, can be clarified starting from its physical meaning and will be more extensively analyzed here after to discuss all involved state and process quantities.

The concept of generalized available energy Ω^R , derived from the adiabatic availability Ψ^R [1.9], constitutes once again the basis of the formulation of the mechanical exergy that now depends should be expressed as:

$$EX^M = \left(\Omega_1^R - \Omega_0^R\right)^M \tag{2.21}$$

where the superscript “M” stands for “Mechanical Reservoir” since the composite system-reservoir undergoes a “work interaction” and the physical meaning becomes the maximum theoretical net useful heat or the maximum theoretical net useful mass withdrawn from the composite system-reservoir AR .

2.3.7.1. Mechanical Exergy of Thermal Processes

The definition of mechanical exergy is the basis for deriving the expression of mechanical entropy using the procedure adopted for thermal exergy and thermal entropy:

$$S_1^M - S_0^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M \tag{2.22}$$

This expression of mechanical entropy can be demonstrated considering that the procedure conceived by Gyftopoulos and Beretta proving the formulation of (thermal) entropy [1], does not impose any restriction concerning the form of energy and generalized available energy that constitute the expression of entropy. Therefore, the same procedure can be considered valid regardless of the physical nature of the properties involved. The minimum amount of weight process corresponds to the maximum amount of heat interaction:

$$\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M = \left(W_{10}^{AR\leftarrow}\right)^{MIN} = P_R V_R \left(\ln V_1 - \ln V_0\right) \tag{2.23}$$

which expresses the (minimum) amount of work interaction absorbed from the mechanical reservoir at constant pressure P_R and constant V_R (total volume coincides with specific volume in the particular case of a reservoir). The Equation (2.13), substituted in the former relation, expresses the mechanical entropy:

$$S_1^M - S_0^M = \overline{R} \cdot \left(\ln V_1 - \ln V_0\right) \tag{2.24}$$

The consequence is that for an adiabatic reversible process implying mechanical work interaction with the external system, the mechanical entropy increases due to the increase of volume while thermal entropy change has to be null as no heat interaction occurs along this process.

The stable equilibrium is proved to be a sufficient condition also for equality of pressure within the AR composite in addition to equal temperature and equal potential [1.4]. The proof assumes stable equilibrium between two interacting systems to derive equality of pressure using the Highest-(Thermal)-Entropy Principle. However, also in this case, pressure and therefore equality of pressure between system and reservoir $P = P_R$ is not accounted for in the definition of entropy property which, instead, should include the mechanical entropy associated to, and determined by, thermodynamic work interaction. A definition of mechanical entropy is here proposed analyzing the work interactions between the system and an (auxiliary) mechanical reservoir behaving at constant pressure P_R .

The weight process represents the experimental measure of the theoretical maximum net useful work interaction $\left(W_{10}^{AR\rightarrow}\right)^{MAX}$ withdrawn from a system A , releasing a corresponding theoretical minimum non-useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MIN}$ to an (auxiliary thermal) reservoir R^T at constant temperature T_R , along whatever conversion, transformation and transfer process from initial state of the system up to its stable equilibrium state with the auxiliary reservoir, according to the definition of generalized available energy and thermal exergy. The inverse (and reversible) process requires the weight process to represent the minimum net useful work released to A while extracting a corresponding maximum non-useful heat from R^T . Indeed, in addition to the theoretical maximum net useful work, the concept of available energy should be extended to the theoretical maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ associated to the theoretical minimum net useful work $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ released to the mechanical reservoir R^M at constant pressure P_R . This symmetric process underpins the definition of mechanical exergy EX^M [2.10-2.13]. In this case, the input work occurs through the interaction of the system A with mechanical reservoir R^M. As work interaction is released to the mechanical reservoir at the same pressure P_R, then it is non-useful work, and consequently, it is no longer useful since it constitutes the non-convertible contribution of input work interaction. Therefore, the mechanical exergy property accounts for the theoretical maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ withdrawn from the system A releasing the theoretical minimum non-useful work $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ to the mechanical reservoir R^M. In this symmetric process, system A interacts with a mechanical reservoir behaving at constant pressure P_R, therefore, the symbol EX^M is adopted with the superscript "M" standing for "Mechanical":

$$EX^{M} = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)^M \tag{2.25}$$

$$EX^{M} = \left(M_{10}^{AR\rightarrow}\right)^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)^C \tag{2.26}$$

and considering the meaning of generalized reservoir again, then:

$$EX^{M} = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^M \tag{2.27}$$

$$EX^{M} = \left(M_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^C \tag{2.28}$$

The above relations express the mechanical exergy corresponding to the amount of generalized mechanical available energy of system A converted into heat interaction $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ at the variable temperature which is different with respect to the constant temperature T_R of the thermal reservoir R^T or converted into mass interaction $\left(M_{10}^{AR\rightarrow}\right)^{MAX}$ at the variable potential μ_R of the chemical reservoir R^C. Indeed, $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ or $\left(M_{10}^{AR\rightarrow}\right)^{MAX}$ is determined by the minimum amount of work interaction $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ released to the mechanical reservoir along the isothermal process or isopotential process where the heat interaction is withdrawn at T_R from the thermal reservoir to be converted into $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ and where the mass interaction is withdrawn at μ_R from the chemical reservoir to be converted into $\left(M_{10}^{AR\rightarrow}\right)^{MAX}$. In fact, work interaction along the isothermal or isopotential expansion process at constant temperature T_R or at constant μ_R, could not be considered useful because it has to be entirely converted into heat by means of an inverse Joule cycle releasing heat (non-useful) to the thermal or chemical reservoir and non-useful work to the mechanical reservoir at a lower and constant pressure.

2.3.7.2. Mechanical Exergy of Chemical Processes

As far as mass interactions between system and reservoir are concerned, the maximum net useful mass $\left(M_{10}^{AR\rightarrow}\right)^{MAX}$ results from the conversion process in which the work input rises up, to higher potential, the mass input withdrawn from the chemical reservoir R^C while releasing, along the isopotential process at constant μ_R, the minimum amount of non-useful work interaction expressed as follows [2.1,2.2]:

$$\left(W_{10}^{AR\rightarrow}\right)^{MIN} = \left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M = \left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M$$

$$= \overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right) \qquad (2.29)$$

The term $\overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right)$ equals the (theoretically minimum) amount of work released to the mechanical reservoir R^M and equals the low temperature heat, withdrawn from the thermal reservoir, converted into high potential mass $\left(M_{10}^{AR\rightarrow}\right)^{MAX}$.

The definition of mechanical exergy, formulated by Equations (2.14) and (2.19), constitutes the basis to derive the expression of mechanical entropy using the same rationale adopted for thermal entropy and chemical entropy: $\left(S_1 - S_0\right)^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M$, and taking into account the mentioned relationship between mechanical generalized available energy and mechanical exergy:

$$\left(S_1 - S_0\right)^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M \qquad (2.30)$$

The former Equation (5), substituted in the latter Equation (6), implies the expression of mechanical entropy [11]:

$$\left(S_1 - S_0\right)^M = \overline{R}\left(\ln V_1 - \ln V_0\right) \qquad (2.31)$$

This expression is a consequence of the Second Law and the stable equilibrium state in a system-reservoir composite AR.

The proof of definition of entropy provided by Gyftopoulos and Beretta [1.4] may be used – mutatis mutandis – as a proof of mechanical entropy as well. In fact, the Second Law statement implies the impossibility of a PMM2 performing, in the case of mechanical entropy, an inverse cycle (instead of direct cycle) so that it may be expressed as the impossibility for mechanical energy to be transferred from a mechanical reservoir at lower pressure P_R to a system at higher pressure P without the contribution of heat interaction. The impossibility of inverse PMM2 expresses the impossibility of any system to undergo a cyclic process that produces no external effect except the heat interaction and the change of another system from an initial state of stable equilibrium to a final state of non-equilibrium. Clearly both process have to be cyclic and therefore for both it is impossible to convert the entire amount of energy content transferred to the other one.

The definition of mechanical entropy can be used to state the Highest-Mechanical-Entropy Principle applicable to those processes determining changes in volume of the system. As regard pressure equality between system and mechanical reservoir, this condition can be proved, using the Highest-Mechanical-Entropy Principle, to be a necessary condition of mutual stable equilibrium between system and reservoir that needs to be complied, in addition to equality of temperature and equality of potential, to ensure the equilibrium state of the composite system-reservoir extending to pressure the stable equilibrium restricted to temperature and potential. On the other hand, the same Highest-Mechanical-Entropy Principle can be adopted to prove the sufficiency of pressure equality or, in different terms, to prove stable equilibrium from pressure equality within system-reservoir composite. This procedure is reported in next sections.

A proof of the above expression can be derived from the Pfaff theorem and Schwarz relation. As concerns interactions, δW is not an exact differential. Indeed $\delta W = dU - \delta Q = C_V dT - TdS$ thus $\partial C_V / \partial T = 0$ and $\partial T / \partial T = 1$. In this case, if the former equation is multiplied by the integrating factor $1/PV$ then it results that $\delta W / PV = C_V dT / PV - TdS / PV = C_V dT / \overline{R} T - dS / \overline{R}$ from which $\partial (1/T) / \partial S = 0$ and $\partial (1/\overline{R}) / \partial T = 0$ so that $dS^M = \delta W / PV = dE_R^M / P_R V_R$ is an exact differential for and represents the mechanical entropy as a state property according to Pfaff theorem.

Figure 2.2. represents a cylinder-piston device operating along and adiabatic reversible process in which contributions to the mechanical exergy are identified:

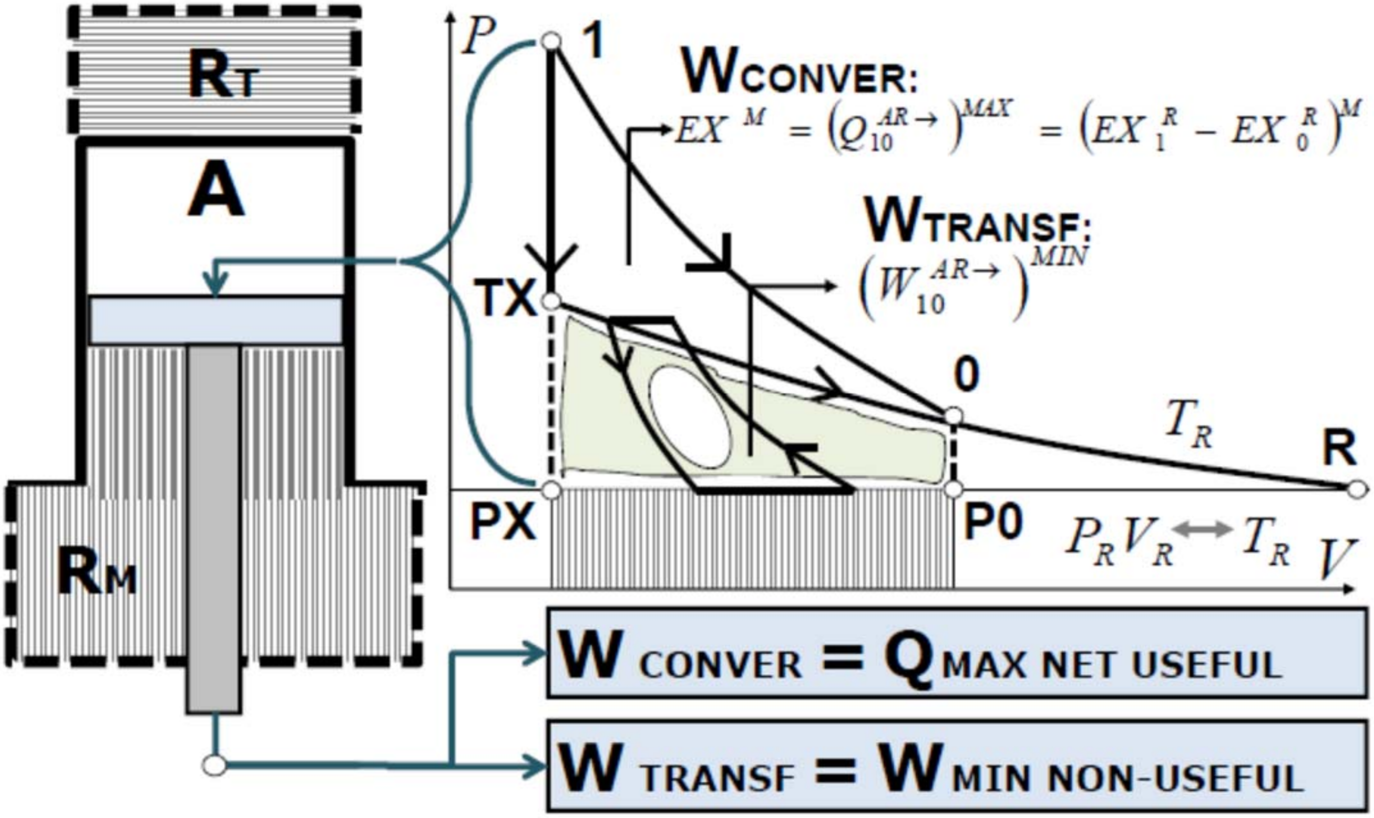


Figure 2.2 – Cylinder-Piston Device and the Mechanical Exergy Contribution

The diagram (P-V) in Figure 2.2 represents a portion of the adiabatic reversible process with constant thermal entropy (usually termed as isoentropic). Since exergy is a state property, then the same amount of work is expected to be obtained through any different process connecting the same initial and final thermodynamic states. To do so, one may think of the adiabatic process replaced by a sequence isovolumic-isothermal connecting the two states at point “0” and point “1”. Once the system A is led to the temperature T_R through the isovolumic 1-TX, the system is still capable of releasing work to the useful external system. In fact, the pressure along the isothermal process remains higher than the pressure of the reservoir, and the product of pressure times volume variation along the same isothermal remains higher with respect to the mechanical reservoir at a constant pressure along the isobaric process. Hence, the work associated to the volume decrease of the reservoir compensates the reduced work associated to the isovolumic process. Nevertheless, the concept of available energy would allow considering the mechanical exergy in terms of “maximum theoretical net useful heat” between the same given states “0” and “1”. To do so, the isovolumic-isothermal process is again analysed in terms, this time, of heat interaction. Once the system has achieved the reservoir temperature due to the release of useful heat along the isovolumic process, the isothermal process remains to bring the system to the final state. The isothermal process would not take place if a corresponding equal quantity of heat were not withdrawn from the reservoir itself. Indeed, the work interaction along the isothermal process at the reservoir temperature requires compensation of the loss of internal energy by means of heat input. One could think of using the work interaction, along with the isothermal process while interacting with the reservoir, to release useful heat. To do so, an intermediate auxiliary Joule cycle should operate between the changing pressure along the isothermal process and the constant pressure P_R of the mechanical reservoir R^M. The lower isobaric process of this Joule cycle would imply temperatures lower than T_R. Though, a thermal reservoir with a temperature lower than T_R does not exist having assumed T_R as the lower bound reference temperature for the minimum non-useful work released to R^M. Moreover, neither a direct cycle (using thermal energy) nor an inverse cycle (using mechanical energy) is suitable to withdraw that residual mechanical internal energy available in A. Hence, that cycle could not operate, and the residual mechanical internal energy of A could not be withdrawn along any reversible cyclic or non-cyclic process. The result is that the content of mechanical internal energy, at the initial state of an adiabatic reversible process, could not entirely be considered as available. The physical meaning is that even the mechanical internal energy transferred as work interaction to the useful external system should be considered a non-isoentropic process so that it makes sense to define a mechanical entropy depending on the volume as extensive state property governing mechanical energy transfer from the system A.

$$EX^{PHYSICAL} = EX_{REV}^{T} + EX_{REV}^{M}$$

$$= W_{REV}^{CONVER} + Q_{REV}^{CONVER} + W_{REV}^{TRANSF} + Q_{REV}^{TRANSF} = \Delta U_{W,Q}^{SYSTEM} + \Delta U_{W,Q}^{RESERVOIR}$$

$$EX^{PHYSICAL} = EX_{REV}^{T} + EX_{REV}^{M} = \left(U_1 - U_0\right)^T + \left(U_1 - U_0\right)^M$$

$$- C_V T_R \left(\ln T_1 - \ln T_0\right) - \overline{R} T_R \left(\ln V_1 - \ln V_0\right)$$

$$+ P_R V_R \left(\ln V_1 - \ln V_0\right) + P_R \left(V_1 - V_0\right)$$

in which:

$- C_V T_R \left(\ln T_1 - \ln T_0\right) - \overline{R} T_R \left(\ln V_1 - \ln V_0\right)$ is the thermal energy loss released to the thermal reservoir;

$+ P_R V_R \left(\ln V_1 - \ln V_0\right) + P_R \left(V_1 - V_0\right)$ is the mechanical energy loss released to the mechanical reservoir.

$EX^{PHYSICAL} = EX_{REV}^{T} + EX_{REV}^{M}$ = Energy used – Energy loss

Hence: Energy = Exergy + Energy loss

2.3.8. Generalized Exergy Related to Generalized Entropy: Exergy of Exergy

All forms of energies and energy transfer through interactions have been so far associated with corresponding exergy components representing additive contributions. This outcome is enlarging the perspective on the physical meaning of this thermodynamic state property. In all cases, the exergy results from heat-to-work and mass-to-work conversion process. Though based on the concept of equivalence and interconvertibility (and the idea that "work is not better than heat") [2.4-2.6], exergy should be derived from opposite work-to-heat and work-to-mass conversion processes; hence exergy can be regarded as the output of a thermodynamic conversion process. For this very reason, by virtue of the definition of mechanical exergy [2.12,2.13], any form of energy and interaction has to be evaluated in the same terms. Hence, the canonical definition addressing to the "maximum theoretical net useful work" remains the one related to thermal exergy as the output of thermal energy input. In the opposite case, the mechanical internal energy and its transfer in the form of work interactions could not be evaluated, as such, in the same "thermal" approach above mentioned, that is, in terms of work interaction directly used by the external useful system. This means that work interaction too must be "thermodynamically" evaluated by converting it into heat or mass interaction. This is the rationale for generalizing the definition of exergy to all forms of energy and interaction in a similar procedure expressed in the following statement:

The generalized exergy is the theoretical maximum net useful interaction deriving from thermodynamic conversion processes operating between two different forms of energy and energy transfer within a system-reservoir composite.

If the above premise and the generalized statement is accounted for, the definition of a thermo-chemical-mechanical reservoir characterized by constant temperature, chemical potential and pressure, implies the additivity of all components constituting the generalized exergy:

$$EX^G = EX^T + EX^C + EX^M \quad \text{or} \quad EX^G = EX^T + EX^C + EX^M_{HEAT} + EX^M_{MASS} \tag{2.32}$$

where, in the second equation, the heat interaction and mass interaction characterizing the mechanical exergy is explicitly expressed.

The internal energy balance of the composite system-reservoir AR, adopting the symbols in [1.9], provides the amount of weight process due to thermal, chemical and mechanical contributions:

$$EX^G = \left(W^{AR\rightarrow}\right) + \left(Q^{AR\rightarrow}\right) + \left(M^{AR\rightarrow}\right)$$

$$= \Delta U^{SYSTEM} + \Delta U^{RESERVOIR}$$

$$= \Delta U_Q^{SYSTEM} + \Delta U^{R,Q} + \Delta U_W^{SYSTEM} + \Delta U^{R,W} + \Delta U_C^{SYSTEM} + \Delta U^{R,C} \tag{2.33}$$

where: $\Delta U^{R,Q} = Q_R$ is the minimum heat interaction with the thermal reservoir; $\Delta U^{R,C} = M_R$ is the minimum mass interaction with the chemical reservoir and $\Delta U^{R,W} = W_R$ is the minimum work interaction with the mechanical reservoir.

The isothermal process realizes energy conversion and at the same time an entropy conversion from thermal entropy to mechanical entropy that occurs due to simultaneous heat interaction and work interaction. Both conversions are accounted for in the physical exergy expression:

$$EX^{G} = \Delta U^{SYSTEM} + \Delta U^{RESERVOIR}$$

$$= (U - U_0) - T_R \cdot \Delta S^{TOTAL,R}$$

$$+ P_R \cdot \Delta V^R - T_R \cdot \Delta S^{T,R} + \mu_R \cdot \Delta S^{C,R} \tag{2.34}$$

where the term $-T_R \cdot \Delta S^{TOTAL,R}$ represents the contribution to entropy conversion only occurring inside the reservoir and the terms $P_R \cdot \Delta V^R - T_R \cdot \Delta S^{T,R} + \mu_R \cdot \Delta S^{C,R}$ represent the contribution transferred from the system to the reservoir. It is noteworthy that entropy conversion is inherent in energy conversion and that entropy conversion requires the additional term that contributes to exergy balance expressed in the above formulation which therefore considers the effect of both energy and entropy conversion processes. Considering that entropy is an additive property constituted by components deduced from the corresponding generalized exergy's components, the generalized entropy may be defined as the sum of thermal, chemical and mechanical terms: $S^G = S^T + S^M + S^C$.

2.3.9. Structure of Internal Energy

The Gibbs-Duhem relation [1.9] constitutes a condition among all intensive properties – temperature, pressure, and chemical potential - defining the state of a heterogeneous system. If the system is homogeneous and composed by one constituent only, there are no phase changes or chemical reaction mechanisms inside the system implying that the system itself is at chemical equilibrium and the Gibbs-Duhem relation is:

$$SdT - VdP + nd\mu = 0 \tag{2.35}$$

Chemical potential μ is defined as the component of internal energy generated by the interactions determined by inter-particle positions and relative distance. Instead, the kinetic potential is due to inter-particle relative velocity. Considering these assumptions, the system model characteristics can be theoretically assimilated to those adopted in the Kinetic Theory of Gas which, in particular, considers molecules undergoing elastic repulsive interaction forces at collision with other molecules and with the wall of the container but otherwise exert no attractive interaction forces (Van der Waals) on each other, or on the container wall. The container walls represent a geometrical volume constraint condition imposed on the system.

In the particular case of the system undergoing an isothermal process, the temperature is constant and the pressure changes due to the change of volume that determines the density of particles and the frequency of particle collisions.

Then, the differential of chemical potential among all atoms or molecules is due to the temperature that is the only inter-particle kinetic energy transformed into inter-particle potential energy due to repulsive collision interactions (attractive interactions are negligible by assumption). Considering that no chemical reactions occur inside the system as assumed, then $d\mu = 0$, as reported by Kotas [2.7] for systems with a fixed chemical composition, and the Gibbs-Duhem relations becomes:

$$SdT = VdP \tag{2.36}$$

where S and V are not null both being inherent properties of any system in any state. If the system undergoes an isothermal reversible process, then the temperature remains constant by definition, so that $dT = 0$; on the other side, dP is not null along the same isothermal process and therefore an inconsistency appears in the previous equation (2.36) where the left side member is null, and the right side is not null. The same inconsistency is displayed if an isobaric process is accounted for using the Gibbs-Duhem relation where pressure remains constant, so that $dP = 0$, and temperature does not. This inconsistency concerns the intensive properties temperature and pressure which determine the thermo-mechanical transformation involving the quantities entropy and exergy correlated to the energy balance. The chemical potential expressed by the Gibbs function reveals that entropy property is variable in the isothermal process and consequently the chemical potential is not constant, which is in contradiction with the assumption set forth.

The chemical potential, appearing in the assumed ideal system model, is due exclusively to repulsive interactions intervening at collisions and depends solely on molecules' kinetic energy associated to velocity, so that temperature constitutes the first contribution to pressure. The second contribution is due to the (specific) volume determining the density of the internal system and consequently the frequency of collisions between molecules and the boundary wall external system (such as, for example, the cylinder-piston device already adopted). The density, instead, does not determine the chemical potential due to attractive interactions depending on relative positions among the molecules which do not exist in the model assumed.

If $d\mu = 0$ and $dT = 0$, and considering attractive interactions as negligible, repulsive interaction potential is equal to the kinetic potential (transformation during collision only). The Gibbs relation:

$$dU = T \cdot dS - P \cdot dV = \delta Q + \delta W \tag{2.37}$$

can be reformulated in different terms adopting thermal entropy and mechanical entropy previously defined:

$$dU = T \cdot \left(dS^{T}\right) - \frac{PV}{\overline{R}} \cdot \left(dS^{M}\right) = \delta Q + \delta W \tag{2.38}$$

and transformed, by using the state equation $PV = \overline{R}T$ valid in this special case, and consistent with the Kinetic Theory of Gases [1.11,1.12], in the following form:

$$dU = T \cdot \left(dS^T\right) - T \cdot \left(dS^M\right) = T \cdot \left(dS^T - dS^M\right) = \delta Q + \delta W \tag{2.39}$$

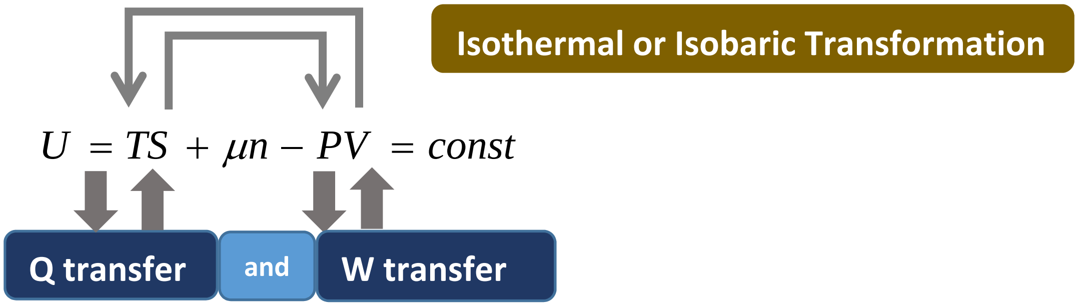
This expression, associated to the temperature, takes into account either heat or work interactions contributing to variations of internal energy.

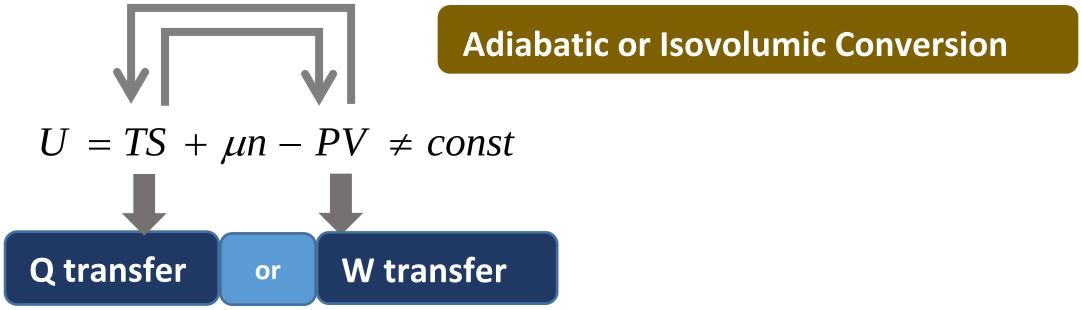
It is noteworthy that, in the case of work interaction, the work put into the system, which is considered positive, corresponds to a decrease of mechanical entropy as per Equations (2.24) and (2.31). This fact is the opposite of heat interaction that is positive if thermal entropy increases. In other terms, heat input causes thermal entropy to increase, and work input causes mechanical entropy to decrease, therefore work depends on the pressure oppositely with respect to heat depending on temperature. If the system releases work, it increases mechanical entropy because mechanical energy, dispersed among all particles constituting the system, progressively becomes similar to the thermal energy, i.e. energy distributed by the velocity of the same set of particles. Increasing volume means that pressure is progressively determined by particles' kinetic energy (temperature) with respect to the contribution of the frequency of collisions among particles and with the external system surface determined by the volume. Pressure is thus progressively the more like temperature as volume increases.

In the framework of the Kinetic Theory of Gases, if conversion cycles are considered, and assuming an ideal system where inter-molecular attractive interactions are null or negligible, isothermal processes in Carnot cycle, or isobaric processes in Joule cycle, imply energy transformation and a corresponding entropy transformation. Instead, adiabatic reversible processes, or isovolumic processes, imply energy conversion and a corresponding entropy conversion. Indeed, for an ideal system characterized by the kinetic energy of particles and no potential energy thereof, the adiabatic reversible (isoentropic) compression process consists of a work interaction implying a transfer of macroscopic work PdV into microscopic inter-particle kinetic energy determining the increase of temperature; hence a non-cyclic conversion occurs. The system undergoes the opposite phenomena in case of the expansion process. Similarly, the isovolumic heating process consists of a heat interaction implying a transfer of macroscopic heat TdS into microscopic inter-particle kinetic energy determining the increase of pressure; hence a non-cyclic conversion occurs. The system undergoes the opposite phenomena in case of the cooling process.

The schema here-after reported represents transformation and conversion processes:

$$U = U(P,T,\mu) = U^{M}(P) + U^{T}(T) + U^{C}(\mu)$$





The physical meaning of entropy property will be treated in the next section 3., an anticipation of the significance is here given relating to the degree of distribution and dispersion of phenomena among the constituting elements of a system. However, along with an isothermal (and isopotential) process, the temperature remains constant while a heat interaction input occurs and a variation of entropy property characterizes the thermal energy transfer from the external to the internal system. Thus, the degree of distribution remains constant since the kinetic energy associated to each and every particle remain constant as the temperature is constant, while entropy property increases or decreases. Hence, it seems that a contradiction between definition and phenomena is occurring. Nevertheless, along with an isothermal process of an ideal system, the internal energy depends on temperature only. Then thermal internal energy is constant and can be assumed that is undergoing a cyclic process for which $Q = W$ and the proof demonstrated by Gyftopoulos, applies. Then heat interaction input corresponds to the work interaction output and, consequently, entropy associated to heat must be compensated by an equal amount of entropy that, instead, has to be associated to work to achieve the overall entropy property balance $S^{T} = S^{M}$

A similar proof can be applied to isopotential (and isothermal) processes for which $M = W$ and consequently

$S^C = S^M$.

To conclude, this is the proof that entropy property is an inherent property of all systems in all states and it is associated to all types of interactions between two systems.

The balance of entropy, along the isothermal expansion reversible process $dU=0$, is deduced from the equation $S^{TOTAL} = S^T - S^M = 0$ where S^T is the thermal entropy input due to heat flowing into the system and $-S^M$ is the mechanical entropy output from the system which is the opposite of the mechanical entropy input flow inherent in the expansion work output from the system itself. The physical meaning is that conversion from a kinetic form into a geometric form, required to convert heat into work, necessitates an increase in mechanical entropy.

Because the mechanical entropy must enter the system because of work output, then the mechanical entropy direction is inverted compared to the thermal entropy direction in the system's entropy balance. Total entropy is consequently constant if either thermal and mechanical entropy enters into the system. The rationale of this statement is that these two entropy components have an opposite origin and elide each other.

If the term ΔS^{TOTAL} is expressed by means of $S^{TOTAL} = S^T - S^M = 0$, the total entropy, resulting from the addition of thermal and mechanical components of entropy, implies that thermal entropy would be constant in an isothermal reversible process that requires heat interaction by means of thermal entropy exchange.

On the other side, pressure does not derive from inter-particle chemical potential and is just the mechanical effect produced by the temperature itself (apparent potential).

The Gibbs relation, expressed in terms of the Equation (19), resolves the apparent inconsistency highlighted in the Gibbs-Duhem relation. In fact, this can be reformulated as follows:

$$dU = T(dS^T - dS^M) + \mu \cdot dn = TdS^T - TdS^M + \mu \cdot dn \qquad (2.40)$$

The Euler relation is obtained from the Gibbs relation by integration at constant temperature and constant chemical potential [1], so that:

$$U = TS^{TOTAL} = T \cdot \left(S^T - S^M\right) + \mu \cdot n = TS^T - TS^M + \mu \cdot n \qquad (2.41)$$

If compared with the classical expression of the Gibbs relation $U = TS + \mu \cdot n - PV$, the term $-PV$ corresponds to the term $-TS^M$. Moreover, in the case of an isothermal process (and absence of chemical reactions so that chemical potential is constant) it requires that total entropy is constant also implying that thermal entropy variation is equal to mechanical entropy variation.

It is noteworthy that, in the case of an ideal system as assumed, internal energy U is associated with the kinetic energy of the molecules, and thus to temperature only; however, internal energy components depend on the terms $\mu \cdot n$ and $-PV$ which both depend on volume as well. This dependency ensures that real systems in which thermodynamic conditions are affected by interactions among molecules that determine the potential energy are characterized by volume which affects the mean distance among particles and therefore the potential generated by the inter-particle actions.

The Euler relation is composed by terms corresponding to the specific (generalized) potential in finite terms. In differential terms, the Euler relations is:

$$dU = TdS^{TOTAL} + S^{TOTAL} dT + \mu \cdot dn + n \cdot d\mu =$$

$$= T \cdot \left(dS^{T} - dS^{M}\right) - \left(S^{T} - S^{M}\right) \cdot dT \ + \mu \cdot dn + n \cdot d\mu$$

$$= TdS^{T} - TdS^{M} + S^{T} dT - S^{M} dT \ + \mu \cdot dn + n \cdot d\mu \tag{2.42}$$

On combining the Gibbs relation and Euler relation expressed in the terms set forth, the Gibbs-Duhem relation $SdT - VdP + \mu \cdot dn = 0$ assumes the form:

$$S^{T} dT - S^{M} dT + nd\mu = \left(S^{T} - S^{M}\right) \cdot dT + n \cdot d\mu = S^{TOTAL} \cdot dT + n \cdot d\mu = 0 \tag{2.43}$$

The superscript "TOTAL" refers to the thermal and mechanical internal energy components. Once the total thermal-mechanical contribution is added to the total chemical-mechanical contribution, then the definition of "Generalized" entropy will have been achieved.

In the above equation (2.43), T constitutes the inter-particle kinetic potential component of internal energy resulting in the PV macroscopic work interaction transferred by means of a weight process; μ constitutes the inter-particle chemical potential component of internal energy resulting in the PV macroscopic work interaction transferred by means of a weight process. The kinetic and chemical constitute the two fundamental potentials at microscopic inter-particle level interacting at macroscopic level that constitute the hierarchical geometric and kinematic structure.

The dualism of kinetic potential and chemical potential constitutes the inherent structure of potentials even in the special case of an ideal system for which inter-particle potential energy in null. In this case, in fact, potential energy still exists in the form of repulsive reaction potential energy that is due to kinetic energy transformed on collision only, without macroscopic effects on the entire system.

This different form of the Gibbs-Duhem relation resolves the apparent inconsistency in the special case of the isothermal ideal process. In fact, $n \cdot d\mu = 0$ because the system model is ideal and $dT = 0$ remains the only condition to be satisfied since dP no longer appears in the Gibbs-Duhem relation as expressed in Equation (2.43). The rationale of these statements can also be found in the behaviour of elements, molecules and atoms, constituting the system as a whole. In fact, in the isothermal process, the temperature and subsequent intermolecular repulsive interactions on each collision are constant and the variations of kinetic potential and chemical potential (due to intermolecular repulsive interactions) are therefore null: $dT = 0$ and consequently $d\mu = 0$. In the case of the isobaric process, temperature and pressure are variable or kinetic potential and chemical potential (due to repulsive interactions at each inter-particle collision) both change along the isobaric process: $dT \neq 0$ and consequently $d\mu \neq 0$. Even in the case of an ideal system, there is dualism and symmetry of kinetic energy and potential energy among the molecules so that $dT > 0$ and $d\mu > 0$.

Pressure is the mechanical effect of the contribution related to kinetic interaction and related potential and chemical interaction and related potential. In this perspective, pressure can be viewed as the outcome of the temperature and chemical potential of a complex multi-particle system, converted into work interaction with the external reservoir and with the external weight process.

Finally, notwithstanding the restrictions assumed for the model adopted, the behaviour of the system is coherent with expectations in terms of phenomena and tendency of the properties in the general case of real systems and processes where each particle experiences attractive interaction with all others, and does not contradict the fundamentals reported in the literature.

Continuous transformation of kinetic energy into potential energy and vice versa occurs at molecular inter-particle level. Therefore, one form is real and the other form is apparent and vice versa.

2.4. Thermodynamic Properties and Processes

The present section is specifically dedicated to outline a summary to characterize and categorize all main thermodynamic properties defining any state, according to the Stable-Equilibrium-State Principle [1.1], and their physical meaning along typical processes that systems undergo throughout components and whole plants. Therefore, the sequence "Properties $\Rightarrow$ Processes" is pursued to provide an overarching prospect. Although all quantities and variables belong to the Classical Thermodynamics, it is deemed worth proposing a logically organized structure of state properties and the relationships among each other, thus representing a rational perspective useful in processes analysis.

2.4.1. State Properties and Process Variables

The difference between state properties and process variable is that the former depends on the state of the system only while the latter is determined by the particular process connecting two different states. In turn, state properties can be intensive if are not depending on the mass of the system, and extensive, if are determined by the amount of the mass.

Potentials (Driving Forces)

P : mechanical potential (pressure);

T : thermal potential (temperature);

μ^C : chemical potential (potential);

μ^N : nuclear and sub-nuclear potential (potential);

Thermodynamic Entropy

S^T associated to S : thermal entropy;

S^C associated to n : chemical entropy;

S^M associated to V : mechanical entropy;

Internal Energy (Euler) in Finite Terms

$U^T = TS$: thermal internal energy or capability to transfer by means of heat interaction;

$U^C = \sum_{i=1}^{r} \mu_i n_i$: chemical internal energy or capability to transfer by means of mass interaction;

$U^M = PV$: mechanical internal energy or capability to transfer by means of work interaction;

Internal Energy in Differential Terms

$dU^T = d(TS) = TdS + SdT$: thermal internal energy differential;

$dU^C = d\left(\sum_{i=1}^{r} \mu_i n_i\right) = \sum_{i=1}^{r} \mu_i dn_i + \sum_{i=1}^{r} n_i d\mu_i$: chemical internal energy differential;

$dU^M = d(PV) = PdV + VdP$: mechanical internal energy differential;

Energy Transfer ⇔ Interaction

$\delta Q_{INT} = TdS$: elementary internal heat interaction;

$\delta Q_{EXT} = d(TS)$: elementary external heat interaction;

$\delta Q_{INT+EXT} = SdT$: elementary total heat interaction;

$\delta M_{INT} = \sum_{i=1}^{r} \mu_i dn_i$: elementary internal mass interaction;

$\delta M_{EXT} = d\left(\sum_{i=1}^{r} \mu_i n_i\right)$ elementary external mass interaction;

$\delta M_{INT+EXT} = \sum_{i=1}^{r} n_i \, d\mu_i$: elementary total mass interaction;

$\delta W_{INT} = -PdV$: elementary internal work interaction;

$\delta W_{EXT} = -d(PV)$: elementary external work interaction;

$\delta W_{INT+EXT} = -VdP$: elementary total work interaction.

The above-listed state and process quantities are those needed to describe any state and process of any system and are correlated with each other to provide a rational schema overarching all thermodynamic energies' analytical formulations. The physical meaning of those quantities allows facilitating the interpretation of thermodynamic analytical functions describing any type of system and phenomena.

The schema of the hierarchical structure of potentials and thermal, chemical mechanical internal energies can be represented in the following Figure 2.1. This schema is meant to highlight the dependence of macroscopic model of a system to the microscopic constituting many-particle modeling. In different terms, the schema describes the dependence of internal energy and available energy, and its thermal, chemical and mechanical contributions, on the interactions among particles and the confinement wall of the space domain of a portion of matter representing the volume constraint of the system. This relationship is underpinned by the model of the system constituted by particles in the assumptions of Kinetic Theory of Gases and the Statistical Mechanics and Statistical Thermodynamics methodologies. Nevertheless, even in the perspective of Quantum Physics, the schema remains valid with the only difference that, individually, each and every particle behaves in a quantized mode according to the particle-in-a-box modeling. The crucial phenomena of this relationship are the collisions among particles and between a particle and the wall of the confined space volume representing the boundary condition of particles motion. In the quantum description, boundary conditions imposed by a confining barrier imply quantization of the allowed values of energy associated with a single particle. Indeed, the expression of the wavefunction Ψ, representing a solution of the Schrodinger equation, is the following [1.10,1.18]:

$$\Psi = \left(\frac{2}{L}\right)^{1/2} \sin \frac{n\pi x}{L} = \frac{1}{2i}\left(\frac{2}{L}\right)^{1/2} \left(e^{ikx} - e^{-ikx}\right) \quad \text{where} \quad k = \frac{n\pi}{L}$$

where n is the quantum number identifying the energy level pertaining to the single particle.

It is noteworthy that quantum description of particle motions allows a discrete series of quantum numbers n so that the energy content of a single particle in turn quantized. Nevertheless, the consequent momentum, hence the velocity at each collision, does not change the essence of the dynamical interaction at a single particle-wall collision. The frequency of collisions, depending on the velocity of particles, is quantized as well. Anyway, quantum discretization does not change the effect on the confinement wall and the resulting pressure caused by the continuity of collisions over time.

The above caveat concerning the classical and quantum correspondence is here needed to validate and generalize all considerations and results achieved so far in defining properties involved in the entropy-exergy relationship.

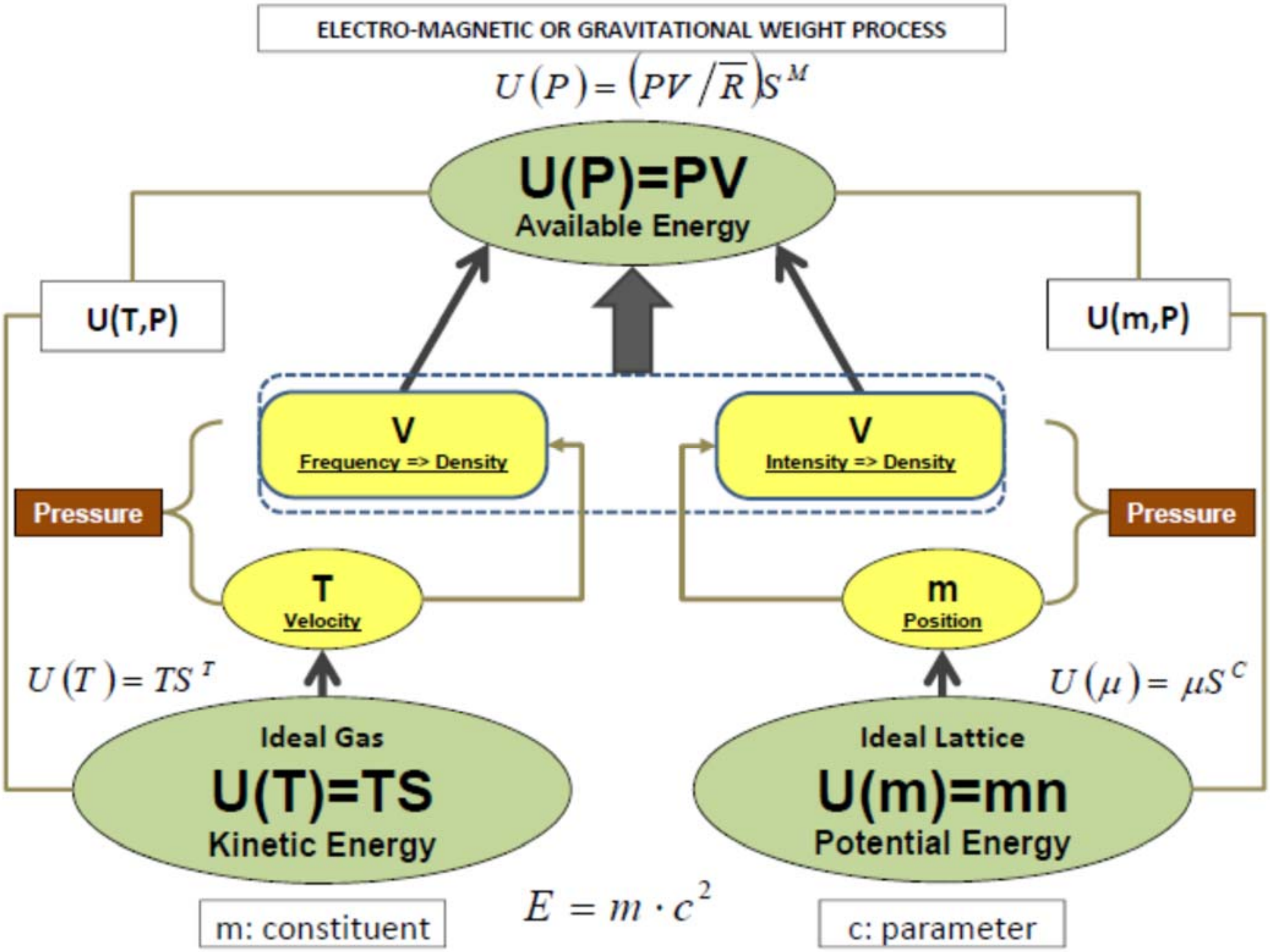


Figure 2.3 – Schema of Thermodynamic Potentials

2.4.2. Control Surface and Balance of Properties

The Control Surface (CS) identifies boundary limits of an internal system with respect to the external system (or environment) to be considered in the balance of properties involved in interaction between the two systems. The balance is here extended to thermal, chemical and mechanical aspects of properties and interactions to achieve a generalized relation applicable to any special case.

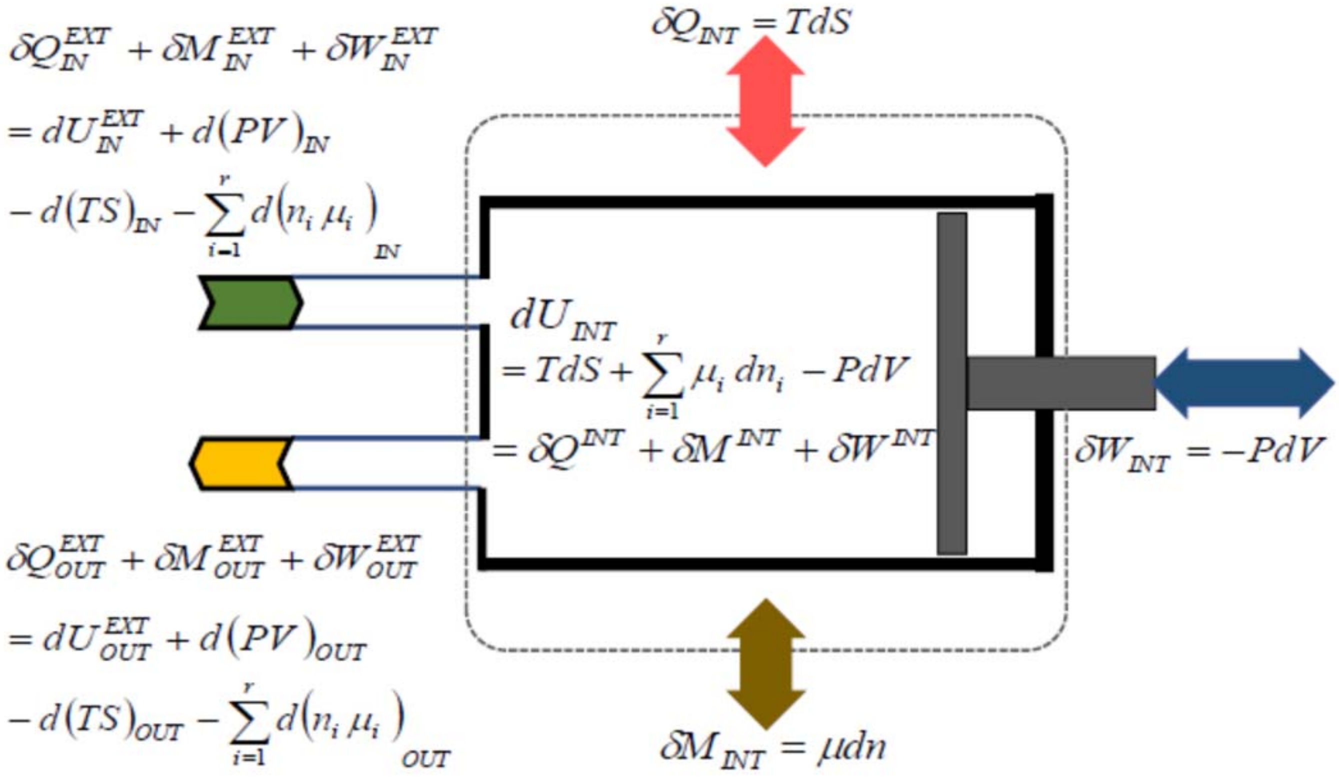


Figure 2.4 – Control Surface and Mass-Energy Balance

With reference to the Control Surface (CS), the overall balance of internal and external fluxes is the following that considers solely external work interaction associated to the entering and exiting infinitesimal mass:

$$dU^{INT} = \left[dU_{OUT}^{EXT} + \delta W_{OUT}^{EXT}\right] - \left[dU_{IN}^{EXT} + \delta W_{IN}^{EXT}\right] + \delta Q^{INT} + \delta M^{INT} + \delta W^{INT}$$

being the external elementary work: $\delta W_{IN}^{EXT} = d(PV)_{IN}$; $\delta W_{OUT}^{EXT} = d(PV)_{OUT}$; and being the internal elementary work: $\delta W^{INT} = -PdV$, then:

$$dU^{INT} = \left[dU_{OUT}^{EXT} + d\left(PV\right)_{OUT}\right] - \left[dU_{IN}^{EXT} + d\left(PV\right)_{IN}\right] - PdV + \delta Q^{INT} + \delta M^{INT}$$

$$= \left[dH_{OUT} - dH_{IN}\right] + \delta W^{INT} + \delta Q^{INT} + \delta M^{INT}$$

As far as work interaction is concerned:

$$\delta W^{INT} + \delta W^{EXT} = -PdV + \left[d\left(PV\right)_{OUT} + d\left(PV\right)_{IN}\right] = \left(-PdV\right)^{INT} + d\left(PV\right)^{EXT} = \left(VdP\right)^{\substack{CONTROL\\VOLUME}}$$

Indeed, $U^M = PV \Rightarrow dU^M = d(PV)$ that is, the differential variation of PV is $d(PV)$ representing the infinitesimal contribution to PV determined by an external infinitesimal amount of the same type of mechanical energy hence consisting of the very $d(PV)$ entering and or exiting the control volume of the system.

It is noteworthy that, in the balance above calculated, the elementary mass entering and exiting through the surface containing the control volume, is assumed contributing with the elementary work interaction transmitted from the external system to the internal system. Though, this is a limitation of the balance because the external heat interaction δQ^{EXT} and the external mass interaction δM^{EXT} should be accounted for in addition to the external work interaction δW^{EXT}. This caveat is here underlined for sake of completeness of the balance and would imply a more extended equation resulting from the thermal chemical and mechanical interactions as specified in Figure 2.2 where these terms are associated to input and output elementary masses. The complete balance equation becomes:

$$dU^{INT} = \left[dU_{OUT}^{EXT} + \delta Q_{OUT}^{EXT} + \delta M_{OUT}^{EXT} + \delta W_{OUT}^{EXT}\right] - \left[dU_{IN}^{EXT} + \delta Q_{IN}^{EXT} + \delta M_{IN}^{EXT} + \delta W_{IN}^{EXT}\right]$$

$$+ \delta Q^{INT} + \delta M^{INT} + \delta W^{INT}$$

being the external elementary heat: $\delta Q_{IN}^{EXT} = d\left(TS\right)_{IN}$; $\delta Q_{OUT}^{EXT} = d\left(TS\right)_{OUT}$

and being the external elementary mass: $\delta M_{IN}^{EXT} = \sum_{i=1}^{r} d\left(\mu_i\, n_i\right)_{IN}$; $\delta M_{OUT}^{EXT} = \sum_{i=1}^{r} d\left(\mu_i\, n_i\right)_{OUT}$

$$dU^{INT}$$

$$= \left[dU_{OUT}^{EXT} + d\left(TS\right)_{OUT} + \sum_{i=1}^{r} d\left(\mu_i\, n_i\right)_{OUT} + d\left(PV\right)_{OUT}\right]$$

$$- \left[dU_{IN}^{EXT} + d\left(TS\right)_{IN} + \sum_{i=1}^{r} d\left(\mu_i\, n_i\right)_{IN} + d\left(PV\right)_{IN}\right]$$

$$+\delta Q^{INT} + \delta M^{INT} + \delta W^{INT}$$

A final remark is specially focused on the fact that the set of differential terms within the square parentheses, but the infinitesimal internal energy $dU_{IN}^{EXT}, dU_{OUT}^{EXT}$, represent the Euler equation relating to the external elementary mass entering and exiting the control surface. Hence, the enthalpy is replaced by the Euler equation:

$$dU^{INT} = dU_{MASS}^{EXT} + dU_{ENVIR}^{EXT} + \delta Q^{INT} + \delta M^{INT} + \delta W^{INT}$$

2.4.3. Internal Energies (or Characteristic Functions)

The purpose of the present section is to discuss the free energies, being part of thermodynamic fundamentals, through a rational paradigm able to allow the definition of corresponding free enthalpies, all depending on the combination of thermodynamic potentials, or intensive properties, characterizing these functions. This brief treatise is basically carried out in the spirit of a pure philosophical speculation that might end up to be beneficial in a theoretical and even experimental use of these functions in applications. To do so, the overall internal energy expressed by Euler equation is considered as the macroscopic result of the sum of particles kinetic energies and particles potential energies:

$$U = U\left(P, T, \mu^C, \mu^N\right) = U^M(P) + U^T(T) + U^C\left(\mu^C\right) + U^N\left(\mu^N\right)$$

$$= -PV + TS + \sum_{i=1}^{r} \mu_i^C n_i^C + \sum_{i=1}^{r} \mu_i^N n_i^N$$

which constitutes a real function of eight variables not independent each other [2.10].

The Euler equation can be regarded as a generalized expression of the First Law in finite terms. In differential terms the Euler equation becomes the following:

$$dU = dU\left(P, T, \mu^C, \mu^N\right)$$

$$= dU^M(P) + dU^T(T) + dU^C\left(\mu^C\right) + dU^N\left(\mu^N\right)$$

$$= -d(PV) + d(TS) + d\left(\sum_{i=1}^{r} \mu_i^C n_i^C\right) + d\left(\sum_{i=1}^{r} \mu_i^N n_i^N\right)$$

$$= -PdV - VdP + TdS + SdT + \sum_{i=1}^{r} \mu^C dn_C + \sum_{i=1}^{r} n_C d\mu^C + \sum_{i=1}^{r} \mu^N dn_N + \sum_{i=1}^{r} n_N d\mu^N$$

$= \delta W + \delta Q + \delta M$ from which, in finite terms: $\Delta U = W + Q + M$

The physical meaning of Euler equation consists of the total thermodynamic energy of the internal system itself. This total internal energy can be transferred i) to the internal useful system (cylinder-piston device components relative motion transmission) by means of internal interactions (non-bulkflow as a closed system) and ii) to the external useful system (reservoir-piston device components relative motion transmission) by means of external interactions (bulk-flow as an open system) corresponding to the components of the differential of each and every term of the Euler equation.

2.4.3.1. Helmholtz Free Energy (Thermal Free Energy)

The canonical definition of Helmholtz free energy in finite terms equals the total internal energy minus the thermal internal energy so that the total internal energy is constituted by chemical internal energy and mechanical internal energy according to the following analytical function:

$A = U - TS = \sum_{i=1}^{r} \mu_i n_i - PV$ from which, the total differential is $dA = \sum_{i=1}^{r} \mu_i \, dn_i - PdV - SdT$ that can be demonstrated using two different proofs.

First Proof Using Gibbs Equation

$$dU = dU^{T} + dU^{C} + dU^{M} = TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV = \delta Q + \delta M + \delta W$$

related to reversible or irreversible processes of internal system undergoing processes interacting with an open or closed external system; taking into account the total differential of thermal internal energy, the Gibbs equation becomes: $TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV = d(TS) - SdT + \sum_{i=1}^{r} \mu_i \, dn_i - PdV$

If the elementary thermal internal energy $d(TS)$ is subtracted from the elementary internal energy dU, then:

$dU - d(TS) = -SdT + \sum_{i=1}^{r} \mu_i \, dn_i - PdV$ from which the following is obtained:

$dA = d(U - TS) = dU - d(TS) = \sum_{i=1}^{r} \mu_i \, dn_i - PdV - SdT$ and finally:

$$dA = dU - dU^{T} = \sum_{i=1}^{r} \mu_i \, dn_i - PdV - SdT = \delta M_{INT} + \delta W_{INT} - \delta Q_{INT+EXT}$$

The integration, over a whatever process, leads to the finite form:

$$A = U - TS = \sum_{i=1}^{r} \mu_i n_i - PV = M_{INT} + W_{INT} - Q_{INT+EXT}$$

representing the “whole” thermodynamic potential U of the internal system due to external and or internal interactions with closed or open external system. Indeed, the total amount of U can be viewed as resulting from the integral of elementary contributions due to variations of generalized entropy with constant total mass per unit of generalized entropy contribution, and or due to variations of total mass with constant generalized entropy per unit of total mass contribution.

Second Proof Using Gibbs-Duhem Equation

From the Euler equation of internal energy

$$U = U^M + U^T + U^C = -PV + TS + \sum_{i=1}^{r} \mu_i n_i$$

$$dU = dU^M + dU^T + dU^C = -d(PV) + d(TS) + d\left(\sum_{i=1}^{r} \mu_i n_i \right)$$

$$dU - d(TS) = -d(PV) + d\left(\sum_{i=1}^{r} \mu_i n_i \right)$$

$$d(U - TS) = -PdV - VdP + \sum_{i=1}^{r} \mu_i dn_i + \sum_{i=1}^{r} n_i d\mu_i$$

From Gibbs-Duhem equation: $-VdP + SdT + \sum_{i=1}^{r} n_i d\mu_i = 0$ => $-VdP + \sum_{i=1}^{r} n_i d\mu_i = -SdT$

substituted in the previous equation, it follows:

$$dA = d(U - TS) = dU - d(TS) = \sum_{i=1}^{r} \mu_i dn_i - PdV - SdT$$

that corresponds to the expression demonstrated with the First Proof.

The above equation applies to reversible and or irreversible, bulkflow and or non-bulkflow, cyclic and or non-cyclic transfer processes of an internal system interacting with a closed or open external system.

During chemical reactions, such as for example the methane combustion $CH_4 + 2O_2 = CO_2 + 2H_2O$, chemical bonds breaking make atoms and or molecules release the chemical bond potential energy into Lennard-Jones inter-particle potential energy (resulting in endogenous or exogenous work input in the multi-particle system itself) or transformed into inter-particle kinetic energy (resulting in endogenous or exogenous heat input in the multi-particle system itself). In turn, the Lennard-Jones inter-particle potential energy can be directly transferred by means of work interaction along adiabatic processes. That said, the physical meaning of thermal free energy differential is:

$$dA = dU - dU^{T} = dU^{C} + dU^{M} = \delta M_{INT} + \delta W_{INT}$$

and integrating over a whatever finite process:

$$A = U - TS = U - U^{T} = U^{C} + U^{M} = \sum_{i=1}^{r} \mu_i n_i - PV = M + W$$

Mass-Work transformation occurs at microscopic level and Mass-Work conversion occurs at macroscopic level

$M \Rightarrow \Delta A$ then

$\Delta U^{C} = W^{C}$ (work of chemical origin - mass interaction)

$\Delta U^{M} = W^{M}$ (work of mechanical origin - work interaction)

$$\Delta A = \Delta U - \Delta U^{T} = \Delta U^{C} + \Delta U^{M} = W^{C} + W^{M}\,;\; I = W^{C} + W^{M}$$

If temperature changes, then A constitutes the amount of work interaction derived from inter-particle potential energy variation of a closed system only as inter-particle kinetic energy due to external system temperature variation is accounted for in the term $-SdT$. The term $U - TS$ is the internal energy, related to inter-particle potential energy and inter-particle kinetic energy, minus the internal (related to system only) thermal contribution associated to inter-particle kinetic energy only $-TS$. Therefore, it represents the inter-particle potential energy which is transferred to the external system by means of maximum net useful work produced by the closed system.

Free energy variation can occur at constant temperature, where temperature remains the same at initial and final state although it can change along the process from initial to final state.

At constant temperature and constant chemical potential, $dA = -PdV$ constitutes the amount of work interaction due to internal energy change of a closed system determined by inter-particle potential energy only as inter-particle kinetic energy does not undergo changes being temperature constant. Indeed, the amount of heat interaction along the isothermal process is accounted for in the free energy definition itself in the term $-d(TS)$. Therefore, free energy represents the maximum net useful work produced by the closed system undergoing a process at constant temperature.

In particular, the amount of work interaction associated to the variation of Helmholtz free energy A is generated by both inter-particle Van der Waals potential energy and inter-particle chemical bonds potential energy. In fact, only thermal energy TS is deducted from the total internal energy U so that the remaining chemical and mechanical contributions are evaluated by means of A and represent the total internal mechanical energy PV

In case of adiabatic reversible process which releases thermodynamic internal work interaction only, the free energy constitutes the amount of work contribution due to inter-particle potential energy (at microscopic level) or due to thermodynamic mechanical energy PV (at macroscopic level) and not to inter-particle kinetic energy (at microscopic level) or not to thermal energy TS (at macroscopic level).

2.4.3.2. Z Free Energy (Chemical Free Energy)

The chemical free energy can be thought as corresponding to the thermal free energy in which the temperature is replaced by the chemical potential. The analytical expression is the following:

$Z = U - \sum_{i=1}^{r} \mu_i n_i = TS - PV$ from which, the total differential is $dZ = TdS - PdV - \sum_{i=1}^{r} n_i\, d\mu_i$ that can be demonstrated using two different proofs as in the previous case.

First Proof Using Gibbs Equation

The Gibbs equation is again considered that can be expressed in the following terms considering the total differential of chemical potential: $dU = TdS + d\left(\sum_{i=1}^{r} \mu_i n_i\right) - \sum_{i=1}^{r} n_i\, d\mu_i - PdV$. If the elementary thermal internal energy $d\left(\sum_{i=1}^{r} \mu_i n_i\right)$ is subtracted from the elementary internal energy dU, then the Z free energy in differential terms is derived:

$$dZ = dU - dU^C = dU^T + dU^M = dU - d\left(\sum_{i=1}^{r} \mu_i n_i\right) = TdS - PdV - \sum_{i=1}^{r} n_i\, d\mu_i$$

and integrating over whatever finite process:

$$Z = U - \sum_{i=1}^{r} \mu_i n_i = U - U^C = U^T + U^M = TS - PV = Q + W$$

The physical meaning is that heat-work transformation occurs at microscopic level and heat-work conversion occurs at macroscopic level.

$Q \Rightarrow \Delta Z$ then $\Delta U^T = W^T$ and $\Delta U^M = W^M$ hence $\Delta Z = \Delta U^T + \Delta U^M = W^T + W^M$

Second Proof Using Gibbs-Duhem Equation

From the Euler equation of internal energy

$$dZ = dU - dU^C = TdS + SdT - PdV - VdP$$

From Gibbs-Duhem equation: $-\sum_{i=1}^{r} n_i \, d\mu_i = SdT - VdP$ that substituted in the previous one gives:

$dZ = TdS - PdV - \sum_{i=1}^{r} n_i \, d\mu_i$ that demonstrates the expression to be proved.

2.4.3.3. Enthalpy (Mechanical Free Energy)

The enthalpy, or mechanical free energy, in finite terms is defined by the following expression:

$H = U + PV = TS + \sum_{i=1}^{r} \mu_i \, n_i$ from which, the total differential is $dH = TdS + \sum_{i=1}^{r} \mu_i \, dn_i + VdP$ that, also in this case, can be demonstrated using two different proofs.

First Proof Using Gibbs Equation

The addition of the term $d(PV)$ to both sides of Gibbs relation (corresponding to mass input and or output through the control volume), then $dU + d(PV) = TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV + d(PV)$, hence:

$d(U + PV) = TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV + PdV + VdP$ from which:

$dH = TdS + \sum_{i=1}^{r} \mu_i \, dn_i + VdP$ corresponding to the given differential expression of enthalpy function.

It should be noticed that U represents the internal energy of the external system entering and exiting the control volume and adding to the internal energy of the internal energy already existing inside the control volume or the cylinder-piston device.

$$dH = dU - dU^M = dU^T + dU^C = \delta Q + \delta M$$

Second Proof Using Gibbs-Duhem Equation

From Euler equation of internal energy: $H = U - U^M = U^T + U^C = TS + \sum_{i=1}^{r} \mu_i \, n_i$ that, in differential terms becomes:

$$dH = dU - dU^{M} = dU^{T} + dU^{C}$$

$$= d(TS) + d\left(\sum_{i=1}^{r} \mu_i n_i\right) = TdS + SdT + \sum_{i=1}^{r} \mu_i dn_i + \sum_{i=1}^{r} n_i d\mu_i$$

From Gibbs-Duhem equation $SdT + \sum_{i=1}^{r} n_i d\mu_i = VdP$, substituting in the above equation,

$dH = TdS + \sum_{i=1}^{r} \mu_i dn_i + VdP$ that corresponds to the above equation.

$$dH = dU^{T} + dU^{C} = \delta Q + \delta M \ ; \quad \delta W^{T} = \delta W^{C} = 0$$

Therefore, at constant pressure and with no heat and mass interactions, enthalpy variations express the amount of thermal energy transformed into chemical energy (endothermic process) or chemical energy transformed into thermal energy (exothermic process).

2.4.3.4. Gibbs Free Energy (Chemical Free Enthalpy)

Differently from thermal, chemical and mechanical free energies, in the case of thermal, chemical and mechanical free enthalpies the thermodynamic potential characterizing the analytical function is twofold, that is temperature-potential, temperature-pressure and potential-pressure. Hence, the terms of differential analytical function in which the differential of the thermodynamic potential (intensive property) appear are two and not only one as in the case of free energies where that term is only one.

In particular, the chemical free enthalpy, commonly denoted as Gibbs free energy, is derived from Euler equation by subtracting the thermal internal energy and the mechanical internal energy with the following expression:

$$G = U - U^{T} - U^{M} = U - TS + PV$$

$$= TS + \sum_{i=1}^{r} \mu_i n_i - PV - TS + PV = \sum_{i=1}^{r} \mu_i n_i$$

In differential terms:

$$dG = d(U - TS + PV) = dU - d(TS) + d(PV) = dU - dU^{T} - dU^{M}$$

$$dG = d(U - TS + PV) = dU - TdS - SdT + PdV + VdP$$

$$dG = TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV - d(TS) + d(PV)$$

from which, substituting the Gibbs equation $dU = TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV$, then:

$$= TdS + \sum_{i=1}^{r} \mu_i \, dn_i - PdV - TdS - SdT + PdV + VdP$$

$$dG = \sum_{i=1}^{r} \mu_i \, dn_i - SdT + VdP$$

In the special case of system interacting with a reservoir R

$$dG = \sum_{i=1}^{r} (\mu_i - \mu_R) dn_i - Sd(T - T_R) + Vd(P - P_R)$$

2.4.3.5. Thermal Free Enthalpy

The chemical free enthalpy is the most common analytical function normally used in Chemistry and Physical chemistry. Though, nothing prevents from thinking of analytical functions derived by means of the association of combination among all thermodynamic potential. Indeed, the thermal free enthalpy is consequent to the subtraction of the chemical and mechanical internal energy from the overall Gibbs equation of the system, that is:

$$J = U - U^C - U^M = U - \sum_{i=1}^{r} \mu_i \, n_i + PV = TS + \sum_{i=1}^{r} \mu_i \, n_i - PV - \sum_{i=1}^{r} \mu_i \, n_i + PV = TS$$

In differential terms:

$$dJ = TdS - \sum_{i=1}^{r} n_i \, d\mu_i + VdP$$

2.4.3.6. Mechanical Free Enthalpy

The mechanical free enthalpy is the result of thermal and chemical internal energies from the overall Gibbs equation:

$$K = U - U^{T} - U^{C} = U - TS - \sum_{i=1}^{r} n_i \mu_i = TS + \sum_{i=1}^{r} \mu_i n_i - PV - TS - \sum_{i=1}^{r} \mu_i n_i = -PV$$

In differential terms:

$$dK = -PdV - SdT - \sum_{i=1}^{r} n_i \, d\mu_i$$

If the Gibbs-Duhem equation is used, then $dK = -PdV - VdP = -d(PV)$ that represents the infinitesimal variation of mechanical internal energy caused by mass entering or exiting the control volume of the system characterized by its own mechanical internal energy $-PV$.

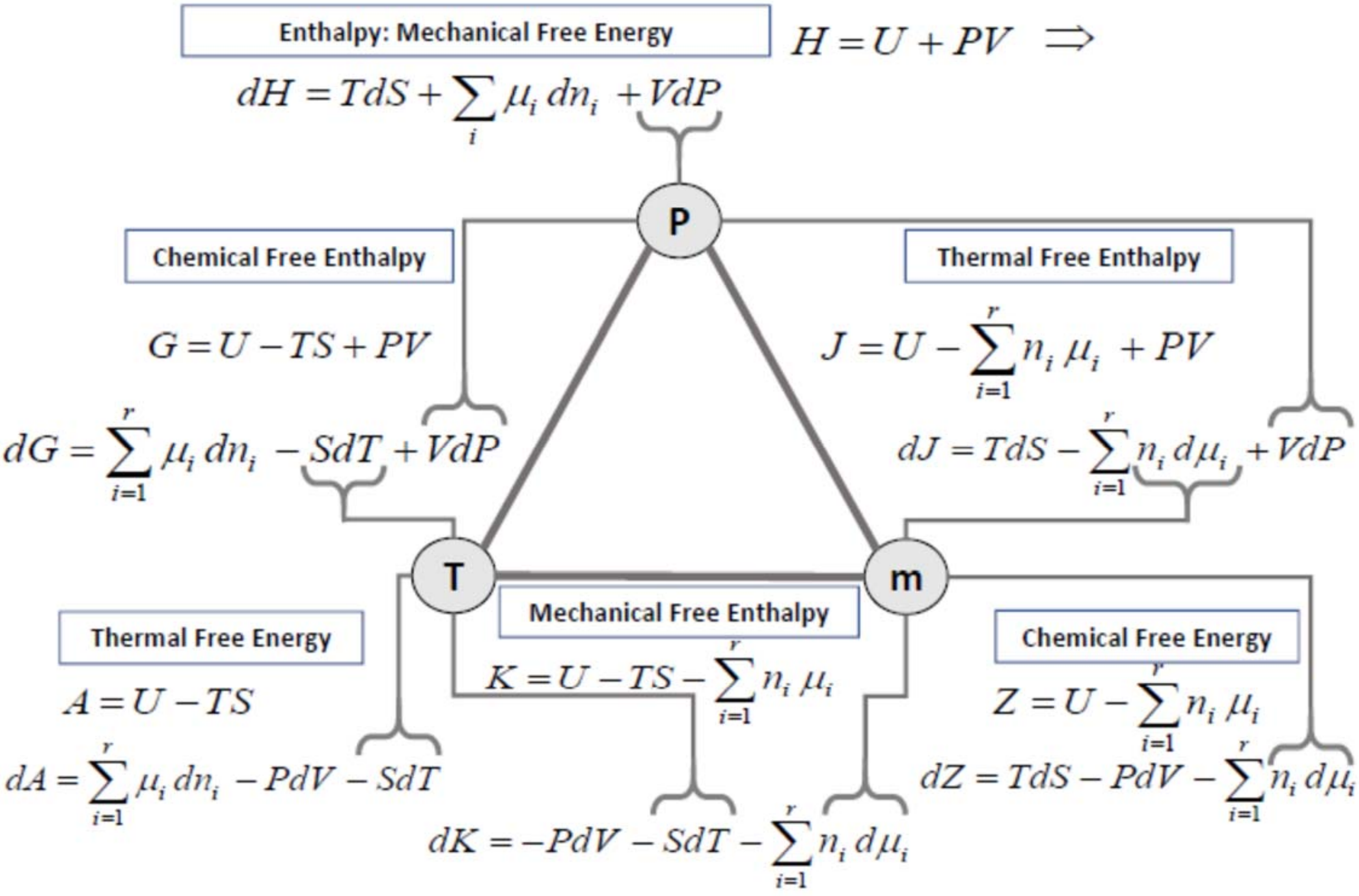
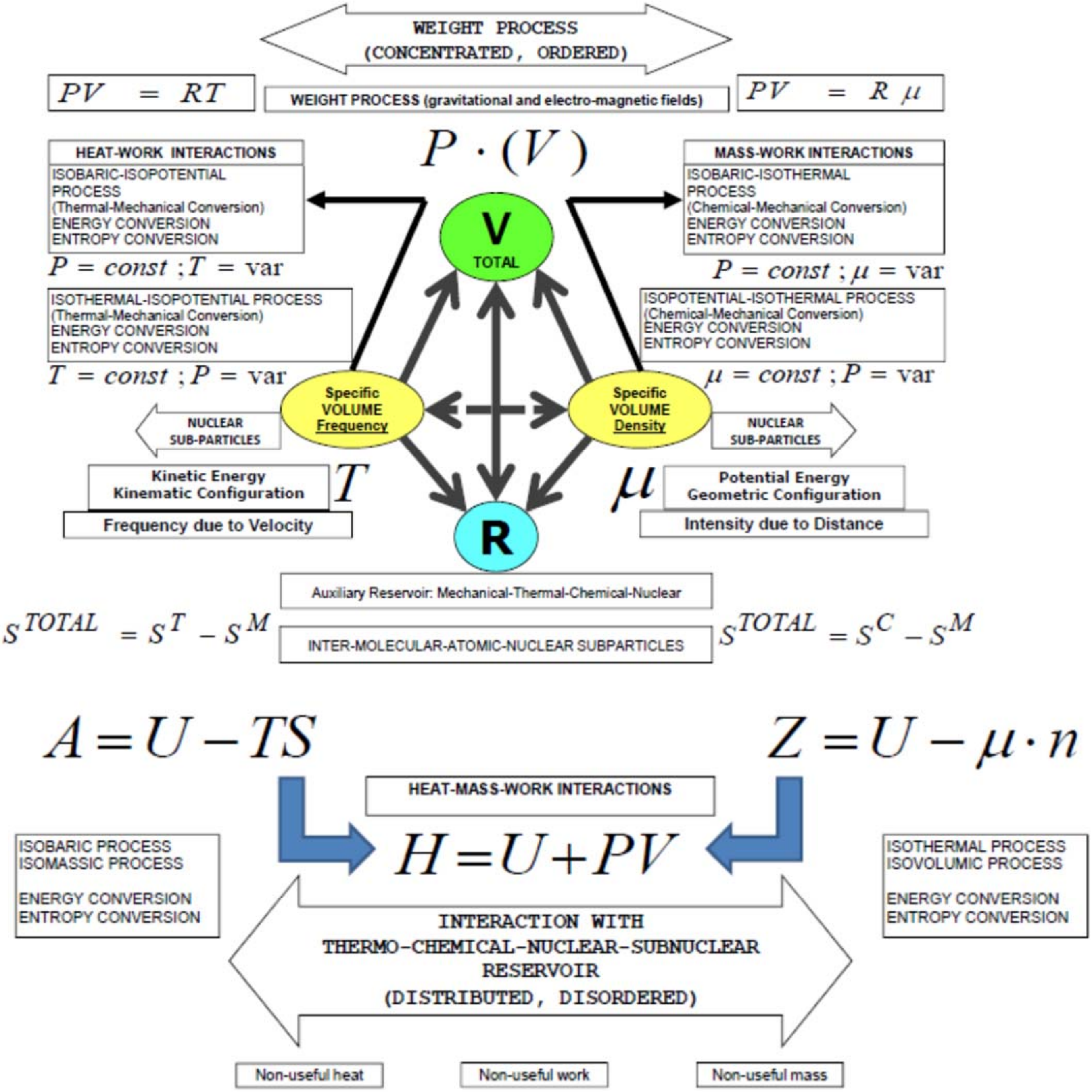


Figure 2.5 – Schema of Internal Energies related to Potentials

This schema is such that in correspondence with vertexes there are free energies and in correspondence with sides connecting vertexes there are free enthalpies. The implication with infinitesimal variation of intensive properties constituting temperature, potential and pressure, is pointed out by arrows.

Thermodynamic Potentials, or Internal Energies here defined, can be correlated to potentials and represented in the diagram here after included. This diagram is designed with four vertexes: three are occupied by the volume and the forth is the reference reservoir. The role of this diagram is to stress the importance of kinematic configurations and geometric configurations, or in different terms, the phase space, in the particles dynamic originating properties and governing processes organized in a rational hierarchical structure. The diagram shows the three thermal, chemical and mechanical free energies, namely, thermal free energy (Helmholtz): $A = U - TS$, chemical free energy: $A = U - n\mu$, mechanical free energy (enthalpy): $H = U + PV$ to point out the interactions and implications with conversion and transformation processes. The diagram also reports two different and "symmetric" equations of state, the thermal-mechanical version $PV = \overline{R}T$ on the left side and the chemical-mechanical version $PV = \overline{R}\mu$ on the right side. This twofold version of state equation is a direct consequence of the dualism and symmetry outcoming from this diagram reproducing the mathematical entities of the phase space, that is positions and velocities (or momenta), in turn "a priori" concepts of microstates of microscopic physical entities.


WEIGHT PROCESS
(CONCENTRATED, ORDERED)
$PV = RT$
WEIGHT PROCESS (gravitational and electro-magnetic fields)
$PV = R\mu$
$P \cdot (V)$
HEAT-WORK INTERACTIONS
ISOBARIC-ISOPOTENTIAL PROCESS
(Thermal-Mechanical Conversion)
ENERGY CONVERSION
ENTROPY CONVERSION
$P = const ; T = \text{var}$
MASS-WORK INTERACTIONS
ISOBARIC-ISOTHERMAL PROCESS
(Chemical-Mechanical Conversion)
ENERGY CONVERSION
ENTROPY CONVERSION
$P = const ; \mu = \text{var}$
V
TOTAL
ISOTHERMAL-ISOPOTENTIAL PROCESS
(Thermal-Mechanical Conversion)
ENERGY CONVERSION
ENTROPY CONVERSION
$T = const ; P = \text{var}$
ISOPOTENTIAL-ISOTHERMAL PROCESS
(Chemical-Mechanical Conversion)
ENERGY CONVERSION
ENTROPY CONVERSION
$\mu = const ; P = \text{var}$
Specific VOLUME Frequency
Specific VOLUME Density
NUCLEAR SUB-PARTICLES
NUCLEAR SUB-PARTICLES
Kinetic Energy
Kinematic Configuration
T
Frequency due to Velocity
μ
Potential Energy
Geometric Configuration
Intensity due to Distance
R
Auxiliary Reservoir: Mechanical-Thermal-Chemical-Nuclear
$S^{TOTAL} = S^{T} - S^{M}$
INTER-MOLECULAR-ATOMIC-NUCLEAR SUBPARTICLES
$S^{TOTAL} = S^{C} - S^{M}$
$A = U - TS$
$Z = U - \mu \cdot n$
HEAT-MASS-WORK INTERACTIONS
ISOBARIC PROCESS
ISOMASSIC PROCESS
ENERGY CONVERSION
ENTROPY CONVERSION
$H = U + PV$
ISOTHERMAL PROCESS
ISOVOLUMIC PROCESS
ENERGY CONVERSION
ENTROPY CONVERSION
INTERACTION WITH
THERMO-CHEMICAL-NUCLEAR-SUBNUCLEAR
RESERVOIR
(DISTRIBUTED, DISORDERED)
Non-useful heat
Non-useful work
Non-useful mass

2.4.4. Thermodynamic Non-Cyclic Processes

The canonical thermodynamic non-cyclic processes are characterized and categorized: isothermal (constant temperature), isopotential (constant attraction-repulsion inter-particle potential), isomassic (constant thermal capacity), isomolar (constant chemical potential of constituents), isovolumic (constant volume), isoentropic (adiabatic reversible), isobaric (constant pressure). All non-cyclic processes are real thus characterized by reversible and non-reversible phenomena inherently constituting components of all states and systems elaborations. Notwithstanding these canonical processes are normally and largely described in papers and textbooks and referred to in the literature, it is worth highlighting those aspects displaying a different way to analyse physical phenomena and properties proposed in the present research.

2.4.4.1. Isothermal-Isopotential Process

In the framework of Kinetic Theory of Gases and Classical Statistical Mechanics and Thermodynamics, constant temperature process (isothermal) means that particles kinetic energy, or thermal internal energy, is constant and is not transferred to the external system by work interaction that, instead, results from variable pressure and variable volume. As clarified in Figure 2.1, the very volume determines the frequency of collisions or mechanical internal energy transfer to the external system. Considering the Euler equation $U = TS - PV$, thermal and mechanical contributions $U^T(T) = TS$ and $U^M(P) = -PV$ are independent each other: this implies that, since the isothermal process requires particles constant velocity, determining constant kinetic energy and therefore constant temperature, there remains the volume variation and variable pressure, hence the collision frequency, to transfer work interaction. The compensation of the mechanical internal energy transferred to the external system by work interaction output, is obtained by means of thermal internal energy transferred to the internal system by heat interaction input (in the particular case of expansion process). While thermal input is occurring, kinetic energy is transferred as work interaction of thermal origin $\delta Q = \delta W$. In the particular case of ideal systems, since the ultimate form of internal energy is constituted by particles kinetic energy, or thermal energy, then if temperature remains constant along an isothermal process, the internal energy remains constant as well. However, it is worth noticing that the invariance of internal energy is originated by the compensation of thermal internal energy decrease and mechanical internal energy increase, or vice versa, intrinsic to the compensation of thermal entropy and mechanical entropy as describe in the previous section 2.3.9. where this compensation mechanism is analysed.

The thermodynamic potentials (or characteristic functions) along process above listed assume the following specific forms.

Internal Energy of Isothermal-Isopotential Process

For isothermal-isopotential processes heat interaction and work interaction occur at constant temperature, therefore:

$$dU = dU^T(T) + dU^M(P) = d(TS) - d(PV) = TdS + SdT - PdV - VdP$$

as by definition of isothermal process $SdT = 0$, and considering the Gibbs equation $\delta Q_{INT} + \delta W_{INT} = TdS - PdV = dU^{T}_{INT} + dU^{M}_{INT} = dU_{INT} = 0$, then $dU = dU^{M}_{INT+EXT} = -VdP$ hence meaning that the internal energy is coincident with the mechanical internal energy depending on variable pressure and variable volume.

Helmholtz Free Energy (Thermal Free Energy) of Isothermal-Isopotential Process

$$dA = -PdV - SdT = -PdV = dU^{M}_{INT} = \delta W_{INT}$$

In case of an ideal system here assumed, the total internal energy U depends on temperature and pressure. Though, the mechanical internal energy too is determined by the kinetic energy of molecules associated to the temperature. This physical fact can be found in the expression of the free energy representing the mechanical work interaction of internal system $dA = -PdV$, withdrawable with the refilling of the very thermal energy input transfer by means of heat interaction, $\delta Q_{INT} = \delta W_{INT}$; moreover, the total internal energy in differential terms is given by $dU = dU^{M} = \delta W_{INT} + \delta W_{EXT} = -VdP$ in which the only contribution come from the total external and internal work interaction $dU^{M} = -VdP$. The comparison between internal energy and thermal free energy is shown here below:

$$U = TS - PV \left\{ \begin{array}{l} dA = dU^{M}_{INT} = -PdV = \delta W_{INT} \\ \\ dU = dU^{M}_{INT} + dU^{M}_{EXT} = -VdP = \delta W_{INT} + \delta W_{EXT} \end{array} \right.$$

2.4.4.2. Isobaric-Isopotential Process

In case of processes at constant pressure, the constant frequency-velocity, or collision momentum, determining constant pressure energy, is associated to constant pressure and variable temperature at the same time to compensate the mechanical internal energy, transferred to the external system by work interaction output, with thermal internal energy transferred to the internal system by heat interaction input (in the particular case of expansion process).

Internal Energy of Isobaric-Isopotential Process

The isobaric-isopotential process needs heat and work interactions implying transformation of thermal internal energy into mechanical internal energy and hence heat interaction into work interaction, and vice versa accompanied by the increase of thermal internal energy associated to the increase of temperature and the increase of mechanical internal energy associated to the increase of volume. Starting from the differential expression of Euler equation:

$$dU = dU^{T} + dU^{M} = dU^{T}(T) + dU^{M}(P) = TdS + SdT - PdV - VdP$$

as by definition of isobaric process $VdP = 0$, and considering the Gibbs equation $\delta Q_{INT} + \delta W_{INT} = TdS - PdV$, then $dU = SdT$ hence meaning that the internal energy is coincident with the thermal internal energy but differing from the Helmholtz free energy illustrated in the following section.

Helmholtz Free Energy (Thermal Free Energy) of Isobaric-Isopotential Process

$$dA = -PdV - SdT = dU^{M} + dU^{T} = \delta W_{INT} + \delta Q_{INT} + \delta Q_{EXT}$$

In case of an ideal system here too assumed, the total internal energy U depends again on temperature and pressure. Though, the mechanical internal energy is again determined by the kinetic energy of molecules associated to the temperature. This physical fact can be found in the expression of the free energy representing the heat interaction and the mechanical work interaction of internal system $dA = -PdV - SdT$, withdrawable with the refilling of the very thermal energy input transfer by means of heat interaction, $\delta Q_{INT} = \delta W_{INT}$ in this case, the heat interaction input is used to increase temperature and thermal internal energy; moreover, the total internal energy in differential terms is given by $dU = dU^{T} + dU^{M} = \delta W_{INT} + \delta Q_{INT} + \delta Q_{EXT} = -PdV - SdT$ in which the only contribution come from the total external and internal work interaction $dU^{M} = -VdP$. The comparison between internal energy and thermal free energy is shown here below:

$$dU = d(TS) - d(PV) \qquad \left\{ \begin{array}{l} dA = dU^{M}_{INT} = -PdV - SdT = \delta W_{INT} - \delta Q_{INT} - \delta Q_{EXT} \\ \\ dU = dU^{M}_{INT} + dU^{M}_{EXT} = -PdV + TdS + SdT = \delta W_{INT} - \delta Q_{EXT} \end{array} \right.$$

2.4.4.3. Isopotential-Isothermal Processes

The isopotential-isothermal process is opposite to the isothermal-isopotential one. The physical meaning is that, in this opposite case, the combined attraction and repulsion interactions among particles are such that the inter-particle potential energy remains constant along the process. This behaviour occurs in solid state matter at high pressure and low temperature so that variations of volume determine negligible variation of pressure, or, more precisely, negligible variation of intensity of interactions between internal system (solid matter) and external system (interaction device).

2.4.4.4. Isovolumic Process

The isovolumic reversible process is characterized be thermal internal energy transfer determined by heat as the only interaction occurring between internal and external systems. This process represents the case in which thermal state and process properties are involved and all other variables and parameters change because of the Stable-Equilibrium-State Principle. $dU^T = dU^T(T) = TdS = \delta Q_{INT}$.

2.4.4.5. Adiabatic-Isopotential Process

Along an adiabatic-isopotential process the conversion of thermal internal energy into mechanical internal energy occurs at macroscopic level. This implies that, at microscopic level, internal kinetic energy of particles is first transformed into internal potential energy of particles and finally is converted into macroscopic mechanical internal energy. In turn, the mechanical internal energy is transferred to the external system by means of work interaction. Indeed, the inter-particle kinetic energy resulting in temperature is continuously transformed into pressure while $-PdV = \delta W_{INT}$

Conversion is defined as a process in which energy undergoes an entropy increase or decrease while undergoing transfer to an external system or by means a whatever interaction or a change into a different energy form.

2.4.4.6. Isomassic Process

An isomassic process is characterized by a constant amount of heat capacity at constant amount of constituents r, or molecules of each and every constituent. Then, by definition, the isomassic process corresponds to the isothermal process in the sense that the number of constituents is constant.

2.4.4.7. Isobaric Process

An isobaric process implies that temperature and chemical potential change this representing the typical case occurring in chemical reactions. During chemical reactions, the work interaction output at constant pressure results from the transfer of chemical internal energy undergoing a chemical-mechanical transformation. While mass interaction input is occurring, chemical reaction is releasing chemical potential internal energy μ in turn transferred as work interaction $\delta M = \delta W_{INT}$. At the same time, the work interaction at constant pressure results from the transfer of thermal internal energy undergoing a thermal-mechanical transformation hence $\delta Q = \delta W_{INT}$. This double process is balanced by the reactions constant K_R that depends of the equilibrium of the reaction itself and represents the amount of chemical energy transformed into thermal energy or, in the opposite way of the reaction, the amount of thermal energy transformed into chemical energy depending on temperature, chemical potential and pressure of the mixture. A common case of isobaric process is the methane combustion $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

2.4.4.8. Isomolar-Isothermal Process

An isomolar process is characterized by a constant amount of chemical potential caused by a variable amount of constituents and their number of molecules. Then, the isomolar process, corresponding to the isothermal process, experiences variations of pressure.

Considering the Euler equation $U = \mu n - PV$, chemical and mechanical contributions $U^C(\mu) = \mu n$ and $U^M(P) = -PV$ are dependent each other: this biunivocal relationship implies that, since the isomolar process requires particles constant position, determining constant potential energy and therefore constant chemical potential, there remains the volume variation and variable pressure, hence the collision intensity, to transfer work interaction. The compensation of the mechanical internal energy transferred to the external system by work interaction output, is obtained with chemical internal energy transferred to the internal system by molar interaction input, in the particular case of expansion process. While molar input is occurring, potential energy is transferred as work interaction of chemical origin $\delta M = \delta W$.

2.4.4.9. Isobaric-Isothermal-Isopotential Process

This is the particular case in which there is no transfer from internal energy to work interaction. Hence, the system behaves as a solid system in which inter-particle kinetic energy or inter-particle potential energy is not transferred to work interaction. Instead, work interaction results only from inter-particle potential energy of chemical bonds among atoms and molecules that constitute an internal barrier preventing internal reactions. In this case, $\frac{1}{2}\sigma_{ij}\varepsilon_{ij} = \delta W$ where σ_{ij} is the tension tensor and ε_{ij} is the deformation tensor [2.3].

2.4.5. Thermodynamic Cyclic Processes

The importance of cyclic processes is ascribed to their capability of ensuring continuous power release to the external useful system. In practice, cyclic processes can be realized by means of open systems or closed systems delimited by a control surface according to eulerian approach. The continuity is realized by: i) continuous bulkflow (non-interaction) for open systems and: ii) continuous interaction (non-bulkflow) for closed systems. Cyclic processes are based on the same thermodynamic state defining the process at the conclusion of each and every cycle.

The continuous power release could be realized in a different way, such as the continuous non-cyclic change of thermodynamic condition along an “infinite” process, in open systems or closed systems, undergone by the same operating mass constituting the internal system. This way focuses on a fixed amount of mass and can be addressed to as the lagrangian approach. However, this process is technically impossible to ensure the continuity of power release and is only conceptually devised and used to define those properties needed to describe phenomena under analysis.

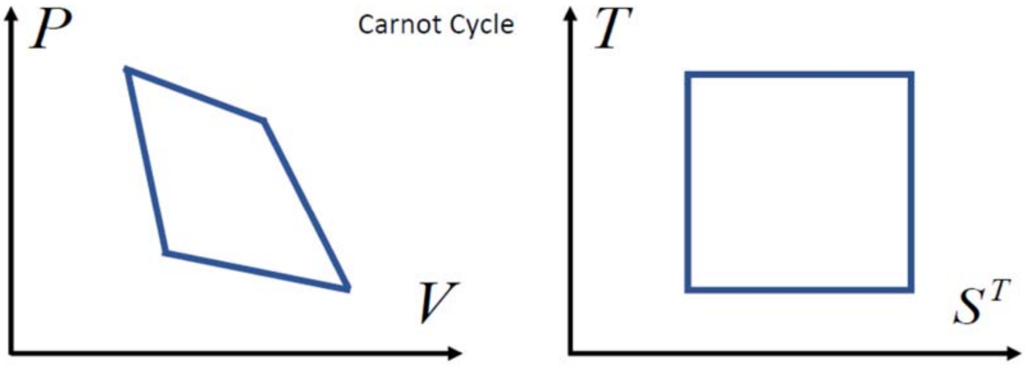
As far as closed systems are concerned, Carnot cycle and Joule cycle can be elaborated by means of heat interactions (isothermal processes) or mass interactions (isopotential processes) with thermal or chemical reservoirs respectively.

Cycles operating in continuous mode result in interactions conversion that can be summarized as:

- Thermo-Mechanical heat-to-work, direct or inverse, cyclic conversion process: $Q=W$
- Thermo-Chemical mass-to-work, direct or inverse, cyclic conversion process: $M = W$

The set of cyclic processes is reported in Figures 2.6a and 2.6b and described more in detail in the following section.

CYCLIC PROCESS - CONTINUOUS POWER - OPEN SYSTEM AND CLOSED SYSTEM
(CONTROL SURFACE OR VOLUME - EULERIAN ANALYSIS)

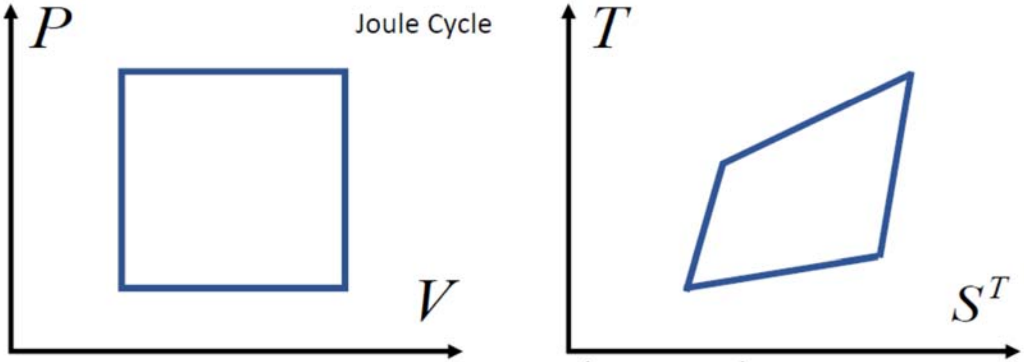


$$\delta Q = TdS^{T} - T_R\, dS^{T} = dS^{T}\left(T - T_R\right)$$

OPEN SYSTEM (BULKFLOW)

$$= TdS^{T}\left(\frac{T - T_R}{T}\right) = TdS^{T}\left(1 - \frac{T_R}{T}\right) = \delta Q\left(1 - \frac{T_R}{T}\right) = \delta W$$

CLOSED SYSTEM (NON-BULKFLOW)



$$\delta W = PdV - P_R\, dV = dV\left(P - P_R\right)$$

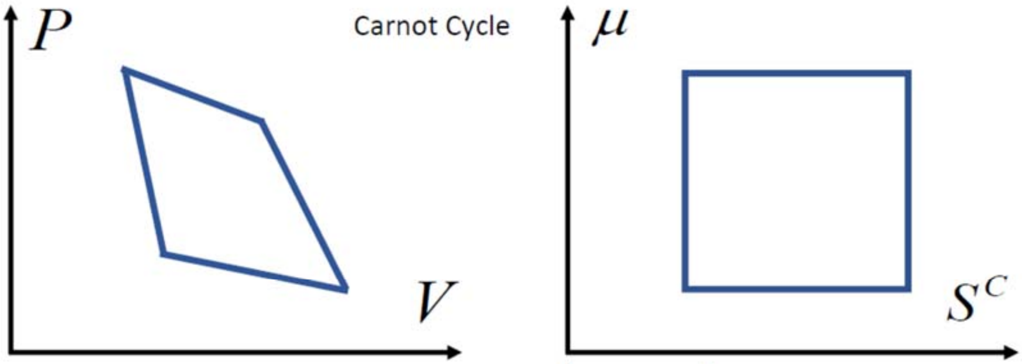
OPEN SYSTEM (BULKFLOW)

$$= PdV\left(1 - \frac{P_R}{P}\right) = \delta W^{REV}\left(1 - \frac{P_R}{P}\right) = dU^{M}\left(P\right)\cdot\left(1 - \frac{P_R}{P}\right) = \delta Q$$

CLOSED SYSTEM (NON-BULKFLOW)

Figure 2.6a – Thermal Aspect of Cyclic Process

CYCLIC PROCESS - CONTINUOUS POWER - OPEN SYSTEM AND CLOSED SYSTEM (CONTROL SURFACE OR VOLUME - EULERIAN ANALYSIS)

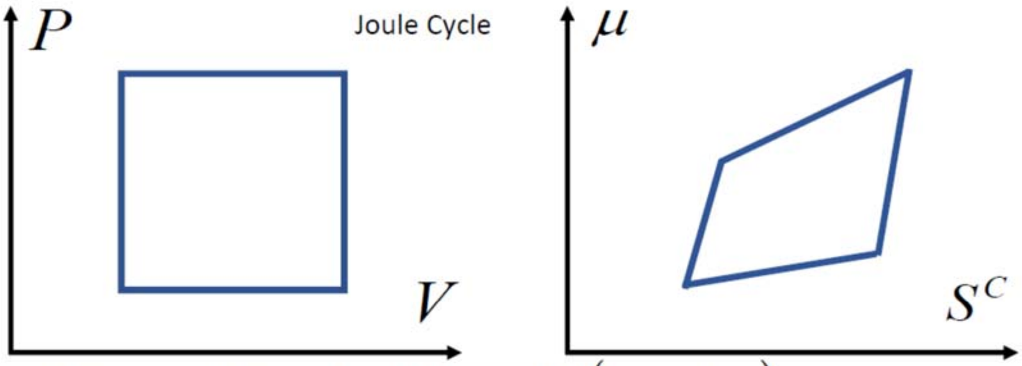


$$\delta M = \mu dS^{C} - \mu_{R} dS^{C} = dS^{C}\left(\mu - \mu_{R}\right)$$

OPEN SYSTEM (BULKFLOW)

$$= \mu dS^{C}\left(\frac{\mu - \mu_{R}}{\mu}\right) = \mu dS^{C}\left(1 - \frac{\mu_{R}}{\mu}\right) = \delta M\left(1 - \frac{\mu_{R}}{\mu}\right) = \delta W$$

CLOSED SYSTEM (NON-BULKFLOW)



$$\delta W = PdV - P_{R} dV = dV\left(P - P_{R}\right)$$

OPEN SYSTEM (BULKFLOW)

$$= PdV\left(1 - \frac{P_{R}}{P}\right) = \delta W^{REV}\left(1 - \frac{P_{R}}{P}\right) = dU^{M}\left(P\right)\cdot\left(1 - \frac{P_{R}}{P}\right) = \delta M$$

CLOSED SYSTEM (NON-BULKFLOW)

Figure 2.6b – Chemical Aspect of Cyclic Process

2.4.5.1. Thermal-Mechanical Conversion Cycles

Canonical Carnot and Joule conversion cycles are symmetric as opposite processes belong to the same type, namely isothermal and isobaric respectively. Opposite isothermal or isobaric processes imply heat input and work output and heat output and work input. Both cycles operate heat-to-work (direct) and work-to-heat (inverse) cycle conversion.

Constant Temperature: Heat Interactions Balance of Carnot Cycle with Adiabatic Processes

$$\delta Q = TdS^{T} - T_R\, dS^{T} = dS^{T}\left(T - T_R\right)$$

$$= TdS^{T}\left(\frac{T - T_R}{T}\right) = TdS^{T}\left(1 - \frac{T_R}{T}\right) = \delta Q\left(1 - \frac{T_R}{T}\right) = dU^{T}\left(T\right)\cdot\left(1 - \frac{T_R}{T}\right)$$

$$= \delta W = \oint_{CYCLE} - PdV$$

where $\eta^{T} = 1 - \frac{T_R}{T}$ is the conversion efficiency.

The counterproof is:

$$\delta Q\left(1 - \frac{T_R}{T}\right) = \delta Q\left(\frac{T_R}{T_R} - \frac{T_R}{T}\right) = T_R\left(dS_R^{T} - dS^{T}\right) = -T_R\left(dS^{T} - dS_R^{T}\right) = -T_R\, d\left(S^{T} - S_R^{T}\right)$$

$$= -\delta Q_R = -\delta W_R$$

Since, in this counterproof, the lower temperature T_R is evidenced out of the parenthesis, then the quantity $-\delta Q_R$ represents the heat interaction output released at the lower temperature of the cycle, hence to the reservoir at T_R.

Constant Pressure: Work Interactions Balance of Joule Cycle with Isovolumic Processes

$$\delta W = PdV - P_R dV = dV\left(P - P_R\right)$$

$$= PdV\left(1 - \frac{P_R}{P}\right) = \delta W^{REV}\left(1 - \frac{P_R}{P}\right) = dU^{M}\left(P\right)\cdot\left(1 - \frac{P_R}{P}\right) = \delta Q$$

It is noteworthy that, as shown in the Figure 2.4a, there is a symmetry of Carnot and Joule cycles, with respect to vertical axes (extensive state properties) if thermodynamic diagrams $P-V$ and $T-S^T$ are compared.

2.4.5.2. Chemical-Mechanical Conversion Cycles

Canonical Carnot and Joule conversion cycles can be operated considering that higher and lower isothermal processes can be replaced by isopotential processes along which mass interactions occurr. This means that semi-permeable membranes replace heat conduction devices and the work output is converted from the mass output, that is, from the chemical potential energy associated to high chemical potential constituent entering the system. In this case, opposite isopotential or isobaric processes imply mass input and work output and mass output and work input. Both cycles operate heat-to-work (direct) and work-to-heat (inverse) cycle conversion.

As far as mass interactions and mass-to-work conversion are concerned:

$$\delta M = \mu dS^C - \mu_R dS^C = dS^C (\mu - \mu_R)$$

$$= \mu dS^C \left(\frac{\mu - \mu_R}{\mu} \right) = \mu dS^C \left(1 - \frac{\mu_R}{\mu} \right) = \delta M \left(1 - \frac{\mu_R}{\mu} \right) = \delta W \quad \text{where} \quad \eta^C = 1 - \frac{\mu_R}{\mu}$$

Also in this case, the conterproof is:

$$\delta M \left(1 - \frac{\mu_R}{\mu} \right) = \delta Q \left(\frac{\mu_R}{\mu_R} - \frac{\mu_R}{\mu} \right) = \mu_R \left(dS_R^C - dS^C \right) = \delta M$$

Constant Pressure: Mass Interactions Balance of Carnot Cycle with Isomolar Processes

$$\mu dS^C - \mu_R dS^C = dS^C (\mu - \mu_R) = \mu dS^C \left(1 - \frac{\mu_R}{\mu} \right) = \delta M^{REV} \left(1 - \frac{\mu_R}{\mu} \right) = dU^C(\mu) \cdot \left(1 - \frac{\mu_R}{\mu} \right)$$

$$dEX^C = \mu \cdot dS^C \cdot \left(1 - \frac{\mu_R}{\mu} \right) = dS^C \cdot (\mu - \mu_R)$$

$$dS^C = \frac{dM}{\mu} \Rightarrow dM = \mu \cdot dS^C$$

Constant Potential: Work Interactions Balance of Joule Cycle with Isomassic Processes

$$\delta W = PdV - P_R dV = dV\left(P - P_R\right)$$

$$= PdV\left(1 - \frac{P_R}{P}\right) = \delta W^{REV}\left(1 - \frac{P_R}{P}\right) = dU^{M}\left(P\right)\cdot\left(1 - \frac{P_R}{P}\right) = \delta M$$

Similarly to the previous case, as shown in the Figure 2.4b, a symmetry of Carnot and Joule cycles, with respect to vertical axes (extensive state properties), appears if thermodynamic diagrams $P - V$ and $\mu - S^C$ are compared.

The symmetry here highlighted results by virtue of the construction of cycles based on different processes adopted in the Joule cycle for which isovolumic processes are used in lieu of adiabatic ones. It is noteworthy that this substitution completes and corroborates the symmetry with respect the Carnot cycle. In different terms, the symmetry results when considering axes $P - V$ versus axes $T - S^T$, and considering axes $P - V$ versus axes $\mu - S^C$.

2.5. Generalized Exergy of Closed and Open Systems

The definition of generalized exergy property is founded on those terms implied in the overall balance of entering and exiting exergy flow streams through the control volume defining the system under analysis. Hence, the generalized exergy is defined as the sum of all exergy components already defined in terms of useful work, useful heat and useful mass:

$EX^{G} = EX^{T} + EX^{C} + EX^{M}_{HEAT} + EX^{M}_{MASS}$ or, grouping terms relating to the type of interaction:

$$EX^{G} = EX^{PHISICAL} + EX^{CHEMICAL} + EX^{MECHANICAL}$$

In differential terms the above equations become:

$$dEX^{G} = dEX^{T} + dEX^{C} + dEX^{M}_{HEAT} + dEX^{M}_{MASS}$$

$$dEX^{G} = dEX^{PHISICAL} + dEX^{CHEMICAL} + dEX^{MECHANICAL}$$

$$= \delta W_{HEAT} + \delta W_{MASS} + \delta Q_{WORK} + \delta M_{WORK}$$

2.5.1. Exergy of Closed Systems

Assuming a closed system with only one constituent operating along a non-flow process, the canonical expression of exergy is the following:

$$EX^{G} = U - U_{R} = U^{INT} - T_{R}\left(S - S_{R}\right) - \mu_{R}\left(n - n_{R}\right) + P_{R}\left(V - V_{R}\right)$$

$$= U^{T} + U^{C} + U^{M} - T_{R}\left(S^{T} - S_{R}^{T}\right) - \mu_{R}\left(S^{C} - S_{R}^{C}\right) + P_{R}\left(S^{M} - S_{R}^{M}\right)$$

$$dEX^{G} = dU^{T} + dU^{C} + dU^{M} - d\left(T_{R}S^{T}\right) - d\left(\mu_{R}S^{C}\right) + d\left(P_{R}S^{M}\right)$$

However, properties related to the reservoir are constant, therefore:

$$dEX^{G} = dU^{T} + dU^{C} + dU^{M} - T_{R}\,dS^{T} - \mu_{R}\,dn + P_{R}\,dV$$

If Gibbs relation $dU = TdS^{T} + \mu dn - PdV$ is used

$$= TdS^{T} + \mu dn - PdV - T_{R}\,dS^{T} - \mu_{R}\,dn + P_{R}\,dV$$

hence:

$$\boxed{dEX^{G} = \underbrace{\left(T - T_{R}\right)dS^{T}}_{\eta^{\substack{DIRECT\\THERMAL}}} + \underbrace{\left(\mu - \mu_{R}\right)dn}_{\eta^{\substack{DIRECT\\CHEMICAL}}} - \underbrace{\left(P - P_{R}\right)dV}_{\eta^{\substack{INVERSE\\MECHANICAL}}} = dQ^{INT} + dM^{INT} + dW^{INT}}$$

This equation of the generalized exergy in differential terms is calculated for cyclic process. Nevertheless, it can be integrated and can be extended to non-cyclic processes.

Equivalent Expressions of Thermal Exergy

As far as the formulation of exergy is concerned, two different equations exist, relating to non-cyclic and cyclic processes of a closed nonflow system, that anyway are equivalent if compared with respect their calculation and application to a same process.

For a non-cyclic process:

$$EX^{T} = U_{1} - U_{0} - T_{R}\left(S^{T} - S_{R}^{T}\right) = \int_{1}^{0}\left(T - T_{R}\right)\cdot dS^{T}$$

For a cyclic process:

$$EX^T = \oint_{CYCLE} \left[U_1 - U_0 - T_R \left(S^T - S_R^T\right)\right] \cdot dS^T = Q\left(1 - \frac{T_R}{T}\right)$$

2.5.2. Exergy of Open Systems

The definision of exergy for open systems needs to account for entering and exiting flows from the external system and the associated components of exergy to be considered in the balance and the definition. The following Figure 2.7. describes all exergy flows being part of the generalized definition of exergy for an open system undergoing a bulk-flow process.

2.5.2.1. Thermal Exergy of Open Systems

The expression of thermal exergy for an open system is derived from the balance of entering and exiting mass through the control surface delimiting the whole system (machinery or any device). As usually resulting, the enthalpy appears in the expression to account for work interaction transmitted by flowing mass. Therefore:

$EX^T = H - T_R S^T$ and, in differential terms

$dEX^T = dH - T_R dS^T$ accounting for heat interactions only

$= dU + d\left(PV\right) - T_R dS^T$

Using the Gibbs relation $dU = TdS - PdV$

$= TdS - PdV + PdV + VdP - T_R dS^T$ hence

$dEX^T = \left(T - T_R\right) \cdot dS^T + VdP$

valid for non-cyclic processes.

2.5.2.2. Chemical Exergy of Open Systems

In analogy to the thermal exergy, the expression of chemical exergy for an open system is derived from the balance of entering and exiting mass through the control surface delimiting the whole system (machinery or any device or set of devices).

$EX^C = H - \mu_R S^C$ and, in differential terms,

$dEX^C = dH - \mu_R dS^C$ accounting for mass interactions only

$= dU + dPV - \mu_R dS^C$

Using the Gibbs relation $dU = \mu dS^C - PdV$

$= \mu dn - PdV + PdV + VdP - \mu_R dS^C$ hence

$dEX^C = (\mu - \mu_R) dS^C + VdP$

2.5.2.3. Mechanical Exergy of Open Systems

$$EX^M = A + P_R V$$

$dEX^M = dA + P_R dV$ accounting for work interactions only

$$= dU - d(TS) + P_R dV$$

Using the Gibbs relation $dU = TdS - PdV$

$$= TdS - PdV - TdS - SdT + P_R dV$$

$$dEX^M = -(P - P_R)dV - SdT$$

Generalized Exergy for Open Systems

Finally, the generalized expression of exergy property for open systems is the result of thermal, chemical and mechanical components and assumes the following form:

$$EX = U - T_R S - \mu_R n + P_R V$$

$$= U^T + U^C + U^M - T_R S^T - \mu_R S^C + P_R S^M$$

$$dEX = dU^T + dU^C + dU^M - d\left(T_R S^T\right) - d\left(\mu_R S^C\right) + d\left(P_R S^M\right)$$

However, properties related to the reservoir are constant, therefore

$$dEX = dU^T + dU^C + dU^M - T_R dS^T - \mu_R dn + P_R dV$$

$$= TdS^T + \mu dn - PdV - T_R dS^T - \mu_R dn + P_R dV$$

Hence:

$$dEX = \left(T - T_R\right)dS^T + \left(\mu - \mu_R\right)dn - \left(P - P_R\right)dV$$

$$\eta^{DIRECT}_{THERMAL} \qquad \eta^{DIRECT}_{CHEMICAL} \qquad \eta^{INVERSE}_{MECHANICAL}$$

Control Surface and Balance

The Control Surface (CS) identifies boundary limits of an internal system with respect to the external system (or environment) to be considered in the balance of entering and exiting exergy flows and other correlated properties involved in interactions between the two systems. The balance is here extended to thermal, chemical and mechanical aspects of properties and interactions to achieve a generalized relation applicable to any particular case. Following input and output flows through the control volume delimiting an open system are accounted for in the definition:

$$dEX_{IN}^{T} = \left(\delta W_{HEAT}^{AR\rightarrow}\right)_{IN}^{MAX} = dU_{IN}^{T} - T_R\, dS_{IN}^{T} + P_R\, dV_{IN}$$

$$dEX_{OUT}^{T} = \left(\delta W_{HEAT}^{AR\rightarrow}\right)_{OUT}^{MAX} = dU_{OUT}^{T} - T_R\, dS_{OUT}^{T} + P_R\, dV_{OUT}$$

$$dEX_{IN}^{C} = \left(\delta W_{MASS}^{AR\rightarrow}\right)_{IN}^{MAX} = dU_{IN}^{C} - \mu_R\, dS_{IN}^{C} + P_R\, dV_{IN}$$

$$dEX_{OUT}^{C} = \left(\delta W_{MASS}^{AR\rightarrow}\right)_{OUT}^{MAX} = dU_{OUT}^{C} - \mu_R\, dS_{OUT}^{C} + P_R\, dV_{OUT}$$

As far as the mechanical exergy, both components associated to heat and mass are considered as a unique input or output term:

$$dEX_{IN}^{M} = \left(\delta Q^{AR\rightarrow}\right)_{IN}^{MAX} + \left(\delta M^{AR\rightarrow}\right)_{IN}^{MAX} = dU_{IN}^{M} + P_R V_R\, dS_{IN}^{M}$$

$$dEX_{OUT}^{M} = \left(\delta Q^{AR\rightarrow}\right)_{OUT}^{MAX} + \left(\delta M^{AR\rightarrow}\right)_{OUT}^{MAX} = dU_{OUT}^{M} + P_R V_R\, dS_{OUT}^{M}$$

The overall exergy balance of a system confined in a control volume is represented in the following Figure 2.7 here after included:

$$dEX_{IN}^{T} = \left(\delta W_{HEAT}^{AR\rightarrow}\right)_{IN}^{MAX} = dU_{IN}^{T} - T_R dS_{IN}^{T} + P_R dV_{IN}$$

$$dEX_{IN}^{C} = \left(\delta W_{MASS}^{AR\rightarrow}\right)_{IN}^{MAX} = dU_{IN}^{C} - \mu_R dS_{IN}^{C} + P_R dV_{IN}$$

$$dEX_{IN}^{M} = \left(\delta Q^{AR\rightarrow}\right)_{IN}^{MAX} + \left(\delta M^{AR\rightarrow}\right)_{IN}^{MAX} = dU_{IN}^{M} + P_R V_R dS_{IN}^{M}$$

$$dEX_{OUT}^{T} = \left(\delta W_{HEAT}^{AR\rightarrow}\right)_{OUT}^{MAX} = dU_{OUT}^{T} - T_R dS_{OUT}^{T} + P_R dV_{OUT}$$

$$dEX_{OUT}^{C} = \left(\delta W_{MASS}^{AR\rightarrow}\right)_{OUT}^{MAX} = dU_{OUT}^{C} - \mu_R dS_{OUT}^{C} + P_R dV_{OUT}$$

$$dEX_{OUT}^{M} = \left(\delta Q^{AR\rightarrow}\right)_{OUT}^{MAX} + \left(\delta M^{AR\rightarrow}\right)_{OUT}^{MAX} = dU_{OUT}^{M} + P_R V_R dS_{OUT}^{M}$$

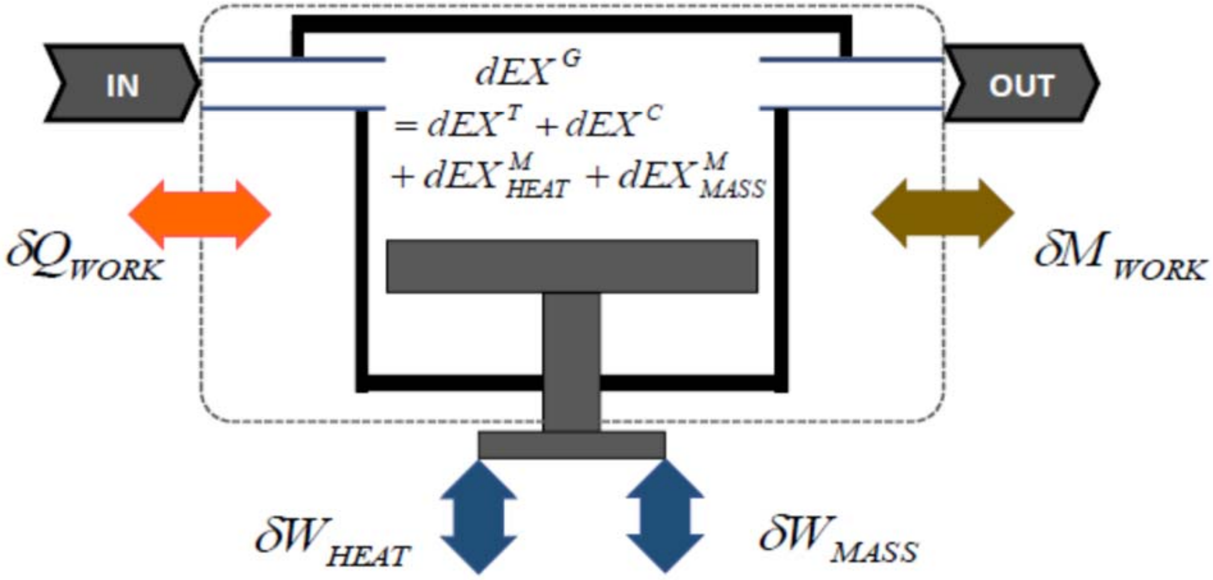


Figure 2.7 - Control Surface and Mass-Exergy Balance

There is a close analogy of the exergy balance with respect to energy balance for open systems. In this specific case too, it has been considered that the entering or exiting mass has its own exergy and conveys thermal, chemical and mechanical exergy exchanged with the external system or environment.

2.6. Exergy Dissipation or Exergy Destruction in Real Processes

Any real process implies that exergy is not conserved due to irreversible phenomena determining a dissipation or, in the current language, exergy destruction. The entropy-exergy relationship correlates the exergy destruction to the corresponding local entropy production and global entropy generation caused by any kind of thermal, chemical and mechanical irreversibility. This correlation is stated by the Gouy-Stodola theorem. A more detailed treatise of this theorem, in the framework of irreversible processes, is included in the section 4. specially dedicated to the non-equilibrium thermodynamics.

3. GENERALIZED THERMODYNAMIC ENTROPY

The rationale behind the elaboration of a generalized thermodynamic entropy is the attempt of defining entropy as the sum of entropy components associated to all forms of energy, energy transfers and interactions occurring in any process. Then, the physical meaning of this generalization consists of the significance of entropy as the "*degree of subdivision of any phenomena among all constituting elements of a system*". From this statement on, any physical observable is characterized by a "disintegration" (or "scattering" or "spreading"), and hence an entropy associated to related states and processes. This definition relies on the fact that entropy is a state and additive property of any system in any state, equilibrium (reversibility) and non-equilibrium (irreversibility). A simple proof of this definition can be found in the following consideration concerning mechanical internal energy transfer by means of the corresponding work interaction along and adiabatic reversible process, hence per se isoentropic in the canonical framework of Classical Thermodynamics. Once the weight process has started, the whole energy content initially concentrated in the system A immediately undergoes a partition between the two interacting entities, namely the internal system and the external useful system connected via the weight process device. This incipient partition is the event triggering the hierarchical, and reversible, "dissipation" process of the initial higher-density or non-dissipated energy content. It will be clarified later that this definition is valid for any "observable" describing any phenomena occurring in any system. Any type of energy flow and the interaction related to energy transfer between two systems is then thermodynamically characterized by the pertaining form of entropy associated to that interaction from macroscopic to microscopic and quantum level of system and phenomena description. This remark corroborates the trend of a large part of the scientific community in believing that entropy may represents the only physical essence of any other physical ontological or phenomenological entity.

An important caveat, already more than once underlined while discussing its definition, is that entropy, being an inherent property of matter [3.1,3.2], does not depend on any external reference system addressed to as a reservoir. This non-dependence was clarified and demonstrated assigning to the reservoir the function of an auxiliary system [3.3,3.4]. A step forward in this direction is the proof that entropy needn't have based on an auxiliary thermal reservoir that has been removed from thermodynamic entropy definition [3.5]. At the same time, Gaggioli pursued the idea that the external reference system is unnecessary in his study of 1998 [2.4] while discussing the available energy and exergy concepts. Meanwhile, the removal of reservoir from the definition of thermodynamic entropy has been confirmed in terms of a theorem inferred by the axiomatic proof provided by Beretta and Zanchini [3.5]. The logical procedure, adopted for this axiomatic proof, is applied to the thermal thermodynamic entropy related to thermal internal energy and the temperature. Nevertheless, from a formal standpoint, nothing prevents to replace the physical properties adopted in assumptions and postulated with ones pertaining to chemical and mechanical aspects removing the assumption limiting the theorem to a non-reacting system. This substitution would allow to validate the proof for any other property playing a role in the characterization of the state of a system, such as chemical potential and pressure in lieu of, or in addition to, temperature. In particular, the stable equilibrium of interacting systems used in the demonstration [3.5] is assumed with respect to the role of the temperature, though no specific mention is done to any other "driving force" that may determine a non-equilibrium state although stable equilibrium is postulated. Indeed, the equality of temperatures is assumed as the unique condition related to the stable equilibrium not considering that, instead, stable equilibrium does not occur with no additional equality of chemical potential and pressure. At this point, it appears the need of a bi-univocal logical inference between stable equilibrium and equality of temperature, potential and pressure jointly representing a generalized potential related to the generalized stable equilibrium a system. The bi-univocal character of this inference implies the necessity and the sufficiency of both conditions, that is, equilibrium and equality. This logical relationship deserves a more accurate investigation to ensure a rigorous axiomatic generalization of theorems derived from a proper extension of axioms and postulates. To do so, the definitions of chemical thermodynamic entropy and mechanical thermodynamic entropy, in addition to the thermal thermodynamic entropy, will be considered as the set of properties to be accounted for.

3.1. Theorem of Necessity and Sufficiency of Stable Equilibrium for Generalized Potential Equality between System and Reservoir

The theorem of necessity and sufficiency of stable equilibrium for the generalized potential equality between system and reservoir is the result of the attempt of extending the methodological schema, underpinning thermodynamics foundations, to all aspects, in particular mechanical, chemical, nuclear and sub-nuclear, besides the thermal aspect that usually represents the main paradigm.

3.1.1. Focus on the Theoretical Background and Main Objectives of the Theorem

The literature reports that equality of temperature, equality of potential and equality of pressure between a system and a reservoir are necessary conditions for the stable equilibrium of the system-reservoir composite or, in the opposite and equivalent logical inference, that stable equilibrium is a sufficient condition for equality. The aim and the first novelty of the present study is to prove that equality of temperature, potential and pressure is also a sufficient condition for stable equilibrium, in addition to necessity, implying that stable equilibrium is a condition also necessary, in addition to sufficiency, for equality. The second novelty is that the proof of the sufficiency of equality (or the necessity of stable equilibrium) is attained by means of the generalization of the entropy property, derived from the generalization of exergy property, which is used to demonstrate that stable equilibrium is a logical consequence of equality of generalized potential. This proof is underpinned by the Second Law statement and the Maximum-Entropy Principle based on generalized entropy which depends on temperature, potential and pressure of the reservoir. The conclusion, based on these two novel concepts, consists of the theorem of necessity and sufficiency of stable equilibrium for equality of generalized potentials within a composite constituted by a system and a reservoir.

3.1.2. Rationale of the Theorem and Reasons for It Is Needed

The interactions occurring within a composite constituted by a system A and a reservoir R determine the state of stable equilibrium which represents the foundation of the Second Law statement reported in the literature and in particular by Gyftopoulos and Beretta [1.9]. The reservoir is defined as an auxiliary system experiencing stable equilibrium states only [1.9]. The mutual stable equilibrium between system and reservoir implies the necessary conditions of equal temperature, chemical potential and pressure of the system-reservoir composite AR. Instead, the canonical definition of entropy, founded on this statement of the Second Law and derived from energy and available energy, is underpinned by the equality of temperature as the sole necessary condition for the stable equilibrium of AR and for this reason is based only on the constant temperature T_R of the reservoir. The chemical potential μ_R and pressure P_R of the reservoir do not appear in the formulation of entropy. A first aim is here to explore the possibility of generalizing the definition of exergy property, and consequently the definition of entropy, considering the equality of chemical potential $\mu = \mu_R$ and pressure $P = P_R$, within the system-reservoir composite, as further necessary conditions of mutual stable equilibrium in addition to equality of temperature and characterizing the definition of generalized entropy by μ_R and P_R in addition to T_R. The second aim is to demonstrate that equality of temperature, equality of potential and equality of pressure are conditions that are also sufficient for stable equilibrium and the proof is attained by means of the generalized entropy derived from the generalized exergy here defined, which is used to derive stable equilibrium as a logical consequence of the equality of generalized potentials.

The following analysis focuses on “simple systems” according to the terminology and definitions adopted by Gyftopoulos and Beretta [1.9] where the system can be large or small, even at molecular or atomic level, and can experience states of equilibrium and non-equilibrium. It is important to underline that the present study does not disprove any of the fundamentals reported in the literature, and on the contrary, based on those thermodynamic foundations, it extends the standpoint and generalizes the related definitions and properties.

The method adopted is based on the assumption that entropy is an inherent property of any system and equality of chemical potential and pressure between system and reservoir constitute necessary conditions of stable equilibrium of the system-reservoir composite, in addition to the equality of temperature. These additional conditions will therefore be accounted for in defining of the generalized exergy which implies that generalized entropy is derived according to the procedure based on the statement that entropy S is proportional to the difference between energy E and available energy Ω [1.9] according to the following expression:

$$\left(S_1 - S_0\right) = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right] \tag{3.1a}$$

and considering that the definition of exergy is directly correlated to the generalized available energy consequent to the generalized adiabatic availability [1.9], then:

$$\left(S_1 - S_0\right) = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right] \tag{3.1b}$$

in which C_R is a constant property depending on the reservoir only.

3.1.3. Thermal Stable Equilibrium as a Sufficient Condition (or Equality of Temperature as a Necessary Condition)

The canonical definition of physical exergy property is based on the amount of heat and work interaction occurring until the system is in a mutual stable equilibrium with the reservoir; in particular, the (thermal) exergy formulated as maximum net useful work, obtained by means of a weight process resulting from the difference of generalized available energy between the (variable) temperature T of system A and the (constant) temperature T_R of reservoir R, is as follows:

$$EX^{T} = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \Omega_1^R - \Omega_0^R \tag{3.2a}$$

$$EX^{T} = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^T = \left(U_1 - U_0\right) - T_R \cdot \left(S_1^T - S_0^T\right) + P_R \cdot \left(V_1 - V_0\right) \tag{3.2b}$$

The term $-T_R \cdot \left(S_1^T - S_0^T\right)$ represents the amount of heat released to the reservoir once the equality of temperature $T = T_R$ between system and reservoir has been achieved at thermal equilibrium.

The term $P_R \cdot \left(V_1 - V_0\right)$ expresses the amount of work released to the reservoir at constant pressure P_R differing from the (variable) pressure P of the system, since system and reservoir are not in mutual stable equilibrium even though the system-reservoir composite AR is in a stable (thermal) equilibrium state due to the equality of temperatures $T = T_R$.

According to the procedure reported in the literature [1.9], the (thermal) entropy is derived from the product of the factor $1/T_R$ times the difference between energy E and generalized available energy Ω which are both measurable properties, while entropy is not directly measurable:

$$\left(S_1 - S_0\right)^T = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^T \tag{3.3a}$$

and considering that (thermal) generalized available energy is directly correlated to thermal exergy, then:

$$\left(S_1 - S_0\right)^T = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^T \tag{3.3b}$$

It should be noted that this definition of entropy property depends solely on temperature T_R and does not include pressure P_R of the mechanical reservoir despite it is appearing in the definition of thermal exergy expressed by Equations (3.2a) and (3.2b) which constitute a term of equations (3.3a) and (3.3b).

Although equality of temperature is a necessary condition of mutual stable equilibrium derived from the Highest-Entropy Principle [1.9], this condition is not unique and therefore cannot be also termed sufficient. In fact, even when two interacting systems are in thermal stable equilibrium due to equal temperatures, these systems may experience (constraints removed) states of nonequilibrium due to a not null difference of (chemical) potential and or pressure. Therefore, equality of temperature, chemical potential and pressure between system and reservoir must constitute the set of necessary conditions ensured by the mutual stable equilibrium of a system-reservoir composite. However, the proof that equal potential and pressure are necessary conditions for stable equilibrium is founded on the Highest-Entropy Principle where the entropy property is defined with respect to a reservoir at constant temperature only [1.9]. Therefore, this Highest-(Thermal)-Entropy Principle should not be able to prove the necessity of potential and pressure because (thermal) entropy does not account for the difference between the potential and pressure of the system and the potential and pressure of the reservoir. Moreover, the procedure adopted to demonstrate the necessity of temperature equality does not explicitly refer to the temperature of reservoir T_R or an intermediate temperature T_{EQ} of equality between system and the reservoir at equilibrium. Hence, the definition of (thermal) entropy should require a generalization extended to the contributions of chemical entropy and mechanical entropy evaluated with respect to a reservoir at constant chemical potential μ_R and constant pressure P_R adopted in the procedure without any specific constraint of reservoir characteristics [1.9].

It is noteworthy that the canonical expression of thermal entropy is proved by means of the concept of impossibility of the Perpetual Motion Machine of the Second Kind (PMM2) which is a consequence of the Second Law expressing the existence and uniqueness of the stable equilibrium state [1.9]. The thermal aspect of entropy definition proof is based on the impossibility of the PMM2 performing a direct cycle converting an amount of heat interaction into work interaction without releasing heat at lower temperature to a thermal reservoir.

3.1.4. Chemical Stable Equilibrium as a Sufficient Condition (or Equality of Potential as a Necessary Condition)

A definition of chemical exergy is proposed by Kotas [2.7] as "The maximum work obtainable from a substance when it is brought from the environmental state to the dead state by means of processes involving interaction only with the environment". Indeed, such an environment is a system behaving as a chemical reservoir which can be characterized according to the definition proposed by Gyftopoulos and Beretta as a "reservoir with variable amounts of constituents". The maximum net useful work withdrawn from the system interacting with the reservoir undergoing a process from initial state 0 to final state 1, corresponding to the chemical exergy EX^C, is expressed by the following equation reported by Kotas [2.7]:

$$EX^C = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \overline{R}T_R \ln\frac{P_1}{P_0} \tag{3.4}$$

where the superscript “C” stands for “Chemical reservoir” since the composite of system and reservoir undergoes an interaction that can be defined as “mass interaction” determining a “useful work” until the system-reservoir composite is not in a state of stable equilibrium. Mass interaction is characteristic of chemical energy transfer and it is moved by the difference of chemical potential between the system and the chemical (isopotential) reservoir.

In the more general case of a mixture consisting of n chemical constituents, according to the definition reported by Moran and Sciubba [2.8]:

$$EX^{C} = \sum_{i}^{n} \left(W_{10}^{AR\rightarrow} \right)_{i}^{MAX} = \overline{R} T_{R} \sum_{i}^{n} x_{i,1} \ln \frac{x_{i,1}}{x_{i,0}} \tag{3.5}$$

where x_i represents the molar fraction of the $i-th$ constituent. The equality of chemical potentials is accounted for as a further necessary condition of mutual stable equilibrium between the system and the reservoir in addition to the equality of temperature [1.9]. This implies a definition of chemical entropy derived from chemical exergy and chemical energy according to the method previously adopted and the general definition of Equations (3.1a) and (3.1b). To do so, if the concept of generalized available (chemical) energy is again considered, the formulation of chemical exergy should be translated as the following expression:

$$EX^{C} = \left(W_{10}^{AR\rightarrow} \right)^{MAX} = \left(\Omega_{1}^{R} - \Omega_{0}^{R} \right)^{C} \tag{3.6a}$$

$$EX^{C} = \left(W_{10}^{AR\rightarrow} \right)^{MAX} = \left(EX_{1}^{R} - EX_{0}^{R} \right)^{C} \tag{3.6b}$$

Now that chemical exergy has been defined, and considering that energy and available energy are additive properties, chemical entropy is an additive property as well. Therefore, chemical entropy may be derived from the chemical potential and the generalized available (chemical) energy which depends on mass interaction:

$$\left(S_1 - S_0 \right)^{C} = \frac{1}{\mu_R} \left[\left(E_1 - E_0 \right) - \left(\Omega_{1}^{R} - \Omega_{0}^{R} \right) \right]^{C} \tag{3.7a}$$

and considering that a correlation between generalized chemical available energy and chemical exergy can be established:

$$\left(S_1 - S_0 \right)^{C} = \frac{1}{\mu_R} \left[\left(E_1 - E_0 \right) - \left(EX_{1}^{R} - EX_{0}^{R} \right) \right]^{C} \tag{3.7b}$$

which expresses the chemical entropy derived from (chemical) energy and chemical exergy, based on the equality of potential that constitutes a necessary condition for mutual stable equilibrium between the system and the chemical reservoir, in addition to equality of temperature [1.9]. This expression depends on the potential of reservoir μ_R and is formally analogous to the thermal entropy Equation (3.3a) and (3.3b). The term $1/\mu_R$ corresponds to the term $1/T_R$ in Equations (3.2a) and (3.2b), so that chemical stable equilibrium is the result of the necessary condition of chemical potential equality between the system and chemical reservoir, given the equality of temperature and pressure of the system-reservoir composite.

3.1.5. Mechanical Stable Equilibrium as a Sufficient Condition (or Equality of Pressure as a Necessary Condition)

The weight process constitutes a device adopted to measure the maximum net useful work extracted from a system A releasing a corresponding minimum non-useful heat to a (thermal) reservoir R^T at constant temperature T_R according to the definition of generalized available energy and thermal exergy here adopted. The inverse (and reversible) process requires the weight process to be the minimum net useful work released to A and extracting a corresponding maximum non-useful heat from R^T. Nevertheless, the weight process can also be regarded as an interaction suitable for calculating the minimum non-useful work $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$, released by system A to the (mechanical) reservoir R^M at constant pressure P_R, associated to the maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ which, in this symmetric process, can be referred to as mechanical exergy EX^M [3.6]. In this case, the weight process occurs through the interaction of system A with mechanical reservoir R^M until the difference of pressure between system and reservoir is null. Due to the fact that the non-useful work is released interacting with the mechanical reservoir, it may be inferred that work, such as heat, is no longer useful since it constitutes the non-convertible component of generalized available energy of the system interacting with the mechanical reservoir.

To summarize, the mechanical exergy property accounts for the maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ extracted from system A releasing the minimum non-useful work to the mechanical reservoir. System A interacts with a mechanical reservoir behaving as an isobaric reservoir R^M. Then, with the symbol EX^M adopting the superscript “M” standing for “Mechanical”:

$$EX^M = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)^M \tag{3.8a}$$

$$EX^M = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^M \tag{3.8b}$$

This relation expresses the amount of generalized available (mechanical) energy of system A converted into heat interaction $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ at higher variable temperature with respect to the thermal reservoir R^T at lower constant temperature T_R. On the other hand, $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ results from the minimum amount of work interaction $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ released to the mechanical reservoir along the isothermal process where the heat interaction is withdrawn from the thermal reservoir to be converted into $\left(Q_{10}^{AR\to}\right)^{MAX}$. The minimum amount of non-useful work interaction, corresponding to the maximum net useful heat withdrawn, at constant temperature T_R, from the thermal reservoir and converted into useful heat at higher temperature, is expressed as follows:

$$\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M = \left(W_{10}^{AR\to}\right)^{MIN}$$

$$= \overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right) \tag{3.9}$$

The term $\overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right)$ equals the (theoretically minimum) amount of work released to the reservoir and is equal to the low temperature heat, withdrawn from the thermal reservoir, converted into high temperature heat $\left(Q_{10}^{AR\to}\right)^{MAX}$.

The definition of mechanical exergy formulated by Equations (3.8a) and (3.8b) is the basis for deriving the expression on mechanical entropy using the same procedure adopted for thermal exergy and thermal entropy:

$$\left(S_1 - S_0\right)^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M \tag{3.10a}$$

taking into account the relationship between generalized mechanical available energy and mechanical exergy:

$$\left(S_1 - S_0\right)^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M \tag{3.10b}$$

the Equation (3.9) $\overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right)$, substituted in the former relation, implies the expression of mechanical entropy [3.6]:

$$\left(S_1 - S_0\right)^M = \overline{R}\left(\ln V_1 - \ln V_0\right) \tag{3.11}$$

This expression is a consequence of the Second Law and the stable equilibrium state in a system-reservoir composite AR. The condition of pressure equality between system and reservoir might prove, using the Highest-(Mechanical)-Entropy Principle, to be an additional necessary condition of mutual stable equilibrium between system and reservoir that needs to be complied, with the equality of temperature and potential to ensure the equilibrium status of the composite system-reservoir as a whole.

The Second Law implies the impossibility of a Perpetual Motion Machine of the Second Kind (PMM2) performing, in this case, an inverse cycle so that it may be expressed as the impossibility for available energy to be transferred from a reservoir at lower pressure P_R to a system at higher pressure P without the contribution of heat interaction. This inverse PMM2 can consequently represent a statement to prove mechanical entropy definition by using the same method adopted to derive the entropy property from the Second Law principle.

3.1.6. Generalized Exergy Related to Reservoir States

The definition of exergy is characterized by the property of additivity because it is defined with respect to an external reference system or to an internal part of the system itself behaving as a reservoir. The definition of a thermo-chemical-mechanical reservoir characterized by constant temperature, chemical potential and pressure implies the property of additivity of the components that constitute the generalized exergy so that:

$$EX^G\left(T, T_R, \mu, \mu_R, P, P_R\right) = EX^T\left(T, T_R\right) + EX^C\left(\mu, \mu_R\right) + EX^M\left(P, P_R\right) \tag{3.12}$$

The additivity of the entropy property can be proved considering the additivity of energy and generalized available energy. On the basis of the additivity of the entropy property, the generalized entropy results from the sum of entropy components each derived from the corresponding exergy component related to the (generalized) potential constituted by temperature, chemical potential and pressure. Therefore, the generalized entropy S^G can be expressed as [3.7]:

$$S^G = S^G\left(T, \mu, P\right) = S^T\left(T\right) + S^C\left(\mu\right) + S^M\left(P\right) \tag{3.13}$$

The generalized entropy is derivable from the generalized exergy if, and only if, the system is in stable equilibrium with a generalized reservoir. This condition implies equality of temperature, chemical potential and pressure between system and reservoir which becomes a set of necessary conditions for the stable equilibrium state of the system-reservoir composite.

3.1.7. Stable Equilibrium as a Necessary and Sufficient Condition for Generalized Potential Equality

One of the most recent statements of the Second Law consists of the existence and uniqueness of stable equilibrium [1.9]. This statement implies that all subsystems of a whole system have to be individually in stable equilibrium and the composite of all subsystems mutually interacting with each other has to satisfy the condition of stable equilibrium as well. On the other hand, entropy property is a consequence of the Second Law founded on stable equilibrium which implies that equality of potential and equality of pressure are additional necessary conditions consequent to stable equilibrium, however potential and pressure of the reservoir do not appear in the definition of entropy property mentioned above. In fact, the formulation of entropy here referred to, is correlated solely to the equality of temperature between system and reservoir and indeed depends solely on the temperature of reservoir T_R. As a further consideration, the proof that potential and pressure are additional necessary conditions of stable equilibrium is based on the Highest-Entropy Principle whereas the definition of entropy is related to equality of temperature only and does not include potential and pressure [1.9]. The reason is that the proof is general, while the concept of entropy has not been generalized as well to comply with the proof procedure. Therefore, there is an apparent inconsistency which may be resolved by means of a generalization of the entropy definition proposed in the previous section.

According to the proof theory, deriving a thesis from a hypothesis implies the logical proof that a hypothesis is sufficient and, vice versa, deriving the hypothesis from the thesis leads to the logical proof that a hypothesis is necessary.

The proof that equality of temperatures, potentials and pressures within the whole composite system-reservoir are necessary condition of stable equilibrium, hence "Equilibrium => Equality", is described by Gyftopoulos and Beretta [1.9] who adopt the Highest-Entropy Principle to prove that temperature-potential-pressure equality is the consequence of individual-and-interacting stable equilibrium.

With an opposite logical procedure, Gaggioli adopts the Lowest-Energy Principle to prove that individual-and-interacting stable equilibrium implies temperature-potential-pressure equality [2.4]. Therefore, the stable equilibrium is a sufficient condition for equality, hence, once again, "Equilibrium => Equality". However, since sufficiency of equilibrium (or necessity of equality) is the sole condition established and proved and, on the other hand, the necessity of stable equilibrium is not proved, then the system-reservoir composite may experience equality of the temperatures, potentials and pressures while the composite itself is not in a stable (or neutral) equilibrium state since the equilibrium is not necessary as well (or equality is not sufficient as well) in contradiction to the assumed stable equilibrium. To resolve this contradiction, reference can be made to the thermal, chemical, mechanical contributions of exergy, which is an additive property, so that the sum of these contributions constitutes generalized exergy as the base for deriving generalized entropy, which is an additive property as well, as demonstrated in previous section above. The only procedure to prove the necessity and sufficiency, without disproving the proofs already provided in the literature, is consequently to demonstrate that equalities (or equilibrium) are necessary and sufficient conditions, thus Gaggioli's statement is also necessary and Gyftopoulos and Beretta's statement is also sufficient, both implying that the inference equality => equilibrium is complementary to the inference equilibrium => equality so that both equilibrium and equality are necessary and sufficient conditions for each other. In different terms, equilibrium is true if and only if equality is true and equality is true if and only if equilibrium is true. Figure 1 represents the hierarchical structure of the statement of necessity and sufficiency conditions.

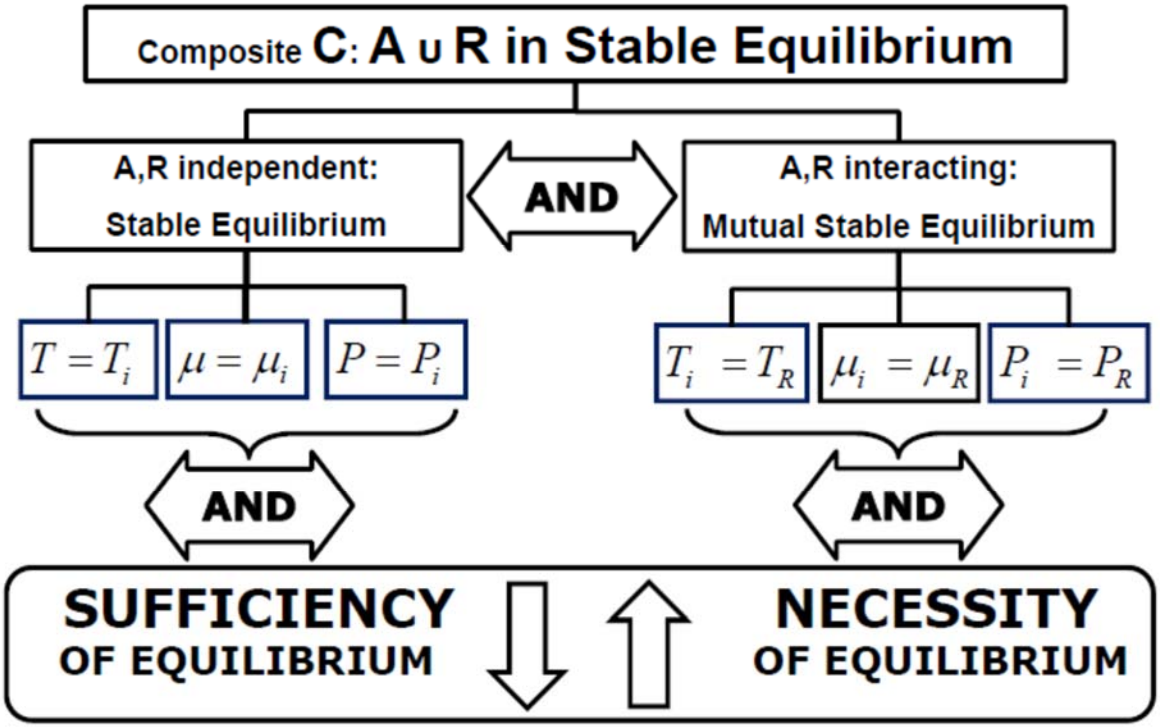


Figure 3.1 – Hierarchical structure of necessity and sufficiency conditions

Thus, Gaggioli adopts the Lowest-Energy Principle and Gyftopoulos and Beretta adopt the Highest-Entropy Principle, and since entropy depends on the difference between energy and generalized available energy as per Equations (3.1a) and (3.1b) which imply the First Law and Second Law respectively, then entropy remains the suitable quantity to attain the proofs of sufficiency as well as necessity. Therefore, entropy property should account for potential and pressure, in addition to temperature in order to constitute the procedure for such a proof. $E = E\left(S^G, n, \beta\right)$ Lowest-Energy Principle ⇔ $S^G = S^G\left(E, n, \beta\right)$ Highest-Entropy Principle. The two principles are mutually correlated to each other. In fact, the Stable-Equilibrium-State Principle establishes the mathematical relationship among all system properties. This relationship also exists between the Lowest-Energy Principle and the Highest-Entropy Principle which are intrinsic to the Stable-Equilibrium-State Principle as stated by the fundamental relations as follows [1]:

$$dE = \left[\left(\frac{\partial E}{\partial S}\right)_{n,\beta}\right]_0 dS + \sum_{i=1}^{r}\left[\left(\frac{\partial E}{\partial n_i}\right)_{S,n,\beta}\right]_0 dn_i + \sum_{j=1}^{s}\left[\left(\frac{\partial E}{\partial \beta_j}\right)_{S,n,\beta}\right]_0 d\beta_j \tag{3.14a}$$

$$dS = \left[\left(\frac{\partial S}{\partial E}\right)_{n,\beta}\right]_0 dE + \sum_{i=1}^{r}\left[\left(\frac{\partial S}{\partial n_i}\right)_{E,n,\beta}\right]_0 dn_i + \sum_{j=1}^{s}\left[\left(\frac{\partial S}{\partial \beta_j}\right)_{E,n,\beta}\right]_0 d\beta_j \tag{3.14b}$$

The proof of the necessity of stable equilibrium (or the sufficiency of generalized potential equality) consists of deriving stable equilibrium from equality and may be established "ad absurdum" assuming that temperatures, potentials and pressures of system and reservoir are equal while the system-reservoir composite is not in stable equilibrium. Indeed, this condition is admitted by the sufficiency of stable equilibrium as the only inference which does not "necessarily" imply that stable equilibrium is a consequence of equality of temperature, potential and pressure in the system-reservoir composite so that the equality may be compatible with nonequilibrium. This equality of generalized potential would thus be able to move the system into a nonequilibrium state without undergoing any net change of the environment, or that would be able to generate a weight process according to a PMM2 which is impossible according to the Second Law statement based on stable equilibrium as assumed. The consequence is that equality must imply stable equilibrium, that is, equality must be a sufficient condition for stable equilibrium (or stable equilibrium must be a necessary condition for equality). The proof of this sufficiency can be based on the Highest-Generalized-Entropy Principle where generalized entropy depends on temperature, potential and pressure of reservoir $S^G = S^G(T, \mu, P) = S^T(T) + S^C(\mu) + S^M(P)$. Having assumed the equality of generalized potential between system and reservoir, generalized entropy has to assume the highest value and the system is thus at stable equilibrium.

3.1.8. Results

Results of the present study consist of a proposal to encompass the Second Law statement by a bi-univocal logical relationship between the stable equilibrium of a system-reservoir composite, assumed as a hypothesis, and the generalized potential equality derived as the thesis of a theorem. The outset is that the literature reports the equality of temperature, potential and pressure between a system and a reservoir as a necessary condition for stable equilibrium of the system-reservoir composite or, in the opposite and equivalent logical inference, that stable equilibrium is a sufficient condition for equality. The method adopted consists of the analysis of the logical relationship between stable equilibrium and equality of generalized potential correlated by the Maximum-Entropy Principle. The first result is the proof that equality of temperature, potential and pressure is also a sufficient condition, in addition to be necessary, for stable equilibrium implying that stable equilibrium is also a necessary condition, in addition to be sufficient, for equality of generalized potential. The second result is that the proof can be achieved if and only if the generalized entropy definition is assumed, which is used to demonstrate that stable equilibrium is a logical consequence of equality of generalized potentials. This proof is underpinned by the Second Law statement conceived in terms of existence and uniqueness of stable equilibrium and using the Maximum-Generalized-Entropy Principle based on the generalized entropy property. The conclusion, derived from these two novel concepts, is stated in terms of the theorem of necessity and sufficiency of stable equilibrium for equality of generalized potentials within a composite constituted by a system and a reservoir.

The necessity and sufficiency of stable equilibrium here enunciated, constitutes a theorem characterized by the bi-univocal logical relationship which renders the theorem valid for both stable equilibrium and generalized potential equality. This theorem represents a rigorous rationale to corroborate the implication between the thermodynamic equilibrium or non-equilibrium state of a system and the intensive properties represented by the thermodynamic potentials, or dynamic driving forces, moving any kind of interaction between two systems or two portions of the same system.

3.2. Highest-Generalized-Entropy Principle for Stable Equilibrium and Non-Equilibrium

The method adopted assumes the equality of temperature, chemical potential and pressure of the composite system-reservoir AR as necessary conditions for mutual stable equilibrium [3.8]. The formulation of the entropy property is derived from exergy, related to a reservoir at constant temperature, constant pressure and constant chemical potential. The reservoir is an auxiliary system only as entropy is an inherent property of any system in any state as assumed. The procedure assumes macroscopic systems as a whole. Instead, microscopic analysis will be pursued to formulate entropy property definition in the perspective of Kinetic Theory of Gases to derive exergy property formulation accounting for microscopic entropy definition. This set of generalized potentials equality constitutes a necessary and sufficient condition for the stable equilibrium of a composite system-reservoir consistent with the Second Law statement [3.8].

3.2.1. Background and Premises

The literature reports that Second Law statement can be enunciated in terms of existence and uniqueness of stable equilibrium for a given value of energy content, compatible with a given composition of constituents and compatible with a given set of parameters of any system A. This statement implies that each subsystem of a whole system has to be individually in stable equilibrium and that the composite of all subsystems mutually interacting with each other has to be in stable equilibrium as well. Stable equilibrium is proved to be a sufficient condition for equality of temperature, equality of potential and equality of pressure, or thermodynamic potentials, in many-particle systems interacting with an external reservoir R by heat, mass and work mutual exchange. Considering the inverse logical inference, the sufficiency of stable equilibrium for equality of thermodynamic potentials is equivalent to the necessity of equality of temperature, potential and pressure, inside the system and between system and reservoir, for stable equilibrium of the composite system-reservoir AR. The proof of sufficiency of stable equilibrium, or equality of thermodynamic potentials, is achieved by Gaggioli through the Lowest-Energy Principle [2.4] and also by Gyftopoulos and Beretta through the Highest-Entropy Principle [1.9].

The Second Law implies the definition of thermodynamic entropy property for a composite resulting from a system A and a reservoir R mutually interacting to determine the state of stable equilibrium of the composite AR [2]. The canonical definition of thermodynamic entropy can be proved by means of the concept of Perpetual Motion Machine of the Second Kind (PMM2) in turn representing a consequence to Second Law statement founded on existence and uniqueness of stable equilibrium [2]. The definitions of thermodynamic entropy reported in the literature are based on the temperature as the unique intensive property, or thermodynamic potential, which specifically characterizes heat interactions. At stable equilibrium, temperature has to be equal in all points of space region occupied by a system and the proof is achieved by the Highest-Entropy Principle. Besides, potential and pressure are additional necessary conditions, for stable equilibrium, to equality of temperature and, for potential and pressure necessity too, the proof is based again on the same Highest-Entropy Principle [2]. Thus, the existence and uniqueness of stable equilibrium implies PMM2 used to define entropy expressed by the temperature which, instead, does not represents the unique thermodynamic potential to be equal in the system for stable equilibrium. Therefore, potential and pressure are necessary conditions for stable equilibrium in addition to temperature, however potential and pressure do not appear neither in the canonical expression of thermodynamic entropy, nor in the Highest Entropy Principle. This logical inconsistency represents the outset of this research and its resolution is the objective to be achieved.

3.2.2. Assumptions and Method

The present analysis focuses on a many-particle system denoted as A constituted by particles interacting each other through inter-particle potential energy, here addressed to as potential, and inter-particle kinetic energy, namely temperature, determined by particles relative position and velocity respectively, and constituting the system configuration at any state. The thermodynamic state of A can be global equilibrium or global non-equilibrium.

The reservoir R consists of an auxiliary system behaving at constant temperature T_R , constant potential μ_R and constant pressure P_R while interacting with A and experiencing stable equilibrium states only. R is assumed to be any subsystem or external system, or a combination of the two, not limited to the environment and moving throughout constant equality of all potentials and for this reason here defined as generalized reservoir.

The method adopted is based on the generalized expression of entropy property $\left(S_1-S_0\right)^G=\frac{1}{C_R}\left[\left(E_1-E_0\right)^T+\left(E_1-E_0\right)^C+\left(E_1-E_0\right)^M-\left(\Omega_1^R-\Omega_0^R\right)^T-\left(\Omega_1^R-\Omega_0^R\right)^C-\left(\Omega_1^R-\Omega_0^R\right)^M\right]$ where C_R is a positive and constant parameter depending on the characteristics of the generalized reservoir only , E is the energy of the system and Ω represents the generalized available energy of the composite AR so that, again in this generalized configuration, entropy remains an inherent property of any system, large or small, valid for equilibrium and non-equilibrium states where the function of the generalized reservoir is only auxiliary.

The set of necessary conditions for stable equilibrium consisting of equality of temperature $T=T_i$, $T_i=T_R$, equality of potential $\mu=\mu_i$, $\mu_i=\mu_R$ and equality of pressure $P=P_i$, $P_i=P_R$, where i represents the $i-th$ subsystem of the whole system, will be accounted for in defining the generalized entropy deduced from generalized exergy property. If reference is made to a generalized reservoir, then the definition of exergy EX^R results correlated to the generalized available energy Ω^R which is considered a particular case of generalized adiabatic availability Ψ^R [2], hence:

$$\left(S_1-S_0\right)^G$$
$$=\frac{1}{C_R}\left[\left(E_1-E_0\right)^T+\left(E_1-E_0\right)^C+\left(E_1-E_0\right)^M-\left(EX_1^R-EX_0^R\right)^T-\left(EX_1^R-EX_0^R\right)^C-\left(EX_1^R-EX_0^R\right)^M\right] \tag{3.15}$$

This definition of thermodynamic entropy is underpinned by equal temperature as the sole necessary condition for the stable equilibrium of AR and for this reason is based only on the constant temperature T_R of the reservoir [3,4]. Instead, the stable equilibrium implies the necessary conditions of equal potential and equal pressure, in addition to equal temperature, of two interacting systems, nevertheless chemical potential μ_R and pressure P_R of the reservoir do not appear in the definition of entropy property. To resolve this inconsistency, the definition of entropy will be generalized so that equality of potential and equality of pressure will be accounted for as necessary conditions of stable equilibrium in addition to equality of temperature to account for μ_R and P_R in addition to T_R . The definition of generalized entropy will be obtained from the generalized exergy here defined and underpins the statement of the Highest-Generalized-Entropy Principle suitable to infer that equality of temperature, equality of potential and equality of pressure are conditions also sufficient for stable equilibrium, in addition to necessity. The proof accounts for independent thermal, chemical and mechanical contributions to the generalized entropy associated to heat, mass and work interactions respectively.

Finally, the proof of definition of entropy property in which $C_R = T_R$ [1.9], is based on the concept of Perpetual Motion Machine of the Second Kind (PMM2) representing a consequence of Second Law statement. A specific characterization of PMM2 will be used to demonstrate that C_R is also proportional to μ_R or P_R .

3.2.3. Necessity and Sufficiency of Temperature Equality (or Sufficiency and Necessity of Thermal Stable Equilibrium)

The canonical definition of physical exergy property is based on the amount of heat and work interactions occurring until the system reaches the mutual stable equilibrium with the reservoir. In particular, the (thermal) exergy between two thermodynamic states $(0,1)$ connected by a process $(1 \rightarrow 0)$, is $EX^T = \left(EX_1^R - EX_0^R\right)^T = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \Omega_1^R - \Omega_0^R$ and corresponds to the maximum net useful work, obtained by means of a weight process resulting from the difference of generalized available energy between the (variable) temperature T of system A and the (constant) temperature T_R of a reservoir R .

Physical exergy canonical definition reported in the literature is $EX^T = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^T = \left(U_1 - U_0\right) - T_R \cdot \left(S_1^T - S_0^T\right) + P_R \cdot \left(V_1 - V_0\right)$ where the term $-T_R \cdot \left(S_1^T - S_0^T\right)$ constitutes the exergy loss corresponding to the amount of heat released to the reservoir once the equality of temperature $T = T_i$, $T_i = T_R$ between system and reservoir has been achieved at thermal equilibrium. The term $P_R \cdot \left(V_1 - V_0\right)$ expresses the amount of work released to the reservoir at constant pressure P_R differing from the (variable) pressure P of the system, as the composite system-reservoir AR is not in stable equilibrium even though AR is in a (restricted) thermal stable equilibrium state due to the equality of temperatures.

According to the procedure reported in the literature [2], thermodynamic (thermal) entropy is defined as $\left(S_1 - S_0\right)^T = \dfrac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^T$ and, taking into account the above mentioned relationship between (thermal) generalized available energy Ω^R and (thermal) physical exergy EX^R :

$$\left(S_1 - S_0\right)^T = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^T \tag{3.16}$$

The above equation of entropy is associated to, and is determined by, heat interaction of system A with the reservoir R at temperature T_R and for this very reason is here specified as thermal entropy. This definition of thermal entropy is proved by means of the impossibility of the PMM2 to perform a direct ideal cycle converting a total amount of heat into work with no heat released at lower temperature or, in other terms, without net effects on the external system. Being energy and generalized available energy defined for equilibrium and non-equilibrium states, thermodynamic entropy is valid for any state as well [1.9, 3.1-3.5].

The expression of thermal entropy property depends solely on temperature T_R and does not include pressure P_R despite it appears in the definition of thermal exergy property and despite pressure equality $P = P_R$ represents a necessary condition of stable equilibrium in addition to temperature equality $T = T_R$. Although the equality of temperature is a necessary condition of stable equilibrium derived through the Highest-(Thermal)-Entropy Principle, this condition is not unique. In fact, even when two interacting systems are in thermal stable equilibrium due to equal temperatures, these systems can experience (constraints removed) states of non-equilibrium due to a not null difference of potential and or pressure between system and reservoir or between two different portions of matter (or sub-systems). Therefore, equality of temperature has to be added to the equality of potential and equality of pressure between system and reservoir and all these equalities have to jointly constitute the set of necessary conditions ensured by the stable equilibrium of a system-reservoir composite. Whilst entropy property being defined solely with respect to the constant temperature of the reservoir T_R , the proof that equal potential and equal pressure are additional necessary conditions for stable equilibrium is founded on the Highest-(Thermal)-Entropy Principle [1.9] which is correlated to the Lowest-(Thermal)-Energy Principle. The reason is that Second Law states the existence and uniqueness of stable equilibrium for each given value of energy related to entropy which is a consequence of Second Law itself. In fact, the fundamental relation of Stable-Equilibrium-State Principle establishes the relationship between energy and entropy, and in particular, energy depending on temperature, potential and pressure within the system at stable equilibrium as reported by Gyftopoulos and Beretta [1.9]:

$dE = \left[\left(\frac{\partial E}{\partial S}\right)_{n,\beta}\right]_0 dS + \sum_{i=1}^{r}\left[\left(\frac{\partial E}{\partial n_i}\right)_{S,n,\beta}\right]_0 dn_i + \sum_{j=1}^{s}\left[\left(\frac{\partial E}{\partial \beta_j}\right)_{S,n,\beta}\right]_0 d\beta_j$, and entropy depending on temperature, potential and pressure as well being the inverse equation of the former:

$dS = \left[\left(\frac{\partial S}{\partial E}\right)_{n,\beta}\right]_0 dE + \sum_{i=1}^{r}\left[\left(\frac{\partial S}{\partial n_i}\right)_{E,n,\beta}\right]_0 dn_i + \sum_{j=1}^{s}\left[\left(\frac{\partial S}{\partial \beta_j}\right)_{E,n,\beta}\right]_0 d\beta_j$. However, the Highest-(Thermal)-Entropy Principle couldn't be able to prove the necessity of equal potential and equal pressure since the canonical definition of (thermal) entropy does not account for the equal potential $\mu = \mu_i$, $\mu_i = \mu_R$ and equal pressure $P = P_i$, $P_i = P_R$ and does not make reference to independent mass interaction or work interaction between system and reservoir. On the other hand, since the proof of necessity of equal temperature does not explicitly refer to the temperature of reservoir T_R (or an intermediate equal temperature at stable equilibrium between system and a subsystem behaving as a reservoir), then entropy used in Highest-(Thermal)-Entropy Principle is intended to be valid also for potential and pressure [1.9]. Hence, the definition of entropy should require a generalization extended to mass and work interactions in order to account for the independent contributions of chemical entropy and mechanical entropy, in addition to the thermal entropy, evaluated with respect to a reservoir at constant potential μ_R and constant pressure P_R to validate its applicability to non-equilibrium states caused by potential and pressure non-equality between system and reservoir.

It is noteworthy that the necessity of equal temperatures within the composite AR implies that the assumption of stable equilibrium determines solely equal temperature and not necessarily equal potential and equal pressure which, therefore, do not ensure stable equilibrium itself as, instead, is assumed. Hence, equality of potential and equality of pressure have to become necessary conditions to be satisfied jointly with equality of temperature. Once equal temperature, potential and pressure within AR are assumed as a set of necessary conditions, then this set of conditions has to be proved to be also sufficient. Therefore, these equality conditions have to be necessary and sufficient with the consequence that stable equilibrium has to be sufficient and necessary condition as well. Thus, stable equilibrium is proved to be a necessary condition if it is derived from equality of temperature, equality of potential and equality of pressure, here addressed to as equality of generalized potential, within AR composite. This bi-univocal logical inference represents the objective of this study and will be proved in following sections.

From differential standpoint, if reference is made to the canonical definition of entropy property $dS^T = \frac{\delta Q}{T} = \frac{dE_R^T}{T_R}$ the term $1/T$ or $1/T_R$ constitutes the integrating factor which makes the heat interaction an exact differential according to Pfaff theorem and Schwarz relation. In fact, considering a process characterized by both heat interaction and work interaction, the Gibbs equation for an ideal gas is $dU = \delta Q + \delta W$ which, by virtue of the state equation $PV = n\overline{R}T$ becomes $dU = C_V dT + 0 \cdot dV$ or $dU = 0 \cdot dT + (\overline{R}T/V) \cdot dV$, is an exact differential. Instead, δQ and δW are not individually exact differential. Indeed, applying the Schwarz relation to the expression $\delta Q = C_V dT + (\overline{R}T/V) \cdot dV$ it follows that $\partial C_V / \partial V = 0$ and $\partial\left(\overline{R}T/V\right)/\partial T = \overline{R}/V \neq 0$ thus the Schwarz relation does not hold and δQ is not a state property. As known, multiplying the expression of δQ by the integrating factor $1/T$ then the ratio $\delta Q/T$ becomes the definition of thermal entropy which is a state property.

3.2.4. Necessity and Sufficiency of Potential Equality (or Sufficiency and Necessity of Chemical Stable Equilibrium)

Stable equilibrium is proved to be a sufficient condition for equality of potential between two interacting systems, in addition to equality of temperature and pressure. The proof reported in the literature assumes stable equilibrium, for a given energy content, to derive equality of potential using the Highest-(Thermal)-Entropy Principle where entropy depends solely on T_R [1.9]. However, potential of the reservoir, and therefore equality of potential, is not accounted for in the definition of entropy property expressed in

Equation (3.2). Since stable equilibrium is achieved once equality of potential is a condition verified in addition to equality of temperature and pressure (restricted stable equilibrium), then entropy equation should include the contribution of chemical entropy, associated to and determined by mass interaction and defined with respect to μ_R and the equality of system and reservoir potential $\mu = \mu_i$, $\mu_i = \mu_R$, in addition to the contribution of thermal entropy associated to heat interaction.

A system A with n chemical constituents is considered interacting with a chemical reservoir R assuming restricted stable equilibrium in the composite system-reservoir undergoing processes at equal temperature and pressure but different chemical potential so that mass can flow from system to the reservoir characterized by variable amount of constituents. The maximum net useful work withdrawn from A interacting with R, undergoing a process from initial state 0 to final state 1, until the system-reservoir composite AR reaches the chemical stable equilibrium state, corresponds to the chemical exergy EX^C, expressed by the following equation reported by Kotas [2.7]: $EX^C = \left(W_{10}^{AR\to}\right)^{MAX} = \overline{R}T_R \ln \frac{P_1}{P_0}$ where the superscript “C” stands for “Chemical reservoir” since the composite of system and reservoir undergoes a “mass interaction” determining a “useful work”. Mass interaction is characteristic of chemical energy transfer and it is moved by the difference of chemical potential between the system and the chemical reservoir. For this reason, the expression of chemical exergy reported by Moran and Sciubba [9] can be expressed as: $EX^C = \sum_i^n n_i \left(\mu_{i,1} - \mu_{i,0}\right)$ where μ_i represents the chemical potential of the $i-th$ constituent. In the general case of a mixture consisting of n chemical constituents, according to the definition [9]: $EX^C = \sum_i^n \left(W_{10}^{AR\to}\right)_i^{MAX} = \overline{R}T_R \sum_i^n x_{i,1} \ln \frac{x_{i,1}}{x_{i,0}}$ where x_i is the molar fraction of the $i-th$ constituent.

A definition of chemical entropy can be derived from chemical energy and chemical exergy according to the method previously adopted and the general definition of Equation (1). To do so, if the concept of (chemical) generalized available energy is again considered, the formulation of chemical exergy should be translated into $EX^C = \left(W_{10}^{AR\to}\right)^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)^C$ which, in case of a chemical reservoir, becomes $EX^C = \left(W_{10}^{AR\to}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^C$. Now that chemical exergy is defined, chemical entropy may be derived from both chemical energy and (chemical) generalized available energy which depend on mass interaction: $\left(S_1 - S_0\right)^C = \frac{1}{\mu_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^C$. Assuming that energy and generalized available energy are additive properties, chemical entropy is an additive property as well and considering that the generalized reservoir allows a correlation between chemical generalized available energy and chemical exergy, then chemical entropy can be formulated as:

$$\left(S_1 - S_0\right)^C = \frac{1}{\mu_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^C \tag{3.17}$$

Chemical entropy is associated to and is determined by mass interaction between A and R at constant potential μ_R. This definition is valid for non-equilibrium, in addition to stable equilibrium, between system and chemical reservoir since it is derived through the same procedure adopted for equation of thermal entropy valid in turn for non-equilibrium states [1.9]. Nevertheless, it follows from the Second Law stated, in this case, as existence and uniqueness of chemical stable equilibrium since thermal and mechanical stable equilibrium are posited as restricted stable equilibrium.

Chemical entropy definition can be proved by means of PMM2. One could imagine a machine with a two-phase fluid operating at constant temperature between two different and constant pressures. The impossibility of PMM2 does not allow to withdrawn work interaction without net changes in the environment here constituted by the reservoir interacting with the system by mass transport. The proof, already provided by Gyftopoulos and Beretta to define the thermodynamic entropy, is general and no specific mention is made to its physical meaning, or to specific assumptions relating to the characteristics of the system, the number and type of particles, the type of potential as well as to the thermodynamic state. This is the rationale behind the generality of the theorems and proofs which, therefore, may be considered still valid also for chemical entropy here defined. This results from the fact that chemical entropy is an inherent property of any system, in any state. Therefore, the chemical entropy can be adopted to state the Highest-Chemical-Entropy Principle which can be assumed as complementary to the Lowest-Chemical-Energy Principle.

Necessity of equality of chemical potential for stable equilibrium can be proved by the Highest-Chemical-Entropy Principle which can also be adopted for the proof of sufficiency to infer chemical stable equilibrium from potential equality. This bi-directional logical implication can be worded as the necessity and sufficiency of chemical potential equality between the system and chemical reservoir, given the equality of temperature and pressure of the system-reservoir composite (restricted stable equilibrium).

Also in this case, from differential standpoint, the chemical entropy as for Equation (3.3) depends on the potential of reservoir μ_R and is formally analogous to the thermal entropy as for Equation (3.2) depending on the temperature of reservoir T_R. The term $1/\mu_R$ in Equation (3) corresponds to the term $1/T_R$ in Equation (3.2) and, in this analogy, Chemical-Mechanical State Equation for an ideal multi-particle system results from the equivalence between inter-particle kinetic energy, associated to the temperature depending on particles relative velocity, and inter-particle potential energy, associated to the density depending on particles relative position, and can be expressed as $PV = \overline{R}\mu$. This state equation is suitable to prove that the term $1/\mu_R$ constitutes the integrating factor which makes the mass interaction an exact differential according to Pfaff theorem so that chemical entropy $dS^C = \frac{\delta M}{\mu} = \frac{dE_R^C}{\mu_R}$ is a state property. Considering the Pfaff theorem for an adiabatic process of a closed system, Gibbs equation is $dU = C^C d\mu = dW = -PdV$ where C^C represents the specific mass (or the amount of mass corresponding to an increase of potential equal to one unit). That said, Gibbs equation can be written as $C^C d\mu + PdV = 0$ or $C^C \frac{d\mu}{\mu} + \frac{\overline{R}}{V} dV = 0$ representing the Pfaff equation.

Applying Schwarz relation to Pfaff theorem, it follows that $\partial\left(C^C/\mu\right)/\partial V=0$ and $\partial\left(\overline{R}/V\right)/\partial\mu=0$ so that it is an exact differential.

In case of adiabatic process of an open system undergoing mass interaction, Gibbs equation assumes the form $dU=dM+dW$. The first consequence is that $dM=C^C d\mu+\frac{\overline{R}\mu}{V}dV$ for which Schwarz relation is not valid anymore since $\partial C^C/\partial V=0$ while $\partial\left(\overline{R}\mu/V\right)/\partial\mu=\overline{R}/V\neq 0$. The second consequence is that $dW=\frac{\overline{R}\mu}{V}dV+0\cdot d\mu$ for which again Schwarz relation is not valid anymore since $\partial\left(\overline{R}\mu/V\right)/\partial\mu=\overline{R}/V\neq 0$ while $\partial\left(0\right)/\partial\mu=0$.

Assuming that $1/\mu_R$ behaves as an integrating factor, then $dS^C=\frac{dM}{\mu}=C^C\frac{d\mu}{\mu}+\frac{\overline{R}}{V}dV$ which fulfils the Schwarz condition being $\partial\left(C^C/\mu\right)/\partial V=0$ and $\partial\left(\overline{R}/V\right)/\partial\mu=0$ therefore representing the definition of chemical entropy as a state property.

3.2.5. Necessity and Sufficiency of Pressure Equality (or Sufficiency and Necessity of Mechanical Stable Equilibrium)

Stable equilibrium is proved to be a sufficient condition also for equality of pressure within the AR composite in addition to equal temperature and equal potential [1.9]. The proof assumes stable equilibrium between two interacting systems to derive equality of pressure using the Highest-(Thermal)-Entropy Principle. However, also in this case, pressure and therefore equality of pressure between system and reservoir $P=P_R$ is not accounted for in the definition of entropy property which instead should include the mechanical entropy associated to and determined by thermodynamic work interaction, in addition to thermal entropy and chemical entropy contributions. A definition of mechanical entropy is here proposed analyzing the work interactions between system and a mechanical reservoir behaving at constant pressure P_R.

The weight process represents the experimental measure of the maximum net useful work interaction $\left(W_{10}^{AR\rightarrow}\right)^{MAX}$ withdrawn from a system A releasing a corresponding minimum non-useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MIN}$ to a (thermal) reservoir R^T at constant temperature T_R [2,3,4] according to the definition of generalized available energy and thermal exergy. The inverse (and reversible) process requires the weight process to represent the minimum net useful work released to A while extracting a corresponding maximum non-useful heat from R^T. On the other hand, in addition to the maximum net useful work, the concept of available energy [1] addresses to the maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ associated to the minimum net useful work $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ released to the mechanical reservoir R^M at constant pressure P_R. This symmetric process underpins the definition of mechanical exergy EX^M [10]. In fact, in this case, the input work occurs through the interaction of system A with mechanical reservoir R^M. As work interaction released to the mechanical reservoir is non-useful work, then it is no longer useful since it constitutes the non-convertible contribution of input work interaction. Therefore, mechanical exergy property accounts for the maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ withdrawn from the system A releasing the minimum non-useful work $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ to the mechanical reservoir. In this symmetric process, system A interacts with a mechanical reservoir behaving at constant pressure P_R therefore the symbol EX^M is adopted with the superscript "M" standing for "Mechanical reservoir":

$$EX^{M} = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(\Omega_1^R - \Omega_0^R\right)^M \tag{3.18a}$$

and considering again the meaning of generalized reservoir, then:

$$EX^{M} = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_1^R - EX_0^R\right)^M \tag{3.18b}$$

This relation expresses the mechanical exergy corresponding to the amount of generalized mechanical available energy of system A converted into heat interaction $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ at variable temperature which is different with respect to the constant temperature T_R of thermal reservoir R^T. Indeed, $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ is determined by the minimum amount of work interaction $\left(W_{10}^{AR\rightarrow}\right)^{MIN}$ released to the mechanical reservoir along the isothermal process where the heat interaction is withdrawn at T_R from the thermal reservoir to be converted into $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$. In fact, work interaction along the isothermal expansion process, could not be considered useful because it has to be entirely converted into heat by means of an inverse Joule cycle releasing heat (non-useful) to the thermal reservoir and non-useful work to the mechanical reservoir at a lower and constant pressure.

Thus, the maximum net useful heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$ results from the conversion process in which the input work rises up to higher temperature the heat input withdrawn from the thermal reservoir constant temperature T_R while releasing, along the isothermal process at constant T_R, the minimum amount of non-useful work interaction expressed as follows [3.6]:

$$\left(W_{10}^{AR\rightarrow}\right)^{MIN} = \left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M = \left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M$$

$$= \overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right) \tag{3.19}$$

The term $\overline{R}T_R\left(\ln V_1 - \ln V_0\right) = P_R V_R\left(\ln V_1 - \ln V_0\right)$ equals the (theoretically minimum) amount of work released to the mechanical reservoir R^M and equals the low temperature heat, withdrawn from the thermal reservoir, converted into high temperature heat $\left(Q_{10}^{AR\rightarrow}\right)^{MAX}$.

The definition of mechanical exergy, formulated by Equations (4a) and (4b), constitutes the basis to derive the expression of mechanical entropy using the same procedure adopted for thermal entropy and chemical entropy: $\left(S_1 - S_0\right)^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]^M$, and taking into account the mentioned relationship between mechanical generalized available energy and mechanical exergy:

$$\left(S_1 - S_0\right)^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M \qquad (3.20)$$

The former Equation (5), substituted in the latter Equation (6), implies the expression of the mechanical entropy [3.6]:

$$\left(S_1 - S_0\right)^M = \overline{R}\left(\ln V_1 - \ln V_0\right) \qquad (3.21)$$

This expression is a consequence of the Second Law and the stable equilibrium state in a system-reservoir composite AR .

The proof of definition of entropy provided by Gyftopoulos and Beretta [1.9] may be used – mutatis mutandis – as a proof of mechanical entropy as well. In fact, the Second Law statement implies the impossibility of a PMM2 performing, in the case of mechanical entropy, an inverse cycle (instead of direct cycle) so that it may be expressed as the impossibility for mechanical energy to be transferred from a mechanical reservoir at lower pressure P_R to a system at higher pressure P without the contribution of heat interaction. The impossibility of inverse PMM2 expresses the impossibility of any system to undergo a cyclic process that produces no external effect except the heat interaction and the change of another system from an initial state of stable equilibrium to a final state of non-equilibrium. Clearly both process have to be cyclic and therefore for both it is impossible to convert the entire amount of energy content transferred to the other one.

The definition of mechanical entropy can be used to state the Highest-Mechanical-Entropy Principle applicable to those processes causing changes in volume of the system. As regard pressure equality between system and mechanical reservoir, this condition can be proved, using the Highest-Mechanical-Entropy Principle, to be a necessary condition of mutual stable equilibrium between system and reservoir that needs to be complied, in addition to equality of temperature and equality of potential, to ensure the equilibrium state of the composite system-reservoir extending to pressure the stable equilibrium restricted to temperature and potential. On the other hand, the same Highest-Mechanical-Entropy Principle can be adopted to prove the sufficiency of pressure equality or, in different terms, to prove stable equilibrium from pressure equality within system-reservoir composite. This procedure is reported in next sections.

As far as the Pfaff theorem and Schwarz relation are concerned, δW is not an exact differential. Indeed $\delta W = dU - \delta Q = C_V dT - TdS$ thus $\partial C_V / \partial T = 0$ and $\partial T / \partial T = 1$. In this case, if the former equation is multiplied by the integrating factor $1/PV$ then it results that $\delta W / PV = C_V dT / PV - TdS / PV = C_V dT / \overline{R}T - dS / \overline{R}$ from which $\partial(1/T)/\partial S = 0$ and $\partial\left(1/\overline{R}\right)/\partial T = 0$ so that $dS^M = \delta W / PV = dE_R^M / P_R V_R$ is an exact differential for and represents the mechanical entropy as a state property according to Pfaff theorem.

Although readers could consider the following clarification as obvious, it is worthy further underline that the concept of mechanical entropy here defined is correlated to the thermodynamic work only and has nothing to do with mechanical work. To better clarify, mechanical work is intended as the transfer work done by an external system behaving as an incompressible fluid, such as a liquid interacting with a hydraulic turbine whereas the thermodynamic work consists of the expansion work done by the internal system behaving as a compressible fluid, such as a vapor (steam) or a gas interacting with the expander of a gas turbine or with a cylinder-piston device.

3.2.6. Generalized Entropy Derived from Generalized Exergy

The definition of exergy is characterized by the property of additivity because it is defined with respect to an internal subsystem of the whole system, or to an external reference system behaving as a reservoir. The generalized reservoir, characterized by constant temperature, constant chemical potential and constant pressure, implies the property of additivity of each one of the components, thermal, chemical and mechanical, constituting the generalized exergy so that the sum of all contributions can be expressed as follows:

$$EX^G = EX^G\left(T, T_R \mu, \mu_R, P, P_R\right) = EX^T\left(T, T_R\right) + EX^C\left(\mu, \mu_R\right) + EX^M\left(P, P_R\right) \qquad (3.22)$$

The generalized exergy can be regarded as the sum of generalized physical exergy, resulting from the sum of thermal exergy and mechanical exergy, and generalized chemical exergy, resulting from the sum of chemical exergy and mechanical exergy: $EX^G = \left(EX^T + EX^M_{HEAT}\right)^{\overset{G}{PHYSICAL}} + \left(EX^C + EX^M_{MASS}\right)^{\overset{G}{CHEMICAL}}$. An expression of the first one can be provided (in section 2.5) through two different procedures based on non-cyclic processes and on cyclic processes, in particular the Carnot and Joule cycles operating between higher and lower temperature and higher and lower chemical potential. A more detailed description of these cycles is included in the next section 4. specifically focusing on equilibrium and non-equilibrium

Likewise, the additivity of the entropy property is proved considering the additivity of energy and generalized exergy from which it is defined. On the basis of the additivity of the entropy property, the generalized entropy is the result of the sum of entropy contributions, each derived from the corresponding exergy contribution, related to the generalized potential constituted by the set of temperature, chemical potential and pressure (T, μ, P) of the system. Therefore, the generalized entropy S^G can be expressed as follows:

$$S^G = S^G(T, \mu, P) = S^T(T) + S^C(\mu) + S^M(P)$$

$$= \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^T + \frac{1}{\mu_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^C$$

$$+ \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M \tag{3.23}$$

The above equation, differently from exergy, depends solely on temperature, chemical potential and pressure of the system, no reference is needed, and no mention is done, to the thermodynamic state of the reservoir. Indeed, the generalized entropy is derivable from generalized exergy for any state of the system, equilibrium or non-equilibrium with respect to generalized reservoir having auxiliary function only. For this reason (and differently from the generalized exergy) as the method expressed in Equation (3.1) is adopted, it depends on the properties of the system only, namely system's generalized potential (T, μ, P) and does not depend on the reservoir's generalized potential (T_R, μ_R, P_R). This condition does not remove the implication of equality of temperature, chemical potential and pressure between system and reservoir which remains a set of necessary conditions for the stable equilibrium state of the system-reservoir composite. Moreover, the generalized entropy can be defined as an extensive and additive property resulting from the sum of entropy contributions (reversibility) and productions, or generations, (irreversibility) associated to each kind of energy content (thermal, chemical, mechanical) transferred between two subsystems of a whole system by means of the related heat, mass or work interaction respectively. Although the generalized entropy depends on temperature, potential and pressure (or generalized potential), by virtue of the Stable-Equilibrium-State Principle, its contributions are correlated to, and dependent on, each one of the specific interaction constituting the transfer of any specific energy namely thermal energy, chemical energy and pressure energy.

The physical meaning of generalized entropy is that each form of energy is characterized by its own specific form of entropy property expressing the contribution or creation associated to energy transfers and respective heat, mass or work interactions. This viewpoint is a further confirmation of the concept of entropy (interpreted as the degree of subdivision of phenomena among subsystems) proposed as the outset of the present section 3. being the one more adequate to any speculative reasoning on this topic.

Going back to Pfaff theorem demonstrated for each one of entropy components, δQ or δW are not separately exact differentials if occurring simultaneously (in parallel), however they become exact differentials if occurring individually and sequentially (in series). As well, δM or δW are not separately exact differentials if occurring simultaneously (in parallel), however they become exact differentials if occurring individually and sequentially (in series).

Although entropy property depends on temperature, potential and pressure (or generalized potential) by virtue of the Stable-Equilibrium-State Principle, its contributions are related to, and dependent on, each one of the specific interaction constituting the transfer of each specific energy, namely thermal energy, chemical energy and pressure energy, constituting the internal energy of whole system.

If the Pfaff exact differential is again applied to the generalized entropy derived from generalized interaction, the following expression ensures that it is a state property:

$$dS^G = \frac{\delta I^G}{P^G} = \frac{dE_R^G}{P_R^G} = \frac{d\left(E^G - EX^G\right)}{P_R^G} \tag{3.23a}$$

A final remark arises from the dependency of entropy property on temperature, chemical potential and pressure (or generalized potential) by virtue of the Stable-Equilibrium-State Principle, expressed as $S = S\left(E, n, \beta\right)$. In effect, its components are related to, and dependent on, each one of the specific interaction constituting the transfer of each corresponding type of energy namely thermal, chemical and mechanical. This relationship confirms the uniqueness of any property and parameter characterizing a system in the stable equilibrium state and the subsequent uniqueness of thermal, chemical and mechanical stable equilibrium. Each kind of these "equilibria" is the prerequisite to derive, as a corollary, the corresponding kind of PMM2 and the kind of entropy inferred by the logical schema adopted for its proof.

3.2.7. Highest-Generalized-Entropy Principle

Assuming all components of the generalized entropy, then the generalized statement of the Highest-Entropy Principle can be founded on the definition of the very generalized entropy property. Hence, it is possible to state that the Highest-Generalized-Entropy Principle results from the contribution of thermal entropy, chemical entropy and mechanical entropy all exhibiting the property of additivity. Then, the Highest-Generalized-Entropy Principle is in turn consistent with, and is the result of the combination of, the Highest-Thermal-Entropy Principle, the Highest-Chemical-Entropy Principle and the Highest-Mechanical-Entropy Principle, each one proved for its corresponding entropy component related to heat, mass and work interaction. Therefore, making reference to the statement formulated by Gyftopoulos and Beretta [1.9], the Highest-Generalized-Entropy Principle implies that, among all states of a system characterized by given values of energy, number of constituents and parameters such as the volume, there exist a unique stable equilibrium, according to the Second Law statement here addressed to, and the generalized entropy of this state is larger than the generalized entropy of any other state with the same value of energy, number of constituents and parameters.

On the other hand, if all states with same value of generalized entropy are considered, and assuming the Stable-Equilibrium-State Principle as the relationship between energy and entropy as reported in previous section 3, one can infer the Lowest-Generalized-Energy Principle implying that among all states of a system characterized by given value of entropy, number of constituents and parameters, the generalized energy of the unique stable equilibrium state is lower than the generalized energy of any other state with the same value of generalized entropy, number of constituents and parameters.

3.2.8. Necessity and Sufficiency of Generalized Potential Equality (or Sufficiency and Necessity of Stable Equilibrium)

The present section is aimed at describing the proof that the generalized potential equality is a condition necessary and sufficient for the stable equilibrium (or that stable equilibrium is a condition sufficient and necessary for the generalized potential equality). This proof is here again reported for sake of completeness and consistency as well as to better clarify the rationale behind the generalization of properties and principles here proposed.

According to the proof theory, deriving a thesis from a hypothesis implies the logical proof of hypothesis sufficiency and, vice versa, deriving the hypothesis from the thesis implies the logical proof of hypothesis necessity. The opposite is valid if thesis is replaced by hypothesis or, consistently, if hypothesis is replaced by thesis. The proof that equality of temperatures, potentials and pressures within the whole composite system-reservoir are necessary condition of stable equilibrium, hence “Equilibrium => Equality”, is described by Gyftopoulos and Beretta who adopt the Highest-Entropy Principle to prove that temperature-potential-pressure equality is the consequence of subsystems individual-and-interacting stable equilibrium. With an opposite logical inference, the proof that individual-and-interacting stable equilibrium is inferred from temperature-potential-pressure equality is achieved by Gaggioli by adopting the Lowest-Energy Principle. Therefore, in both cases, stable equilibrium is a sufficient condition for equality, hence, once again, “Equilibrium => Equality”. As sufficiency of equilibrium (or necessity of equality) is the sole condition established and proved and, on the other hand, the necessity of stable equilibrium (or sufficiency of equality) is not proved, then the system-reservoir composite can experience equality of temperature, potential and pressure while the composite itself is not in a stable equilibrium state since the equilibrium is not necessary as well (or equality is not sufficient as well) in contradiction to the assumed stable equilibrium. To resolve this contradiction, stable equilibrium has to be sufficient and necessary condition for equality of generalized potential or, vice versa, equality of generalized potential has to be necessary and sufficient condition for stable equilibrium. Reference can be made to the thermal, chemical, mechanical contributions of entropy, which is an additive property, so that the sum of these contributions constitutes generalized entropy which is the base of Highest-Generalized-Entropy Principle. To prove the necessity and sufficiency, without disproving the proofs already provided in the literature, one has to demonstrate that equality (or equilibrium) is necessary and sufficient conditions, thus Gaggioli’s statement is also necessary and Gyftopoulos and Beretta’s statement is also sufficient, both implying that the inference “Equality => Equilibrium” is complementary to the inference “Equilibrium => Equality” so that both equilibrium and equality are necessary and sufficient conditions for each other. In different terms, stable equilibrium is true if and only if generalized potential equality is true and vice versa generalized potential equality is true if and only if stable equilibrium is true. Figure 1 represents the hierarchical structure of the statement of necessity and sufficiency conditions.

Thus, Gaggioli adopts the Lowest-Energy Principle and Gyftopoulos and Beretta adopt the Highest-Entropy Principle, and since entropy depends on the difference between energy and generalized available energy which express the First Law and Second Law respectively, then entropy remains the suitable quantity to attain the proofs of both sufficiency and necessity. Therefore, entropy property should account for equality of potential and equality of pressure, in addition to equality of temperature, in order to constitute the procedure for such a proof. First and Second principles are mutually correlated to each other: $E = E\left(S^G, n, \beta\right)$ Lowest-Energy Principle $\Leftrightarrow$ $S^G = S^G(E, n, \beta)$ Highest-Entropy Principle. In fact, the Stable-Equilibrium-State Principle establishes the mathematical relationship among all system properties at stable equilibrium. This relationship also exists between the Lowest-Energy Principle and the Highest-Entropy Principle which are intrinsic to the Stable-Equilibrium-State Principle as stated by the above fundamental relations [2].

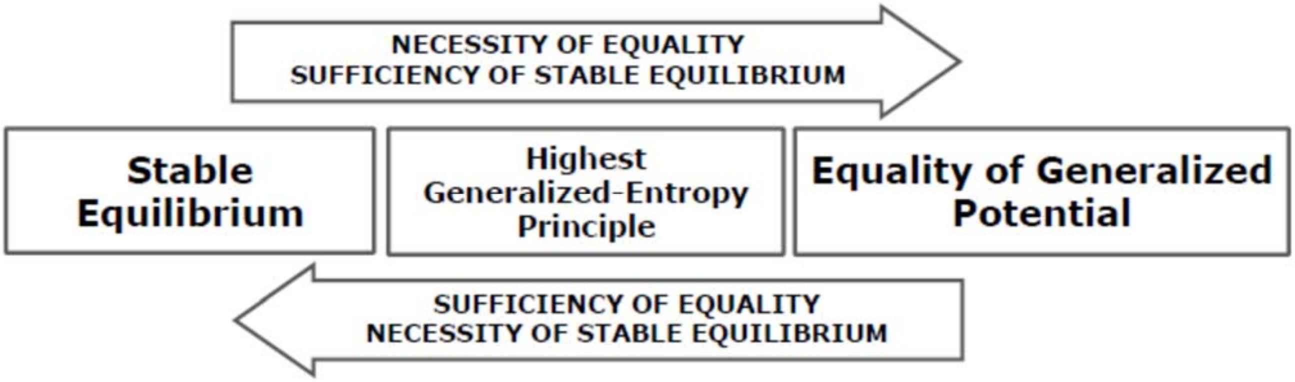


Figure 3.2 – Hierarchical structure of logical relationship between stable equilibrium and generalized potential equality between system and reservoir

The proof of the necessity of stable equilibrium (or the sufficiency of generalized potential equality) consists of deriving stable equilibrium from equality and may be established through the “reductio ad absurdum” assuming that temperature, potential and pressure of system and reservoir are equal while the system-reservoir composite is not in stable equilibrium. Indeed, this condition is admitted by the sufficiency of stable equilibrium as the only condition which does not “necessarily” imply that stable equilibrium is a consequence of equality of temperature, potential and pressure in the system-reservoir composite so that the equality may be compatible with non-equilibrium. This equality of generalized potential would thus be able to move the system into a non-equilibrium state without undergoing any net change of the environment, or, would be able to generate a weight process by means of a PMM2 which is impossible according to the Second Law statement based on stable equilibrium as assumed. The consequence is that equality must imply stable equilibrium, that is, equality must be a sufficient condition for stable equilibrium (or stable equilibrium must be a necessary condition for equality). The proof of this sufficiency can be based on the Highest-Generalized-Entropy Principle where generalized entropy depends on thermal, chemical and mechanical contributions associated to heat, mass and work interactions between system and reservoir $S^G = S^G(T, \mu, P) = S^T(T) + S^C(\mu) + S^M(P)$. Indeed, entropy property depends on temperature, potential and pressure, however this relationship does not “suffice” to prove stable equilibrium. For instance, adiabatic reversible process, namely isoentropic, causes changes in pressure as well as in temperature but equality of temperature does not in turn imply equality of pressure between system and reservoir. Instead, equality of temperature, potential and pressure associated to heat, mass and work interactions respectively, each individually identified as an additive contribution, ensures stable equilibrium. Adopting once again the paradigm of “reductio ad absurdum”, if equality of generalized potential is not associated to stable equilibrium, then the system can undergo a process due to whatever interaction, bringing it to stable equilibrium with an increase of entropy due to even one type of interaction moved by not equal potential that is impossible as equality is an assumption and being stable equilibrium associated to the highest generalized entropy. Having assumed the equality of generalized potential between system and reservoir, then generalized entropy has to assume the highest value with respect to any other state with non-null difference of temperature, potential and pressure. Therefore, each thermal, chemical and mechanical contribution of generalized entropy, has to be individually the highest. To do so, each individual heat, mass or work interaction, determined by the difference of temperature, potential and pressure respectively, has to be able to bring the system itself to the stable equilibrium state.

Finally, on the basis of the bi-univocal logical inference between stable equilibrium and generalized potential equality, and also considering the validity of Stable-Equilibrium-State Principle which correlates stable equilibrium with all properties characterizing the system in each thermodynamic state, the Second Law statement can be enunciated in terms of existence and uniqueness of generalized potential equality state for each given value of energy content compatible with a given composition of constituents and compatible with a given set of parameters of any system. This statement can be extended to and remains valid also for neutral equilibrium.

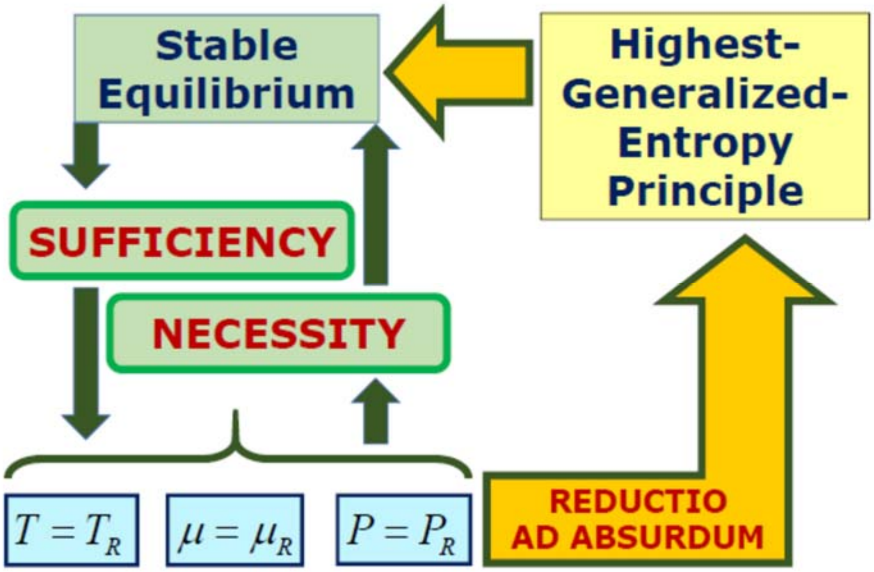


Figure 3.3 – Logical Schema of Theorem Proof

The necessity and sufficiency of stable equilibrium constitutes a logic tautology according to the meaning provided by the Proposition Logics and therefore is always true likewise the non-contradiction statement. In the present case under discussion, the statement “necessity and sufficiency of stable equilibrium” is true or is false because a system may be or may not be in stable equilibrium, there are not other possibilities. If only necessity or sufficiency is true, then the stable equilibrium can be true and false at the same time. Instead, from a linguistic viewpoint, the hypothesis of the theorem does not contain the thesis, therefore it is not at all a language tautology because stable equilibrium and equality of potentials are not the same concept.

3.2.9. Considerations and Future Developments

There is a couple of concluding considerations of arguments developed in the present study. Firstly, it consists of a proposal to encompass the Second Law statement by a bi-univocal logical inference between stable equilibrium, assumed as a hypothesis, and the generalized potential equality derived as the thesis of a theorem of necessity and sufficiency of stable equilibrium. The second result is that the proof is achieved by means of the definition of the Highest-Generalized-Entropy Principle in which the generalized entropy is derived from the generalized exergy property.

A consequence emerging from the generalized definition of entropy is that chemical entropy is an intrinsic and independent property of any system in any state and represents and additional contribution, with respect to thermal entropy, determined by the chemical potential of the system itself characterized by its atomic and molecular configuration, regardless the content of thermal entropy. Moreover, the chemical entropy characterizes mass interactions of a system with a reservoir even in case no heat interactions are occurring while mass is entering or leaving the system. On the other hand, by analogy with the thermal exergy, the work interaction, representing the quantity defining the mechanical exergy, can also be correlated to the chemical exergy associated to an amount of mass interaction released to the system. As far as chemical entropy is concerned, its usefulness may be envisaged in the description of atomic and molecular systems undergoing non-equilibrium phenomena determining specific intermediate and final geometrical configurations along processes. In particular, optimization methods and techniques can include the chemical entropy to provide a system's evolution schema suitable to describe organized structures and their self-assembling and self-organizing capabilities especially in living systems at molecular and cellular level. The definition of generalized entropy can be also extended to Quantum Physics domain to account for the contribution of quantum thermodynamic properties within the framework of an overarching and unified theory. The extension of the applicability and use of the generalized thermodynamic entropy and its components is analysed in the next section 4. In particular, certain essential adaptation of this property to nuclear and sub-nuclear level displays its powerful significance beyond the usual meaning adopted in the description of physical phenomena. An extension of this generalized paradigm to definitions, properties and theorems relating to few-particle systems and non-equilibrium states will be based on, and account for, recent treatments on the definition of thermodynamic entropy property [3.4,3.5]. This recent rigorous and formalized framework of axioms and theorems does not need the concept of reservoir to define thermodynamic entropy for each given value of energy content of the system which depends solely on the temperature. Nevertheless, the extension to few-particle systems in non-equilibrium states would involve potential and pressure of the systems, in addition to temperature, aimed at generalizing the definition of thermodynamic entropy to all kinds and forms of potential characterizing matter at molecular, atomic and sub-nuclear level.

3.2.10. Summary and Outcomes

A sequence of crucial points in the logical rationale underpinning the framework of foundations under discussion is here after summarized to highlight the reasons why a more general paradigm is deemed of fundamental importance.

Among all statements of the Second Law reported in the literature, the one established on the assumption of existence and uniqueness of stable equilibrium has been devised and developed with its corollaries. The stable equilibrium implies thermal equilibrium, chemical equilibrium and mechanical equilibrium or, more in general, the equality of all thermodynamic potentials (dynamic driving forces) acting among systems' macroscopic parts and microscopic particles. A corollary of the stable equilibrium is the non-existence of Perpetual Motion Machines of the Second Kind (PMM2), that is, the impossibility, for any device, of withdrawing any form of energy from a system in stable equilibrium with no use of a second system characterized, at least, by one thermodynamic potential different from each other. Hence, energy flows if two subsystems interact each other in turn implying the subdivision of energy itself and the creation of entropy because of its very definition, as anticipated at the outset of the present section 3. where the main definitions are provided. In turn, the PMM2 is adopted in the proof of the entropy definition related to temperature, hence it is the definition of a thermal entropy property. The highest-(thermal)-entropy principle is applied to prove that the stable equilibrium implies the equality of temperature, potential and pressure while thermal entropy determines thermal energy and heat interaction only. Using a property related to temperature only, to prove a statement related to all kind of thermodynamic potentials, represents a logical incompleteness and inconsistency, thus introducing an incongruity. Indeed, a system containing a constant overall amount of internal energy $U = TS + \sum_{i=1}^{r} \mu_i^C n_i^C + \sum_{i=1}^{k} \mu_i^N n_i^N - PV$ and assuming constant thermal intensive and extensive properties, behaves with variations of remaining independent parameters not ensuring the stable equilibrium as a whole. The Gibbs Phase Rule $F = r + 2 - q$ of a heterogeneous state with q coexisting phases [1.9] ensures at least one independent intensive property in such a system at stable equilibrium. At this point, a couple of questions rise up concerning the reasons why i) entropy relates to thermal stable equilibrium only and reservoir's temperature without accounting for chemical stable equilibrium and mechanical stable equilibrium and reservoir's chemical potential and pressure respectively, ii) entropy relates to the equality of temperature only while equality of chemical potential and equality of pressure are additional necessary conditions for stable equilibrium, and iii) entropy relates to temperature and thermal stable equilibrium only and is used in the proof of sufficiency of chemical and mechanical stable equilibrium for the equality of chemical potentials and pressures respectively.

To remove the abovementioned incongruities, equality of temperature, potential and pressure have to imply thermal, chemical and mechanical equilibria and this opposite proof needs chemical entropy and mechanical entropy, in addition to thermal entropy, to enunciate and adopt a highest-generalized-entropy principle to be used in the proof. Therefore, necessity and sufficiency of stable equilibrium is proved if and only if the existence of mechanical entropy is admitted and included in the set of entropy components to account for all kinds of thermodynamic potentials moving energies among interacting systems. A further consequence of the generalized entropy is that the proof of each one of the components needs to specialize the idea of PMM2 requiring specific useful, used and lost interaction specially devised for any particular case. maybe it makes sense to think of a "generalized PMM2" consisting of a device suitable to extract any form of energy from a system in stable equilibrium state where all kind of thermodynamic potentials are accounted for. This more advanced analysis is reported in next section 4. where the non-existence of PMM2 is discussed jointly with the non-existence of Maxwell’s demon.

Both Highest-Generalized-Entropy Principle and Lowest-Generalized-Energy Principle are able to prove the theorem of necessity and sufficiency of stable equilibrium. This twofold option can be recognized in the fact that the First Law is the conservative aspect of Second Law and the Second Law is the evolutionary aspect of First Law. The two laws are inherently correlated in the respect of the Stable-Equilibrium-State Principle [1.9] and constitute the ultimate essence of any other physical law.

3.3. Thermal and Chemical Aspect in Equation of State and Relation with Generalized Thermodynamic Entropy

The definition of entropy property, proved by Gyftopoulos and Beretta and discussed in the present research, is derived by replacing the heat interaction Q, appearing in Clausius canonical formulation, with the difference between energy E and available energy Ω^R of a system A interacting with an external reference system, or reservoir, R, times a parameter $1/C_R$ characteristic of the reservoir: $S_1 - S_0 = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]$ where it is proved that $C_R = T_R$ and T_R is the constant temperature of R. The genesis of this theory has been largely observed from all facets in previous section. Nevertheless, it is worth highlighting an aspect that may shed a light on a different, though complementary, aspect. In fact, the physical meaning of this expression is that entropy variation can be regarded as the amount of non-useful heat released by the system, along whatever process between initial and final states, to the reservoir at T_R. Indeed, energy minus the available energy results in the non-available energy. The available energy is defined with respect to the reservoir R and hence corresponds to the exergy EX^R, in turn depending on a fixed reference thermodynamic state, both being additive state properties. Therefore, the above expression of entropy can be turned into the one already written: $S_1 - S_0 = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]$. However, considering that exergy is defined as the maximum net useful work withdrawable from a system-reservoir composite, here the physical meaning is that entropy corresponds to the minimum net non-useful heat released by the system to the reservoir at T_R. As anticipated, the consequence is that the concept of heat interaction Q is not more used in this definition that, instead, implies entropy being an inherent property of matter, hence it does not depend on whatever external reference system or reservoir is assumed [3.3]. The role of the reservoir is therefore auxiliary only and recent studies demonstrate that entropy can be defined with no use of the reservoir concept [3.5], as already clarified in previous sections.

To corroborate this conception, the theory underpinning exergy and the entropy-exergy relationship has been elaborated also by Gaggioli who has authored an overarching treatise of all fundamental aspects of the methodology based on this property [2.3-2.6]. Significant concepts, among those demonstrated by Gaggioli, are equivalence and interconvertibility of heat and work interactions [2.4-2.6]. The equivalence is here extended in order to imply the interconvertibility between heat and work interactions and between mass and work interactions occurring between system and the reservoir. In this extension, the thermodynamic efficiency of the conversion processes heat-to-work or mass-to-work is equal to the opposite conversion process work-to-heat or work-to-mass and reflects the dualisms and the symmetries constituting one of the paradigms of the present research. The interconvertibility also derives from the assumption that available energy of a system-reservoir composite is a unique state property, regardless the specific process undergone from initial state to stable equilibrium state of the composite itself, and regardless the specific interaction established between two physical entities.

Specifically, mass interaction is here intended as the amount of chemical constituent moles input, and or output, through the control volume of the system determining variations of the inter-particle potential energy, or chemical internal energy of the system. Then, the concepts of equivalence and interconvertibility allow to infer that the definition of exergy, consisting of the maximum net useful work withdrawable from a system-reservoir composite, can be considered in its symmetric meaning as the maximum net useful heat or mass that can be extracted from the same system in the identical thermodynamic state with respect to the constant conditions of the reservoir. In other terms, the statement of equivalence stating that “work is not better than heat” [2.4-2.6] should be extended as “work is not better than mass”, or, more in general, one could assess that “work interaction is not better than heat or mass interaction”. These statements are the premise to think of the definition of mechanical exergy EX^M as a quantifier of the amount of maximum net useful heat or maximum net useful mass resulting from the opposite processes producing the maximum net useful work, this latter representing the canonical definition of exergy reported in the literature. That said, on the basis of the twofold relation of equivalence and inter-convertibility, a duplication of the mentioned relation to heat and mass interactions can be equally formalized by the expressions of mechanical exergy EX^M adopting the symbolism in [1.9]:

$$EX^{T} = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_{1}^{R} - EX_{0}^{R}\right)^{T} \tag{3.24}$$

Thermal Exergy corresponding to the maximum net useful work due to thermal-energy-to-work conversion process, implying the minimum non-useful heat released to the reservoir;

$$EX^{C} = \left(W_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_{1}^{R} - EX_{0}^{R}\right)^{C} \tag{3.25}$$

Chemical Exergy corresponding to the maximum net useful work due to chemical-energy-to-work conversion process, implying the minimum non-useful mass released to the reservoir;

$$EX^{M} = \left(Q_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_{1}^{R} - EX_{0}^{R}\right)^{M} \tag{3.26}$$

Mechanical Exergy corresponding to the maximum net useful heat due to mechanical-energy-to-heat conversion process implying the minimum non-useful work released to the reservoir;

$$EX^{M} = \left(M_{10}^{AR\rightarrow}\right)^{MAX} = \left(EX_{1}^{R} - EX_{0}^{R}\right)^{M} \tag{3.27}$$

Mechanical Exergy corresponding to the maximum net useful mass due to mechanical-energy-to-mass conversion process implying the minimum non-useful work released to the reservoir.

The above definitions, considering that exergy is a non-conservative additive state property, lead to formulate the generalized exergy $EX^G = EX^T + EX^C + EX^M$ that can be regarded as the maximum net useful interaction (heat, mass or work) between system and the reservoir that represents the reference system determining the exergy content of the system thermodynamic state. The physical meaning of the generalized exergy lies in the equivalence and interconvertibility characteristic among all interactions occurring in whatever process, reversible or irreversible, thus requiring that all involved interactions be evaluated in terms of exergy property. Finally, the generalized exergy accounts for each and every kind of interaction involved in the process from any thermodynamic state to the stable equilibrium state. Considering the relationship between exergy and entropy, as expressed by the equation discussed so far, it is a logical consequence to derive an alternative formulation of entropy from exergy on the basis of previous definitions. Nevertheless, entropy definition can be generalized to account for all contributions of internal energy deriving from temperature (inter-particle kinetic energy), potential (inter-particle potential energy) and pressure (determined by both kinetic energy and potential energy) in a perspective of microscopic description of statistical physics correlated to the macroscopic phenomena and properties. Hence, a generalized entropy S^G definition can be stated as the result of thermal S^T, chemical S^C and mechanical S^M reversible contributions and irreversible productions: $S^G = S^T + S^C + S^M$. A corollary of this formulation consists of the elaboration of an equation of state centered on the chemical potential, $PV = n\overline{R}\mu$, in analogy to the one centered on the temperature, $PV = n\overline{R}T$, usually preferred in the literature. Furthermore, the set of temperature, chemical potential and pressure is regarded as a conventional generalized potential used to formulate the generalized state equation as proved in the remaining sections of the present chapter. The demonstration starts with a logical rationale behind the need of admitting the existence of the mechanical entropy property introduced in the previous part of this research.

3.3.1. Generalized Thermodynamic Entropy Definition

Gibbs relation expressing the First Law for a system composed by 1 mole of r chemical constituents and the volume V as the only parameter that confines the system (control mass and control volume), is:

$$dU = TdS + \mu_1 dn_1 + ... + \mu_r dn_r - PdV \tag{3.28}$$

from which (thermal) entropy, associated to thermal internal energy, with units of measure in $J/(mol \cdot K)$ is obtained, expressed in differential terms, as follows:

$$dS^T = (dU - \mu_1 dn_1 - .... - \mu_r dn_r + PdV)/T \quad \text{or}$$

$$dS^T = \frac{dU}{T} - \frac{\mu_1 dn_1}{T} - . ... - \frac{\mu_r dn_r}{T} + \frac{PdV}{T} \tag{3.29}$$

The additivity of the generalized thermodynamic entropy property, implying the balance of all contributions, underpins its derivation based on Gibbs relation in Equation (3.28) from the combination of thermal, chemical and mechanical components of internal energy, referred to as U^T, U^C and U^M respectively. Two forms can be used to express the generalized thermodynamic entropy property. The first form considers the temperature T as an integrating factor [3.6-3.8]:

$$dS^G = dS^T + dS^C + dS^M$$

$$= \frac{dU}{T} = \frac{d\left(U^T + U^C + U^M\right)}{T} \quad \text{hence}$$

$$dS^G = dS^T + \frac{\mu_1 dn_1}{T} + \cdots + \frac{\mu_r dn_r}{T} - \frac{PdV}{T} \tag{3.30}$$

The second form considers the chemical potential μ as an equivalent integrating factor:

$$dS^G = dS^T + dS^C + dS^M$$

$$= \frac{dU}{\mu} = \frac{d\left(U^T + U^C + U^M\right)}{\mu} \quad \text{hence}$$

$$dS^G = \frac{TdS}{\mu} + \frac{\mu_1 dn_1}{\mu} + \cdots + \frac{\mu_r dn_r}{\mu} - \frac{PdV}{\mu} \tag{3.31}$$

From above expressions of dS^G, entropy derived from Gibbs relation is associated to all thermal, chemical and mechanical interactions occurring in closed and or open systems. Considering an adiabatic reversible process, identified by definition as isoentropic because experiencing work interaction only (no heat or mass interaction occur), would imply that no entropy variation occurs. This conclusion seems to be in contradiction with the fact that Gibbs relation is based on a definition of entropy accounting for all forms of energy and interactions, as derived from Equations (3.30) and (3.31). In fact, an isoentropic process requires that entropy, appearing in Gibbs relation, should not be considered as a total entropy: instead, it is an entropy contribution associated to thermal and or chemical internal energy and heat and or mass interaction only and. for this very reason, it is not associated to mechanical energy and work interaction. While the generalized definition of entropy, derived from Gibbs relation itself and expressed in Equations (3.30) and (3.31), accounts for all contributions appearing in the relation itself, including the very mechanical term. The isoentropic process therefore displays an incoherence. Moreover, an adiabatic reversible process cannot be isoentropic, again as a consequence of Gibbs relation, thus it has to be characterized by a change in mechanical entropy S^M constituting a contribution, in addition to thermal entropy S^T and chemical entropy S^C, implicitly accounted for in the Gibbs relation. This apparent contradiction, is resolved considering that the generalized definition of entropy, under the two forms of equations (3.30) and (3.31), is extended to encompass thermal entropy, chemical entropy and mechanical entropy contributions related to thermal, chemical and mechanical internal energy components associated to heat, mass and work interactions with the reference external system or reservoir R . According to this rationale, the definition of mechanical entropy and chemical entropy has been proposed [3.6-3.8], for sake of homogeneity, under the same formulation previously established for the expression of thermal entropy adopted in the present elaboration. On this basis, it would be also possible to extend the concept of adiabatic availability by addressing to “non-interaction availability” in the sense that no heat, no mass and no work interaction occur between system and reservoir, or among different portions of the system itself.

The differential form of the definition of thermal entropy S^T, referred to 1 mole of any chemical constituent or set of chemical constituents of the system, can be expressed as:

$$dS^T = \frac{\delta Q}{T} = \frac{dE_R^T}{T_R} = \frac{d\left(E^T - EX^T\right)}{T_R} \tag{3.32}$$

where the term $1/T$ constitutes the integration factor which makes the elemental heat interaction δQ an exact differential according to Pfaff theorem [3.6-3.8]. As usual, T_R is the constant temperature of the reservoir R.

Contributions of entropy components resulting from Gibbs relation, as above demonstrated, imply the equivalence of State Equation specially expressed for all forms of internal energy.

3.3.2. Mechanical-Thermal State Equation

The canonical mechanical-thermal State Equation of an ideal gas results from the equivalence between inter-particle kinetic energy associated to the temperature depending on particles relative velocity, and the pressure generated by particles kinematic configuration, that is:

$$PV = n\overline{R}T \tag{3.33}$$

where $\overline{R} = \frac{J}{mol \cdot K}$ is the universal constant of gases. For ideal gases $\bar{R}$ is constant since the inter-particle potential energy is constantly null except at collisions when it is (partially or totally) transformed into the inter-particle kinetic energy to which it is hence equivalent. In case of real gases, as well as real liquid and solid matter, $\bar{R}$ is no more constant and correction factors become part of the state equation. In turn, the equivalence of units of measure of this State Equation is analyzed resulting in $J = mol \cdot \frac{J}{mol \cdot K} \cdot K = J$ from which $J = J$ that is identically verified. The physical meaning, in the framework of statistical physics and the Kinetic Theory, is that the content of macroscopic mechanical internal energy of a system as a whole is equivalent to the content of its thermal internal energy determined by microscopic inter-particle kinetic energy of the constituting particles of whatever system, as assumed by the thermal-mechanical State Equation.

Vice versa, if pressure, associated to the density depending on particles collision frequency, is considered, then a thermal-mechanical State Equation should appear as:

$$TS^{T} = \frac{PV}{n\overline{R}}S^{M} \tag{3.34}$$

Units of measure of this equation are $K \cdot \frac{J}{mol \cdot K} = \frac{1}{mol} \cdot \frac{mol \cdot K}{J} \cdot J \cdot \frac{J}{mol \cdot K}$ from which $\frac{J}{mol} = \frac{J}{mol}$ that is verified as in the previous equivalence. The equivalence of units of measure of both members of the two State Equations are therefore congruent. This fact proves that, at microscopic level, both temperature and pressure result from the kinetic energy of particles interacting each other and interacting with the system confinement wall.

3.3.3. Mechanical-Chemical State Equation

The differential form of the definition of chemical entropy S^{C}, referred to one mole of any chemical constituent or set of chemical constituents of the system, can be expressed as:

$$dS^{C} = \frac{\delta M}{\mu} = \frac{dE_{R}^{C}}{\mu_{R}} = \frac{d\left(E^{C} - EX^{C}\right)}{\mu_{R}} \tag{3.35}$$

The term $1/\mu$ constitutes the integrating factor which makes the elemental mass interaction δM an exact differential again according to Pfaff theorem [3.6-3.8]. This results from the fact that chemical entropy, as thermal entropy, is an inherent property of any system, in any state.

On the other hand, a mechanical-chemical State Equation can be envisaged resulting from the equivalence between inter-particle potential energy, associated to the potential depending on particles relative position, and the pressure generated by particles geometric configuration, associated to the density depending on particles relative position, and can be expressed as:

$$PV = n\overline{R}\mu \tag{3.36}$$

In this case, considering that the unit of measure of the chemical potential μ is J/mol the units of measure equivalence implies that:

i) from mechanical-chemical State Equation $PV = n\overline{R}\mu$ then $J = mol \cdot \frac{J}{mol \cdot K} \cdot \frac{J}{mol} \Rightarrow 1 = \frac{J}{mol \cdot K}$ corresponding to $J = mol \cdot K$;

ii) from $PV = n\overline{R}T$, then $\overline{R} = \frac{PV}{nT}$ so that units of measure equivalence $\overline{R} = \frac{J}{mol \cdot K}$ using the $J = mol \cdot K$, becomes $\overline{R} = \frac{J}{J}$ and, by virtue of mechanical-thermal State Equation, then $J = mol \cdot \frac{J}{J} \cdot K = mol \cdot K = J \Rightarrow J = J$

iii) substituting $\overline{R} = \frac{J}{J}$ again in the mechanical-chemical State Equation $PV = n\overline{R}\mu$ then $J = mol \cdot \frac{J}{J} \cdot \frac{J}{mol}$ from which $J = J$ that is identically verified also in this case and hence confirms the physical equivalence between mechanical internal energy and the content of its chemical internal energy determined by inter-particle potential energy assumed by the mechanical-chemical State Equation.

Similarly to the previous case of the mechanical-thermal State Equation, here the physical meaning is adopted again from the framework of statistical physics and the kinetic theory. Hence, the content of macroscopic mechanical internal energy of a system as a whole is equivalent to the content of its chemical internal energy determined by microscopic inter-particle potential energy of the constituting particles of the same system, as assumed by the mechanical-chemical State Equation.

The above points i), ii) and iii) include equations that are to be intended as units of measure equivalences only and are not numerical equalities. Those equations are equalities in case proper values are assigned to all properties and parameters. In particular, $\overline{R} = k_B N_A$ where k_B is the Boltzmann constant and N_A is the Avogadro number. Thus $k_B = \frac{\overline{R}}{N_A}$ so that, in terms of units of measure, $k_B = \frac{J}{mol \cdot K} \cdot \frac{mol}{molecules} = \frac{J}{molecules \cdot K}$. Therefore, being $\overline{R} = \frac{J}{mol \cdot K}$ and $k_B = \frac{J}{molecules \cdot K}$, then the following equivalences apply $J = \overline{R} \cdot mol \cdot K$ and $J = k_B \cdot molecules K$; hence, the combination of the two equivalences $J = mol \cdot \frac{J}{mol \cdot K} \cdot K = molecules \cdot \frac{J}{molecules \cdot K} \cdot K = J$

proves that $\overline{R}$ and k_B are equivalent in terms of units of measure and, more precisely, are dimensionless, whereas they have different numerical values. The consequence is that, as $\overline{R}$ and k_B satisfy the units of measure equivalence, then $J = mol \cdot K$ is true for the specific case referred to one mole and $J = molecules \cdot K$ is in turn true for the general case of all molecules constituting any system at microscopic level.

Also in this case, if pressure, associated to the density depending on particles collision intensity, is considered, then a chemical-mechanical State Equation should become:

$$\mu S^{C} = \frac{PV}{n\overline{\overline{R}}} S^{M} \tag{3.37}$$

Again, the equivalence of units of measure is $\frac{J}{mol} \cdot \frac{J}{mol \cdot K} = \frac{1}{mol} \cdot \frac{mol \cdot K}{J} \cdot J \cdot \frac{J}{mol \cdot K}$ from which $\frac{J}{mol} = \frac{J}{mol}$ that is identically verified. This fact again proves that, at microscopic level, both potential and pressure result from the potential energy of particles interacting each other.

Considering that, from the set of expressions of State Equation, $T = \frac{PV}{n\overline{\overline{R}}}$ and $\mu = \frac{PV}{n\overline{\overline{R}}}$, then the unit of measure equivalence of $T = \mu$, expressed as $K = \frac{J}{mol}$ is proved.

It is noteworthy that, in terms of dimensional analysis of properties, and equivalence of units of measure, considering that $J = mol \cdot K$, the thermal entropy is $\frac{J}{mol \cdot K} = 1$ and the chemical entropy is $\frac{J/mol}{J/mol} = 1$, thus, the two properties are dimensionless. From physical point of view this result confirms that entropy represents an indicator of the subdivision, among all available degrees of freedom, of whatever physical quantity defining the state or process of a system, no matter the nature of quantity and system under consideration. In different terms, “Entropy is the ratio between macro (multi-particle) energy and a representative particle energy, thus dimensionless”.

3.3.4. Generalized State Equation

As regard the differential form of mechanical entropy S^{M}, appearing as a contribution in Gibbs equation:

$$dS^{G} = \frac{dU}{PV} = dS^{T} + dS^{C} + dS^{M}$$

$$= \frac{TdS}{PV} + \frac{\mu_1 dn_1}{PV} + ... + \frac{\mu_r dn_r}{PV} + \frac{PdV}{PV} \tag{3.38}$$

the following expression has been proposed [3.6-3.8]:

$$dS^{M} = \frac{\delta W}{PV} = \frac{dE_{R}^{M}}{P_R V_R} = \frac{d\left(E^{M} - EX^{M}\right)}{P_R V_R} \tag{3.39}$$

where the term $1/PV$ in turn constitutes the integrating factor which makes the work interaction an exact differential according to Pfaff theorem [12,13].

Considering both thermal-mechanical and chemical-mechanical contributions, their combination becomes $TS^T + \mu S^C = \frac{PV}{n\overline{R}} S^M$ from which the following Generalized State Equation is derived:

$$PV = \frac{n\overline{R}}{S^M}\left(TS^T + \mu S^C\right) \tag{3.40}$$

Coming back to the initial discussion on internal energy, the terms representing finite contributions (per mole) can be written as thermal internal energy $U(T) = TS^T$, chemical internal energy $U(\mu) = \mu S^C$ and mechanical internal energy $U(P) = \frac{PV}{n\overline{R}} S^M$. As above reported, $T = \frac{PV}{n\overline{R}}$ and $\mu = \frac{PV}{n\overline{R}}$ so that:

$$U = U(T, \mu, P) = U(T) + U(\mu) + U(P)$$

$$= TS^T + \mu S^C + \frac{PV}{n\overline{R}} S^M$$

$$= \frac{PV}{n\overline{R}} S^T + \frac{PV}{n\overline{R}} S^C + \frac{PV}{n\overline{R}} S^M$$

$$U = \frac{PV}{n\overline{R}}\left(S^T + S^C + S^M\right) = \frac{PV}{n\overline{R}} S^G = P^G S^G \tag{3.41}$$

where P^G represents the generalized thermodynamic potential and S^G the generalized thermodynamic entropy. Then the equivalence of all forms of internal energy is established and, on this basis, the sum of thermal, chemical and mechanical entropies can be defined as generalized thermodynamic entropy: $S^G = S^T + S^C + S^M$. Hence, the Generalized State Equation can be also expressed in the following form:

$$PV = n\overline{R}P^G \tag{3.42}$$

The dimensional equivalence of units of measure is $\frac{J}{mol} = \frac{J}{mol} \cdot \frac{mol \cdot K}{J} = 1$ that results identically verified.

The canonical definition of thermal entropy addresses to the degree of distribution of kinetic energy among the particles constituting the system: “Entropy as defined by Quantum Thermodynamics as a measure of the distribution of a system’s internal energy at any given instant of time amongst the available internal degrees of freedom, i.e., the energy eigenlevels of the system” [3.10]. For this very reason, thermal entropy S^T can be regarded as a kinematic entropy addressing to the relative velocity microscopic configuration. Similarly, the definition of chemical entropy S^C is based on the distribution of potential energy among the particles constituting the system hence the definition of geometric entropy seems addressing to the relative position microscopic configuration. Finally, the mechanical entropy S^M accounts for density of energy depending on the volume of the system considered as the only parameter governing work interaction moving the (gravitational or electro-magnetic) weight process of the external system. Volume determines frequency of collisions in the case of kinetic energy generating the work of kinetic origin, and determines intensity of interactions in the case of potential energy generating the work of potential origin.

Finally, using the same formulation of entropy adopted for thermal, chemical and mechanical contributions, a definition of Generalized Thermodynamic Entropy is the following:

$$dS^G = \frac{d\left(E^G - EX^G\right)}{P^G} \tag{3.43}$$

The generalized state equation here derived is such that it remains valid in the setting of the Stable-Equilibrium-State Principle in turn overarching the Lowest-Generalized-Energy Principle and the Highest-Generalized Entropy Principle, all organized in the structure represented in the Figure 3.4:

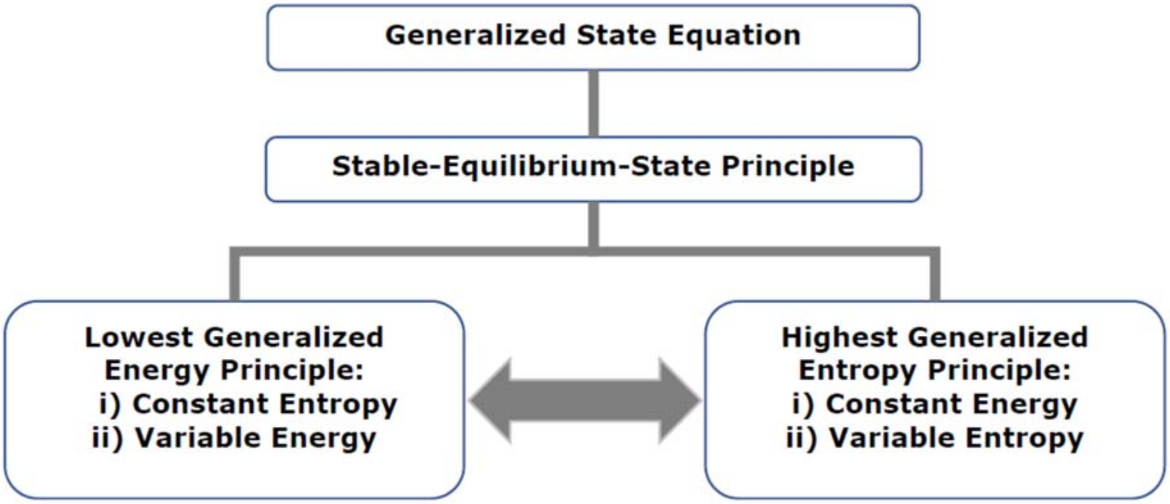


Figure 3.4 - Stable-Equilibrium-State Principle related to Generalized State Equation

This paradigm attempts to corroborate the ansatz concerning the tendency toward a unique governing law of everything that can be thought as belonging to the physical universe. To complete this guess, the information universe should be put beside, as will be more clearly explained in the following section 4.

Lowest-Energy Principle and Highest-Entropy Principle represent the paradigm underpinning reversible and irreversible contributions to be accounted for in the overall balance for the optimization of processes and the design of systems by means of extrema principles discussed in next section 4. with global and local approaches.

This paradigm is obviously valid for processes occurring in isolated systems and in closed or open systems experiencing irreversible processes. In isolated systems, energy remains constant and generalized entropy increases. In closed or open systems, entropy can remain constant under the condition that thermal, chemical or mechanical energy necessarily increases as it enters the system to compensate the entropy increase by means of a reduction of entropy determined by the increase of temperature or chemical potential implying increase of thermal energy or chemical energy or decrease of specific volume implying increase of mechanical energy (or increase of density).

3.3.5. Perspective on State Equation of Real Systems and Irreversible Processes Connecting Non-Equilibrium States

The definition of Generalized Thermodynamic Entropy, resulting from thermal, chemical and mechanical contributions and production processes, is the property accounted for extending the canonical state equation considering both thermal or chemical aspects of entropy-exergy relationship and the dependency between microscopic state and macroscopic parameters and properties of any system in any state. The physical meaning of State Equation is assumed deriving from statistical physics and the microscopic configuration of any system correlated to the macroscopic thermodynamic state. Consequently, thermal-mechanical and chemical-mechanical aspects of state equation have been analyzed and specific direct and inverse formulations have been proposed as the components of a generalized state equation. Hence, the formulation of the generalized state equation is derived accounting for all forms of energy and entropy properties characterizing any thermodynamic state of a system.

Outcomes of the present research can be regarded as a theoretical paradigm highlighting an extended perspective on studies already published [18,19] on the State Equation of real systems and their properties along irreversible processes among non-equilibrium states.

3.4. Concepts of Exergy and Entropy in Equilibrium and Non-Equilibrium Thermodynamics

The concept of exergy and its canonical definition reported in the previous sections has been devised for equilibrium or quasi-equilibrium states and processes. The adoption of this property has not been considered a suitable and fit-for-purpose approach to be extended to far-from-equilibrium phenomena, typically occurring in complex systems and living systems, to ensure rigorous treating of analyses and optimization design.

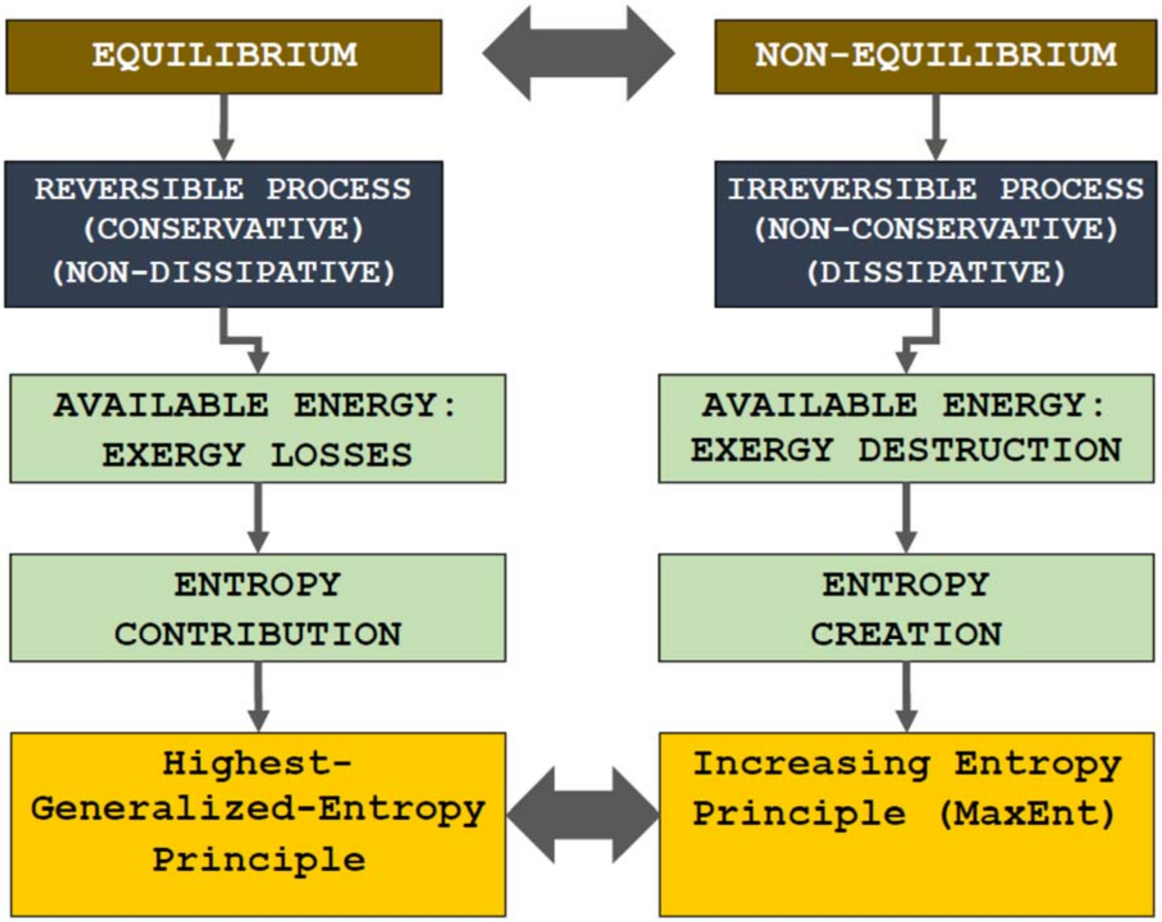


Figure 3.5 – Equilibrium and Non-Equilibrium Relationship

Nevertheless, the entropy-exergy relationship and the validity of the concept of entropy to any system in any state has triggered and promoted researches to achieve a definition of exergy for irreversible phenomena and non-equilibrium processes [2.13,2.14]. Accordingly, the definition of thermodynamic entropy has been extended and the procedure has been recently developed [3.5]. On the other hand, reference has been made to the temperature representing the thermodynamic driving force moving processes: here, the intent is to extend the axiomatic formalism to potential (chemical and nuclear) and pressure to provide and overarching formalize and rational framework of theorems applicable to all systems and technologies.

This caveat is deemed necessary to anticipate all topics treated in the following section specially dedicated to Non-Equilibrium Thermodynamics.

4. NON-EQUILIBRIUM THERMODYNAMICS

The present part of the research discusses the basic foundations of Non-Equilibrium Thermodynamics and provides a focus on both Equilibrium and Non-Equilibrium states and processes representing the ideal and real essence of all phenomena occurring in any system. The perspective adopted to treat this topic is extended to both physical and informational aspects representing fundamental pillars in a unitary approach to non-equilibrium. The informational aspect is though mentioned, and not extensively treated, however an overview on recent disciplines and theories is provided to ensure the completeness of such a perspective. Notwithstanding there is no specific treatise on informational topics, the link and relationship between physical-thermodynamic and informational aspects is clearly highlighted and corroborated to envisage implications and developments emerging from this relationship and from the outcomes of the present research. As far as systems are concerned, the attempt is to extend the treatise to all cases encountered in applications, thus open systems are always considered beside closed and isolated ones.

The challenge launched in this treatise of non-equilibrium, is to, once again, attempt (it is not the first time in the scientific community) the huge, and almost impossible, endeavor of a syncretism of all disciplines and theories overarching the non-equilibrium as one of fundamental and ultimate essences of the “physis” in its broader meaning.

4.1. Irreversible Phenomena and Processes

Non-equilibrium processes determine energy dissipation and the consequent irreversibility implying that the system could not be restored back to its initial state with no net effects on the external system or environment.

Cascade cause-effect: Non-Equilibrium (states) => Dissipation (processes) => Irreversibility (phenomena)

This statement can be regarded as applicable to all forms of energy characterizing states and processes of a system. In terms of thermal, chemical and mechanical internal energy, the phenomena leading a system to a non-reversible state can be first ascribed to the dissipation of energy form itself:

i) Thermal irreversible conversion: from high temperature and low thermal entropy to low temperature and high thermal entropy;
ii) Chemical irreversible conversion: from high potential and low number of moles (or low chemical entropy) to low potential and high number of moles (or high chemical entropy);
iii) Mechanical irreversible conversion: from high pressure and low volume (or low mechanical entropy) to low pressure and high volume (or high mechanical entropy).

The set of all irreversible phenomena and processes occurring in any system, under driving forces that are gradients, gives origin to the Non-Equilibrium Thermodynamics.

The main distinction is between heat transport (heat transmission) and mass transport (or mass transmission). Fluxes are moved locally by thermodynamic potentials. The following canonical cases can be regarded as fundamental because dissipation phenomena can be characterized and categorized as heat, mass and work dissipation. The breakdown usually recognized in the literature, and corresponding to the preceding, is:

- Heat transport caused by temperature gradient: conduction, convection, radiation (Fourier Law);
- Mass transport caused by concentration gradient: diffusion (Fick Law);
- Work transport caused by pressure gradient: transmission (Newton Law).

These phenomena are commonly pertaining to the domain of Thermo-Hydraulics and Fluid-Dynamics disciplines.

Real phenomena occur through the combination and the complementary coexistence of the above i), ii) and iii) irreversible conversion processes due to dissipation phenomena. Different type of transport processes simultaneously occurring and interfering may determine non-linear behavior. At the same time, there can be irreversible conversions from one form of energy to a different one. The following Figure 4.1 provides correlations of all possible dissipative conversion processes and depicts the prospect of these types of irreversibilities in relation to the thermodynamic potentials driving processes, and mutual relationships.

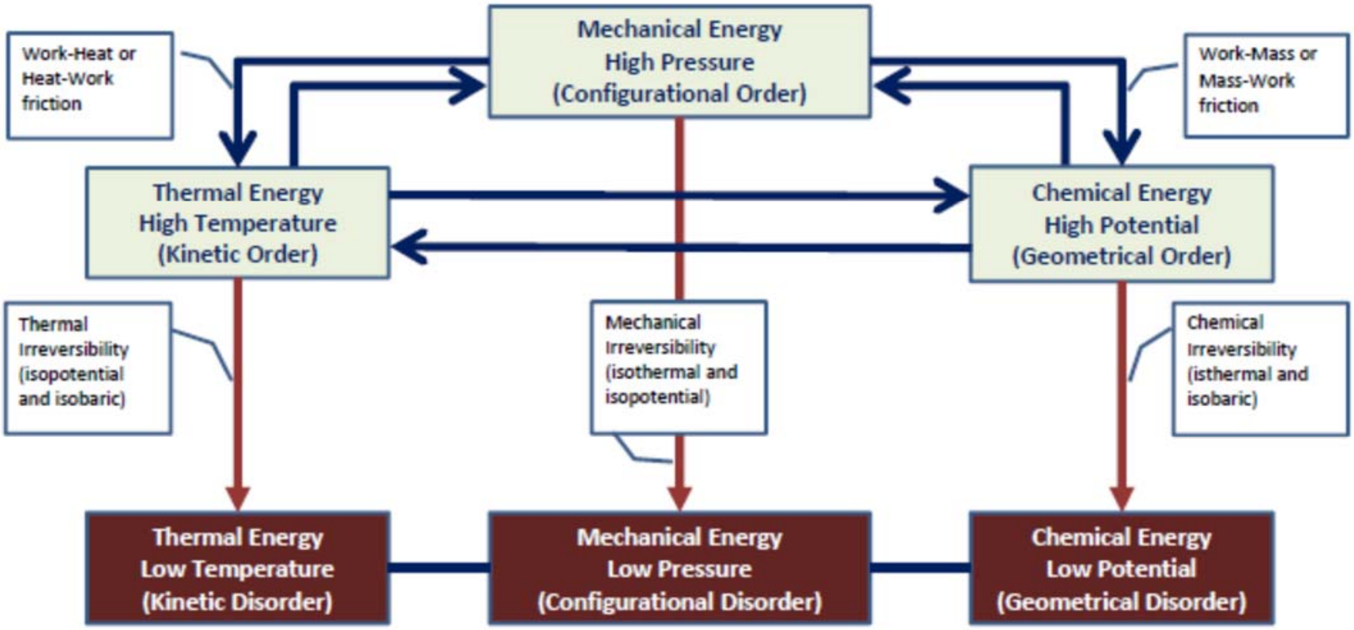


Figure 4.1 – Prospect of dissipative conversion processes

Different forms of irreversibility can be recognized in specific dissipative processes along which irreversible conversions take place from a form of energy to a different one. A canonical case of non-equilibrium process of internal energy dissipation is the unrestrained expansion of a gas representing the practical experiment of mechanical irreversibility [2.7]. Moreover, considering irreversible conversions, the stirring operation represents the conversion of mechanical energy, through the work interaction, into thermal internal energy

[2.7]. The stirring itself can be thought as an irreversible conversion of mechanical energy, through the work interaction, into chemical internal energy. The opposite irreversible conversions are admitted and evaluated in terms of exergy as a broader use of heat and work equivalence and interconvertibility explained by Gaggioli in his article dated 1998 [2.4]. If a control surface is assumed to define inward and outward entropy flows, then entropy balances and entropy efficiencies can be calculated for any process occurring in any system.

4.1.1. Mechanical Irreversible Conversion

In case of irreversible process, reference can be made to the classical cylinder-piston device where the piston separates the cylinder into two chambers with two systems at different thermodynamic conditions. A dissipative process behaves without interactions with the external environment therefore a fixed volume cylinder with internal moving piston is assumed. This is the configuration used to discuss the adiabatic availability. An ideal gas with no interaction among molecules except collisions, is assumed to fill the volume on the left side of the cylinder at high pressure and the right side at low pressure. The temperature is the same in both portions of the system and the piston is supposed to be adiabatic, that is with null thermal conductivity so that no heat interactions is allowed between the two portions of cylinder volume. The cylinder is provided with a partition wall that keeps separated a high pressure portion of overall gas from a low pressure remaining portion, both at same temperature. Then, the difference of pressure between the two portions is due to the frequency of collisions resulting increased in the lower sub-volume. The mechanical internal energy $-PV$ is therefore associated to the density of inter-particle kinetic energy and not to the extension of kinetic energy which is equally distributed over the two sub-volumes.

Once the partition wall is instantaneously removed or blown out from a valve in which fluid lamination occurs, the gas distributes over the whole volume with a pressure that is intermediate between the high pressure gas portion and the low pressure gas portion. Instead, the temperature remains constant as no heat interaction occurred along the totally irreversible process. The same experiment carried out using a real gas determines a decrease of temperature. The reason is that the higher the volume the higher the distance among molecules and the lower the inter-particle potential energy transformed into inter-particle kinetic energy resulting in lower temperature. This is the case in which the dissipation has an effect on both the main (mechanical) and the secondary (thermal) forms of energy (blue and red arrows in the Figure 4.1).

As far as other types are concerned, a similar behavior can be ascribed to the thermal irreversible conversion and to the chemical irreversible conversion. In the first case, the piston is supposed with infinite thermal conductivity so that the temperature is hold the same in both portions. In the second case, the piston is realized with permeable and adiabatic material so that only mass interaction is allowed.

4.1.2. Thermal Irreversible Conversions

Processes where the heat interaction occurs within a system at uniform pressure and uniform chemical potential (absence of chemical reactions), in all portions of the confined volume, imply the thermal irreversible conversion of thermal internal energy from higher temperature to lower temperature. These non-equilibrium processes are irreversible because the only result achieved at stable equilibrium is a different arrangement of the same amount of thermal internal energy among all particles constituting the system. That is, no interaction output is released to the environment.

4.1.3. Chemical Irreversible Conversions

In analogy with the thermal irreversible conversions, processes where the mass interaction occurs within a system at uniform pressure and uniform temperature, in all portions of the confined volume, imply the chemical irreversible conversions of chemical internal energy from higher chemical potential to lower chemical potential. In this case too non-equilibrium processes are irreversible because the only result achieved at stable equilibrium is a different arrangement of the same amount of chemical internal energy among all particles constituting the system. That is, no interaction output is released to the environment.

4.1.4. Entropy Production

All kinds of dissipation phenomena occurring within any system undergoing real processes have been generalized by Onsager introducing linear reciprocal relations between thermodynamic forces and fluxes. Those reciprocal relations are here reported [4.1,4.2]: $J_i = \sum_k L_{ik} X_k$ and $L_{ik} = L_{ki}$. The validity of these relations is true under hypotheses of local equilibrium and microscopic reversibility ensured by linear phenomena and small forces. Thus, local equilibrium describes global non-equilibrium.

If local equilibrium conditions stated by Onsager are fulfilled, then the entropy production, as defined by Prigogine [4.3-4.5], is minimum for stationary non-equilibrium states.

The dynamic instability at microscopic level described by Prigogine to provide the rationale behind the irreversibility, notwithstanding the deterministic and reversible dynamic laws (Loschmidt paradox), is correlated with the probabilistic character of Quantum Physics governing dynamic and motion of elemental microscopic particles. Dissipative processes far from equilibrium, transitory of stationary, imply dissipative structures [4.6], temporary or permanent respectively.

Starting from Prigogine who derived the minimum entropy production principle, Ziegler has devised the maximum entropy production principle at local level that apparently seems in contrast with the previous one.

4.1.5. Entropy Generation

The opposite viewpoint, with respect to the local entropy production, is represented by the global entropy generation. This approach has been developing in two directions centered on the minimum and maximum entropy generation principle.

The minimum entropy generation principle is the pillar of the “constructal theory”, applied to closed and open systems, conceived and developed by Bejan [4.9-4.14] and further enhanced by Sciubba [4.15-4.17] in the framework of entropy generation minimization (EGM) methods. The idea, and the objective behind the constructal theory, is to understand the criteria and the way in which natural phenomena shape the architecture of macroscopic non-living and living organized systems and devices. One of the most important statements of the constructal law is: “For a finite-size flow system to persist in time (to survive) its configuration must evolve in such a way that it provides an easier access to the currents that flow through it”. The concurrent trends are: i) the increase of reversible work interaction moving mass flow rate with increase of section area and ii) decrease irreversible work interaction due to moving mass flow rate with increase of section area. The opposite trends remain concurrent. The constructal theory basically starts with a search for the “minimum resistance to the flow” of some quantity whose transport is driven by a gradient of a physical parameter. Instead, the EGM minimizes the total entropy generation rate (viscous plus thermal), i.e. the total rate of irreversibility in the transport process. An experimental proof of EGM optimum has been carried out on a straight pipe conveying a given mass flow rate from a single source to a double delivery sink. It has been compared to a fixed branched pipe in order to investigate the existence (and uniqueness) of EGM minimum point corresponding to an optimized configuration. This is an approach to render this problem similar to the one with multi-point delivery (or gathering in case of opposite flow direction). This experimental proof accounts for multi-purpose systems to evaluate delivery of heat, mass and work, also including information. The constructal theory explains the reason behind the tendency of branching of the (heat or mass) transporting structure and demonstrates that it is the “function” that creates the “shape”. But it does so by positing together different assumptions, such as the ratio of entrance and exit diameters of ducts or a fixed volume of fluid or minimal length or fixed elementary geometry. By contrast, the use of EGM does not require additional phenomenological assumptions, and permits to treat any conceivable geometry and any physical phenomenon, solely on the basis of the Second Law of Thermodynamics which is a conceptual and practical extension with respect to the constructal theory. A rigorous proof of EGM enunciated as a theorem can be stated as follows: entropy generation minimization is a condition necessary and sufficient for tree-shape geometrical configuration optimization or, vice versa, tree-shape geometrical configuration is a condition necessary and sufficient of entropy generation minimization. This logical procedure would request the necessity proof and the sufficiency proof. Analytical representations can be complemented by numerical descriptions as the first are more strongly correlated to physical meaning of EGM method and the second provide quantitative assessment of problems and the opportunity of getting a sensitivity analysis of the methodology adopted to achieve the demonstration.

The constructal theory is underpinned by the Gouy-Stodola theorem and the leading concept is that the overall power consumed by any apparatus or network is affected by the dissipated energy flows depending on entropy generation rates. Hence, the entropy generation minimization is beneficial to efficiencies of balances and metabolism of cells and organisms. Minimizing entropy generation requires the evaluation of all forms of thermal, chemical and mechanical irreversible phenomena and the mutual inter-dependence at macroscopic and microscopic levels, all participating to the global epiphenomena arising from complex interactions among constituting elements and their assemblies. In this regard, the hierarchical structure of configurations is analyzed in the continuation of this section to focus on mechanisms governing the transition through hierarchical levels of macro-meso-micro-scopic systems. The constructal theory envisages the tree-shaped geometry configuration of interaction (mass, heat, work) systems as a differentiating constraint for changes. Indeed, the differentiation represents the adaptation and optimization process during transient metamorphosis, or physio-morpho-genesis of individual (ontogenesis), and during transient evolution or physio-morpho-genesis of species (“filogenesi” in Italian language).

On the opposite side of entropy generation approach, a theory has been recently proposed by Grazzini and Lucia [4.18-4.20] aimed at demonstrating that the non-equilibrium evolution of systems obeys to the maximum entropy generation principle.

It is worth highlighting that, in the framework of the generalized definitions of thermodynamic entropy, all optimization methods underpinned by the extrema principles and theories remain valid also with respect to any single component of entropy; In this regard, extrema principles should address to the generalized thermodynamic entropy creation (to overarch generation and production) thus extending to all components the use of this analysis logical schema. As an example, the EGM could be adopted in terms of “chemical entropy generation minimization” specially applied to specific chemical processes of interest. Moreover, a combination of “thermal entropy and chemical entropy generation minimization” constitute an extended application to more complex systems and phenomena.

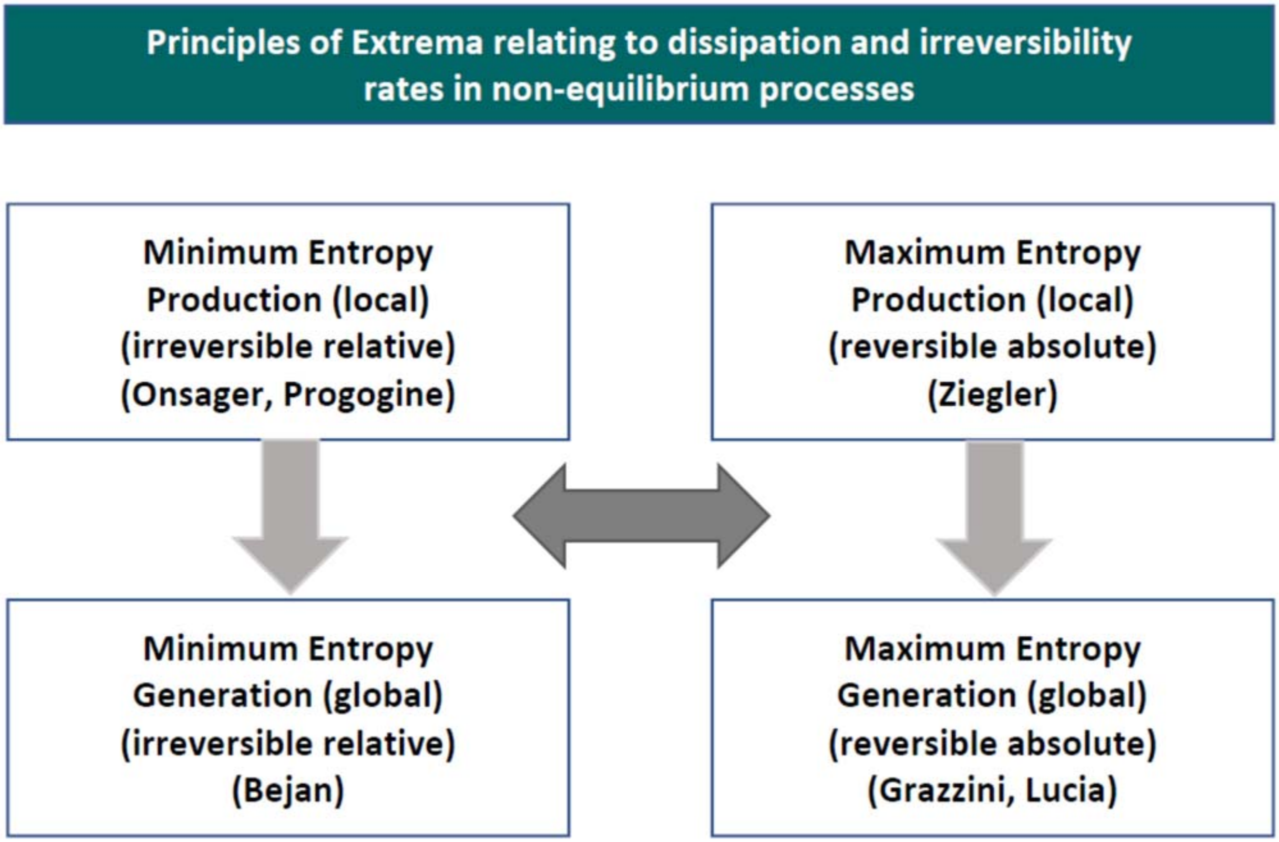


Figure 4.2 – Principles of Extrema

For sake of clarity, the Figure 4.2 summarizes the extrema principles considered in the analysis of open systems. These principles are not in contradiction with each other, however each one has a specific field of application that outlines the context of validity as explained by U. Lucia [4.15]. In order to achieve an overarching integration of these principles, they are listed and characterized here after:

- **Minimum Entropy Production**: proved by Prigogine provided the validity of local equilibrium governed by Onsager reciprocal relations;
- **Maximum Entropy Production**: proved by Ziegler provided the validity of local equilibrium governed by Onsager reciprocal relations;
- **Minimum Entropy Generation**: developed by Bejan through the constructal theory (internal needs of an open system);
- **Maximum Entropy Generation**: devised by Grazzini and Lucia underpinned by the variational calculus and Noerther's theorem (external interaction between system and environment).

There is a first difference between local and global non-equilibrium conditions: the entropy production is only a local approach thus representing a limitation with respect to the global approach of entropy generation as needed in applications and engineering design. Moreover, one should consider that the local description of a system should consider particle in their quantum nature and behavior deeply affecting the laws of dissipation mechanisms and the implication up to global level.

As far as the entropy production is concerned, the minimum entropy production principle was stated by Prigogine for local non-equilibrium.

Concerning entropy generation, the minimum can be considered as a relative minimization with respect to fixed boundary conditions such as mass flow rate, density, pressure, volume, characterizing fluxes within the system. Instead, the maximum generation should rather be evaluated in terms of maximization correlated to the maximum mass flow rate intake along mass interactions, and the associated entropy reversible variations (entropy contributions), between system and environment. In this regard, assigning to maximum and minimum extrema the proper physical significance, the above principles are therefore not in contrast with one another.

Considering the transient change of systems configuration, entropy generation, at global scale, is correlated to the evolution while entropy production, at local scale, is correlated to the so-called metamorphosis of an individual system.

In this regard, local and global non-equilibrium should be described by means of the generalized thermodynamic entropy to include all contributions and interactions within the system and between system and environment.

$$\left(S_2 - S_1\right)_{system} = S_{rev}^{\leftarrow} + S_{irr}$$

$S_{rev}^{\leftarrow}$: entropy contribution due balance of entropy property associated to inward and outward reversible interactions between system and reservoir

S_{irr} : entropy creation due to balance of entropy property associated to irreversible interactions occurring among internal subsystems

The generalized entropy production is expressed as $S_{IRR}^{G} = S_{IRR}^{T} + S_{IRR}^{C} + S_{IRR}^{M}$ in which the components of all forms entropy creation associated to the energy dissipation appear.

4.1.4. Gouy-Stodola Theorem

The Gouy-Stodola theorem states that exergy destruction is directly related to entropy produced along any irreversible process [1.17]:

$$EX_{DESTR} = T_R S_{GEN} \tag{4.1}$$

This expression embeds all contributions due to thermal, chemical and mechanical dissipation and can be explicated in the three components determined by thermal, chemical and mechanical dissipation. Then, the variation of exergy can be subdivided into its reversible and irreversible components:

$$\Delta EX^{T} = \Delta EX^{T}_{REV} + \Delta EX^{T}_{DESTR} = \left(H_2 - H_1\right) - T_R\left(S_2^{REV} - S_1^{REV}\right)^{T} - T_R\left(S^{IRR}\right)^{T} \tag{4.2}$$

$$\Delta EX^{C} = \Delta EX^{C}_{REV} + \Delta EX^{C}_{DESTR} = \left(H_2 - H_1\right) - \mu_R\left(S_2^{REV} - S_1^{REV}\right)^{C} - \mu_R\left(S^{IRR}\right)^{C} \tag{4.3}$$

$$\Delta EX^{M} = \Delta EX^{M}_{REV} + \Delta EX^{M}_{DESTR} = (H_2 - H_1) - \mu_R(S_2^{REV} - S_1^{REV})^{M} - \mu_R\left(S^{IRR}\right)^{M} \tag{4.4}$$

4.2. Hierarchical Structure of Thermodynamic and Informational Entropy

The title of the present section addresses both the thermodynamic and informational aspects of entropy concept to propose a unitary perspective of its definitions as an inherent property of any system in any state. However, the treatise is here focused on physical aspects as a prerequisite to extend the conceptual framework to information science to pursue the attempt of achieving an overarching and unitary theory.

On the one side, the term "generalized thermodynamic entropy" addresses the physical aspect of phenomena occurring in any system. On the other side, the definition of "generalized informational entropy" is the corresponding property of interest developed in the domain of Information Science and Geometry. The novelties here proposed concern: (i) the generalization of thermodynamic entropy and its hierarchical structure associated to multi-scale system configuration; and (ii) the possibility (and, for a rigorous approach, the need) of extending to information science the generalization of foundations and properties in the thermodynamic domain with the aim of achieving a complete and consistent conceptual framework. The intent is here to highlight correlations among different facets of the theoretical and methodological building under elaboration by the community of physicists and information scientists.

4.3. Thermodynamics-Information Relationship Schema

The following main points represent the context in which the present study is placed:

(i) Thermodynamic foundations framework in the conception of Hatsopoulos, Gyftopoulos and Beretta [1.4,1.5,4.7,4.8] claim that thermodynamic entropy is an inherent property of matter in its broader sense related to any system, large or small, in any state, equilibrium or non-equilibrium, even at macroscopic non-statistical level with no need for any microscopic statistical rationale [1.11,1.12].

(ii) The inherent character of entropy extends its validity to any scale of physical dimensions, hence classical and quantum mechanics equations of any particle are in compliance with the inherent essence and physical meaning of entropy including non-statistical and statistical methods of mechanics and thermodynamics [1.18]. In addition, quantum thermodynamics and the unified quantum theory of mechanics and thermodynamics [4.23-4.26] have demonstrated that irreducible uncertainties and probabilistic nature of phenomena are the ultimate root causes of irreversibility existing in microscopic dynamics.

(iii) Nevertheless, according to an information-based conception, a different school of thought has devised proofs that information and Shannon informational entropy [4.27,4.28] are in turn inherently associated to physic states of matter, as demonstrated by Jaynes [4.29,4.30], Landauer [4.31,4.32], and Karnani, Paakkonen and Annila [4.33]. Therefore, Boltzmann and Gibbs statistical entropy are correlated to Shannon entropy and this relationship is not only a formal correspondence and homology. Both thermodynamic aspect and informational aspects are inherent to any system in any state and the implication of quantum mechanics in quantum information theory advocates this principle [4.34]. Indeed, informational entropy is in turn an inherent property of matter as any physical state is characterized by an amount of information and a corresponding amount of uncertainty that depends on the scale of the system up to quantum where Heisenberg indetermination principle constitutes a physical fundamental. The statement that information is a physical entity does not disprove that entropy is an inherent property of matter. Instead, both represent different expressions of a unique fundamental and elementary characteristic of the phenomenological physical reality.

(iv) Information is an inherent property of any system in any state since it is associated to the state of properties. Consequently, the relationship between thermodynamic and informational viewpoints represent an intrinsic property of any system in any state being the two viewpoints coexisting and complementary. Any microscopic up to macroscopic scale of classical (and non-statistical) thermodynamics is affected by this correlation and generalization of theorems or properties can be adopted in the domain of information theory, as explained by Kafri [4.35].

The main objective is here to discuss the hierarchy characterizing any system and the subsequent structure of thermodynamic and informational entropy deriving from this multi-level description. The interest relies in extending these findings to achieve a correspondence and equivalence between thermodynamic entropy and informational entropy and their respective role in the description of complex abiotic and or biotic systems.

4.4. Considerations on Physical Aspect of Second Law and Thermodynamic Entropy

One of the paradigms of Thermodynamics conceptual architecture is founded on axiomatic definitions and demonstrations of principles and theorems developed by Keenan, Hatsopoulos, Gyftopoulos and Beretta. The First Law and Second Law have been reformulated and, in their perspective, the Second Law statement asserts the existence and uniqueness of stable equilibrium state for a given system A composed by r constituents, described by S parameters and characterized by a constant energy content [1.9]. A corollary of this statement is the impossibility of "Perpetual Motion Machine of the Second Kind (PMM2)" which has been adopted to demonstrate an alternative formulation of thermodynamic entropy as a non-conservative, additive and state property. In particular, this definition of entropy property for macroscopic states and processes, in the framework of Classical Thermodynamics, has been founded on its nature inherent to all systems, large or small, in all states, equilibrium and non-equilibrium. On this basis, its definition has been derived replacing the heat interaction Q, appearing in Clausius definition, with the difference between energy E and available energy Ω^R of a system A interacting with an external reference system, or reservoir R, times a parameter C_R characteristic of the reservoir $S_1 - S_0 = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right]$ where it is proved that $C_R = T_R$ and T_R is the constant temperature of R. The physical meaning of this expression is that the entropy variation is determined by the amount of non-useful heat released by the system, along whatever process between initial and final states, to the reservoir. Indeed, the energy minus the available energy results into the non-available energy. The available energy is defined with respect to a reference system and hence corresponds to the exergy EX^R, in turn depending on a fixed reference thermodynamic state, both being additive state properties. Therefore, the above expression of entropy can be turned in the one considering exergy in lieu of available energy $S_1 - S_0 = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]$. Considering that exergy is defined as the maximum net useful work withdrawable from a system interacting with a reservoir, here the physical meaning is that entropy corresponds to the minimum net non-useful heat released by the system to the reservoir. The consequence, as anticipated, is that the concept of heat interaction Q is not more used in this definition [3.2-3.5]

To complete the discussion of the physical meaning, this definition assumes that entropy expressed in Equation (1) is an inherent property of matter, hence it does not depend on whatever external reference system or reservoir is assumed [3.1–3.5]. The role of the reservoir is therefore auxiliary only and recent studies demonstrate that entropy can be defined with no use of the reservoir concept [3.5]. The available energy is replaced by the exergy property, in turn conceived and defined as a non-conservative and additive state property [2.3–2.6] to provide components of exergy associated to all contributions of available energy of a system interacting with a reservoir. The entropy-exergy relationship ensures that the exergy method, adopted in the design and optimization of processes and plants [2.7], properly accounts for non-equilibrium and irreversible phenomena focused by Second Law analyses.

A summary of the logical rationale underpinning the framework of foundations under discussion is described in the following sequence to highlight the reasons of a more general paradigm:

(1) The Second Law statement is based on the existence and uniqueness of stable equilibrium.
(2) Stable equilibrium implies thermal equilibrium, chemical equilibrium and mechanical equilibrium.
(3) Corollary of stable equilibrium is the impossibility of Perpetual Motion Machine of the Second Kind (PMM2).
(4) PMM2 is adopted in the proof of the entropy definition related to temperature, hence it is the definition of a thermal entropy property.
(5) Highest-(thermal)-entropy principle is applied to prove that stable equilibrium implies the equality of temperature, potential and pressure while thermal entropy determines thermal energy and heat interaction only, this representing a logical incompleteness and inconsistency thus introducing an incongruity [29–31].
(6) To remove the incongruity, equality of temperature, potential and pressure has to imply thermal, chemical and mechanical equilibria and this opposite proof needs chemical entropy and mechanical entropy, in addition to thermal entropy, to assert a highest-generalized-entropy principle to be used in the proof [29–31].

As entropy requires the concept of exergy, in turn derived from the available energy of the composite system-reservoir, then the formulation of chemical exergy and mechanical exergy, in addition to thermal exergy, is needed to achieve the chemical entropy and mechanical entropy, in addition to thermal entropy, as components of the generalized thermodynamic entropy property, which enables demonstrating the necessity and sufficiency of stable equilibrium for equality of temperature, potential and pressure, thus proving the Second Law with a complete and consistent logical rationale. This paradigm should also be valid at microscopic level, more rigorously at any dimensional scale of matter up to elementary particles obeying to quantum mechanics. For this very reason, the following sections focus on the extension of all components of thermodynamic entropy to each and every mesoscopic level constituting a multi-scale system in the perspective of statistical and quantum physics.

4.5. Second Law Statements Related to Thermal or Chemical Potentials

Among all statements of Second Law reported in the literature, the existence of uniqueness of stable equilibrium of a system constitutes the principle from which the non-existence of an ideal Perpetual Motion Machine of the Second Kind (PMM2) is inferred [1.9]. PMM2 implies that a system does not exist which is capable of converting a given amount of thermal energy at high temperature into mechanical energy with no production of thermal energy at lower temperature. This represents a statement of the Second Law enunciated by Kelvin and Planck in the sense that the PMM2 undergoes a direct heat-to-work ideal conversion cycle process. Besides, the statement of Clausius addresses to the impossibility of converting thermal energy at low temperature into thermal energy at high temperature with no contribution of mechanical energy input. In this case, the PMM2 can be regarded as undergoing an inverse work-to-heat ideal conversion cycle process. The rationale behind the impossibility of PMM2 is the non-existence of Maxwell’s demon [4.36]. The concept of Maxwell’s demon, implied with the Second Law, consists of a being or a device capable of selecting and separating particles of any system with higher kinetic or potential energy from particles with lower kinetic or potential energy, with no net effects on the surrounding environment interacting with the system. In other terms, there is no means to select and separate particles at higher velocity from particles at lower velocity and particles at lower relative distance from particles at higher relative distance. If it existed, this selective segregation would be able to revert an irreversible process or to generate the availability of the system equivalent to a reduction of thermodynamic entropy property between the initial non-equilibrium state and the final stable equilibrium state.

The non-existence of PMM2 is adopted to demonstrate the formulation of entropy property as used in the proof developed by Gyftopoulos and Beretta [1.9], however, the concept of PMM2 can be generalized to chemical potential that depends on particles relative position determining the system geometry, in addition to the thermal aspect that depends on particles relative velocity determining the system kinematics. Hence, considering that mass interaction, occurring in open systems, assumes the same role of heat interaction in closed systems, the Second Law can be regarded in terms of mass interactions in addition to heat interactions. A consequence of the extended types of interactions governed by the Second Law, in the specific case of cyclic processes, is that the definition of entropy property can be expressed in terms of thermal or chemical cycle efficiency. For thermal processes at constant chemical potential and variable pressure, the following canonical expression of heat cycle efficiency applies: $W = Q \cdot \left(1 - \frac{T_R}{T}\right) = Q\,\eta^T$. On the other side, accounting for chemical processes at constant temperature and variable pressure, the following expression of mass cycle efficiency corresponds to, and is homologous to, the previous one and is based on inter-particle potential energy (chemical potential) in lieu of inter-particle kinetic energy (temperature): $W = M \cdot \left(1 - \frac{\mu_R}{\mu}\right) = M\,\eta^C$. It is noteworthy that the Phase Rule $F = C + 2 - P$ ensures at least two independent intensive properties that, in the case of isopotential or isothermal processes, consist of temperature and pressure or potential and pressure, respectively.

The formulation of mass cycle efficiency can be proved adopting the rationale proposed by Gyftopoulos for the heat cycle efficiency [4.21]. Assuming a reversible process to convert mass interaction into work interaction the balance of energy and entropy relating to the conversion cycle of the internal system is evaluated. The system undergoes an input of mass interaction M at high potential μ associated to chemical entropy input $S^C = \frac{M}{\mu}$ to be converted into work interaction W. The entropy balance of the cyclic process requires that an equal amount of chemical entropy output, corresponding to $\frac{M}{\mu}$, be associated to mass interaction released at low potential μ_R. However, the release of entropy at μ_R must necessarily be associated to a mass interaction $\mu_R S^C = \mu_R \frac{M}{\mu}$. Hence, the overall interactions balance is $W = M - \mu_R \frac{M}{\mu} = M \cdot \left(1 - \frac{\mu_R}{\mu}\right)$ in which the cycle efficiency corresponds to the formulation assumed: $W = M \cdot \left(1 - \frac{\mu_R}{\mu}\right)$. The non-completeness of energy transfer occurs after reaction since before reaction no contribution and no Maxwell demon can act to increase the amount of energy transfer [4.21,4.22]. Both thermal and chemical aspects of Second Law, according to the above highlighted dualism and symmetry relating to closed and open systems, underpin all definitions of the Second Law in terms of non-existence of PMM2. The set of statements of Second Law accounting for thermal, chemical and mechanical interactions is discussed in the following section.

4.6. Perpetual Motion Machines of Second Kind (PMM2) as a Corollary of Second Law

The Perpetual Motion Machine of the Second Kind (PMM2) is a corollary directly derived from the Second Law enunciated in terms of existence and uniqueness of stable equilibrium. With reference to the previous section, temperature and potential drive those processes occurring in thermal-mechanical PMM2 or in chemical-mechanical PMM2, then the following set of statements can be characterized by the properties involved, categorized by the process occurring and classified in terms of specific PMM2 definition. It is intended that ideal direct or inverse cycle conversions are reversible processes moving the systems through stable equilibrium states.

4.6.1. Non-Existence of Thermal-Mechanical PMM2

Thermal–Mechanical aspect relating to heat-to-work or work-to-heat interactions conversion occurring in closed systems can be characterized and categorized as follows:

1. Mechanical aspect of non-existence of PMM2 performing an ideal direct heat-to-work conversion cycle implies that it is not possible to convert a given amount of thermal energy at high temperature into

mechanical energy with no production of thermal energy at lower temperature (Kelvin–Planck and Poincaré); in this case, the PMM2 canonical efficiency is $\eta^{DIRECT}_{THERMAL} = 1 - \frac{T_R}{T}$.

2. Thermal aspect of non-existence of PMM2 performing an ideal inverse work-to-heat conversion cycle implies that it is not possible to convert a given amount of thermal energy at low temperature into thermal energy at high temperature with no contribution of mechanical energy input (Clausius and Thompson).
3. Mechanical aspect of non-existence of PMM2 performing an ideal inverse work-to-heat conversion cycle implies that it is not possible to convert a given amount of mechanical energy at high-pressure-low-volume into thermal energy with no production of mechanical energy at low-pressure-high-volume.
4. Thermal aspect of non-existence of PMM2 performing an ideal direct heat-to-work conversion cycle implies that it is not possible to convert a given amount of mechanical energy at low-pressure-high-volume into mechanical energy at high-pressure-low-volume with no contribution of thermal energy input.

4.6.2. Non-Existence of Chemical-Mechanical PMM2

Chemical-mechanical aspect relating to mass-to-work or work-to-mass interactions conversion occurring in open systems:

5. Mechanical aspect of non-existence of PMM2 performing an ideal direct mass-to-work conversion cycle implies that it is not possible to convert a given amount of chemical energy at high potential into mechanical energy with no production of chemical energy at lower potential; in this case, the PMM2 canonical efficiency is $\eta^{DIRECT}_{CHEMICAL} = 1 - \frac{\mu_R}{\mu}$.
6. Chemical aspect of non-existence of PMM2 performing an ideal inverse work-to-mass conversion cycle implies that it is not possible to convert a given amount of chemical energy at low potential into chemical energy at high potential with no contribution of mechanical energy input.
7. Mechanical aspect of non-existence of PMM2 performing an ideal inverse work-to-mass conversion cycle implies that it is not possible to convert a given amount of mechanical energy at high-pressure-low-volume into chemical energy with no production of mechanical energy at low-pressure-high-volume.
8. Chemical aspect of non-existence of PMM2 performing an ideal direct mass-to-work conversion cycle implies that it is not possible to convert a given amount of mechanical energy at low-pressure-high-volume into mechanical energy at high-pressure-low-volume with no contribution of chemical energy input.

4.6.3. Physical Meaning of PMM2 Impossibility

One of consequences of the Second Law, or from a different perspective, the ultimate cause of irreversibility intrinsic to all processes, is the subdivision of systems configuration among levels of a hierarchical structure. In the special case of a molecule, once rigid constraints determining the whole mass to behave as a unique physical entity are removed, then the consequent distribution and dispersion of all components of internal energy is spread among increased available degrees of freedom of vibrating atoms or groups of atoms. The non-existence of Maxwell's demon hence prevents to reverse any process attempting to bring the system back to its original configuration. As the existence of Maxwell's demon is impossible, the reverse process from a lower to a higher hierarchical level is impossible as well since a PMM2 does not exist that is able to convert the entire amount of energy of a hierarchical level into energy of a higher level in the whole system configuration hierarchy.

The importance of a complete characterization of all types of PMM2 is ascribed to the fact that the impossibility of PMM2 is a corollary of Second Law and implies a cycle efficiency $\eta < 1$ in any conversion processes. The ultimate cause of impossibility of PMM2 is the inter-particle collision characterized by the quantum uncertainty that determines microscopic irreversibility, as demonstrated by Lucia [4.37]. The not complete conversion of energy determines the available energy and, consequently, exergy used in the formulation of thermodynamic entropy and its components, as demonstrated in the following sections. By virtue of the intrinsic correlation between physical and informational content of systems and phenomena, the impossibility of PMM2 can be retrieved in any calculation process and device hence providing a proof of the Landauer's principle [4.38–4.41].

4.7. Hierarchical Configuration and Levels of Multiscale Mesoscopic Systems

Thermodynamic systems can be regarded as a set of many-particles or few-particles as assumed in the framework of statistical physics and kinetic theory. Interactions among particles depend on relative velocity and relative position thus determining the kinetic energy and potential energy representing fundamental components of the internal energy characterizing any state of any system. The internal energy, at each available state, is subdivided in, and accommodated among, all translational and rotational degrees of freedom of the system which can be regarded as constituted by hierarchical levels with respect to the aggregation of masses of particles. The transitions among levels have been treated by Grmela et al. [4.42–4.45] in a rigorous and axiomatic mathematical formalism demonstrating the classical and quantum implication of entropy between two different levels accounting for non-equilibrium dissipative and non-dissipative dynamics. One of the major outcomes of Grmela analysis is that dissipative and non-dissipative dynamics are coupled in reduction and extension from one level to another one. On this basis, the attempt is here to investigate the possibility of specializing the definition of entropy by replicating its intrinsic structure for all coexisting levels of a hierarchical structure shaping the configuration of a multiscale mesoscopic system including quantum scale. In this perspective, physical and informational domain should remain a unique paradigm.

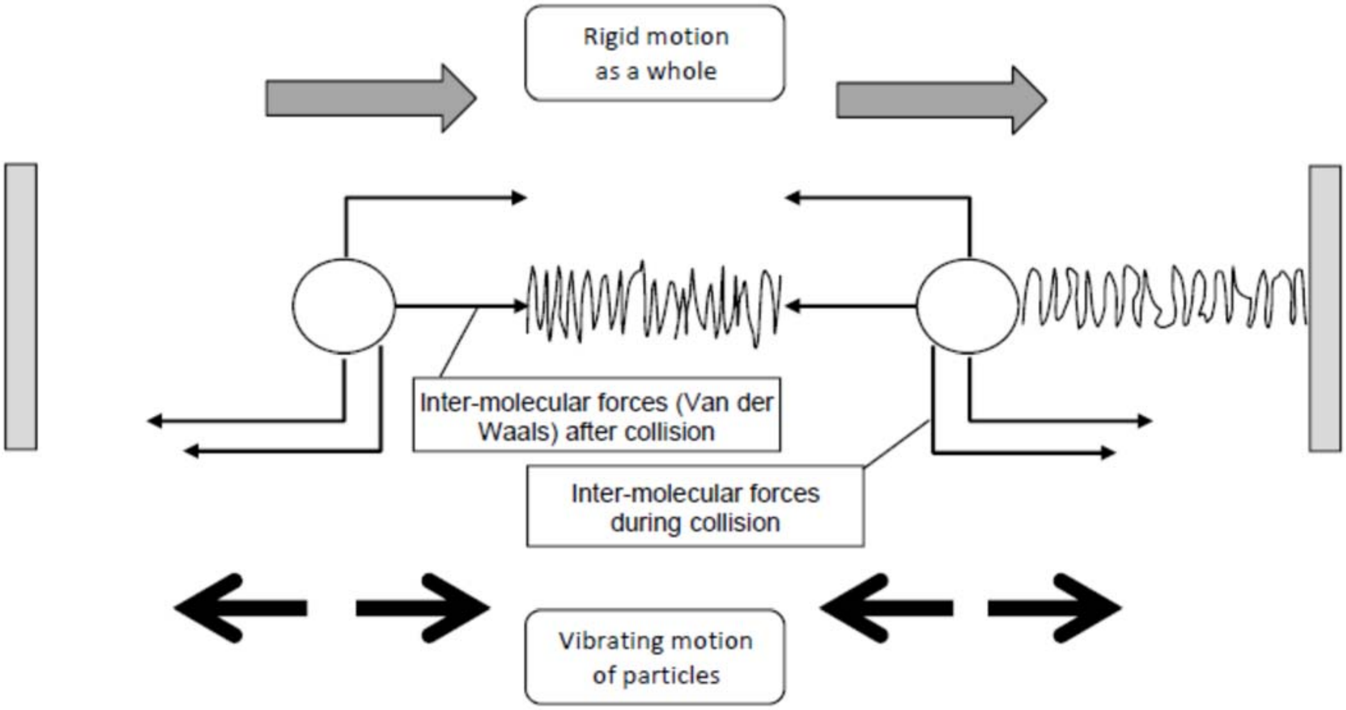
4.7.1. Maxwell's Demon and Degrees of Freedom

As far as the hierarchical configuration is concerned, vibrational (translational and rotational) degrees of freedom are considered pertaining to a lower hierarchical level. Indeed, aggregates of particles, such as atoms bonded in a molecule or protons and neutrons bonded in the nucleus of an atom, behave differently from the same particles with no binding constraints. Then, removal of constraints determines an increase of degrees of freedom hence the configuration of the system has implications on equilibrium and non-equilibrium phenomena occurring within it. The main consequence is that, if particles are bounded to each other and constitute a rigid whole, then kinetic energy and potential energy of the rigid whole itself can be entirely transferred to the external system as work interaction. Instead, free independent particles of the same system with equal content of internal energy are not more able to transfer the entire amount of internal energy by means of work interaction to the external system. The ultimate reason of this limit is that a Maxwell's demon does not exists that is capable to select positions and velocities of particles in such a way to move the system back to thermodynamic potentials characterizing non-equilibrium configurations.

4.7.2. Degrees of Freedom and Hierarchical Levels

The hierarchical configuration of thermodynamic systems, both many-particle of few-particle, is related to the geometric and kinematic framework of constraints and degrees of freedom determining properties and phenomena occurring along processes. In a unitary perspective, macroscopic and microscopic systems should behave consistently and laws not to be in contradiction. Thus, the relationship between the macroscopic (continuum) view of Classical Thermodynamics and its microscopic (particles) view as conceived in the framework of Classical and Quantum Statistical Thermodynamics, is here assumed as reported by Kline [1.17]. Differently from Classical Thermodynamics, the microscopic description of a system, in the fundamental assumptions and physical model proposed by Gibbs, is the ensemble constituted by number of replica $\overline{N}$ of a system containing n_i particles. Gibbs ensembles are suitable to account for independent or dependent particles as occurring in solid state of matter, liquids or gases. The internal energy associated to each and every particle is distributed according to Gibbs canonical distribution of fractions $p_i = n_i \big/ \overline{N}$ of molecules n_i (out of the total amount of molecules *N*) in the state i $p_i = n_i \big/ N = e^{-\beta\varepsilon_i} \Big/ \sum_i e^{-\beta\varepsilon_i}$ where $\beta = 1 \big/ k_B T$ and $Q = \sum_i e^{-\beta\varepsilon_i}$ is the Gibbs canonical partition function derived from the statistical thermodynamic entropy formulation $S = k_B \ln W$ where k_B is the Boltzmann constant and *W* is the number of different particles configurations. The partition function describes a configuration, in terms of positions and velocities of the phase space, resulting from the distribution of particle energies among the energy levels allowable for a given thermodynamic state of a microscopic system in stable equilibrium [1.10-1.12]. The relationship between macroscopic and microscopic representation model of a system is the rationale behind the conception of entropy defined in terms of degree of distribution of phenomena among the elements constituting a system [3.10]. The typical thermodynamic system considered in statistical physics is composed of molecules. However, each and every molecule is in turn composed of atoms constrained by electro-magnetic forces acting as chemical bonds. Atoms move in three translational and three rotational vibration modes while the molecule itself moves as a whole along its three translational and three rotational degrees of freedom. These two different modes (external dynamics and internal vibration) establish a hierarchical relationship within a molecule so that positions and velocities, at a higher Hierarchical Level (HL1) of the molecule as a whole, imply different thermodynamic properties with respect to a lower Hierarchical Level (HL2) where sub-molecules and atoms behave independently within their own degrees of freedom. Vibration modes of motion, in the perspective of translation and rotation at lower hierarchical level, should be considered as a consequence of constraints suitable: (i) to separate two hierarchical levels; and (ii) to allow relative velocities and displacements; hence, constraints fulfilling these requirements can only be interactions constituting dynamical correlations among particles. The increase of degrees of freedom and constraints has an impact on the content of information that the system accommodates and needs for the extraction of energy along any process. In this regard, a superpositions of multiscale systems modeling is adopted addressing to macro-level (macroscopic), meso-level (mesoscopic) micro-level (microscopic) and quantum-level (quantum-scopic) representing hierarchical levels implied in equilibrium and non-equilibrium thermodynamic processes. The importance and criticality of hierarchical models of systems in equilibrium or non-equilibrium is corroborated by current studies reported in the literature [4.42-4.45]. Referring to the energy levels available in a given state of the system defined in Statistical Physics, should be regarded in the following breakdown:

$$\varepsilon_i = \varepsilon_i^{TRANSLAT} + \varepsilon_i^{ROTAT} + \varepsilon_i^{VIBRATION} \tag{4.5}$$



$$\varepsilon_i^{HL-HIGHER} = \varepsilon_i^{TRANSLAT} + \varepsilon_i^{ROTAT} \tag{4.6}$$

$$\varepsilon_i^{HL-LOWER} = \varepsilon_i^{\substack{VIBRATION\\TRANSLAT}} + \varepsilon_i^{\substack{VIBRATION\\ROTAT}} \tag{4.7}$$

The above Equations (4.6) and (4.7) formally express the hierarchical paradigm deriving from the subdivision of a physical entity into interacting elements and the consequent degrees of freedom availability increase. The transition to subdivided particles occurs through stochastic change of Hamiltonian equation and is governed by the same probabilistic mechanism as in intrinsic quantum collisions and particles motion dynamics. This mechanism is a further demonstration of the fact that the thermodynamic entropy undergoes changes as soon as interactions intervene between two or more parts of a system, according to the definition discussed at the outset of previous section 3. The elementary interaction implies subdivision and hence irreversible dissipation of physical and informational energy with increase of entropy which undergoes a non-homogeneous partition between two hierarchical levels. Then, the logical schema of dissipation phenomena is:

Systems Interaction $\Longrightarrow$ *Energy Subdivision* $\Longrightarrow$ *Hierarchical Configuration* $\Longrightarrow$ *Irreversible Dissipation*

The elementary subdivision occurring in a two-particle system, such as a bi-atomic molecule, intrinsically embeds the loss of exergy related to the physical creation of thermodynamic entropy; at the same time, this operation implies the increase of degrees of freedom and the subsequent loss of information. The multiple double implication paradigm is*: Interaction* ⇔ *Subdivision* ⇔ *Dissipation*, inherently implying physical and informational variations intrinsically correlated. Restoring the initial status from the final, requires an input of coupled energy and information. The reverse process would be: *Interaction* ⇔ *Conversion* ⇔ *Organization,* occurring in terms of physical and informational aggregation. This operation needs an input consisting of physical and informational work interaction.

The formal correspondence between Boltzmann-Gibbs Entropy and Shannon Information confirms the relationship between Statistical Physics and Information Theory. However, information is inherently associated to physical states of system and, on the other side, physical properties and phenomena inherently embed information. This bi-directional relationship constitutes the rationale to extend thermodynamic principles and properties, at any mesoscopic hierarchical level, to informational aspect of any system. Therefore, thermodynamic information (or information of thermodynamics) and informational thermodynamics (or thermodynamics of information) can be regarded as the two aspects of a thermodynamic-informational duality of the ultimate essence of any interaction (classical and quantum, non-statistical and statistical) occurring among any particle in any state. In this duality, an interaction, as a transfer of property, corresponds to communication as a transfer of information. The relationship is overarching any level of the hierarchy from classical to quantum scale. This fundamental fact concerns any portion of matter as a unique entity, that is physical and informational, and is accounted for by the existence of a generalized thermodynamic and informational entropy property. This fact also justifies the Landauer's principle and translates irreversible dissipation phenomena into a corresponding informational logical schema ending up with corroborating the very non-existence of the Maxwell's demon.

4.8. Generalized Thermodynamic Entropy and Exergy Properties

A consequence of Second Law, and its corollary consisting of the non-existence of PMM2, is the definition of entropy property of a system *A* that, beside the classical formulation of Clausius $S_1 - S_0 = \int_0^1 \frac{\delta Q}{T}$ in finite terms, has been expressed in the following form already discussed in previous here again reported for sake of clarity: $S_1 - S_0 = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]$ where C_R is the constant characterizing an external reference system *R* behaving as a reservoir, *E* is the internal energy determined by temperature, chemical potential and pressure, and EX^R is the exergy of the system resulting from thermal, chemical and mechanical components. In all cases, the thermodynamic entropy remains an inherent property of any system, large or small, in any state, equilibrium or non-equilibrium. Therefore, the reservoir behaves as a thermal-chemical-mechanical auxiliary system only. Since the parameters characterizing the reservoir are temperature, chemical potential and pressure, for this very reason the generalized exergy expresses the maximum theoretical net useful (and generalized) interaction available within the system-reservoir composite; then, this definition relates to the thermal entropy S^T , chemical entropy S^C and mechanical entropy S^M .

4.8.1. Thermodynamic Entropy Components

As the thermodynamic entropy has been proved to be an inherent property of any system in any state, hence it has to relate to all forms of interactions at any hierarchical level. The reference external system R is auxiliary only and for this very reason can be the same for all hierarchical level of the system configuration, and, therefore, it should result from the following components [3.6-3.8]:

Thermal Entropy: $(S_1 - S_0)_{HL}^T = \frac{1}{T_R}\left[(E_1 - E_0) - (EX_1^R - EX_0^R)\right]_{HL}^T$ (4.8)

Chemical Entropy: $(S_1 - S_0)_{HL}^C = \frac{1}{\mu_R}\left[(E_1 - E_0) - (EX_1^R - EX_0^R)\right]_{HL}^C$ (4.9)

Mechanical Entropy: $(S_1 - S_0)_{HL}^M = \frac{\overline{R}}{P_R V_R}\left[(E_1 - E_0) - (EX_1^R - EX_0^R)\right]_{HL}^M$ (4.10)

Then entropy is derived from exergy and can be calculated based of the amount of work interaction along a so called “mechanical process” in which a mass undergoes displacements in the same direction of gravitational or electro-magnetic field force. All S^T, S^C, S^M components of thermodynamic entropy above defined are extensive and additive properties as a consequence of their definition. Indeed, the additivity of entropy is a consequence of the additivity of energy and exergy appearing as terms of the entropy formulation [1.9]. In particular, exergy is directly derived from the generalized available energy that has been proved to be additive by virtue of the interaction of a system with the reservoir considered as the external reference system accounted for in its definition.

The concept of equivalence and interconvertibility demonstrated by Gaggioli [2.4–2.6], further corroborates the need of entropy contributions specially defined for thermal, chemical and mechanical forms of energy and interaction. To do so, the definition of generalized thermodynamic entropy consists of the sum of terms expressing thermal, chemical and mechanical contributions of entropy property being extensive and additive for any system in any state [3.6-3.8]:

$$S^G = S^T + S^C + S^M \tag{4.11}$$

where S^T is the thermal entropy, or kinematic entropy, S^C is the chemical entropy, or geometric entropy, and S^M is the mechanical entropy characterizing, respectively, heat, mass and work interactions with useful external system and non-useful external reservoir. The physical meaning of these contributions can be clarified in relation to the microscopic model of the system constituted by a set of few particles or many particles in the framework of Statistical Physics perspective. These contributions are characterized by inter-particle kinetic energy associated to particles relative velocity and inter-particle potential energy associated to particles relative position. Then, thermal entropy and chemical entropy represent, respectively, the degree of distribution of inter-particle kinetic energy and the degree of dispersion of inter-particle potential energy among available degrees of freedom characterizing the system configuration at all hierarchical levels.

In addition, mechanical entropy accounts for the density of inter-particle kinetic energy caused by the collision frequency determined by the volume and the density of inter-particle potential energy caused by the repulsion intensity determined by the volume as well.

The configuration of any system and the hierarchy established by the set of constraints and degrees of freedom determines the hierarchical structure of entropy property as the consequence of the existence of hierarchical levels HL of the system partition. It is here assumed that entropy is a measure of the degree of sub-division of phenomena and properties among all accessible levels and degrees of freedom characterizing the hierarchical configuration of a system [44]. This dissipative sub-division process is intrinsically irreversible along non-equilibrium processes and through different levels according to Equations (2) and (3). This fact is reflected in the concept of entropy for non-equilibrium states [4.47-4.48] and non-equilibrium dynamics, as presented in different well-known theories such as the General Equation for Non-Equilibrium Reversible Irreversible Coupling (GENERIC) [4.43,4.44] and the Steepest-Entropy-Ascent (SEA) [4.49] are not at all discussed and their validity not criticized. On the contrary, these theories should be corroborated by their extension and application to configurations characterized by the stratification and superimposition of coexisting physical layers organized as hierarchical levels, in the sense here described, underpinning the complexity of multi-scale systems and considering the dualism ascribed to physical–informational character of matter. However, on an evolutionary time scale, the hierarchical architecture of complex systems is determined by the Maximum Entropy Production Principle [4.50] (overarching SEA and GENERIC) as the effect of Second Law acting on multi-level biotic systems evolution, as described by Annila [4.51].

The non-existence of Maxwell's demon represents the inherent physical limit preventing the upgrade of the entire amount of energy at a certain hierarchical level to a higher level. Hence, a hierarchical structure of entropy property definitions is founded on this intrinsic property and is represented in Figure 4.2:

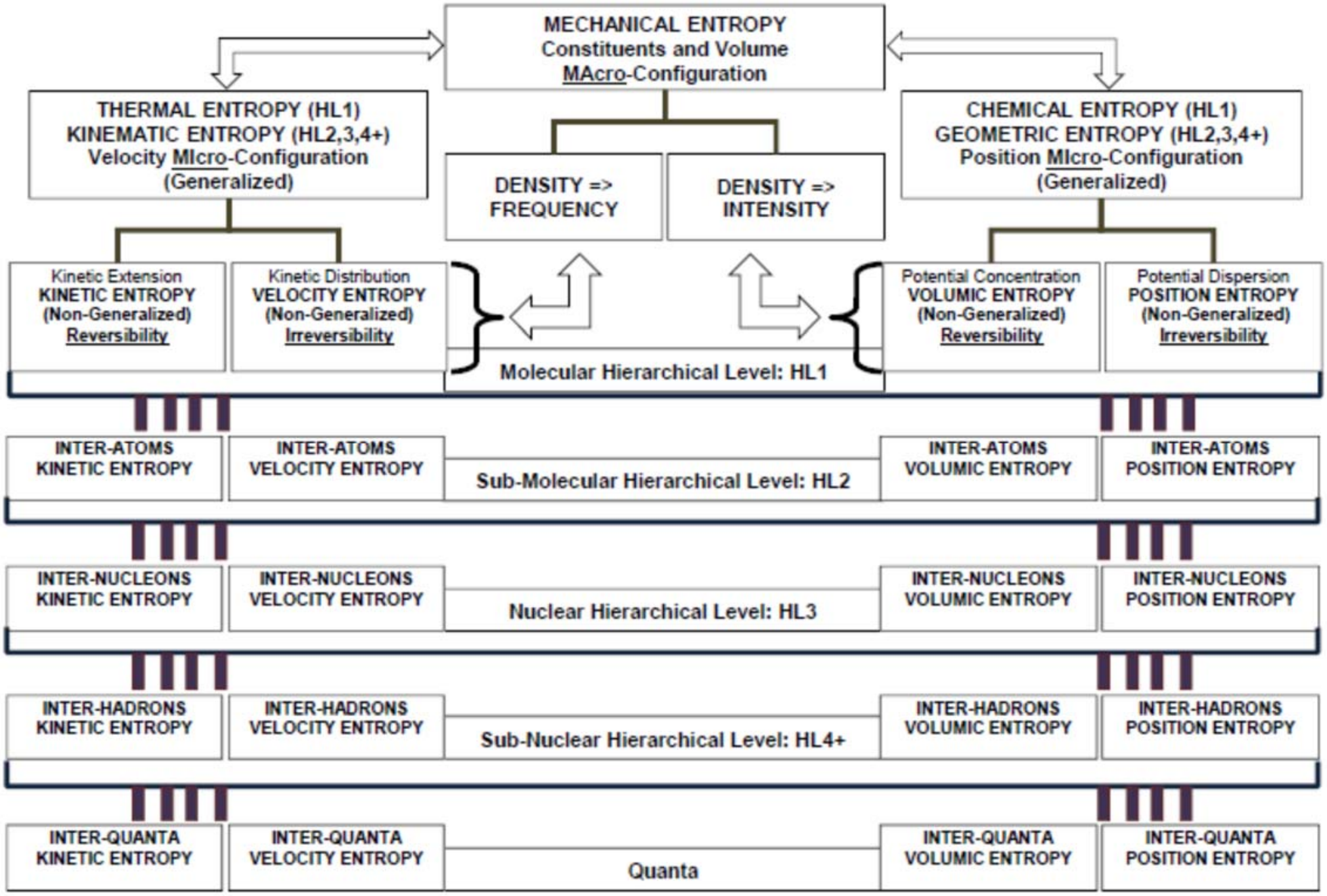


Figure 4.3 - Hierarchical structure of generalized thermodynamic entropy property

The sum extended to all hierarchical levels leads to the generalized thermodynamic entropy expressed as:

$$S^{G} = S^{G}_{HL\,1} + S^{G}_{HL\,2} + S^{G}_{HL\,3} + S^{G}_{HL\,4+} \qquad (4.12)$$

The definition in terms of density and frequency spans from classical and statistical thermodynamics is adopted to describe the origin of energy and entropy contributions due to kinetic energy and potential energy of a microscopic system up to the quantum mechanics domain. At quantum level, the Schrodinger equation $\hat{H}\,\Psi = \left(\hbar^{2}/2m\right)\nabla^{2}\Psi + V\Psi = E\Psi$ is constituted by the Hamiltonian operator resulting from the sum of a kinetic operator and a potential operator of the wavefunction Ψ. Interestingly, the duality wave-particle can be recognized in all terms of Schrodinger equation. In the left side member of the equation each term is constituted by an operator, representing the particle-trajectory dual character of waves, times the wavefunction, representing the wave-transmission dual character of particles. In the right side of the equation, the eigenvalue represented by the energy is associated to the particle-trajectory while the wavefunction is again associated to the wave-transmission in space and time. This dualism relies on the twofold essence of Schrodinger equation terms in which operators and eigenvalues of observables address to the mass nature and eigenfunctions address to the phenomenological ondulatory nature of any physical entity. Solutions of wavefunction are affected by boundary conditions determining the quantization of observable levels typically occurring in the particle-in-a-box case where indetermination of positions and momenta result from discrete separations among energy levels. The higher the dimensions of the physical domain available to the particle, the lower the difference between two adjacent levels. The limit to infinite makes the particle behaving in a classical mode, and vice versa. One can envisage that, enlarging or reducing the space dimensions, a whole paradigm gives the perspective spanning from stars (macroscopic cosmological particle objects) to strings (microscopic ultimate wave entities), through the hierarchical subdivision above discussed.

This definition extends the hierarchical levels to the scale of atomic, nuclear and sub-nuclear systems where quantum mechanics provides the equations describing the motion of particles [1.18]. However, the ultimate origin of Second Law is rationalized in the conceptual paradigm of quantum thermodynamic that governs equilibrium and non-equilibrium processes at fundamental microscopic level. The irreversibility is inherent due to quantum states being “characterized by irreducible intrinsic probabilities” [4.23–4.26], and the physical entropy is an intrinsic and non-statistical property of matter. The steepest-entropy-ascent (SEA) of microscopic dynamics at atomistic scale is contextualized and implemented in Intrinsic Quantum Thermodynamics (IQT) [4.52]. IQT is supplemented with First and Second Laws of Thermodynamics in addition to postulates of Quantum Mechanics. This superposition gives rise to non-linear dynamics responsible of quantum dissipation resulting from the irreversible relaxation of any state of a particle up to the stable equilibrium state caused by changes occurring within the system, regardless any other interaction with the external system. The ultimate cause of this non-equilibrium behavior is the endogenous statistic nature of quantum phenomena. Quanta are therefore carriers of inherent irreversibility.

Given this paradigm, the definition of entropy can be rephrased in terms of degree of (reversible or irreversible) dissipation of an observable among all constituting wave-particle physical entities constituting a system.

A couple of remarks should be here underlined. Firstly, IQT appears as the intent of nature to ensure the probabilistic extension of interaction to any particle of a system with any other particle belonging to the same system, even isolated. All possibilities and opportunities are experienced within the system to foster both dissipation and construction processes. Secondly, non-equilibrium processes result in constructive sequences opposite to dissipative processes up to stable equilibrium where, instead, neither construction nor dissipation occur. The validity of these two facts can be extended to a single particle within a confined space isolated from the external environment. Then, one can infer that the intrinsic non-equilibrium of a single particle determines the “intrinsic” constructive self-organization of a whole set of mutual interacting particles.

4.8.2. Exergy Contributions

Based on the entropy-exergy relationship, the generalized exergy property EX^G can be defined in the canonical terms of maximum net useful interactions withdrawn from a system-reservoir composite [3.6–3.8]. The generalized exergy consists of the sum of thermal, chemical and mechanical contributions relating to each and every hierarchical level or, adopting the definitions here proposed, thermal exergy or kinematic exergy EX^T, chemical exergy or geometric exergy EX^C and mechanical exergy EX^M :

$$EX^G = EX^T + EX^C + EX^M \tag{4.13}$$

where $EX^T = \left(W_{10}^{AR\rightarrow}\right)_{HEAT}^{MAX}$ is the maximum net useful work due to heat-to-work conversion direct cycle implying the minimum non-useful heat released to the reservoir; $EX^C = \left(W_{10}^{AR\rightarrow}\right)_{MASS}^{MAX}$ is the maximum net useful work due to mass-to-work conversion direct ideal cycle implying the minimum non-useful mass released to the reservoir; $EX^M = \left(Q_{10}^{AR\rightarrow}\right)_{WORK}^{MAX}$ is the maximum net useful heat due to work-to-heat conversion inverse ideal cycle implying the minimum non-useful work released to the reservoir; and $EX^M = \left(M_{10}^{AR\rightarrow}\right)_{WORK}^{MAX}$ is the maximum net useful mass due to work-to-mass conversion inverse ideal cycle implying the minimum non-useful work released to the reservoir.

On the other hand, this expression applies to all hierarchical levels, then:

$$EX^G = EX_{HL1}^G + EX_{HL2}^G + EX_{HL3}^G + EX_{HL4+}^G \tag{4.14}$$

Nuclear fission and fusion reactions Second Law analyses based on exergy method represent a possible application of these expressions. In the case of nuclear reactions, binding energies and kinetic energies of particles and nuclei fragments, associated to the mass defect, are accounted for to calculate all components of exergy and deriving the generalized thermodynamic entropy variation. In addition, fission and fusion represent processes of particles subdivision or assembling, respectively, between two different hierarchical levels. The inherent relationship between thermodynamic and informational aspect can be evaluated considering the modifications occurring to degrees of freedom and bonds involved in these reactions.

4.9. Hierarchical Structure of Thermodynamic Entropy and Exergy Properties

The geometric and kinematic configuration of a system at any state affects the hierarchical properties describing phenomena occurring among all particles and sub-particles. One of the most important consequences is that kinetic energy and potential energy at different hierarchical levels could not be characterized by the same “availability”. Once the kinetic energy or potential energy has been spread and subdivided into contributions pertaining to the degrees of freedom of a certain hierarchical level, then this amount of energy could not be transferred back to the whole molecule. Indeed, the non-existence of Maxwell’s demon prevents the internal linear-angular vibration kinetic energy to be entirely converted into translation-rotation kinetic energy of the particle behaving as a whole. While vibrating, this energy undergoes continuous transformation from kinetic energy into potential energy, and vice versa, along the vibration motion degrees of freedom and could not be entirely transferred back to the particle as a whole rigid body. This implies the irreversibility of dispersion of particles positions from a higher hierarchical level to a lower one. A similar conclusion holds for internal bond potential energy. Once again, a Maxwell’s demon does not exist that is capable of selecting and separating particles with higher bond potential energy from those particles with lower bond potential energy. Thus, internal bond potential energy cannot be entirely transferred back to the higher hierarchical level where the particles behave as a rigid whole. In turn, this implies the irreversibility of distribution of particles velocities from a higher hierarchical level to a lower one.

Considering hierarchical levels requires a clarification concerning the meaning of macroscopic and microscopic terms. Macroscopic is intended as the set of particles, even only one particle, constituting the system, contributing to the macroscopic parameters characterizing the whole system; neither the absolute or relative dimensions of system particles and container nor the dimensional scale difference or the number of particles, determine the meaning of macroscopic model of a system. Microscopic means that the parameter characterizing the system as a whole are generated and derived from the properties describing phenomena involving all particles constituting the system. Therefore, even one sphere interacting with its container, with same or different order of magnitude of dimensions, can be considered under a microscopic non-statistical or microscopic statistical perspective. Classical and quantum conceptual frameworks and methods apply to their own dimensions range of particles and containers considering the proper approximations and validity limitations stated by those theories.

If a system with a hierarchically structured configuration is considered, the internal energy can be expressed by means of all components contributing to the entire amount pertaining to a given state of the macroscopic system:

$$U = U\left(P, T, \mu\right) = U^{M}\left(P\right) + U^{T}\left(T\right) + U^{C}\left(\mu\right)$$

$$+\sum_{i=1}^{HLs} E_{HLi}^{KINETIC} + \sum_{i=1}^{HLs} E_{HLi}^{POTENTIAL} = -PV + TS + \mu n + \sum_{i=1}^{HLs} E_{HLi}^{KINETIC} + \sum_{i=1}^{HLs} E_{HLi}^{POTENTIAL} \qquad (4.15)$$

P : determined by the kinetic energy and potential energy of particles per unit of volume;

T : kinetic energy per unit of particles; and

μ : potential energy per unit of mole.

The hierarchical levels breakdown structure is the following:

(a) Zeroth Hierarchical Level (HL0): The system is considered as a macroscopic rigid whole.

(b) First Molecular Hierarchical Level (HL1): Phase-Constituent, the macroscopic system is considered as a set of atoms and/or molecules; $-PV$ (mechanical internal energy); translational–rotational kinetic energy; and translational–rotational potential energy.

(c) Second Sub-Molecular Hierarchical Level (HL2). Atoms and sub-molecules, as component elements of molecules, constitute a microscopic system: $+TS + \mu n$ (vibration-translational/vibration-rotational kinetic energy and vibration-translational/vibration-rotational potential energy).

(d) Third Nuclear Hierarchical Level (HL3). Nucleons (protons and neutron) and electrons constitute atoms or group of atoms of group of molecules: $E_{HL3}^{KINETIC} + E_{HL3}^{POTENTIAL}$(vibration-translational/vibration-rotational kinetic energy and vibration-translational/vibration-rotational potential energy).

(e) Fourth Sub-Nuclear Hierarchical Level (HL4). Sub-nuclear hadrons and particles constitute a nucleus: $E_{HL\,4}^{KINETIC} + E_{HL\,4}^{POTENTIAL}$ (vibration-translational/vibration-rotational kinetic energy and vibration-translational/vibration-rotational potential energy).

Exergy is a non-conservative and additive state property. In the case of hierarchical structure of exergy, mentioned in the previous section, the generalized expression can be stated for any system characterized by hierarchical levels considering that exergy is an additive property:

$$EX^{G} = EX_{HL1}^{G} + EX_{HL2}^{G} + EX_{HL3}^{G} + EX_{HL4+}^{G}$$

$$EX_{HL1}^{G} > EX_{HL2}^{G} > EX_{HL3}^{G} > EX_{HL4+}^{G} \tag{4.16}$$

The above inequalities are the consequence of the relationship between the hierarchical structure of molecular configuration and entropy and exergy properties definition for equilibrium and non-equilibrium states. In fact, the generalized exergy represents the maximum net useful interaction (work, heat, mass), that can be extracted from all hierarchical levels of a system characterized by a hierarchical configuration with HLi levels.

As said, entropy is an inherent property of any system, large (many-particle) or small (few-particle) and is characterized by its own hierarchical configuration. Hence, nuclear energy is determined by nuclear entropy defined based on kinetic energy and potential energy distribution among all nucleons and particles constituting a single atom.

The point is that a machine does not exist which is capable to govern the process of progressive distribution of initial high density energy in a sub-system to be transferred as work interaction. In other terms, an elemental device, such as a cylinder-piston or electro-magnetic field, which is capable of collecting and transferring the inter-particle kinetic energy and potential energy to the external system via work interaction does not exist.

The transition from internal energy to external energy with respect to the external system implies an entropy increase due to irreversible conversion of external energy to internal energy that prevents the opposite process.

The definition of entropy property for a given hierarchical level S_{HL} can be expressed considering the distribution of kinetic energy and potential energy among all degrees of freedom pertaining to that level:

$$dS_{HL}^{KINEMATIC} = \frac{\delta Q^{HL}}{T^{HL}} = \frac{dE_{R}^{HL}}{T_{R}^{HL}} \quad \text{and} \quad dS_{HL}^{GEOMETRIC} = \frac{\delta M^{HL}}{\mu^{HL}} = \frac{dE_{R}^{HL}}{\mu_{R}^{HL}} \tag{4.17}$$

and, in the generalized form extended to all types of interactions:

$$dS^{G} = \frac{\delta I^{G}}{P^{G}} = \frac{dE_{R}^{G}}{P_{R}^{G}} = \frac{d\left(E^{G} - EX^{G}\right)}{P_{R}^{G}} \qquad (4.18)$$

where P^{G} and P_{R}^{G} represent the generalized potential of system and reservoir, respectively.

4.9.1. Macroscopic Level

At macroscopic level, the expression of entropy property, derived from energy and exergy properties, can be applied to a microscopic system in which few particles interact, as in the case of fission or fusion nuclear reactions:

$$\left(S_{1}^{MECHANICAL} - S_{0}^{MECHANICAL}\right)^{HL} = \frac{\overline{R}}{P_{R}^{HL} V_{R}^{HL}} \left[\left(E_{1} - E_{0}\right)^{M} - \left(EX_{1}^{R} - EX_{0}^{R}\right)^{M}\right]^{HL} \qquad (4.19)$$

$$\left(S_{1}^{KINEMATIC} - S_{0}^{KINEMATIC}\right)^{HL} = \frac{1}{T_{R}^{HL}} \left[\left(E_{1} - E_{0}\right)^{K} - \left(EX_{1}^{R} - EX_{0}^{R}\right)^{K}\right]^{HL} \qquad (4.20)$$

$$\left(S_{1}^{GEOMETRIC} - S_{0}^{GEOMETRIC}\right)^{HL} = \frac{1}{\mu_{R}^{HL}} \left[\left(E_{1} - E_{0}\right)^{P} - \left(EX_{1}^{R} - EX_{0}^{R}\right)^{P}\right]^{HL} \qquad (4.21)$$

in which T_{R}^{HL} represents the temperature and μ_{R}^{HL} the potential of the reservoir considered as an auxiliary reference system.

It is noteworthy that the thermodynamic state of the reservoir does not affect the entropy content at any hierarchical level since the reservoir is an auxiliary reference system only, therefore a unique reservoir can be considered as the reference system for all hierarchical levels.

As the above definition of entropy property is to be considered valid for many-particle or few-particle, this expression has to be valid for few particles involved in the particular case of nuclear reactions. To do so, the calculation of energy and exergy would allow calculating the three contributions of entropy property.

4.9.2. Microscopic Level

At microscopic level, the classical statistical mechanics and thermodynamics describe the system in terms of substructures by means of the method established by Gibbs for dependent and distinguishable particles whose expression of statistical canonical thermodynamic entropy property is the following expression in which positions and velocities in the phase space are identified:

$$S = k_{B} \ln W = k_{B} \ln W^{p} + k_{B} \ln W^{q} = k_{B} N \sum_{i} \frac{n_{i}}{N} \ln \frac{n_{i}}{N} = k_{B} N \sum_{i} w_{i} \ln w_{i} \qquad (4.22)$$

where k_{B} is the Boltzmann constant and $k_{B} = \frac{\overline{R}}{N_{A}}$ where N_{A} is the Avogadro number. N is the number of particles constituting the system. W is the weight of the most probable microscopic configuration of the system determining the macroscopic state. The weight is the number of different microscopic configurations corresponding to the number of possible distributions of particles among the particle kinetic and potential energy levels available at a given state. w_i represents the fraction of particles in the state i out of all states corresponding to all different kinematic configurations and geometric configurations.

Being the phase space composed by coordinates related to both velocities p_n and positions q_n of each and every particle n , then two different expressions can be stated, for both contributions, as follows:

$$S_{HL}^{KINEMATIC}=k_B \log W^p = k_B \sum_i N_i\, p_i^p \ln p_i^p \tag{4.23}$$

representing the Kinematic Entropy associated to the fraction p_i^p of particles in the kinematic state i related to the velocity phase space; and

$$S_{HL}^{GEOMETRIC}=k_B \log W^q = k_B \sum_j N_j\, p_j^q \ln p_j^q \tag{4.24}$$

representing the Geometric Entropy associated to the fraction p_j^q of particles in the geometric state j related to the position phase space. This term is here adopted to include the "configurational entropy", related to particles position in the phase space, and the "conformational entropy" addressing to all possible arrangements of complex molecules as occurring in macromolecules involved in biological systems; being entropy an extensive and additive state property, then the sum of different contributions can be expressed as:

$$S_{HL} = S_{HL}^{KINEMATIC} + S_{HL}^{GEOMETRIC} = k_B N \sum_i \left(p_i^p \ln p_i^p + p_j^q \ln p_j^q \right) \tag{4.25}$$

The transition from a certain level to a lower level implies a (quantum) increase of the entropy pertaining to the starting level and therefore can be defined as the entropy of entropy. This recursive term originates from the cascade dissipation of energy along the progressive subdivision descending levels through the hierarchical configuration of systems. Mathematically, the formal expression of generalized entropy, considering that entropy is a non-conservative and additive state property, is given by:

$$S^G = S_{HL1}^G + S_{HL2}^G + S_{HL3}^G + S_{HL4+}^G \text{ with } S_{HL1}^G < S_{HL2}^G < S_{HL3}^G < S_{HL4+}^G \tag{4.26}$$

4.10. Non-Equipartition Theorem of Entropy

The inter-dependency between Statistical Mechanics and Kinetic Theory suggests the correlation between the Boltzmann molecular distribution function and the equipartition theorem of energy for a system in a stable equilibrium state.

A many-particle or few-particle system constituted, in the most general case, by three-dimensional complex molecules can be described adopting the phase space in which positions and velocities of particles are analytically represented. The distribution of the total amount of energy of the system occurs, for an individual particle, among the following degrees of freedom: 3 rigid-translational + 3 rigid-rotational = 6. These degrees of freedom accommodate the inter-molecule potential energy depending on relative positions, and inter-molecule kinetic energy depending on relative velocity. In addition, each and every molecule is allowed 3 vibro-translational + 3 vibro-rotational = 6 degrees of freedom, constituting a lower hierarchical level, once again characterized by relative (inter-atomic) positions and velocities. The equipartition theorem of energy [1.10-1.12] establishes that the total amount of internal energy is spread among all available degrees of freedom and all levels of the system hierarchical configuration; moreover, one degree of freedom accommodates a portion of internal energy equal to $k_B T/2$ where k_B is the Boltzmann constant and T is the absolute temperature. Consequently, the equipartition of energy implies that each and every degree of freedom accommodates an equal portion of overall internal energy content of a system accounting for all kind of energy that the system experiences. However, those degrees of freedom, pertaining to lower hierarchical levels associated to the internal configuration of particles, determine an irreversible degradation of properties characterizing the system.

Non-existence of Maxwell's demon implies that equipartition of energy among degrees of freedom and therefore between two given hierarchical levels does not allow to bring back the whole amount of energy to upper levels. Indeed, no being or device is able to select molecules velocity or position to invert the system configuration. The amount of energy available to be transferred to the upper hierarchical level is the portion converted along a conversion cycle operating between two constant inter-particle temperatures, namely T^{HLi} and T^{HLi+1} or between two constant inter-particle potential namely μ^{HLi} and μ^{HLi+1}. If multiple levels are accounted for, the final available energy as maximum net useful work at the upper level under consideration, resulting from conversion of heat interaction or mass interaction, is given by:

$$W_{HL} = Q\prod_{i=0}^{i=HL}\eta^{HLi} \quad \text{and} \quad W_{HL} = M\prod_{i=0}^{i=HL}\eta^{HLi} \tag{4.27}$$

A consequence of the hierarchical structure of systems is that kinetic energy and potential energy are equally distributed among all hierarchical levels and their degrees of freedom. Instead, entropy property is not equally distributed along whatever chemical and nuclear processes. Indeed, as a Maxwell demon does not exist, energy associated with a degree of freedom at a lower hierarchical level could not be entirely transferred to a higher hierarchical level. Therefore, if the overall content of energy is equally distributed among a higher number of hierarchical levels and lower degrees of freedom corresponding to each level, then the amount of energy available to be transferred by work interaction to a weight process is lower. This irreversibility, related to the Second Law, is the essence of the non-equipartition theorem of entropy which would be complementary to the equipartition theorem of energy derived from the First Law. The non-equipartition implies the maximum entropy principle at each hierarchical level and a proposal has been already elaborated for superstatistical systems [4.53].

As far as processes are concerned, even equilibrium states can determine irreversible process in case a lower hierarchical level is implied in the interactions among different portions of the system.

The non-equipartition theorem of entropy is determined by systems configuration subdivision relating to degrees of freedom and constraints among constituting particles and reflects the fact that distributed and dispersed systems maximize entropy along irreversible processes. The spontaneous tendency of these processes is to extend to all levels of coexisting hierarchical structures, nested in any system, reversible and irreversible phenomena along steady conservative or non-conservative processes [4.50]. Instead, in the opposite direction, the tendency to maximize energy dissipation in non-equilibrium processes induces the system evolution to generate hierarchically structured configurations [4.51]. However, a morphogenetic counter-tendency appears along transient constructive evolution as in the constructional theory [4.9,4.13] and the entropy generation minimization method [4.15,4.16] representing the driving project of systems architecture shaping, parts assembling and matter aggregation. The following logical relations between these paradigms are established for equilibrium or non-equilibrium phenomena:

i. Equipartition theorem of energy: Reversible and irreversible conversion processes and maximum entropy production principle $\Rightarrow$ multi-scale configuration of systems emerging from energy dissipation along hierarchical levels.

ii. Non-equipartition theorem of entropy: Reversible and irreversible conversion processes and entropy generation minimization paradigm $\Rightarrow$ constructive evolution of systems through self-organizing capability and shaping of optimized hierarchical configurations.

Hence, the constructive evolution would describe the complementary trend of thermodynamic and informational phenomena occurring in a system, in the opposite sense with respect to the Non-Equipartition Theorem of Entropy centered on its physical and informational significance implied in hierarchical configuration of systems driven by dissipation processes.

Future developments may envisage applications of the methodologies here discussed to biotechnologies or nanotechnologies and nano-systems [4.54-4.56] in which the self-assembling and self-organizing capabilities are used as tools to govern matter manipulation.

4.11. Hybridization of Dissipation and Construction

The previous paragraphs illustrate the concept that the dualism and the relation arising from thermodynamic and informational aspect of entropy property play a fundamental role in matter and phenomena description of multi-scale and mesoscopic systems characterized by hierarchical configurations. This conceptual schema, underpinned by the physical nature of information and the informational content of physical states, is recognized as inherent to any system and provides an overarching and unitary perspective over the domain from classical through statistical to quantum physics. The non-existence of Maxwell's demon, implied with the Second Law, represents the fundamental rationale behind the hierarchical levels definition and analysis. The thermodynamic efficiency of conversion cycles underpinned by the Second Law statement has been specialized for ideal cycles governed by chemical potentials to further extend the common approach based on temperatures. Consequently, an extension of a corollary of the Second Law, consisting of the impossibility of PMM2, to all thermal–mechanical and chemical-mechanical conversion processes, is a further result here outlined. The definition of generalized thermodynamic entropy and exergy properties have been proposed with the intent of extending to all hierarchical levels constituting the system configuration thus implying the calculation of entropy and exergy balance and efficiency in Second Law analyses. Finally, the irreversibility associated to the hierarchical configuration of a system, related to the Second Law, is the essence of the non-equipartition theorem of entropy which would be complementary to the equipartition theorem of energy derived from the First Law. A counter-tendency is revealed by the capability of systems in displaying constructive evolutive capabilities in shaping structures in the direction of entropy generation minimization opposite to the maximum entropy production determining hierarchical configurations of multi-level structures.

The following drawing gathers those main concepts described so far in a graphical representation to provide a whole point of view.

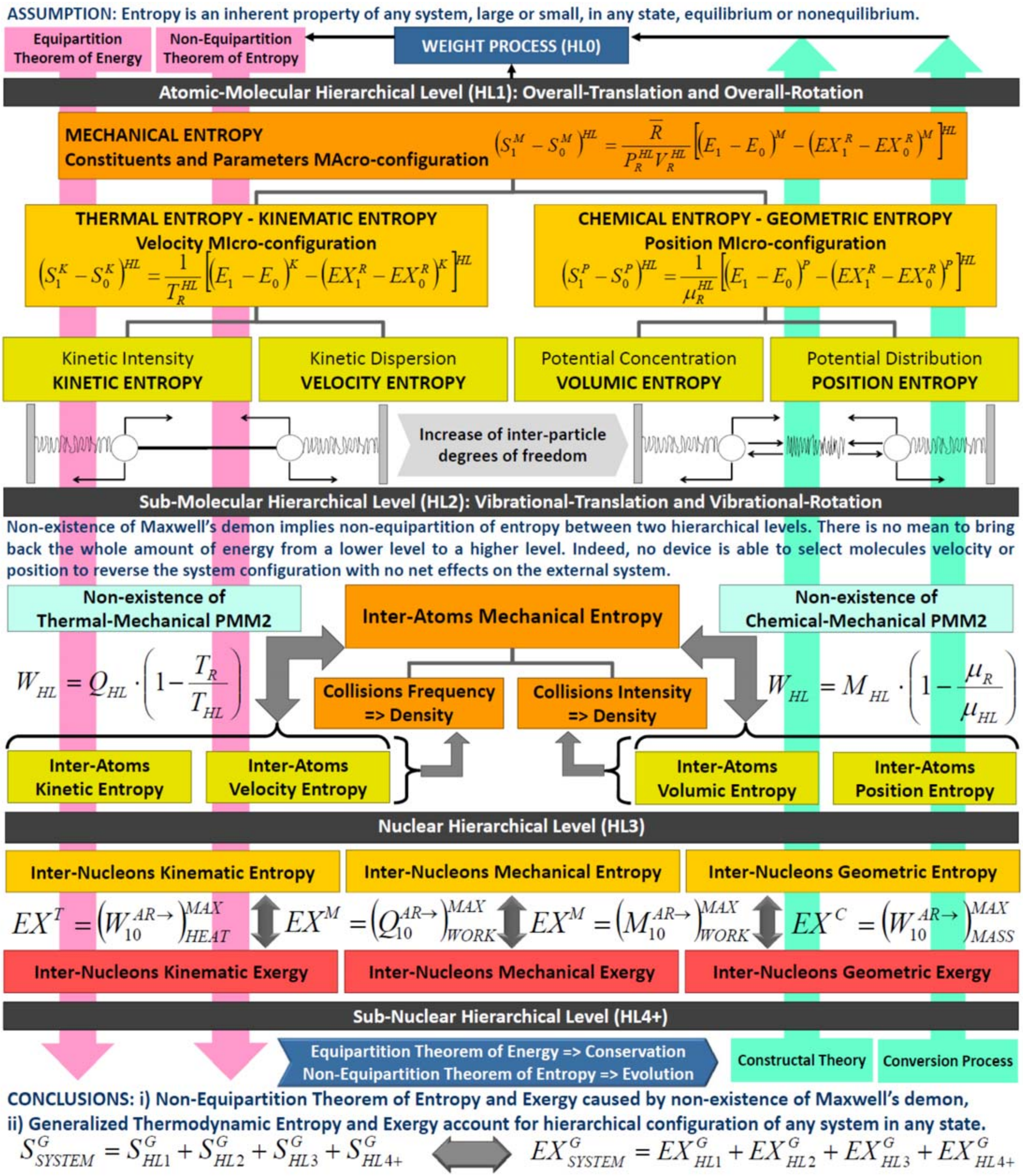


Figure 4.4 – Counter-tendency of complex systems

There are two physical opposite tendencies emerging in the above representation: i) the occurrence of dissipation implies hierarchical structures generation through subdivision (Annila), that can be termed as dissipative hierarchization (disorder); ii) the existence of hierarchical structures require aggregation through organization (Bejan), that can be termed as constructive organization. Common driving forces of these opposite processes are finite differences of potentials as well as states and processes far from equilibrium. The logical paradigm "order-disorder-organization", advocated by Morin (mentioned in the Introduction) [1.23], can be viewed in terms of "mass-energy-dissipation-construction". In fact, this complex dynamic evolutive process, specifically referred to living systems, can be regarded as:

"mass-energy interaction ⟹ hierarchical subdivision ⟹ fisio-morpho-genetic assembling"

In this sense, the downward process implies the hierarchical structure configuration generation through subdivision and dissipation compensated by the upward process creating the use of mass and energy content of the system for structures organization processes. In this counter-tendency, molecular machines intervene in physical and informational assembling and organizing processes. This dialectical method presumes what can be described as a *hybridization* of thermodynamic dissipation and construction processes of systems and phenomena and the integration of thermodynamic and informational components accounting for contribution and creation of properties describing any system in any state along this non-finite change process.

4.12. Extrema Principles and Hierarchical Configurations

Considering again the hierarchical configuration of systems previously discussed, and the lower hierarchical levels pertaining to quantum physics domain, the extrema principles and non-equilibrium dynamics assume different adaptations and specializations, the most outstanding, among others, here after mentioned.

A premise already posited when dealing with the set of extrema principles [4.20], is that Onsager and Prigogine are not in contradiction with Ziegler if the Minimum Entropy Production Principle is attributed to irreversible phenomena in quasi-equilibrium and the Maximum Entropy Production Principle (MEPP) [4.50] is concerning far-from-equilibrium dynamics, according to the local and microscopic modeling and equations belonging to the GENERIC and SEA theories.

Steepest-Entropy-Ascent (SEA)

In the context of the maximum entropy production principle, the Steepest-Entropy-Ascent (SEA) principle has been demonstrated by Beretta [4.49] to establish a univocal dynamic evolution from a far-from-equilibrium state toward the stable equilibrium. The uniqueness of all parameters defining dynamic states could be translated in a "Non-Equilibrium-State Principle" that would become the opposite complement of the Stable-Equilibrium-State Principle already enunciated [1.9]. A question here arises whether a correlation of SEA with the brachistochrone function in mechanics and thermodynamics [4.68] could enable a circular closure between the highest and lowest levels of physical descriptions.

General Non-Equilibrium Reversible Irreversible Coupling (GENERIC)

On a different, though concurrent, side of researches dealing with non-equilibrium, the General Non-Equilibrium Reversible Irreversible Coupling (GENERIC) has been proposed by Ottinger and Grmela. However, it has been demonstrated by Beretta that the GENERIC is a version of, and can be contextualized to, the SEA [4.49]. The existence and uniqueness of SEA along a non-equilibrium process could be assumed as the prerequisite to define the corresponding non-equilibrium temperature [4.59]. In addition, though, non-equilibrium potential and non-equilibrium pressure should even be defined to provide the complete set of thermodynamic potentials governing any process. Being inherently non-linear and probabilistic physical entities, quanta are carriers of irreversibility in thermal, chemical and mechanical processes and, in all these processes, high energy density flows toward low energy density of quanta.

Non-Equilibrium Potentials

Then, temperature, potential and pressure could be globally defined considering that macroscopic phenomena and non-equilibrium processes occur with the unique constraint of the Steepest-Entropy-Ascent. This means that, being entropy generation such that its production rate has to be the steepest, then no other irreversible processes can be arranged in the system. The irreversible components of entropy are correlated to the driving forces moving thermal, chemical and mechanical irreversible processes such that: $S_{IRR}^{T} \Leftrightarrow T_{IRR}$, $S_{IRR}^{C} \Leftrightarrow \mu_{IRR}$, $S_{IRR}^{M} \Leftrightarrow P_{IRR}$. Hence, the existence and uniqueness of non-equilibrium entropy implies the existence and uniqueness global temperature, potential and pressure regardless their local and time variation.

The Second Law is a statement of existence and uniqueness of stable equilibrium and the Highest-Entropy Principle is a consequence accounting for irreversibility of processes occurring in isolated systems and also expressed by the adiabatic availability. Therefore, Second Law states the entropy generation $\dot{S}_{gen}$ as a principle.

The constructal theory and EGM constitute a holistic paradigm starting from elemental to complex which is complementary to the opposite reductionist paradigm, from complex to elemental, addressed to by “deconstructal” classical science [4.10]. The multiple options offered by non-heuristic, meta-heurist, semi-heuristic, quasi-heuristic, full-heuristic methodology should be properly selected case by case.

Heuristic approach to EGM proceeds by reduction of local entropy generation. Local irreversibilities due to local non-equilibrium. The step forward to constructal standpoint toward geometric tree-shaped configuration is related to global non-equilibrium and the relationship between local and global irreversible processes.

Heuristic-Holistic relationship: from heuristic to holistic paradigm. The method itself is governed by tree-shaped geometric configuration.

The hierarchical configuration of entropy generation systems displays a breakdown through elemental components and assembled components as describe in the figure here after shown:

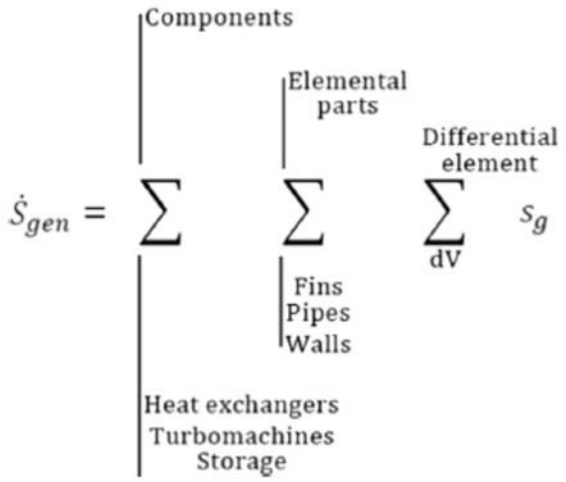


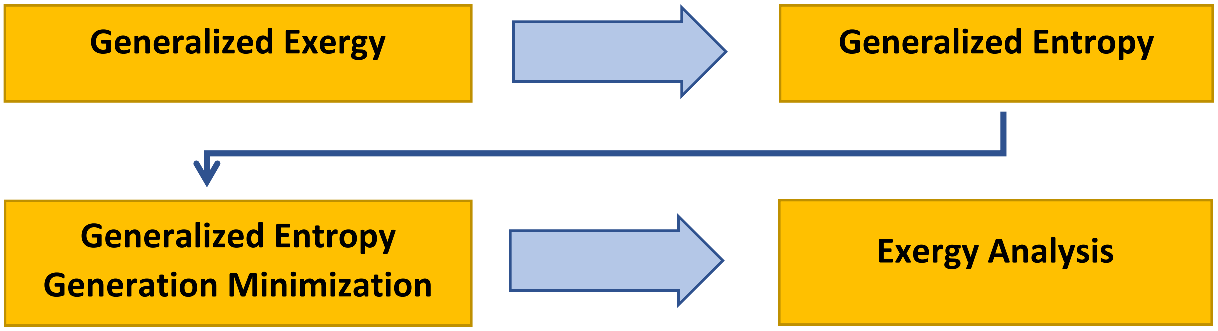
Fig. 5. Hierarchy of entropy generation formulation [20].

Bifurcations constitute as system aimed at distributing and elaborating in parallel which modulate and subdivide mass flows with same differences of thermodynamic potentials or driving forces (theoretically reversible processes)

The EGM methodology can be extended to chemical and nuclear reactions so that the method can be generalized to all thermal, chemical, nuclear and mechanical interactions.

Generalized EGM Method

Tri-furcated or multi-furcated branches to reduce irreversibility at constant aspect ratio $a_r = H/L$ taking into account mass interactions (chemical reactions) and or heat interactions (thermal operations) separately occurring or combined together. The Shape Factor: SF = surface / volume (or = perimeter / surface) representing a geometrical parameter to be assumed or optimized.



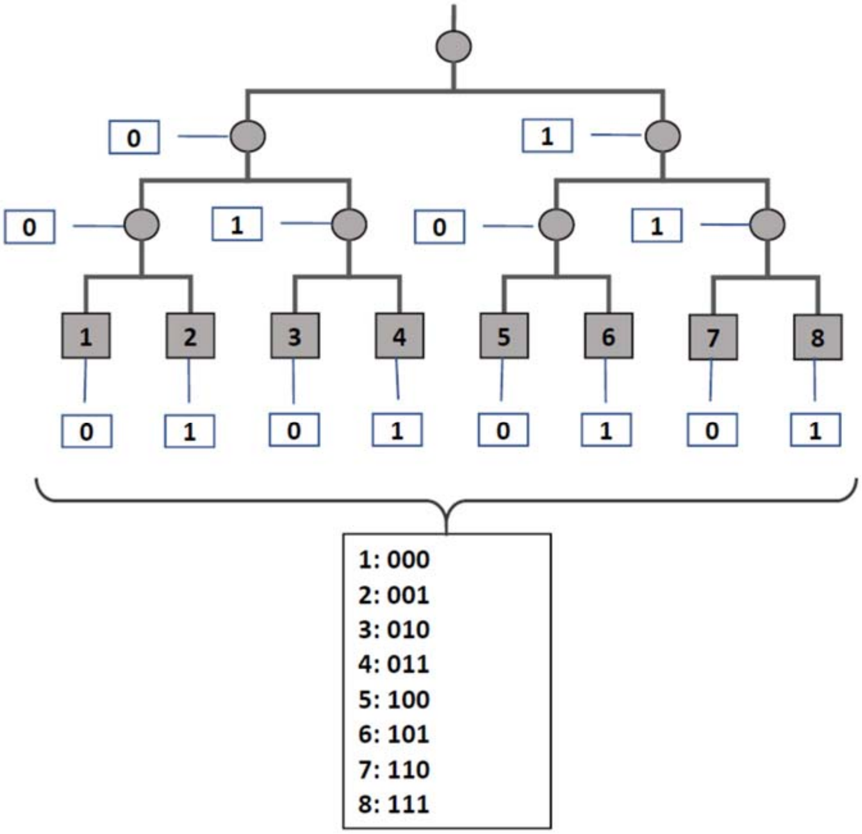
Generalized Entropy Generation Minimization (GEGM) methodology resulting from the summation of thermodynamic components and information components. The concept of efficiency is extended to generalized entropy efficiency and generalized exergy efficiency.

4.13. Informational Aspect of Thermodynamics

The outset of the information theory is ascribed to Shannon and Weaver who devised the concept of informational entropy in the framework of the mathematical theory of information and communication [4.27,4.28].

Informational Entropy and Information

The dual aspect of physical essence of any portion of matter is the informational content. The concept of information is characterized by bifurcations according to Shannon and Weaver paradigm of sequential selection among alternative options at each generalization-particularization level of a branch-configured tree-shaped hierarchical structure. To depict a graphical description of its meaning, the informational entropy property can be viewed as characterized by bifurcations according to Shannon and Weaver paradigm of sequential selection among alternative symbols or options at each generalization-particularization level of a branch-configured tree-shaped hierarchical structure.



The sequence of successive selections of symbols is measured by a reduction of uncertainty (increase of certainty) or restriction of selection degree of freedom: information is a measure of this reduction [4.70], and can be expressed as $I = c \log_2 N$. Instead, the informational entropy is a measure of uncertainty relating to degrees of freedom of choices. Then, informational entropy and information, dealing with the amount of degrees of freedom and the reduction of them respectively, are complementary.

Beside the Shannon entropy, an introduction to the logical entropy was proposed by D. Ellerman (2013) as a measure of information.

Information content is associated to energy and entropy storage in a system. Each and every state of a thermodynamic system constitutes a bit of information.

Shannon informational entropy is expressed as $I_S = \sum_i p_i \ln p_i$ where p_i is the probability of a given character appearing by chance out of a defined alphabet of characters.

From mathematical and formal standpoint, this expression of informational entropy is similar to the one formulated by Boltzmann and Gibbs for many-particle systems consisting of microscopic characteristics and properties obeying to Maxwell's statistical mechanics and thermodynamics laws.

Shannon entropy: $H = k \sum_{j=1}^{N} p_i \log\left(\frac{1}{p_i}\right)$

From maximum informational entropy inference to the partition function that does not exclude any probability or event as a characteristic of an ergodic property [Shannon, Jaynes].

von Neumann entropy $S = -Tr\left(\rho \ln \rho\right)$ is describing quantum particles.

Generalized Informational Exergy

Considering the correspondence and the inherent relationship between physical and informational aspect, the informational exergy is an informational interaction conveying a rule or schema (logical inference or syllogism), or a set of rules or schema thereof, determining the content of information within the receiving system [2.9]. In this sense, informational entropy and informational exergy are mutually complementary and the latter is considered corresponding to the genetic "information" contained in the DNA code of living systems. The correspondence and the inherent relationship between physical and informational aspect of any portion of matter entitles to reproduce the paradigm of eight types of cycles and impossible PMM2 previously set up and recognized in any matter and energy conversion process. Same balances and efficiencies could be defined considering entering and exiting information flows as well as the generalized informational entropy created as a consequence of informational irreversibilities.

Organized structures have a content of information such that they provide a contribution in terms of thermodynamic and information energy and information entropy associated determined by phenomena occurring within the system.

Landauer’s Principle

The Landauer's Principle [4.31,4.32] is a physical principle pertaining to the lower theoretical limit of energy consumption of computation. The statement is termed as: "any logically irreversible manipulation of information, such as the erasure of a bit or the merging of two computation paths, must be accompanied by a corresponding entropy increase in non-information-bearing degrees of freedom of the information-processing apparatus or its environment". Another way of phrasing Landauer's principle is that if an observer loses information about a physical system, the observer loses the ability to extract work from that system. The Landauer’s principle establishes a direct correspondence between physical and informational behavior of a system or a set of physical constituting elements. Hence, any physical occurrence translates into an informational content. The Landauer’s Principle confirms the non-existence of Maxwell’s demon. In fact, there always exists a minimum bit of energy associated to a bit of information that is input in the system. Therefore, the Maxwell’s demon needs energy to separate particles with different values of properties and the second law is not disregarded and remains still valid.

4.14. Thermodynamics and Information Relationship Schema

The following Figures 4.5a and 4.5b provide a representation of the thermodynamic and informational aspects relationship schema relying on the twofold essence: on the one side, entropy is an intrinsic property of any substance, hence information is inherently associated to any thermodynamic state and process; on the other side, information is inherently associated to physical states and processes, hence it undergoes the same governing laws. This schema is a quadrilateral configuration characterized by those significant facets of the relationship between thermodynamic and informational aspects. To enlarge the overview, the Figure 4.4c reports the disciplines, in the domain of Information Science, undergoing by the scientific community a strong momentum and progress in recent times.

Gyftopoulos [3.1,4.21] and Hatsopoulos [4.22] have proved that entropy is an inherent property of all systems, large or small, in all states, equilibrium and non-equilibrium. Thus, knowledge of system state and processes, advocated by Maxwell and Boltzmann, do not address to any physical or information meaning.

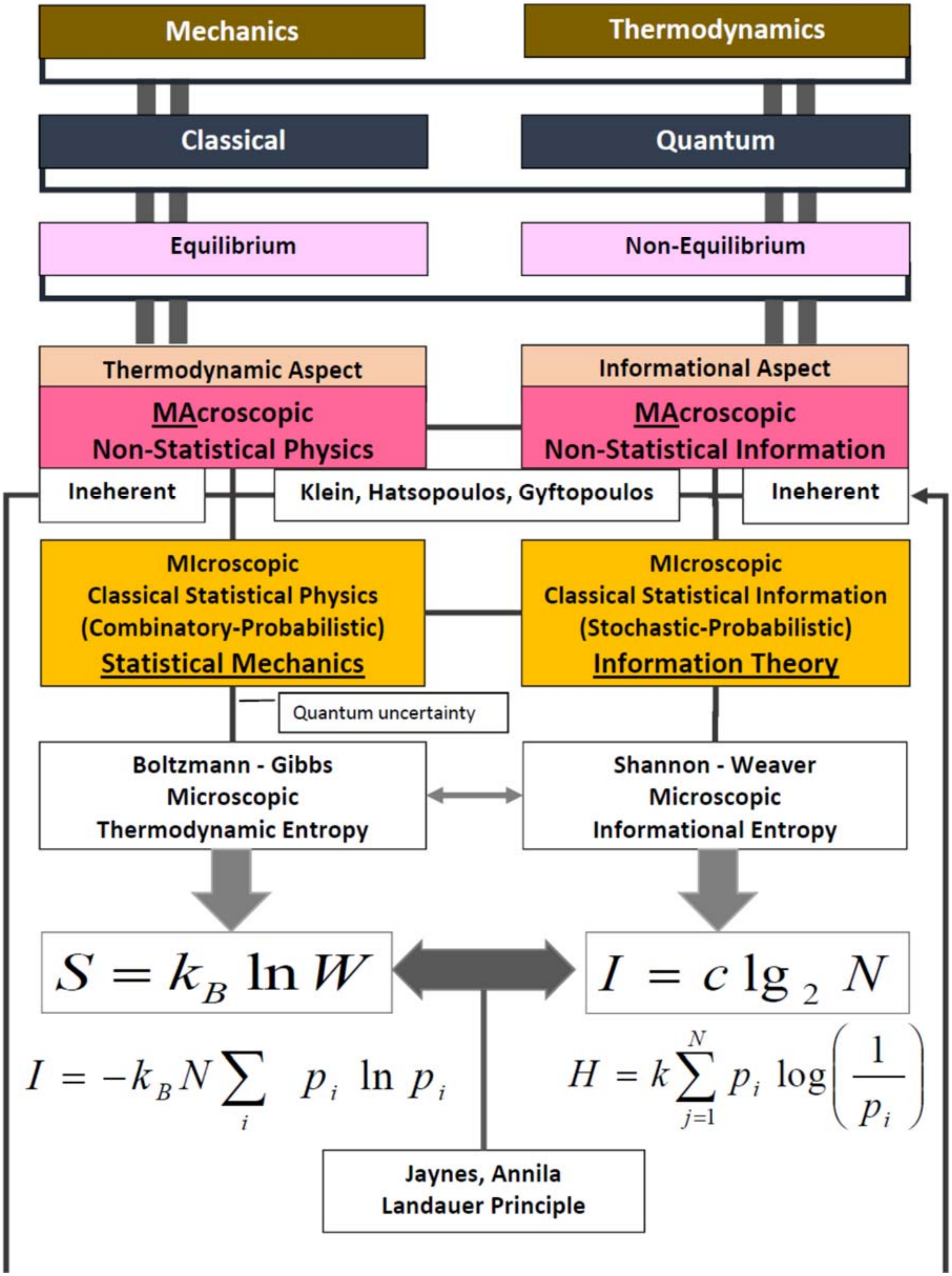


Figure 4.5a – Thermodynamic and Informational Aspects Relationship Schema – Non-Quantum

The above Figure 4.5a is continued in the below Figure 4.5b. representing the role of Quantum Physics and Quantum Information in the relationship between thermodynamic aspect and informational aspect.

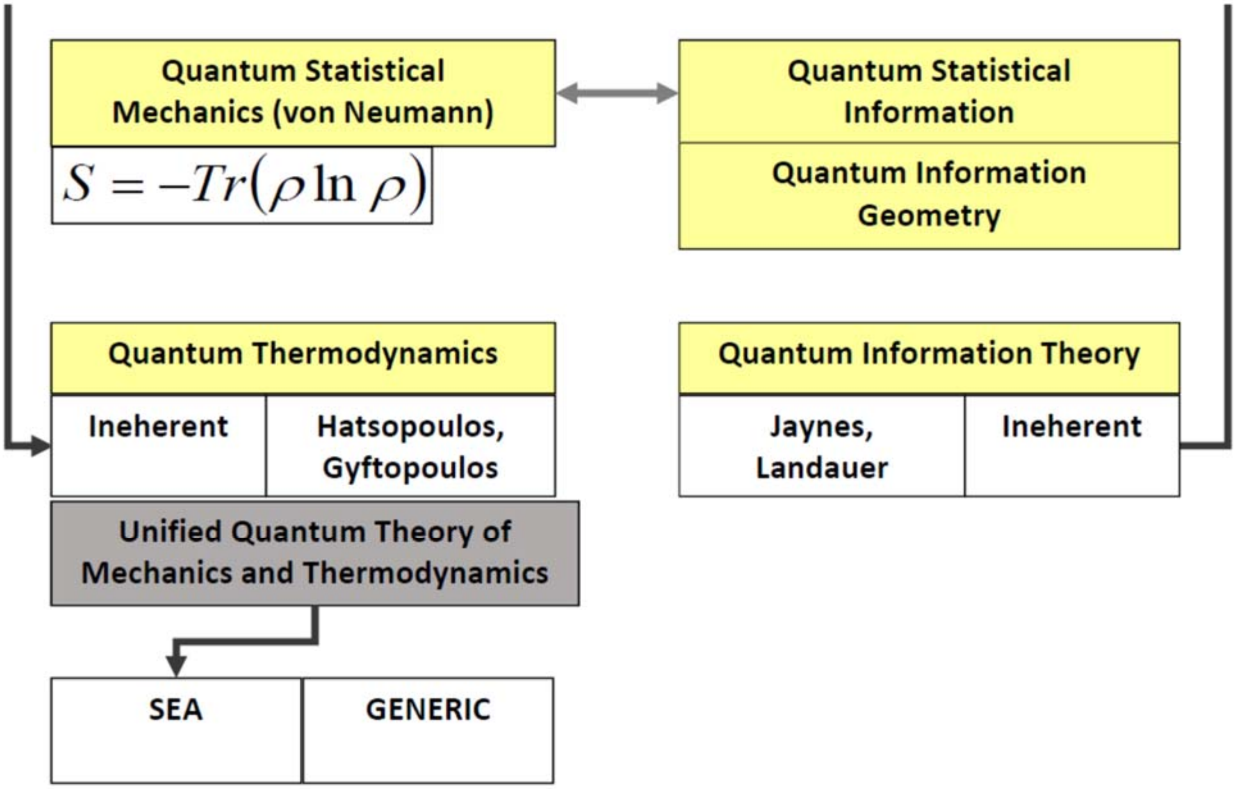


Figure 4.5b – Thermodynamic and Informational Aspects Relationship Schema – Quantum

The Figure 4.5c here below is intended to identify disciplines and methodologies originated by pioneering papers published by Shannon, Weaver, Jaynes and Landauer and today representing the ground of researches, developments and applications in technology.

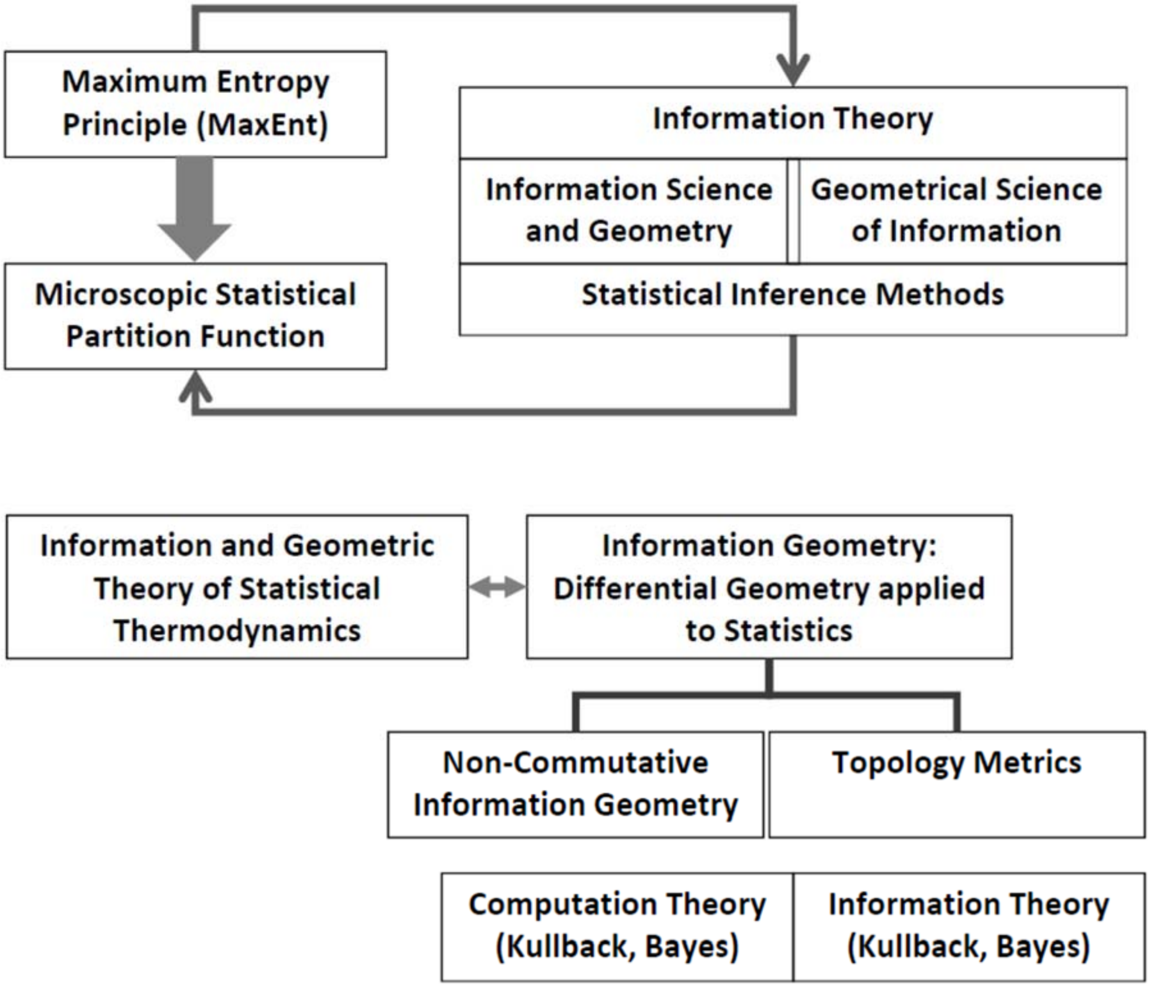


Figure 4.5c – Disciplines in the Domain of Information Science

The schema in Figures 4.5a and 4.5b, representing the relationship between thermodynamic aspect and informational aspect, can be viewed as pivoted on the following bi-univocal relationship:

Hierarchical generalized thermodynamic entropy ⇔ *Hierarchical generalized informational entropy*

where both properties inherently constitute the intrinsic essence of any physical entity in any state. This bi-univocal relationship between physical and informational aspect at fundamental quantum level has been recently presented through the convergence of Schrodinger and Von Neumann thought on quantum and probability as irreducible characters of matter that obeys to non-causal laws [4.71]. Then, the cause of dissipation is not the lack of information, being instead an inherent and irreducible character of matter representing an "epistemic and ontic indeterminism" [4.71] anticipated by Heisemberg in his uncertainty, or indeterminacy, principle.

This twofold essence should per reflected and should be part of all those extrema principles, and related theories, already mentioned concerning the sole thermodynamic aspect. The Figure 4.6 provides the set of principles and theories with a specific mention of both thermodynamic and informational aspects and related laws to which all portions of matter in the universe should obey.

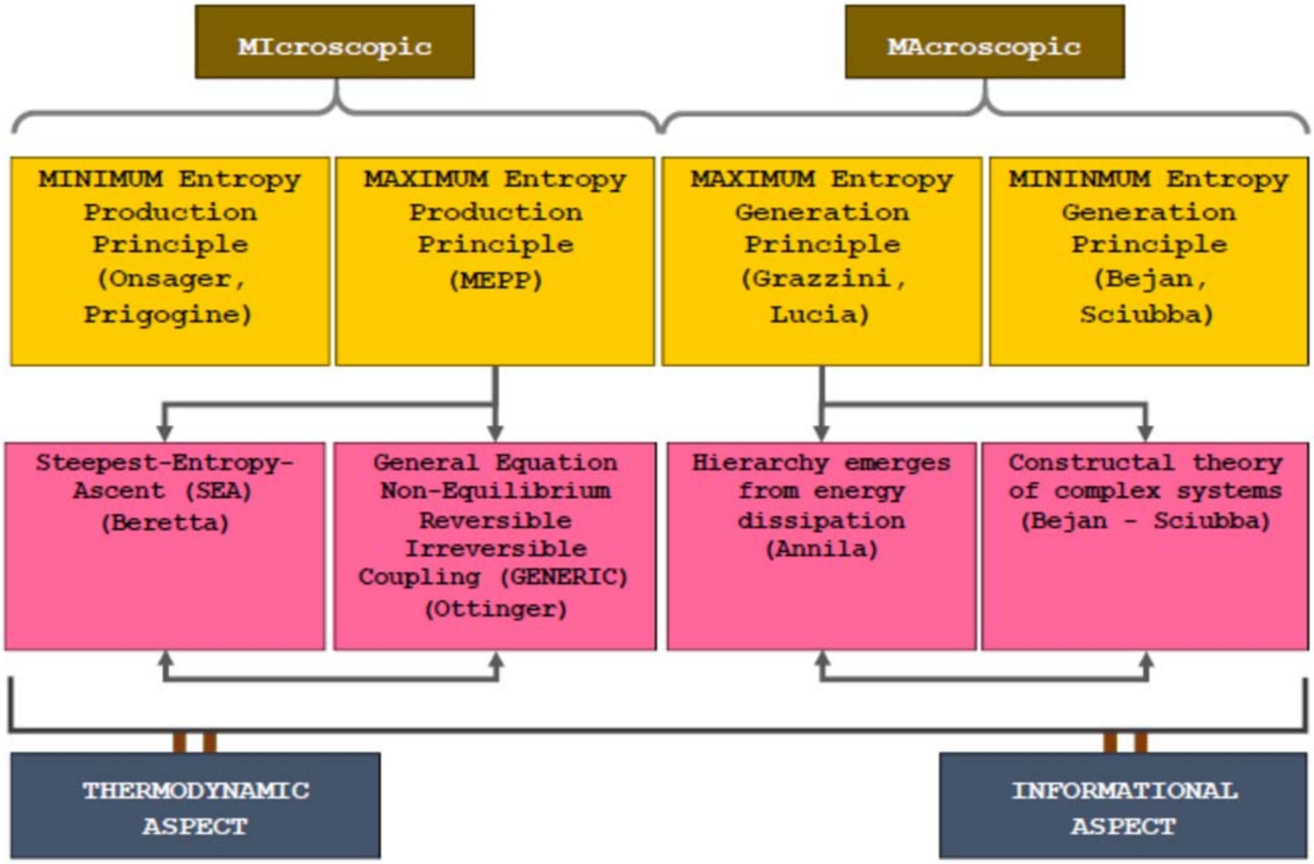


Figure 4.6 – Extrema Principles and Related Theories

An interesting connection that is worth considering in the right portion of the Figure 4.6 is the one headed by the maximum entropy generation principle. This extremum principle is the one governing, on the one side, the "evolutionary" construction of macroscopic shapes architectures suitable to maximize flows and the growth of systems or set of systems; on the other side, hierarchical configurations emerging in such a way to maximize the effect of irreversible dissipation associated to the reversible conservation of the maximized flows. It seems there is a collaborative reciprocal effect justifying, with particular evidence, the "design" of biosystems in any expression. The entropy generation minimization principle can be viewed as the complement to optimize the design through a more detailed level of development. All extrema principles and their theoretical and experimental developments, represent the ground to look at the Fourth Law as a complement, a completion and the culmination of the whole conceptual building underpinned by First, Second and Third Laws. In this framework of principles and laws, the "Least Action Principle", summarized by the null variation of the Hamiltonian function $\delta L = 0$, seems to be the ultimate fundamental law governing everything. This perspective should represent the methodological framework to continue the research in the domain of complex and living systems to attempt, and achieve, an overarching and encompassing science. As a first step in this direction, it would be worth considering that, in non-equilibrium phenomena, physical dissipative processes of the internal system can become constructive with respect to the geometry of the external system through the informational exergy intended as an interaction withdrawn under the form of informational interaction between internal and external system. The informational exergy compensates the thermodynamic dissipation by means of the organizing and ordering informational interaction with the external system. This local-to-global interaction transports constructive information from the internal system to the external one in the respect of the paradigm interaction-subdivision-assembling previously proposed.

4.15. State-of-the-Art in Non-Equilibrium Thermodynamics Advancement

As far as Non-Equilibrium Thermodynamics is concerned, most recent advancements on the fundamental properties and definitions, among others, have been being developed by Beretta and Zanchini, adopting an axiomatic paradigm, and by Sciubba and Zullo, who are oriented on a more analytic approach. Beretta has demonstrated the SEA is equivalent to the GENERIC. Sciubba and Zullo have proved that the uniqueness of non-equilibrium exergy variation on space and time depends on fixed boundary conditions. A step forward would allow to combine the above outcomes and to define a non-equilibrium temperature to be intended as a unique distribution in space and time of the local temperature the systems assumes along a non-equilibrium process starting from a given thermodynamic state and boundary conditions.

4.16. Fourth Law and Extrema Principles

The set of extrema principles and their mutual relationships constitute the ground to discuss the Fourth Law in its multiple facets and looking forward in the direction of an overarching and unitary perspective. So far, there have been different version of the statement addressing to the emergence of complexity and epi-phenomenological properties of systems.

5. FISSION AND FUSION NUCLEAR REACTIONS EXERGY ANALYSES

The interest in applying the exergy method to fission and fusion nuclear reactions arises from the need of optimizing and comparing the performance and sustainability of different types of nuclear processes and plants. The confrontation among various technologies should account for entropy and exergy variations in the overall balances to achieve more accurate, rigorous and physically realistic results.

As far as the theoretical framework, as well as the methodological philosophy, are concerned, two different models and expressions can be adopted for few particle systems representing the case of elemental fission and fusion nuclear reactions:

i) Macroscopic perspective leading to the formulation based on Gyftopoulos and Beretta theory: entropy is derived from exergy
ii) Microscopic perspective leading to the formulation based on Boltzmann and Gibbs theory: exergy is derived from entropy

One of the advantages offered by Gyftopoulos and Beretta theory is that entropy property can be calculated based of the amount of work interaction along a so called “weight process” in which a mass undergoes displacements in the same direction of gravitational field forces. This could be also replicated considering an electro-magnetic field and an electric charged body moving within it. Hence, the procedure “i)” will be adopted. However, to corroborate the results, the calculation will be executed according to the procedure “ii)” to prove, at least, the convergence of results coming from microscopic and macroscopic model and phenomena described by pertaining properties.

The concept of irreversibility of any process, and in particular nuclear fission and fusion reactions, is related to the incapability of systems to maintain all forms of energy involved in whatever phenomena occur, at the same hierarchical level and, therefore, subdividing the properties defining the state of a system among lower levels with no possibility of transfer back to higher levels. Nuclear fission and fusion reactions are processes where the particle system undergoes transmutations and changes of configuration so that different levels of the hierarchical structure of the system are involved. The subdivision of particles constituting a system into sub-particles determines a multiplication of velocities and positions configurations and the consequent loss of phenomena homogeneity and reversibility. In case of velocity distribution, the probability of equal and opposite velocity become much lower. In case of position dispersion, the capability to transfer inter-particle potential energy into work interaction is reduced.

5.1. Fission and Fusion Elemental Nuclear Reactions

The present section describes the main characteristics of fission and fusion nuclear reactions that will be further analyzed in terms of exergy method to provide a thermodynamic appraisal in terms of Second Law. Typical reactions are those occurring in industrial nuclear reactors.

5.1.1. Nuclear Fission

Nuclear reactions can be classified in two main categories: i) radioactivity decay and ii) nuclear interactions.

In particular, nuclear interactions concern the collision of a neutron with a nucleus resulting in elastic scattering, inelastic scattering, neutron capture and capture with fission. Nuclear fission implies transmutations in the sense that products result are chemical elements different from reacting ones. Nuclear fission is here considered for Second Law Analyses.

It is noteworthy that an analogy exists between chemical reactions and nuclear reactions. In both cases, reactions imply a change of system's configuration of characteristics and properties of reactants and products.

A typical nuclear decay determining a more stable configuration of the nucleus is the following β^- decay [5.1,5.2]:

$$n \rightarrow p^+ + \beta^- + \overline{\nu_e} + \Delta E^{KINETIC} + \gamma$$

which, in case of a specific atom ${}_Z X^A$ becomes

$${}_Z X^A \rightarrow {}_{Z+1}Y^A + e^- + \overline{\nu_e} + \Delta E^{KINETIC} + \gamma$$

A typical nuclear interaction is represented by the nucleus fission such as Uranium fission described by the following reaction:

$${}_{92}U^{235} + {}_0 n^1 \rightarrow {}_{92}U^{236*} \rightarrow {}_{Z1}X^{A1} + {}_{Z2}Y^{A2} + 2{,}43\,{}_0 n^1 + \Delta E^{KINETIC}$$

The delayed neutrons production reaction represents a decay reaction of fission products in nuclear reactors and occurs as:

$${}_Z X^A \rightarrow {}_Z Y^{A-1} + {}_0 n^1 + \Delta E^{KINETIC}$$

Industrial nuclear plants operate with the following reactions using fertilization of natural Uranium and Thorium (fertile fuels) by means of neutron capture:

Uranium:

$${}_{92}U^{238} + {}_0 n^1 \rightarrow {}_{92}U^{239*} \rightarrow {}_{92}U^{239} + \gamma$$

$${}_{92}U^{239} \rightarrow {}_{93}Np^{239} + \beta^- + \overline{\nu} \rightarrow {}_{94}Pu^{239} + \beta^- + \overline{\nu}$$

Thorium:

$$_{90}Th^{232} +_0 n^1 \rightarrow _{90}Th^{233*} \rightarrow _{90}Th^{233} + \gamma$$

$$_{90}Th^{233} \rightarrow _{91}Pa^{233} + \beta^- + \overline{\nu} \rightarrow _{92}U^{233} + \beta^- + \overline{\nu}$$

These neutron capture reactions, occurring in the bulk fuel material, are accompanied by the typical fission reaction used of enriched part of fuel bulk as follows:

$$_{92}U^{235} +_0 n^1 \rightarrow _{92}U^{236\,*} \rightarrow {}^{140}_{54}Xe^{239} +_{38}Sr^{94} + 2\,_0 n^1$$

that represents a mass balance of fission products generated along the reaction.

The irreversibility of fission process can be subdivided in two phases. The first phase consists of the removal of bond constraints due to internucleon attraction strong forces, this implying that the unique mass of the nucleus is subdivided into fission fragments. This determines a leap to a lower hierarchical level that prevents the conversion of the total amount of internucleon potential energy back to the higher level. In fact, once a system constituted by a unique mass is subdivided into fragments, then the entire amount of inter-particle repulsion potential energy is not more capable to be entirely transferred to the external system. Indeed, two particles only can undergo the same displacement of a theoretical elemental cylinder-piston device moving parts. All additional particles undergo intermediate displacements between the maximum of cylinder and piston and zero at the center of their distance. The second phase of the irreversible fission process is the temperature reduction from the higher temperature, corresponding to the entire inter-nucleons potential energy transformed into fragments kinetic energy, to the temperature inside the fuel rod centerline.

A fission nuclear reaction is caused by the collision between a neutron and a nucleus. Before the reaction occurs, the nucleus is bounded, as a whole, by mutual attractive strong interactions among protons and neutrons. Nucleus behaves as a rigid system and linear-angular vibration relative motion among the constituting particles is allowed only. During fission reaction, neutron kinetic energy is transferred to the nucleus to overcome the fission potential energy barrier due to inter-nucleons bond potential energy determined by attractive strong forces. Once this barrier has been achieved, the “potential hole” is crossed and the inter-nucleon potential energy due to repulsive electro-magnetic forces between fission fragments results higher than the attractive strong force. This excess of force implies that inter-fragments repulsive electro-magnetic forces generate the inter-fragments electro-magnetic potential energy (Lennard-Jones potential). If an ideal cylinder-piston device existed, that potential energy could be entirely transferred as work interaction to the external system. Theoretically, from purely geometrical-kinematic point of view, nothing prevents to think of the viability of this process. Electro-magnetic field would be able to accomplish this operation. However, in the real case, this device is not foreseen, for technological or design reasons, such as in actual nuclear reactors, then the potential energy due to repulsive forces between the two fission fragments is converted intro inter-fragments kinetic energy, that is no more capable to be entirely transferred back into work interaction. This means that there has been a change of hierarchical level, from sub-molecular, or atomic, to subatomic, implying an irreversible distribution of velocities pertaining to fission fragments.

In fact, it happens that inter-particle repulsion electro-magnetic forces are not individually used to transfer the entire electro-magnetic potential energy into work interaction. Indeed, if a spherical system is considered, then the fission process produces a multiplication of system sub-particles spreading over the whole volume. In this distributed configuration, the lower the distance from the sphere center, the lower the displacement between two interacting particles and hence the lower the amount of inter-particle potential energy transferred as work interaction to the external system. Only in case of infinite radius of the sphere, the displacement nearby the sphere center is not null. This differential displacement proves that nuclear fission determines the aforementioned change of the hierarchical level of entropy definition. Therefore, even in case of potential energy, other than the case of kinetic energy, there is no mean to recover the entire amount of kinetic energy or potential energy when many particles or few particles are produced as a consequence of subdivision of a whole particle into two or more sub-particles. This irreversible process associated to the subdivision of a system has a lower bound in the threshold leading from two interacting particles to three interacting particles. Indeed, three particles constitute the three-body system assumed by Poincaré to demonstrate that, in this case, equations governing the motion of three bodies have non-converging solution this representing a complex behavior associated to the irreversibility of any process occurring within it.

The conversion from inter-particle potential energy to inter-particle kinetic energy implies a mass increase. Actually, the following process occurs:

$$\Delta E^{\substack{ATTRACTION \\ POTENTIAL}} \rightarrow \Delta E^{\substack{REPULSION \\ POTENTIAL}} \Leftrightarrow \text{ constraints removal}$$

$$\Leftrightarrow \text{ energy conversion and mass increase;}$$

repulsive electro-magnetic potential energy $\Leftrightarrow$ γ radiation $\Leftrightarrow$ mass reduction $\Delta E = \Delta m^{TOTAL} \cdot c^2$

This relationship then derives from the particle system reduction of its overall potential energy hence the excess of potential energy is conserved and transformed into mass and released under form of radiation energy transferred to the external system.

In case of nuclear fission due to neutron collisions, the atom nucleon bonds are broken and nucleons attractive potential energy is converted into repulsive potential energy in turn transformed into kinetic energy. As said, the quantum transformation of potential energy into kinetic energy implies an increase of total mass.

As here above clarified, in term of Second Law logic schema, a reaction from nucleons attraction potential energy, due to strong forces, to nucleons repulsive potential energy, due to electro-magnetic forces, implies an energy conversion because the “degree of distribution” of attraction potential energy is lower with respect to the case of repulsion potential energy, hence thermodynamic entropy increases thus the reaction is not a transformation in which entropy is constant. Indeed, the system is subdivided into two or more sub-systems and a hierarchical level quantum change occurs so that entropy property undergoes a quantum increase. Strong attractive interactions among nucleons behave as a constraint and hold the nucleus as a whole mass. Instead, electro-magnetic repulsive interactions act on the fragments of subdivided nucleus into multi-particle systems. The transition from a higher to a lower hierarchical structure level is caused by a decrease of mass concentration and a corresponding increase of mass distribution of both particles and interactions.

Actually, the maximum net useful work due to repulsive interactions potential energy could be transferred by work interaction $\Delta E^{\substack{REPULSION\\POTENTIAL}} \rightarrow W_{HL}$ and the work of sub-particle origin is withdrawn by means of the elemental cylinder-piston device capable of transferring the entire inter-particle repulsion potential energy, of each and every sub-particle, into work interaction.

With reference to the expression of Kinematic Entropy and Geometric Entropy at microscopic level, the following contributions determine entropy property changes caused by the process from rigid constraints to dynamic interactions among all available degrees of freedom:

1. N : number of particles or sub-particles
2. W^p : number of micro-states due to variation of velocity degree of freedom
3. W^q : number of micro-states due to variation of position degree of freedom

$\Delta E^{\substack{REPULSION\\POTENTIAL}} \rightarrow \Delta E^{\substack{KINETIC\\FRAGMENTS}} \Leftrightarrow$ degrees of freedom availability

$\Leftrightarrow$ energy transformation and mass increase;

Once the rigid constraints have been removed, the inter-particle electro-magnetic repulsion forces start acting and their potential energy, frozen by the removed rigid constraints, is released and transformed into kinetic energy with increase of temperature.

The total balance of whole process through nuclear reactions determines the transformation from initial bound attractive potential energy to final kinetic energy implying a conversion of mass:

$$\Delta E^{\substack{ATTRACTION\\POTENTIAL}} - \Delta E^{\substack{KINETIC\\FRAGMENTS}} = \Delta m^{TOTAL} \cdot c^2$$

The relativistic term $\Delta m^{TOTAL} \cdot c^2$ accounts for the transition from a higher hierarchical level to a lower hierarchical level of entropy property associated to the system energy or, in different terms, from a concentrated form of energy to a more distributed one. Hence, this term expresses the amount of energy needed to reverse the process from the lower to the higher hierarchical level. The non-existence of Maxwell demon is proved by the relativistic term. Or, in different terms, accounting for the contribution of each and every nucleon:

$$\left(\sum_{i=1}^{n} E_{1i}^{\substack{ATTRACTION\\POTENTIAL}} + \sum_{i=1}^{n} E_{1i}^{\substack{NUCLEON\\KINETIC}}\right) - \left(\sum_{i=1}^{N} E_{2i}^{\substack{FRAGMENTS\\POTENTIAL}} + \sum_{i=1}^{N} E_{2i}^{\substack{FRAGMENTS\\KINETIC}}\right) = \Delta m^{TOTAL} \cdot c^2$$

where n is the number of nucleons and N is the number of fission fragments.

Considering the amount of elementary work interaction resulting from bound attractive potential energy, the following definition of "work of nuclear origin", due to nuclear interactions, can be stated, in elemental terms: $\delta m = \delta W_{HL}$.

As regard the definition of thermal exergy EX^T , the maximum net useful work is represented by the amount of work interaction resulting from the electro-magnetic repulsive forces acting among fission fragments. Nevertheless, the withdrawable maximum work interaction takes into account that neutrino produced by the reaction is lost and with no mean it can contribute, gamma radiation cannot be used as well. By virtue of the duality wave-particle, γ radiation can be accounted for as a mass particle.

In all above nuclear reactions $\Delta E^{KINETIC}$ corresponds to the difference of bound attraction potential energy converted into repulsion interaction potential energy of reaction fragments in turn transformed into kinetic energy of fragments themselves. The conversion from bound attraction potential energy to repulsion interaction potential energy constitutes the threshold from a concentrated mass system to a distributed mass system. Indeed, the initial nucleus behaves as a unique physical entity and all forms of energies, namely potential energy and kinetic energy, are associated to a unique mass as a whole. This implies that all quantum processes are reversible hence no additional amount of energy is needed to make the opposite process occurring. Bounds act as constraints ensuring that the process is reversible in the same form. The calculation of generalized exergy is based on the difference of energy available before and after the fission reaction occurs.

The Q-value of the reaction is about 210 MeV and is subdivided in the following contributions (in MeV):

1) Kinetic energy of fission fragments:	170
2) Kinetic energy of prompt neutron:	10
3) Prompt γ :	10
4) Decay of fission fragments:	
4.1) Kinetic energy of delayed neutrons:	negligible
4.2) Energy associated to β^- :	5
4.3) Energy associated to delayed γ :	5

4.4) Energy associated to $\overline{\nu}$: 10

Neutrinos associated to β^- decay are not recovered and energy associated to neutrinos has to be considered irreversibly lost.

Therefore, the amount of Q-value to be accounted for as thermal internal energy and transferred to the cooling medium by means of heat interaction is equal to 200 MeV. This implies that, in terms of thermal exergy, the maximum net useful work is derived considering the amount of heat interaction converted into work interaction.

The calculation of thermal exergy requires the evaluation of the temperature corresponding to the kinetic energy of fission fragments in correspondence of the centreline of fuel rods. After nucleus fission process has completed, fragments move accelerating away from each other due to Coulomb electro-magnetic repulsion forces. To do so, reference can be made to the Equipartition Theorem of Energy that is demonstrated in the framework of Classical Statistical Mechanics and the Kinetic Theory of Gases. The theorem correlates the temperature with the total kinetic energy accommodated among all available degrees of freedom of the system components constituted, in the case of a fission nuclear reaction, by the fission products.
The mean energy calculated for a particle in oscillation motion, along one direction, is given by:

$$\overline{E}^{x} = \overline{E}^{y} = \overline{E}^{z} = \frac{1}{2}\overline{E}^{KINETIC} + \frac{1}{2}\overline{E}^{POTENTIAL} = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T$$

Nuclear reactions occur along three spatial dimensions, therefore the total mean energy is the following:

$$\overline{E} = \frac{3}{2}\overline{E}^{KINETIC} + \frac{3}{2}\overline{E}^{POTENTIAL} = \frac{3}{2}k_B T + \frac{3}{2}k_B T = 3k_B T$$

Fragment motion immediately after the fission is the initial phase of the oscillation motion that generates heat interaction and transmission through the entire fuel rod and the core. Therefore, during this initial phase of the motion, the potential energy due to electro-magnetic repulsive forces is transformed into kinetic energy and the sum of the two contributions can be considered constant and equal to $3k_B T$. Then, assuming that the mean total energy corresponds to Q-value = 200 MeV, it is straight forward possible to calculate the absolute temperature of the reacting nuclear fuel, conventionally considered at the centreline of a fuel rod.

Considering that 1 eV = $1{,}602\cdot 10^{-19} J$ or 1 MeV = $1{,}602\cdot 10^{-13} J$ and Boltzmann constant is $k_B = 1{,}38064852 \times 10^{-23}\frac{m^2 \cdot kg}{s^2 \cdot K} = 1{,}38064852 \times 10^{-23}\frac{J}{K}$ or $k_B = 8{,}617 \times 10^{-5}\frac{eV}{K} = 8{,}617 \times 10^{-11}\frac{MeV}{K}$

and $N_A = 6{,}022 \times 10^{23} \dfrac{1}{mol}$, then the following equality is valid: $Q - vaue = 3k_B T$, from which the fission temperature is calculated as $T^{FISSION} = \dfrac{Q - vaue}{3k_B}$ then from which $T^{FISSION} = \dfrac{200}{3 \times 8{,}617 \times 10^{-11}}$ $\cong 7{,}7 \times 10^{11} K = 7{,}7 \times 10^{2} \times 10^{3} \times 10^{6} K$.

5.1.2. Nuclear Fusion

Among nuclear processes, nuclear fusion [5.7] is characterized by the arrangement of two nuclei undergoing a reconfiguration resulting in transmutations of reactants into different products with higher atomic number. Nuclear fusion will be also considered for Second Law Analyses.

5.2. Nuclear Reaction Irreversibility and Exergy Destruction

Once the inter-nucleons attraction bond of strong interactions has been overcome by the electro-magnetic Coulomb repulsive interaction, then the kinetic energy of fission fragments is released to the surrounding fuel bulk and the temperature itself is decreased to the fuel rods temperature. This decrease of temperature is responsible of the decrease of thermal exergy due to the fission reaction process. Indeed, the high temperature difference is not used to produce work interaction thus it is irreversibly lost. To summarize, the following steps are responsible for the exergy loss and destruction during fission process:

i) Nucleus, as a whole rigid mass, undergoes attractive strong forces among nucleons in opposition to repulsive Coulomb electro-magnetic forces. Strong forces act as a constraint among nucleons and ensure the stability of nucleus. Inter-particle electro-magnetic repulsion potential energy constitutes the theoretical available energy entirely withdrawable only in case no more than two parts of the nucleus result from fission and therefore undergo repulsive interaction and drive the two moving parts of an ideal elemental cylinder-piston device; this available energy corresponds to the electro-magnetic repulsion potential energy $E^{REPULSION}_{POTENTIAL}$

ii) Once the fission has occurred, and strong interactions have been overcome, then the nucleus becomes a multi-particle system constituted by more than two fission fragments characterized by inter-particle electro-magnetic repulsion potential energy. This step determines an increase of number of particles as fragments produced by the fission and therefore makes the system moving from a higher to a lower hierarchical level at which entropy increases due to non-equipartition theorem of entropy [4.57]. Hence, the available energy is $E^{REPULSION}_{POTENTIAL} \cdot \eta^{C}$

iii) The inter-particle electro-magnetic repulsion potential energy is transformed into inter-particle kinetic energy corresponding to fission temperature and the available energy is $E^{KINETIC}_{FRAGMENTS} \eta^{T}$

iv) Fission temperature kinetic determined by inter-particle kinetic energy of fragments is irreversibly converted into lower temperature of nuclear fuel calculated at the centreline of fuel rods.

These four steps determine the irreversible decrease of initial exergy content of each and every atom of nuclear fuel and should be included among all contribution to the exergy balance of the reactor's core.

Once exergy has been calculated, then the balance of entropy property along the fission process can be derived considering the expression $S_1 - S_0 = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]$ in which EX^R is the thermal exergy calculated, as above, with respect to the reservoir R. Hence, it must be, at least, of the same order of magnitude of the entropy change calculated by means of the Boltzmann expression of a microscopic system.

5.3. Mass Defect and Binding Energy

Total binding energy of a nucleus is expressed as the difference of protons, neutrons and nucleus mass in the two states of composed nucleus and isolated nucleons [5.1-5.3]:

$$B(A, Z) = 931 \cdot \left[Z \cdot m_H \cdot c^2 + m_n (A - Z) \cdot c^2 - M\right]$$

where the binding energy is expressed in MeV and 1 Atomic Mass Unit (AMU) = 931 MeV.

The total binding energy of a nucleus is calculated by means of the Weizsacker's formula derived from the liquid drop model [5.1]:

$$B(A, Z) = a_1 A - a_2 A^{2/3} - a_3 \frac{(A - 2Z)^2}{A} - a_4 \frac{Z^2}{A^{1/3}} \pm \frac{a_5}{A^{3/4}}$$

- attractive energy = $a_1 A$
- surface tension effect = $-a_2 A^{2/3}$
- nucleus composition term = $-a_3 \cdot \frac{(A-2Z)^2}{A}$ where $A - 2Z$ represents the excess of neutrons with respect to the number of protons in the nucleus
- repulsive energy = $-a_4 \cdot \frac{Z^2}{A^{1/3}}$
- spin effect = $\pm \frac{a_5}{A^{3/4}}$ where the plus sign applies to even-even nuclei and the minus sign applies to odd-odd nuclei

The total binding energy of one nucleus of uranium ${}_{92}U^{238}$ can be assumed equal to 1785 MeV [Glasstone, Edlund] and constitutes the theoretical available energy that a nucleus can release under certain conditions defined at i) and using an ideal device. Hence, $E^{\substack{REPULSION\\POTENTIAL}} = 1785$ MeV. The nuclear exergy available after phase i) is completed, is dictated by the lower hierarchical level and expressed as $E^{\substack{REPULSION\\POTENTIAL}} \cdot \eta^{C} = E^{\substack{REPULSION\\POTENTIAL}} \cdot \left(1 - \frac{\mu_R}{\mu}\right)$ where μ is the nucleon repulsion potential energy at the instant of nucleus fission into fragments and μ_R is the nucleon repulsion potential energy of the reservoir corresponding to the entire volume of the nuclear reactor confined by the reflector shield. The nucleon repulsion potential energy μ for uranium ${}_{92}U^{238}$ is equal to the nucleon binding energy (7,6 MeV/nucleon); μ_R is the nucleon binding energy of the reservoir or, in different term, the potential energy in stable equilibrium state corresponding to the higher mass of the isolated nucleon in stable equilibrium state. The reservoir is characterized by μ_R in the conditions allowed within the nuclear core. On the one hand, neutrons are produced and tend to the maximum dispersion where $\mu > \mu_R$. On the other hand, the nuclear fission process produces fragments more stable than the originating nucleus and distributed in the gas plenum of fuel rods. Fragments and neutrons, apart from each other, constitute the configuration corresponding to μ_R . The thermodynamic state of R corresponds to the one occurring after the fission reaction Q-value of 200 MeV has been released to the coolant flowing through the core. Therefore, the difference between the initial binding energy of nucleus and the q-value energy of fission reaction represents the amount of available energy irreversibly lost along the process from a unique system to a set of fragments:

$$\Delta EX^{\substack{NUCLEAR\\FISSION}} = W^{\substack{NUCLEUS\\POTENTIAL\\ENERGY}} - W^{\substack{FRAGMENTS\\KINETIC\\ENERGY}} = E^{\substack{REPULSION\\POTENTIAL}} - E^{\substack{KINETIC\\FRAGMENTS}} \eta^{T}$$

$$= 1785 - 200 \cdot \left(1 - \frac{298}{1793}\right) = 1785 - 200 \cdot 0{,}834 = 1785 - 166{,}8 = 1618{,}2 \quad MeV$$

Thus, the amount of exergy change $\Delta EX^{\substack{NUCLEAR\\FISSION}} = 1618{,}2 MeV$ constitutes the amount of available work interaction that is irreversibly lost along fission process of a single nucleus interacting with a neutron. This mean that a large part of the initial mechanical energy consisting of the binding potential energy of the whole nucleus is lost because of the subdivision of the nucleus in three or more fragments that implying a change from a higher to a lower hierarchical level. The initial binding potential energy theoretically useful as work interaction, constitutes the content of mechanical exergy EX^{M} undergoing dissipation into thermal exergy corresponding to the exergy of nucleus fragments immediately after the fission.

5.4. Reasons of Interest for Fission and Fusion Elemental Reactions Second Law Analyses

The interest in developing Second Law analyses founded on exergy method applied to fission and fusion nuclear reactions can be found in: i) the observation of physical phenomena and nuclear processes through a thermodynamic standpoint; ii) the need of adopting a more extended approach to nuclear reactors design in the perspective of the optimization and confrontation of different types of technologies and plant configurations. The exergy method focuses on irreversible phenomena associated to non-equilibrium states and processes occurring in all macroscopic and microscopic physical systems. The degree of irreversibility of non-equilibrium processes is correlated to the amount of exergy destruction representing the indicator of the degree of dissipation of all energy and interaction forms. For these reasons, it is worth applying this method to nuclear reactions with the aim of extending the overall plant mass and energy balances and evaluate exergy efficiencies. To do so, an analysis of concepts underpinning the definitions of thermodynamic entropy and exergy properties is here summarized to demonstrate their implications in nuclear physics.

Usually, second law analyses consider the conventional plant or the nuclear reactor or both jointly combined to achieve an overall balance. As far as light water boiling technology and Boiling Water Reactors (BWR) power units are concerned, a study was carried out by Dunbar et al. on an operating plant [5.8]. As regards light water pressurized technology, more recent studies are reported in the literature for Pressurized Water Reactors (PWR) [5.9] and Multipurpose Advanced Reactor inherently Safe (MARS) [5.10]. Despite the accuracy of those studies, no specific mention is provided on the elemental nuclear reaction and the implication on the behavior and performance of plant core. Though, here the purpose is to bridge this gap with the analysis focusing on the elementary fission or fusion nuclear reaction representing the crucial process stage occurring in the core of fission power plants or in the plasma chamber of ITER (under construction) or DEMO (under design) fusion reactors.

As regard the nuclear physical aspect, the literature reports studies focusing on the exergy analysis of nuclear radiation along decay processes [5.11,5.12]. In particular, classical and quantum statistical methods have been adopted to evaluate exergy based on barions motion and momentum to achieve exergy fluxes calculated by means of physical parameters characterizing the particles motion [5.11,5.12]. These evaluations are underpinned by statistical models to describe nuclear fuel bulk reactions occurring in operational industrial plants. The present research focuses on the thermodynamic processes occurring within the core of reactors. Here, the intent is to analyze the elemental fission and fusion reactions and to propose an alternative method based on binding potential energy among protons and neutrons, calculated on the basis of mass defect in different physical states [5.13]. The objective is to evaluate the thermodynamic state and process variables governing nuclear reactions and to provide the bases to achieve a complete evaluation of plant configurations and a confrontation among different technologies. This perspective allows to assess the balance and efficiency that should be accounted for in an overall Second Law analysis based on exergy method here adopted to provide an operative tool for calculations in applications and reactors design. To do so, Second Law analyses need to be carried out adopting measurable properties and for this very reason the exergy method, and the formulation of thermodynamic entropy defined by Hatsopoulos, Gyftopoulos and Beretta will be adopted as described in the following sections.

5.5. Second Law Analysis and Exergy Method Applied to Nuclear Reactions

Nuclear reactions can be regarded as elemental non-equilibrium irreversible processes occurring in few-particle systems constituted by nuclei, neutrons and other sub-nuclear particles interacting because of collisions occurring at defined thermodynamic conditions. The definition of entropy property of a system A, beside the classical formulation of Clausius $S_1 - S_0 = \int_0^1 \frac{\delta Q}{T}$, has been expressed by Hatsopoulos, Gyftopoulos and Beretta in the following form [7-11]:

$$S_1 - S_0 = \frac{1}{C_R}\left[\left(E_1 - E_0\right) - \left(\Omega_1^R - \Omega_0^R\right)\right] \tag{5.1}$$

where C_R is a constant characterizing an external reference system R behaving as a reservoir, E is the internal energy determined by the temperature associated to the kinetic energy of interacting particles and reaction products, and Ω^R is the available energy of the system interacting with the reservoir. The literature reports the proof that $C_R = T_R$ [1.9]. Moreover, it has been proved that entropy is an inherent property of any system, large or small, in any state, equilibrium or non-equilibrium and, for this reason, the reservoir behaves as an auxiliary system only [1.9]. The definition of thermal entropy can be expressed in the form:

$$S_1^T - S_0^T = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^T \tag{5.2}$$

where the available energy Ω^R is replaced by the thermal exergy EX^R. This expression has been proved [1.9] by means of the concept of non-existence of Perpetual Motion Machine of the Second Kind (PMM2). Indeed, the non-existence of PMM2 implies the impossibility of a complete thermal-mechanical conversion of thermal energy into work thus meaning that the energy conversion efficiency $\eta^T < 1$. This logical inference can be replicated for nuclear-mechanical conversion of mass into work where mass interaction is associated to the potential energy, or binding energy, among particles constituting a system. Hence, the definition of nuclear entropy can be assumed to be:

$$S_1^N - S_0^N = \frac{1}{\mu_R^N}\left[\left(E_1^N - E_0^N\right) - \left(EX_1^R - EX_0^R\right)\right]^N \tag{5.3}$$

where $C_R = \mu_R^N$ and μ_R^N is the reference nuclear potential of the reservoir and E^N is the binding potential energy associated to strong interactions among nucleons. The method here adopted is founded on the binding energies calculated in terms of mass defects before and after a nuclear reaction according to the approach already used and reported in the literature by Badescu and Isvoranu [5.11,5.12] and by Hermann [5.13]. The Figure 1 describes the curves of binding potential energy for nuclei involved in fission and fusion reactions respectively.

In this particular case, the non-existence of PMM2 implies the impossibility of a complete nuclear-mechanical conversion of nuclear potential into work thus meaning that the energy conversion efficiency $\eta^N < 1$.

Finally, the mechanical entropy S^M accounts for the density of: (i) interparticle kinetic energy correlated to the frequency of collisions, and (ii) the potential energy correlated to the intensity of actions both depending on the volume. Hence, the following expression:

$$S_1^M - S_0^M = \frac{\overline{R}}{P_R V_R}\left[\left(E_1 - E_0\right) - \left(EX_1^R - EX_0^R\right)\right]^M \tag{5.4}$$

in which $\frac{1}{C_R} = \frac{\overline{R}}{P_R V_R}$, constitutes an additional term of the generalized thermodynamic entropy suitable to characterize the mechanical internal energy PV associated to pressure and volume. As entropy is an additive property, the generalized definition is obtained by the sum of its thermal, nuclear and mechanical components: $S^G = S^T + S^N + S^M$ [3.7,3.8].

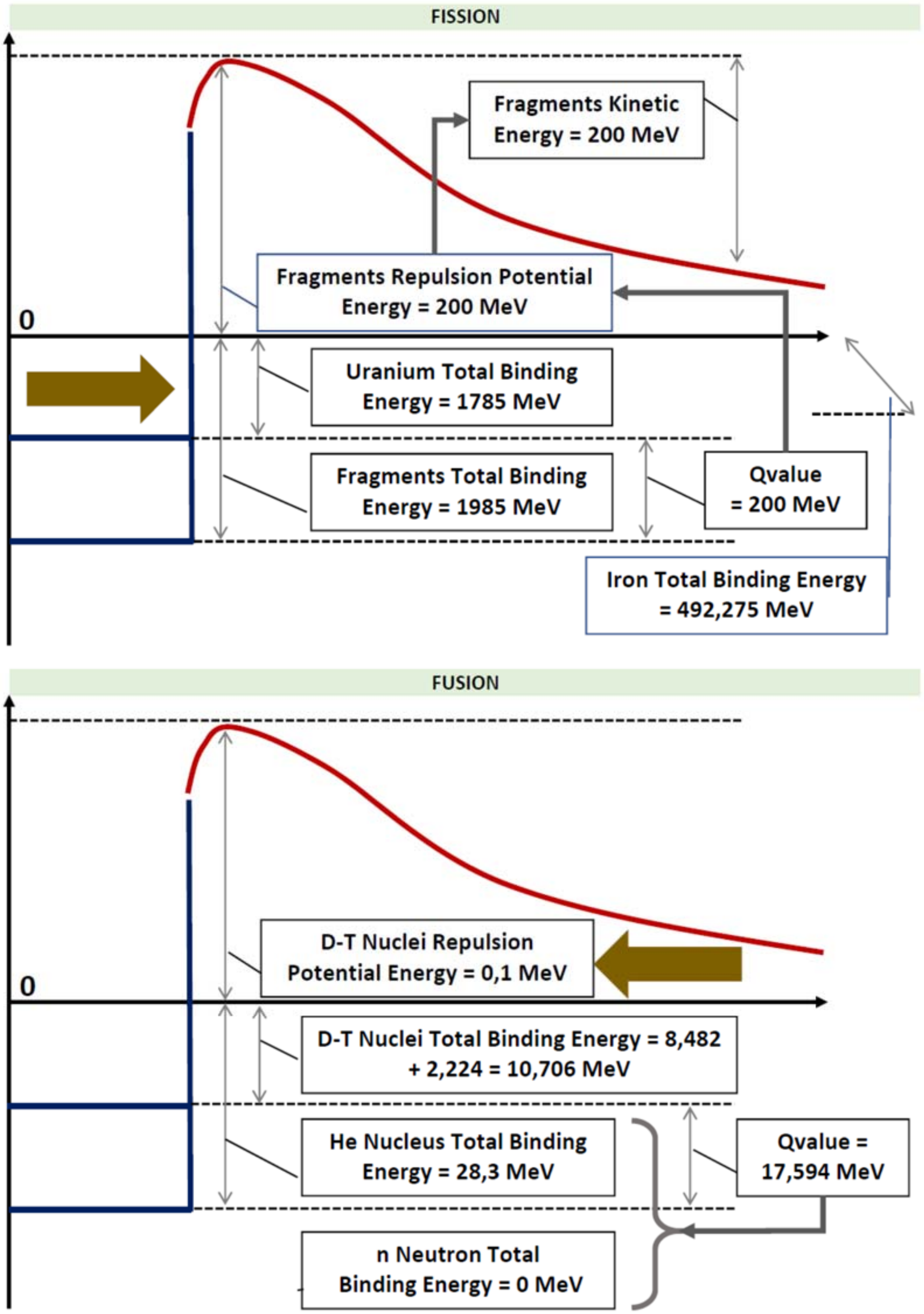


Figure 5.1 - Binding potentials in fission and fusion nuclear reactions. The horizontal x-axis represents the distance between interacting particles, the vertical y-axis represents the inter-particle energy.

With reference to the definitions of entropy related to exergy here enunciated, and being *AR* the composite of mutually interacting system *A* and reservoir *R*, the generalized exergy balance of an individual fission or fusion nuclear reaction can be expressed by means of different exergy contributions: thermal exergy producing available work interaction $EX^T = \left(W_{10}^{AR\rightarrow}\right)_{HEAT}^{MAX}$, nuclear exergy producing work interaction $EX^N = \left(W_{10}^{AR\rightarrow}\right)_{MASS}^{MAX}$, mechanical exergy producing heat interaction $EX^M = \left(Q_{10}^{AR\rightarrow}\right)_{WORK}^{MAX}$, mechanical exergy producing mass interaction $EX^M = \left(M_{10}^{AR\rightarrow}\right)_{WORK}^{MAX}$; therefore, the expression of generalized exergy is the following [4.57]:

$$EX^{G}_{\substack{NUCLEAR\\REACTION}} = EX^T + EX^N + EX^M$$

$$= \left(W_{10}^{AR\rightarrow}\right)_{HEAT}^{MAX} + \left(W_{10}^{AR\rightarrow}\right)_{MASS}^{MAX}$$

$$+ \left(Q_{10}^{AR\rightarrow}\right)_{WORK}^{MAX} + \left(M_{10}^{AR\rightarrow}\right)_{WORK}^{MAX} \tag{5.5}$$

This definition of generalized exergy of nuclear reactions is underpinned, on the one side, by the concept of equivalence between heat interaction and work interaction and the equivalence between mass interaction and work interaction; on the other side, the inter-convertibility of heat-to-work and work-to-heat as well as the inter-convertibility of mass-to-work and work-to-mass is a counter-proof of the equivalence above mentioned [2.3-2.6]. It is worth using the expressions above discussed for nuclear processes since energy and exergy are measurable properties. Moreover, the thermodynamic state of reference system behaving as a reservoir, can be arbitrarily selected being an auxiliary system only in the definition of thermodynamic entropy [3.1,3.2] and its components [3.7,3.8]. Hence, the calculation of entropy can be directly derived once thermodynamic states before and after nuclear reactions are defined. This method, usually adopted for many-particle systems and properties describing macroscopic systems in plant optimization [2.7], will be here specially applied to elemental fission and fusion processes as demonstrated in the following sections.

5.6. Fission Nuclear Reaction Exergy Analysis

A typical Uranium ${}_{92}U^{235}$ fission reaction is represented by the following process [5.1-5.4]:

$${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236*}$$

$$\rightarrow {}_{Z1}X^{A1} + {}_{Z2}Y^{A2} + 2{,}43\,{}_{0}n^{1} + Qvalue \tag{5.6}$$

Before the fission occurs, strong attraction interactions among nucleons behave as a constraint and hold the nucleus as a unique whole system. The nucleus fission produces fragments ${}_{Z1}X^{A1}$, ${}_{Z2}Y^{A2}$ composed by nuclei of lower atomic number, with respect to the uranium atomic number, neutrons and gamma radiation. The increase of particles mass dispersion and interactions distribution among fragments causes the transition from a concentrated mass, characterized by a unique position and velocity, to a subdivided configuration. This transition implies that positions are dispersed and velocities distributed with random spectra compared with the initial nucleus, due to the intrinsically probabilistic statistical and quantum nature of phenomena at microscopic nuclear and sub-nuclear level. Once the inter-nucleons attraction bond barrier has been overcome during the fission, fragments move accelerating away from each other due to electro-magnetic repulsion interactions. The repulsion potential energy existing immediately after the fission is transformed into fragments kinetic energy released to the surrounding fuel bulk and the fission temperature is decreased to the fuel rods temperature. The fission temperature is conventionally calculated considering the relation $k_B T = 210 MeV$ where $k_B = 8{,}617 \times 10^{-11}\, MeV/K$ is the Boltzmann constant and $1MeV = 1{,}602 \cdot 10^{-13}\, J$.

This temperature difference is not used in a conventional industrial reactor to produce work interaction hence it is irreversibly dissipated. The reaction is not reversible because the heat interaction amount released is not sufficient to reverse back the nucleus to its original configuration thus requiring an inverse fusion reaction with heat input. In fact, the fission determines the stochastic distribution of velocity vectors pertaining to each and every fission fragment in such a way to prevent the occurrence of any reversible process back to the initial unique mass state with energy associated to the nucleus center of mass. Thus, nucleus fission into fragments increases the degree of velocity distribution and position dispersion among all particles, hence increases the entropy property characterizing the thermodynamic state change after fission process. The entity of entropy increase caused by the two different contributions above identified is the objective of the following analysis.

The definition of generalized thermodynamic entropy S^G variation, outlined in the previous section and here adopted, requires the calculation of the generalized exergy EX^G variation that can be expressed in the following terms taking into account the contribution balance of all components:

$$\Delta EX^{G}_{\substack{NUCLEAR\\FISSION}} = \left(\Delta EX^{M} + \Delta EX^{T} + \Delta EX^{N}\right)_{\substack{NUCLEAR\\FISSION}}$$

$$= -\left[\left(EX^{M} + EX^{T} + EX^{N}\right)^{\substack{BEFORE\\FISSION}}\right] - \left[-\left(EX^{M} + EX^{T} + EX^{N}\right)^{\substack{AFTER\\FISSION}}\right] \qquad (5.7)$$

Before the fission, the mechanical exergy EX^M consists of the capability, of colliding neutron and target nucleus kinetic energy, to be converted into thermal energy along a reversible process, however for moderated neutrons this component is negligible. The thermal exergy EX^T related to the fuel bulk temperature characterizing target nucleus with respect to the environment, is negligible. The nuclear exergy EX^N associated to the nucleus binding potential energy, is equal to the sum of inter-nucleons strong attraction potential energy and inter-nucleon electro-magnetic repulsion potential energy $E^{\substack{NUCLEUS\\BINDING}} = E^{\substack{ATTRACTION\\POTENTIAL}} + E^{\substack{REPULSION\\POTENTIAL}}$. This resulting potential energy can be theoretically transferred as maximum net useful work interaction along a mass-to-work direct conversion cycle with efficiency η^N. Hence, only nuclear exergy is available before fission. The total binding potential energy of one nucleus of uranium ${}_{92}U^{235}$ can be assumed equal to about $1785\,MeV$ [5.1] and constitutes the theoretical available potential energy $E^{\substack{NUCLEUS\\BINDING}}$ that the nucleus can release in the form of repulsion potential energy among all nucleons.

After the fission, fragments with lower atomic number and atomic mass are generated. The initial nucleus binding potential energy of the starting whole nucleus is transformed into two contributions constituted by: i) fragments binding potential energy, and ii) repulsion potential energy in turn transformed into fragments kinetic energy expressed as $Qvalue$ representing the useful energy released along the fission reaction. Hence, thermal energy only is available that can be converted into mechanical energy and transferred as work interaction to the external system along a heat-to-work conversion direct cycle with efficiency η^{T}. This implies that in turn, thermal exergy only is available after fission.

The overall exergy balance, based on the definition of exergy property components before and after fission, is the following:

$$\Delta EX^{G}_{\substack{NUCLEAR\\FISSION}} = -\left[\left(0+0+M^{\substack{NUCLEUS\\BINDING\\ENERGY}}\,\eta^{N}\right)^{\substack{BEFORE\\FISSION}}\right] = -\left[-\left(0+Q^{\substack{FRAGMENTS\\KINETIC\\ENERGY}}\,\eta^{T}+0\right)^{\substack{AFTER\\FISSION}}\right] \tag{5.8}$$

In case of nucleus fission, η^{T} and η^{N} are the efficiencies of ideal direct conversion cycles operating between the reservoir and the system thermodynamic conditions corresponding to kinetic energy and the potential energy of fission fragments. Interactions in the above equation can be expressed in terms of energy transfer associated to interacting particles before and after fission:

$$\Delta EX^{G}_{\substack{NUCLEAR\\FISSION}} = -\left[\left(0+0-E^{\substack{NUCLEUS\\BINDING}}\,\eta^{N}\right)^{\substack{BEFORE\\FISSION}}\right] - \left[-\left(0-E^{\substack{FRAGMENTS\\KINETIC}}\,\eta^{T}+0\right)^{\substack{AFTER\\FISSION}}\right] \tag{5.9}$$

The $Qvalue$ of a nuclear fission is about $210\,MeV$ and it is calculated with the measurement of mass defect of nuclei before and after fission [20]. The $Qvalue$ is partitioned in the following contributions (in MeV): kinetic energy of fission fragments = 170; kinetic energy of prompt neutron = 10; prompt γ = 10. Moreover, as concerns the decay of fission fragments: kinetic energy of delayed neutrons = negligible; energy associated to β^{-} = 5; energy associated to delayed γ = 5; energy associated to neutrinos $\overline{\nu}$ = 10 taking into account that neutrinos (generated by β^{-} decay) are not recovered and their energy is irreversibly lost. In addition to the mass defect, equal to the amount of thermal energy release and the associated thermal entropy contribution, nuclear fissions also determine a subdivision of the initial nucleus mass into fragments hence implying thermal entropy production due to inherently stochastic distribution of fragments velocities. Considering that the mechanical exergy is null before and after fission, then the calculation of generalized thermodynamic entropy for nuclear fission results from the following expression:

$$\Delta S^{G}_{FISSION} = \left(S_1 - S_0\right)^T + \left(S_1 - S_0\right)^N$$

$$= \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX^R_1 - EX^R_0\right)\right]^T + \frac{1}{\mu^N_R}\left[\left(E_1 - E_0\right) - \left(EX^R_1 - EX^R_0\right)\right]^N \tag{5.10}$$

As the reservoir is an auxiliary external reference system, its thermodynamic state can be arbitrarily selected to simplify the calculation. To this end, it can be assumed that reservoir conditions are those existing before the fission occurs. Then, temperature and nuclear potential of the reservoir are: $T_R = 298\,K$ corresponding to the environmental initial temperature of target nucleus and neutron before fission; $\mu^N_R = \mu^N_1$ $= -E^{NUCLEUS}_{\substack{BINDING \\ FRAGMENTS}} \Big/ n_1 = 1785/4{,}43 \cong 40\ 3 MeV$ is the nuclear potential corresponding to the ratio of binding potential energy over the number n_1 of fragments after fission, with minus sign. Once the fission has occurred, then for the selected thermodynamic state of the reservoir, the calculation of entropy change can be separated for thermal process and nuclear process.

As concerns the thermal entropy variation related to the reference temperature:

$$\left(S_1 - S_0\right)^T = \frac{1}{T_R}\left[\left(E_1 - E_0\right) - \left(EX^R_1 - EX^R_0\right)\right]^T$$

$$= \frac{1}{298}\left[210 - \left(200 \cdot \left(1 - \frac{T_R}{T_1}\right) - 0\right)\right]^T \tag{5.11}$$

It should be noticed that the whole amount of $Qvalue$, released as thermal energy along the nucleus fission, can be assumed as subdivided among 2 fission fragments and 2,43 neutrons as a mean value, that is 4,43 particles generated from 2 initial interacting particles, namely neutron and target nucleus. Therefore, by virtue of the equipartition theorem of energy among all fission fragments, each particle has associated an amount of kinetic energy equal to $210/4{,}43 \cong 47{,}4 MeV$ constituting the thermal potential to be accounted for:

$$\left(S_1 - S_0\right)^T = \frac{1}{298}\left[210 - \left(200 \cdot \left(1 - \frac{0{,}025 \cdot 10^{-6}}{47{,}4}\right) - 0\right)\right]^T \tag{5.12}$$

$$\cong 0{,}0336 \quad MeV \ /K$$

where the heat-to-work conversion efficiency has been assumed as $\eta^{T} \cong 1$ being the final fission temperature far much higher than the initial reference temperature: hence, the energy released during fission can be considered equal to the thermal exergy content and the increase of thermal entropy is due to the kinetic energy associated to lost neutrinos.

As concerns the nuclear entropy variation related to the reference nuclear potential:

$$(S_1 - S_0)^N$$

$$= \frac{1}{\mu_R^N}\left[\left(E_1^{\substack{FRAGMENTS\\BINDING}} - E_0^{\substack{NUCLEUS\\BINDING}}\right)\right]^N$$

$$+ \frac{1}{\mu_R^N}\left[-\left(E_1^{\substack{FRAGMENTS\\BINDING}}\left(1-\frac{\mu_R^N}{\mu_1^N}\right)\right)\right]^N$$

$$+ \frac{1}{\mu_R^N}\left[-\left(E_0^{\substack{NUCLEUS\\BINDING}}\left(1-\frac{\mu_R^N}{\mu_0^N}\right)\right)\right]^N \qquad (5.13)$$

where binding energies before fission and after fission are those calculated by means of the mass defect as reported in the literature [5.1]; nuclear potentials account for the number of particles, hence $\mu_0^N = 1985 MeV$ and $\mu_1^N = \mu_R^N = 403 MeV$ as assumed, thus:

$$(S_1 - S_0)^N$$

$$= \frac{1}{403}\left[(1785 - 1985) - \left(0 - 1985 \cdot \left(1 - \frac{403}{1985}\right)\right)\right]^N$$

$$\cong 3{,}4\, MeV/K$$

The positive increase pertaining to both thermal and nuclear components of entropy variation above calculated confirms that a fission reaction determines an increase of fragments velocities associated to the velocity distribution and position dispersion caused by the increase of the number of particles generated from a unique nucleus.

Finally, the variation of the generalized thermodynamic entropy resulting from the sum of its components is:

$$\Delta S_{FISSION}^{G}$$

$$= \left(S_1 - S_0\right)^T + \left(S_1 - S_0\right)^N$$

$$\cong 0{,}0336 \ MeV / K + 3{,}4 \, MeV / K$$

$$\cong 3{,}4336 \ MeV / K$$

The amount of $Qvalue$ is available as thermal energy and transferred to the cooling medium assumed at $573K$ (typical average temperature of the coolant in a Light Water Reactor) by means of heat interaction. In terms of thermal exergy, this implies that the maximum net useful work is derived considering the amount of heat interaction converted into work interaction by a reversible process between the fragments temperature and the cooling medium temperature. However, the temperature corresponding to $E^{\substack{FRAGMENTS \\ KINETIC}}$ is much higher, therefore the thermal exergy between fission temperature and cooling medium temperature is irreversibly lost. The $Qvalue$ is the amount of inter-fragments repulsion potential energy $E^{\substack{REPULSION \\ POTENTIAL}}$ transformed into inter-fragments kinetic energy $E^{\substack{FRAGMENTS \\ KINETIC}}$, resulting from the nucleus fission, that can be finally withdrawn by the cooling medium from the temperature of fuel rods. However, an additional amount is recovered from structures and the coolant itself. Hence, the difference between the initial binding energy of the nucleus and the $Qvalue$ of the fission process represents the amount of available energy irreversibly dissipated, corresponding to the exergy destruction, along the process starting from a unique system and ending to a set of fragments. The generalized exergy balance is:

$$\Delta EX^{G}_{\substack{NUCLEAR \\ FISSION}}$$

$$= -\left[\left(-E^{\substack{NUCLEUS \\ BINDING}} \eta^N\right)^{\substack{BEFORE \\ FISSION}}\right]$$

$$= -\left[-\left(E^{\substack{FRAGMENTS \\ KINETIC}} \eta^T - E^{\substack{FRAGMENTS \\ BINDING}} \eta^N\right)^{\substack{AFTER \\ FISSION}}\right] \tag{5.14}$$

As the difference of thermodynamic potentials between nuclear fuel and external environment (reservoir) is high, then $\eta^N \cong 1$ can be assumed, therefore:

$$\Delta EX^{G}_{\substack{NUCLEAR \\ FISSION}}$$

$$= -\left[(-1785) - \left(200 \cdot \left(1 - \frac{298}{573} \right) - 1985 \right) \right]$$

$$= -[-1785 - 200 \cdot 0{,}48 + 1985] = -104 MeV$$

The above amount of generalized exergy decrease $\Delta EX^{G}_{\substack{NUCLEAR\\FISSION}} = -104 MeV$ expresses the available mechanical exergy EX^{M} irreversible destruction along the fission process of a single neutron and target nucleus. The reason of irreversibility implying exergy destruction is that a fraction of the initial binding energy of the whole nucleus is irreversibly dissipated because of: i) the subdivision of the nucleus into three or more fragments determining a change from high density energy to low density energy, and ii) the lower temperature, assumed at $573K$, of $Qvalue$ heat-to-work conversion with respect to the fission temperature that makes the available energy, immediately after the fission, as a quasi-exergy. Finally, considering the definition of exergy efficiency $\eta^{EX} = 1 - EX_{DESTR} / EX_{INPUT}$, the figure relating to an elemental fission reaction of ${}_{92}U^{235}$ is:

$$\eta^{EX}_{FISSION} = 1 - \Delta EX^{\substack{NUCLEAR\\FISSION}}_{DESTR} \Big/ \Delta EX^{\substack{NUCLEUS\\BINDING}}_{AVAILABLE} \tag{5.15}$$

$$= 1 - (200 - 104)/200 = 0{,}52$$

The enhancement of fission nuclear plants overall efficiency can be achieved by means of optimized plant configurations such us cogeneration to produce process heating in addition to the generation of electric power [5.16].

5.7. Fusion Nuclear Reaction Exergy Analysis

A typical fusion nuclear reaction occurs through the following process [5.6,5.7]:

$${}_{1}H^{2} + {}_{1}H^{3} \rightarrow {}_{2}He^{4}(3{,}5MeV) + {}_{0}n^{1}(14{,}1MeV) \tag{5.16}$$

where ${}_{1}H^{2}$ and ${}_{1}H^{3}$ are isotopes of hydrogen, Deuterium (D) and Tritium (T) respectively. Thermodynamic conditions to allow this reaction are generated inside the plasma chamber where electro-magnetic field are suitable to confine charged particles. Differently from fission, the fusion process is generated by colliding nuclei with an initial kinetic energy far much higher than the inter-nuclei kinetic energy corresponding to the environment temperature; those nuclei move along the same direction and opposite way to ensure that the collision occurs. This additional nuclei’s kinetic energy is needed to overcome the electro-magnetic repulsion potential energy acting before short-radius strong interactions among nucleons prevail. After the fusion, the system results to be more stable with a higher binding potential energy implying a release of energy consisting of the $Qvalue = 17{,}594 MeV$ representing the net useful available energy transferred to the external system. The $Qvalue$ corresponds to the thermal energy used by the heat transfer system conveying this thermal interaction to be converted into work interaction in turn released to be utilized by the external useful system. Fusion results from colliding ${}_1H^2$ and ${}_1H^3$ nuclei and the subsequent transmutation into ${}_2He^4$ with higher atomic number and by-production of one neutron. An increase of reaction products kinetic energy, due to the fusion processes and corresponding to the $Qvalue$, occurs. The amount of $Qvalue$ is calculated with the measurement of mass defect of nuclei before and after fusion [5.6]. Differently from fission, nuclear fusion creates an aggregation of the initial nuclei masses into one unique nucleus hence implying thermal entropy decrease due to the annihilation of the stochastic distribution of initial nuclei velocities.

The exergy balance of a nuclear fusion can be stated as follows:

$$\Delta EX^{G}_{\substack{NUCLEAR\\FUSION}} = \Delta EX^{M} + \Delta EX^{T} + \Delta EX^{N}$$

$$= -\left[\left(EX^{M} + EX^{T} + EX^{N}\right)^{\substack{BEFORE\\FUSION}}\right]$$

$$-\left[-\left(EX^{M} + EX^{T} + EX^{N}\right)^{\substack{AFTER\\FUSION}}\right] \tag{5.17}$$

Before the collision occurs, Deuterium and Tritium nuclei undergo an increase of velocity along the same direction and opposite ways needed to provide the thermodynamic conditions for nuclei fusion. To do so, an amount of work interaction input is used to increase the kinetic energy $E^{\substack{NUCLEI\\KINETIC}}$ of nuclei up to a range of $116 \cdot 10^{6} K$ to $1160 \cdot 10^{6} K$ corresponding to a range of $10 keV$ to $100 keV$. This work interaction is associated to the mechanical exergy $EX^{M} = Q^{\substack{NUCLEI\\KINETIC\\ENERGY}}$ calculated in terms of maximum net useful heat output resulting in the transfer of thermal energy associated to the temperature of colliding nuclei. Instead, the work interaction associated to the mechanical exergy $EX^{M} = M^{\substack{NUCLEI\\POTENTIAL\\ENERGY}}$ calculated in terms of maximum net useful mass, is negligible because both strong and electro-magnetic interactions are negligible at the distance between particles before the collision. The thermal exergy $EX^{T} = W^{\substack{NUCLEI\\KINETIC\\ENERGY}}$ relating to the temperature of nuclei equal to the environment temperature before entering the confined plasma can be considered null. The nuclear exergy $EX^{N} = W^{\substack{NUCLEI\\POTENTIAL\\ENERGY}}$ of Deuterium and Tritium is null as the binding potential energy $E^{\substack{NUCLEI\\BINDING}}$ of individual interacting nuclei is equal to the sum of ${}_1H^{2} = 2{,}224 MeV$ and ${}_1H^{3} = 8{,}482 MeV$ and it couldn't be converted into maximum net useful work being in a more stable configuration with respect to isolated protons and neutrons as reported in the Figure 5.1.

After the collision has occurred, products velocity is distributed over random directions so that are characterized by products kinetic energy $E_{KINETIC}^{PRODUCTS}$ determining the thermal energy being transferred as heat interaction output $Q_{\substack{KINETIC\\ENERGY}}^{PRODUCTS}$ to the external system by means of the first wall, the breading blanket and divertors constituting the main components of the primary heat transfer system from plasma chamber of a fusion reactor. The binding potential energy $E_{BINDING}^{PRODUCTS}$ of ${}_2He^4$ formed after collision is equal to $28{,}3MeV$ representing the mass interaction output $M_{\substack{POTENTIAL\\ENERGY}}^{PRODUCTS}$. The mechanical exergy EX^M after the fusion process is null since the whole content of energy is released under the form of thermal energy. Based on these contributions, the exergy balance is the following:

$$\Delta EX_{\substack{NUCLEAR\\FUSION}}^{G}$$

$$= -\left[\left(Q_{\substack{KINETIC\\ENERGY}}^{NUCLEI} + W_{\substack{KINETIC\\ENERGY}}^{NUCLEI} + W_{\substack{POTENTIAL\\ENERGY}}^{NUCLEI}\right)^{\substack{BEFORE\\FUSION}}\right]$$

$$-\left[-\left(0 + Q_{\substack{KINETIC\\ENERGY}}^{PRODUCTS}\eta^T + M_{\substack{POTENTIAL\\ENERGY}}^{PRODUCTS}\eta^N\right)^{\substack{AFTER\\FUSION}}\right] \tag{5.18}$$

that can be expressed as:

$$\Delta EX_{\substack{NUCLEAR\\FUSION}}^{G}$$

$$= -\left[\left(E_{KINETIC}^{NUCLEI}\eta^T + 0 + E_{POTENTIAL}^{NUCLEI}\eta^N\right)^{\substack{BEFORE\\FUSION}}\right]$$

$$-\left[-\left(0 + E_{KINETIC}^{PRODUCTS}\eta^T + E_{POTENTIAL}^{PRODUCTS}\eta^N\right)^{\substack{AFTER\\FUSION}}\right] \tag{5.19}$$

It is noteworthy that, before fusion, the attraction potential energy between Deuterium and Tritium due to strong interactions $E^{\substack{NUCLEI \\ POTENTIAL}}$ is negligible. Instead, after fusion, the importance of attraction strong interactions potential energy becomes prevailing and provides an additional contribution to the products kinetic energy that is to be accounted for in the $Qvalue$. In terms of exergy balance, the attraction potential energy could not be transferred as useful work thus implying that it does not contribute to the exergy balance so the difference between before and after only contributes

The calculation of generalized thermodynamic entropy for nuclear fusion thus results in the following expression:

$$\Delta S^{G}_{FUSION} = (S_1 - S_0)^T + (S_1 - S_0)^N$$

$$= \frac{1}{T_R}\left[(E_1 - E_0) - (EX_1^R - EX_0^R)\right]^T$$

$$+ \frac{1}{\mu_R^N}\left[(E_1 - E_0) - (EX_1^R - EX_0^R)\right]^N \qquad (5.20)$$

As concerns the thermal entropy variation related to the temperature, assuming, also in this case, that T_R corresponds to the environmental initial temperature of target nucleus and neutron before fusion, then:

$$(S_1 - S_0)^T = \frac{1}{T_R}\left[(E_1 - E_0) - (EX_1^R - EX_0^R)\right]^T \qquad (5.21)$$

In the special case of fusion reaction, T_R can be assumed equal to the temperature of ${}_1H^2$ and ${}_1H^3$ before nuclei collision, that is:

$T_R = 10keV = 0{,}01MeV = 116 \cdot 10^6 K$, so that:

$$(S_1 - S_0)^T$$

$$= \frac{1}{116 \cdot 10^6}\left[17{,}594 - \left(17{,}594 \cdot \left(1 - \frac{T_R}{T_1}\right) + 0{,}01 \cdot \left(1 - \frac{T_R}{T_0}\right)\right)\right]$$

that, using the numerical values becomes:

$$= \frac{1}{116 \cdot 10^6}\left[17{,}594 - \left(17{,}594 \cdot \left(1 - \frac{0{,}01}{17{,}594}\right) + 0{,}01 \cdot \left(1 - \frac{0{,}01}{0{,}01}\right)\right)\right]$$

$$\cong \frac{1}{116 \cdot 10^{6}} \left(-17{,}594 - 17{,}594 \cdot 0.9994 \right) \cong 9{,}1 \cdot 10^{-5} \cdot 10^{-6}\ MeV\ /K$$

This result demonstrates that the variation of thermal entropy along a nuclear fusion is negligible by virtue of the high temperature of products before and after the collision and nuclei aggregation has occurred. Though, the even negligible increase of thermal entropy reveals that the available energy, or the $Qvalue$, is released under the subdivided thermal form of energy associated to the thermal entropy positive variation. It is noteworthy that this variation is substantially lower with respect to the case of nuclear fission. Indeed, the rationale behind this difference is twofold: i) fission implies increase of particles as fragments of the initial target nucleus while fusion does not since it creates two products, Helium and neutron, from two reactants, Deuterium and Tritium; ii) the Helium nucleus has an atomic number, and therefore a mass number, higher than Deuterium or Tritium hence implying a higher mass concentration in one nucleus thus determining a decrease of thermal entropy associated to an increase of kinetic energy density.

As far as the nuclear entropy variation related to the nuclear potential is concerned, the following expression applies:

$$\left(S_1 - S_0 \right)^N = \frac{1}{\mu_R^N} \left[\left(E_1 - E_0 \right) - \left(EX_1^R - EX_0^R \right) \right]^N \tag{5.22}$$

where μ_R^N can be assumed equal to the nuclear potential of ${}_1H^2$ and ${}_1H^3$ before nuclei collision, that is $\mu_R^N = 2{,}224\, MeV + 8{,}482\, MeV = 10{,}706\, MeV$, then the previous expression is as follows:

$$\left(S_1 - S_0 \right)^N$$

$$= \frac{1}{\mu_R^N} \left\{ \left(E_1 - E_0 \right) \right\}$$

$$+ \frac{1}{\mu_R^N} \left\{ - \left[\left(\mu_1^N n_1^N \right) \cdot \left(1 - \frac{\mu_1^N}{\mu_1^N} \right) - \left(\mu_0^N n_0^N \right) \cdot \left(1 - \frac{\mu_1^N}{\mu_0^N} \right) \right] \right\} \tag{5.23}$$

that, using the numerical values, becomes:

$$= \frac{1}{10{,}706} \left[\left(10{,}706 - 28{,}3 \right) - \left(10{,}706 \cdot \left(1 - \frac{10{,}706}{10{,}706} \right) - 28{,}3 \cdot \left(1 - \frac{10{,}706}{28{,}3} \right) \right) \right]$$

$$= \frac{1}{10{,}706} \left[\left(-17{,}594 \right) - \left(-17{,}594 \right) \right] = 0\, MeV/K$$

In this case, the variation of nuclear entropy is null since there is no variation of the number of particles between the initial and final states of the reaction: thus, from a physical standpoint, there is no change in the degree of subdivision of the binding energy content before and after releasing the $Qvalue$. Moreover, it has been assumed that, for two interacting particles, the nuclear potential μ_R^N equals the potential energy of the system hence the whole amount of potential energy is transferred as work interaction to the useful external system. Instead, from three interacting particles on, the nuclear potential would progressively decrease as the progressive increase of the number of particles is accounted for. Hence, the variation of nuclear entropy becomes positive because of the not complete transfer of nuclear potential into work interaction in the respect of Second Law.

The number of particles before and after the reaction is conserved although mass aggregation is not, hence the variation of entropy depends on both distribution of mass and velocity caused by the collision and the consequent fusion process.

The variation of exergy property, calculated before and after ${}_1H^2$ and ${}_1H^3$ nuclei collision, can be assumed as the maximum net useful interaction expressing the definition of generalized exergy. Therefore:

$$-\Delta EX^{G}_{\substack{NUCLEAR\\FUSION}}$$

$$=\left(0{,}1\eta^{T}+0+2{,}224\eta^{N}+8{,}482\eta^{N}\right)^{BEFORE}_{FUSION}$$

$$-\left(0-17{,}594\eta^{T}+28{,}3\eta^{N}\right)^{AFTER}_{FUSION}$$

$$-\Delta EX^{G}_{\substack{NUCLEAR\\FUSION}}=6{,}274MeV$$

where it is assumed that $\eta^{N}\cong 1$ from plasma chamber fusion temperature to blanket temperature assumed $823\,K$ and $\eta^{T}=\left(1-\frac{298}{823}\right)=0{,}638$ from blanket to environment temperature at $298K$, then a decrease of exergy occurs in fusion process equal to $\Delta EX^{G}_{\substack{NUCLEAR\\FUSION}}\cong -6{,}274MeV$

The physical meaning of this result is that almost the entire amount of energy released along a nuclear fusion process constitutes the available energy, in terms of generalized exergy, deriving from the decrease of mass subsequent to the increase of inter-nucleon potential energy with respect to the isolated nucleons before fusion. The decrease of exergy is accompanied by a decrease of entropy due to a different configuration of the whole system in which an increase of level in the hierarchical structure is due to the mass fusion ${}_1H^2+{}_1H^3\rightarrow{}_2He^4+n$. Indeed, free hydrogen isotopes result in a bind system of higher mass. To do so, a fraction of initial nuclei kinetic energy $E^{NUCLEI}_{KINETIC}$ is adsorbed during fusion reaction. Then, the fusion process is irreversible due to the destruction of a part of initial exergy content that does not completely compensate the entropy reduction due to fusion of D and T nuclei.

Finally, the exergy efficiency is:

$$\eta^{EX}_{FUSION} = 1 - \Delta EX^{NUCLEAR\ FUSION}_{DESTR} \Big/ \Delta EX^{NUCLEI\ BINDING}_{AVAILABLE} \tag{5.24}$$

$$= 1 - (17,594 - 11,22)/17,594 = 0,638$$

This is a theoretical result that is to be reduced taking into account the real processes occurring in the plasma chamber of a fusion reactor.

5.8. Outcomes

Two main conclusions can be outlined from the present research. Firstly, the model of few-particle thermodynamic systems is adopted to determine all phenomena and properties, involved in nuclear fission and fusion processes. This investigation has been carried out in the perspective of the Second Law analysis based on the exergy method adopted to calculate entropy property variations. The second result concerns the consequence of decrease or increase of nuclei atomic number and mass number subsequent to elemental fission and fusion nuclear reactions and therefore the subdivision or aggregation of atomic nuclei. The role of entropy property, in these special cases, is to quantify the impact on energy and exergy balances, along nuclear fission or fusion processes, responsible of the different behavior of a few-particle system. A conclusive consideration arising from the aforementioned results is that nuclear physics and physics of elementary particles undergo non-equilibrium processes. In this regard, irreversibilities determined by non-equilibrium states and processes are governed by extrema principles, rooted on entropy property variations, such as the maximum entropy production principle [4.50], representing an innovative contribution to analysis methods and researches in those fields.

6. PERFORMANCE COMPARATIVE MODEL

Nuclear plants, based on fission or fusion reactions, are design according to different technologies. Among the most recent pertaining to III+ and IV generation, considered in the present study, there are the ABWR (boiling reactor) and the AP1000 (pressurized reactor).

Balances consist of equations establishing the equality among process variables and state properties to identify parameters concurring to the design of a nuclear plant in both cases of steady or transient operating conditions.

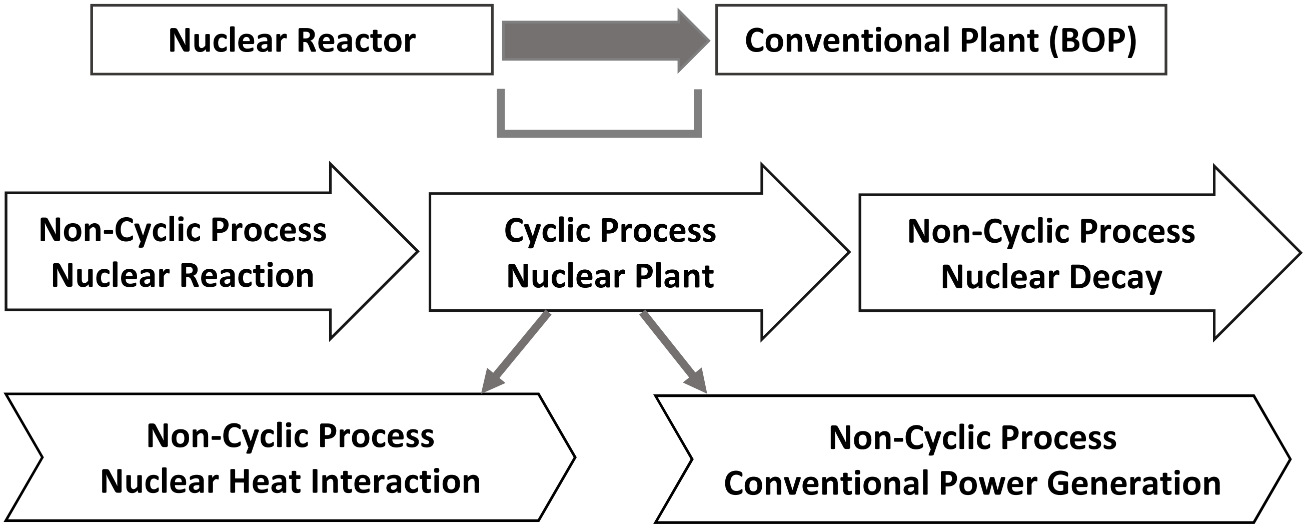
Process variables balances concern heat interactions, mass interactions and work interactions. State properties balances account for energy, exergy, entropy properties depending on system design parameters. The intent is here to identify those components and parameters that more significantly affect a first approximation first and second law analysis aimed at providing an initial design of plants and components.

6.1. Nuclear Plant Configuration and Process Breakdown Structure

In order to carry out analyses and the optimized design of a nuclear plant, the first approach is to break down the overall configuration into the parts and component and the set of processes into all phenomena occurring in it.

6.1.1. Plant Configuration

The overall plant can be regarded as subdivided in two blocks. Core: Nuclear Reactor. Balance of Plant (BOP) or Conventional Plant: Physical-Chemical Processes.



6.1.2. Plant Breakdown Structure

The analysis of nuclear reactor and BOP is executed for the main plant components to investigate the higher exergy destruction processes in order to optimize components exergy efficiency and overall plant exergy efficiency taking into account avoidable/unavoidable irreversibility [6.1,6.2] and endogenous/exogenous irreversibility [6.1,6.2] determining, for each and every main component, the behaviour of the overall nuclear plant and vice versa.

An indicative work breakdown structure of main components of a boiling or pressurized nuclear reactor is represented in the following Figure 6.1 where the steam generator is highlighted as the components determining the difference between the two types of plant configuration.

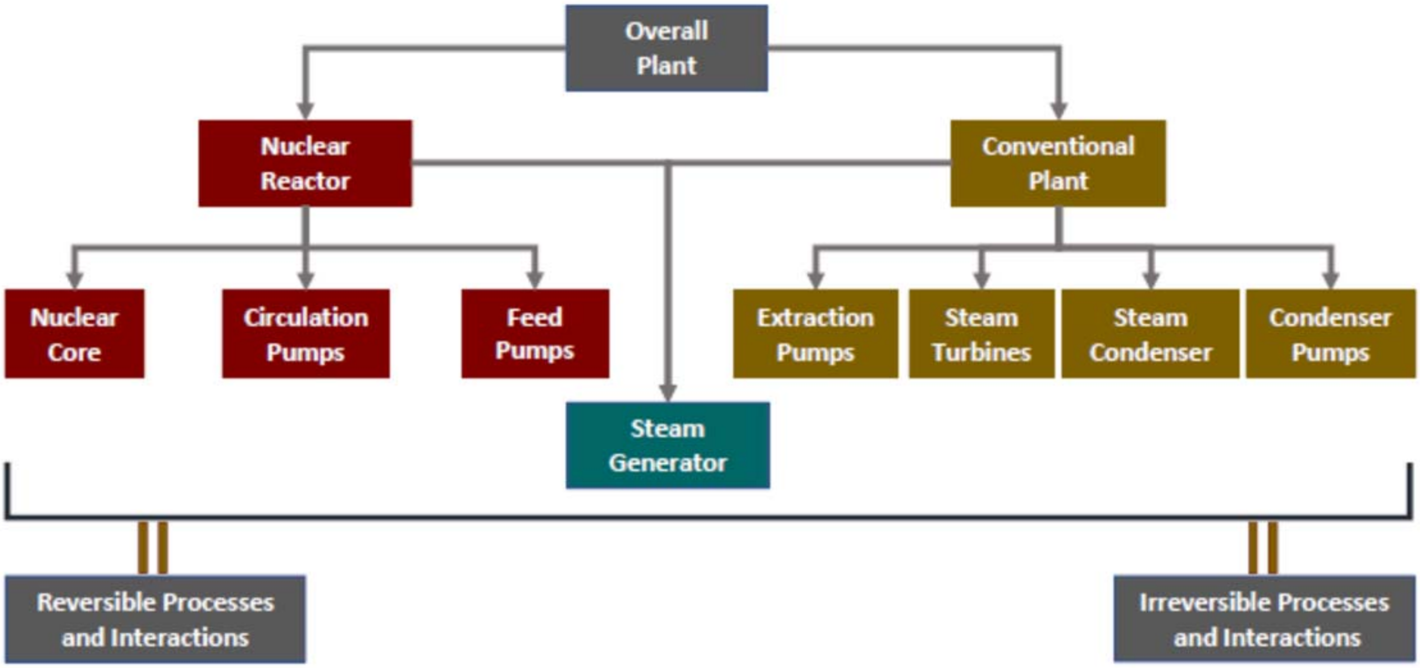


Figure 6.1 – Boiling and Pressurized Plant Components

6.1.3. Process Breakdown Structure

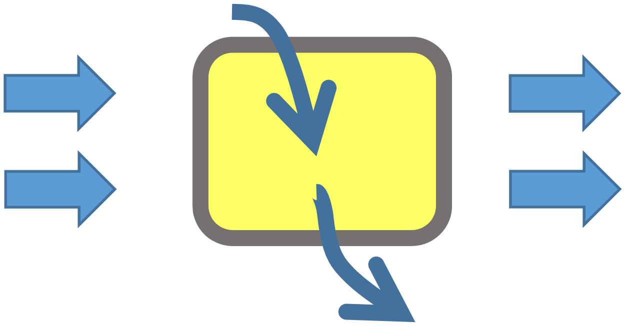
As reported in the schema of the previous section, all components and main parts of the overall plant experience both reversible and irreversible phenomena and interactions that contribute to the overall balances and partial balances. In particular, reversible contribution of properties and irreversible production of properties shall be accounted for in the balances to identify devices and machinery that, more than others, affect the performance of a nuclear plant.

6.2. Balances

Balances can be calculated by means of two procedures: i) by component according to the “eulerian” approach, and: ii) by stream according to the lagrangian approach. The first approach focuses on irreversibilities and exergy destruction of each and every device and for this very reason allows to identify and optimize less performing operations. The second approach focuses on the fluid and requires the knowledge of all conditions along the process thus requiring a greater analytical and numerical accuracy. Here, balances are considered in the first approach with respect to a properly selected portion of the whole plant delimited by a control surface according to the eulerian analysis accounting for interactions with the external system. For a nuclear power station, this portion shall include the reactor vessel and the conventional plant. In turn, two separate poertions will enclose the nuclear reactor and the conventional plant.

Integral balance rates can be considered valid for any balance and any quantity, such as mass, momentum, density, energy, entropy, exergy, mass interaction, heat interaction, work interaction, and their combination:

$$\frac{dG}{dt} = \sum_{INLET} \dot{G}_i - \sum_{OUTLET} \dot{G}_i \pm \dot{Z}$$



where:

$\frac{dG}{dt}$: first derivative of a generalized state property with respect to time;

$\sum_{INLET} \dot{G}_i - \sum_{OUTLET} \dot{G}_i$: exogenous contribution of open system (state properties);

$\pm \dot{Z} = \pm \dot{Z}^{REV} \pm \dot{Z}^{IRR}$: endogenous contribution of closed system (inward or outward process interactions).

The most significant balances are described in the following section and represent a typical paradigm useful to analyse main processes of a nuclear plant. Reference is made to the symbology adopted in the literature referred to in the previous sections.

6.2.1. Mass Balance

Main mass streams through the control volume of a nuclear plant are represented by: i) input enriched nuclear fuel and output depleted nuclear fuel, ii) cold cooling water input from the environment and output heated cooling water released back to the environment.

For transient state:

$$\frac{dM}{dt} = \sum_{INLET} \dot{m}_i - \sum_{OUTLET} \dot{m}_i \pm \dot{m}_{PROD}$$

where:

$\frac{dM}{dt}$: first derivative of total mass with respect to time;

so that, in case of stationary state in which $\frac{dM}{dt} = 0$ then $\sum_{Streams} \dot{m} = 0$

6.2.2. Interaction Balance

The interaction balance accounts for all interactions contributing to the state of the system. Interactions occur by means of heat transmission, mass transport and work transfer between the internal system, defined by a control surface and volume, and the external system with respect to the boundary. In particular, mass interaction needs a more accurate clarification. In fact, usually mass transport is typical of open systems for which a bulk-flow through system boundaries allows the continuity of processes and phenomena occurring in the system. Mass interaction accounts for the special case of closed system where ideal semi-permeable separation walls allow the theoretical input and or output of individual constituents characterized by specific chemical or nuclear potential transmitted inward or outward the internal system. Therefore, mass interaction relates to chemical constituents and nuclei particles and sub-particles characterizing all processes in fission or fusion reactions occurring in nuclear plants. In different terms the mass interaction implies a molar variation of one or more constituents.

Interactions constitute the form of energy transfer associated to heat, mass and work exchanged between the system and the reservoir, or environment or between different parts of the plant. Nuclear plants perform an open cyclic process for which state property of a unit mass undergoing a complete cycle (Lagrangian analysis) display the same values at the end of a complete cycle. Therefore, a balance of interactions with external system, namely environment, can be written considering all interactions through the control surface separating the nuclear plant from those facilities directly operating in the surrounding environment. Two different interaction balances can be stated for a nuclear plant as follows:

1) Overall Plant Balance
2) Nuclear Reactor Balance + Conventional Plant Balance

The interactions balance is aimed at highlighting all external and internal contributions to the overall processes resulting from the canonical types of interactions:

a) Heat Interaction (reversibility) => Heat Transmission Phenomena (irreversibility), flux loss
b) Mass Interaction (reversibility) => Mass Transport Phenomena (irreversibility), fluid friction
c) Work Interaction (reversibility) => Weight Process

In particular, differently from mass balance accounting for mass rate of inward and outward streams, the mass interaction balance corresponds to chemical and the nuclear particles potential energy associated to mass moli, similarly to particles kinetic energy associated to heat interaction.

The overall balance results from the sum of partial balances relating to the main parts of the plant, namely nuclear and conventional. In turn, the interaction balances result from the energy balances of each and every plant component.

In particular, the overall cycle could be considered pertaining to the right side of tetrahedron in which temperature accounted for in Carnot and Joule cycles is replaced by nuclear potential at a lower hierarchical level with respect to chemical potential. The evaluation of nuclear entropy can be demonstrated by means of the general proof that considers entropy property associated to all forms of interactions [4.21].

For a cyclic process, the interaction balance is the following:

$$\dot{Q} + \dot{M} + \dot{W} = 0$$

And, in the case of a nuclear plant, the overall plant balance due to all streams or flows can be subdivided in the following relationship where steady state processes are assumed:

$$\frac{d}{dt}\left(M^{\leftarrow}_{\substack{ENRICHED\\FUEL}} + W^{\leftarrow}_{\substack{CIRCUL\\PUMPS}} + W^{\leftarrow}_{\substack{FEED\\PUMPS}} + W^{\leftarrow}_{\substack{CONDENSER\\PUMPS}} \right)$$

$$= \frac{d}{dt}\left(M^{\rightarrow}_{\substack{DEPLETED\\FUEL}} + Q^{\rightarrow}_{\substack{STEAM\\CONDENSER}} + W^{\rightarrow}_{\substack{HP\_STEAM\\TURBINES}} + W^{\rightarrow}_{\substack{LP\_STEAM\\TURBINES}} \right)$$

As the control boundary includes the overall plant, then the above equations do not account for heat interaction output from the nuclear core and heat interaction input to the steam produced in the core and expanded in the high pressure and low pressure steam turbines.

6.2.3. Energy Balance

The energy balance takes into account the energy variation due to all interactions occurring between internal system on the one side and useful external system and reference external system (reservoir) on the other side:

$$\frac{dU}{dt} = \sum_{INLET} \dot{E}_i - \sum_{OUTLET} \dot{E}_i + \dot{Q} + \dot{M} + \dot{W} = \sum_{INLET} \dot{m}_i \, h_i - \sum_{OUTLET} \dot{m}_i \, h_i + \dot{Q} + \dot{M} + \dot{W}$$

6.2.4. Exergy Balance

The equation of total overall generalized exergy balance can be expressed focusing on both exergy reversible contribution and exergy irreversible destruction components, as follows:

$$\Delta EX^G = \Delta EX^G_{CONTR} + EX^G_{DESTR}$$

where in particular: $EX^G_{DESTR} = T_R S^G_{PROD}$ and S^G_{PROD} is the generalized entropy production summarized along all processes.

The balance of exergy can be executed once the thermodynamic state of the reference system or reservoir R constituted by the environment, has been specified. Conventionally, reservoir conditions are the following: $T_R = 298K$, $P_R = 0{,}1MPa$

$$\frac{dEX^G}{dt} = \sum_{INLET} \dot{EX}_i^G - \sum_{OUTLET} \dot{EX}_i^G + \int \left(1 - \frac{T_R}{T}\right) d\,\dot{Q} + \int \left(1 - \frac{\mu_R}{\mu}\right) d\,\dot{M} + \int \left(1 - \frac{P_R}{P}\right) d\,\dot{W} + \dot{EX}^G_{DESTR}$$

where:

$\dot{EX}^G_{DESTR} = \dot{EX}^T_{DESTR} + \dot{EX}^C_{DESTR} + \dot{EX}^M_{DESTR}$ is the generalized exergy destruction subdivided into contributions due to thermal exergy destruction, chemical exergy destruction and mechanical exergy destruction.

In finite terms, $\dot{Q}_{FISSION} = q^{III} \cdot V_{CORE}$

where $q^{III} = E_{FISS} \cdot \sigma_{FISS} \cdot \Phi_n \cdot \rho_{UO2} \cdot \dfrac{N_A}{M_{UO2}\left(\overline{X}\right)} \overline{X}$

To calculate the exergy destruction in the fuel, T_{FISS} is variable along the core axis according to Bessel function.

6.2.5. Entropy Balance

The balance of entropy property accounts for all entropy contribution due to reversible processes and all entropy generation due to irreversibility occurring in real systems and fluids. Indeed, entropy is an inherent property of any system, large or small, in any state, stable equilibrium and non-equilibrium. Therefore, entropy is associated to each and every form of interaction between internal system and the reservoir, even though entropy itself does not depend on the particular thermodynamic state of the reservoir thus considered auxiliary only.

Nuclear Reactor

Reversible Process

Nuclear Fuel Mass Interaction: $M^{\leftarrow}_{\substack{ENRICHED\\URANIUM}} + M^{\rightarrow}_{\substack{DEPLETED\\URANIUM}} = 0$

Coolant Mass Interaction: $M^{\leftarrow}_{\substack{REACTOR\\COOLANT}} + M^{\rightarrow}_{\substack{GENERATOR\\HEATER}} = 0$

Coolant Energy Balance

$$Q^{\rightarrow}_{\substack{FISSION\\REACTION}} - Q^{\leftarrow}_{COOLANT} = 0$$

$$Q^{\rightarrow}_{\substack{FISSION\\REACTION}} = mc_P\left(T^{REACTOR}_{OUT} - T^{REACTOR}_{IN}\right)$$

Coolant Exergy Balance

$$EX^{REACTOR}_{INLET} = \left(U^{REACTOR}_{INLET} - U^{R}\right) - T_R\left(S^{REACTOR}_{INLET} - S^{R}\right)$$

$$EX^{REACTOR}_{OUTLET} = \left(U^{REACTOR}_{OUTLET} - U^{R}\right) - T_R\left(S^{REACTOR}_{OUTLET} - S^{R}\right)$$

Irreversible Process

Reactor Coolant

Interaction Balance: $W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} - Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}} = 0$

In PWR plants circulation jet pumps overall power can rise up to 5 MW.

Energy Balance: $Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}} = m\int_{T_{IN}}^{T_{OUT}} c_P(T)dT = mc_P\left(T^{REACTOR}_{OUT} - T^{REACTOR}_{IN}\right)$

Exergy Balance

$$W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} - \left(H_{OUT} - H_{IN}\right) - T_R\left(S_{OUT} - S_{IN}\right)$$

Conventional Plant

Reversible Process

Steam Generator

$$Q^{\leftarrow}_{\substack{STEAM\\GENERATOR}} + W^{\leftarrow}_{\substack{FEED\\PUMP}} = W^{\rightarrow}_{\substack{STEAM\\TURBINE}} + Q^{\rightarrow}_{CONDENSER}$$

where:

$M^{\leftarrow}_{URANIUM}$: mass interaction; this is not a steady state interaction however, considering the periodic refuelling of enriched uranium, can be assimilated to a continuous feed of matter.

$W^{\leftarrow}_{PUMP}$: work interaction: this interaction is associated to the power needed by the feed pump to circulate water through the core for moderation and cooling

$W^{\rightarrow}_{TURBINE}$: work interaction

$Q^{\rightarrow}_{CONDENSER}$: heat interaction

Irreversible Process

Energy Balance

The energy balance is related to those plant components representing the most important in terms of power and thermodynamic criticality. Indeed, as the process is cyclic, the overall balance is null since all thermodynamic properties assume same values at the initial and final points of the cyclic process. Instead, it is worth representing the energy balance of each component to evaluate its own contribution to the overall balance and the relating phenomena occurring through the component itself.

$$\left(U^{T}\right)^{COOLANT}_{out} - \left(U^{T}\right)^{COOLANT}_{in} = Q^{\leftarrow}_{FISSION}$$

$$\left(U^{N}\right)_{out}^{CORE}-\left(U^{N}\right)_{in}^{CORE}=M_{FISSION}^{\leftarrow}$$
$$\left(U^{M}\right)_{out}^{CORE}-\left(U^{M}\right)_{in}^{CORE}=H_{out}-H_{in}=Q_{HYDR}^{\rightarrow}=W_{HYDR}^{\leftarrow}$$

6.3. Definition of Exergy Efficiency

The definition of exergetic efficiency is based on the input exergy flows defined as “fuel” and the output exergy flows defined as “product”. In addition, the exergy losses and exergy destruction flows are accounted for. In fact, exergy losses are constituted by the amount of exergy property associated to reversible interaction with external system or reservoir. Moreover, exergy destruction represents the amount of irreversible contribution due to internal processes and or interactions with the reservoir.

In this approach, the exergy balance can be regarded as the balance of exergy fuels EX_{F_j} and exergy products EX_{P_i} combined in the following equation:

$$\sum_{j=1}^{m}\Delta EX_{F_j}-\sum_{i=1}^{n}\Delta EX_{P_i}=EX_{DESTR}^{IRR}$$

This exergy balance equation is the basis for the definition of exergy efficiency expressed as the ratio of utilized exergy output over used exergy input.

According to the Second Law and considering the exergy rates, the exergy efficiency or “rational efficiency”, as termed by Kotas [2.7], can be stated: $\Psi=\frac{\sum\Delta\dot{EX}_{OUTPUT}}{\sum\Delta\dot{EX}_{INPUT}}\leq 1$ where the difference between $\Delta\dot{EX}_{OUTPUT}$ and $\Delta\dot{EX}_{INPUT}$ depends on the degree of irreversibility of the process.

As far as the exergetic efficiency is concerned, that is $\eta^{EX}=\frac{used\cdot EX}{utilized\cdot EX}$:

$$\eta^{EX}=\frac{\sum_{i=1}^{n}EX_{P_i}}{\sum_{j=1}^{m}EX_{F_j}}=1-\frac{EX_{D}+EX_{L}}{\sum_{j=1}^{m}EX_{F_j}}$$

where:

EX_{P_i} : exergy of input streams of “fuels” corresponding to the utilized exergy

EX_{F_j} : exergy of output streams or “products” corresponding to the used exergy

EX_D : exergy destruction

EX_L : exergy losses

In the above expression, exergy losses EX_L are identically null by definition. In fact, the loss is represented by the thermal energy being discharged by heat interaction to the reservoir (or environment), at the same temperature of the reservoir itself so that no available energy can be withdrawn from that flow. From a different standpoint, one could infer that for reversible processes the exergetic efficiency is unitary because there is no exergy destruction while the exergy loss is in effect a thermal energy loss. That is, in case of reversible processes, input total exergy has to equal output total exergy. Therefore, the expression of the exergetic efficiency is the following:

$$\eta^{EX} = \frac{\sum_{i=1}^{n} EX_{P_i}}{\sum_{j=1}^{m} EX_{F_j}} = 1 - \frac{EX_D}{\sum_{j=1}^{m} EX_{F_j}}$$

This expression will be adopted as a performance indicator to provide a comparative analysis among different types of nuclear plants accounted for in the present research.

The overall exergetic efficiency accounts for the exergetic efficiency of each and every plant component. If an approximate approach is adopted, the main components are evaluated. Anyway, the overall efficiency is the results of product of efficiency of components operating in series and the expression is the following:

$$\eta^{EX}_{OVERALL} = \prod_{j=1}^{n} \eta^{EX}_{j} = \prod_{j=1}^{n} 1 - \frac{EX_D}{EX_{F_j}} = 1 - \frac{EX_D}{\sum_{j=1}^{m} EX_{F_j}}$$

Unitary exergy efficiency cannot be achieved as exergy is an inherent property of any system in any state, as entropy property is. Indeed, even in the particular case of kinetic energy and potential energy associated to the center of mass releasing work interaction in a hydraulic turbine, not all the energy content is transferred by work interaction to the external system [2.6]. The concepts of equivalence and inter-convertibility between heat and work constitute the proof of this limitation and are base of arguments treated in the previous sections 2. and 3. of the present research.

It should be noticed that, as the expression of exergetic efficiency directly depends on exergy destruction, then balances are segregating all those processes being irreversible so that it is straightforward to detect irreversibilities determining a reduction of exergetic efficiency.

It is worth clarifying that, for a cyclic process, the following expression of a overall cycle thermodynamic indicator $\frac{\eta_{REAL}^{EN}}{\eta_{IDEAL}^{CARNOT-DIRECT}}$ cannot be considered an exergetic efficiency because it depends on the specific cycle and processes regardless the amount of irreversibilities occurring along the real cycle under evaluation. Indeed, this expression, that depends on the shape of the cycle, is <1 even in case of reversible processes while, in the case of ideal processes, the exergetic efficiency should be $=1$.

The overall nuclear plant process can be uncoupled and separated into the two main parts represented by the nuclear reactor and the conventional plant. Hence, the overall closed system (non-bulkflow) cyclic process is subdivided in two combined open systems (bulk-flow) non-cyclic processes.

The conventional plant is limited by the conditions of steam at the HP steam turbine inlet and the cooling water at the reactor vessel inlet. The conventional plant includes the regeneration process using the steam extracted from HP steam turbine and LP steam turbines as well as the reheating process.

Efficiency Function

A mention is deemed worth relating to the analytical function describing the thermo-mechanical heat-to-work conversion efficiency achieved along a direct cycle:

$\eta = 1 - \frac{298}{T} = 1 - 298T^{-1}$ calculating the first derivative: $\eta' = \frac{d\eta}{dT} = 298T^{-2}$ this function is represented by a hyperbolic function.

6.4. Exergy Destruction in Real Processes

As regard irreversible phenomena and processes as well as the consequent exergy destruction, the following type of irreversibility occur in whatever real process [6.1,6.2]:

- Avoidable and Unavoidable
- Endogenous and Exogenous

Reversible processes increase the efficiency with an increase of generalized potential difference between system and reservoir

Irreversible processes decrease dissipation (or increase of efficiency) with decrease of generalized potential differences between system and reservoir

The two above phenomena are opposite.

Avoidable – Unavoidable

The unavoidable irreversibility that determines the exergy destruction $EX_{IRR,k}^{UNAV}$ is generated by technological limitation that cannot be further reduced because of too high cost increase or not existence of technological improvement or alternative solutions.

The difference between total and unavoidable exergy destruction within a component is the avoidable exergy destruction to be considered in the improvement of the component: $EX_{IRR,k}^{AV} = EX_{IRR,k} - EX_{IRR,k}^{UNAV}$ where the value of unavoidable exergy destruction within the k-th component is calculated by: $EX_{IRR,k}^{UNAV} = EX_{PRODUCT,k}^{REAL}\left(EX_{IRR,k} / EX_{PRODUCT,k}\right)^{UNAV}$ thus for calculating the value of $\left(EX_{IRR,k} / EX_{PRODUCT,k}\right)^{UNAV}$ a system in which only unavoidable exergy destructions occur within each component should be simulated.

Endogenous – Exogenous

The endogenous irreversibility, and the consequent exergy destruction, can be evaluated considering the component under analysis with its real behavior while all other components of the plant are accounted for behaving as ideal system.

Proper Orthogonal Decomposition

A procedure adopted for an exergy or thermos-economical optimization is represented by the Proper Orthogonal Decomposition (POD). It is based on the model order reduction of non-linear phenomena analyzed by means of a set of numerical or experimental data.

7. ABWR AND AP1000 FISSION REACTORS EXERGY ANALYSIS

A first premise for an optimization of nuclear plants design is the comparative analysis among nuclear technology typologies to assess the differences, enhancements and possible improvements that nuclear design could undergo.

Typologies of nuclear reactors considered in the present study are those based on fission reaction and technology maturity characterizing generations III+ industry:

- ABWR: advanced boiling water reactor $(3926\,MWt)$;
- AP1000: advanced passive pressurized water reactor $(3400\,MWt)$.

Main characteristics affecting energy and exergy balances in steady state operating conditions are here described in order to define those properties and interactions contributing to all balances of interest providing figures for a first order performance assessment. Analyses here carried out are focusing on exergy flow balance, to do so, all remaining balances, in particular mass flow rates and thermal and mechanical power are assumed with figures, data and information reported in the literature and specially in ARIS-IAEA database mentioned in references.

7.1. ABWR

ABWR reactors represent a design class belonging to the Generation III+ technology already in operation.

The ABWR nuclear plant design consists of a boiling water reactor type and represents an advanced version of Generation III+ technology with a large industrial application. One of the main characteristics of ABWR design is that the steam produced in the reactor core is directly conveyed to high pressure and low pressure steam turbines with no intermediate steam generator or other equipment. Therefore, there is no separation between the primary circuit and the secondary or conventional (or balance of plant BOP). The steam title at core outlet is about 14,5%; before entering the high pressure (HP) turbine, the steam is separated, dehydrated and conveyed to HP turbine inlet. Steam turbine arrangement is 1/0/3 HP/MP/LP type with 1 reheating stage and steam extraction stages for feedwater heating regeneration process. In particular, the extraction steam from the HP turbine supplies the last stage of feedwater heating and extraction steam from the low pressure (LP) turbines supplies the first four stages.

Advanced Boiling Water Reactor (ABWR) is a technology based on boiling feed water process. A significant ABWR feature improvements with respect to previous BWR technologies is represented by jet pumps replaced by pumps located inside the reactor vessel; the addition of 10 reactor internal pumps (RIP) mounted on the bottom of the reactor pressure vessel (RPV) which achieve improved performance while eliminating large recirculation pumps in containment and associated large-diameter and complex piping interfaces with the RPV (e.g. the recirculation loop found in earlier BWR models); only the RIP motor is located outside of the RPV in the ABWR; each RIP has a nominal capacity of 6912 m^3/h. The internal pumps reduce the required pumping power for the same flow to about half that required with the jet pump system with external recirculation loops. Thus, in addition to the safety and cost improvements due to eliminating the piping, the overall plant thermal efficiency is increased. Eliminating the external recirculation piping also reduces occupational radiation exposure to personnel during maintenance.

The Emergency Core Cooling System (ECCS) has been improved in many areas, providing a very high level of defense-in-depth against accidents, contingencies, and incidents.

Eighteen SORVs (safety overpressure relief valves), ten of which are part of the ADS (automatic depressurization system), ensure that RPV overpressure events are quickly mitigated, and that if necessary, that the reactor can be depressurized rapidly to a level where low pressure core flooder (LPCF, the high-capacity mode of the residual heat removal system, which replaces the LPCI and LPCS in previous BWR models) can be used.

Further, LPCF can inject against much higher RPV pressures, providing an increased level of safety in the event of intermediate-sized breaks, which could be small enough to result in slow natural depressurization but could be large enough to result in high pressure corespray/coolant injection systems' capacities for response being overwhelmed by the size of the break.

The RPV and Nuclear Steam Supply System (NSSS) have significant improvements, such as the substitution of RIPs, eliminating conventional external recirculation piping loops and pumps in the containment that in turn drive jet pumps producing forced flow in the RPV. RIPs provide significant improvements related to reliability, performance and maintenance, including a reduction in occupational radiation exposure related to containment activities during maintenance outages. These pumps are powered by wet-rotor motors with the housings connected to the bottom of the RPV and eliminating large diameter external recirculation pipes that are possible leakage paths. The 10 internal recirculation pumps are located at the bottom of the annulus downcomer region (i.e., between the core shroud and the inside surface of the RPV). Consequently, internal recirculation pumps eliminate all of the jet pumps in the RPV, all of the large external recirculation loop pumps and piping, the isolation valves and the large diameter nozzles that penetrated the RPV and needed to suction water from and return it to the RPV. This design therefore reduces the worst leak below the core region to effectively equivalent to a 2-inch-diameter (51 mm) leak. The conventional BWR3-BWR6 product line has an analogous potential leak of 24 or more inches in diameter. A major benefit of this design is that it greatly reduces the flow capacity required of the ECCS.

7.1.1. ABWR Nuclear Reactor

Main components determining exergy balance and efficiency of the ABWR reactor are the core, containing the burning fuel assemblies, composed by fuel rods, and the cooling system constituted by the circulating water moved, by means of circulation pumps, throughout the core channels.

7.1.1.1. Core Fuel

The temperature of fuel particles at the centreline of fuel rods represents a crucial parameter for thermal-hydraulic design. The maximum allowable temperature is limited, in steady state operation, at $1300\,°C$ for fuel and clad material integrity reasons. However, the temperature after an elemental nuclear fission is much higher and it undergoes a strong reduction due to the moderator and the fragments and neutrons velocities distribution along a strongly irreversible process. This determines a corresponding strong exergy destruction directly proportional to the temperature difference between the elemental reaction temperature and the maximum allowable fuel temperature. Therefore, the larger amount of exergy destruction occurs within the core fuel. A first appraisal of the fission temperature subsequent to the release of the $Qvalue$ is given by $200\,MeV$ translated in terms of K degrees. Considering that $3k_B T = 200\,MeV$ with $k_B = 8{,}617 \times 10^{-11}\,MeV/K$ and $N_A = 6{,}022 \times 10^{23}\,\frac{1}{mol}$ then the following equality is valid: $Qvalue = 3k_B T$, from which the fission temperature is calculated as $T^{FISSION} = \frac{Qvalue}{3k_B} = \frac{200}{3 \times 8{,}617 \times 10^{-11}} \cong 7{,}7 \times 10^{11} K = 7{,}7 \times 10^{2} \times 10^{3} \times 10^{6} K$. This temperature is far much higher than the reference temperature of environment and in terms of heat-to-work conversion efficiency can be considered as unitary $\eta^T \cong 1$. Hence exergy equals the amount of energy released by the fission so that: $EX^T \cong Qvalue$.

This result, however, cannot be considered as useful since that amount of exergy is not used, as such, in any fission reactor being this operation technologically impossible. Instead, the presence of a moderator drastically reduces the temperature from fission temperature to the fuel rods temperature and imposes the destruction of that exergy available in the fuel.

A second step of temperature decrease, with a consequent exergy destruction process, is caused by the temperature difference between the fuel and the cooling water along the channels among fuel assemblies and fuel rods. In operation, the fuel allowable temperature is $873K$ ($600\,°C$) and the coolant rises from $278K$ $(5°C)$ to $288K$ $(15°C)$. Fuel is a solid component undergoing thermal exergy destruction from fuel rod centreline to peripherical edge.

As far as the heat interaction and thermal power balance is concerned, a design parameter is volumic heat q^{III} used to calculate the overall thermal power $\dot{q}_{FISSION}$:

$$\dot{q}_{FISSION} = q^{III} \cdot V_{CORE}$$

Where $\dot{q}_{FISSION}$ is the fission heat interaction per unit of volume and V_{CORE} is the volume of the fuel in the reactor core.

ABWR overall design data gathered in ARIS-IAEA database and documentation are the following [7.2]:

Maximum linear heat generation rate: 44 kW/m

Average linear heat generation rate: 13,6 kW/m

Considering that the overall length of fuel rod is 4,47 m, then the resulting total heat generation rate is $\dot{q}_{FISSION} = 13,6 \times 4,47 = 60,79\, kW$

The above thermal power is produced by one out of the total number of fuel rods equal to 80224 so the overall thermal power produced by the reactor core is:

$$\dot{Q}_{FISSION} = 60,79 \times 80224 = 4876816{,}96 kWt \cong 4876{,}8 MWt$$

However, considering $\dot{Q}_{FISSION} = 3926\ MWt$ as the core nominal thermal power, then $\dot{q}^{ROD}_{FISSION} = 3926/80224 = 0{,}0489\, MW/rod = 48{,}9\, kW/rod$

$$\dot{q}_{FISSION} = 48{,}9/4{,}47 = 10{,}9\, kW/m$$

The nuclear core can be considered as a system generating an amount of heat interaction constituting the transfer of the thermal energy transformed from nuclear energy released along the fission process. Hence, $\dot{Q}_{FISSION}$ is the amount to be accounted for in the overall exergy balance:

$$\frac{dEX^T}{dt} = \dot{EX}^T = \dot{Q}_{FISSION} \cdot \eta^T = \dot{Q}_{FISSION} \cdot \left(1 - \frac{T_R}{T_{FUEL}}\right)$$

where $T_R = 298\,K$ and $T_{FUEL} = 873\,K$, therefore:

$$\dot{EX}^T_{FUEL} = 3926 \cdot \left(1 - \frac{298}{873}\right) = 2585{,}8 MW$$

representing an exergy input within the core control volume.

7.1.1.2. Core Cooling System

The cooling water flowing through the core channels undergoes two heating processes. The first is a heat interaction in the range of subcooled conditions: sensible heat is input in water mass to increase its temperature. The second is a heat interaction in the range of saturated water: latent heat is input to increase the moisture title. ABWR core inlet and outlet cooling water process conditions (saturated water) are the following [7.2]:

T_{IN}^{CORE} = 278 °C; H_{IN} = 1236,7 kJ/kg; S_{IN} = 3,07 $kJ/kg\ K$

T_{OUT}^{CORE} = 288 °C; H_{OUT} = 1289,8 kJ/kg; S_{IN} = 3,16 $kJ/kg\ K$

The cooling water undergoes a heat interaction process that determines an increase of its temperature of about 10 degrees and a generation of steam with a 15% title. This implies an increase of thermal exergy due to increase of temperature determined by the sensible heat interaction, and chemical exergy due to increase of chemical potential determined by the latent heat interaction.

Considering that $\overline{R} = 8{,}3143\, kJ\ /(kmol\ \cdot K)$, the exergy balance can be calculated for each and every step of the heating process through the reactor vessel:

Feedwater Inlet in the Reactor Vessel

The water inlet temperature in the reactor pressure vessel is $215{,}6°C = 488{,}6K$ and before the water inlet in the core channels it undergoes a heating interaction by means of mixing with the recirculating water in the reactor vessel so that the water inlet temperature in the core is up to $278°C = 551K$. The recirculating water mass flow rate is $14502\, kg/s$ and the feed water mass flow rate vaporized to deliver steam is $2122\, kg/s$.

$$\Delta \dot{EX}^{T} = \dot{m}\left[\left(H_{OUT} - H_{IN}\right) - T_R\left(S_{OUT}^{T} - S_{IN}^{T}\right)\right] = \dot{m}\left[\left(H_{OUT} - H_{IN}\right) - T_R\,\overline{R}\left(\ln T_{OUT} - \ln T_{IN}\right)\right]$$

Feedwater Inlet in the Core Channels

The whole amount of thermal power produced by fission reactions occurring in fuel rods is released to the cooling water (feedwater) flowing throughout core channels. The thermal exergy variation is given by the following expression:

$$\Delta \dot{EX}^{T} = \dot{m}\left[\left(H_{OUT} - H_{IN}\right) - T_R\,\overline{R}\left(\ln T_{OUT} - \ln T_{IN}\right)\right]$$

Overall Exergy Flow Balance Variation of Feedwater

As it is a state property, the overall thermal exergy variation of feedwater can be calculated considering the thermodynamic state at initial and final states. As far as cooling water is concerned, one can consider conditions at condenser outlet and nuclear core outlet as saturated steam. On this basis, the overall thermal exergy increase is calculated considering that the condenser operates at $P^{COND} = 11{,}75\, kPaA$ and $T_{OUT}^{COND} = 187\,°C = 460\, K$

and the feedwater is heated between the two temperatures condenser outlet and reactor core outlet at $T_{OUT}^{CORE} = 288\,^{\circ}C = 561K$ with the corresponding enthalpies $H_{OUT}^{COND} = 794{,}5\,kJ/kg$ and $H_{OUT}^{CORE} = 2768{,}9\,kJ/kg$ and entropies $S_{OUT}^{COND} = 2{,}207\,kJ/kgK$ and $S_{OUT}^{CORE} = 5{,}797\,kJ/kg\,K$

The thermal exergy variation of feedwater is calculated as:

$$\Delta \dot{EX}^{T} = 2122 \times \left[\left(2768{,}9 - 794{,}5\right) - 298\left(5{,}797 - 2{,}207\right)\right]$$

$$= 2122 \times \left[1974{,}4 - 1069{,}82\right] = 1919518{,}76kW \cong 1919MW$$

that is positive by virtue of the continuous heating process from coldest point of the circuit at condenser exit, through regeneration preheaters, up to the hottest point of the circuit at reactor core exit point.

Thermal Exergy Variation in Nuclear Core

$$\Delta \dot{EX}_{CORE}^{T} = \dot{m}\left[\left(H_{OUT} - H_{IN}\right) - T_{R}\left(S_{OUT} - S_{IN}\right)\right]^{T}$$

$$= 2122 \times \left[1477{,}1 - 298 \times \left(5{,}7821 - 3{,}1594\right)\right] = 2122 \times \left[1477{,}1 - 781{,}5646\right]$$

$$= 1475926{,}12kW \cong 1475{,}9MW$$

$$\Delta \dot{EX}_{CORE}^{T} = 1475{,}9MW$$

7.1.2. ABWR Conventional Plant

Main components of the conventional plant are feedwater preheaters, moisture separation, reheaters, low pressure and high pressure steam turbines, and the main steam condenser.

Feedwater Preheating and Reheating Regeneration System

An amount of steam is extracted from steam turbine circuit to be input in cooling water regenerator heat exchangers. ABWR conventional plant configuration is provided with two steam extraction nozzles from the HP steam turbine and with two nozzles per each LP cylinder. HP steam is conveyed to two high pressure feed water heaters; LP steam is conveyed to four low pressure feed water heaters. This extraction of steam at higher temperature and higher pressure with respect to the feedwater water is the cause of exergy destruction that is to be accounted for in the overall balance.

Steam Reheating

ABWR Rankine cycle foresees 1 stage of steam reheating in between the HP steam turbine outlet and LP steam turbines inlet.

HP and LP Steam Turbines

Steam enters the HP steam turbine with the following conditions. Steam exits the LP steam turbine in the same conditions that conventionally are assumed as the condenser inlet conditions above considered. The mass flow rate in the turbines progressively reduces because of the steam extractions, at different pressures, conveyed to feedwater preheater allowing the increase of whole process performance due to thermal regeneration.

Interactions Balance

As regard water circulation through the nuclear reactor, the interaction balance is the following:

Interaction Balance: $W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} - Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}} = 0$

This balance expresses the fact that the entire amount of mechanical power (work interaction rate) requested to move the pumps is irreversibly converted into thermal power (heat interaction) thus representing an additional heat input to be accounted for in the energy balance of cooling system. In ABWR plants circulation pumps overall power can rise up to 8,3 MW. $Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}} = \Delta H = H^{COOLANT}_{OUT} - H^{COOLANT}_{IN}$

$= m \int_{T_{IN}}^{T_{OUT}} c_P(T)dT = mc_P\left(T^{REACTOR}_{OUT} - T^{REACTOR}_{IN}\right)$ where $c_P = 5{,}7\, kJ/kg \cdot {}^\circ K$ at 300 °C

Circulation jet pumps move the cooling water throughout the core with an overall mass flowrate of 14502 kg/s and an overall power of 10x830 kW = 8300 kW. Water internal friction makes the mechanical power entirely irreversibly dissipated into heat power.

The interaction balance is: $W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} = Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}}$

$$EX^{M}_{DESTR} = W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} = Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}} = 8300\ kW = 8{,}3MW$$

The heat power input represents an additional contribution with respect to the amount of heat power transmitted from the burning nuclear fuel in the core. Therefore, a part of the exergy destructed is partially recovered.

Overall Exergy Balance

$$\Delta \dot{EX}^{G}_{OVERALL} = \left[-\Delta \dot{EX}^{T}_{FUEL} + \Delta \dot{EX}^{C}_{CORE} \right]^{\substack{NUCLEAR \\ REACTOR}}$$

$$+ \left[\Delta \dot{EX}^{T}_{PREHEATER} + \Delta \dot{EX}^{T}_{REHEATER} + \Delta \dot{EX}^{M}_{TURBINE} + \Delta \dot{EX}^{C}_{CONDENSER} \right]^{\substack{CONVENTION\ AL \\ PLANT}}$$

Overall Cycle Thermodynamic Indicator

The overall cycle thermodynamic indicator is expressed as the ratio of real energy efficiency over the ideal Carnot cycle efficiency: $I_{OVERALL} = \dfrac{\eta^{EN}_{REAL}}{\eta^{CARNOT-DIRECT}_{IDEAL}}$

This expression allows to calculate the exergy efficiency based on the design data of ABWR nuclear reactor. The extreme temperatures to be considered for the ideal direct cycle efficiency calculation are the following:

- Maximum temperature of fuel at steady condition: $873K$
- Temperature of external reference system: $25°C = 298K$

Hence: $I_{OVERALL} = 1 - \dfrac{298}{873} = 0{,}659$

$$I_{OVERALL} = \frac{0{,}344}{0{,}659} = 0{,}522$$

7.2. AP1000

The AP1000 nuclear plant design consists of a pressurized water reactor type and represents, together the ABWR, a Generation III+ technology with a large industrial application. The main difference between ABWR and AP1000 is the presence of the steam generator representing a separating component between the primary circuit and the secondary or conventional (or balance of plant BOP).

Process conditions of the conventional plant are similar to those pertaining to ABWR reactors. Main difference characterizing the design of primary circuit in the nuclear reactor involve the water and steam conditions and mass flow rate affecting the overall plant power delivered to the electrical grid. In fact, the cooling water primary circuit operates at $15{,}5MPa$ requested to rise the cooling water temperature at higher value with respect the secondary feedwater to ensure similar steam conditions at the exit of steam generator. Furthermore, the core is cooled by liquid water for its entire height with the advantage of an enhanced withdrawable thermal power produced by fissions.

7.2.1. AP1000 Nuclear Reactor

Main components determining exergy balance and efficiency of the ABWR reactor are the core, containing the burning fuel assemblies, composed by fuel rods, and the cooling system constituted by the circulating water moved, by means of circulation pumps, throughout the core channels.

7.2.1.1. Core Fuel

The nuclear parameters characterizing the core of AP1000 design are different with respect to ABWR being different the overall thermal power released. The average linear heat rate is $q^{I} = 18{,}7\,kW/m$ and the average core power density is $q^{III} = 109{,}7\,MW/m^{3}$. Considering that the equivalent core diameter is $3{,}04m$ and the active core height is $4{,}267m$, then the equivalent core volume is $30{,}97m^{3}$ therefore the overall thermal power is given by $q^{III} \cdot V_{CORE} = 3397{,}41MW$ approximated by the nominal thermal power of $3400MW$.

7.2.1.2. Core Cooling System

The AP1000 reactor cooling system is constituted by circulation jet pumps designed to move the coolant through the fuel channels in the nuclear core and in the primary circuit constituted by and the steam generator tubes (tube side). In AP1000 plants circulation jet pumps overall power can rise up to 5 MW and the pressure increase through the pumps is 4 bars. This power is an additional contribution to the core thermal power coming from the interaction balance: $W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} - Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}} = 0$ which implies that the entire amount of mechanical power is dissipated into thermal power. The energy balance of cooling water through the nuclear core can be written as:

$$\overset{\leftarrow}{\dot{Q}}_{\substack{ADDITIONAL\\HEAT}} = \dot{m}\,\Delta H = \dot{m}\left(H_{OUT}^{COOLANT} - H_{IN}^{COOLANT}\right) = m\int_{T_{IN}}^{T_{OUT}} c_P(T)\,dT = mc_P\left(T_{OUT}^{REACTOR} - T_{IN}^{REACTOR}\right)$$

where: $c_P = 5{,}7\,kJ/(kgK)$ at 300 °C

Core Exergy Balance

Core inlet and outlet cooling water process conditions (saturated water) and exergy variations are the following (considering that the mean temperature rise across the core is $45{,}2°C$).

Core coolant inlet temperature: $T_{IN}^{CORE} = 279{,}4°C$; H_{IN} = 1236,7 kJ/kg; $S_{IN} = 3{,}07\,kJ/(kgK)$
Inlet coolant specific thermal exergy: $EX_{IN}^{T} = H_{IN} - T_R S_{IN}$ where $T_R = 298K$
$EX_{IN} = 1236{,}7 - 298\times 3{,}07 = 322{,}14\,kJ$
Core coolant outlet temperature: $T_{OUT}^{CORE} = 324{,}7°C$; $H_{OUT} = 1491{,}6\,kJ/kg$; $S_{OUT} = 3{,}497\,kJ/(kgK)$
Outlet coolant specific thermal exergy: $EX_{OUT}^{T} = H_{OUT} - T_R S_{OUT} = 1491{,}6 - 298\times 3{,}497 = 449{,}494\,kJ$
The specific thermal exergy variation is: $\Delta EX^{T} = EX_{OUT}^{T} - EX_{IN}^{T}$ and considering that:
$H_{OUT} = H_{IN} + W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} + Q^{\leftarrow}_{\substack{ADDITIONAL\\HEAT}}$, therefore:
$$\Delta EX^{T} = EX_{OUT}^{T} - EX_{IN}^{T} = \left(H_{OUT} - H_{IN}\right) - T_R\left(S_{OUT} - S_{IN}\right) = W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} + Q^{\rightarrow}_{\substack{FISSION\\REACTION}} - EX_{DESTR}$$

Thermal Power from Reactor = $\dot{m}Q^{\rightarrow}_{\substack{FISSION\\REACTION}}$ = 3400000 kW => $Q^{\rightarrow}_{\substack{FISSION\\REACTION}}$ = 3400000 / 14300 = 237,76 kJ/kg

Mechanical Power from Circulation Pumps $\dot{m}$ = 14300 Kg/s

$W^{\rightarrow}_{\substack{CIRCUL\\PUMP}}$ = 5 MW => $EX_{\substack{CIRCUL\\PUMPS}}$ = 5000 / 14300 = 0,35 kJ/kg

$Q^{\rightarrow}_{\substack{FISSION\\REACTION}}$ = 3400000 / 14300 = 237,76 kJ/kg

$Q^{\rightarrow}_{\substack{FISSION\\REACTION}}\eta = Q^{\rightarrow}_{\substack{FISSION\\REACTION}}\left(1 - \frac{T_R}{T}\right)$ =237,76 (1-293/552,4)=237,76 * 0,469 = 111,51 kJ/kg

Balance

$$\Delta EX = \sum EX_{OUT} - \sum EX_{IN} = \left(H_{OUT} - T_R S_{OUT}\right) - \left(H_{IN} - T_R S_{IN}\right) - W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} - Q^{\rightarrow}_{\substack{FISSION\\REACTION}}\eta$$

= 466,98 - 337,19 $- W^{\rightarrow}_{\substack{CIRCUL\\PUMP}} - Q^{\rightarrow}_{\substack{FISSION\\REACTION}}$

= - 466,98 + 337,19 + 111,51 + 0.35 = - 17,93 kJ/kg

ΔEX = - 17,93 kJ/kg

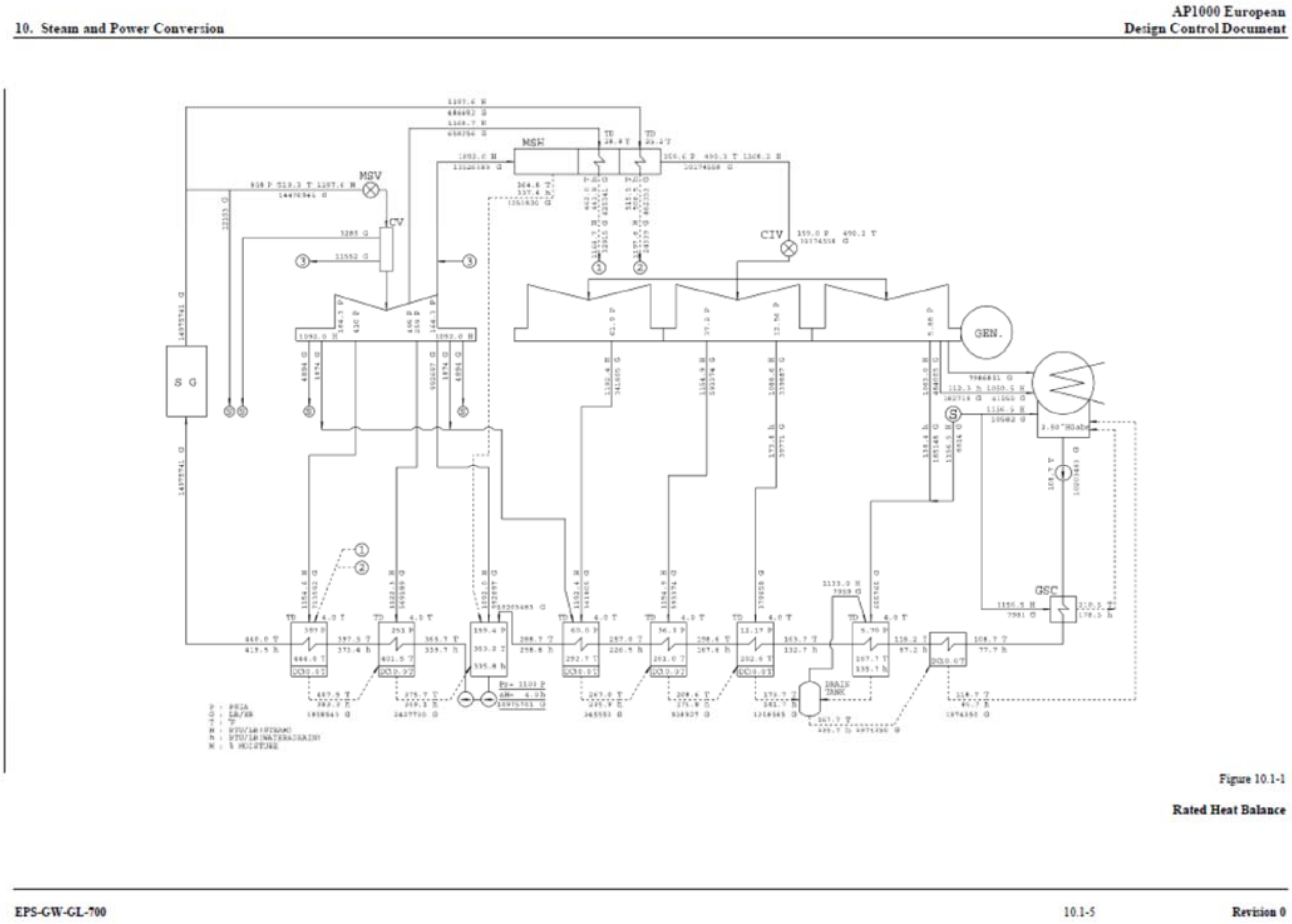
$$\dot{EX}_{OUT} = \dot{m}\left[\left(H_{OUT} - H_{IN}\right) - T_R\left(S_{OUT} - S_{IN}\right)\right]$$

7.2.1.3. Steam Generator

Once the coolant has been conveyed to the steam generator, the water undergoes a heat interaction along the tubes of the tube bundle.

7.2.2. AP1000 Conventional Plant

The conventional plant here considered is constituted by the following main components, namely, high pressure and low pressure steam turbines, main condenser and regenerating feedwater preheaters, moisture separator and reheaters and the condenser.



10. Steam and Power Conversion

AP1000 European
Design Control Document

Figure 10.1-1

Rated Heat Balance

EPS-GW-GL-700 10.1-5 Revision 0

Figure 7.1 – AP1000 Conventional Plant

7.2.2.1. High Pressure and Low Pressure Steam Turbines

The turbine is a 1800-rpm, tandem-compound, six-flow, reheat unit with 52-inch (1.32 m) last-stage blades (TC6F 52-inch, 1.32 m LSB). The high-pressure turbine element includes one double-flow, high-pressure turbine. The low-pressure turbine elements include three double-flow, low-pressure turbines and two external moisture separator/reheaters (MSRs) with two stages of reheating.

Steam from each of two steam generators enters the high-pressure turbine through four stop valves and four governing control valves After expanding through the high-pressure turbine, exhaust steam flows through two external moisture separator/reheater vessels. The external moisture separators reduce the moisture content of the high-pressure exhaust steam from approximately 10 to 13 percent at the rated load to 0.5 percent moisture or less.

The AP1000 employs a 2 stage reheater, of which the first stage reheater uses the extraction steam from the high pressure turbine and the second reheater uses a portion of the main steam supply to reheat the steam to superheated conditions. The reheated steam flows through separate reheat stop and intercept valves in each of six reheat steam lines leading to the inlets of the three low-pressure turbines. Turbine steam extraction connections are provided for seven stages of feedwater heating. Steam from the extraction points of the high-pressure turbine is supplied to high-pressure feedwater heater No. 6 and No. 7. The high-pressure turbine exhaust also supplies steam to the deaerating feedwater heater (stream "S" in the PFD). The low-pressure turbine third, fourth, fifth, and sixth extraction points supply steam to the low-pressure feedwater heaters No. 4, 3, 2, and 1, respectively. The external moisture separator/reheaters use multiple vane chevron banks (shell side) for moisture removal. The moisture removed by the external moisture separator/reheaters drain to a moisture separator drain tank and is pumped to the deaerator. Condensed steam in the reheater (tube side) is drained to the reheater drain tank, flows into the shell side of the No. 7 feedwater heater, and cascades to the No. 6 feedwater heater.

Following sections are specially focused on the calculation of exergy destruction for all main components more largely affecting the performance of AP1000 plant.

7.2.2.2. First Feedwater Preheater

Hot side

Inlet

Saturated steam (93%, 75,86°C) from LP turbine: mass flow rate is $60{,}98\,kg/s$ at $P_{IN} = 0{,}04\,MPa = 40\,kPa$,

$H_{IN}^{STEAM-SAT} = 2472{,}54\,kJ/kg$; $S_{IN}^{STEAM-SAT} = 7{,}2\,kJ/(kgK)$;

Condensate from LP turbine: mass flow rate is $20{,}81\,kg/s$ at $P_{IN} = 0{,}04\,MPa = 40\,kPa$

$H_{IN}^{COND} = 321{,}92\,kJ/kg$ $\quad S_{IN}^{COND} = 1{,}02\,kJ/(kgK)$

Saturated steam (95,5%, 185,29°C) from Steam Generator and HP turbine: mass flow rate is $0{,}83\,kg/s$ at $P_{IN} = 1{,}13\,MPa = 1130\,kPa$;

$H_{IN}^{STEAM-SAT} = 2690{,}02\,kJ/kg$; $S_{IN}^{STEAM-SAT} = 6{,}347\,kJ/(kgK)$;

Saturated steam (98,5%, 94,8°C) from Drain Tank: mass flow rate is $1\,kg/s$ at $P_{IN} = 0{,}084\,MPa = 84\,kPa$;

$H_{IN}^{STEAM-SAT} = 2635{,}36\, kJ/kg$; $S_{IN}^{STEAM-SAT} = 7{,}325\, kJ/(kgK)$;

Outlet

Condensate: mass flow rate is $83{,}63\, kg/s$ at $P_{OUT} = 0{,}0393\, MPa = 39{,}3 kPa$ and $T_{OUT} = 75{,}39\,°C = 348{,}39\, K$

$H_{OUT} = 315{,}64\, kJ/kg$; $S_{OUT} = 1{,}02\, kJ/(kgK)$

$$\Delta \dot{EX}^{T}_{HOT} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m}_{OUT} \cdot ex^{T}_{OUT} - \dot{m}_{IN} \cdot ex^{T}_{IN}$$

$$= 83{,}63 \times (315{,}64 - 298 \times 1{,}02) - 60{,}98 \times (2472{,}54 - 298 \times 7{,}2)$$

$$- 20{,}81 \times (321{,}92 - 298 \times 1{,}02) - 0{,}83 \times (2690{,}02 - 298 \times 6{,}347) - 1 \times (2635{,}36 - 298 \times 7{,}325)$$

$$= 976{,}8 - 19936{,}8 - 373{,}75 - 662{,}83 - 452{,}51 = -20449{,}09 kW = -20{,}45 MW$$

Cold Side

Inlet

Feedwater: the mass flow rate of feedwater is $1285{,}64\, kg/s$ at $P_{IN}^{FEEDWATER} = 1{,}1 Mpa = 1100\, kPa$ and $T_{IN} = 47{,}9°C = 320{,}9 K$;

$H_{IN} = 202{,}83 kJ/kg$; $S_{IN} = 0{,}676\, kJ/(kgK)$

Outlet

Feedwater: the mass flow rate of feedwater is $1285{,}64\, kg/s$; at $P_{OUT}^{FEEDWATER} = 1{,}1 Mpa = 1100\, kPa$ and $T_{OUT} = 73{,}17\,°C = 346{,}17\, K$;

$H_{OUT} = 308{,}66\, kJ/kg$; $S_{OUT} = 0{,}993\, kJ/(kgK)$

$$\Delta \dot{EX}^{T}_{COLD} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m}_{OUT} \cdot ex^{T}_{OUT} - \dot{m}_{IN} \cdot ex^{T}_{IN}$$

$$= 1285{,}64 \times [(308{,}66 - 298 \times 0{,}993) - (202{,}83 - 298 \times 0{,}676)]$$

$$= 1285{,}64 \times [12{,}746 - 1{,}382] = 1461{,}01 kW = 1{,}46 MW$$

First feedwater preheater balance: $\Delta \overset{\bullet}{EX}{}^{T} = \Delta \overset{\bullet}{EX}{}^{T}_{HOT} + \Delta \overset{\bullet}{EX}{}^{T}_{COLD} = -20{,}45 + 1{,}46 = -18{,}99 MW$

7.2.2.3. Second Feedwater Preheater

Hot side

Inlet

Saturated steam at $P_{IN}^{STEAM-SAT} = 0{,}0839\, MPa = 83{,}9 kPa$: the total mass flow rate of saturated steam extraction from LP steam turbine is $47{,}84\, kg/s$. Dry steam mass flow rate is $42{,}83\, kg/s$ and condensate mass flow rate is $5{,}01\, kg/s$, therefore the moisture of saturated steam is 0,89 dry steam and 0,11 condensate. The inlet and outlet conditions are the following.

$H^{STEAM-DRY} = 2666{,}74\, kJ/kg$; $H^{COND} = 396{,}62\, kJ/kg$

$$H_{IN}^{STEAM-SAT} = x^{STEAM-DRY} H^{STEAM-DRY} + x^{COND} H^{COND}$$

$$= 0{,}89 \times 2666{,}74 + 0{,}11 \times 396{,}62 = 2373{,}4 + 43{,}63 = 2417{,}03\, kJ/kg$$

$S^{STEAM-DRY} = 7{,}418\, kJ/(kgK)$; $S^{COND} = 1{,}479\, kJ/(kgK)$

$$S_{IN}^{STEAM-SAT} = x^{STEAM-DRY} S^{STEAM-DRY} + x^{COND} S^{COND}$$

$$= 0{,}89 \times 7{,}418 + 0{,}11 \times 1{,}479 = 6{,}6 + 0{,}16 = 6{,}76\, kJ/(kgK)$$

Condensate: mass flow rate $118{,}3\, kg/s$ at $P_{IN} = 0{,}248\, MPa = 248\, kPa$ and $T_{IN} = 98{,}1°C = 371{,}1 K$ mixed to saturated steam at $H_{IN}^{COND} = 533{,}71\, kJ/kg$; $S_{IN}^{COND} = 1{,}604\, kJ/(kgK)$

Outlet:

Condensate: mass flow rate $166{,}14\, kg/s$ at $P_{OUT} = 0{,}0839\, MPa = 83{,}9 kPa$ and $T_{OUT} = 78{,}72\, °C = 351{,}72\, K$;

$H_{OUT}^{COND} = 329{,}159\, kJ/kg$; $S_{OUT}^{COND} = 1{,}06\, kJ/(kgK)$

$$\Delta \overset{\bullet}{EX}{}^{T}_{HOT} = \overset{\bullet}{EX}{}^{T}_{OUT} - \overset{\bullet}{EX}{}^{T}_{IN} = \overset{\bullet}{m}_{OUT} \cdot ex_{OUT}^{T} - \overset{\bullet}{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 166{,}14 \times (329{,}159 - 298 \times 1{,}06) - 47{,}84 \times (2417{,}03 - 298 \times 6{,}76) - 118{,}3 \times (533{,}71 - 298 \times 1{,}604)$$

$= 2206{,}17 - 19257{,}99 - 6591{,}44 = -23643{,}26 kW = -23{,}64 MW$

Cold side: the mass flow rate of feedwater is $1285{,}64\ kg/s$, $P^{FEEDWATER} = 1{,}1 Mpa$

Inlet: $T_{IN} = 73{,}17\,°C = 346{,}17\,K$; $H_{IN} = 306{,}706\,kJ/kg$; $S_{IN} = 0{,}99\,kJ/(kgK)$

Outlet: $T_{OUT} = 92{,}55\,°C = 365{,}55\,K$; $H_{OUT} = 388{,}046\,kJ/kg$; $S_{OUT} = 1{,}22\,kJ/(kgK)$

$$\Delta \dot{EX}^{T}_{COLD} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m} \cdot \left(ex^{T}_{OUT} - ex^{T}_{IN}\right)$$

$$= 1285{,}64 \times \left[(388{,}046 - 306{,}706) - 298(1{,}22 - 0{,}99)\right] = 1285{,}64 \times \left[81{,}34 - 68{,}54\right] = 16456{,}19 kW = 16{,}46 MW$$

Second feedwater preheater balance: $\Delta \dot{EX}^{T} = \Delta \dot{EX}^{T}_{HOT} + \Delta \dot{EX}^{T}_{COLD} = -23{,}64 + 16{,}46 = -7{,}18 MW$

7.2.2.4. Third Feedwater Preheater

Hot Side

Inlet

Superheated steam: $P^{STEAM-SH}_{IN} = 0{,}248\,MPa = 248\,kPa$: the total mass flow rate of superheated steam extraction from LP steam turbine is $74{,}76\ kg/s$

$H^{STEAM-SUP}_{IN} = 2686{,}3\,kJ/kg$; $S^{STEAM-SH}_{IN} = 7{,}05\,kJ/(kgK)$

Condensate: mass flow rate $43{,}54\ kg/s$ at $P_{IN} = 0{,}414\,MPa = 414\,kPa$ and $T_{IN} = 130{,}55\,°C = 403{,}55\,K$

$H^{COND}_{IN} = 548{,}7\,kJ/kg$; $S^{COND}_{IN} = 1{,}64\,kJ/(kgK)$

Outlet

Condensate: mass flow rate $118{,}3\,kg/s$ at $P_{OUT} = 0{,}248\,MPa = 248\,kPa$ and $T_{OUT} = 98{,}11\,°C = 371{,}11\,K$

$H^{COND}_{OUT} = 548{,}7\,kJ/kg$; $S^{COND}_{OUT} = 1{,}64\,kJ/(kgK)$

$$\Delta \dot{EX}^{T}_{HOT} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m}_{OUT} \cdot ex^{T}_{OUT} - \dot{m}_{IN} \cdot ex^{T}_{IN}$$

$$= 118{,}3 \times (548{,}7 - 298 \times 1{,}64) - 74{,}76 \times (2686{,}3 - 298 \times 7{,}05) - 43{,}54 \times (548{,}7 - 298 \times 1{,}64)$$

$$= 7095{,}6 - 43764{,}5 - 2611{,}53 = -39280{,}43 kW = -39{,}28 MW$$

Cold Side: the mass flow rate of feedwater is $1285{,}64\, kg/s$ at $P^{FEEDWATER} = 1{,}1 MPa$

Inlet: $T_{IN}^{FEEDWATER} = 92{,}55\,°C = 365{,}55\,K$; $H_{IN}^{FEEDWATER} = 389{,}84\, kJ/kg$; $S_{IN}^{COND} = 1{,}22\, kJ/(kgK)$

Outlet: $T_{OUT}^{FEEDWATER} = 125\,°C = 398\,K$; $H_{OUT}^{FEEDWATER} = 526{,}84\, kJ/kg$; $S_{OUT}^{COND} = 1{,}58\, kJ/(kgK)$;

$$\Delta \dot{EX}^{T}_{COLD} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m}_{OUT} \cdot ex_{OUT}^{T} - \dot{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 1285{,}64 \times \left[(526{,}84 - 298 \times 1{,}58) - (389{,}84 - 298 \times 1{,}22) \right]$$

$$= 1285{,}64 \times [56 - 26{,}28] = 38209{,}22 kW = 38{,}21 MW$$

Third feedwater preheater balance: $\Delta \dot{EX}^{T} = \Delta \dot{EX}^{T}_{HOT} + \Delta \dot{EX}^{T}_{COLD} = -39{,}28 + 38{,}21 = -1{,}07 MW$

7.2.2.5. Fourth Feedwater Preheater

Hot Side

Inlet

Saturated steam (88% steam, 185,4°C) from HP Turbine: $P_{IN}^{HP-STEAM-SAT} = 1{,}133\, MPa = 1133\, kPa$; the mass flow rate of superheated steam extraction from HP steam turbine is $0{,}236\, kg/s$;

$H_{IN}^{HP-STEAM-SAT} = 2540\, kJ/kg$; $S_{IN}^{HP-STEAM-SAT} = 6{,}02\, kJ/(kgK)$

Superheated steam (160°C) from LP Turbine: $P_{IN}^{LP-STEAM-SH} = 0{,}427\, MPa = 427\, kPa$; the mass flow rate of superheated steam extraction from HP steam turbine is $43{,}1\, kg/s$;

$H_{IN}^{LP-STEAM-SH} = 2773{,}5\, kJ/kg$; $S_{IN}^{LP-STEAM-SH} = 6{,}95\, kJ/(kgK)$

Outlet: condensate mass flow rate $43{,}54\, kg/s$ at $P_{OUT}^{COND} = 0{,}4137\, MPa = 413{,}7\, kPa$ and $T_{OUT} = 130{,}55\,°C = 403{,}55\, K$

$H_{OUT}^{COND} = 548{,}7\, kJ/kg$; $S_{OUT}^{COND} = 1{,}64\, kJ/(kgK)$

$$\Delta \dot{EX}^{T}_{HOT} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m}_{OUT} \cdot ex_{OUT}^{T} - \dot{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 43{,}54 \times (548{,}7 - 298 \times 1{,}64) - 0{,}236 \times (2540 - 298 \times 6{,}02) - 43{,}1 \times (2773{,}5 - 298 \times 6{,}95)$$
$$= 2611{,}53 - 176{,}06 - 30273{,}44 = -27837{,}97 kW = -27{,}84 MW$$

Cold Side: the mass flow rate of feedwater is $1285{,}64\ kg/s$ at $P^{FEEDWATER} = 1{,}1 MPa$

Inlet: $T_{IN}^{FEEDWATER} = 125\,°C = 398\,K$; $H_{IN}^{FEEDWATER} = 526{,}84\ kJ/kg$; $S_{IN}^{COND} = 1{,}581\ kJ/(kgK)$

Outlet: $T_{OUT}^{FEEDWATER} = 142{,}61\,°C = 415{,}61 K$; $H_{OUT}^{FEEDWATER} = 601{,}97\ kJ/kg$; $S_{OUT}^{COND} = 1{,}765\ kJ/(kgK)$;

$$\Delta \dot{EX}^{T}_{COLD} = \dot{EX}^{T}_{OUT} - \dot{EX}^{T}_{IN} = \dot{m}_{OUT} \cdot ex_{OUT}^{T} - \dot{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 1285{,}64 \times [(601{,}97 - 298 \times 1{,}765) - (526{,}84 - 298 \times 1{,}581)]$$
$$= 1285{,}64 \times [76 - 55{,}7] = 26098{,}49 kW = 26{,}1 MW$$

Fourth feedwater preheater balance: $\Delta \dot{EX}^{T} = \Delta \dot{EX}^{T}_{HOT} + \Delta \dot{EX}^{T}_{COLD} = -27{,}84 + 26{,}1 = -1{,}74 MW$

7.2.2.6. Fifth Feedwater Preheater (Mixer)

Inlet

Feedwater: the mass flow rate of feedwater is $\dot{m}_{IN}^{FEEDWATER} = 1285{,}64\ kg/s$ at $P^{FEEDWATER} = 1{,}1 MPa$ and $T_{IN}^{FEEDWATER} = 142{,}61\,°C = 415{,}61 K$;

$H_{IN}^{FEEDWATER} = 601{,}97\ kJ/kg$; $S_{IN}^{COND} = 1{,}765\ kJ/(kgK)$;

Saturated steam (88% steam, 185,4°C) from HP Turbine: $P_{IN}^{HP-STEAM-SAT} = 1{,}133\ MPa = 1133\ kPa$; the mass flow rate of steam is $125{,}08\ kg/s$

$H_{IN}^{HP-STEAM-SAT} = 2540\ kJ/kg$; $S_{IN}^{HP-STEAM-SAT} = 6{,}02\ kJ/(kgK)$

Condensate from Moisture Separator (MS): mass flow rate $\dot{m}_{IN}^{COND-MS} = 170{,}33\ kg/s$;
$P_{IN}^{COND-MS} = 1{,}1 MPa = 1100\ kPa$; $T_{IN}^{COND-MS} = 184{,}9\,°C = 457{,}91 K$

$H_{IN}^{COND-MS} = 784{,}79\ kJ/kg$; $S_{IN}^{COND-MS} = 2{,}178\ kJ/(kgK)$

Condensate: $\overset{\bullet}{m}_{IN}^{COND} = 305,89\ kg/s$ at $P_{IN}^{COND} = 1,73\,MPa = 1730\ kPa$ and $T_{IN}^{COND} = 190,94\,°C = 463,94\,K$

$H_{IN}^{COND} = 812\ kJ/kg$; $S_{IN}^{COND} = 2,28\,kJ/(kgK)$

Outlet

Feedwater: the mass flow rate of feedwater is $\overset{\bullet}{m}_{OUT}^{FEEDWATER} = 1886,94\ kg/s$ at $P_{OUT}^{FEEDWATER} = 8,68\,MPa$ and $T_{OUT}^{FEEDWATER} = 185,39\,°C = 458,39\,K$;

$H_{OUT}^{FEEDWATER} = 790,14\,kJ/kg$; $S_{OUT}^{FEEDWATER} = 2,181\,kJ/(kgK)$

Fifth feedwater preheater (mixer) balance: $\Delta \overset{\bullet}{EX}{}_{MIXER}^{T} = \overset{\bullet}{EX}{}_{OUT}^{T} - \overset{\bullet}{EX}{}_{IN}^{T} = \overset{\bullet}{m}_{OUT} \cdot ex_{OUT}^{T} - \overset{\bullet}{m}_{IN} \cdot ex_{IN}^{T}$

$$= 1886,94 \times (790,14 - 298 \times 2,181) - 1285,64 \times (601,97 - 298 \times 1,765) - 125,08 \times (2540 - 298 \times 6,02)$$

$$-170,33 \times (784,79 - 298 \times 2,178) - 305,89 \times (812 - 298 \times 2,28)$$

$$= 264552,76 - 97708,64 - 93314,68 - 23121,62 - 40548,78 = 9859,04kW = 9,86MW$$

In this case, the variation of exergy is positive as an input of work interaction by feedwater pumps compensate the decrease of exergy due to the exergy destruction in the mixer. However, this work interaction input is dissipated into work interaction so that the entire amount calculated represents the exergy destruction occurring in this fifth preheater.

7.2.2.7. Sixth Feedwater Preheater

Hot Side

Inlet

Saturated steam (90% steam, 206,6°C) from HP Turbine: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{IN}^{HP-STEAM\ -SAT} = 71,72\ kg/s$ at $P_{IN}^{HP-STEAM\ -SAT} = 1,78\,MPa = 1780\ kPa$;

$H_{IN}^{HP-STEAM\ -SAT} = 2610,47\,kJ/kg$; $S_{IN}^{HP-STEAM\ -SAT} = 5,98\,kJ/(kgK)$

Condensate: mass flow rate $\dot{m}_{IN}^{COND} = 234{,}18\,kg/s$ at $P_{IN}^{COND} = 2{,}74\,MPa = 2740\,kPa$ and $T_{IN}^{COND} = 208{,}61\,°C = 481{,}61\,K$

$H_{IN}^{COND} = 891{,}55\,kJ/kg$; $S_{IN}^{COND} = 2{,}41\,kJ/(kgK)$

Outlet

Condensate: mass flow rate $\dot{m}_{OUT}^{COND} = 305{,}89\,kg/s$ at $P_{OUT}^{COND} = 1{,}73\,MPa = 1730\,kPa$ and $T_{OUT}^{COND} = 190{,}94\,°C = 463{,}94\,K$

$H_{OUT}^{COND} = 812\,kJ/kg$; $S_{OUT}^{COND} = 2{,}244\,kJ/(kgK)$

$$\Delta\dot{EX}_{HOT}^{T} = \dot{EX}_{OUT}^{T} - \dot{EX}_{IN}^{T} = \dot{m}_{OUT}\cdot ex_{OUT}^{T} - \dot{m}_{IN}\cdot ex_{IN}^{T}$$

$$= 305{,}89\times(812 - 298\times 2{,}244) - 71{,}72\times(2610{,}47 - 298\times 5{,}98) - 234{,}18\times(891{,}55 - 298\times 2{,}41)$$

$$= 43830{,}37 - 59415 - 40599{,}79 = -56184{,}41\,kW = -56{,}18\,MW$$

Cold Side

Inlet

Feedwater: the mass flow rate of feedwater is $\dot{m}_{IN}^{FEEDWATER} = 1886{,}94\,kg/s$ at $P_{IN}^{FEEDWATER} = 8{,}68\,MPa = 8680\,kPa$ and $T_{IN}^{FEEDWATER} = 185{,}39\,°C = 458{,}39\,K$;

$H_{IN}^{FEEDWATER} = 790{,}14\,kJ/kg$; $S_{IN}^{FEEDWATER} = 2{,}181\,kJ/(kgK)$

Outlet

Feedwater: the mass flow rate of feedwater is $\dot{m}_{OUT}^{FEEDWATER} = 1886{,}94\,kg/s$ at $P_{OUT}^{FEEDWATER} = 8{,}68\,MPa = 8680\,kPa$ and $T_{OUT}^{FEEDWATER} = 203{,}05\,°C = 476{,}05\,K$;

$H_{OUT}^{FEEDWATER} = 868{,}53\,kJ/kg$; $S_{OUT}^{FEEDWATER} = 2{,}348\,kJ/(kgK)$

$$\Delta\dot{EX}_{COLD}^{T} = \dot{EX}_{OUT}^{T} - \dot{EX}_{IN}^{T} = \dot{m}_{OUT}\cdot ex_{OUT}^{T} - \dot{m}_{IN}\cdot ex_{IN}^{T}$$

$=1886{,}94\times\left[(868{,}53-298\times2{,}348)-(790{,}14-298\times2{,}181)\right]$

$=1886{,}94\times\left[168{,}83-140{,}2\right]=54023{,}09kW=54MW$

Sixth feedwater preheater balance: $\Delta \overset{\bullet}{EX}^{T}=\Delta \overset{\bullet}{EX}^{T}_{HOT}+\Delta \overset{\bullet}{EX}^{T}_{COLD}=-56{,}18+54=-2{,}18MW$

7.2.2.8. Seventh Feedwater Preheater

Hot Side

Inlet

Saturated steam (94% steam, 230,6°C) from HP Turbine: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{IN}^{HP-STEAM-SAT}=89{,}9\,kg/s$ at $P_{IN}^{HP-STEAM-SAT}=2{,}83MPa=2830\,kPa$;

$H_{IN}^{HP-STEAM-SAT}=2685{,}6\,kJ/kg$; $S_{IN}^{HP-STEAM-SAT}=5{,}99\,kJ/(kgK)$

Saturated steam from first Reheater: $P_{IN}^{STEAM-SAT}=3{,}41MPa=3410\,kPa$ and $T_{IN}^{STEAM-SAT}=238{,}89°C=511{,}89K$; saturated steam (95%) mass flow rate is $4{,}15\,kg/s$; and condensate mass flow rate is $78{,}79\,kg/s$;

$H_{IN}^{STEAM-SAT}=2718{,}4\,kJ/kg$; $S_{IN}^{STEAM-SAT}=5{,}964\,kJ/(kgK)$

$H_{IN}^{COND}=1032{,}28\,kJ/kg$; $S_{IN}^{COND}=2.69\,kJ/(kgK)$

Saturated steam from second Reheater: $P_{IN}^{STEAM-SAT}=5{,}57\,MPa=5570\,kPa$ and $T_{IN}^{STEAM-SAT}=268{,}61°C=541{,}61K$; saturated steam (99%) mass flow rate is $3{,}07\,kg/s$; and condensate mass flow rate is $58{,}26\,kg/s$;

$H_{IN}^{STEAM-SAT}=2785{,}62\,kJ/kg$; $S_{IN}^{STEAM-SAT}=5{,}895\,kJ/(kgK)$

$H_{IN}^{COND}=1178{,}12\,kJ/kg$; $S_{IN}^{COND}=2.963\,kJ/(kgK)$

Outlet

Condensate: mass flow rate $\overset{\bullet}{m}_{OUT}^{COND}=234{,}18\,kg/s$ at $P_{OUT}^{COND}=2{,}74\,MPa=2740\,kPa$ and $T_{OUT}^{COND}=208{,}61\,°C=481{,}61K$

$H_{OUT}^{COND} = 891{,}55\,kJ/kg$; $S_{OUT}^{COND} = 2{,}41kJ/(kgK)$

$$\Delta \overset{\bullet}{EX}{}_{HOT}^{T} = \overset{\bullet}{EX}{}_{OUT}^{T} - \overset{\bullet}{EX}{}_{IN}^{T} = \overset{\bullet}{m}_{OUT} \cdot ex_{OUT}^{T} - \overset{\bullet}{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 234{,}18 \times (891{,}55 - 298 \times 2{,}41) - 89{,}9 \times (2685{,}6 - 298 \times 5{,}99) - 4{,}15 \times (2718{,}4 - 298 \times 5{,}964)$$

$$- 78{,}79 \times (1032{,}28 - 298 \times 2{,}69) - 3{,}07 \times (2785{,}62 - 298 \times 5{,}895) - 58{,}26 \times (1178{,}12 - 298 \times 2{,}963)$$

$$= 40599{,}79 - 80962{,}14 - 3905{,}68 - 18173{,}7 - 3158{,}75 - 17195{,}2 = -82795{,}68kW = -82{,}79MW$$

Cold Side

Inlet

Feedwater: the mass flow rate of feedwater is $\overset{\bullet}{m}{}_{IN}^{FEEDWATER} = 1886{,}94\,kg/s$ at $P_{IN}^{FEEDWATER} = 8{,}68\,MPa = 8680\,kPa$ and $T_{IN}^{FEEDWATER} = 203{,}05\,°C = 476{,}05\,K$;

$H_{OUT}^{FEEDWATER} = 868{,}53\,kJ/kg$; $S_{IN}^{FEEDWATER} = 2{,}348\,kJ/(kgK)$

Outlet

Feedwater: the mass flow rate of feedwater is $\overset{\bullet}{m}{}_{OUT}^{FEEDWATER} = 1886{,}94\,kg/s$ at $P_{OUT}^{FEEDWATER} = 8{,}68\,MPa = 8680\,kPa$ and $T_{OUT}^{FEEDWATER} = 226{,}67\,°C = 499{,}67\,K$;

$H_{OUT}^{FEEDWATER} = 975{,}76\,kJ/kg$; $S_{OUT}^{FEEDWATER} = 2{,}568\,kJ/(kgK)$

$$\Delta \overset{\bullet}{EX}{}_{COLD}^{T} = \overset{\bullet}{EX}{}_{OUT}^{T} - \overset{\bullet}{EX}{}_{IN}^{T} = \overset{\bullet}{m}_{OUT} \cdot ex_{OUT}^{T} - \overset{\bullet}{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 1886{,}94 \times [(975{,}76 - 298 \times 2{,}568) - (868{,}53 - 298 \times 2{,}348)]$$

$$= 1886{,}94 \times [210{,}5 - 168{,}8] = 78685{,}4kW = 78{,}68MW$$

Seventh feedwater preheater balance: $\Delta \overset{\bullet}{EX}{}^{T} = \Delta \overset{\bullet}{EX}{}_{HOT}^{T} + \Delta \overset{\bullet}{EX}{}_{COLD}^{T} = -82{,}79 + 78{,}68 = -4{,}11MW$

7.2.2.9. Steam Generator

Hot Side (Tube Side)

Inlet

Coolant: the mass flow rate of coolant (cooling water) in the tube side of the steam generator is $\dot{m}_{IN}^{COOLANT} = 14300\ kg/s$ at $P_{IN}^{COOLANT} = 15{,}5MPa = 15500\ kPa$ and $T_{IN}^{COOLANT} = 324{,}75°C = 597{,}7K$;

$H_{IN}^{COOLANT} = 1482{,}29\ kJ/kg$; $S_{IN}^{COOLANT} = 3{,}473\ kJ/(kgK)$

Outlet

Coolant: the mass flow rate of coolant (cooling water) in the tube side of the steam generator is $\dot{m}_{OUT}^{COOLANT} = 14300\ kg/s$ at $P_{OUT}^{COOLANT} = 15{,}5MPa = 15500\ kPa$ and $T_{OUT}^{COOLANT} = 279{,}4°C = 552{,}4K$;

$H_{OUT}^{COOLANT} = 1229{,}27\ kJ/kg$; $S_{OUT}^{COOLANT} = 3{,}034\ kJ/(kgK)$

$$\Delta \dot{EX}_{HOT}^{T} = \dot{EX}_{OUT}^{T} - \dot{EX}_{IN}^{T} = \dot{m}_{OUT} \cdot ex_{OUT}^{T} - \dot{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 14300 \times [(1229{,}27 - 298 \times 3{,}034) - (1482{,}29 - 298 \times 3{,}473)]$$

$$= 14300 \times [325{,}14 - 447{,}37] = -1747889kW = -1747{,}89MW$$

Cold Side (Shell Side)

Inlet

Feedwater: the mass flow rate of feedwater is $\dot{m}_{IN}^{FEEDWATER} = 1886{,}94\ kg/s$ at $P_{IN}^{FEEDWATER} = 8{,}68MPa = 8680\ kPa$ and $T_{IN}^{FEEDWATER} = 226{,}67°C = 499{,}67K$;

$H_{IN}^{FEEDWATER} = 975{,}76\ kJ/kg$; $S_{IN}^{FEEDWATER} = 2{,}568\ kJ/(kgK)$

Outlet

The total mass flow rate of feedwater is $\dot{m}_{OUT}^{FEEDWATER} = 1886{,}94\ kg/s$ at $P_{OUT}^{FEEDWATER} = 5{,}57MPa = 5570\ kPa$ and $T_{OUT}^{FEEDWATER} = 270{,}72°C = 543{,}72K$; the total mass flow rate is partitioned in three streams with following mass flow rates, enthalpies and entropies pertaining to each and every stream.

First Preheater:

The mass flow rate of saturated steam (94%, 270,8°C) to the first preheater is $\dot{m}_{OUT}^{FIRST-PREHEATER} = 1{,}52\; kg/s$ at $P_{OUT}^{FIRST-PREHEATER} = 5{,}57\, MPa = 5570\, kPa$ and $T_{OUT}^{FIRST-PREHEATER} = 270{,}72\,°C = 543{,}72\,K$;

$H_{OUT}^{FIRST-PREHEATER} = 2690{,}02\; kJ/kg$; $S_{OUT}^{FIRST-PREHEATER} = 5{,}748\; kJ/(kgK)$

Second Reheater:

The mass flow rate of superheated steam to the second reheater is $\dot{m}_{OUT}^{SECOND-REHEATER} = 61{,}32\; kg/s$ at $P_{OUT}^{SECOND-REHEATER} = 5{,}57\, MPa = 5570\, kPa$ and $T_{OUT}^{SECOND-REHEATER} = 270{,}72\,°C = 543{,}72\,K$;

$H_{OUT}^{SECOND-REHEATER} = 2785{,}62\; kJ/kg$; $S_{OUT}^{FIRST-PREHEATER} = 5{,}927\; kJ/(kgK)$

HP Steam Turbine

The mass flow rate of saturated steam (99,8%) to the HP steam turbine is $\dot{m}_{OUT}^{HP-TURBINE} = 1824{,}09\; kg/s$ at $P_{OUT}^{HP-TURBINE} = 5{,}57\, MPa = 5570\, kPa$ and $T_{OUT}^{HP-TURBINE} = 270{,}72\,°C = 543{,}72\,K$;

$H_{OUT}^{HP-TURBINE} = 2785{,}62\; kJ/kg$; $S_{OUT}^{HP-TURBINE} = 5{,}927\; kJ/(kgK)$

$$\Delta \dot{EX}_{COLD}^{T} = \dot{EX}_{OUT}^{T} - \dot{EX}_{IN}^{T} = \dot{m}_{OUT} \cdot ex_{OUT}^{T} - \dot{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 1{,}52 \times (2690{,}02 - 298 \times 5{,}748) + 61{,}32 \times (2785{,}62 - 298 \times 5{,}927) + 1824{,}09 \times (2785{,}62 - 298 \times 5{,}927)$$

$$- 1886{,}94 \times (975{,}76 - 298 \times 2{,}568)$$

$$= 1485{,}22 + 62508{,}01 + 1859429{,}92 - 397193{,}32 = 1526229{,}83 kW = 1526{,}23 MW$$

Steam generator balance: $\Delta \dot{EX}^{T} = \Delta \dot{EX}_{HOT}^{T} + \Delta \dot{EX}_{COLD}^{T} = -1747{,}89 + 1526{,}23 = -221{,}66 MW$

7.2.2.10. Moisture Separator and Reheater (MSH)

Hot Side

Inlet

Saturated steam (95%, 241°C) from HP turbine to first reheater: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{IN}^{HP-STEAM-SAT} = 82{,}94\,kg/s$ at $P_{IN}^{HP-STEAM-SAT} = 3{,}41MPa = 3410\,kPa$;

$H_{IN}^{HP-STEAM-SAT} = 2718{,}4\,kJ/kg$; $S_{IN}^{HP-STEAM-SAT} = 5{,}964\,kJ/(kgK)$

Saturated steam (99,8%) from steam generator to second reheater: the mass flow rate of superheated steam is $\overset{\bullet}{m}_{IN}^{HP-STEAM-SAT} = 61{,}32\,kg/s$ at $P_{IN}^{HP-STEAM-SAT} = 5{,}57\,MPa = 5570\,kPa$; $T_{OUT}^{HP-STEAM-SAT} = 270{,}72°C = 543{,}72\,K$

$H_{IN}^{HP-STEAM-SAT} = 2785{,}62\,kJ/kg$; $S_{IN}^{HP-STEAM-SAT} = 5{,}927\,kJ/(kgK)$

Outlet

Condensate to mixer: mass flow rate $\overset{\bullet}{m}_{OUT}^{COND-MS} = 170{,}33\,kg/s$; $P_{OUT}^{COND-MS} = 1{,}1MPa = 1100\,kPa$; $T_{OUT}^{COND-MS} = 184{,}9°C = 457{,}91K$

$H_{OUT}^{COND-MS} = 784{,}79\,kJ/kg$; $S_{OUT}^{COND-MS} = 2{,}178\,kJ/(kgK)$

Saturated steam to seventh feedwater preheater: $P_{OUT}^{STEAM-SAT} = 3{,}41MPa = 3410\,kPa$ and $T_{OUT}^{STEAM-SAT} = 238{,}89°C = 511{,}89K$; saturated steam (95%) mass flow rate is $4{,}15\,kg/s$; and condensate mass flow rate is $78{,}79\,kg/s$;

$H_{OUT}^{STEAM-SAT} = 2718{,}4\,kJ/kg$; $S_{OUT}^{STEAM-SAT} = 5{,}964\,kJ/(kgK)$

$H_{OUT}^{COND} = 1032{,}28\,kJ/kg$; $S_{OUT}^{COND} = 2{,}69\,kJ/(kgK)$

Saturated steam to seventh feedwater preheater: $P_{OUT}^{STEAM-SAT} = 5{,}57\,MPa = 5570\,kPa$ and $T_{OUT}^{STEAM-SAT} = 268{,}61°C = 541{,}61K$; saturated steam (99%) mass flow rate is $3{,}07\,kg/s$; and condensate mass flow rate is $58{,}26\,kg/s$;

$H_{OUT}^{STEAM-SAT} = 2785{,}62\,kJ/kg$; $S_{OUT}^{STEAM-SAT} = 5{,}895\,kJ/(kgK)$

$H_{OUT}^{COND} = 1178{,}12\,kJ/kg$; $S_{OUT}^{COND} = 2{,}963\,kJ/(kgK)$

$$\Delta \overset{\bullet}{EX}{}_{HOT}^{T} = \overset{\bullet}{EX}{}_{OUT}^{T} - \overset{\bullet}{EX}{}_{IN}^{T} = \overset{\bullet}{m}_{OUT} \cdot ex_{OUT}^{T} - \overset{\bullet}{m}_{IN} \cdot ex_{IN}^{T}$$

$$=170,33\times(784,79-298\times 2,178)+4,15\times(2718,4-298\times 5,964)+78,79\times(1032,28-298\times 2,69)$$

$$+3,07\times(2785,62-298\times 5,895)+58,26\times(1178,12-298\times 2,963)$$

$$-82,94\times(2718,4-298\times 5,964)-61,32\times(2785,62-298\times 5,927)$$

$$=23121,62+3905,68+18173,7+3158,75+17195,2-78057,16-62508,01$$

$$=-75010,22kW=-75,01MW$$

Cold Side

Inlet

Saturated steam (88%, 185,4°C) from HP turbine: the mass flow rate of saturated steam is $\dot{m}_{IN}^{HP-STEAM-SAT}=1452,32\ kg/s$ at $P_{IN}^{HP-STEAM-SAT}=1,13MPa=1130\ kPa$;

$H_{IN}^{HP-STEAM-SAT}=2540\ kJ/kg$; $S_{IN}^{HP-STEAM-SAT}=6,02\ kJ/(kgK)$

Outlet

Superheated steam to LP turbines: the mass flow rate is $\dot{m}_{OUT}^{LP-STEAM-SH}=1281,99\ kg/s$ at $P_{OUT}^{LP-STEAM-SH}=1,1MPa=1100\ kPa$ and $T_{OUT}^{LP-STEAM-SH}=254,61°C=527,61K$;

$H_{OUT}^{LP-STEAM-SH}=2949,83\ kJ/kg$; $S_{OUT}^{LP-STEAM-SH}=6,897\ kJ/(kgK)$

$$\Delta\dot{EX}_{COLD}^{T}=\dot{EX}_{OUT}^{T}-\dot{EX}_{IN}^{T}=\dot{m}_{OUT}\cdot ex_{OUT}^{T}-\dot{m}_{IN}\cdot ex_{IN}^{T}$$

$$=1281,99\times(2949,83-298\times 6,897)-1452,32\times(2540-298\times 6,02)$$

$$=1146770,82-1083488,81=63282,01kW=63,28MW$$

Moisture separator and reheater balance:

$$\Delta\dot{EX}^{T}=\Delta\dot{EX}_{HOT}^{T}+\Delta\dot{EX}_{COLD}^{T}=-75,01+63,28=-11,73MW$$

7.2.2.11. HP Steam Turbines

The calculation of mechanical exergy balance accounts for the output mass flow rate to the moisture separator and reheater (MSH) equal to the input mass flow rate to the HP steam turbines, thus neglecting the steam extraction to feedwater preheaters and to the condenser. This mass flow rate represents the 79,6% of the total input mass flow rate through the MSV valve. This approximation is assumed to simplify the calculation that, instead, would require the calculation of mechanical exergy for any expansion step, with variable mass flow rates, specific volumes and enthalpies. The reference environment condition to calculate the mechanical exergy are: $P_R = 0{,}1 MPa = 100 kPa$ and $V_R = 0{,}845\, m^3/kg$ so that $P_R V_R = 84{,}5\, kJ/kg$. The universal gas constant of water steam is $\overline{R} = 461{,}5 J/(kg \cdot K) = 0{,}4615 kJ/(kgK)$.

Hot Side

Inlet

Saturated steam (99,8%, 270,72°C) from steam generator to HP turbine: the mass flow rate of superheated steam is $\overset{\bullet}{m}_{IN}^{HP-STEAM-SAT} = 1452{,}32\, kg/s$ at $P_{IN}^{HP-STEAM-SAT} = 5{,}57\, MPa = 5570\, kPa$; $T_{IN}^{HP-STEAM-SAT} = 270{,}72\,°C = 543{,}72\, K$

$H_{IN}^{HP-STEAM-SAT} = 2785{,}62\, kJ/kg$;

$v_{IN}^{HP-STEAM-SAT} = 0{,}0351 m^3/kg$;

$$\left(S_{IN}^{HP-STEAM-SAT}\right)^M = 0{,}4615 \times \ln 0{,}0351 = 0{,}4615 \times (-3{,}349) = -1{,}545\, kJ/(kgK)$$

$$\left(EX_{IN}^{HP-STEAM-SAT}\right)^M = H_{IN}^{HP-STEAM-SAT} + P_R V_R \left(\overline{R} \ln v_{IN}^{HP-STEAM-SAT}\right)$$

$$= 2785{,}62 + 84{,}5 \times (-1{,}545) = 2655{,}07\, kJ/kg$$

The non-useful work interaction released to the environment, and constituting the inherent mechanical exergy destruction along the steam expansion process at inlet conditions is:

$$\left(EX_{IN}^{HP-STEAM-SAT}\right)_{DESTR}^M = P_R V_R \left(\overline{R} \ln v_{IN}^{HP-STEAM-SAT}\right) = -130{,}55\, kJ/kg$$

Outlet

Saturated steam (88%, 185,4°C) to MSH: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{OUT}^{HP-STEAM-SAT} = 1452{,}32\, kg/s$ at $P_{OUT}^{HP-STEAM-SAT} = 1{,}13 MPa = 1130\, kPa$;

$H_{OUT}^{HP-STEAM-SAT} = 2540\ kJ/kg$;

$v_{OUT}^{HP-STEAM-SAT} = 0.152\, m^3/kg$;

$\left(S_{OUT}^{HP-STEAM-SAT}\right)^M = 0{,}4615 \times \ln 0{,}152 = 0{,}4615 \times (-1{,}884) = -0{,}869\ kJ/(kgK)$

$$\left(EX_{OUT}^{HP-STEAM-SAT}\right)^M = H_{OUT}^{HP-STEAM-SAT} + P_R V_R \left(\overline{R} \ln v_{OUT}^{HP-STEAM-SAT}\right)$$

$$= 2540 + 84{,}5 \times (-0{,}869) = 2466{,}57\, kJ/kg$$

The non-useful work interaction released to the environment, and constituting the inherent mechanical exergy destruction along the steam expansion process at outlet conditions is:

$$\left(EX_{OUT}^{HP-STEAM-SAT}\right)_{DESTR}^M = P_R V_R \left(\overline{R} \ln v_{OUT}^{HP-STEAM-SAT}\right) = -73{,}43\, kJ/kg$$

$$\Delta \dot{EX}^M = \dot{EX}_{OUT}^M - \dot{EX}_{IN}^M = \dot{m}_{OUT} \cdot ex_{OUT}^T - \dot{m}_{IN} \cdot ex_{IN}^T$$

$$= 1452{,}32 \times (2466{,}5 - 2655{,}07) = -273863{,}98 kW = -273{,}86 MW$$

The same above $\Delta \dot{EX}^M$ calculated considering non-useful work interactions corresponding to the mechanical exergy destruction is finally:

$$= 1452{,}32 \times (-73{,}43 + 130{,}55) = 82956{,}52 kW = 82{,}956 MW$$

Cold Side

The cold side of a steam turbine is represented by the work interaction (or mechanical power) corresponding to the enthalpy variation along the steam expansion process. Hence, it is calculated by the difference between input and output enthalpies of same streams included in the balance of hot side.

Saturated steam (99,8%) from steam generator to HP turbine: the mass flow rate of superheated steam is

$\dot{m}_{IN}^{HP-STEAM-SAT} = 1452{,}32\ kg/s$ at $P_{IN}^{HP-STEAM-SAT} = 5{,}57\, MPa = 5570\ kPa$;

$T_{IN}^{HP-STEAM-SAT} = 270{,}72\,°C = 543{,}72\, K$;

$H_{IN}^{HP-STEAM-SAT} = 2785{,}62\, kJ/kg$;

Saturated steam (88%, 185,4°C) to MSH: the mass flow rate of saturated steam is

$\dot{m}_{OUT}^{HP-STEAM-SAT} = 1452{,}32\ kg/s$ at $P_{OUT}^{HP-STEAM-SAT} = 1{,}13 MPa = 1130\ kPa$;

$H_{OUT}^{HP-STEAM-SAT} = 2540\ kJ/kg$;

$\overset{\bullet}{m}^{HP-STEAM-SAT} \left(H_{OUT}^{HP-STEAM-SAT} - H_{IN}^{HP-STEAM-SAT}\right)$

$= 1452{,}32 \times (2540 - 2785{,}62) = -356718{,}84 kW = -356{,}7 MW$

HP steam turbines balance: $\Delta \overset{\bullet}{EX}^{M} = \Delta \overset{\bullet}{EX}{}^{M}_{HOT} + \Delta \overset{\bullet}{EX}{}^{M}_{COLD} = -273{,}86 + 356{,}7 = 82{,}84 MW$

The fact that the resulting exergy flow is positive means that the exergy flow output is released to the external system (represented by the electrical grid). This power is reduced with respect to the enthalpy variation (times the mass flow rate) due to the mechanical internal energy loss to the external mechanical reservoir according to the very definition of mechanical exergy characterizing the mechanical internal energy of the saturated steam. This mechanical exergy variation constitutes the mechanical exergy destruction along the saturated steam expansion process.

7.2.2.12. LP Steam Turbines

According to the assumption posited for HP steam turbines, in the case of LP steam turbines too the calculation of mechanical exergy balance accounts for the equality of output mass flow rate to the condenser and input mass flow rate to the LP steam turbines, thus neglecting the steam extraction to feedwater preheaters. This mass flow rate represents the 78,5% of the total input mass flow rate through the CIV valve. The reference environment conditions to calculate the mechanical exergy and the universal gas constant of water steam are the same.

Hot Side

Inlet

Superheated steam from second reheater to LP turbines: the mass flow rate is $\overset{\bullet}{m}{}_{IN}^{LP-STEAM-SH} = 1006\ kg/s$ at $P_{IN}^{LP-STEAM-SH} = 1{,}1 MPa = 1100\ kPa$ and $T_{IN}^{LP-STEAM-SH} = 254{,}61°C = 527{,}61 K$;

$H_{IN}^{LP-STEAM-SH} = 2949{,}83 kJ/kg$;

$v_{IN}^{LP-STEAM-SH} = 0{,}213 m^3/kg$

$\left(S_{IN}^{LP-STEAM-SH}\right)^M = \overline{R}\left(\ln v_{IN}^{LP-STEAM-SH}\right) = 0{,}4615 \times \ln 0{,}213 = 0{,}4615 \times (-1{,}546) = -0{,}713\ kJ/kg$

$\left(EX_{IN}^{LP-STEAM-SH}\right)^M = H_{IN}^{LP-STEAM-SH} + P_R V_R \left(S_{IN}^{LP-STEAM-SH}\right)^M$

$$= 2949{,}83 + 84{,}5 \times (-0{,}713) = 2889{,}58\, kJ/kg$$

The non-useful work interaction released to the environment, and constituting the inherent mechanical exergy destruction along the steam expansion process at inlet conditions is:

$$\left(EX_{IN}^{LP-STEAM-SAT}\right)_{DESTR}^{M} = P_R V_R \left(\overline{R} \ln v_{IN}^{LP-STEAM-SAT}\right) = -60{,}25\, kJ/kg$$

Outlet

Saturated steam (90%, 45°C) to condenser: the mass flow rate of saturated steam is

$$\overset{\bullet}{m}_{OUT}^{LP-STEAM-SAT} = 1006\ kg/s \text{ at } P_{OUT}^{CONDENSER} = 0{,}0091\, MPa = 9{,}1 kPa\ ;\ T_{OUT}^{CONDENSER} = 45\,°C = 318\, K$$

$$H_{OUT}^{LP-STEAM-SAT} = 2583{,}2\, kJ/kg\ ;$$

$$v_{OUT}^{LP-STEAM-SAT} = 15{,}258\, m^3/kg\ ;$$

$$\left(S_{OUT}^{LP-STEAM-SAT}\right)^{M} = 0{,}4615 \times \ln 15{,}258 = 0{,}4615 \times (2{,}725) = 1{,}257\ kJ/(kgK)$$

$$\left(EX_{OUT}^{LP-STEAM-SAT}\right)^{M} = H_{OUT}^{LP-STEAM-SAT} + P_R V_R \left(\overline{R} \ln v_{OUT}^{LP-STEAM-SAT}\right)$$

$$= 2583{,}2 + 84{,}5 \times (1{,}257) = 2689{,}42\, kJ/kg$$

The non-useful work interaction released to the environment, and constituting the inherent mechanical exergy destruction along the steam expansion process at outlet conditions is:

$$\left(EX_{OUT}^{LP-STEAM-SAT}\right)_{DESTR}^{M} = P_R V_R \left(\overline{R} \ln v_{OUT}^{LP-STEAM-SAT}\right) = 106{,}22\, kJ/kg$$

$$\Delta \overset{\bullet}{EX}^{M} = \overset{\bullet}{EX}_{OUT}^{M} - \overset{\bullet}{EX}_{IN}^{M} = \overset{\bullet}{m}_{OUT} \cdot ex_{OUT}^{T} - \overset{\bullet}{m}_{IN} \cdot ex_{IN}^{T}$$

$$= 1006 \times (2689{,}42 - 2889{,}58) = -201360{,}96 kW = -201{,}36 MW$$

The same above $\Delta \overset{\bullet}{EX}^{M}$ calculated considering non-useful work interactions corresponding to the mechanical exergy destruction is finally:

$$= 1006{,}22 \times (106{,}22 + 60{,}25) = 82956{,}52 kW = 166{,}47 MW$$

Cold Side

For sake of clarity, it is here repeated that the cold side of a steam turbine is represented by the work interaction (or mechanical power) corresponding to the enthalpy variation along the steam expansion process. Hence, it is calculated by the difference between input and output enthalpies of same streams included in the balance of hot side.

Superheated steam from second reheater to LP turbines: the mass flow rate is $\overset{\bullet}{m}_{IN}^{LP-STEAM-SH} = 1006\ kg/s$ at $P_{IN}^{LP-STEAM-SH} = 1{,}1 MPa = 1100\ kPa$ and $T_{IN}^{LP-STEAM-SH} = 254{,}61°C = 527{,}61K$;

$H_{IN}^{LP-STEAM-SH} = 2949{,}83\, kJ/kg$;

Saturated steam (90%, 45°C) to main steam condenser: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{OUT}^{LP-STEAM-SAT} = 1006\ kg/s$ at $P_{OUT}^{CONDENSER} = 0{,}0091\, MPa = 9{,}1 kPa$; $T_{OUT}^{CONDENSER} = 45\,°C = 318\,K$

$H_{OUT}^{LP-STEAM-SAT} = 2583{,}2\, kJ/kg$;

$$\overset{\bullet}{m}^{LP-STEAM-SAT} \left(H_{OUT}^{LP-STEAM-SAT} - H_{IN}^{LP-STEAM-SAT}\right)$$

$$= 1006 \times (2583{,}2 - 2949{,}83) = -368829{,}78 kW = -368{,}8 MW$$

LP steam turbines balance: $\Delta \overset{\bullet}{EX}^{M} = \Delta \overset{\bullet}{EX}_{HOT}^{M} + \Delta \overset{\bullet}{EX}_{COLD}^{M} = -201{,}36 + 368{,}8 = 167{,}44 MW$

7.2.2.13. Main Steam Condenser

Hot Side

Inlet

Saturated steam (90%, 45°C) from LP turbine: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{IN}^{LP-STEAM-SAT} = 1006{,}34\, kg/s$ at $P_{IN}^{CONDENSER} = 0{,}0091\, MPa = 9{,}1 kPa$; $T_{IN}^{CONDENSER} = 45\,°C = 318\,K$

$H_{IN}^{LP-STEAM-SAT} = 2583{,}2\, kJ/kg$; $S_{IN}^{LP-STEAM-SAT} = 8{,}165\ kJ/(kgK)$

Saturated steam (91,5%, 75,86°C) from LP turbine: the mass flow rate of saturated steam is $\overset{\bullet}{m}_{IN}^{LP-STEAM-SAT} = 5{,}17\ kg/s$ at $P_{IN}^{LP-TURBINE} = 0{,}04\, MPa = 40\, kPa$;

$H_{IN}^{LP-STEAM-SAT} = 2443,46\,kJ/kg$; $S_{IN}^{LP-STEAM-SAT} = 7,1\,kJ/(kgK)$

Condensate from LP turbine: the mass flow rate of condensate is $\dot{m}_{IN}^{COND} = 23\,kg/s$ at $P_{IN}^{COND} = 0,04\,MPa = 40\,kPa$ and $T_{IN}^{COND} = 62\,°C = 335\,K$

$H_{IN}^{COND} = 261,21\,kJ/kg$; $S_{IN}^{COND} = 0,856\,kJ/(kgK)$

Saturated steam (95,5%, 185,29°C) from Steam Generator and HP turbine: the mass flow rate of saturated steam is $\dot{m}_{IN}^{HP-STEAM-SAT} = 1,33\,kg/s$ at $P_{IN} = 1,13\,MPa = 1130\,kPa$;

$H_{IN}^{HP-STEAM-SAT} = 2690,02\,kJ/kg$; $S_{IN}^{STEAM-SAT} = 6,347\,kJ/(kgK)$;

Outlet

Feedwater to preheaters: the mass flow rate of feedwater is $\dot{m}_{OUT}^{FEEDWATER} = 1285,64\,kg/s$ at $P_{OUT}^{FEEDWATER} = 0,0091\,MPa = 9,1\,kPa$ and $T_{OUT}^{FEEDWATER} = 42,6°C = 315,6\,K$

$H_{OUT}^{FEEDWATER} = 178\,kJ/kg$; $S_{OUT}^{FEEDWATER} = 0,6\,kJ/(kgK)$

Main steam condenser hot side balance: $\Delta \dot{EX}_{HOT}^{T} = \dot{EX}_{OUT}^{T} - \dot{EX}_{IN}^{T} = \dot{m}_{OUT} \cdot ex_{OUT}^{T} - \dot{m}_{IN} \cdot ex_{IN}^{T}$

$$= 1258,64 \times (178 - 298 \times 0,6) - 1006,34 \times (2583,2 - 298 \times 8,165) - 5,17 \times (2443,46 - 298 \times 7,1)$$

$$- 23 \times (261,21 - 298 \times 0,856) - 1,33 \times (2690,02 - 298 \times 6,347)$$

$$= -1006,9 - 150779,92 - 1694 - 140,8 - 1062,16 = -154683,78\,kW = -154,68\,MW$$

Cold Side

As far as the cold side of main steam condenser is concerned, it can be assumed that the temperature of external cooling medium is coincident with the reservoir $T_R = 25°C = 298K$, so that the thermal exergy variation of the cold side of the main steam condenser is null.

Main steam condenser balance: $\Delta \dot{EX}^{T} = \Delta \dot{EX}_{HOT}^{T} + \Delta \dot{EX}_{COLD}^{T} = -154,68 + 0 = -154,68\,MW$

7.3. ABWR and AP1000 Exergetic Efficiency Calculation and Comparison

On the basis of the exergy destruction calculated for any of the main components of the conventional plant and the exergy input released from the nuclear core, the calculation of the overall exergetic efficiency can be carried out for both ABWR and AP1000 nuclear plant design. Notwithstanding the detailed analysis and calculation of exergy destruction in all main plant components has been carried out for the conventional part of AP1000 design only, an evaluation and estimation is feasible considering an adequate scale out of thermal power and mass flow rates circulating among all components.

The expression adopted for the exergetic efficiency is the following:

$$\eta^{EX} = 1 - \frac{\sum_{COMPONENTS} \dot{EX}^{G}_{DESTR}}{\dot{EX}_{INPUT}}$$

Considering first the AP1000 plant components exergy destruction set forth starting from the first preheater through all plant components up to the main steam condenser:

$$\sum_{COMPONENTS} \dot{EX}^{G}_{DESTR} = 18{,}99 + 7{,}18 + 1{,}07 + 1{,}74 + 9{,}86 + 2{,}18 + 4{,}11 + 221{,}66 + 11{,}73 + 82{,}96 + 166{,}47 + 154{,}68$$

$$= 682{,}63MW$$

$$\dot{EX}_{INPUT} = \dot{Q}_{FISSION} = 3400 \times \left(1 - \frac{298}{873}\right) = 2239{,}4MW$$

$$\eta^{EX}_{AP1000} = 1 - \frac{682{,}63}{2239{,}4} = 0{,}69$$

Considering the thermal power ABWR: 3926 MWt and AP1000 3400 MWt, the ratio of power 3926/3400 = 1,15 so that the amount of exergy destruction can be estimated by a scale up of the exergy destruction of AP1000. However, the exergy destruction of the steam generator has to be removed since this component is not part of the ABWR plant configuration:

$$\sum_{COMPONENTS}^{ABWR} EX^{G}_{DESTR} = \left(\sum_{COMPONENTS}^{AP1000} EX^{G}_{DESTR} - EX^{STEAM-GENERATOR}_{DESTR} \right) \times 1{,}15 = (682{,}63 - 221{,}66) \times 1{,}15 = 530{,}11MW$$

$$\dot{EX}_{INPUT} = \dot{Q}_{FISSION} = 3926 \times \left(1 - \frac{298}{873}\right) = 2585{,}85MW$$

$$\eta_{ABWR}^{EX} = 1 - \frac{530{,}11}{2585{,}85} = 0{,}79$$

As a final outcome, the comparison between the two exergetic efficiencies values above calculated confirms that, in case of indirect Rankine process of AP1000, the exergy destruction occurring in the steam generator is affecting the overall performance that remains lower with respect to the direct Rankine process of ABWR where the steam generator is missing.

8. EU DEMO FUSION REACTOR EXERGY ANALYSIS

Purpose of the present study is the exergy analysis of EU DEMO pulsed fusion power plant considering the Primary Heat Transfer Systems, the Intermediate Heat Transfer System (IHTS) including the Energy Storage System (ESS) as a first option to ensure the continuity of electric power released to the grid. A second option here considered is a methane fired auxiliary boiler replacing the ESS. The Power Conversion System (PCS) performance is evaluated as well in the overall balance. The performance analysis is based on the exergy method to specifically assess the amount of exergy destruction determined by irreversible phenomena along the whole cyclic process. The pulse and dwell phases of the reactor operation are evaluated considering the state of the art of the ESS adopting molten salts alternate heating and storage in a hot tank followed by a cooling and recovery of molten salt in a cold tank to ensure the continuity of power release to the electrical grid. An alternative plant configuration is evaluated on the basis of an auxiliary boiler replacing the ESS with a 10% of the power produced by the reactor during pulse mode.

8.1. Description of Fusion Reaction and Plant Configuration

EU DEMO [8.1] is the pulsed fusion power plant under design in the framework of the international cooperation coordinated by the Eurofusion Consortium.

The nuclear fusion with the most suitable characteristics for the industrial use is the reaction between deuterium and tritium [8.2]:

$$_1D^2 + {}_1T^3 \rightarrow {}_2He^4(3.5MeV) + n(14.1MeV).$$

The generation of Tritium, not available in the amount needed to fuel the reaction, is obtained by means of a breeding nuclear reaction occurring with Lithium nuclei, stored in the blanket of plasma chamber, according to the following reactions [8.2]:

$$_3Li^6 + n(14.1MeV) \rightarrow {}_2He^4(3.5MeV) + {}_1T^3 + 4.78MeV$$

$$_3Li^7 + n \rightarrow {}_2He^4 + {}_1T^3 + n - 2.47MeV$$

These reactions, ensuring the continuity of the nuclei fusion process, rely on the Tritium production in the Breeding Zone (BZ) of the blanket where thermal power is produced in addition to the amount generated by neutrons in the First Wall (FW). BZ and FW are components of the Primary Heat Transfer Systems (PHTS) and both provide a contribution to the overall thermal power conveyed to the Power Conversion System (PCS) producing the electric power released to the external grid. Two main concepts are actually proposed and developed for the EU-DEMO: Helium-Cooled Pebble Bed (HCPB) [8.3] and Water-Cooled Lithium Lead (WCLL) [8.4]. The WCLL concept, selected as reference in this paper, is based on liquid lithium-lead eutectic as breeder and water to remove the generated heat into the blanket (through tubes inserted into the BZ and into the FW). The BZ and FW Primary Heat Transfer Systems (PHTS) are the water circuits, derived from the Pressurized Water Reactors (PWR) fission power plant technology, capable to produce steam for the turbine.

Other additional heat sources are the divertor (DIV) and the vacuum vessel (VV), but the power generated is limited and at low temperature (130 – 210 °C). For this, is not possible to use DIV and VV power to produce steam and then are used as feedwater regeneration preheaters to raise the electrical efficiency.

The EU-DEMO WCLL 2017 configuration [8.4] has been used in the calculations.

DEMO is designed to operate in a pulsed mode through two alternated phases corresponding to a plasma burn and a dwell period. This operating sequence implies that the production of thermal power in BZ and FW of the reactor, and released to the PHTS, is not continuous and therefore this does not assure a continuity in the delivery of power from the PCS to the electric grid. The duration of plasma burn mode (pulse phase) is 2 hours while the duration of reduced heating power mode (dwell period) is 10 minutes during which only the decay heat is produced. The decay heat is approximately equal to 1% of the reaction heat produced during pulse mode thus creating a discontinuity in electric power release.

To provide a continuous power generation, an Intermediate Heat Transfer System (IHTS) is foreseen. This solution in the design of DEMO fusion reactor and the related Balance of Plant (BOP) has led to a configuration of the IHTS constituted by the secondary sides of Intermediate Heat Exchangers (IHX) and the Energy Storage System (ESS) consisting of two molten salt tanks operating at different temperatures [8.5]. An alternative option, here compared with the molten salt ESS, is represented by a natural gas (methane) fired boiler specially designed to generate the superheated steam conveyed to high pressure and low pressure steam turbines. Figures 1a-1b and 2a-2b show the simplified process flow diagram of the whole system including main systems and components constituting the plant configuration with ESS and with auxiliary boiler, respectively both in pulse and dwell operating modes.

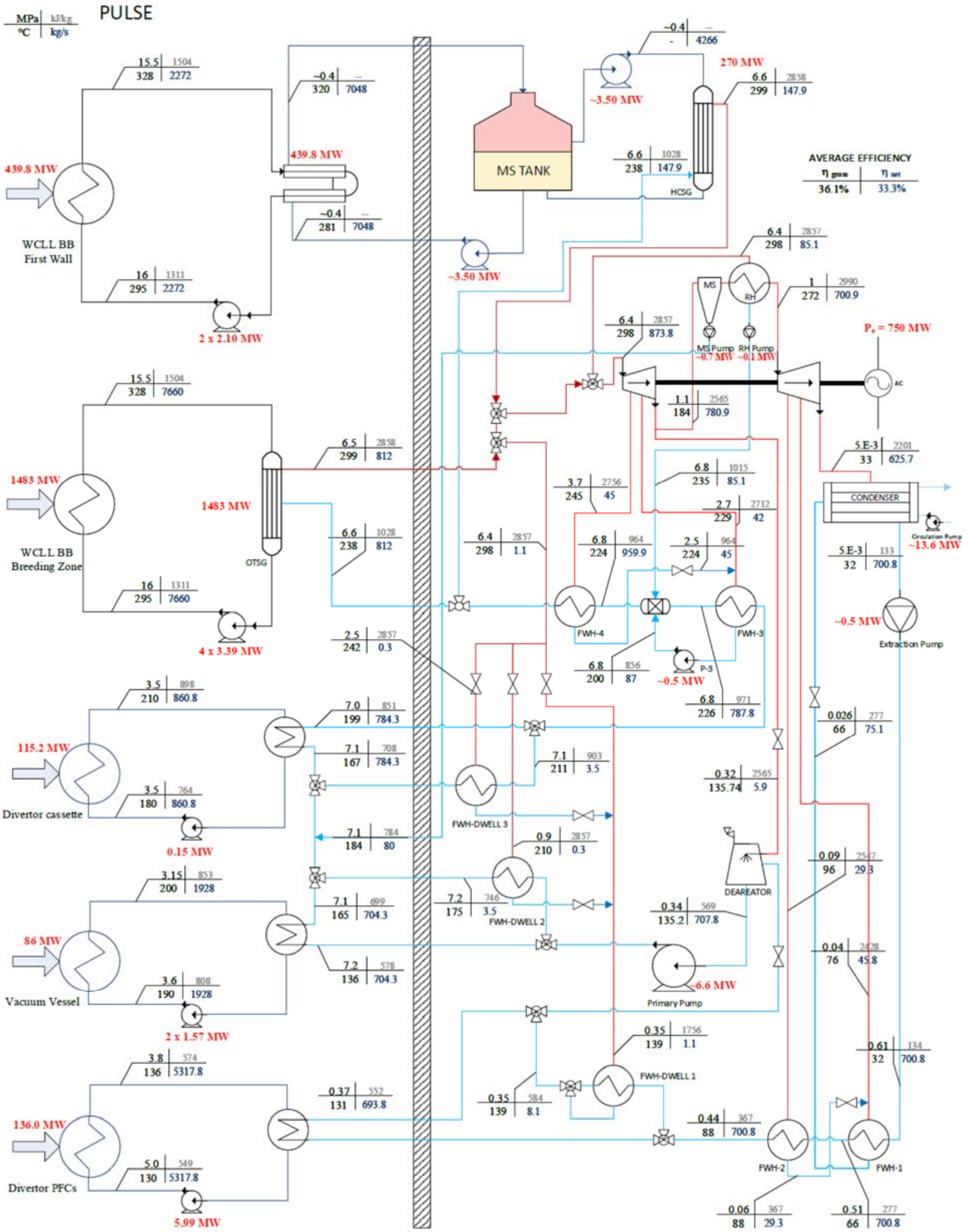


Figure 1a – Process Flow Diagram of DEMO with ESS Configuration (pulse mode)

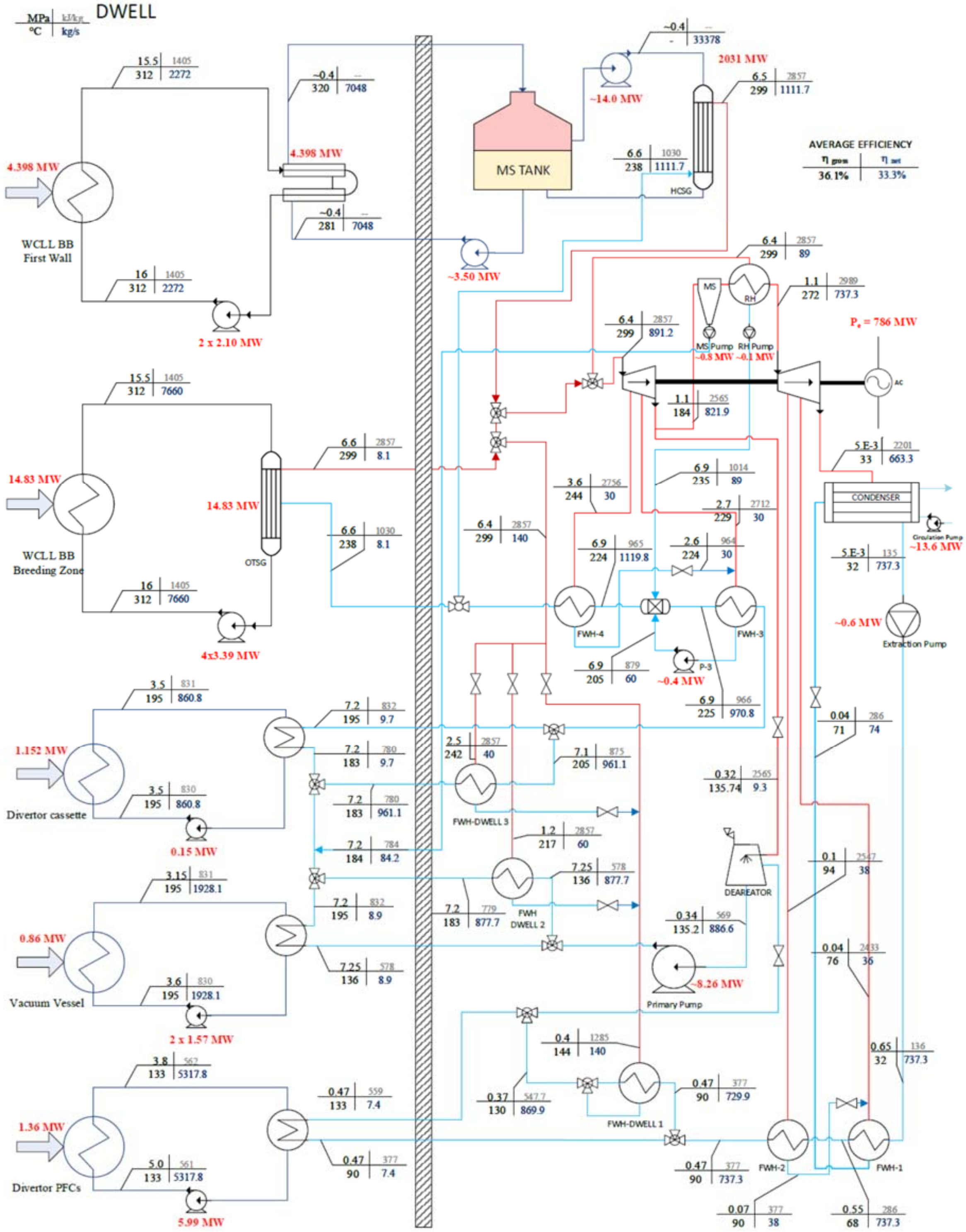


Figure 1b – Process Flow Diagram of DEMO with ESS Configuration (dwell mode)

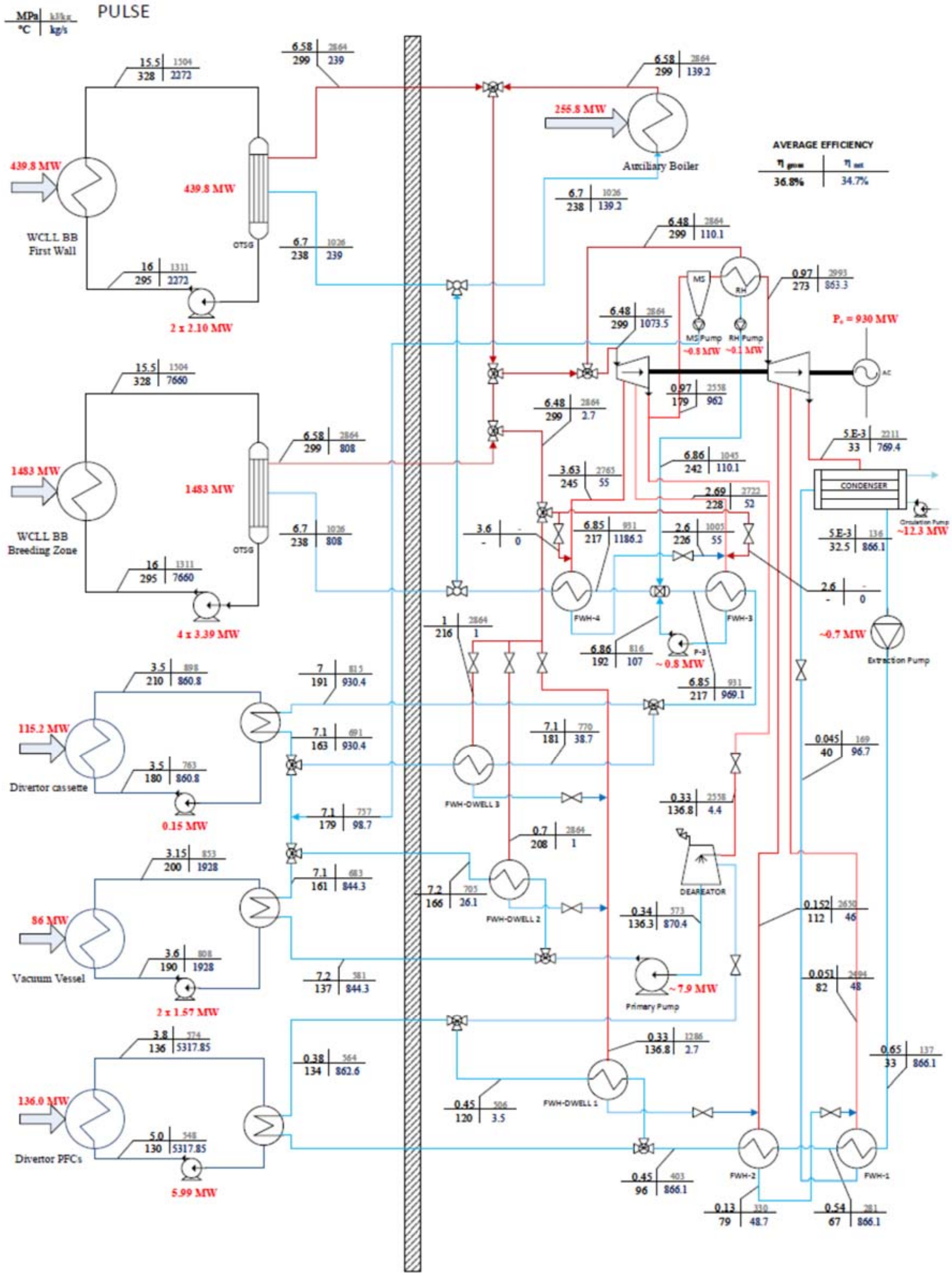


Figure 2a – Process Flow Diagram of DEMO with Auxiliary Boiler Configuration (pulse mode)

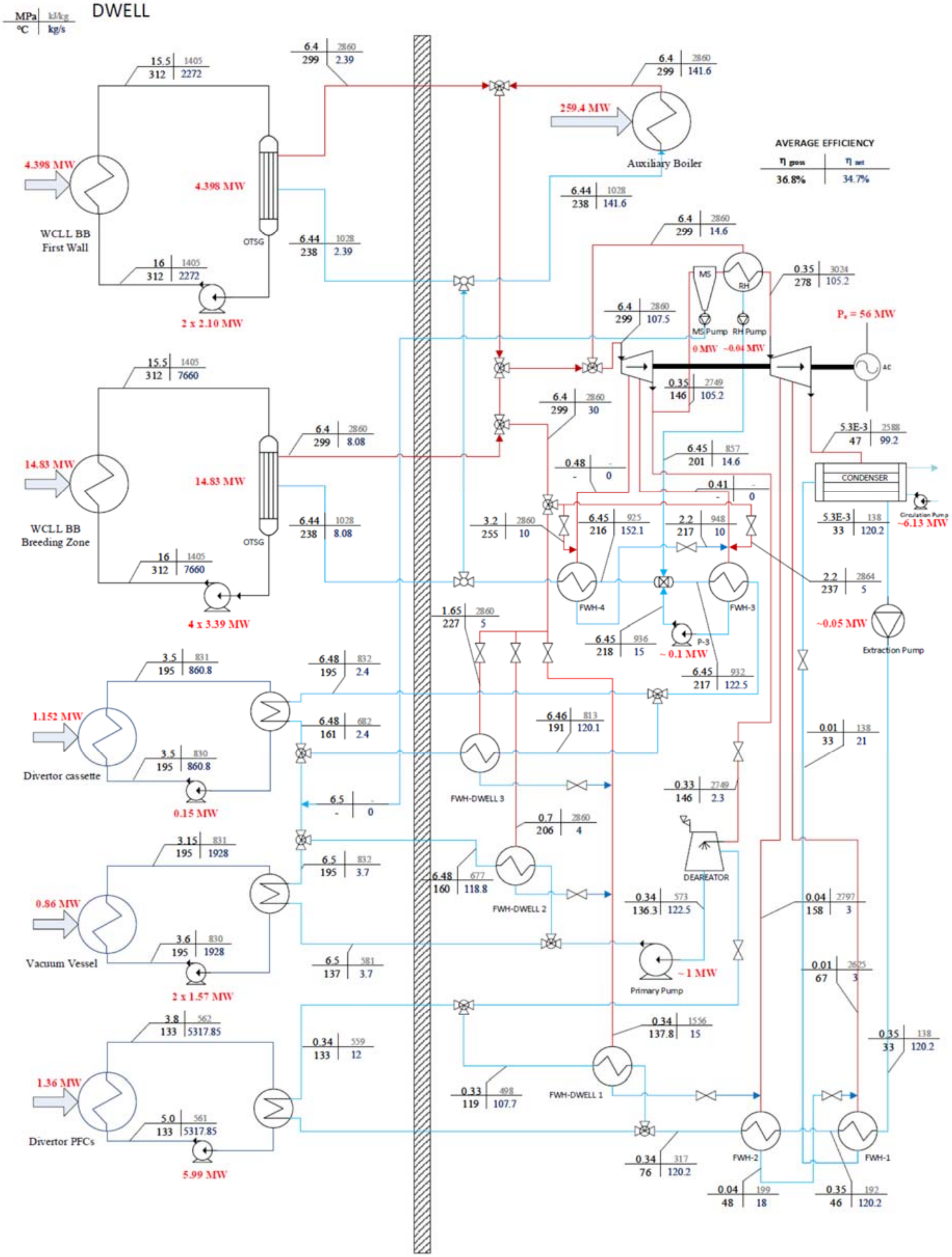


Figure 2b – Process Flow Diagram of DEMO with Auxiliary Boiler Configuration (dwell mode)

8.2. Energy Storage System Configuration

The Energy Storage System (ESS) is part of the Intermediate Heat Transfer System (IHTS) designed to feed the PCS releasing steady-state electric power to the electricity grid. The current design of the ESS is constituted by two different tanks filled in with molten salt and connected by a pipeline in which molten salt flows in two directions depending on the operating phase of the reactor [8.5]. During the pulse phase, the molten salt is moved from the cold tank to the hot tank after heat exchange with the cooling water conveyed from the FW PHTS. The hot tank stores the high temperature molten salt heated through two intermediate water-salt heat exchangers. The cold tank recovers the low temperature molten salt cooled during the dwell phase to produce the superheated steam conveyed to turbines of the PCS. This configuration requires the pumping of molten salt from the cold tank to the hot tank during dwell mode and vice versa during the opposite mode.

As far as the molten salt is concerned, HITEC is the commercial product of a ternary salt characterized by chemical, physical and thermodynamic properties suitable for process conditions requested by the ESS plant. HITEC is a eutectic mixture of water-soluble and inorganic salts of potassium nitrate KNO_3 , sodium nitrate $NaNO_3$ and sodium nitrite $NaNO_2$ [8.6] with the following composition:

- 7% of NaNO3, molecular weight 84.995 g/mol
- 40% of NaNO2 molecular weight 69.000 g/mol
- 53 % of KNO3 molecular weight 101.103 g/mol

with a molecular weight of the mixture equal to 87,134 g/mol.

The design of the ESS relies on the following parameters characterizing the physical properties and the behaviour of molten salt during heating and cooling phases:

- Liquid Phase Specific Heat
- Melting-Solidification Latent Heat
- Maximum Allowable Temperature
- Solidification Temperature
- Viscosity v/s Temperature
- Salt mass used in ESS system

HITEC molten salt specific heat at constant pressure is $C_P = 0.373\,cal/gr°C = 1.56\,kJ/(kg \cdot K)$ and it is suggested to be considered as constant value with temperature independence. However, expressions are available in the literature [8.7] to calculate enthalpy and entropy for ESS design.

During the pulse (2 h) the BZ PHTS thermal power ($1483\,MWth$) is delivered to the PCS. The FW PHTS delivers a thermal power of $439.8\,MWth$ to the ESS: a fraction of this power is transferred to the PCS, $265.9\,MWth$, and $173.9\,MWth$ are stored during the pulse phase corresponding to a stored energy of

$1.25 \times 10^6 MJ$ that will be delivered to the PCS during the dwell time. The thermal power during the pulse period is transferred from the ESS to the PCS through one Helical Coil Steam Generator (HCSG). The hot molten salt flows in shell side and transfers thermal energy to water flowing in the tube side. The molten salt temperature cycle is $280 - 320°C$. The feedwater enters in the HCSG with an inlet temperature of $238°C$ and exits with an outlet temperature of $299°C$ at $6.41 MPa$. The HCSG mass flow rate of HITEC is $4375.4\, kg/s$, and the feedwater mass flow rate, calculated with the enthalpy balance, is $284.1\, kg/s$.

During the dwell time ($600 s$), the mass flow of molten salt from hot to cold tanks is $33436\ kg/s$. The ESS tank contains $20062\, tons$ of molten salt at the beginning of dwell, thus about $11000\, m^3$ are needed to store this mass. In this phase, the ESS delivers power to PCS through four HCSGs. The average power available in dwell mode is approximately $2086 MWth$, thus the power of each HCSG is $521.5 MWth$. It is noteworthy that, one out of the four HCSGs is the one operating during pulse time to transfer $265.9 MWth$, as described. The thermal power recovered from Divertor Cassette, Divertor Plasma Facing Components (PFC) and Vacuum Vessel (VV), is used in the feedwater regenerative preheating through specifically designed heat exchangers.

Figure 1 shows the PHTS boundary conditions accounted for in the design of the PCS carried out by means of GateCycle^{TM} application. The output data and information have been gathered in a spreadsheet here adopted for further calculations of interest.
The objective of the present study is to provide a Second Law analysis of all components based on the exergy method to adopt a rigorous and complete approach to assess dissipation phenomena having an impact in the efficiency of the plant.

8.3. Methane Fired Steam Generator Configuration

An alternative option to the ESS, here evaluated and compared with the ESS, consists of an auxiliary natural gas (methane) fired steam generator to produce superheated steam during the dwell phase. Design parameters of this steam generator are derived from the process data of fusion reactor considering that the thermal power to be released during the dwell phase to ensure the continuity is some $254 MW$ corresponding to the 10% of the thermal power produced during pulse mode. It is assumed a thermal energy efficiency equal to 86% considering that the economizer is missing since the feed water pre-heating occurs using the heat interaction in divertors and vacuum vessel. The fuel considered in the present analysis is 100% methane with a Low Heating Value (LHV) equal to $802.3 kJ/mol = 50147.5\, kJ/kg$. The auxiliary boiler is assumed to operate at rated power during both pulse and dwell modes. Indeed, the constant duty prevents thermal fatigue and represents and additional thermal power contribution during pulse mode.

8.4. Exergy Method and Assumptions

The literature reports definitions and applications relating to exergetic properties underpinning the exergy method and the Second Law analysis [2.7,2.8]. The ESS is essentially characterized by the contribution of thermal energy transfer by means of heat interactions occurring in different types of exchangers. In addition, the mechanical exergy balance is accounted for. Calculation of exergy are based on the process conditions and properties deriving from the IHTS design and optimization; all data and information relating to stream interested in the present verification analysis of IHTS are those reported in the literature [8.1] as the result of a design project. Hence, dimensions and materials of plant components are not directly involved in this exergy analysis and, therefore, are not addressed to along calculations. Finally, the exergy balance is obtained from the algebraic sum of contributions pertaining to all components constituting the ESS.

As far as the dissipation processes are concerned, the heat and mass interaction flows internally to water and molten salt are neglected.

Two options are considered for the PCS supply during dwell phase:

i) ESS with molten salt hot and cold tanks;

ii) methane fuelled fired boiler for steam production.

As far as the reference system *R* is concerned, the environment conventional conditions corresponding to $25°C = 298K$ and $1bar$ is assumed. Therefore, water is in sub-cooled liquid state and its reference thermodynamic properties to calculate exergy are the specific enthalpy $h_R = 104.877 kJ/kg$ and the specific entropy $s_R = 0.367 kJ/(kg \cdot K)$.

Among those thermodynamic properties of molten salt in the liquid state implied in the exergy analysis, the following expressions are here adopted for enthalpy and entropy [8.7]:

$$H - H_R = \int_{298,15}^{T_{MELT}} C_P dT + \Delta H_{MELT} + \int_{T_{MELT}}^{T} C_P dT = 0.8 \times 10^{-1} T^2 + 27.75T - 14568.9 \frac{J}{mol}$$

$$S - S_R = \int_{298,15}^{T_{MELT}} \frac{C_P}{T} dT + \frac{\Delta H_{MELT}}{T_{MELT}} + \int_{T_{MELT}}^{T} \frac{C_P}{T} dT = 1.6 \times 10^{-1} T + 27.75 \ln T - 202.83 \frac{J}{mol \cdot K}$$

These properties are calculated with respect to the reference environment condition and are specially defined to calculate the thermal exergy variations along the ESS process. In order to ensure the uniformity with the unit of measure system here adopted, the numerical results of above functions are divided by the molecular weight of the molten salt to obtain J/kg and $J/(kgK)$ respectively.

Calculations have been carried out on the basis of GateCycle^{TM} program output resulting from the design of plant configuration as described in the process flow diagram [8.8].

8.4.1. Thermal Exergy

The canonical definition of specific thermal exergy for open bulkflow systems, through the control volume defining the contributing streams to the plant, is the following [2.7,2.8]:

$$ex^T = (h - h_R) - T_R (s - s_R)$$

in which h and s are the specific enthalpy and specific entropy at the generic thermodynamic condition of the system and h_R and s_R are the same properties at the reference state conditions of the reservoir represented by the environment. the above expression is used to evaluate the exergy balance of all heat exchangers operating in the plant. As far as the thermal exergy rates, the following expression is adopted that accounts for mass flowrates:

$$\dot{EX}^{T} = \dot{m} \cdot (h - h_R) - T_R (s - s_R)$$

8.4.2. Chemical Exergy

The comparison of performances provided by the two plant configuration options under discussion needs to evaluate the chemical exergy of the methane combustion process in the auxiliary boiler. To do so, the canonical definition of specific molar chemical exergy for open systems is adopted. The special case of hydrocarbons can be handled considering the following typical combustion reaction:

$$aCO_2 + \frac{b}{2} H_2O \leftrightarrow C_aH_b + \left(a + \frac{b}{4}\right) O_2$$

The chemical exergy relies on the molar fractions of constituents and is expressed in the form here reported [2.7,2.8] based on the difference of hydrocarbon chemical potential μ before and after the reaction at the reference system represented by the environmental reservoir R:

$$EX^{C} = \sum_{i=1}^{r} \left(W_{10}^{AR\rightarrow}\right)_i^{MAX} = \overline{R} T_R \sum_{i=1}^{r} n_i \ \ln \frac{x_i^{RR}}{x_i^{R}}$$

where r is the number of constituents or chemical species i in the system, n_i is the number of moles of the $i-th$ constituent, x_i is the molar ratio of the $i-th$ constituent with respect to the total amount of system's mass. The superscript RR indicates the restricted reference system in stable equilibrium, that is a thermodynamic state with temperature and pressure equal to those pertaining to the reservoir R (or environment). Though, reactant and product substances are usually not existing in the reference environment, hence the chemical exergy has to be calculated with respect the elementary substance constituting reactants and products and existing in the environment. The special case of hydrocarbons can be handled considering the following canonical reaction above reported. In this case too, the equilibrium reaction equation has to account for chemical potentials of species within the environment, again denoted with the superscript R, is:

$$a\mu_{CO_2}^{R} + \frac{b}{2}\mu_{H_2O}^{R} = \mu_{C_aH_b}^{R} + \left(a + \frac{b}{4}\right)\mu_{O_2}^{R}$$

where $\mu^R_{CO_2}$, $\mu^R_{H_2O}$, $\mu^R_{C_aH_b}$, $\mu^R_{O_2}$ specifically denote the chemical potential of each substance in the same reference reservoir state of the reacting hydrocarbon, for example, the standard conditions of $25°C$ and $1BarA$. Solving the above relation for $\mu^R_{C_aH_b}$:

$$\mu^R_{C_aH_b} = a\mu^R_{CO_2} + \frac{b}{2}\mu^R_{H_2O} - \left(a + \frac{b}{4}\right)\mu^R_{O_2}$$

used in all cases in which compounds, such as hydrocarbons C_aH_b, are not present in the reference environment.

Inserting this expression of $\mu^R_{C_aH_b}$ in the definition of chemical exergy $EX^C = \sum_i^n n_i \left(\mu_i^{RR} - \mu_i^R\right)$ with unitary hydrocarbon's number of moles, $n_i = n_{C_aH_b} = 1$ above stated and considering $1mol$, the specific molar chemical exergy is:

$$\overline{ex}^C_{C_aH_b} = \mu^{RR}_{C_aH_b} - \mu^R_{C_aH_b} = \mu^{RR}_{C_aH_b} - \left[a\mu^R_{CO_2} + \frac{b}{2}\mu^R_{H_2O} - \left(a + \frac{b}{4}\right)\mu^R_{O_2}\right]$$

The chemical potential $\mu^{RR}_{C_aH_b}$ of the hydrocarbon is equal to its molar Gibbs function $G = U - TS + pV = H + pV$, hence, using the expressions $\mu_i^{RR} = \overline{g}_i\left(T_R, p_R\right) + \overline{R}T_R \ln x_i^{RR}$ and $\mu_i^R = \overline{g}_i\left(T_R, p_R\right) + \overline{R}T_R \ln x_i^R$ the following is obtained:

$$\overline{ex}^C_{C_aH_b}$$

$$= \left[\overline{g}_{C_aH_b} + \left(a + \frac{b}{4}\right)\overline{g}_{O_2} - a\overline{g}_{CO_2} - \frac{b}{2}\overline{g}_{H_2O}\right]_{T_R, p_R} + \overline{R}T_R \ln\left[\frac{\left(x^R_{O_2}\right)^{a+b/4}}{\left(x^R_{CO_2}\right)^a\left(x^R_{H_2O}\right)^{b/2}}\right]$$

where x_i is the molar fraction of each i-th constituent appearing in the equation and $\bar{g}_i$ is the molar Gibbs chemical potential at standard conditions of T_R = 298.15 K and P_R = 101.325 kPa.

8.4.3. Mechanical Exergy

The use of mechanical exergy is specially devised and here adopted to evaluate the second law performance of steam turbines [2.12,2.13]. The mechanical exergy does not account for the operating fluid mass kinetic energy and gravitational or electro-magnetic potential energy of the whole mass referred to its center of gravity. These components, termed as kinetic exergy and potential exergy respectively, are neglected when considering the balance of a plant. Then mechanical exergy accounts for internal mechanical energy $U^M = U^M(p) = -pV$ that depends on pressure and volume entering and exiting the control volume identifying the elemental machine stage operating along an adiabatic process of a steam turbine. An adiabatic reversible process is defined as isoentropic since no heat interactions occur along the expansion (or compression) process. Then, the thermal exergy defined in terms of maximum net useful work, with null variation of entropy in the expression $EX^T = (H - H_R)^T - T_R(S^T - S_R^T)$, should be coincident with the enthalpy change between input and output states, $\Delta EX^T = W = H_{OUTPUT} - H_{INPUT}$. Though, this definition is pertaining to thermal exergy associated to the thermal internal energy $U^T = U^T(T) = TS$ while the adiabatic expansion releasing internal work is associated to the mechanical component of internal energy. Instead, the mechanical exergy, should be defined as the maximum net useful heat depending on the difference of mechanical internal energy between inlet and outlet operating fluid states. The definition $EX^M = (H - H_R)^M + p_R V_R(S^M - S_R^M)$ is suitable to evaluate this capability associated to pressure and the volume with respect to the pressure and specific volume of the reference state of the reservoir. The term $p_R V_R(S^M - S_R^M)$ represents the mechanical exergy loss or the non-useful work released to the reservoir at $p_R V_R$. Indeed, this term accounts for the fact that, although the variation of enthalpy equals the work interaction released to the external useful system, the capability in terms of work-to-heat conversion through and ideal cycle is not the same due to the different pressure-to-volume relationship that determines a different available mechanical internal energy. The energy loss in terms of non-useful work interaction released to the reservoir has to be accounted for in the exergy balance of steam turbines. Hence, for a steam turbine stage the following equations apply:

Input: $EX_{IN}^M = H_{IN} + p_R V_R(S_{IN}^M - S_R^M)$

Output: $W_{OUT}^{EXT} \Leftrightarrow EX_{OUT}^M = \left(Q_{IN-OUT}^{AR\rightarrow}\right)_{WORK}^{MAX}$

$$EX_{OUT}^M = H_{OUT} + p_R V_R(S_{OUT}^M - S_R^M)$$

$$EX_{DESTR}^M$$

The steam turbine mechanical exergy balance along a real process is the following:

$$\Delta EX^M = \Delta EX_{REV}^M + \Delta EX_{IRR}^M = (H_{OUT} - H_{IN}) + p_R V_R\left(S_{OUT}^{REV} - S_{IN}^{REV}\right)^M + p_R V_R\left(S^{IRR}\right)^M$$

where the term $p_R V_R(S^{IRR})^M$ represents the mechanical exergy destruction.

8.4.4. Irreversible Processes and Exergy Destruction

Real processes imply irreversible phenomena determining an amount of entropy production. The Gouy-Stodola theorem ensures the direct relationship between entropy production and exergy destruction as expressed by the following relation [2.7]:

$$EX_{DESTR}^{T} = T_R S_{IRR}^{T}$$

A formulation extended to all type of irreversible processes should account for chemical exergy destruction and mechanical exergy destruction, according to the following generalized version of Gouy-Stodola theorem:

$$EX_{DESTR}^{G} = EX_{DESTR}^{T} + EX_{DESTR}^{C} + EX_{DESTR}^{M} = T_R S_{IRR}^{T} + \mu_R S_{IRR}^{C} + p_R V_R S_{IRR}^{M}$$

that considers the generalized reservoir conditions at T_R, μ_R, and p_R ensuring the equality of all thermodynamic potentials at the stable equilibrium state.

8.4.5. Exergy Balance and Exergy Efficiency

The calculation of exergy balance of a component is obtained considering the difference of exergy content of entering and exiting mass of the same stream through the control volume. However, in case of a single stream entering without exiting or, vice versa, exiting without entering, the exergy property has to be calculated based on the canonical definition with respect to the external reference system or environment.

The exergy balance is calculated in terms of exergy rate to account for the total exergy associated to the amount of mass contributing to the balance of any plant component. Therefore, for each component the balance is expressed in terms of exergy flows (MW).

As far as the overall efficiency is concerned, the fuel and product streams are used in the literature to define the exergetic efficiency as follows:

$$\eta_{OVERALL}^{EX} = \prod_{j=1}^{n} \eta_j^{EX} = \prod_{j=1}^{n} 1 - \frac{EX_D}{EX_{F_j}} = 1 - \frac{EX_D}{\sum_{j=1}^{m} EX_{F_j}}$$

where the symbols D and F stand for destruction and fuel respectively. Anyway, for sake of clarity and uniformity, the term input (or inlet) denoted by the symbol IN will be here used in lieu of fuel.

Exergy Input:

$$\dot{EX}_{FUEL}^{PULSE} = \dot{EX}_{INPUT}^{BZ-OTSG-HOT} + \dot{EX}_{INPUT}^{FW-IHX-HOT} + \dot{EX}_{INPUT}^{DIV-CAS} + \dot{EX}_{INPUT}^{DIV-PFC} + \dot{EX}_{INPUT}^{VV}$$

$$\dot{EX}_{FUEL}^{DWELL}=\dot{EX}_{INPUT}^{BZ-OTSG-HOT}+\dot{EX}_{INPUT}^{HCSG-HOT}+\dot{EX}_{INPUT}^{DIV-CAS}+\dot{EX}_{INPUT}^{DIV-PFC}+\dot{EX}_{INPUT}^{VV}$$

Exergy Destruction:

$$\dot{EX}_{DESTR}^{PULSE}=\Delta\dot{EX}_{PULSE}$$

$$\dot{EX}_{DESTR}^{DWELL}=\Delta\dot{EX}_{DWELL}$$

To calculate the exergy rates efficiency, exergy fuel flows considered are thermal power withdrawn from the Breeding Zone, First Wall, Divertor Cassette, Divertor PFCs, and Vacuum Vessel.

The pulse-dwell sequence can be considered as a series of exergy contributions. The exergy efficiency pertaining to both modes can be calculated in terms of exergy rates. However, the expression of the overall exergy efficiency relating to the whole pulse-dwell sequence has to be obtained in terms of amount of exergy calculated along pulse and dwell time periods. The overall exergy efficiency accounts for the sum of exergy input and the sum of exergy destruction contributions during pulse and dwell modes. The expression of overall exergy efficiency characterizing ESS and auxiliary boiler configurations become the following:

$$\eta_{PULSE+DWELL}^{EX}=1-\frac{EX_{\substack{DESTR\\PULSE+DWELL}}}{EX_{\substack{INPUT\\PULSE+DWELL}}}=1-\frac{EX_{\substack{DESTR\\PULSE}}+EX_{\substack{DESTR\\DWELL}}}{EX_{\substack{INPUT\\PULSE}}+EX_{\substack{INPUT\\DWELL}}}=1-\frac{\dot{EX}_{PULSE}^{DESTR}\cdot\tau_{PULSE}+\dot{EX}_{DWELL}^{DESTR}\cdot\tau_{DWELL}}{\dot{EX}_{PULSE}^{INPUT}\cdot\tau_{PULSE}+\dot{EX}_{DWELL}^{INPUT}\cdot\tau_{DWELL}}$$

where τ_{PULSE} and τ_{DWELL} are the time duration of pulse and dwell modes.

8.5. Exergy Analyses with ESS

Two main phases, pulse and dwell, characterize the periodic dynamic process of thermal energy loading and unloading of the molten salt storage system. This alternate operation ensures the constant electric power input in the grid as an output of Power Conversion System (PCS). Analyses along both pulse and dwell processes account for all components and the results are those produced by GateCycle™ and the spreadsheet adopted to gather all data and information and to carry out the exergy analyses based on those previous pre-design and balances [8.8]. Following figures are specially focusing on BZ PHTS and FW PHTS directly conveyed to the OTSG and to PCS to highlight main components of the PHTS representing the fuel exergy input in the expression of exergy efficiency. Instead, Divertor Cassette, Divertor PFCs and Vacuum Vessel components, used for feedwater pre-heating in both pulse and dwell modes, are anyway duly accounted for in balances and efficiencies calculations, in particular for the exergy destruction contributions due to irreversible phenomena in all plant components.

8.5.1. Pulse Mode Exergy Balance

The calculation of thermal exergy variation requires enthalpy and entropy corresponding to the inlet and outlet states of water, steam and molten salts. The following figures are obtained from water and steam tables. As concerns the chemical, physical and thermodynamic properties of HITEC reference is made to data available from commercial data sheets and literature.

8.5.1.1. BZ PHTS

During the pulse mode (2 hours) the primary cooling water flowing through the BZ of the plasma chamber conveys a thermal power, equal to $2 \times 741.5 = 1483 MWth$, to two Once Through Steam Generator (OTSG) from which superheated steam is delivered to PCS steam turbines.

The OTSG primary side (hot) pressure is $15.5 MPa$ and the total water mass flow rate is $2 \times 3847 = 7694 \ kg/s$

The OTSG secondary side (cold) pressure is assumed $6.41 MPa$ and super-heated steam is produced and conveyed to the steam turbines of the Power Conversion System (PCS). The secondary side water mass flow rate per each OTSG is $2 \times 406 = 812 \ kg/s$.

BZ OTSG Primary (shell-side)

Primary cooling water inlet and outlet temperatures: $T_{INLET}^{BZ-OTSG-HOT} = 328°C = 601K$ and $T_{OUTLET}^{BZ-OTSG-HOT} = 295°C = 568K$.

BZ OTSG Secondary (tube-side)

Feedwater coolant inlet and superheated steam outlet temperatures are: $T_{INLET}^{BZ-OTSG-COLD} = 238°C = 511K$ and $T_{OUTLET}^{BZ-OTSG-COLD} = 299°C = 572K$.

BZ OTSG Thermal Exergy Destruction

The thermal exergy balance of OTSG results from the contributions due to the thermal exergy release along the shell side and the thermal exergy increase along the tube side. Therefore, the thermal exergy destruction is calculated by means of the following component balance expression:

$$\Delta \dot{EX}_{BZ-OTSG}^{DESTR} = \Delta \dot{EX}_{BZ-OTSG-HOT}^{T} + \Delta \dot{EX}_{BZ-OTSG-COLD}^{T}$$

8.5.1.2. FW PHTS

The FW PHTS is designed to recover the thermal power $439.8 MWth = 2 \times 219.9 MWth$ produced during the pulse mode (2 h) and use it to store thermal energy ($1.25 \times 10^{6} MJ$) in the molten salt that will be used during the dwell phase to produce electric power ensuring the continuity to the power output into the electrical grid. The two Intermediate Heat Exchangers (IHX) transfer the thermal power, recovered from FW PHTS by the cooling water flowing in the primary side at $15.5MPa$ with a mass flowrate of $2272\ kg/s$, to the HITEC molten salt circulating in the secondary side with a mass flowrate of $4375.4\ kg/s$ from the cold tank to the hot tank.

FW IHX Tube Side

The two Intermediate Heat Exchangers (IHX) are specifically designed to convey heat interaction from FW to the molten salt to be stored in the hot tank. IHX primary side (hot) water temperatures are the following:

$T_{INLET}^{FW-IHX-HOT} = 328°C = 601K$ and $T_{OUTLET}^{FW-IHX-HOT} = 295°C = 568K$;

FW IHX Shell Side

During the 2 hours pulse mode, IHX secondary side (cold) HITEC molten salt mass flow rate from cold to hot tank is $4375.4\ kg/s$. The inlet and outlet temperatures are: $T_{INLET}^{FW-IHX-COLD} = 280°C = 553K$ and $T_{OUTLET}^{FW-IHX-COLD} = 320°C = 593K$.

The thermal entropy is calculated considering that molten salts undergo an isovolumic process and therefore, considering that the expression is $\Delta S^T = \int_0^1 \frac{C_V dT}{T} \cong \int_0^1 \frac{C_P dT}{T} = C_P \ln\frac{T_1}{T_0} = C_P \ln\frac{T_{OUTLET}}{T_{INLET}}$ applied to the sensible heat and latent heat during melting so that the thermal exergy is: $\Delta \dot{EX}^{FW-IHX-COLD} = \dot{m}(\Delta H - T_R \Delta S^T)^{FW-IHX-COLD}$ where the experimental expression of enthalpy and thermal entropy for molten salts depending on the temperature is shown in the previous section 2 and is reported in the literature [8.6,8.7].

IHX Thermal Exergy Destruction

The thermal exergy balance of IHXs results from the contributions due to the thermal exergy release along the shell side and the thermal exergy increase along tube side. Therefore, the thermal exergy destruction is calculated by means of the following component balance expression:

$$\Delta \dot{EX}_{FW-IHX}^{DESTR} = \Delta \dot{EX}_{FW-IHX-HOT}^{T} + \Delta \dot{EX}_{FW-IHX-COLD}^{T}$$

Pulse Mode Mechanical Exergy Balance

During the pulse mode, the circulation through OTSG and IHX requires mechanical power to be spent and dissipated along the circuit.

BZ OTSG Mechanical Exergy Destruction

The amount of mechanical power moving the BZ cooling water through OTSG shell side is $7.2MW$

As regard the tube side of OTSGs, the mechanical power results from the contribution of condenser extraction pump equal to $0.3MW$, and the circulation pump equal to $5MW$ resulting in a total amount of $5.3MW$, therefore:

$$\Delta \dot{EX}^{M}_{BZ-OTSG} = 12.5MW$$

FW IHXs Mechanical Exergy Destruction

The power moving the FW cooling water through IHXs tube side is $2.1MW$. For IHXs shell side, molten salts are moved from the cold tank to the hot tank by means of pumps delivering a mechanical power equal to $3.5MW$, therefore:

$$\Delta \dot{EX}^{M}_{IHX} = 5.6MW$$

BZ OTSGs and FW IHXs Mechanical Exergy Balance

Finally, the total amount of mechanical power during pulse mode results in the destruction of mechanical exergy dissipated along the motion and resulting in the pressure loss; the balance of mechanical exergy destruction is the following:

$$\Delta \dot{EX}^{M}_{PULSE} = \Delta \dot{EX}^{M}_{BZ-OTSG} + \Delta \dot{EX}^{M}_{FW-IHX}$$

$$= (7.2 + 0.3 + 5)_{BZ-OTSG} + (2.1 + 3.5)_{FW-IHX} = 12.5 + 5.6 = 18.1MW$$

Pulse Mode Total Exergy Balance.

The total exergy balance related to pulse mode includes the OTSG and IHX thermal exergy and mechanical exergy flow.

$$\Delta \dot{EX}_{PULSE} = \Delta \dot{EX}^{T}_{PULSE} + \Delta \dot{EX}^{M}_{PULSE}$$

Finally, Table 1 summarizes the exergy analysis of this configuration in pulse mode.

Table 1 – DEMO Exergy Input and Exergy Destruction with ESS in Pulse Mode

DEMO Configuration with ESS - Pulse Mode					
PRIMARY HEAT TRANSFER SYSTEM COMPONENT	**MASS FLOW RATE (kg/s)**	**SPECIFIC ENTROPY (kJ/(kg*K))**	**SPECIFIC EXERGY (kJ/kg)**	**EXERGY INPUT RATE (MW)**	**EXERGY DESTRUCTION RATE (MW)**
BZ OTSG Hot Inlet (primary shell side)	7694.67	3.5085	462.723	3560.5	-45.138
FW IHX Hot Inlet (primary shell side)	2272	3.7057	402.888	915.361	-4.2091
Divertor Cass. Hot Inlet (primary shell side)	860.8	2.4220	180.978	155.786	-2.4613
Divertor PFCs Hot Inlet (primary shell side)	5317.85	1.69430	73.91	393.040	-6.6047
Vacuum Vessel Hot Inlet (primary shell side)	1927.68	2.3283	163.659	315.484	-6.3492

8.5.2. Dwell Mode Exergy Balance

Similarily to the case of pulse mode, the thermal exergy balance in dwell mode requires enthalpy and entropy properties corresponding to the inlet and outlet states of molten salts, water and superheated steam flowing through four Helical Coil Steam Generators.

8.5.2.1. Helical Coil Steam Generators

The Helical Coil Steam Generators (HCSG) are designed to transfer the thermal energy stored in the hot molten salt to the feedwater to generate the superheated steam to be expanded in steam turbines. During dwell time of 10 minutes, the hot molten salt stored in the hot tank is delivered to four HCSGs before being recovered in the cold tank. The molten salt flows from hot tank to cold tank through HCGS shell side and releases the thermal power to the feedwater flowing in the tube side with a mass flow rate of $4 \times 255 = 1020 \; kg/s$ $(3672 \; t/h)$ at $6.41 MPa$ and exits as superheated steam conveyed to be expanded in steam turbines of PCS.

HCSG Shell Side

The HCSG shell side molten salt temperatures are [5]: $T_{INLET}^{HCSG-SHELL} = 320°C = 593K$ and $T_{OUTLET}^{HCSG-SHELL} = 280°C = 553K$.

The enthalpy is calculated as: $\Delta H^{HCSG-SHELL} = C_P\left(T_{OUTLET}^{HCSG-SHELL} - T_{INLET}^{HCSG-SHELL}\right)$; the absolute value of enthalpy variation is equal during pulse and dwell phases as no energy accumulation is foreseen in the molten salts. Also in this case, the thermal entropy is calculated by means of the same expression already adopted, for the pulse phase in this case expressing an entropy decrease due to cooling corresponding to the entropy increase of molten salt heating during the pulse phase.

The thermal exergy flow input needed to calculate the exergy efficiency is the following:

$$\dot{EX}_{INPUT}^{HCSG-PRIMARY} = \dot{m}\left[\left(H_{INLET}^{HCSG-PRIMARY} - H_R\right) - T_R\left(S_{INLET}^{HCSG-PRIMARY} - S_R\right)\right]$$

$$= \dot{m} \cdot \left[C_P\left(T_{INLET}^{HCSG-SHELL} - T_R\right) - T_R C_P \ln \frac{T_{INLET}^{HCSG-SHELL}}{T_R} \right]$$

HCSG Tube Side

Feedwater temperature in tube side is increased by the heat interaction with the molten salt releasing a thermal power. Hence, from liquid water at $T_{INLET}^{HCSG-TUBE} = 238°C = 511K$ to superheated steam $T_{OUTLET}^{HCSG-TUBE} = 299°C = 572K$ conveyed to the high pressure steam turbine.

So far, a thermal exergy balance has been calculated. However, mechanical exergy balance due to pressure loss along interconnecting piping designed to convey molten salt should be accounted for in both pulse and dwell phases to achieve an overall assessment of thermal and mechanical dissipation phenomena occurring in the ESS during both operating phases. To do so, the mechanical exergy destruction rate is calculated considering that it corresponds to the mechanical power delivered by pumps to all circulating fluids.

Dwell Mode Mechanical Exergy

During dwell mode, molten salt is moved from the hot tank to the cold tank by means of pumps delivering mechanical power equal to $14MW$. Therefore:

$$\Delta \dot{EX}_{DWELL}^{M} = \Delta \dot{EX}_{HCSG}^{M} = 14\,MW$$

Dwell Mode Total Exergy Balance

The total exergy balance during dwell mode includes the HCSG thermal exergy and mechanical exergy flow.

$$\Delta \dot{EX}_{DWELL} = \Delta \dot{EX}_{DWELL}^{T} + \Delta \dot{EX}_{DWELL}^{M}$$

The exergy analysis in dwell mode is shown in table 2.

Feedwater Pre-Heaters

The thermal power produced in the Divertor Cassette, Divertor PFCs and Full Vacuum is conveyed to the regeneration system design to pre-heat the feedwater before inlet in OTSG during both pulse and dwell modes and to IHX during pulse mode only. Pre-heaters are U-Tubes and Shell heat exchangers.

Table 2 – DEMO Exergy Input and Exergy Destruction with ESS in Dwell Mode

DEMO Configuration with ESS - Dwell Mode					
PRIMARY HEAT TRANSFER SYSTEM COMPONENT	**MASS FLOW RATE (kg/s)**	**SPECIFIC ENTROPY (kJ/(kg*K))**	**SPECIFIC EXERGY (kJ/kg)**	**EXERGY INPUT RATE (MW)**	**EXERGY DESTRUCTION RATE (MW)**
MS HCSG Hot Inlet (primary shell side)	10196.39	3.5084	458.257	4672.57	-60.3293
BZ OTSG Hot Inlet (primary shell side)	50,97	3.5085	462.723	23.58555	-0.3149
Divertor Cass. Hot Inlet (primary shell side)	860.8	2.2803	155.758	134.076	-0.01237
Divertor PFCs Hot Inlet (primary shell side)	5317.80	1.66291	70.4727	374.760	-0.3764
Vacuum Vessel Hot Inlet (primary shell side)	1927,68	2.2809	155.447	299.652	-0.3255

8.5.3. Exergy Balance and Efficiency

The overall exergy balance of the IHTS, including the ESS, is calculated over the two pulse and dwell phases to take a pulse-dwell closed cycle as the reference unit operation. In order to properly compare the two phases, the exergy efficiency is calculated based on the exergy amount during each reactor operating mode time duration. Therefore:

$$\Delta EX_{OVERALL} = \Delta EX_{PULSE} + \Delta EX_{DWELL}$$

8.5.3.1. Pulse Mode

The exergy efficiency during pulse mode is calculated by means of the following expression:

$$\eta^{EX}_{PULSE} = 1 - \frac{\Delta \dot{EX}^{OVERALL-DESTR}_{PULSE}}{\dot{EX}^{BZ-OTSG-HOT}_{INPUT} + \dot{EX}^{FW-IHX-HOT}_{INPUT} + \dot{EX}^{DIV-CAS}_{INPUT} + \dot{EX}^{DIV-PFC}_{INPUT} + \dot{EX}^{VV}_{INPUT}}$$

8.5.3.2. Dwell Mode

The exergy efficiency during dwell mode is calculated by means of the following expression:

$$\eta^{EX}_{DWELL} = 1 - \frac{\Delta \dot{EX}_{DWELL}}{\dot{EX}^{DWELL}_{FUEL}} = 1 - \frac{\Delta \dot{EX}_{DWELL}}{\dot{EX}^{HCSG-SHELL}_{INPUT}}$$

$$\eta^{EX}_{DWELL} = 1 - \frac{\Delta \dot{EX}^{OVERALL-DESTR}_{DWELL}}{\dot{EX}^{BZ-OTSG-HOT}_{INPUT} + \dot{EX}^{HCSG-HOT}_{INPUT} + \dot{EX}^{DIV-CAS}_{INPUT} + \dot{EX}^{DIV-PFC}_{INPUT} + \dot{EX}^{VV}_{INPUT}}$$

8.6. Exergy Analyses with Auxiliary Boiler Replacing ESS

A viable alternative solution to reduce plant layout complexity and due to molten salt tanks and connection piping is to replace the ESS with an auxiliary boiler. This fired steam generator is evaluated being fuelled by natural gas (100% methane CH_4) and provides thermal power production during the dwell phase. The design thermal duty of this steam generator is about $254MW$ as it is foreseen that, during dwell phase, 10% of the mass flow rate, and hence thermal power released with respect to pulse phase, is considered for plant operation. Moreover, to avoid thermal fluctuations and consequent thermal fatigue, the auxiliary steam generator is operated in continuous mode during both pulse and dwell phases to ensure a constant duty. This implies that the thermal power released by the auxiliary boiler has to be considered during pulse mode in addition to that thermal power not used for molten salt heating. Therefore, the entire thermal power produced by the reactor during pulse mode is available for the PCS and provided by four OTSG operating in parallel to use the thermal power generated in both breeding zone and first wall. The combustions reaction can be written as follows:

$$\alpha CH_4 + x\left(O_2 + 3{,}76N_2\right) \rightarrow aCO_2 + bH_2O + cN_2 + dO_2$$

The standard specific molar chemical exergy of methane, with respect to the reference reservoir R represented by the environment at $T_R = 298.15K$ and $p_R = 101.325kPa$ is [8.9]:

$$\overline{ex}^{C}_{CH_4} = \mu_{CH_4}\left(T_R, p_R\right) - \mu^{R}_{CH_4}\left(T_R, p_R\right) = 831.2kJ/mol$$

Considering the molar weight of methane equal to $16.04\,g/mol$, then the specific chemical exergy is:

$$ex^{C}_{CH_4} = \frac{831.2kJ/mol}{16.04g/mol} \cong 51.82kJ/g = 0.05182kJ/kg$$

The Lower Heat Value (LHV) of the methane is $802.3kJ/mol = 50147.5\,kJ/kg$, then the mass flowrate expressed in mol/s of methane needed to produce $254MW$ of thermal power is the following:

$$254\,MW = 254\,\frac{MJ}{s} = 254 \times 1000\,\frac{kJ}{s}$$

obtained considering an auxiliary boiler with no economizer as pre-heating is no needed, then its design implies a lower thermal efficiency equal to $\eta_{BOILER} = 0{,}86$. Thus, the methane mass flowrate is:

$$\frac{\dot{Q}}{\eta_{BOILER} \cdot LHV} = 254 \times \frac{1}{0.86} \times 1000 \frac{kJ}{s} \times \frac{1}{802.3}\frac{mol}{kJ} \cong 368.14\frac{mol}{s}$$

and, to express the mass flowrate in kg/s, the molar weight is used:

$$368.14\frac{mol}{s} \times 16.04\frac{g}{mol} \cong 5905\frac{g}{s} = 5.905\frac{kg}{s}$$

This is the mass flowrate that is to be accounted for exergy balance with the option of auxiliary boiler to producing $254MW$ of thermal power.

The air mass flowrate, considering air excess of 10%, is equal to $117.32\,kg/s$.

The temperature at the centre of the burning flame in the combustion chamber can be assumed at $2000°C = 2273K$.

The rate of exergy destruction is calculated as follows [2.7]:

$$\Delta \dot{EX}_{DESTR} = \Delta \dot{EX}^{T}_{DESTR} + \Delta \dot{EX}^{C}_{DESTR} = \dot{EX}_{IN} - \Delta \dot{EX}_{OUT}$$

$$= 0.02 \times 5.905 \times 50147.5 \times \left(1 - \frac{298}{2273}\right) \quad \text{(heat losses to environment)}$$

$$+ 117.32 \times 281.7 + 5.905 \times 1.06 \times 50147.5 \quad \text{(thermal exergy input + chemical exergy input)}$$

$$- (5.905 + 117.32) \times 957.42$$

$$= 5145.96 + 33049 + 313888 - 117978 = 234104 \ kJ/s = 234 \ MW$$

Tables 3 and 4 include all calculated values pertaining to pulse and dwell mode respectively, of the configuration with auxiliary boiler.

Table 3 – DEMO Exergy Input and Exergy Destruction with Auxiliary Boiler in Pulse Mode

DEMO Configuration with Auxiliary Boiler - Pulse Mode					
PRIMARY HEAT TRANSFER SYSTEM COMPONENT	**MASS FLOW RATE (kg/s)**	**SPECIFIC ENTROPY (kJ/(kg*K))**	**SPECIFIC EXERGY (kJ/kg)**	**EXERGY INPUT RATE (MW)**	**EXERGY DESTRUCTION RATE (MW)**
BZ+FW OTSG Hot Inlet (primary shell side)	9981.8	3.5085	462.723	4618.84	-69.6097
Auxiliary Burner CH4 LHV Inlet	5.905	11.59	50147	313.88	-234
Divertor Cass. Hot Inlet (primary shell side)	860.8	2.4220	180.978	155.78	-3.360
Divertor PFCs Hot Inlet (primary shell side)	5317.85	1.6943	73.9096	393.04	-5.11430
Vacuum Vessel Hot Inlet (primary shell side)	1927.68	2.32834	163.659	315.484	-6.31249

Table 4 – DEMO Exergy Input and Exergy Destruction with Auxiliary Boiler in Dwell Mode

DEMO Configuration with Auxiliary Boiler - Dwell Mode					
PRIMARY HEAT TRANSFER SYSTEM COMPONENT	**MASS FLOW RATE (kg/s)**	**SPECIFIC ENTROPY (kJ/(kg*K))**	**SPECIFIC EXERGY (kJ/kg)**	**EXERGY INPUT RATE (MW)**	**EXERGY DESTRUCTION RATE (MW)**
BZ+FW OTSG Hot Inlet (primary shell side)	65.35	3.50847	462.7231	30.23896	-0.51394
Auxiliary Burner CH4 LHV Inlet	5.905	11.59	50147	313.882	-234
Divertor Cass. Hot Inlet (primary shell side)	860.8	2.28033	155.7577	134.07627	-0.01043
Divertor PFCs Hot Inlet (primary shell side)	5317.85	1.6629	70.4727	374.76322	-0.17262
Vacuum Vessel Hot Inlet (primary shell side)	1927.684	2.2809	155.447	299.6523	-0.0429048

8.6.1. Exergy Balance and Efficiency

Similarly to the configuration with ESS, also in the case with the auxiliary boiler, the exergy efficiency is calculated based on the exergy amount during each reactor operating mode time duration.

8.6.1.1. Pulse Mode

$$\eta_{PULSE}^{EX} = 1 - \frac{\Delta \dot{EX}_{PULSE}}{\dot{EX}_{FUEL}^{PULSE}} = 1 - \frac{\Delta \dot{EX}_{PULSE}}{\dot{EX}_{INPUT}^{OTSG-SHELL}}$$

8.6.1.2. Dwell Mode

$$\eta_{DWELL}^{EX} = 1 - \frac{\Delta \dot{EX}_{DWELL}}{\dot{EX}_{FUEL}^{DWELL}} = 1 - \frac{\Delta \dot{EX}_{DWELL}}{\dot{EX}_{INPUT}^{OTSG-SHELL}}$$

8.7. Exergy Efficiency of the Overall Pulse-Dwell Cycle

The comparison of performances achieved by the two configurations of BOP should summarize the properties along both pulse and dwell modes to merge the results in one indicator, namely the exergy efficiency. To do so, the efficiency is calculated considering the amount of exergy input and destruction, instead of use the rates as previously done. Then, input and destruction exergy rates must be multiplied by the duration of pulse and dwell mode to obtain an exergy amount that can be summed up and used in the efficiency expression. Thus, considering all figures calculated for ESS and auxiliary boiler configuration during pulse and dwell modes, the following result is obtained.

8.7.1. Configuration with ESS

The exergy efficiency of the configuration with ESS requires the calculation of input exergy and destruction exergy during both pulse and dwell phases.

8.7.1.1. Pulse (7200 s)

Input: $\dot{EX}_{\substack{INPUT \\ PULSE}} \times \tau_{PULSE} = EX_{\substack{INPUT \\ PULSE}} = 5340MW \times 7200s = 38.448 \times 10^6 MJ$

Destruction: $\dot{EX}_{\substack{DESTR \\ PULSE}} \times \tau_{PULSE} = EX_{\substack{DESTR \\ PULSE}} = 552MW \times 7200s = 3.9744 \times 10^6 MJ$

8.7.1.2. Dwell (600 s)

Input: $\dot{EX}_{\substack{INPUT \\ DWELL}} \times \tau_{DWELL} = EX_{\substack{INPUT \\ DWELL}} = 5504MW \times 600s = 3.3024 \times 10^6 MJ$

Destruction: $\overset{\bullet}{EX}_{\substack{DESTR\\DWELL}} \times \tau_{DWELL} = EX_{\substack{DESTR\\DWELL}} = 586MW \times 600s = 0.3516 \times 10^{6} MJ$

$$\eta_{ESS}^{EX} = 1 - \frac{EX_{\substack{DESTR\\PULSE}} + EX_{\substack{DESTR\\DWELL}}}{EX_{\substack{INPUT\\PULSE}} + EX_{\substack{INPUT\\DWELL}}} = 1 - \frac{3.9744 + 0.3516}{38.448 + 3.3024} = 1 - \frac{4.326}{41.7504} = 0.8964$$

8.7.2. Configuration with Auxiliary Boiler

The exergy efficiency of the configuration with auxiliary boiler requires the calculation of input exergy and destruction exergy during both pulse and dwell phases.

8.7.2.1. Pulse (7200 s)

Input: $\overset{\bullet}{EX}_{\substack{INPUT\\PULSE}} \times \tau_{PULSE} = EX_{\substack{INPUT\\PULSE}} = 5914MW \times 7200s = 42.5808 \times 10^{6} MJ$

Destruction: $\overset{\bullet}{EX}_{\substack{DESTR\\PULSE}} \times \tau_{PULSE} = EX_{\substack{DESTR\\PULSE}} = 839MW \times 7200s = 6.0408 \times 10^{6} MJ$

8.7.2.2. Dwell (600 s)

Input: $\overset{\bullet}{EX}_{\substack{INPUT\\DWELL}} \times \tau_{DWELL} = EX_{\substack{INPUT\\DWELL}} = 1168MW \times 600s = 0.7008 \times 10^{6} MJ$

Destruction: $\overset{\bullet}{EX}_{\substack{DESTR\\DWELL}} \times \tau_{DWELL} = EX_{\substack{DESTR\\DWELL}} = 305MW \times 600s = 0.183 \times 10^{6} MJ$

$$\eta_{CH4}^{EX} = 1 - \frac{EX_{\substack{DESTR\\PULSE}} + EX_{\substack{DESTR\\DWELL}}}{EX_{\substack{INPUT\\PULSE}} + EX_{\substack{INPUT\\DWELL}}} = 1 - \frac{6.0408 + 0.183}{42.5808 + 0.7008} = 1 - \frac{6.2238}{43.2816} = 0.8562$$

All results related to exergy efficiency above achieved are summarized in the following Table 5:

Table 5 – DEMO Exergy Efficiencies

DEMO Exergy Efficiencies		
	Exergy Rates Efficiency	**Exergy Efficiency**
with ESS		
Pulse	0.8965	
Dwell	0.8935	
Overall		0.8964
with Auxiliary Boiler		
Pulse	0.8581	
Dwell	0.7382	
Overall		0.8562

8.8. Results

Main result of the present research is a performance evaluation based on exergy method adopted to calculate balances and efficiencies of components and systems constituting the overall plant. The second Law, underpinning the exergy method, focuses on dissipative phenomena implying entropy production and exergy destruction representing performance indicator to detect solution for the design enhancement. The PHTS, IHTS, ESS and PCS of DEMO fusion reactor and balance of plant assessed by means of the exergy method reveals that the efficiency of the system designed with molten salts remains higher with respect to the alternative solution with an auxiliary boiler replacing the ESS. However, the difference of exergy efficiency between the solutions here considered could suggest the suitability of both configurations. Indeed, the strong exergo-dissipative combustion reaction that would lower the performance with the auxiliary boiler is mitigated by the thermal power reduction to 10% during dwell mode. Though, this solution determines a higher stress level and fatigue in steam turbine components. On the other side, the ESS with molten salt ensures the continuity of full power release; moreover, this configuration could undergo design improvements based on optimized shapes of intermediate heat exchangers derived from the entropy generation minimization underpinning the Constructal Law and Constructal Thermodynamics approach specifically applied to heat interactions phenomena and heat exchangers design. Anyway, the selection of the most suitable option requires a more accurate evaluation of the balance of plant in terms of reliability and economics considering the location of the plant and the need of additional infrastructures. The present preliminary exergy analysis can be considered the outset of a more extended evaluation of economic assessments of nuclear fusion plants on the basis of studies already carried out [8.10] and looking forward the adoption of the theory of exergetic cost and the exergo-economic and exergo-environmental analyses and methodologies [8.11].

9. CONCLUSIONS AND FUTURE RESEARCHES

Considering all aspects analysed in the present thesis, main conclusions and subsequent future researches envisaged can be summarized as follows.

9.1. Main Achievements and Original Outcomes

Main conclusions concern on the one side the theoretical and methodological aspect and, on the other side, direct applications to industrial nuclear plants.

The three additive components of exergy discussed in this study constitute the components of generalized exergy that depends on temperature, pressure and chemical potential and, at microscopic level, on the kinetic energy and potential energy generated by interactions among all particles constituting a system. Moreover, three components of entropy property have been inferred from the corresponding exergy components. In particular, chemical exergy and entropy are correlated to the molecular structure of matter due to the composite of molecules geometry and chemical bonds characteristics. The aim of seeking a property related to molecular or supra-molecular architecture is to obtain a method able to predict a-priori stability as well as capability in self-assembling processes and the related intermediate phases of chemical compounds that are not available in the environment and which could undergo a building process by means of nano-sciences technologies. Such a method would make it possible to design materials characterized by properties that could be evaluated prior to being realized and to confirm predictions by means of experiments and laboratory tests.

Most significant and original outcomes can be summarized in the following points:

- Definition of generalized thermodynamic exergy and thermodynamic entropy properties;
- Theorem of necessity and sufficiency of stable equilibrium and Highest-Generalized-Entropy principle for stable equilibrium and non-equilibrium
- Perspective of the State Equation extended to both thermal aspect and chemical aspect; relationship of State Equation with generalized thermodynamic entropy property; analysis of Gibbs equation incoherence and demonstration of units of measure equivalence; generalization of ideal state equation taking into account kinetic and potential energy due to inter-particle kinematic and geometric configurations;
- Hierarchical structure of thermodynamic entropy defined for mesoscopic systems: non-equipartition theorem on entropy, complementary to the equipartition theorem of energy for microscopic systems;
- Fission and fusion elemental reactions second law analyses based on exergy method: thermodynamic and informational aspect accounted for in nuclear physics;
- Simplified exergy balances and efficiencies calculations of ABWR and AP1000 fission nuclear reactors considering nuclear core and conventional plant;
- Preliminary exergy analysis of EU DEMO pulsed fusion reactor with molten salts energy storage system and auxiliary boiler configurations.

9.2. Future Researches

The perspective adopted from the achievements of the present study sheds a light on the future researches starting from the Disciplines Architecture mentioned in the Introduction section. The main points are highlighted in the following paragraphs.

Fission Nuclear Reactors Technology Generation IV

The comparative analysis of performances provided by fission nuclear reactors gen IV would give continuity and a wider prospect in evaluating performances and life cycle assessment including nuclear fuels treatment “from ore to green field”. Finally, the method of Entropy Generation Minimization (EGM) associated with the Extended Exergy Accounting (EEA) could be further generalized to provide an overarching paradigm for analysing the whole process and nuclear life cycle assessment.

Fusion Nuclear Reactors

EU DEMO design activities are underway and solution are proposed to pursue the most optimized solutions. The combined first and second law analyses may provide optimized solution for the balance of plant and, in particular, the energy storage system that a pulsed fusion reactor needs to ensure constant power released to the electric grid.

Molecular Machines

From non-existence of PMM2 cases to the role of molecular machines and molecular motors in self-assembling and self-organizing processes of Nanosciences, Nanotechnologies and Biotechnologies [4.53,4.54]. Atomic and molecular microscopic domain needs Quantum Physics considerations and Quantum Thermodynamics paradigm.

Quantum discretization of a hierarchical level through particle machines efficiency related to finite differences of driving forces constituting boundary conditions.

Nanotechnologies

Analysis of self-organizing and self-assembling processes and self-organized supra-molecular architectures to use the governing laws for prediction and control.

Biotechnologies

Biochemistry, citology, staminal cells and molecular genetics and biotetchnology represent parts of the broader domain where complexity underpins the three characteristics of living systems, that is, methabolisms, reproduction, individual methamorphosis (ontogenesis) and species evolution (filogenesis). Here, the bio-physical-thermodynamical and bio-physical-informational ultimate nature of systems and phenomena play a central and integral role in the epiphenomenology [9.9-9.12]. Self-organization is one of the most outstanding appearences in living systems and studies are ongoing on different directions. In this perspective, information and self-organization [9.13,9.14] constitute the complement of the physical "universe" in which science is the "observer" and the "protagonist" at the same time. The complex thinking taught by Edgar Morin and the dialectic "Order-Disorder-Organization" is the logical paradigm to treat nature complexity. The migration from Complexity of Physics to Physics of Complexity will lead to a new era of science and epistemology.

Fourth Law

Open systems and extrema principles lay questions and research opportunities in the direction of the Fourth Law. In this regard, the following issues, disputes and debates would suggest, if not recommend, to pursue deeper investigations:

- Maxwell's demon: there are attempts in recent publications to look for a way to escape the non-existence of the demon. This topic is dealing with quantum physics and represents an issue involving intrinsic quantum thermodynamics and quantum information theory; on the other hand, a "god", instead of a demon, able to assemble and organize things or, better, physical entities, would more easily get the credit of constructive capabilities displayed by complex systems and, even much more evidently, by living systems;
- Absolute entropy or universal entropy: these terms, already adopted in the literature, could be borrowed to somehow combine the generalized thermodynamic entropy and the generalized informational entropy in a definition with a significance more directed to the essence of entities in the phenomenological universe;
- In an isolated system, non-equilibrium states and processes imply energy dissipation and generalized thermodynamic entropy increase that could be thought as compensated by information creation and generalized informational entropy decrease associated to self-assembling and self-organization of the system;
- A Fourth Law conjecture would take into account the very absolute entropy, or universal entropy, intended as the sole property able to represent the unique governing law of physics as mentioned somewhere in this thesis and ever aspired in the scientific community.

Biology, Biotechnology and Molecular Genetics represent domains where the Fourth Law would govern constructive processes resulting from self-assembling and self-organizing capabilities of complex systems in the opposite direction with respect to the configuration subdivision and hierarchical levels multiplications as an effect of dissipation. Those phenomena, in contrast with each other, shed light, and open enlarged perspectives, on life and the reason why life has emerged in the physical universe, both representing the most amazing, most difficult to be understood, and so far, impossible to be resolved, mysteries.

APPENDIX 1 – SYMBOLOGY AND UNITS OF MEASURE

Symbology

A : generic thermodynamic system
A : atomic mass
E : energy
e : specific energy
EX : exergy
ex : specific exergy
g: specific Gibbs free energy
H: enthalpy
h: specific enthalpy
M : mass interaction
$\dot{m}$: mass flow rate
n: number of moles
Q : heat interaction
r : number of constituents
S : entropy
s : specific entropy
T : temperature
U : internal energy
u : specific internal energy
V : volume
v : specific volume
W : work interaction
x : molar fraction
Z : atomic number

Greek Symbols

β : parameters of a thermodynamic system
Γ : mass flowrate
η : efficiency
μ : potential

Superscript

C : Chemical
HL : Hierarchical Level
M : Mechanical
N : Nuclear
T : Thermal

Subscript

R : Reservoir

Unit of Measure

International unit of measure system (SI) is adopted:

Heat: J
Length: m
Mass: kg , $moli$
Power: W, kW, MW
Pressure: Pa
Energy: J
Entropy: $J/Kg^{\circ}K$
Exergy: J
Specific Heat: $J/Kg^{\circ}K$
Section: Barn
Temperature: $^{\circ}K$
Time: s
Work: J

Unit of Measure Translation Factors

Mass flow rate

$1 kg/s = 3{,}6\, ton/hr$; $1 ton/hr = 0{,}277778\, kg/s$

$1 lb/hr = 0{,}000126\, kg/s$; $1 kg/s = 7936{,}64\, lb/hr$

Pressure

$1 PSIA = 6{,}895 kPa = 0{,}006895 MPa$

$1 kPa = 0{,}01 Bar$; $1 Bar = 100 kPa$

$1 cal/gr°C = 4186{,}8\, J/kg\, K = 4{,}1868\, kJ/kgK$

Enthalpy

$1\, Btu/lb = 2{,}326\, kJ/kg$; $1 kJ/kg = 0{,}4299\, Btu/lb$

1 g = $N_A A$; where N_A : Avogadro number; A

$1 eV$ = $1{,}602 \cdot 10^{-19}\, J$ = $4{,}444 \cdot 10^{-26}\, kWh$

$1 MeV$ = $1{,}602 \cdot 10^{-16}\, J$

Unit of Measure Suffix

M : mega or million

APPENDIX 2 – Thermophysical Properties of Substances and Constants Factors

Boltzmann constant

$$k_B = 1{,}38064852 \times 10^{-23} \frac{m^2 \cdot kg}{s^2 \cdot K} = 1{,}38064852 \times 10^{-23} \frac{J}{K}$$

$$k_B = 8{,}617 \times 10^{-5} \frac{eV}{K} = 8{,}617 \times 10^{-11} \frac{MeV}{K}$$

Universal Gas Constant

$$\overline{R} = 8314{,}34 J / kmol \cdot K = 8{,}314 kJ / kmol \cdot K$$

Universal Gas Constant of Water Steam

$$\overline{R} = 461{,}5 J / (kg \cdot K) = 0{,}4615 kJ / (kg \cdot K)$$

Avogadro Number

$$N_A = 6{,}022 \times 10^{23} \frac{1}{mol}$$

Constant Factors

Mechanical-Thermal Equivalence Factor: $4{,}1855 J / Cal$

Water

Specific Heat c_P :

- 5,75 $kJ/kg \cdot K$ at 300°C
- 4,19 $kJ/kg \cdot K$ at 25°C

Uranium Dioxide

Specific Heat c_P :

- 247 $\frac{J}{kg \cdot °C}$ at 100 °C
- 0,065 $\frac{cal}{g \cdot K}$ at 700 K

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