The Future of Thermoeconomics after the School of Zaragoza

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Abstract:

Thermoeconomics was born as a combination of the Second Law of Thermodynamics and Economics in search of the process of cost formation. Linking the physical origin of cost with irreversibility is the central paradigm of Thermoeconomics. Irreversibility is best identified in energy systems, so Thermoeconomics has concentrated on them without extending its scope to other industrial systems, such as chemical or metallurgical processes. As well as to cost accounting for the irreversibilities of all commodities from the cradle to the grave. The concept of cost is universal, so there is no reason not to extend applications to geological, biological, or purely economic systems. The accumulation of irreversibilities can quantify (in kWh) the destruction of the (natural) resources used to produce a commodity, from the cradle to the market and beyond its degradation as waste and its return to the cradle. It is the natural cost of any human activity - subject to its calculation assumptions. This requires an extension of thermodynamics, which we could reasonably call thermoeconomics. At the University of Zaragoza, we have developed the concepts of Thanatia and thermodynamic rarity to identify the loss of the Mineral Capital of the Planet. We also have identified the idea of waste as external irreversibility, the basis of Circular Thermoeconomics. We have also proposed the idea of a new and more precise function that could be used for the diagnosis of processes that we call Relative Free Energy. All these new concepts need further development, which we invite future researchers to develop. Today's economy is disconnected from physics; prices do not internalise the destruction of natural resources. Our vision is that thermoeconomics provides a bridge between the two, valuing nature in such a way as to replace what has been destroyed and regenerate what has been degraded. In effect, thermoeconomics becomes the economics of physics.

Keywords:

Exergy, Dead State, Thanatia, Pristinia, Circular Thermoeconomics, Relative Free Exergy

1. Preamble

Cost, in its physical expression, accounts for the loss of natural resources. In other words, cost accounts for the irreversibilities accumulated in the formation of any product or service. This is the central paradigm of thermoeconomics, which will be analysed in section 4..

The economy sees nature as a supplier of raw materials or solace. It is designed to value the exchange of services between humans. We do not pay nature for its resources, we only pay the extractor, not what is extracted. Nor do we pay for its regeneration or even its depreciation. To overcome this shortcoming, the economy includes as externalities those unavoidable repairs of the natural environment. Money has been created to measure exchanges between individuals or organisations, it is a human construct that nature does not understand, as it only follows the principle of action and reaction.

The second law of thermodynamics is conclusive: degradation is a physical and unavoidable process in any real activity, and this degradation can be measured with entropy generation. So why not use thermodynamics to account for the loss of the planet's natural resources?

As not all energy is usable, exergy is a better alternative analysis when dealing with natural systems. Exergy is not a conservative property and is partly destroyed in every real process. We call the destroyed exergy irreversibility, which, in turn, is related to the entropy generated in the process and thus its degradation (Gouy-Stodola Law): $I = T_0 S_g$.

While the cost accounts for the loss of natural resources, this loss could be identified with the accumulated irreversibility from cradle to commodity. To do this, we need only extend the concept of dead state to assess exergies. In other words, we have opened up thermodynamics to evaluate the planet's resources. The expectations are immense.

From the intersection of thermodynamics and economics comes thermoeconomics, which we consider the concept of cost to be central. Thermoeconomics, in our opinion, is not only about valuing the physical cost in

monetary units but the more objective cost can and should be measured in physical units, kWh. In this way, costs are left out of the vagaries and fluctuations of money. Strange as it may seem, it is linking economics with nature again, as the early physiocrats did, who considered nature as the source of all wealth because they believed that it regenerated itself. Interestingly, when the value of a currency is in doubt, the gold carat is used as a safe haven.

Thermoeconomics should draw on and recognise many concepts of economics, but it can also complement and illuminate others that conventional economics calls shadow costs, i.e. those that are not accountable or are subjectively valued as externalities.

On the other hand, many authors have built bridges between thermodynamics and economics, among them Nicholas Georgescu-Roegen with his book "The Law of Entropy and the Economic Process" [1] marked the foundation of ecological economics, although he called it bioeconomics. However, this term has been used more recently to relate biology to economics for better utilisation of biological resources and by extension natural resources. Another important author and father of biophysical economics is Charles Hall who developed the concept of energy return on energy investment (EROI) and described its Implications in the book "Energy and the Wealth of Nations: An Introduction to Biophysical Economics". [2]. Incidentally, he previously called it Thermoeconomics. Nor should we forget the contributions of Howard Odum [3] and collaborators on the concept of emergy, to say the least.

In this paper, we do not seek to make an extensive review of the use of the name Thermoeconomics and the work of numerous authors who linked thermodynamics, biology, ecology, physics, etc., with economics. We simply focus on a view of thermoeconomics from the concept of exergy and the immense room for future development by integrating the extraction of geological resources with economics. This new view of thermoeconomics allows us to assess the planet's mineral resources and can be a guide to evaluate the damage our civilisation is inflicting on it. It helps to clarify its costs and to act accordingly.

The purpose of this article is twofold: on the one hand, we describe, from the Zaragoza school of thermoeconomics, its conceptual advances and the needs for future development based on them. We have divided it into four parts: The first deals with Thanatia, exergy costs and rarity. The second is Pristinia, a planetary model for assessing the degradation of fertile soils. The third is the principles of a new Circular Thermoeconomics based on the thermodynamic concept of waste. And finally, an introduction to Relative Free Energy as a new thermodynamic function that depends on both the fluid and the machine at work. It opens a new perspective on the diagnosis of thermal systems.

2.   Thanatia, a planetary reference state for exergy calculation

One of humanity's biggest problems in the coming decades, if not centuries, is the fast destruction of the planet's natural resources, especially non-renewable minerals. In fact, they are extracted, processed, used and, in the last stage, we disperse them into the earth's crust, the oceans or pollute the atmosphere and fresh waters. Therefore, it would be an immense contribution of thermoeconomics to planetary sustainability to construct a physical theory to evaluate the periodic cost of this destruction to at least minimise and manage it.

Ecological economists have resorted to the law of entropy as an uncountable and even immeasurable metaphor. On the contrary, we believe that thermoeconomics can expand its explanatory capacity and appraise this destruction based on the concepts of cost and irreversibility.

We note that the entropic generation, and with it, the irreversibility of the processes, depends on the reference state we choose. In conventional process exergy analysis, the choice of a reference state is linked to the type of problem we want to solve, i.e. we explicitly or implicitly delimit the relevant costs/irreversibilities. Consequently, if we want to evaluate the destruction of the planet's resources, we need to define a reference environment, also called *dead state*, that allows us to evaluate the costs of both resource depletion and waste generation at the planetary level.

The most important property of a reference environment, RE, is that it actually acts as an attractor of our system's intensive properties. Spontaneous evolution is found in the difference in temperatures, or pressures, or concentration, or composition, of a system with its environment. Therefore, it is necessary to define the temperature, pressure, composition and concentration of all chemical substances composing the reference state that can interact with the system. Their exergy loss in both quantity and quality will make it possible to assess the degradation of the planet's mineral resources.

Thanatia would represent a hypothetical end state of the current exponential trajectory of human-induced degradation: The Earth's crust, hydrosphere and atmosphere would have reached the maximum dissipation of all spent materials [4]. Although this scenario is hypothetical and indicates a final depletion, it is purely instrumental and devoid of social or economic connotations, which would obviously take place long before it is reached. This model was developed by Alicia Valero in her PhD thesis in 2008 [5], with the current geochemical

and geological information on the atmosphere, hydrosphere and crust described below.

The crepuscular or twilight atmosphere would be produced after all conventional fossil fuel reserves have been depleted, with an atmospheric injection of about 2,000 Gigatonnes of carbon. According to previously published simulations, the crepuscular atmosphere would have a carbon dioxide content of 683 ppm, an average surface temperature of 17°C (maximum carbon dioxide-induced warming of 3.7°C above pre-industrial temperatures), a pressure of 1.021 bar and a composition, by volume, of 78.8% N2, 20.92% O2, 0.93% Ar and 0.0015% trace gases. (Note that, even if the atmosphere were filled with anthropogenic CO_2, it would be "only" 0.07% [6]).

Saline water accounts for about 97.5% of the entire hydrosphere; the other 2.5% is kept as freshwater, almost all of it in the form of ice, mainly in Antarctica and Greenland. The rest is marginal, although it may seem immense to us, found in groundwater, lakes, rivers, soil and moisture in the atmosphere and biosphere. Only 0.3% of the total amount of freshwater is concentrated in lakes, reservoirs and river systems, yet this is the part of the hydrosphere that we all need to live and is most at risk of being polluted. In addition, due to climate change, a significant part of the glaciers and other ice in the cryosphere is melting. Therefore, we assume that the crepuscular hydrosphere would have the current chemical composition of the oceans at an average temperature of about 17°C. That is, it is implicitly assumed that all ice sheets will have molten and dissolved into saline waters.

According to the US Geological Survey [7] the mass of non-fuel industrial mineral resources worldwide is of the order of 10^{15} kg. Furthermore, the World Energy Council [8] estimates the amount of available conventional and unconventional fossil fuels to be about 10^{16} kg. This means that all concentrated mineral resources of fuel and non-fuel origin represent only 0.001% of the total mass of the Earth's upper continental crust (about 10^{22} kg, according to [9]. Therefore, without any significant error, we can state that the crepuscular continental crust can approximate the average mineralogical composition of the present-day Earth's upper crust [10].

The problem we faced was to identify what type and how many significant and distinct (in a thermodynamic sense) minerals are present in the upper continental crust. To do so, we proposed a model based on the mineralogical composition studied by Grigoriev [11], which would ensure consistency between species and chemical elements. The resulting crustal model comprises at least the 292 most common minerals.

In short, the current state of the biosphere is incredibly close to Thanatia. In our hypothetical reference state, the atmosphere would have reached the state predicted by long-term climate change models. Even if the amount of CO_2 doubled, there would be less carbon dioxide than argon, and this noble gas is considered a trace element. Even if all mineral deposits were increased tenfold in the Earth's crust, the crust would contain no more than 0.01% of them (less than the crustal mass estimation error). Thus, whereas if all commercially exploitable mineral deposits disappeared, the composition of the crust would be virtually the same. Accordingly, the dispersion and degradation of all already used materials mean nothing compared to the amount of common rocks (mostly silicates) that are mostly found in the crust.

As for the hydrosphere, the pollution of all freshwaters and the melting of the Arctic, Greenland and Antarctic ice would have a quantitatively more significant effect, but not more than 2.5% of the total waters of the blue planet. The hydrological cycle driven by solar radiation would still exist, but it must be accountable that water in the atmosphere is only 0.00093% of the total water while rivers account for 0.00015% of all the water on the planet [5]. Therefore, we hold that the hydrosphere of Thanatia would be composed almost entirely of standard salt water.

The present Earth is not in the equilibrium state, whose continental masses evolve slowly in geological times, but more rapidly and spontaneously in chemical terms towards Thanatia. This is by the logic of the second law and there is no catastrophism in it. How fast we get to Thanatia does depend on human beings. But before we get there, one can imagine, without too much difficulty, that economic and perhaps civilisational collapse will be reached sooner as a possible end of the Anthropocene period [12].

2.1. The exponential behaviour of mining demand and the exergetic "U".

Our society does not comprehend exponential behaviour. The extraction of minerals on the planet is growing at such a rate that by 2050 more than twice (or perhaps three times) as much will be consumed as is extracted today, and by 2050 more minerals will have been extracted than in the entire history of human civilisation. Agriculture is heavily dependent on phosphate mines. A mobile phone requires more than 35 chemical elements; a conventional or electric vehicle requires more than 50; and renewable energies, electrochemical storage, and green hydrogen production require huge quantities of rare metals. Therefore, it is necessary to review the message of entropy: its exponential character will help us to understand and assess those behaviours.

It is relevant to analyse the phenomenon of mixtures thermodynamically. As is well known, the irreversibility of a mixing process takes the form:

$$I = -R\,T_0 \sum_{i=1}^{n} x_i \ln x_i = -R\,T_0\,\ln 10 \sum_{i=1}^{n} x_i \log_{10} x_i,$$

where x_i are the mole fractions of the n substances to be mixed. And for the case of a mixture between two substances A and B

$$I = -R\,T_0\,[x_A \ln x_A + (1 - x_A)\ln(1 - x_A)] \quad \text{(kWh)} \qquad \text{and} \qquad \frac{dI}{dx_A} = -R\,T_0\left[\ln\frac{x_A}{1 - x_A}\right]$$

This equation is symmetric around x = 0.5, where it has a minimum, and is asymptotic with x_i = 0. This means that the irreversibility increases exponentially when wanting to decontaminate A from B, or B from A. The separation of the last contaminating particles requires an exponentially increasing exergy. We call this behaviour the exergetic "U".

This exergetic "U" is incredibly important from a practical point of view. Oregrades of many mineral deposits are usually at very low concentrations of the 10^{-1}, 10^{-2},...,10^{-n} type. These low ranges imply that when depleting a mine with an initial concentration of 10^{-1} and reducing it to one of 10^{-2}, the exergy required for the same amount of extraction is multiplied by 10, and so on by 100, 1000,..., whereas what remains are declining residual traces. For example, this trend is historically proven with gold, where its ore grades have been reduced by several orders of magnitude over the last 120 years [13]. In addition, as the actual processes are far from reversible, extraction and beneficiation of minerals require an amount of energy several orders of magnitude higher than the thermodynamic minimum.

It is not our technological ignorance that imposes such behaviour, but thermodynamics, which describes the ideal case of separation. In other words, even if today's mining operations operate gigantic equipment, the physical decline of global oregrades will require more and more energy per tonne of ore extracted.

Unfortunately, metallurgical processes are also subject to the law of entropy. The energy costs for the reduction, purification and refining of metals are even much higher and always far from their thermodynamic minimum the more we want to purify them.

In other words, the law of entropy is evident in the earth's crust. It is not an orderly reservoir of minerals, like in a "department store". This phenomenon had to be added to the Thanatia theory. Many techno-optimistic messages say that there are enough minerals to sustain global development based on new technologies because abundant minerals are in the earth's crust. Apart from the fact that there are unexplored areas with some constraints, they forget that mineral concentrations are not homogeneous, but declining. The best oregrades are first exploited -"low-hanging fruits"- then decline until they become unviable. So energy, water, tailings movement, environmental, social and economic impacts will grow exponentially, perhaps in decades or centuries.

2.2. Exergy, extraction and replacement costs and thermodynamic rarity

The chemical reactivity of non-fossil minerals is very weak and undistinguishable among them. Therefore, their chemical exergy cannot be used to create a theory to value them. Their demand is linked to the physicochemical properties of the chemical elements or compounds obtained from them. To become useful, they are extracted, beneficiated, processed and refined. And all these operations require energy from chemical or electrical sources. So instead of valuing minerals by their exergy content, through, for instance, the well-known Reference Environment by Szargut [14], we have to value them by the amount of exergy needed to process them from cradle to market, i.e. by their exergy cost of extraction, which can be measured in kWh.

The value of a mine is linked to its mineral concentration or oregrade. This value decreases as the mine is exploited. So, the variation of their costs is also important because it is an indicator of mine depletion and, by extrapolation, of the loss of the planet's mineral capital.

However, extracting cobalt is not the same as extracting aluminun. The latter is abundant in the earth's crust, and the former is very scarce. So scarcity is also an indication of value. Whereas we relate the value of scarcity to the physical cost of forming it, we have a problem because the exergy cost depends on the limits of analysis we choose. The resources used to measure it have a cost that expresses the amount of resources used to produce them, and so on, down to the cradle. This accounting has to start from the earth's crust, which can only be measured in exergetic terms once a reference state describing the dead state of the crust itself has been defined.

Note the linkage of the search for natural costs with the need to identify the terrestrial biosphere as the cradle or reservoir and the origin of all chemical elements. To value these costs, a theory is needed to define the "physical effort" in extracting the minerals. Exergy is the key, but quantifying it requires a reference environment, which we call *Thanatia*, as previously explained. An economic theory of costing mineral scarcity without defining a physical reference environment would be highly controversial.

In addition, mineral deposits often contain a variety of metallic compounds that are extracted together (metal companions). In the beneficiation or downstream processes, allocating costs between products and waste is necessary. This brings us back to the exergy analysis.

Let us clarify concepts. We call *exergetic cost of extracting and processing a mineral* the amount of exergetic

resources needed to extract a mineral and process it until the market of a given commodity. Therefore, all commodities should have their cost measured in kWh, for example. Whereas, if standardised energy consumption data were available for all mines, it would be possible to classify and catalogue these costs. The lack of standardised data from mines around the world is disappointing.

However, these costs do not consider the scarcity of metals in the upper crust. Indeed, whereas a metal is very scarce, its composition in Thanatia will be of the 10^{-n} type, with a very high n. For example, n is 9 for cobalt, while aluminium is 3. In other words, aluminum is a million times more abundant in the crust than cobalt. Extracting 1 kg of cobalt from Thanatia with the same technology would require a million times more waste rock removal than 1 kg of aluminum. However, the price of cobalt is not a million times higher than that of aluminum, which shows that the market may be more or less sensitive to extraction costs but not at all to geological scarcity. Therefore, the loss of mineral capital from the earth must be sensitive to genuine geological scarcity to know the limits of depletion.

To properly assess geological scarcity, it is necessary to resort to the exergetic "U", which formulates an exponential behaviour for the consumption of exergy in the systematic replenishment from Thanatia to the mine. Continuing with the example of cobalt, its concentration in present-day mines is of the order of 10^{-3}, so the cost of replenishing that mine from Thanatia would require one million times the energy of current cobalt extraction. No current or future economy could bear such costs, which makes cobalt management a global problem.

Consequently, we define "replacement cost of an ore (at zero level)" as the exergy that would be necessary to replace, with current technology, the concentration of an ore found in its mine from its concentration in Thanatia [15]. In essence, this cost is an avoided cost or bonus that nature offers us for free (see Figure 1). An imaginary cost can be assessed by measuring the energy it would take to concentrate a chemical from a common rock to a concentration equal to that of the mine. Examples of these avoided costs are presented in Thanatia's books [4, 16].

When the replacement costs of metals that are not as scarce as cobalt or gold are assessed, the replacement cost of some metals is close to their extraction cost. This is the case for rare earths, which are more common than copper but very expensive to extract and separate. To solve this paradox, we proposed the concept of thermodynamic rarity [17], which is defined as the sum of the replacement cost plus the extraction cost. Indeed, some metals are scarce but feasible to obtain, such as cobalt, and others are abundant but difficult to separate, such as rare earths. And all the others are in the middle of this range.

However, the idea of replacement from Thanatia is extremely radical because long before reaching Thanatia, extraction would be stopped as technically unfeasible. Therefore, we scale the concept of rarity to an R_1, R_2, R_3 that would correspond to a replacement cost from a concentration 10, 100 or 1000 times higher than that of the metal in Thanatia. Logically, the rarity calculated from the concentration in Thanatia would be R_0.

Skinner [18] and others consider that there is a mineralogical barrier whereby the extraction of a metal does not make sense because of the immense impacts it would cause. Although this barrier can be variable, we consider it one-for-all-metals with a concentration ten times lower than the current minimum for gold extraction. That is, 0.2 gr/tn rock. This would imply removing and treating 500 tn of waste rock per kg of metal.

Moreover, some authors, [19,20] and notably UNEP [21] have focused their concerns based on "mass" scarcity. We believe it is better to approach the concept of energy scarcity, which we call thermodynamic rarity. This concept considers the actual ore grades and is based on physical phenomena. On the contrary, geological mass scarcity becomes meaningless when we look at the magnitude of the earth's crust. Whereas the crust contains 10^{22} tn of rocks and, for example, cobalt has a concentration of 10^{-9} /ton crust, what is several thousand tons of annual extraction versus 10^{11} tn total cobalt, most of it dispersed in the crust that can never be mined?. i.e. cobalt is not massively scarce, but exergetically scarce. It is rare.

The accompanying figure explains the exergetic path of a metal from Thanatia to the mine and then to the market. X represents the concentration of the metal. X=1 would be the pure metal. X_B is the concentration after the beneficiation process. X_m is the metal concentration in current mines; X_L is the concentration in landfills, while X_C is the concentration in the crust (in Thanatia). The mineralogical barrier is somewhere in the red zone for each metal.

Unfortunately, the lack of statistics on mining and metallurgical energy consumption means that many concepts described here have yet to be developed. We leave it to young researchers to assess the mineral capital losses of the planet, as well as to outline and evaluate the mining capital losses of countries or mines over time, as well as market failures, and why not, a different way to hold nature's value. The theory outlined here does not ignore the databases of Life Cycle Analyses but complements them. Their data are fundamental to assessing all the physical impacts of mining. Indeed, water consumption, waste rock movement, reagent use, greenhouse gas emissions, ecosystem destruction and other pollution and consumption are necessary to fully assess the current degradation of mineral resources and the need to conserve them for future generations.
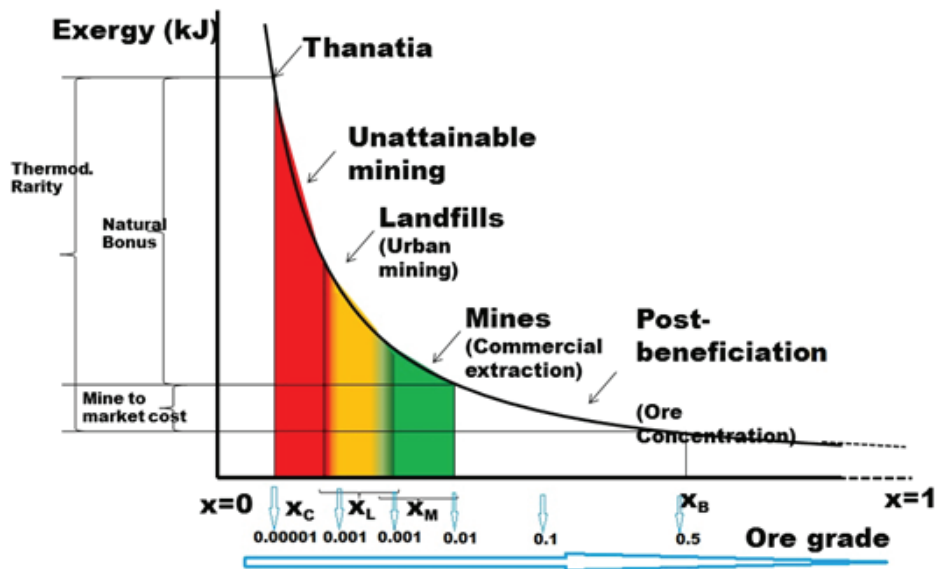
Figure 1: The concept of Thermodynamic Rarity

A final thought in this section: What has been described could perfectly well be called a Thermodynamics of Sustainability. According to the ecological economist J.M.Naredo [22] "Thermodynamics is the Economics of Physics". However, by introducing the concept of cost with all its meanings, in our opinion, the name Thermoeconomics fits better. Not only does it live up to the name it was given in the sixties, but thermodynamics extends its applications to the field of economics, not with metaphors but by quantifying the value of nature that our society ignores, perhaps due to a lack of method, or an excessive interest in forgetting it. It must also be said that by incorporating the word economy in the name, we are honouring all economic mathematics and all the concepts that have been developed until today, for example, input-output analysis, or Lagrange multipliers, to say the least.

## 3. Pristinia, is exergy appropriate for assessing soil fertility?

When we studied the use of exergy to assess the loss of the planet's mineral capital, we found that fertile soils were left out of our analysis. The problem of soil degradation is even faster than that of mineral depletion, Fertile soils are neither abiotic nor biotic but an amazing mixture. Could soil fertility be assessed through exergy? We have done so, but there is a lack of researchers in soil science and thermodynamicists who want to go into this area.

The sustainability of agroecosystems is an important issue considering that food demand will continue growing as the global population increases. A 49 per cent increase in agricultural production is expected to be required by 2050 [17]. In the last decades, crop production yield has been raised by means of employing intensive agriculture based on high inputs of inorganic fertilizers and pesticides, resulting in severe environmental impacts, erosion, and soil quality loss. In fact, the agricultural sector causes approximately 25 per cent of the global greenhouse gases [23]. Besides, degradation caused in soils threatens around 40 per cent of the land area. In Europe, it is estimated that there are 12 million hectares affected by erosion [24].

Compared with the 15 km de upper crust, fertile soils only occupy, on average 15 cm, of topsoil. They are a complex system composed of three main structures: physical, chemical and biological structures. First, their physical texture comprises a variable clay, sand and silt composition. Second, its chemical composition with an inorganic part of at least 19 nutrients and a rich and varied organic part is essential to improve the physical characteristics and as food for the soil biota. The 19 inorganic nutrients are divided into macronutrients like N, P, K, Mg, Ca and S, then micronutrients like Fe, Mn, Cu, Ni, Mo, B, Zn and Cl, and then, other beneficial elements essential for certain species or under specific conditions like Na, Si, Co, Se and Al. Third, their biological content consists of macro and microbiota with bacteria, fungi and viruses. Besides that, water, air and a specific range of temperatures are vital needs.

It is clear that the Thanatia model is not suitable for assessing soil fertility. Moreover, each area of the globe has different local textures and fertility also depends on climate. Therefore, it is necessary to establish a suitable

methodology to serve as a starting point for assessing soil degradation. We adopt a new strategy, proposing an optimum soil that allows us to analyse all real soils as deviations from an optimum towards Thanatia, Figure 2. Accordingly, we introduce a perfect fertile planetary crust, OPTSOIL [25], composed of nutrients, OPTNUT, and organic matter, OPTSOM, that is invariant and independent of different local textures, but not independent of its water content and aeration. We call this imaginary, copiously fertile crust Pristinia as opposed to Thanatia, a dead state referring to abiotic resources. Thus, any real agricultural soil will be in an intermediate state between Pristinia and Thanatia.
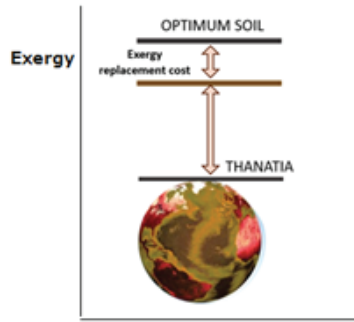
Figure 2: Degraded soils are between Thanatia and an optimal soil in nutrients, organic matter and biota.

The departure of each agricultural soil from the optimum soil can be associated with a sum of physical, chemical and biological causes that can be assessed exergetically. The idea is to evaluate a spectrum of actual degradations of agroecosystems, including those occurring in the soil, and to see the physical cost of their regeneration. For this purpose, the concept of exergy replacement cost is used. As shown in Figure 3, the exergy costs of mechanical processes, fertilisers, pesticides and plant protection products, water and diffuse emissions generated in the agricultural process are quantified. In addition, the substitution processes necessary to return the soil from the final state to the initial state (or optimum state) have been defined and evaluated. In this sense, losses due to erosion, nutrient amendments, organic matter, salinity and acidification are quantified through their exergy costs.
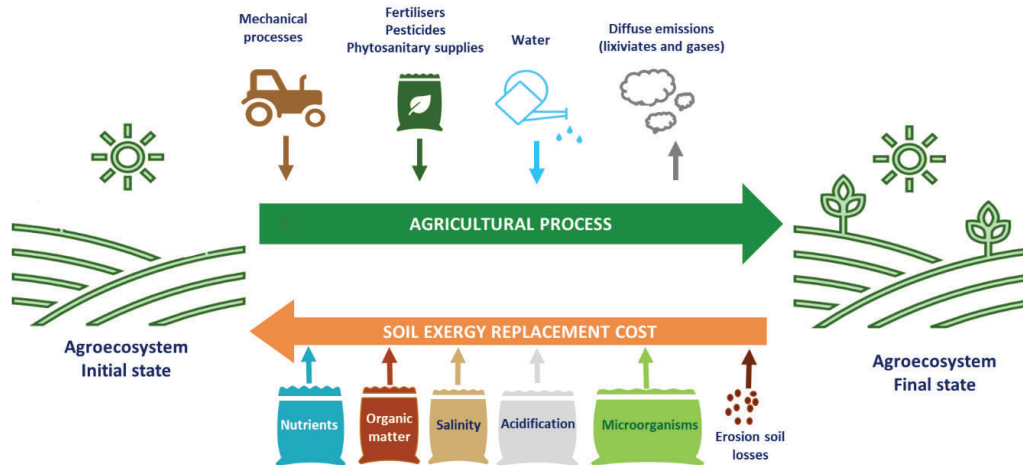
Figure 3: Graphical summary of the exergy-based methodology for the evaluation of agroecosystems.

These are the foundations of an incipient line of work. The next steps should focus on the importance of soil microbiota, OPTMIC, using Jorgensen's concept of eco-energy [26], also in evaluating organic matter in terms

of CO_2 sequestration achieved, which is controversial because of the difficulty of demonstrating its long-term stabilisation. Further development will aim to assess soil considering not only its agricultural production and carbon sequestration functions but all the different ecosystem services it provides, such as habitat provision, biodiversity, water regulation and purification, and environmental quality, among others.

Even with these drawbacks, our methodology has been awarded with a recognition of a reference document from the European Committee for Standardization (CEN).with the title: "Methodology to quantify the global agricultural crop footprint including soil impacts" [27].

This European CWA specifies a methodology for identifying, characterising, and implementing a single indicator to assess the quality and degradation of agricultural soils and the overall impact of the agriculture processes. The agriculture impacts are assessed through the associated mechanical, fertilisation and irrigation activities. Furthermore, soil impacts are evaluated accounting for soil erosion and parameters such as nutrients, texture, and organic matter. The developed methodology allows a simple but robust assessment of soil biogeochemical processes and the loss of fertility and degradation

4. Waste and Circular Thermoeconomics

The concept of waste has not been sufficiently analysed in thermoeconomics. By waste, we mean any unwanted material or energy flow, solid, liquid or gaseous, or a heat, noise or any radiative flow. From a thermodynamic point of view, it is simply the external irreversibility that generates entropy outside the system under analysis. Waste is harmful because it still has exergy and we have to consume it to get rid of it.

Every time we produce, we generate waste. And every product, sooner or later, also becomes waste. This consideration is important because it allows us to distinguish between waste from production processes and the end-of-use waste of material goods. The former corresponds to the remains of the resources used in the processes; let us call them primary waste because they are produced simultaneously as the products are obtained. The latter corresponds to the degradation or elimination of material goods of an inorganic nature or to the discarding of parts of organic substances. Municipalities usually collect this type of waste, and we call it here secondary waste. Their treatment, reduction and disposal require more energy, water and raw materials, which constitute the input for their processing, while new products and tertiary waste are produced, which constitute their output. Thermoeconomic analysis can therefore be applied to them.

Thermoeconomics enables to obtain a coherent and significant set of costs in a given energy structure [28]. Costing allocation essentially looks for the amount of resources needed to produce both intermediate and final products. The irreversibility cost formula [29] allows to calculate the (direct) exergy cost as the exergy content of a flow plus the sum of the irreversibilities generated to produce that flow.

$$B_i^* = B_i + \sum_{j}^{n} \phi_{ij} \, I_j \tag{1}$$

The coefficients ϕ_{ij} represent the part of the irreversibility of the equipment -j- that has been generated to produce one unit of the flow -i-. These coefficients depend exclusively on the definition of the production structure of the plant and the definition of the efficiency of each of its components. Therefore, this formula is the connection between thermodynamics and the second law (exergy and irreversibility) and economics (costs) derived from the definition of the productive purpose of the plant components.

As waste is an integral part of the production, just as one assesses the process of product cost formation, the process of waste cost formation must also be evaluated. Considering that waste has exergy, it is rational to think it could still be used for production. But there is a lack of technology and a surplus of ignorance of nature. Externalisation' is the endorsement of the harms we cause outside the production system. At best, we pay money, in the form of taxes or fines, for society to mitigate them, or we send them to those countries that accept them in return for payment, thus creating an increasingly unequal world. Otherwise, society must adapt to environmental degradation, leaving the burden on future generations.

A responsible society must "internalise" waste and its costs. For this, it is necessary to develop techniques that rigorously assess, for example, both the CO_2 emitted and the CO_2 avoided in each waste treatment process.

Many thermoeconomic analysts have focused on proposing costing assessment procedures for polygeneration plants [30, 31]. Some of these analyses assess the costs of waste remediation or abatement [32], which must then be added to the cost of the products. The result is clear: the cost of the products increases. And the more complex the waste, the higher the costs added to production and, thus the higher the prices of all goods. This is something that today's society does not easily accept.

However, whereas waste has exergy, it can be used to improve the plant's or plants' efficiency in a cyclical production chain and thus reduce production costs, creating the positive effect of reducing resource consumption and waste emissions.

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In many cases, this use of waste energy requires new industrial processes and/or new companies that make up the links in the industrial chains. It is clear that innovation can come from the thermoeconomic analysts themselves, leaving behind more or less irrelevant procedural discussions on achieving a better cost allocation.

The process of waste cost formation must be a priority objective in this new Circular Thermoeconomics. Waste costs must be rigorously assessed because they are the compass for decisions to improve production processes, both within production plants and/or in increasingly complex industrial chains. Whereas we internalise waste costs, eq. (1) will also be accountable for these wastes as (external) irreversibilities. The coefficients ϕ_{ij} also contain information on the internalisation of waste. Therefore, if external irreversibilities (wastes) are recovered, the production costs are reduced. The keyword recycling must be intrinsically related to efficiency and cost. It can be used interchangeably by thermoeconomics, circular economy and industrial symbiosis.

Although it may seem to direct ideas to one's advantage, using exergy makes it possible to quantify any material or energy waste in kWh. This makes it possible to create a general theory based on exergy. Furthermore, exergy can be evaluated with any other energy indicator, e.g. in kg or natural gas equivalent. This allows us to convert it into CO_2 equivalent emitted in the production or, alternatively, to evaluate the CO_2 equivalent savings between two production structures. This is important because it gives rigour to the huge simplifications of GHG emission calculations that are made today in increasingly complex systems.

When applying thermoeconomics to the exergy recovery process of waste, a pinch point of recoverability always appears where total recycling is unattainable because a further increase in recycling does not correspond to the same efficiency increase. The "pinch points" of waste must be identified and systematically diminished. Reality imposes the fact that it is not possible to recycle everything. Hence we should not speak of Circular Economy but of Spiral Economy [33]. The latter makes it possible to assess the degree of spiralling of a material cycle, understood as the percentage of exergy loss with respect to the exergy brought into play in the whole cycle. In this way, spirality can be related to the concept of pinch point, as the economically viable exergy percentage of recovery of a residual flow, measured in the potential for narrowing of its intensive properties of the type ΔT, ΔP, etc.

It is remarkable to see that the search for better energy efficiency is often linked to reduced material efficiency. Nonetheless, this fact has been systematically forgotten. For example, cars, which are nothing more than mobility production plants, consume less and less fuel per kilometre, but we forget that the material complexity of their digitisation has radically reduced their material efficiency. A vehicle from 50 years ago contained only steel, aluminium, copper, rubber, glass, wood and some plastic. Today's vehicles contain more than 55 chemical elements, with a myriad of plastics, alloys and micro-components full of critical raw materials. Their non-recyclability is notorious, and they are not designed to recover their spare parts. Circular thermoeconomics can provide striking answers to this problem because whereas the exergy costs of extraction and replacement of the materials are involved in the analysis, it is possible to assess the relationship between exergy savings and the exergy invested in obtaining them, ExROI. The results obtained yield important conclusions on how our society is squandering the earth's mineral capital in favour of a pseudo-energy efficiency of all processes. This is a strong reason to recycle materials, especially the most critical ones.

The message we can give is that goods are cheap because we internalise the price of products, neither the cost of the scarcity of natural resources nor the impact our waste has on planetary habitability.

Nature closes its material cycles, because the waste generated by one living becomes the resources of others, making the biosphere-geosphere complex a sustainable system driven by solar energy and the planet's internal heat. Nature has its rhythms and the closing of these cycles can even take geological time, as is the case with fossil resources. On the contrary, our society is in a hurry and lets its waste go underground (landfills), turn into gases (incineration) or be diluted in the atmosphere and the hydrosphere.

This is no small task, the production of waste and the depredation of natural resources are closely related to the nine planetary boundaries that Rockstrom et al, [34] point out: climate change, ocean acidification, stratospheric ozone, nitrogen and phosphorous cycle, global freshwater use, deforestation and topsoil degradation, biodiversity loss, chemical pollution, and atmospheric aerosol loading. To these must be added, among others, the more recently reported phenomena such as oceanic pollution by microplastics or the massive extraction of critical raw materials to sustain new digital and renewable technologies.

Against this scenario, thermoeconomicists cannot close their eyes to the most efficient use of waste. Beyond the processes of remediation or abatement of waste, it is necessary to think about the use and reuse of industrial and individual waste. This is the origin of Circular Thermoeconomics. We must learn from nature. The waste of one production plant should be the resource of another. We must design to make the use of waste materially and energetically viable. Cyclical industrial chains must be created to give new life to waste. The concepts of industrial symbiosis and urban-industrial symbiosis must be extended to the whole productive system, which will affect a social change of attitudes.

An introduction to Circular Thermoeconomics can be found in [35]. We invite new researchers to develop both
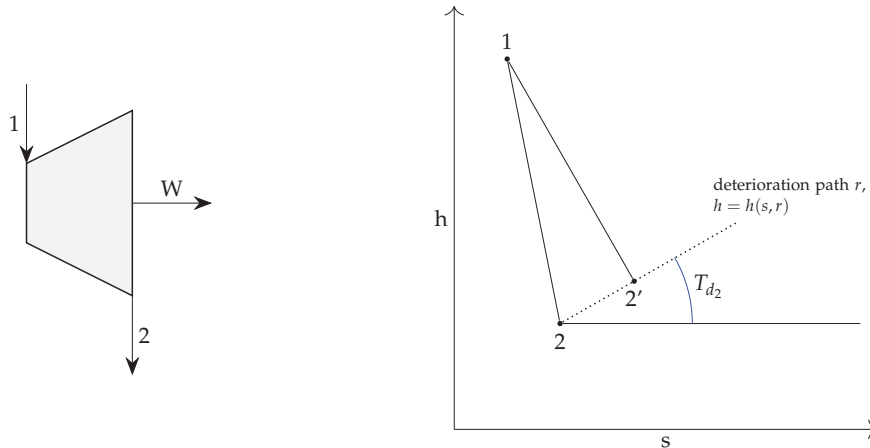
Figure 4: The deterioration path of a turbine.

this theory and its multiple applications that have been proposed with these reflections.

5.   Exergy or Relative Free Energy?

There is a consensus among practitioners that exergy is the thermodynamic property that best distributes production costs among various streams, which then helps to establish the economic costs of the streams that interact in any energy system. However, the exergy calculation has the shortcoming that it depends on the reference environment applied, which in turn is an arbitrary selection of the user and not a physical behaviour of the system under analysis. If this is the case, the concept of exergy efficiency, although more precise than the first law efficiency, still depends on the chosen reference environment.

This problem is even worst in thermoeconomic diagnoses of very complex plants using exergy costs, since the chains of causation may induce wrong malfunctions and dysfunctions. There might be a consensus regarding which is the most suitable. However, convergent opinions are not mathematical proofs. Is it possible to find a better function to get rid of this problem? The answer will need future research, perhaps the "relative free energy function" has the "way" of solving this problem. This section explains why is it.

Any machine that uses a working fluid is designed to change its intensive properties, such as its pressure, temperature, chemical potential or electromagnetic potential, making its energy transfer to another part of the machine.

Suppose now that the working fluid malfunctions due to intrinsic reasons of the machine. If the fuel quality, f, does not change, it will be necessary to increase the amount of fuel to get the same product, P. Then, this excess fuel becomes dissipated in the form of heat.

The enthalpy and entropy balances of the working fluid process, under the conditions (h_1, s_1) and P constant, will be:

$(h_1 - h_2)\, dm = m\, dh_2$
$(s_2 - s_1)\, dm + m\, ds_2 = dS_g$

As the deterioration process of the machine is compensated by higher fuel consumption, both dm and the entropy generated are positive. So is the heat dissipated, $m\, dh_2$, and the entropy increase of the fluid, $m\, ds_2$. If one defines the deterioration temperature of flow in state #2 as the quotient:

$T_{d_2} \equiv dh_2/ds_2$

the result of the combined balances is as follows:

$$\left(\frac{dm}{dS_g}\right)_r = \frac{T_{d_2}}{(h_1 - h_2) - T_{d_2}\,(s_1 - s_2)}\;, \tag{2}$$

where r is the deterioration path in the (h, s) plane of the outflow, as show in Figure 4 for the case of a turbine.

Equation (2) states that any deterioration process in an energy component has an associated T_d in the exit stream of supplying fuel. This parameter possesses temperature dimensions even if it is not a gauging temperature; it can be calculated by measuring the quotient dh_2/ds_2 experienced by the output stream of the component's fuel.

This equation is the mathematical expression of the relationship between the additional consumption of the resource needed to compensate for an internal degradation of the machine when the output of the machine is kept constant.

Equation (2) and the function ℓ, whose variation is defined as:

$$\ell_1 - \ell_2 \equiv h_1 - h_2 - T_d(s_1 - s_2)$$

where presented in [36], and was called the *relative free energy*, RFE. It is surprisingly similar to the exergy variation of the working fluid, which may explain the attachment and intuition of process analysts to exergy. However, RFE is mathematics while exergy comes from consensus.
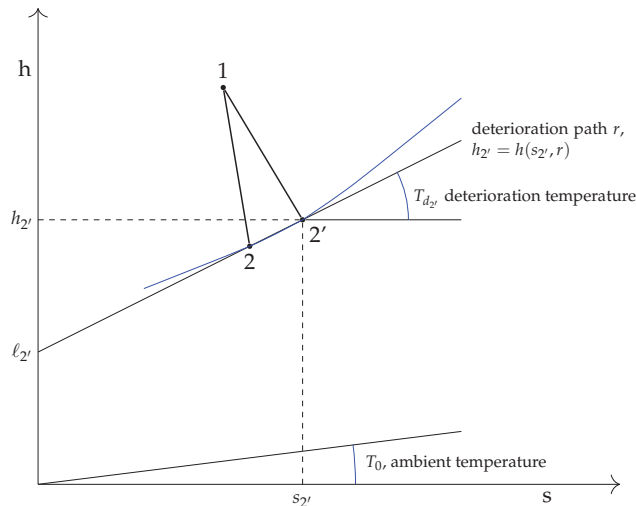
However, the deterioration temperature no longer depends on the chosen reference temperature for exergy calculations. Although T_d has temperature dimensions, is not a gauging temperature; it can be calculated by measuring the ratio dh_2/ds_2 experienced by the machine´s fuel at its output.

For a given deterioration cause r of a machine, a geometric path in the (h, s) plane of the possible exit flow states can be identified. Let $h_2 = h_2(s_2, r)$ be the function describing this outflow deterioration path, and it can be considered as the mathematical description of the effects on the exiting flow caused by such deterioration.

As it is shown in Figure 5 the intersection of the tangent line of the deterioration path r with the h- axis is and its slope is T_d:

$$\ell = h - T_d\,s \tag{3}$$

It means ℓ is a function of T_d, with the caveat that both l, h and s refer to the same zero state.

Figure 5: Geometric representation of relative free energy and deterioration temperature.

In reference [37] is shown that (3) is the Legendre transform of the deterioration r.

According to the definition of relative free energy (3), the expression (2) could be written as:

$$\left(\frac{dm}{dS_g}\right)_r = \frac{T_d}{\ell_1 - \ell_2} \tag{4}$$

Note that this equation is always positive, under the specified conditions. Moreover, since $T_d > 0$, then $\ell_1 > \ell_2$, i.e., the working flow has lost part of its relative free energy. In fact, for the same deterioration, $dS_g = const$, the higher the T_d, the greater the amount of resource required to yield the same product. This trade-off is not linear because whereas the numerator increases, the denominator also decreases. On the contrary, when T_d tends to T_0, the impact of this compensation will decrease. Only in the case where $T_d = T_0$, the decrease of relative free energy will coincide with the exergy decrease.

As the environment is an attractor, the T_d of the components of an installation will decrease until it reaches T_0, just as the relative free energy will tend to exergy.

In order to evaluate T_d, it is necessary to know the cause(s) of machine deterioration and its behaviour, which is additional information to be incorporated into the plant diagnosis. In other words, the cost of a malfunction is directly related to the physical behaviour of the machine.

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The relative free energy function, ℓ, is the amount of specific energy of the exiting stream of a fuel, which is not affected by the deterioration of the machine. In fact, when the exit flow changes its state owing to the deterioration, h and s, vary by following the path $h_r = h_r(s_r)$. Consequently, the following expression is obtained:

$$d\ell_2 = dh_r - \left(\frac{dh}{ds}\right)_r ds_r = 0 \qquad \text{or} \qquad \ell_2 = \text{const.} \tag{5}$$

Besides that, a new definition of efficiency (or its inverse specific consumption), For example, in a turbine it is:

$$k_L = \frac{F_L}{P_L} = \frac{\mathcal{L}_1 - \mathcal{L}_2}{W} = \frac{H_1 - H_2 - T_d\,(S_1 - S_2)}{W} \tag{6}$$

Where $\mathcal{L}$ is the corresponding extensive property of ℓ, i.e. $\mathcal{L} = m\ell$. This "relative" efficiency, k_L, has an astounding property that exergy lacks.

When a malfunction in the turbine follows a trajectory r at W constant, it follows:

$$\ell_1\,dm = \ell_2\,dm + W\,dk_L \tag{7}$$

because $\ell_1 - \ell_2$ is constant along trajectory r. Therefore:

$$\frac{dk_L}{k_L} = \frac{dm}{m} \tag{8}$$

in other words, any additional percentage of malfunction following a trajectory r at W constant result in an additional percentage of the mass of fuel entering the turbine. This property is very promising for simplifying the mathematical apparatus of plant diagnosis. Note instead that exergy does not fulfil this property since:

$$ex_1\,dm = ex_2\,dm + m\,dex_2 + W\,dk \qquad dex_2 \neq 0$$

which may induce false dysfunctions. Furthermore, the definition of k_L incorporates the information of the physical behaviour of the machine through T_d, whereas the unit exergy consumption is a black box to what happens inside the machine.

A noteworthy observation is that companies usually account for the resource consumption per unit of output of their installation. This accounting at the facility level is the one we propose in this section at the component machine level. Therefore, whereas we have for each cause of deterioration, r, the derivative $(\partial m_{local}/\partial S_g)$ and whereas we could evaluate how the amount of local equipment resources is related to the facility resources (of the same quality), i.e., $(\partial m_{plant}/\partial m_{local})$, we could obtain a new theory of energy system diagnostics. In theory our proposal would obtain the derivative: $(\partial m_{plant}/\partial S_g)$,that is $(\partial F_T/\partial S_g)$, where F_T are the plant resources. Note that what says "plant" here could also mean any disaggregated part of the overall plant structure, without needing to resort to the reference environment. This is what companies need for good energy consumption management, i.e. the genuine costs of the deterioration of each and every component of their installation.

Perhaps, the described procedure is much simpler than assessing the diagnosis using exergy costs:

$$\left(\frac{\partial Ex_{plant}}{\partial Ex_{local}}\right)_r$$

Regrettably, actual installations may have several simultaneous causes of degradation and their impact on overall efficiency would not necessarily be the sum of each cause separately.

Thanks to the Legendre transform we have shown that the RFE and the deterioration temperature are as real as the actual path of degradation of the working fluid in a machine. They have a physical basis and are not merely theoretical inventions. Unlike other thermodynamic functions that only depend on the equilibrium states of the system, the pair (RFE, T_d) only exists whereas the machine exists. It is like transferring the deterioration message from the machine to thermodynamics,

Incredibly, it was first presented in 1992 at the ECOS conference [36], with the earliest work by Alefeld at the University of Munich [38] that went almost unnoticed, perhaps because of the excessive cult of exergy. In spite of this, the use of this function in diagnostic applications and cost assessment of malfunctions in industrial energy systems is still to be developed. We leave it to future thermoeconomics practitioners to develop such ideas.

6. Conclusions

Science to be positive must be quantifiable and predictive. In general, the use of the messages of the second law of thermodynamics in the social sciences and in economics is more philosophical than operational. In

contrast, by redefining cost as a sum of irreversibilities and setting it up from the cradle to the market, we are connecting Thanatia with economics. That is Physics with Economics in a quantifiable and predictive way.

The first ideas of thermoeconomics and its very name are due to Myron Tribus, Robert Evans and Yehia El-Sayed in the sixties of the last century [39, 40]. It was created before Georgescu-Roegen published his book *The law of entropy and the economic process* [1] which claimed that economics had forgotten the concept of irreversibility. Unfortunately, thermoeconomics focused mainly on analysing industrial thermal systems, forgetting the message of its own name.

We believe that beyond converting irreversibility into money and weighing it against investments in production equipment, it is necessary to measure economic activities in terms of irreversibility in order to give value to the services provided by the planet.

The concept of a planetary dead state, Thanatia, allows the loss of mineral capital to be assessed in terms of quality and quantity. What is rare is valuable and must be conserved. We can move from the yes/no dichotomy to the physical quantification of nature's losses. And thus weigh the nature we lose against what we gain by engaging in any activity. And in doing so we will give value to the regeneration, repair, replacement and restoration of materials that are key to sustaining humanity for many generations to come. The supply of planetary wealth is not of an economic origin of the demand/supply equilibrium type, but of planetary limits. And in the face of this phenomenon, agreements between people or between countries are not valid, but rather in the assumption of the irreversibility that will condition the future of humanity itself.

Available mineral phosphates are limited to sustain the supply of a few generations. Electric mobility is limited by the enormous amount of chemical elements, more than 50, needed for high-tech vehicles. The digital economy is based on the profusion of non-recyclable microchips and printed circuit boards, extremely short-lived and full of rare metals. The same is true for renewable energy. The energy transition must be accountable for its material impact.

Similarly, current agricultural practices are degrading fertile soils which are the scarcest natural resource of all. Again, it is the second law that allows us to objectively evaluate all deviations from a model copiously fertile crust, called Pristina, as opposed to Thanatia. With the exergy methodology, we have a single indicator to value all the factors that intervene and form the soil. The recognition of this methodology awarded as a reference document from the European Committee for Standardization opens the door to refining and developing its applications.

Another major global problem is the production of waste, not only solid but also liquid, gaseous, noise, heat and radiation of all kinds. They are produced at the same time as we manufacture goods and consume them. They disturb and above all affect the planet in the form of climate change, pollution and the degradation of ecosystems. Whereas they do this damage, it is because they still have exergy. Harnessing them minimises remediation and abatement costs. Society must learn to internalise waste in order to give it new life and avoid its effects. To this end, industrial symbiosis must be generalised, in which the waste or by-product of one company is the resource of another, trying to close cycles (spirals) of all materials. This activity implies the promotion of a new industrial sector that will need to assess (and optimise) all the losses and savings that occur. The circular thermoeconomics outlined here will be an important branch of the future of second law analysis.

Last but not least, the relative free energy and its conjugate, the deterioration temperature, can take a step beyond the use of exergy in the diagnosis of energy systems, and above all to explain why the diagnosis should not depend on the analyst's choice of reference state. Throughout history, the emergence of new basic functions has been a far-reaching scientific event that has opened up new avenues and applications of thermodynamics. As such, it deserves to be welcomed by the thermoeconomic community.

In short, we at the Zaragoza School of Thermoeconomics believe that the "second law analysis" should be expanded to apply it to important problems facing our civilisation, such as the conservation of the planet's energy, water and material resources; the diagnosis and intelligent management of fertile soils to feed current and future living beings; and the minimisation of waste by closing material supply chains, promoting new industrial sectors for waste recovery, still in its infancy. The Thermodynamics of Sustainability of the future must include Thermoeconomics and all theoretical developments that help with these problems are welcome.

Acknowledgments

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