

Exergy analysis and resource accounting

by

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## **Author's declaration**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

## **Abstract**

The objective of this thesis is to establish the utility and limitations of using exergy (a thermodynamic measure of energy quality, or ability to perform work) as a resource consumption metric, and to investigate what role exergy may play in resource consumption decision-making. To do so, this thesis assessed three exergy-based resource consumption methodologies: the Exergy Replacement Cost; Eco-exergy; and Emergy. Furthermore, fundamental properties of exergy were revisited, including the exergy reference state, and the derivations of both concentration and non-flow exergy.

The results of the analysis indicate three significant problem areas with applying exergy toward resource valuation. First, the exergy derivation level conflicts with the resource valuation level regarding important requirements and assumptions: the exergy reference environment is modelled as an infinitely large system in internal chemical equilibrium, and this is incomparable to the real world; and, the derivation of non-flow exergy values items based solely upon chemical concentrations, whereas at the resource consumption level, work producing items are valuable based primarily upon chemical reactivity. Second, exergy proponents have not adequately addressed the many different and critical perspectives of exergy, including exergy as: harmful or helpful; organizing or disorganizing; a restricted or unrestricted measure of potential useful work; and applied to value systems or specific items. Third, none of the resource consumption methodologies properly apply exergy: the Exergy Replacement Cost primarily focuses on mineral upgrading; Eco-exergy is improperly derived from exergy; and Emergy has switched from being energy-based to exergy-based without any reformulation of the methodology.

For the reasons provided above, among others, this author concludes there is currently no justified theoretical connection between exergy and resource value, and that there is a disjunction between how exergy is derived and how it is applied. Non exergy-based applications for the three resource consumption methodologies are proposed.

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I would like to thank Christy for putting up with me these past two years. It has been an awesome adventure so far.

I would like to thank the Government of Canada (via NSERC) for funding this research over the past two years.

Finally, I would like to thank my friends, family, and stuffed animals for allowing me to use the word ‘exergy’ in casual conversation.

## Dedication

I dedicate this thesis to all those poets out there who struggle to understand thermodynamics. It turns out you're not alone!

*Exergy, exergy, burning bright  
Oh what power! Oh what might!  
No matter how hard I may try  
I'll never match your quality.*

*Adapted (and improved) from 'The Tiger', by William Blake.*

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# Chapter 1 – Introduction

The objective of this thesis is to establish the utility and limitations of using exergy as a resource consumption metric, and to investigate what role exergy may play in resource consumption decision-making. Exergy is a thermodynamic measure of energy quality, or ability to perform work, as defined more fully below in section 1.1.1.

The United Nations states that “energy is central to sustainable development” (UN 2008). Without appropriate sources of energy, a society will be unable to maintain or improve its standard of living (IISD 2008). Some of the problems related to energy and resource use are using resources too quickly (such as fossil fuels), the environmental impact due to resource extraction, and the wastes generated due to resource and energy use (Wall and Gong 2000; Rosen and Dincer 2001; Rosen 2002; Dincer and Rosen 2005). These problems are considered a critical challenge for the United Nations Millennium Development Goals (Takada and Fracchia 2007).

Understanding the relationship between energy, resources, and sustainability requires a means of quantifying resources and resource consumption. This thesis explores three thermodynamic approaches to valuing resources for the purpose of quantifying resource consumption. All three thermodynamic approaches relate to exergy in some regard.

## **1.1 Exergy and resource consumption**

### **1.1.1 What is exergy?**

Exergy is a thermodynamic concept derived from the second law of thermodynamics (for a complete derivation, see Bejan 1998, chs. 3 and 5). There are several definitions of exergy, all of which encompass the same basic idea, but vary in which the derivation assumptions are made explicit. In this thesis, exergy is defined based on the work of Wall (1977), and reiterated by Cornelissen and Valero in their recent dissertations on exergy (Cornelissen 1997, ch. 1; Valero 2008, ch. 1):

*The exergy of a system in a certain environment is the amount of mechanical work that can be maximally extracted from the system in this environment*

Exergy has also been defined via the reverse process, creating a material from the reference environment, as provided Szargut (2005, ch. 1):

*Exergy expresses the amount of mechanical work necessary to produce a material in its specified state from components common in the natural environment in a reversible way, heat being exchanged only with the environment.*

Fraser and Kay (2003) provide a third definition of exergy that explicitly references that exergy is concerned with useful work (work that may turn a shaft or lift a weight):

*Exergy is the maximum useful to-the-dead-state work*

For the purpose of the thesis, the three definitions of exergy above are nominally equivalent. However, in Chapter 6, this author will argue for better refinement of the exergy concept, and this would include a more explicit definition of exergy.

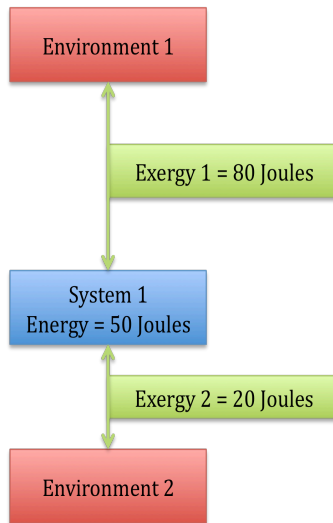
Exergy is commonly referred to as the *quality* of the energy (Wall 1977; Szargut, Morris et al. 1988; Cornelissen 1997; Rosen and Dincer 2001; Kay 2002; Sciubba 2003; Rosen, Dincer et al. 2008, to name but a few), where *quality* is understood as *the ability to perform useful work* (such as lifting a weight). Similarly, exergy is also considered to be the *useful* part of matter or energy (Dincer and Rosen 2005). While interpreting exergy in terms of quality or usefulness allows for helpful interpretations, this may cause confusion at times because exergy is formally an extensive concept (Sciubba 2001; Dincer and Rosen 2007 ch. 1), whereas quality and usefulness are intensive. However, in most situations, it is possible to determine whether the author is using exergy extensively or intensively based upon the context.

### **1.1.2 The properties of exergy**

Before developing the argument between exergy and resource consumption, three properties of exergy must be briefly mentioned. These three properties are generally understood as advantages of exergy over other thermodynamic concepts, specifically energy. While the veracity of these three properties will be examined in detail in this thesis, they provide initial justification for using exergy. However, it must be noted that the claims made concerning the general properties do not represent the conclusions of this thesis, but rather serve as an introduction to why exergy is useful to explore further.

### 1.1.2.1 Context sensitive

First, exergy is *context sensitive* as a result of being formulated with respect to a reference environment (Wall 1977; Wall and Gong 2000; Rosen and Dincer 2001; Rosen and Dincer 2004; Valero 2008). The farther a system is (thermodynamically) from its reference environment, the greater the exergy will be. This concept is shown heuristically in Figure 1-1.



**Figure 1-1 - Exergy changes with reference environment**

In Figure 1-1, the system is thermodynamically farther from Environment 1 than from Environment 2, and consequently the system has more exergy with respect to Environment 1. By contrast, regardless of what reference environment is chosen the system maintains the same internal energy of 50 Joules. As can be seen, energy is not considered to be context sensitive, whereas exergy is.

While not shown in Figure 1-1, a system in thermodynamic equilibrium with a reference environment has no exergy (Rosen and Dincer 1997; Rosen, Dincer et al. 2008). By consequence, the reference environment itself may not be a source of exergy because it is in internal stable equilibrium (Rosen and Dincer 1997).

### 1.1.2.2 Universal

Secondly, exergy is *universal* because all thermodynamic systems can be compared based on their exergy content. In other words, exergy quantifies all resources under the same unit (Wall 1977; Cornelissen and Hirs 2002). Exergy proponents cite the value of the

universality of exergy in the context of lifecycle assessments (Cornelissen 1997; Cornelissen and Hirs 2002).

To once again contrast exergy with energy, exergy proponents claim that energy is not universal, and may be misleading at times because not all forms of energy have the same quality (Cornelissen 1997; Cornelissen and Hirs 2002). For example, in lifecycle assessments that use energy as the primary unit, quality factors must often be applied to account for different energy forms (Berthiaume, Bouchard et al. 2000; Gong and Wall 2000). By contrast, researchers argue that an exergy lifecycle assessment automatically accounts for the different forms of energy and their respective qualities, and thus allows all energy forms to be assessed within one unit (Wall 1977; Cornelissen and Hirs 2002).

### **1.1.2.3 Not conserved**

Third exergy is *not conserved* in real processes (Wall 1977; Rosen and Dincer 1997; Bejan 1998; Wall and Gong 2000; Dincer and Rosen 2005; Dincer and Rosen 2007 ch. 1; Rosen, Dincer et al. 2008). Whereas energy can never be created nor destroyed, exergy may never be created and can only be destroyed (or conserved in a reversible process) (Wall 1977; Wall and Gong 2000 ch. 1; Dincer and Rosen 2005; Dincer and Rosen 2007).

Exergy is not conserved because it is a concept derived from the second law of thermodynamics. The connection between exergy and the second law of thermodynamics is best understood via the Guoy-Stodola theorem, shown in Equation (1.1):

$$B_{\text{destroyed}} = T^{\circ} S_{\text{gen}} \quad (1.1)$$

Where  $B_{\text{destroyed}}$  is exergy destroyed,  $T^{\circ}$  is the temperature of the reference environment, and  $S_{\text{gen}}$  is the amount of entropy produced.

The Guoy-Stodola theorem effectively states that work lost is proportional to the entropy produced (Bejan 1998 ch. 3; Dincer and Rosen 2005). Exergy proponents often interpret the work lost to be the exergy potential itself (Cornelissen 1997; Wall and Gong 2000; Valero 2008 ch. 5). The Guoy-Stodola theorem and the interpretation of work lost as

being the exergy will be discussed in section 6.3.1, specifically with regards to the concentration exergy.

### **1.1.3 The breadth of exergy**

In part due to the three properties of exergy listed above, exergy is applied in several disciplines, thereby creating the potential for dialogue between disciplines. Some of the disciplines that adopt exergy are:

**Ecology and systems thinking** (Jorgensen and Mejer 1977; Odum 1983; Kay 1984; Odum 1988; Kay 1991; Kay and Schneider 1992; Odum 1994; Schneider and Kay 1994; Jorgensen, Nielsen et al. 1995; Odum 1995; Odum 1995; Odum 1996; Jorgensen, Mejer et al. 1998; Kay, Boyle et al. 1999; Jorgensen, Patten et al. 2000; Bossel 2001; Jorgensen 2001; Jorgensen 2001; Kay, Allen et al. 2001; Svirezhev 2001; Svirezhev 2001; Ulgiati and Brown 2001; Jorgensen, Verdonschot et al. 2002; Kay 2002; Brown, Odum et al. 2004; Jorgensen, Odum et al. 2004; Bastianoni, Nielsen et al. 2005; Ho and Ulanowicz 2005; Jorgensen, Ladegaard et al. 2005; Homer-Dixon 2006; Jorgensen 2006; Jorgensen 2006; Susani, Pulselli et al. 2006; Ulanowicz, Jorgensen et al. 2006; Jorgensen 2007; Jorgensen and Nielsen 2007; Kay 2008; Kay and Boyle 2008; Ulanowicz, Goerner et al. 2008)

**Resource accounting** (Wall 1977; Wall 1987; Wall 1990; Wall, Sciubba et al. 1994; Wall 1998; Zaleta-Aguilar, Ranz et al. 1998; Gong and Wall 2000; Wall and Gong 2000; Valero, Ranz et al. 2002; Chen 2005; Chen 2006; Chen and Ji 2007; Huang, Chen et al. 2007; Valero 2008; Jiang, Zhou et al. 2009)

**Lifecycle assessments** (Cornelissen 1997; Cornelissen and Hirs 2002)

**Engineering** (Crane, Scott et al. 1992; Rosen and Dincer 1997; Rosen and Gunnewiek 1998; Dincer and Rosen 1999; Rosen and Dincer 1999; Berthiaume, Bouchard et al. 2000; Rosen and Dincer 2001; Daniel and Rosen 2002; Gogus, CamdalI et al. 2002; Rosen 2002; Rosen 2002; Rosen 2002; Rosen 2002; Giampietro and Little 2003; Rosen and Scott 2003; Rosen and Scott 2003; Rosen and Dincer 2004; Dincer and Rosen 2005; Hepbasli and Dincer 2006; Dincer and Rosen 2007; Dincer and Rosen 2007; Favrat, Marechal et al. 2007; Ao, Gunnewiek et al. 2008; Hepbasli 2008; Rosen, Dincer et al. 2008; Utlu and Hepbasli 2008)

#### **1.1.4 The argument to use exergy to measure resource consumption**

The argument to use exergy to measure resource consumption begins with the ‘observation’ that resource consumption is not well quantified using matter or energy, primarily because both are conserved (Wall 1977 ch. 5; Cornelissen 1997, ch. 5; Gong and Wall 2000; Rosen, Dincer et al. 2008; Valero 2008, ch. 1). In other words, from the perspective of the first law of thermodynamics there is no such thing as resource consumption, and resource consumption is improperly defined (Connelly and Koshland 2001; Cornelissen and Hirs 2002).

To quantify how the important aspects of a resource change during consumption, exergy proponents invoke the second law of thermodynamics by noting that resource consumption is in fact analogous to the degradation of the resource *quality* (Wall 1977; Connelly and Koshland 2001; Cornelissen and Hirs 2002). In other words, the exergy destruction of a resource is a measure of the amount by which the value of the resource is consumed, and the exergy of a resource is a measure of the value of a resource (Brodiński ; Wall 1977; Gong and Wall 2000; Wall and Gong 2000; Cornelissen and Hirs 2002; Rosen 2002; Szargut, Ziebik et al. 2002; Sciubba 2003; Dincer and Rosen 2005; Szargut 2005; Valero 2008).

The argument presented above appears to form the basis for using exergy as a measure of resource consumption, and underlies the three resource consumption methodologies that will be presented in this thesis. This argument will be revisited in Chapter 6.

### **1.2 Justification for the research program**

As mentioned at the beginning of this chapter the purpose of this thesis is to examine the abilities of exergy to contribute to the discussion of resource consumption. After outlining the breadth of exergy in various disciplines (section 1.1.3), and the argument for adopting exergy as a measure of resource valuation and resource consumption (section 1.1.4), there must be a valid reason why the topic should be revisited. There are two primary arguments for revisiting the fundamental connection between exergy and resources: first, there is a need for self-reflexive research regarding exergy theory; and



second, there are already some cracks appearing in the theory of exergy. Each of these arguments will be discussed separately.

### **1.2.1 The need for self-reflexive research**

The need for self-reflexive research is a result of how the exergy concepts have been applied with respect to resource consumption. While many exergy researchers argue for exergy as a measure of resources and resource consumption (Brodianski ; Wall 1977; Gong and Wall 2000; Wall and Gong 2000; Cornelissen and Hirs 2002; Rosen 2002; Szargut, Ziebik et al. 2002; Sciubba 2003; Dincer and Rosen 2005; Szargut 2005; Valero 2008), there has been little to no validation of the argument. For the most part, the argument has been applied as a law, most often in the realm of exergy lifecycle assessments and resource accounting tools (Cornelissen 1997; Bakshi 2002; Cornelissen and Hirs 2002; Hau and Bakshi 2004; Hau and Bakshi 2004).

Between the conceptual understanding of exergy as a measure of resource value, and the application of this concept as a law, there is a large theoretical jump that must be made, and this jump contains implicit and potentially unjustified assumptions. This research attempts to seek out those assumptions, make them explicit, and further the discussion. Ultimately, if the assumptions are valid and exergy is an appropriate measure of resources and resource consumption, then nothing is lost and greater theoretical validation is obtained. By contrast, if there are some cracks in the theory, they should be addressed.

### **1.2.2 Some cracks in the theory – the example of exergy and waste impact**

A second argument for re-examining the underlying theory connecting exergy and resource value is that there are already cracks appearing in application of exergy. This section briefly describes the difficulties several authors have encountered in trying to relate the exergy embodied in a waste to the subsequent impact of that waste.

For the most part, the same authors who propose exergy as a measure of resource consumption also argue that exergy measures waste impact. The argument relating exergy to waste impact is essentially that since exergy measures how far a system is out

of equilibrium from its environment, then it also measures of the potential for the system to cause harm (Crane, Scott et al. 1992; Cornelissen 1997; Rosen and Dincer 1997; Ayres, Ayres et al. 1998; Rosen and Gunnewiek 1998; Rosen and Dincer 1999; Sciubba 1999; Sciubba 2001; Rosen 2002; Rosen 2002; Chen and Ji 2007; Dincer and Rosen 2007; Huang, Chen et al. 2007; Talens, Villalba et al. 2007; Ao, Gunnewiek et al. 2008; Rosen, Dincer et al. 2008). A consequence of the exergy-based measure of waste impact is that a system in equilibrium with the environment has no exergy and no ability to cause harm (Rosen and Dincer 1997), and this has led to the promotion of zero exergy emission processes (Cornelissen and Hirs 2002).

Despite the intuitive relationship between exergy and waste impact, there are some methodological problems that have emerged. For example, Rosen's work in the 1990s found little correlation between exergy and waste impact (Rosen and Dincer 1997; Rosen and Dincer 1999); however, he still continues to argue for the connection (Rosen and Dincer 2001; Dincer and Rosen 2007; Ao, Gunnewiek et al. 2008; Rosen, Dincer et al. 2008). Ayres and Favrat both claim that exergy cannot measure toxicity (Ayres, Ayres et al. 1998; Favrat, Marechal et al. 2007). Szargut argues impact is not likely proportional to exergy (Szargut 2005, ch. 5), and this contradicts other authors that claim exergy is additive (and thereby also proportional) (Sciubba 1999; Sciubba 2001; Chen and Ji 2007; Huang, Chen et al. 2007).

To add to the confusion, some authors claim that the exergy embodied in the waste is the minimum work *required* to bring the waste into equilibrium with the reference environment (Creys and Carey 1997; Rosen and Dincer 1997; Rosen and Dincer 1999; Sciubba 1999; Chen and Ji 2007), while others claim the exergy embodied in waste is a measure of work that may be *produced* by bringing the waste into equilibrium with the reference environment (Hellstrom 1997; Hellstrom 2003). Furthermore, some authors are not even consistent about whether the exergy embodied in a waste represents work potential, or work required (Zaleta-Aguilar, Ranz et al. 1998). It should be noted, however, that relating the exergy embodied in a waste to the work required to clean up that waste is directly contradictory to the definition of exergy provided in section 1.

At this point it should be apparent that the basic theory connecting exergy to waste impact is not as solidly grounded as the conceptual argument and intuitive appeal originally suggest. While sorting out the difficulties relating exergy to waste impact is certainly grounds for future research, it will not be explored here, if only because many of the contradictions have already been exposed. Ideally, however, the cracks in the theory relating exergy to waste impact are adequate justification for revisiting the theory of exergy and resource value.

### **1.3 Methodology**

What is presented in this thesis is a theoretical, exploratory, and iterative assessment of exergy and resource consumption. Each of these three qualifiers must be briefly addressed. The research is largely theoretical (and only rarely draws on empirical findings) for two primary reasons. First, the underlying connection between exergy and resources is a theoretical connection, and must be addressed through theoretical means. Second, the few empirically based studies of exergy and resource consumption already begin with the assumption that exergy measures consumption, and by doing this, the research essentially validates itself, thereby making self-reflexive empirical research quite difficult.

The research program is exploratory because there is no defined body of literature that explicitly addresses the relationship between exergy and resource consumption, and this is because the relationship between exergy and resource consumption has not been validated. The data (the articles analyzed) was collected largely based on snowball sampling, and there was no a priori guarantee that any of the required argumentation linking exergy to resource consumption had in fact been codified.

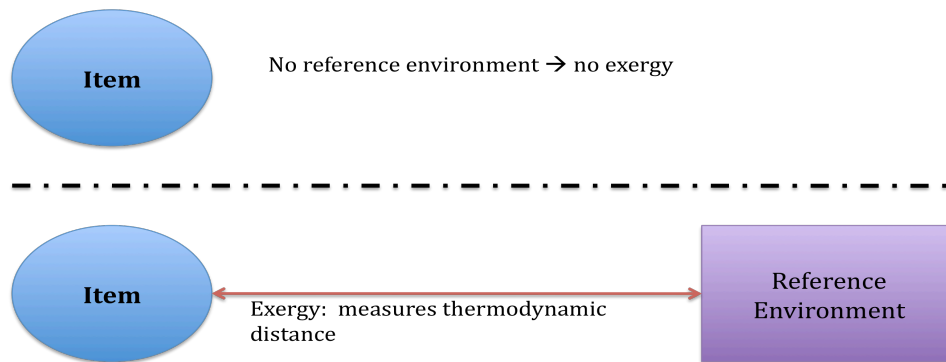
The research is iterative largely as a result of it being exploratory. What is presented in this thesis is a linear schematic of a process that has undergone multiple iteration and many different formats. For example, examining the relationship between exergy and waste impact was once considered to be equal in importance to discussing exergy and

resource consumption. However, once this author determined that exergy and resource consumption was weaker in terms of self-reflexivity, the research focused more on this theme. Since the research is iterative, there is the possibility for further iterations, and at some point the decision must be made as to when one should stop. In this case the decision to stop was based on obtaining sufficient data to draw preliminary conclusions that may foster constructive debate among different exergy proponents.

To explore the relationship between exergy and resource consumption, this thesis is divided into two different parts. The first part (Chapter 2) will be a discussion of the predominant reference state formulations that are used to quantify exergy. The second part (Chapters 3 – 5) will explore the different methodologies that attempt to explicitly link exergy with resource consumption. Each of these parts is introduced in the following two sections.

### 1.3.1 Part 1 - Exergy and the reference state

Exergy is always measured with respect to a reference environment, and according to Antonio Valero, exergy is meaningless without a reference state (Valero 2006). The reason exergy requires a reference environment is by formulation not an inherent state property of an item, but rather a pseudo-property (a state property of an item and its reference state). The pseudo-property nature of exergy is visualized in Figure 1-2.



**Figure 1-2 - Exergy as a pseudo-property**

If the properties of the reference environment are fixed, then exergy effectively becomes a state property. Within engineering thermodynamics there has been a push to standardize the reference environment such that it would have constant temperature, pressure, and composition, and this would essentially turn exergy into a state property.

The justification for standardization within engineering is that without it, exergy would change spatially and temporally (Bejan 1998). Furthermore, using exergy as a state property greatly simplifies analysis. At this point, however, it is not altogether clear as to whether adopting a standardized referent environment is justified when applying exergy to quantify resource consumption.

In Chapter 2, the different formulations of the exergy reference environment will be discussed. Depending on how the environment is formulated, there are consequences for how exergy relates to resource value and resource consumption. Chapter 2 is also important to understand the three methodologies linking exergy to resource consumption that serve as the focus for the three subsequent chapters of Part 2.

### **1.3.2 Part 2 – Exergy resource consumption methodologies**

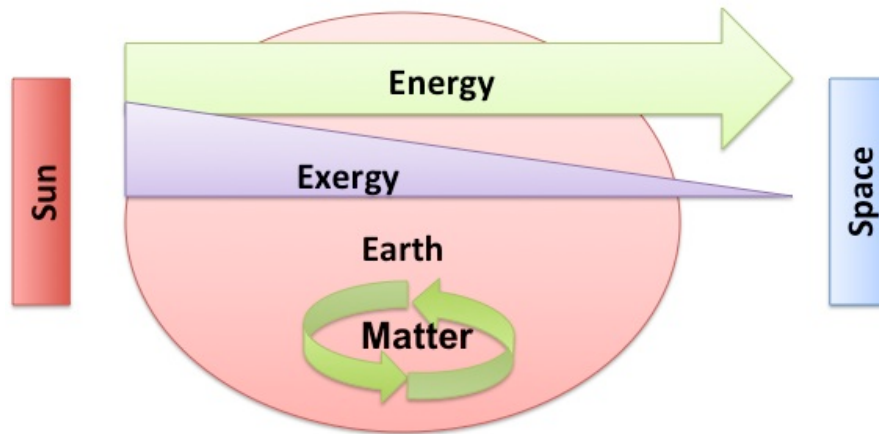
In part 2 of the thesis, three different exergy-based resource consumption methodologies will be explored. Each methodology takes a different approach to resource consumption, and adopts a different method of valuing a resource based on exergy. In many respects, the three methodologies represent the only widely available theory linking exergy to resource consumption. The three methodologies are: the Exergy Replacement Cost by the Exergoecology group (Chapter 3), Eco-exergy by Jorgensen (Chapter 4), and Emergy by Odum et al. (Chapter 5).

The discussions in Chapters 3 – 5 address the exergy resource consumption methodologies in general, as well as the explicit use of exergy within the methodology. In certain cases, the result is a broader discussion than would otherwise be expected in a thesis focused primarily on exergy. There are two reasons for such an expansion. First, the resource consumption methodologies are often quite dependent upon exergy and this makes disaggregation quite difficult. Second, such an expansion allows for some preliminary conclusions to be drawn concerning the limitations of any thermodynamically based resource consumption methodology. These preliminary conclusions may provide constructive theory for future thermodynamic resource consumption methodologies.

One important issue that will be addressed in each chapter is how exergy and the exergy-based resource consumption methodology provide limits to resource consumption. This issue will be briefly introduced in the following subsection.

### 1.3.2.1 Limits to resource consumption

Several exergy researchers have provided exergy and energy budgets of the Earth (Wall 1977; Odum 1996; Szargut 2003; Chen 2005; Jorgensen 2006; Valero 2008). A simple conceptual diagram is provided by Wall (Wall 1977; Wall and Gong 2000), and shown in Figure 1-3.



**Figure 1-3 - Exergy and energy balance of Earth,  
Source: (adapted from Wall 1977; Wall and Gong 2000)**

Figure 1-3 indicates that while there is a terrestrial balance of inflow and outflow energy, exergy is destroyed. Furthermore, the destruction of solar exergy drives flows of energy and matter on the Earth, thereby sustaining living processes (Wall 1977).

While Figure 1-3 serves as a good first heuristic for understanding how exergy drives living processes on the Earth, there are several qualifications that must be first. A first, relatively minor qualification is that different authors propose different amounts incoming solar exergy, including: Chen - 173,300 TW, Wall and Gong - 160,000 TW, and Brodiansky - 158,000 TW (Brodianski ; Wall and Gong 2000; Chen 2005). Second, a comparatively small amount of exergy is provided by deep Earth heat and the tides (Wall and Gong 2000), and this is not shown in Figure 1-3. Third, approximately 30 percent (or 52,000 TW) of the incoming solar exergy is reflected back into space (Wall and Gong 2000; Chen 2005).

The fourth and most important point is that the incoming solar exergy is several orders of magnitude larger than the amount of exergy consumed by humans. Wall and Gong claim the sun provides 13,000 times more exergy than humans consume (Wall and Gong 2000). It is the exergy that reaches the Earth, but is not consumed by humans, that drive global process. For example, the exergy destroyed by the hydrosphere is approximately 7,000 times more than the exergy destroyed by humans (Wall 1977). This difference in magnitude has led several authors to claim that there is no possible method for humans to substitute technological capital for environmental services (Giampietro 1992; Kay and Boyle 2008). Each of the three methodologies discussed in this thesis implicitly or explicitly adopts a unique approach to addressing limits to resource consumption, in general, and the orders of magnitude difference between incoming solar exergy and the exergy available for sustainable human consumption, specifically. Every effort will be made to explicitly codify the different approaches to resource consumption in such a way that they may be critiqued.

#### **1.4 *Boundaries and limitations***

In this section, three boundaries to the thesis will be addressed. These boundaries affect the scope of the thesis and the manner in which issues are addressed. Each boundary will be outlined in what follows.

##### **1.4.1 *Non-flow chemical exergy***

The first boundary is that for most practical purposes, only non-flow chemical exergy is discussed (i.e., non-flow exergy at constant temperature and pressure). The three methodologies discussed in this research are also limited to non-flow chemical exergy, and this author will attempt to remain consistent.

Exergy proponents appear to justify the non-flow chemical exergy limitation by arguing that for resources, the changes in thermo-mechanical exergy (due to temperature and pressure fluctuations) are smaller in magnitude and less important than changes in chemical exergy (Jorgensen 2006, ch. 3; Susani, Pulselli et al. 2006).

There is one glaring exception to the boundary of using non-flow chemical exergy, and this pertains to solar energy. Solar energy has no non-flow chemical exergy because photons do not have a chemical potential (Bejan 1998, ch. 9).

#### **1.4.2 Ambiguities and assumptions**

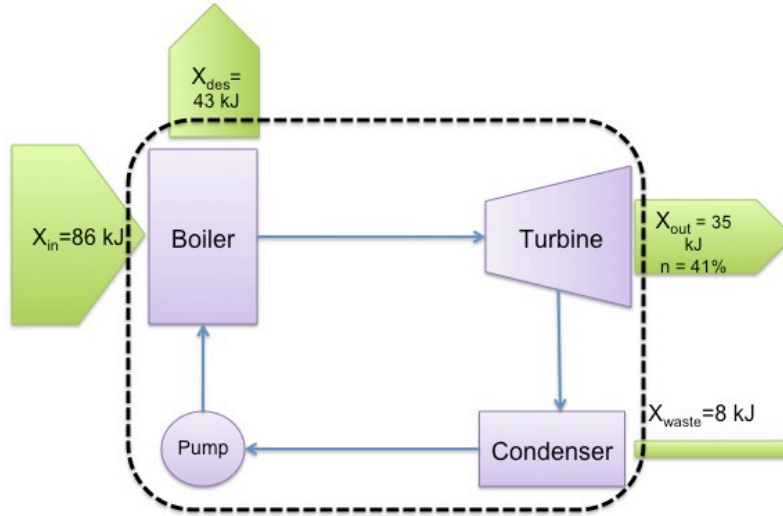
The second boundary in this thesis is the ambiguity surrounding both exergy and exergy-based methodologies. An example of such an ambiguity is found in section 1.2.2, which describes the cracks in theory with regard to exergy as a measure of waste impact. The fact that certain authors relate the exergy of a waste to the work potential derived from the waste, while other authors claim the exergy of the waste is the work required to clean up the waste, and even other authors claim it is both, is indicative of some underlying conceptual ambiguities.

In the following chapters, there will be situations where assumptions must be made as to what an author is attempting to say. A specific example that will appear in Chapter 2 concerns the Exergoecology formulation of a reference state. While criticizing a different author for formulating an *equilibrium* reference state, the Exergoecology group proposes a reference state characterized at separate times as being *thermodynamically dead*, *an entropic planet*, *a crepuscular planet*, and a *dissipated Earth* (Szargut, Valero et al. 2005; Valero 2008, chs. 1 and 5). How these four expressions relate to one another and differ from *equilibrium* is not altogether clear. The different use of terms may be purely a nuance, or could represent a fundamental conceptual difference.

#### **1.4.3 From system to item**

The third boundary in the thesis relates to the conceptual jump of using exergy to analyze systems compared with using exergy to analyze specific items. Exergy was originally developed and applied as an analysis tool, generally within the discipline of engineering systems analysis. For example, exergy may be applied to analyze a power generation system, such as the Rankine cycle shown in Figure 1-4. In Figure 1-4, the Rankine cycle system is delineated by the dashed line.

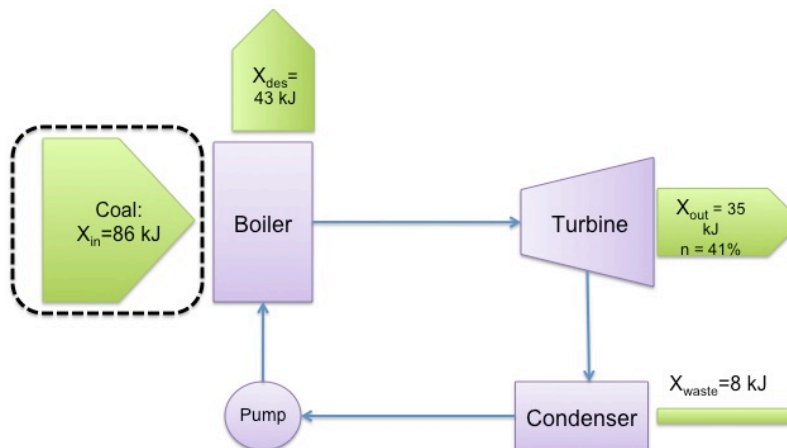




**Figure 1-4 - Exergy analysis of a Rankine cycle**

As a systems analysis tool, exergy may help locate inefficiencies and irreversibilities within the process or system at hand. For example, in the Rankine example of Figure 1-4, much of the incoming exergy is destroyed within the boiler, and therefore the boiler would be an ideal location to improve efficiency and reduce losses.

In the chapters that follow, exergy analysis is not applied to systems, but rather to specific items. In the example of the Rankine cycle of Figure 1-4, the item of interest would be the incoming exergy source, such as coal. The conceptual change from system to item is shown in Figure 1-5.



**Figure 1-5 - Exergy analysis of a specific item**

Within the exergy literature, most example applications of exergy as a measure of resource consumption focus on systems model (Figure 1-4) of exergy analysis (see, for instance: Rosen and Dincer 1997; Dincer and Rosen 1999; Gong and Wall 2000; Rosen 2002; Szargut, Ziebik et al. 2002; Rosen, Dincer et al. 2008). Whether a systems tool is applicable and relevant to apply intrinsic value to a specific item is not discussed, and in this respect is simply assumed.

The conceptual shift from systems-based to item-specific has been noted in the literature. In a recent article, Antonio Valero describes how the shift from ‘systems-analysis diagnosis’ (systems-based) to a quantification of the ‘exergy resources on Earth’ (item-specific) involve “definitions of the environment, reference or dead state [that] are extremely different” (2006).

There are two limitations that arise out of the conceptual shift from exergy as a systems-based tool to exergy as an item-specific tool. First, most of the reflexive research concerning exergy (such as sensitivity analyses relating exergy and the reference environment) does not directly relate to exergy as an item-specific tool. Second, there is no clear distinction between exergy as systems-based and exergy as item-specific. The item-specific coal in Figure 1-5 is an input to the systems-based Rankine cycle in Figure 1-4. Where one conceptual lens is dropped and the other is picked up is not altogether clear.

## **1.5 Conclusion**

As was previously mentioned, the objective of this thesis is to establish the utility and limitations of exergy as a resource consumption metric. Within this context, the research will ideally achieve two end goals: examine the utility of exergy as a measure of resource consumption and resource valuation; and evaluate the current exergy-based resource consumptions methodologies.

In the process of clearing the ambiguities and assumptions present in the exergy literature, this author may unintentionally misinterpret certain concepts and arguments.

While all attempts have been made to avoid such misinterpretations, at the very least by the ambiguities and assumptions more explicit, this author may engender both positive debate and more rigorous formulations in the future.

Finally, the discussions in this thesis may seem to harshly criticise a select few groups of researchers, namely the Exergoecology group, Jorgensen, and the Emergy group. These three groups are overly critiqued primarily because they are the only groups attempting to theoretically connect the formulation of exergy to its application towards resource consumption. For this reason, these three groups should be lauded for their efforts.



## Chapter 2 – The Exergy Reference State

This chapter will introduce and critique the predominant formulations of the exergy reference environment. According to Antonio Valero, exergy is meaningless without a reference state (Valero 2006). Furthermore, Rosen claims that the reference environment must be completely specified (Rosen and Dincer 1997; Dincer and Rosen 1999; Rosen and Dincer 1999; Rosen 2002; Rosen, Dincer et al. 2008).

Despite the importance of the reference environment to exergy analysis, relatively few authors appear to seriously question their choice of reference environment formulations. For example, when assessing the relationship between exergy and environmental impact, Rosen adopted Szargut's reference environment formulation<sup>1</sup> (Rosen and Gunnewiek 1998), despite claiming that Szargut's formulation is "economic in nature, and is vague and arbitrary with respect to the selection of reference substances", and is "not similar to the natural environment" (Rosen and Dincer 1997).

There are three broad categories of reference state formulations that are proposed in the literature and will be discussed in this chapter: process dependent, equilibrium, and defined reference states.

As a final comment, this thesis relies heavily on the work of the Exergoecology group, which includes Jan Szargut, Antonio Valero and Alicia Valero. In certain instances, a citation from a member of the group is described as from the entire group because many of the publications are joint publications.

### **2.1 Process dependent reference states**

The first formulation of reference states is known by several names, including process dependent reference states (Rosen and Dincer 1997; Rosen and Dincer 1999; Dincer and Rosen 2007 chapter 3), environmental reference states (Ahrendts 1980), and partial

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<sup>1</sup> Szargut's reference environment formulation will be discussed in detail in this chapter.

reference states (Szargut, Valero et al. 2005; Valero 2008 chapter 5). Despite the different names, these reference state formulations (which will be called process dependent for simplicity) are generally the same.

Process dependent reference states determine the exergy of an item only relative to a specific process at hand. For example, a hydrocarbon may produce work via combustion or oxidation in a fuel cell, and depending upon which process is chosen, the exergies will differ. Two commonly used process dependent reference environments are those proposed by Bosnjakovic, and Baer and Schmidt, both in 1963 (as cited in Ahrendts 1980; Rosen and Dincer 1999)<sup>2</sup>.

Process dependent reference states fall into the category of systems-based exergy analysis (as mentioned in Chapter 1). As such, process dependent reference states are not directly applicable to the item-specific use of exergy in the following chapters. For this reason, process dependent reference states are only briefly discussed.

### **2.1.1 Critique of process dependent reference states**

Process dependent reference states are criticized because the models are only valid for specific processes under specific conditions (Ahrendts 1980; Szargut, Valero et al. 2005; Valero 2008). In other words, the reference environment is formulated to mimic the environment only in the manner applicable to the energy pathway chosen. Any time a new substance or process is introduced, then a new reference environment would need to be developed, or new substances must be added to the current environment (Ahrendts 1980).

Ahrendts (1980) claims that partial reference environments often contain substances in multiple phases and out of equilibrium (such as the air-water environment proposed by Gaggioli and Petit). According to Ahrendts, the models must have air saturated with water so as to achieve equilibrium (1980).

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<sup>2</sup> Unfortunately, all these articles in German, and are thus inaccessible to this author.

The Exergoecology group claims that since partial reference environments account for blocked energy pathways (inaccessible energy modes), they therefore do not represent a true dead state (where a dead state has no process limitations) (Szargut, Valero et al. 2005; Valero 2008). By consequence partial reference environments are not useful for application in the valuation of natural capital (resources) (Szargut, Valero et al. 2005; Valero 2008).

Much of the criticism of process dependent reference states appears to misunderstand the purpose of process dependent reference states. Most notably are the critiques by Ahrendts that process dependent reference states should be in equilibrium, and by Szargut et al. and Alicia Valero that process dependent reference states account for blocked energy pathways. By forcing equilibrium and ignoring blocked energy pathways, it is likely that process dependent reference states would be less relevant to the specific processes they are designed to model. The point of contention appears to hinge on the concept that process dependent models are systems-based models, whereas the reference of Ahrendts, and Szargut et al. and Valero, are item-specific.

## **2.2 Equilibrium reference states**

The second generic reference environment formulation is the equilibrium reference state developed by Ahrendts in 1980. Ahrendts postulated that with a fixed temperature and knowing original chemical components, equilibrium conditions may be determined (Ahrendts 1980). To do so, Ahrendts used the composition of the atmosphere, the ocean as well as 15 elements that amounted to 99 percent by mass of the Earth's crust (Ahrendts 1980). The elements, in the correct concentrations, were allowed to react experimentally. The model contained compounds in the three phases (solid, liquid and gaseous) (Ahrendts 1980).

In formulating a reference state, Ahrendts listed three criteria (1980):

1. The reference environment should be in thermodynamic equilibrium.
2. The exergies of the substances should not be so high so as to mask irreversibilities and inflate process efficiencies.

- The reference environment should not reduce the appeal of exergy as a measure of worth; it should give value to scarce products from a thermodynamic and economic perspective.

As can be seen, criteria 2 and 3 are subjective, and can have a great impact on the final choice for the reference environment (and consequently the exergy values). Furthermore, Ahrendts' criteria contain requirements relating to exergy as both systems-based (criteria 2), and item-specific (criteria 3).

### 2.2.1 Developing the models

To develop the equilibrium reference state models, Ahrendts manipulated two parameters: the constraints on the equilibrium, and the thickness of the Earth's crust (from 1 to 1000 meters). Equilibrium was constrained in order to maintain atmospheric oxygen, because in a complete equilibrium, there would be none. To maintain atmospheric oxygen, the energy pathway that resulted in the formation of nitric acid was blocked. With such a constrained equilibrium, and a crustal thickness of 1 meter, Ahrendts computed exergies similar to those of Gaggioli and Petit, Baehr and Schmidt, and Szargut (Ahrendts 1980). Despite the similarities to other reference environment formulations, Ahrendts discarded that possible reference state because it violated his first criterion.

After the initial trial described above, Ahrendts focused on complete equilibrium models by manipulating only the crustal thickness. With a crustal thickness of 1000 meters, the model exergies were such that 'valuable oxygen' was burned in the presence of 'worthless' fossil fuels, which Ahrendts labelled as a paradox (Ahrendts 1980). This 'paradox' is shown in Table 2-1.

**Table 2-1 –Chemical exergies of various substances based on crust thickness**

		Crust thickness (m)			
		1	10	100	1000
		Exergy (kJ per kg)			
Substance	O <sub>2</sub>	12.9	33.5	38.6	420.7
	C	392.0	370.0	371.0	4.0
	CH <sub>4</sub>	802.0	760.0	756.0	7.0

**Source: (adapted from Ahrendts 1980)**



The reference model Ahrendts finally chose was one of complete equilibrium with a crustal thickness of one (1) meter. The model differed from what was observed in the natural environment, but the chemical exergy differences were generally low, and there was no issue of a high exergy for oxygen (and a low exergy for fossil fuels) (Ahrendts 1980). Therefore, Ahrendts' three criteria were met.

### **2.2.2 Critique of equilibrium reference states**

Ahrendts' model has received considerable criticism from the Exergoecology group. For example, according to Szargut et al., the equilibrium models are not empirically correct, and therefore fail what Szargut defines as the Earth Similarity Criterion (this will be defined shortly) (Szargut, Valero et al. 2005). Similarly, Antonio Valero et al. critique Ahrendts' reference environment because most metals form part of the 1 percent of the crust that Ahrendts neglected in his models (Valero, Ranz et al. 2002).

From a different perspective, Szargut et al. and Alicia Valero claim the Earth is not in thermodynamic equilibrium, as shown by James Lovelock's work, and therefore an equilibrium environment is not relevant (Szargut, Valero et al. 2005; Valero 2008). Furthermore, Alicia Valero and Antonio Valero et al. claim that Ahrendts' reference environment does not even represent a potentially thermodynamically degraded Earth (Valero, Ranz et al. 2002; Valero 2008).

While not a critique, per se, Ahrendts' article on equilibrium reference states does not contain a calculation methodology<sup>3</sup>. However, for substances available in Ahrendts' reference environment, this author assumes that exergy is calculated based upon the concentration exergy, as will be described in section 2.3.1.

As a final critique, Antonio Valero claims Ahrendts' model is not an absolute model, but rather depends on subjective parameters, such as the crust thickness and the number of compounds included in the model (Valero, Ranz et al. 2002). Antonio Valero et al.'s last critique could be packaged into a larger critique of the Ahrendts' model, namely: there is

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<sup>3</sup> The methodology is likely presented in the German version which is inaccessible to this author

tension between the objective criterion requiring equilibrium and the subjective criteria demanding that the exergies not be too high, nor too different from empirical results.

### **2.2.3 Updates on Ahrendts' model**

In recent years, Ahrendts' model has been revived in two different forms. In 1999, Diederichsen updated Ahrendts' model with one containing more elements, and also allowed for a changing ocean depth<sup>4</sup> (cited in Valero 2008ch. 5). According to Alicia Valero, while Diederichsen's model is closer to meeting the Earth Similarity Criteria, it still diverges when the crustal depth is greater than 0.1 meters (Valero 2008). Despite the noted improvements, Diederichsen's model is subject to the same criticism directed at Ahrendts.

The second revival of Ahrendts' model is in the work of ecologist S.E. Jorgensen. In his efforts to research of ecological thermodynamic, Jorgensen developed an analogue of exergy, known as Eco-exergy (Jorgensen and Nielsen 2007). While Eco-exergy is the focus of Chapter 4, the reference environment formulation deserves mention now.

According to Jorgensen, the reference environments for an ecosystem are the adjacent ecosystem, and this is not altogether useful in ecology. Therefore, Jorgensen proposed that the reference environment for an ecosystem be that same ecosystem, but at thermodynamic equilibrium: all components at their maximum oxidation state (nitrogen as nitrate, etc) (Jorgensen 2001; Jorgensen, Ladegaard et al. 2005; Jorgensen 2006).

Similar to Ahrendts, Jorgensen places some personal restrictions on the reference environment. In Jorgensen's case, the reference environment must be one that accounts for the high improbability, and therefore high value, of life (Susani, Pulselli et al. 2006). Similarly, the choice to use the same ecosystem, as opposed to surrounding ecosystems is a subjective criteria imposed by Jorgensen.

Nominally, Jorgensen's reference environment is similar to Ahrendts', except that Jorgensen's model does not contain all the major substances in the world, but rather the

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<sup>4</sup> Diederichsen's work is also in German, so all citations must be cited via other researchers.

major substances in the ecosystem. However, the detailed analysis of Jorgensen's work performed in Chapter 4 will show that Jorgensen does not in fact use an equilibrium model in his exergy analogue.

### **2.3 Defined reference states**

The third reference state formulation discussed is the defined reference state, first proposed by Szargut in 1957 (cited in Ahrendts 1980; Szargut 2005). Defined reference states are used by the Exergoecology group, which includes most notably Szargut, Alicia Valero, and Antonio Valero. Furthermore, defined reference states appear to be widely used within the engineering community (for instance, see Wall 1977; Cornelissen 1997; Wall 1998; Rosen and Dincer 1999; Chen and Ji 2007). This section describes the most recent revision to defined reference states based on Szargut's original methodology.

According to Szargut (2005), defined reference states are predicated upon understanding the world as a non-equilibrium open system that will never achieve thermodynamic equilibrium due to the constant influx of solar energy. For this reason, an equilibrium world cannot be used as an exergy reference environment (Ahrendts 1980; Szargut 2005). Instead, Szargut proposed to define a reference substance for every substance in the environment. The exergy of a substance can be determined by a balanced chemical reaction between the specific substance, its reference substance, and other reference substances. Similar to Ahrendts' reference state, Szargut's model contains compounds in the solid, liquid and gaseous phases.

Reference substances are chosen based on natural abundance in the world<sup>5</sup> (the Earth Similarity Criterion) and a low Gibbs free energy of formation (the stability criterion). The qualitative method for choosing reference substances may be understood as a two-step procedure (Szargut, Valero et al. 2005; Valero 2008):

1. Among a group of potential reference substances for a given atom that all meet both the Earth Similarity Criteria (abundance) and the stability threshold (have a low Gibbs free energy of formation), choose the most abundant.

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<sup>5</sup> Based on the latest geochemical data.

2. Among a group of potential reference substances that all meet the Earth Similarity Criterion, but none of which meet the stability threshold, choose the most stable (lowest Gibbs free energy of formation)

Despite the simplicity of the two steps, there are several issues to complicate Szargut's methodology. First, the stability threshold is not fixed, but rather depends on each substance (Valero 2008). Second, reference species must be chosen such that no chemical reaction may be formulated between reference species. The reason for this requirement is that if reference species do not interact, then there is no problem of maintaining equilibrium between reference substances (Szargut, Valero et al. 2005)<sup>6</sup>.

### **2.3.1 Exergy calculation method**

In the defined reference states model every element is assigned a reference species based on the 'optimization' of the Earth Similarity Criterion and the stability requirement (as mentioned above). The reference species may be gaseous, liquid or solid depending on a number of factors. Szargut details his calculation methodology in both his works and the work of the Exergoecology group. This section will briefly describe the methodology for both reference and non-reference substances for two reasons. First, Szargut's method essentially serves as the basis for all three exergy-based resource consumption methodologies in the following three chapters. Second, Szargut's method highlights the fact that non-flow chemical exergy is based upon the chemical potential and the concentration exergy, and these two modes of exergy are quite different.

#### **2.3.1.1 Exergy of reference substances**

The defined reference environment contains three ideal mixtures of reference substances, one for each of the three phases: a solid mixture for the earth; a liquid mixture for aqueous environments; and a gaseous mixture for the atmosphere. For the solid and gas phases, Szargut calculates the exergy of a reference substance by assuming they are ideal gases, and therefore uses the concentration exergy equation, shown in Equation (2.1) (Szargut 2005):

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<sup>6</sup> It appears Szargut is stating that it is impossible to *balance* a chemical reaction equation containing only reference species

$$b_{ch,i} = -RT^o \ln x_i \quad (2.1)$$

Where R is the ideal gas constant 8.314 E-3 kJ/mol\*K, T<sup>o</sup> is 298.15 K, and x<sub>i</sub> is the molar fraction of the reference substance in its respective environment (solid or gaseous). At this point, Szargut et al. have not been empirically justified the assumption of the Earth's crust being similar to an ideal gas mixture.

While Szargut does not provide a formula to calculate the exergies of aqueous reference species, he does admit that certain characteristics of the aqueous reference exergies are dependent upon ideal gas assumptions (Szargut, Morris et al. 1988) However, Valero et al. provide values for the exergies of aqueous reference substances, and the formula was determined to be what is shown in Equation (2.2):

$$b_{ch,i}^o = -RT^o \ln m_n + (0.5z b_{ch,H_2}^o - RT^o [2.303z(pH) + \ln(\gamma)]) \quad (2.2)$$

Where R and T<sup>o</sup> are defined as above, z is the number of elementary positive charges of the reference ion,  $b_{ch,H_2}^o$  is the chemical exergy of hydrogen gas (236.09 kJ/mol), m<sub>n</sub> is conventional standard molarity of the reference species in seawater, γ is the activity coefficient (molarity scale) of the reference species in seawater, and the pH of seawater is 8.1. According to Morris, the terms relating to the charge of the reference ion (as well as the pH of water) are derived from standard electrochemistry (Morris and Szargut 1986).

As a final comment regarding aqueous reference species, some of the more common compounds may not be chosen for one of two reasons (Szargut, Morris et al. 1988; Szargut 2005): first, they lead to negative exergy values for solid substances; and second, thermodynamic theory is not sufficiently exact to determine their exergy.

For the purpose of illustration, Table 2-2 provides the molar fraction (chemical concentration) and concentration exergies of some gaseous reference species. The molar fractions are provided by the Exergoecology group, and represent a standard atmospheric composition (Szargut 2005; Szargut, Valero et al. 2005).

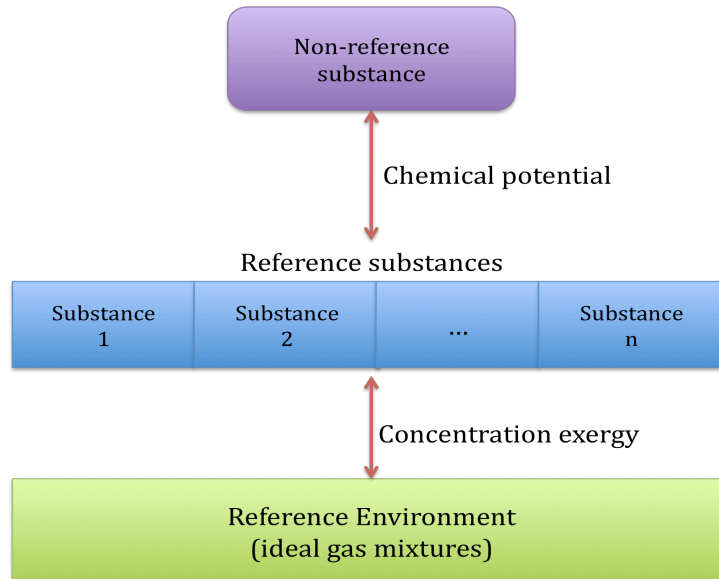
**Table 2-2 - Exergy of gaseous reference substances**

Substance	Molar fraction (%)	Exergy (kJ/mol)
Ar	0.906000	11.65
CO <sub>2</sub>	0.033500	19.82
D <sub>2</sub> O	0.000342	31.18
H <sub>2</sub> O	2.200000	9.45
He	0.000485	30.31
Kr	0.000097	34.30
N <sub>2</sub>	75.78000	0.69
Ne	0.001770	27.10
O <sub>2</sub>	20.390000	3.94

Source: (adapted from Szargut 2005, ch. 2)

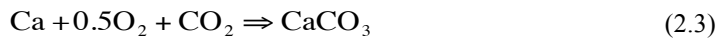
**2.3.1.2 Determining the exergy of non-reference species**

Once the exergy of reference substances have been calculated, the exergy of non-reference substances may be determined. Unlike reference species, non-reference substances have exergy based upon both chemical reactivity and concentration exergy. However, the concentration exergy component of non-reference species only appears as the work required to concentrate the reference species. This essentially two-step procedure is shown in Figure 2-1.



**Figure 2-1 - Separating concentration and chemical exergies**

To calculate the exergy of non-reference substances, Szargut proposes to first calculate the exergy of the pure elements<sup>7</sup>, and then use the exergy of the elements to calculate the exergy of compounds. To calculate the exergy of elements, a reference reaction is composed between the elements at hand and its reference substance. The only substances that may take place in the formation reaction are the element at hand, its reference substance, and other reference substances (often CO<sub>2</sub> and O<sub>2</sub>). An example provided by Szargut (2005) is the reference reaction for the element calcium shown in Equation (2.3), where the reference substance for calcium is calcium carbonate, and oxygen and carbon dioxide are other reference substances present simply to balance the reaction:



The exergies of the various reference substances are shown in Table 2-3.

**Table 2-3 – Exergy of reference substances for calcium**

Reference species	Formula	Exergy (kJ/mol)	ΔG formation (kJ/mol)
Carbon	CO <sub>2</sub>	19.87	NA
Oxygen	O <sub>2</sub>	3.97	NA
Compound	Formula	Exergy (kJ/mol)	ΔG formation (kJ/mol)
Calcium carbonate	CaCO <sub>3</sub>	16.3	-738.6

**Source: (Szargut 2005 App. 1)**

With the exergy values of the reference substances known, the exergy of the specified element is calculated using Equation (2.4):

$$b_{ch,element}^o = -\Delta_r G^o + \sum_{products} B_{ch}^o - \sum_{reactants} B_{ch}^o \quad (2.4)$$

Once the exergy of the elements has been calculated, then the exergy of a compound may be calculated using the reaction of formation (shown in Equation (2.5)):

$$b_{ch,compound}^o = \Delta_f G^o + \sum_{elements} n_{el} b_{ch,el}^o \quad (2.5)$$

where Δ<sub>f</sub>G<sup>o</sup> is the Gibbs free energy of formation of the compound.

### 2.3.1.3 Determining the exergy of liquid fuels

The only case where the above equations for exergy are not employed is the calculation of exergy for liquid fuels. In this case of liquid fuels, exergy values are determined using

<sup>7</sup> The ‘elements’ are in atomic form, with the notable exceptions of: Br<sub>2</sub>, Cl<sub>2</sub>, D<sub>2</sub> (deuterium), F<sub>2</sub>, H<sub>2</sub>, I<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> (Szargut 2005, Table 2.2).

correlations based on the lower heating value of the fuel (Morris and Szargut 1986; Szargut 2005; Valero 2008 ch. 5).

### **2.3.2 Critique of defined reference states**

The first critique of defined reference states is that the proponents of defined reference states use ambiguous terms both in their methodology, and in their critiques of other methodologies. For example, the Exergoecology group refers to the reference environment as a thermodynamically dead planet, an entropic planet, a crepuscular planet, and a dissipated Earth (Valero, Ranz et al. 2002; Szargut, Valero et al. 2005; Valero 2008). Alicia Valero defines in words ‘thermodynamically dead Earth’, ‘crepuscular planet’, and ‘entropic planet’, as (Valero 2008):

*a dead planet where all materials have reacted, dispersed and mixed and are in a hypothetical chemical equilibrium. A degraded Earth would still have an atmosphere, hydrosphere and continental crust. Nevertheless, there would not be any mineral deposits, all fossil fuels would have been burned and consequently, the CO<sub>2</sub> concentration in the atmosphere would be much higher than it is now. Similarly, all water available in the hydrosphere would be in the form of salt water, due to the mixing processes.*

While no definition of ‘dissipated Earth’ has been found, this author must assume it is similarly defined. Valero does not describe how these four terms above differ from ‘equilibrium’, especially given that the definition provided above includes the term ‘hypothetical chemical equilibrium’. Furthermore, the Exergoecology group does not explain how a thermodynamically dead planet fits in with the Earth Similarity Criterion. For example, despite Alicia Valero’s claim of CO<sub>2</sub> concentrations being far higher (as mentioned in the definition of thermodynamically dead), Szargut’s reference environment adopts a CO<sub>2</sub> concentration that is identical to current CO<sub>2</sub> concentrations in the atmosphere (see Table 2-2).

If thermodynamically dead, dissipated Earth, and entropic planet do in fact refer to ‘equilibrium’, then this author notes two contradictions:

1. The Exergoecology group critiques Ahrendts’ equilibrium reference environment on the basis that the Earth is not in thermodynamic equilibrium, and therefore the



reference environment should not be an equilibrium reference environment.

However, they then propose their own equilibrium reference environment.

2. The Exergoecology group proposes an equilibrium reference environment, and yet bases the components of the reference environment on the most common components in the non-equilibrium Earth. In this respect, there is a strong likelihood that their reference environment does not meet their self-imposed requirements of equilibrium. On the other hand, if thermodynamically dead, dissipated Earth, and entropic planet do not refer to equilibrium, then the terms must be redefined.

The Exergoecology group appears to be aware of the contradictions mentioned above, as Alicia Valero stated in her dissertation that (Valero 2008)

*the reference environment based on Szargut's criterion should not be considered as a dead [reference environment], but rather as a mathematical tool for obtaining standard chemical exergies of the elements.*

By this admission, Szargut's methodology is subject to some of the same criticism that Szargut et al. and Alicia Valero directed at process dependent reference environments described in sections 2.1.1 and 2.2.2 (Szargut, Valero et al. 2005; Valero 2008).

Aside from the contradiction, there are other critiques of defined reference states. As mentioned in the introduction to this chapter, critics claim the reference components are often chosen for economic or sometimes arbitrary reasons (Ahrendts 1980; Rosen and Dincer 1997; Dincer and Rosen 2007). These critiques are likely due to the ambiguity associated with the Earth Similarity Criterion and the Stability Criterion.

An important weakness of Szargut's methodology is that some substances end up with negative non-flow chemical exergies (Ahrendts 1980). While negative exergies are possible in flow systems, they are formally impossible for non-flow systems based on the very definition of non-flow exergy (Ahrendts 1980; Bejan 1998, chs. 3 and 5).

Alicia Valero notes two weaknesses with Szargut's approach. First, Szargut's reference environment only contains one reference substance per atom (in the periodic table),

whereas a true degraded Earth would have more. Secondly, the abundance measurements of the reference substances used by Szargut are current measurements, as opposed to concentrations of the degraded Earth (Valero 2008). Neither of these limitations can be assessed until the degraded Earth is properly redefined.

One final critique relates to correlating the exergy of liquid fuels to their lower heating value. By using lower heating values to calculate the exergy of liquid fuels, Szargut appears to be adopting a process dependent reference state (where the chosen process is combustion) as opposed to a defined reference state. If this is the case, then the exergy of liquid fuels may not be used to validate Szargut's model, and in fact serve as a limitation to Szargut's model in that the model cannot account for liquid fuels.

### **2.3.3 Updates on Szargut's model**

As has been mentioned, Szargut's model has been updated with recent geochemical data. Ranz proposed one variation of Szargut's model. Ranz' model differed from Szargut's in that where Szargut used a mixed criterion of abundance and stability, Ranz' criterion was based solely upon abundance (Valero, Ranz et al. 2002; Valero 2008). In a critique of Ranz' approach, the Exergoecology group claims that since the most abundant compound are not necessarily the most stable (they may have higher exergies), this would lower the apparent value of resources (Valero, Ranz et al. 2002; Valero 2008).

## **2.4 Reference environments – a recap**

This final section will attempt to summarize the current state of reference environment formulations. The comments listed below involve the defined and equilibrium reference states (Ahrendts and Szargut et al.), because they are the principle formulations of item-specific reference environments.

### **2.4.1 Self-defined criteria**

The first comment is that the proponents of different groups are using their own requirements for a reference environment to judge other formulations. For example, Ahrendts criticizes both defined and process dependent reference states because neither of them are based upon equilibrium, which is a requirement for Ahrendts. Similarly, the proponents of Szargut's methodology criticize other reference environment formulations

for failing to meet the Earth Similarity Criterion, which is a unique feature of Szargut’s reference state. The end result is tension and confusion regarding what the fundamental characteristics of a reference environment must be. Need reference environments be in equilibrium<sup>8</sup>? Must the components of the reference environment resemble what the current Earth looks like? Or should the components resemble an (potentially unrealizable) equilibrium Earth? These are important questions that have implications for exergy analysis.

To further the discussion of self-defined criteria, this author argues that many of the requirements made by both Ahrendts and the Exergoecology group are subjective. Table 2-4 provides examples of subjective requirements made by different authors.

**Table 2-4 - Requirements for reference environments**

Author	Requirement	
	Reference environment	Exergy values
Ahrendts (Ahrendts 1980)	<ul style="list-style-type: none"> <li>• 3 phases</li> <li>• Non-flow chemical exergy</li> <li>• Fixed temperature</li> </ul>	<ul style="list-style-type: none"> <li>• Exergy of a substance match the value of a scarce product from a thermodynamic and economic sense.</li> <li>• Not be too high such that efficiencies are inflated.</li> </ul>
The Exergoecology group (Szargut, Valero et al. 2005; Valero 2008)	<ul style="list-style-type: none"> <li>• 3 Phases</li> <li>• Non-flow chemical exergy</li> <li>• Fixed temperature and pressure</li> </ul>	<ul style="list-style-type: none"> <li>• Be sufficiently high so as to not reduce the thermodynamic value of natural capital.</li> <li>• Physical state (gaseous, aqueous, solid) of certain reference substances chosen to avoid negative exergies.</li> </ul>
Jorgensen (Jorgensen 2001; Jorgensen 2006)	<ul style="list-style-type: none"> <li>• Does not want the reference state of an ecosystem to be the surrounding ecosystems.</li> </ul>	<ul style="list-style-type: none"> <li>• Accounts for the high improbability, and therefore high value, of life.</li> </ul>

As a final comment on the self-defined criteria, the proponents of various reference environments fail to meet their own criteria. For example, Ahrendts requires that the reference environment provide the absolute exergy of a substance, and yet he determines the final reference environment based on notions such as intuitive appeal (Ahrendts 1980). Similarly, the Exergoecology group requires a thermodynamically dead Earth,

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<sup>8</sup> This question is answered indirectly in Chapter 6. The current derivation of the exergy reference environment (such as Bejan 1998), require a reference environment in internal stable equilibrium.

and then go as far as to admit that their reference environment is not thermodynamically dead (Valero 2008). Furthermore, based on the Exergoecology critique of equilibrium reference environments, this author questions whether Szargut's reference environment was designed to be thermodynamically dead. For example, the Earth Similarity Criterion requires the reference substances to mimic the non-equilibrium Earth.

#### **2.4.2 Different understandings of exergy value**

Along a different line of reasoning, neither Ahrendts nor the Exergoecology group adequately addresses the difference between concentration exergy and chemical potential (i.e. Figure 2-1). For example, in Szargut's defined reference states, the reference species only have an exergy value based upon their concentration exergies, whereas non-reference species have exergy value based upon concentration exergies and chemical potential. Likewise Ahrendts' does not mention how the exergies are in fact calculated from the equilibrium reference environment.

This author notes that Alicia Valero does address some of the differences between chemical potential and concentration exergy, and this will be discussed in Chapter 3. However, an in depth discussion of whether chemical potential and concentration exergy both represent work potential has not been found. Section 6.3.1 will re-examine the subject.

#### **2.4.3 Limited scope**

While not discussed in this chapter, the limited scope of these reference environments was introduced in Chapter 1. Both reference environment formulations are developed to measure non-flow chemical exergy, and for this reason are blind to other forms of exergy, including solar exergy, thermo-mechanical exergy, nuclear exergy, kinetic exergy, potential exergy, and flow exergy (in all forms).

In the case of Ahrendts' reference environment, temperature is held constant while pressure varies with changing partial pressures (Ahrendts 1980). For Szargut's defined reference environment, both temperature and pressure are constant (Szargut 2005, ch. 2; Valero 2008, ch. 5).

A third manner in which the scope is limited is that both equilibrium and defined reference state formulations ignore whether the exergy is accessible or not. As mentioned in section 2.1.1, the Exergoecology group critiques process dependent reference environment formulations because they account for restricted exergy.

#### **2.4.4 Confusions about the meaning of ‘environment’**

One important point underlying this chapter is that both Ahrendts’ and the Exergoecology group appear to be confused regarding the purpose of their reference environment formulations. There is a tendency in both groups to view their reference environments as being analogues to the natural environment of this world (for example, the Earth Similarity Criterion). This confusion lies at the heart of the debate regarding reference environments. To help contrast the difference between the reference environment and the natural environment, two descriptions of ‘environment’ are provided; one relates to the exergy reference environment while the other defines an ecosystem, which forms part of our natural environment.

*“The reference environment is in stable equilibrium, and has all parts at rest relative to one another. No chemical reactions can occur between the reference environment components. Further, the reference environment acts as an infinite system, is a sink and source for heat and materials, and experiences only internally reversible processes in which its intensive state remains unaltered (i.e., its temperature, pressure and chemical potentials for each of the components present remains constant)” (Rosen and Dincer 1999).*

*“[An ecosystem is] an open, hierarchical, self-designing system of subsystems that in turn are an interconnected, interrelated, interacting network of information generating direct and indirect effects (Mitsch and Jorgensen 2004, cited in Gattie, Kellam et al. 2007)*

These two descriptions of the environment are quite at odds with each other. In order to match the properties of the Earth, both Ahrendts and the Exergoecology group appear to compromise in their respective reference state formulations. Ahrendts chose to begin with the premise of equilibrium, and then adjusted the parameters to make the reference

environment similar to the Earth, thereby abandoning true equilibrium. By contrast, the Exergoecology group appears to have begun with a reference environment similar to the Earth, and then adjusted the parameters to bring the reference environment closer to thermodynamic equilibrium. Section 6.3.1 will revisit the fundamental formulation of the reference environment based on the exergy derivation of Bejan (1998).

#### **2.4.5 Ontological concerns**

A second source of confusion regarding the purpose of exergy reference environments is that an ontological argument may emerge<sup>9</sup>. This ontological argument is best illustrated by examining the Exergoecology reference environment as a two-step process:

1. The reference environment is formulated based upon the most common components of the Earth. Because of this, the reference environment derives meaning from these common components of the Earth.
2. The exergy of the components of the Earth (including the most common components) are determined based on the reference environment. In other words, the common components of the Earth derive their meaning from the reference environment.

The ontological argument essentially states that the components of the Earth are measured with respect to a reference environment that is itself derived from the components of the Earth. For this reason, the reference environment and its individual components simultaneously provide meaning to each other in a circular manner.

One interesting result of the circular reference is that since Szargut et al.'s reference environment is made up of components, each of which has exergy, then the reference environment as a whole may have exergy. Furthermore, the reference environment has exergy with respect to itself. While it is formally impossible for the reference environment to have exergy (as seen from Rosen's definition of the reference environment given above), Alicia Valero (2008, ch. 6) calculates the exergy of the Earth, and this is somewhat analogous to calculating the exergy of the reference environment.

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<sup>9</sup> Ontology - a branch of philosophy concerned with the nature of reality Midgley, G. (2000). Systemic intervention: Philosophy, Methodology, and Practice. New York, Kluwer Academic / Plenum Publishers.

#### **2.4.6 What do these points indicate?**

The problems mentioned above are not necessarily insurmountable, but do indicate that from a methodological perspective, the present formulations of the of exergy reference environment are still quite tenuous. The ambiguous language and internal contradictions indicate the exergy reference environment is ill defined. Furthermore, there appears to be two mutually exclusive end goals in the formulation of the exergy reference environment: relevance and thermodynamic consistency. In broad terms, Ahrendts attempts to be thermodynamically consistent at the expense of relevance, whereas Szargut et al. attempts the opposite. While they both seem to compromise between relevance and consistency (as mentioned above in section 2.4.4), there is no guarantee that the compromises are beneficial.

#### **2.5 Conclusion**

This chapter introduced and discussed three reference state formulations, most notably Ahrendts' equilibrium reference states and Szargut's defined reference states. The purpose of the discussion was both to elucidate some of the conceptual shortcomings with the current reference state formulations, as well as provide necessary theoretical groundwork for the following three chapters.

The somewhat loose methodological foundations of exergy with regard to the reference state impacts the credibility of the three item-specific exergy-based resource consumption methodologies that will be described in the following chapters. Furthermore, the problems listed in section 2.4 indicate the need for some critical thinking regarding fundamental relevance of exergy from an item-specific perspective.

The following chapter will begin the discussion of the three exergy-based resource consumption methodologies. The first methodology to be explored is the Exergy Replacement Cost, which follows directly from Szargut's defined reference state. Following that, both Eco-exergy and Emergy will be introduced, both of which are farther from the fundamental basis of exergy.





## Chapter 3 – The Exergy Replacement Cost

The first resource consumption methodology that will be assessed is the Exergy Replacement Cost. The Exergy Replacement Cost recently emerged from the Exergoecology group, which includes Alicia Valero, Antonio Valero, and Jan Szargut (Valero, Ranz et al. 2002; Szargut, Valero et al. 2005; Valero 2008). Under the Exergy Replacement Cost (Valero, Ranz et al. 2002; Szargut, Valero et al. 2005; Valero 2008, 159):

*The thermodynamic value of a natural resource can be defined as the minimum work necessary to produce it with a specific structure and concentration from common materials in the environment. The process should be reversible and heat should only be exchanged with the environment.*

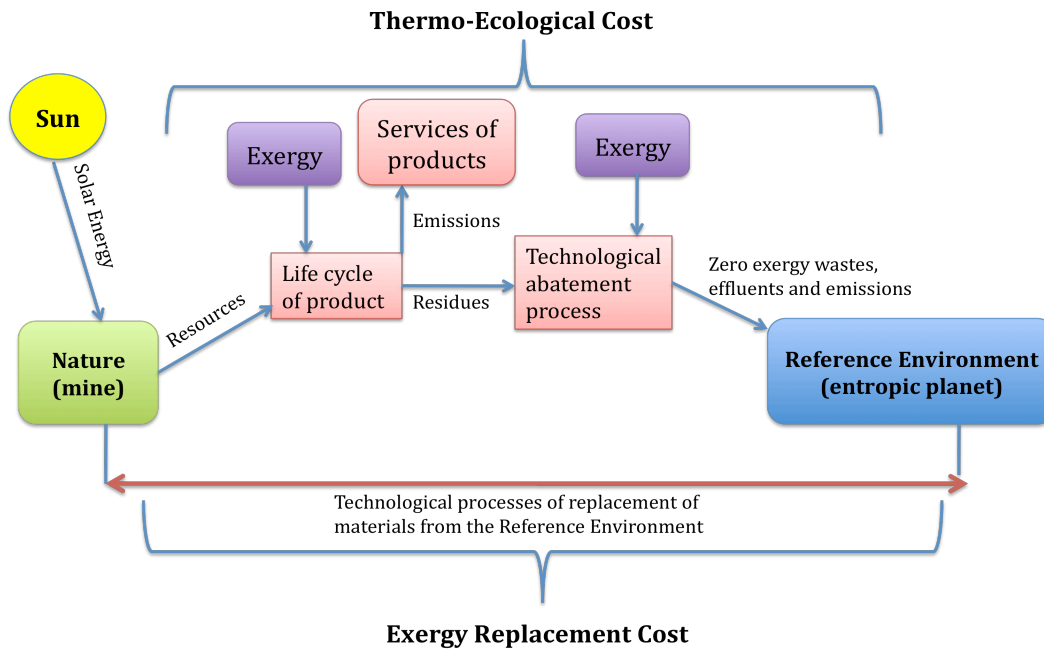
The definition of the Exergy Replacement Cost is identical to Szargut's (2005, ch. 1) definition of exergy provided in Chapter 1 (section 1.1.1) of this thesis, and this is acknowledged by the Exergoecology group (Valero, Ranz et al. 2002; Szargut, Valero et al. 2005; Valero 2008).

### 3.1.1 Scope of the Exergy Replacement Cost

While the Exergoecology group proposes the Exergy Replacement Cost as a measure of resource value (Valero 2008 chs. 1 and 5), the focus is primarily minerals. For example, Alicia Valero describes the scope of the Exergy Replacement Cost as determining the “physical stock available in the current continental crust” (Valero 2008). For the assessment of biotic resources, Alicia Valero refers to Jorgensen's Eco-exergy (Valero 2008), which is discussed in Chapter 4.

The Exergoecology group is sometimes ambiguous regarding the scope of the Exergy Replacement Cost, as members of the group consistently use the expressions ‘natural resources’ and ‘ecosystems’, both of which include biotic and other non-mineral resources. While the problem is largely semantic, the ambiguity can cause confusion.

According to the Exergoecology group, the Exergy Replacement Cost differs from standard extraction costs in that extraction costs assess the cost from the ‘mine to the market’, while the Exergy Replacement Cost assesses the thermodynamic cost from the ‘entropic planet<sup>10</sup> to the mine’ (Valero 2008). The difference between extraction cost and replacement cost is shown in Figure 3-1, adapted from Valero (2008, ch. 1). The only differences between Figure 3-1 and Alicia Valero’s diagram are the words in brackets, and they will be discussed next.



**Figure 3-1 - Exergy Replacement cost**  
**Source: (adapted from Valero 2008)**

From Figure 3-1, this author deduces that the reference environment is the entropic planet, which is not the same as nature, where nature is defined to be the mine. Valero’s diagram makes no mention of the market, and therefore it is difficult to see how the Exergy Replacement Cost in fact compares to the extraction cost. This author will attempt to sort out the confusion in section 3.2.2.

<sup>10</sup> As mentioned in Chapter 2, the Exergoecology group uses the terms ‘entropic planet’, ‘thermodynamically dead planet’, ‘dissipated Earth’ and ‘crepuscular planet’ interchangeably.

### 3.1.2 The Exergy Replacement Cost equations

The Exergy Replacement Cost follows directly from Szargut's defined reference states, and for this reason, the reference state chosen for the Exergy Replacement Cost is Szargut's defined states. A critique of the choice of reference environments will be provided in section 3.2.1.

According to the Exergoecology group, there are two different methods by which an item has value (Valero 2008):

1. Non-flow chemical exergy - the work necessary to develop the structure, as calculated by the reversible formation reaction, shown in Equation (4.1):

$$b_{ch,i} = \Delta G_{f,i} + \sum_j r_{j,i} b_{ch,j} \quad (4.1)$$

where  $\Delta G_{f,i}$  is the Gibbs normal standard free energy of substance  $i$ ,  $r_{j,i}$  is the amount of moles of element  $j$  per mole of substance  $i$ , and  $b_{ch,j}$  is the standard chemical exergy of element  $j$  contained in substance  $i$ . Equation (4.1) is explained in Chapter 2 (section 2.3.1).

2. Concentration exergy - the work necessary to bring the substance from its average concentration in the Earth's crust to the required concentration<sup>11</sup>, shown in Equation (4.2).

$$b_{c,i} = -RT^o \left[ \ln x_i + \left( \frac{1-x_i}{x_i} \right) \ln(1-x_i) \right] \quad (4.2)$$

where  $R$  is the universal gas constant (8.314kJ/kmole K),  $T^o$  is the reference environment temperature (298.15K) and  $x_i$  is the molar concentration of the substance.

The Exergy Replacement Cost is the sum of the non-flow chemical and concentration exergies, shown in Equation (4.3) (Valero 2008).

$$B_{total,i} = n_i [b_{ch,i} + b_{c,i}] \quad (4.3)$$

While the Exergy Replacement Cost equations are conceptually quite simple, the concentration exergy appears to be double counted. As described in Chapter 2 (Figure 2-1), the chemical exergy already includes the concentration exergy. For reference

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<sup>11</sup> A simplified version of the concentration exergy is derived in section 6.3.1

species, the chemical exergy is only the concentration exergy. The exergy of non-reference species is determined based on the exergy of reference species, and therefore the concentration exergy is once again included. To avoid double counting, Equation (4.2) would need to be removed, with the focus simply on chemical exergy.

A second confusing aspect of the concentration exergy, Equation (4.2), is the meaning of the ‘average concentration in the Earth’s crust to the required concentration’. Is the average concentration in the Earth’s crust the same as the concentration in the reference environment? Does the required concentration refer to the mineral as a pure substance? It is worth noting that if the ‘required’ concentration is not the material in a pure substance, then the concentration exergy may need to be *subtracted from*, as opposed to *added to*, the chemical exergy. The reason for this is that since the chemical exergy already contains the material as a pure substance (as mentioned above), anything less than purity would result in a loss of exergy.

### **3.2 Critiques of the Methodology**

The Exergy Replacement Cost is a relatively new methodology for assessing resource value and resource consumption. For this reason, what follows is believed to be a first critique of the Exergy Replacement Cost.

#### **3.2.1 Reference Environment Issues**

A first concern of the Exergy Replacement Cost is how it is dependent upon the choice of reference environments. Notwithstanding the problems with the concentration exergy mentioned above, the Exergy Replacement Cost is defined identically to exergy, with Szargut’s defined reference state as the chosen reference state formulation. Due to the equivalence between the Exergy Replacement Cost and the definition of exergy, all the weaknesses of Szargut’s reference environment formulation are directly applicable here.

In Chapter 2, the various reference environment formulations were discussed and several problems were elucidated. To avoid repeating information, the reader is encouraged to review Szargut’s defined reference state in Chapter 2 (section 2.3). The important points to note are that Szargut’s reference environment contains internal contradictions

(including negative exergies), assumes ideal gases, and in fact does not represent a ‘thermodynamically dead’ reference environment (Valero 2008, ch. 6). If a different reference environment was chosen (such as Ahrendts’ equilibrium environment), then the value of individual resources would likely change dramatically. Which is why Ranz’ defined reference state, based purely on abundance, was rejected (Chapter 2, section 2.3.3).

### **3.2.2 Methodological issues**

The second concern with the Exergy Replacement Cost is based on some confusion with what the Exergy Replacement Cost actually represents. Formally, the Exergy Replacement Cost is the exergy, as defined by the Exergoecology group. However, as mentioned above in section 3.1.1, Alicia Valero compares the Exergy Replacement Cost to the thermo-ecological cost: claiming the latter measures from the mine to the market, while the former measures from the entropic planet to the mine (Valero, Ranz et al. 2002; Valero 2008). In many respects these two different costs are incomparable: Exergy Replacement Cost is a state property of an item<sup>12</sup>, while the thermo-ecological cost is a cumulative (lifecycle) cost.

The Exergoecology group appears to address the confusion above by proposing two different Exergy Replacement Costs, which for the purpose of this thesis are labelled the ‘state-property’ Replacement Cost and the ‘lifecycle’ Replacement Cost. Whereas the state property Replacement Cost is the exergy (as defined by Szargut), the Exergoecology group acknowledges the true Replacement Cost is higher than the theoretical replacement cost as there will always be irreversibilities in a process (Valero, Ranz et al. 2002; Valero 2008). For this reason, the lifecycle Replacement Cost is a measure of the actual amount of work required to refine a mineral resource.

The connection between the state-property and lifecycle Replacement Costs is via two scaling factors,  $k_{ch}$  and  $k_c$ , that multiply the chemical and concentration exergies. The corresponding equation is shown in Equation (4.4):

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<sup>12</sup> Formally the Exergy Replacement Cost is not a state property, but since the reference state has been fixed it is effectively a state property (section 1.3.1).

$$B_{lifecycle,i} = k_{ch,i}B_{ch,i} + k_{c,i}B_{c,i} \quad (4.4)$$

The scaling factors,  $k_{ch}$  and  $k_c$ , vary depending on the mineral. Table 3-1 lists the first twenty k-values, as provided by Alicia Valero (Valero 2008, Table 5.7).

**Table 3-1 - Selected  $k_{ch}$  and  $k_c$  values,**

Substance	$k_c$	$k_{ch}$	Substance	$k_c$	$k_{ch}$
Ag	7042	10	Cs	N.A.	1
Al	2250	8	Cu	343	80.2
As	80	10	F	2	1
Au	422,879	1	Fe	97	5.3
Ba	N.A.	1	Ga	N.A.	1
Be	112	1	Ge	N.A.	1
Bi	90	10	Hf	N.A.	1
Cd	804	10	Hg	1707	10
Co	1261	10	In	N.A.	10
Cr	37	1	K	39	1

**Source: adapted from (Valero 2008)**

While Table 3-1 is not complete, it is representative of the k-values. In general,  $k_c$  fluctuates a great deal, from a low of unity to a high of over 400,000. By contrast,  $k_{ch}$  generally stays within one order of magnitude (from 1 to 10), with a high of 188 for U, which is not shown here (Valero 2008, Table 5.7).

Table 3-1 indicates very little correlation between the state-property and lifecycle Replacement Costs. Furthermore, since the variation in  $k_c$  is over several orders of magnitude, it impossible to predict even rough estimates of the lifecycle Replacement Cost from the state-property Replacement Cost of an unknown compound or element. With such a wide divergence (almost 5 orders of magnitude) between the state-property and lifecycle replacement costs, some of the underlying assumptions of the Exergy Replacement Cost must be re-examined. This author argues there are three critical assumptions that require re-examining, and each will be explained.

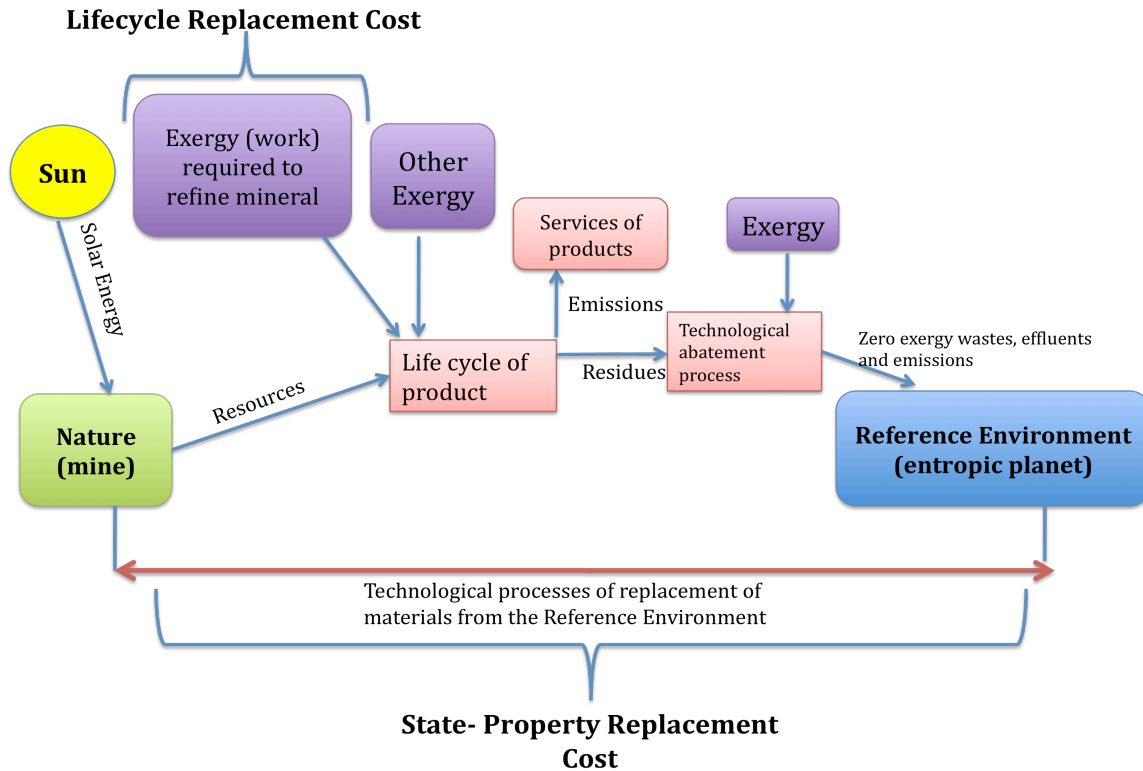
First, the reference environment may be incorrectly formulated. For example, Szargut's defined reference state assume that the solid phase is an ideal gas mixture (Szargut 2005), as mentioned in Chapter 2 (section 2.3.1.1). The reason provided by Szargut for

choosing an ideal gas mixture is that “the external layer of the Earth’s crust is a very complicated mixture of solid solutions [and] it is not possible to calculate exactly the concentration exergy of solid reference species” (Szargut 2005). This does not appear to be sufficient theoretical justification for such an assumption.

Second, the concentration exergy may not be a relevant characteristic of non-fuel minerals. Non-fuel minerals are not used to produce work, and it is likely that they cannot produce useful work. In this respect, this author questions why a work related measure is applied to characterize a non work-producing system.

Third, the concentration exergy may not even a relevant form of exergy regardless of whether a mineral is work producing or not. To the best of this author’s knowledge, some of the assumptions regarding the concentration exergy, such as the presence of a semi-permeable membrane, have not been adequately justified. The derivation and assumptions regarding the concentration exergy will be discussed in Section 6.3.1.

From a different perspective, the lifecycle Replacement Cost also appears to contradict the description of the Exergy Replacement Cost provided by Alicia Valero (and mentioned in section 3.1.1). The lifecycle Replacement Cost essentially quantifies the amount of work required to refine a mineral from a mine. In this respect, the lifecycle Replacement Cost starts from the mine and moves towards the market. By contrast, Alicia Valero describes the Exergy Replacement Cost as moving from the entropic planet to the mine. These differing interpretations are shown in Figure 3-2, where interpretations of both the state-property and lifecycle Replacements costs are shown.



**Figure 3-2 - Interpretations of state-property and lifecycle Replacement Costs**

If the interpretation of Figure 3-2 is correct, then the lifecycle Replacement Cost is more similar to the thermo-ecological cost than it is to the state-property Replacement Cost.

### 3.2.3 Summarizing the critiques

The critiques provided above indicate the Exergy Replacement Cost is lacking in refinement. There is sufficient ambiguity in terms to cause confusion. In the defence of the Exergoecology group, the ambiguity may be due to the novelty of the theory, and further refinement may eliminate many of the critiques.

One specific area of concern relates to whether the lifecycle Replacement Cost has any relationship to exergy. The lifecycle Replacement Cost appears to be concerned solely with the amount of work required to refine minerals. By revisiting the original definition of exergy (the amount of mechanical work that can be maximally extracted from the system in [its] environment), this author questions whether this specific thermodynamic concept has any relevance to mineral processing. In this regard, the preliminary conclusions drawn from the widely divergent k-values indicate that there is no relevance.

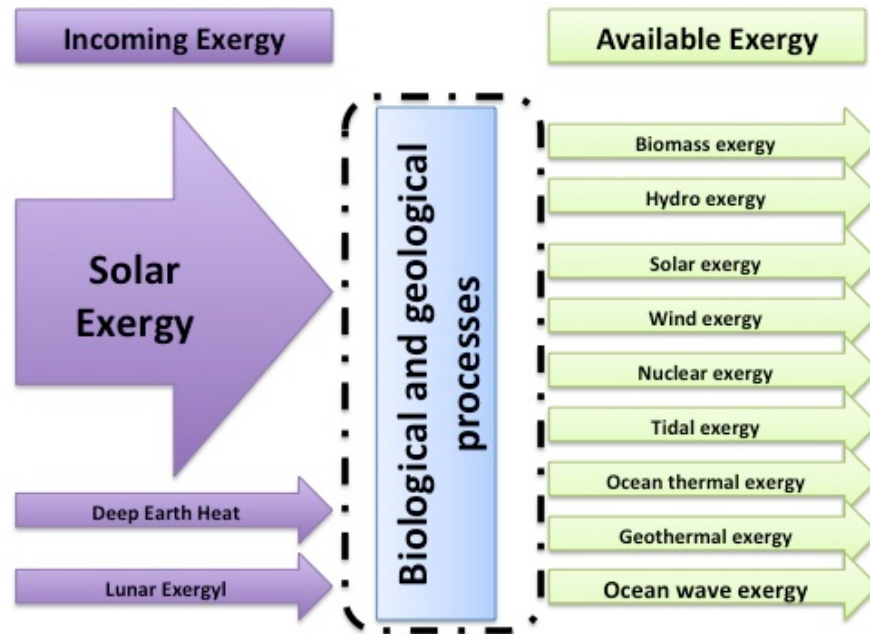


### **3.3 Limits to Resource Consumption**

The last topic to discuss regarding the Exergy Replacement Cost concerns how it sets limits upon resource consumption. In Chapters 4 and 6 of her dissertation, Valero surveys the current resources available for humankind (Valero 2008). Within the survey, all the major resources (such as solar, nuclear, biomass, wind, fossils) are catalogued into three sections: theoretically available, potentially achievable, and currently used, where potentially available exergy provides an upper limit to resource consumption that is technologically, rather than ecologically, derived (Valero 2008).

According to Valero, the theoretically available renewable exergy amounts to approximately 43,000 TW (Valero 2008), which is one third of the total non-reflected solar exergy (173,000 TW, 30 percent of which is reflected, as mentioned in Chapter 1). By contrast, the potentially available renewable exergy amounts to roughly 80 TW (Valero 2008), which amounts to 0.2 percent of the theoretically available exergy. Valero concludes that since there is so much energy available there is no energy crisis, and rather the world is in fact suffering from a material crisis because non-fuel minerals cannot be replaced by renewable resources (Valero 2008).

While not explicitly stated, the Exergoecology group appears to adopt a black box approach to resource consumption in that they ignore biological and geological processes and are concerned mainly with the exergy available from specific resources. In essence, the Exergoecology approach is more of a bookkeeping tool. A heuristic of this approach is provided in Figure 3-3.



**Figure 3-3 - Exergoecology approach to resource consumption (not to scale)**

It is difficult to interpret the Exergoecology understanding of resource consumption. For example, despite concluding that non-fuel mineral resources are the critical problem facing the world, the Exergoecology group does not explain how the Exergy Replacement Cost fits into an understanding of resource consumption. *If there is such an ample supply of renewable exergy (as found by Valero), and if exergy characterizes resource and mineral consumption (which is the Exergoecology argument) then it is difficult to conclude that the world is facing a mineral crisis.* In other words, there should be ample exergy available to bring minerals from the entropic planet back to the mine.

A second problem with the Exergoecology approach to resource consumption is that the resources listed above may not be calculated using Szargut's defined reference states. Szargut's defined reference state can only quantify non-flow chemical exergy, and therefore is blind to every form of exergy listed in Figure 3-3, with biomass the only potential exception. However, for biomass, Alicia Valero refers to Jorgensen's Eco-exergy, because the Exergy Replacement Cost is developed for mineral resources (Valero 2008, ch. 1).

This author notes that Figure 3-3 does not include fossil fuels, and the Exergoecology approach does calculate the exergy of fossil fuel resources. However, as was mentioned in Chapter 2 (section 2.3.1.3), liquid fuels are not calculated based upon Szargut's defined reference states, but rather based upon correlations with the lower heating value. In Chapter 2 (section 2.3.2), this author argues that by using heating value correlations to determine exergy, the Exergoecology group is adopting a process dependent reference environment.

The purpose of the above critique is not to claim that the Exergoecology approach is wrong, but rather incomplete. The relationships between the state-property Replacement Cost, the lifecycle Replacement Cost, and the limits to resource consumption are not adequately developed or justified. More specifically, the apparent use of different exergy calculation methodologies (Szargut's defined reference states for Exergy Replacement Costs, process dependent reference states for most resources) may signify a lack of internal consistency. Furthermore, by separating all resources into different categories, it is difficult to see how the resources may be compared to one another, and whether this comparison is performed via the Exergy Replacement Cost. While these problems are not necessarily insurmountable, they do require further discussion.

### **3.4 Conclusion**

In this chapter the Exergy Replacement Cost was assessed both as a measure of the utility of exergy, and for the potential of the Exergy Replacement Cost to inform resource consumption. After a preliminary analysis, there are several issues that have arisen and deserve mention. A summary of the Exergy Replacement Cost is provided in Table 3-2 below.

Many of the limitations regarding the Exergy Replacement Cost are potentially due to ambiguously defined terms and concepts. There is confusion regarding what the reference environment represents, and what the Exergy Replacement Cost measures.

With respect to the utility of exergy within the Exergy Replacement Cost, no firm conclusion can be drawn, but preliminary indications are not positive. The k-values of Table 3-1 serve as a first indication there is little to no correlation between non-flow chemical exergy and mineral refining. The lack of correlation in k-values may be attributed to inappropriate assumptions regarding the reference environment (such as ideal gas assumptions), the potential irrelevance of the concentration exergy to characterise non work-producing systems, and even possibly the irrelevance of the concentration exergy in general. There are possibly other reasons for the disjunction between the state-property and the lifecycle Replacement Cost that have not been noted here.

With respect to providing limits to resource consumption, the Exergoecology group is unclear in their proposal. By ignoring biological and geological processes (as shown in Figure 3-3), the Exergoecology approach appears to be primarily a bookkeeping approach. Furthermore, the use of multiple exergy calculation methodologies requires further clarification.

While the Exergy Replacement Cost is proposed as a means of valuing resources, this author proposes to frame the Exergy Replacement Cost only with respect to mineral refining. Effectively, the Exergy Replacement Cost would serve as a catalogue that would relate a mineral's purity to the work required to refine the mineral. Furthermore, due to the widely variant k-values, the Exergy Replacement Cost would be descriptive as opposed to predictive, and would not be directly related to exergy.

The advantage of using Exergy Replacement Cost purely for mineral refining is that the Exergy Replacement Cost is predicated upon a wealth of geological and geochemical data. The k-values also represent empirical data produced that may prove to be very useful within a larger resource consumption methodology.

**Table 3-2 - Summary of Exergy Replacement Cost**

Exergy Replacement Cost - Summary	
Definition of resource value	<ul style="list-style-type: none"> <li>• The value of a natural resource is the minimum work necessary to produce it with a specific structure and concentration from common materials in the environment. This definition is equivalent to Szargut's definition of exergy.</li> </ul>
Reference state	<ul style="list-style-type: none"> <li>• Szargut's defined reference state.</li> </ul>
Assumptions	<ul style="list-style-type: none"> <li>• The exergy of all resources can be compared and is related to the Exergy Replacement Cost.</li> <li>• The concentration exergy is a relevant characteristic of non work-producing resources.</li> <li>• Assumes Szargut's reference state is an appropriate reference state.</li> </ul>
Limitations	<ul style="list-style-type: none"> <li>• Exergy Replacement Cost only properly defined for mineral resources.</li> <li>• The value of a resource is dependent upon the formulation of the reference state.</li> <li>• Ambiguous terminology limits critical discussion. Further refinement of the Exergoecology approach is needed.</li> </ul>
Approach to resource consumption	<ul style="list-style-type: none"> <li>• Divide all the specific resources into their respective categories (wind, biomass, hydro, fossil, nuclear).</li> <li>• Account for resources independently of one another.</li> <li>• Apply different exergy calculation methodologies for difference resources because none of the energy resources appear to be well defined by the Exergy Replacement Cost.</li> </ul>
Empirical validation	<ul style="list-style-type: none"> <li>• Distinguishes between state-property Replacement Cost (which is the exergy) and lifecycle Replacement Cost (which appears to be the work required to process minerals). Empirical evidence (Table 3-1) shows there is no correlation between state-property and lifecycle Replacement Costs.</li> <li>• Confusion as to whether lifecycle Replacement Cost is a Replacement Cost, and not simply the work required to refine minerals.</li> </ul>
This author's proposed use	<ul style="list-style-type: none"> <li>• Methodology focused on describing the amount of work required to refine mineral deposits. This application does not relate to exergy, but it does take advantage of the currently compiled geological data.</li> </ul>



## Chapter 4 – Eco-exergy

The second resource consumption methodology assessed in this thesis is Eco-exergy. Eco-exergy was developed by S.E. Jorgensen in the late 1990s, although he had already been using it (or an analogue thereof) as an indicator in aquatic ecology for more than two decades (Jorgensen and Mejer 1977; Jorgensen 1988). While Eco-exergy has been applied primarily within the ecological modelling community, Jorgensen has proposed Eco-exergy as an indicator of sustainability due to its claimed ability to be used for thermodynamic and ecological applications (Bastianoni, Nielsen et al. 2005; Jorgensen 2006; Susani, Pulselli et al. 2006).

### 4.1.1 Eco-exergy and ecological development

According to Jorgensen, the Eco-exergy approach is based on the observation<sup>13</sup> that the level of development of an ecosystem is related to the distance between the ecosystem and thermodynamic equilibrium (Jorgensen 2006; Jorgensen and Nielsen 2007). In other words, the exergy of an ecosystem measures the organization of the ecosystem in the forms of “organisms, complex biochemical compounds and [the] complex ecological network” (Jorgensen 2006)<sup>14</sup>. Jorgensen codifies the observation into a proposed 4<sup>th</sup> law of thermodynamics (Jorgensen 2006):

*If a system receives an input of exergy, it will use this exergy after the maintenance of the system far from equilibrium has been covered, to move the system further from thermodynamic equilibrium. If more than one pathway to depart from equilibrium is offered, the one yielding the most gradients, and the most Eco-exergy storage ( $dEx/dt$  is maximum) under the prevailing conditions, to achieve the most ordered structure furthest from equilibrium will tend to be selected.*

Other authors have proposed similar 4<sup>th</sup> laws of thermodynamics, and there is the potential for confusion. What primarily distinguishes Jorgensen’s 4<sup>th</sup> law is that

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<sup>13</sup> Jorgensen does not clarify who made the observation.

<sup>14</sup> Jorgensen never clearly defines ‘complexity’. However, it will be seen that ‘complexity’ is used to define the improbability of life.

Jorgensen proposes the end goal of ecological self-organization is to increase the storage of Eco-exergy (Jorgensen 2006) – where Eco-exergy will be derived in section 4.2.

There are two concerns that arise with Jorgensen’s approach to exergy and ecological development. First, Jorgensen does not distinguish between exergy inputs that are helpful (organizing) and exergy inputs that are harmful (disorganizing). As was mentioned in Chapter 1, there is ongoing discussion concerning how exergy may be a measure of waste impact. For example, while nuclear wastes added to an ecosystem would represent an exergy input, this exergy input would likely be harmful to the ecosystem and promote disorganization (as opposed to self-organization). How Jorgensen’s 4<sup>th</sup> law would reconcile this problem is not apparent.

The second concern regards Jorgensen’s observation that the level of development of an ecosystem is related to the distance between the ecosystem and thermodynamic equilibrium (Jorgensen 2006; Jorgensen and Nielsen 2007). The work of several ecologists, most notably the Resilience Alliance, has shown that ecological collapse and reorganization is an intrinsic and integral part of ecological development (Kay, Boyle et al. 1999; Gunderson and Holling 2002; Walker and al. 2002; Homer-Dixon 2006; Walker and Salt 2006). During the reorganization phase, the exergy stored up in the ecosystem is released (Kay, Boyle et al. 1999), and this would arguably reduce the stored Eco-exergy as well. In this respect, Jorgensen’s ‘observation’ appears to ignore the quasi-cyclical nature of ecological development, because it focuses primarily on the growth phase of ecosystems.

#### 4.1.2 The Eco-exergy equation

While Eco-exergy will be derived in section 4.2, it is helpful to immediately introduce how Eco-exergy relates to resource value. There are several interchangeable equations for Eco-exergy, the simplest being the Eco-exergy of a single organism shown in Equation (5.1) (Jorgensen 2006, ch. 3):

$$b_{organism,i} = \beta_i c_i (\mu - \mu_o)_{detritus} \quad (5.1)$$

where  $\beta_i$  is a dimensionless complexity factor relating the ratio of information to chemical exergy in the organism,  $c_i$  is the mass of the organism in grams, and  $(\mu - \mu_o)_{detritus}$



is the chemical exergy of detritus, calculated to be 18.7 kJ per gram (Jorgensen 2006; Susani, Pulselli et al. 2006). The dimensionless complexity factor,  $\beta$ , will be introduced at the end of the formal derivation of Eco-exergy.

#### **4.1.3 The scope of Eco-exergy**

While Eco-exergy equation primarily characterizes organisms, the scope of Eco-exergy includes organisms, non-living resources and other items (or systems) of interest (Susani, Pulselli et al. 2006). For example, Jorgensen calculates the Eco-exergy of a house, a book, a picture and a crystal (Susani, Pulselli et al. 2006), as well as various mineral resources (including chromium, nickel, zinc and copper) (Jorgensen 2006, ch. 4). The scope of Eco-exergy, and its ability to value resources and items will be discussed further in section 4.4. The salient point is that Jorgensen attempts to quantify all resources and items via Eco-exergy.

#### **4.2 The derivation of Eco-exergy**

Unlike the Exergy Replacement Cost, which was formulated to match the definition of exergy, Eco-exergy is a composite function of thermodynamics and information theory. By incorporating non-energy based information theory, i.e., information is not related to energy microstates as in statistical mechanics, Eco-exergy is no longer a thermodynamically pure concept, and therefore the derivation of Eco-exergy is not accounted for by the derivation of exergy that is found in thermodynamic texts (such as Bejan 1998 ch. 5). By this token, the derivation of Eco-exergy must be analyzed to ensure it is properly developed from first principles.

The derivation of Eco-exergy is presented in part in several articles and chapters by Jorgensen (including, Jorgensen, Nielsen et al. 1995; Jorgensen 2001; Jorgensen 2006 ch. 3; Susani, Pulselli et al. 2006). All the derivations provided by Jorgensen contain logical jumps and/or unstated assumptions, both of which increase the difficulty of properly formulating a critique. What follows in this section an attempt to complete the derivation by synthesizing Jorgensen's partial derivations, and by making explicit the unstated assumptions. The two primary sources for the derivation presented below are (Jorgensen 2006; Susani, Pulselli et al. 2006), as they were determined to be the most complete.

#### 4.2.1 The Eco-exergy reference state

The first step in deriving Eco-exergy is the formulation of a reference state. According to Jorgensen, since the reference state for an ecosystem would be the surrounding ecosystems, the standard exergy concept is inappropriate (Jorgensen 2006 ch. 3). Instead, Jorgensen proposes the reference state be the very same ecosystem at thermodynamic equilibrium, with all elements at their maximum oxidation state, and at standard temperature and pressure (298.15 K, 101.325 kPa) (Jorgensen 2001; Jorgensen 2006 ch. 3; Susani, Pulselli et al. 2006). For example, nitrogen would be as nitrate ( $\text{NO}_3^-$ ). According to Jorgensen, all the components required for life would be present, but in their most stable form (Susani, Pulselli et al. 2006).

Nominally, the reference state described by Jorgensen above is a modification of Ahrendts' equilibrium reference state (Ahrendts 1980), which was discussed in Chapter 2. However, there are some conceptual differences between the two, as the Eco-exergy reference state is chosen so as to distinguish between living and non-living matter, something that Ahrendts' reference state does not account for (Susani, Pulselli et al. 2006). The distinction is based on the so-called 'complexity' of the exergy.

There are several problems relating to Jorgensen's proposed reference state. First, Jorgensen is ambiguous regarding the reference state. For example, in one publication, Jorgensen claims that the reference state is detritus (organic matter) rather than thermodynamic equilibrium (Fonseca, Marques et al. 2000). Furthermore, when calculating the Eco-exergy of abiotic resources (such as mineral and fossil resources), Jorgensen appears to adopt Szargut's defined reference state values (for example, see Jorgensen 2006, ch. 4; Susani, Pulselli et al. 2006).

A more important problem regarding the Eco-exergy reference state is that it appears Jorgensen has not in fact produced a model for what an ecosystem would be composed of at thermodynamic equilibrium. In this respect, the Eco-exergy reference state is still undefined (de Witt 2005).

### 4.2.2 The derivation steps

In this section, Eco-exergy will be derived in a step-wise manner. The steps are chosen in an attempt to elicit the principal assumptions in the derivation.

#### Step 1 – Setting up the concentration and beginning with chemical exergy

To begin the derivation, Jorgensen begins with the formula for non-flow chemical exergy, shown in Equation (5.2):

$$B = \sum_i N_i (\mu_i - \mu_{i,o}) \quad (5.2)$$

Jorgensen's first step is to change the chemical exergy equation from chemical potentials to concentrations, and this is based on the definition of the chemical potential shown in Equation (5.3) (see Bejan 1998):

$$\mu_i - \mu_{i,o} = RT^o \ln \frac{c_i}{c_{i,o}} \quad (5.3)$$

Using Equation (5.3), Jorgensen rewrites the non-flow chemical exergy to that which is shown in Equation (5.4) (Jorgensen 2006, ch. 4):

$$b = RT^o \sum_c c_i \ln \frac{c_i}{c_i^{eq}} \quad (5.4)$$

Where  $c_i$  and  $c_i^{eq}$  represent the concentration of component in the ecosystem, and in the reference state respectively. There are several important points to be made concerning Equation (5.4). First, Equation (5.4) no longer represents the total Eco-exergy, but rather the Eco-exergy per unit mass, because Equation (5.4) sums up concentrations (the  $c_i$ 's in front of the natural logarithm). Jorgensen does not mention this change from total Eco-exergy to Eco-exergy per unit mass. Secondly, no explanations are provided as to what these concentrations are (even whether they are mass or volume concentrations), or how they are measured.

A third point of note is that switching from chemical potentials to concentration exergies requires that every chemical present in the system is also present in the reference environment; otherwise the exergy would be infinite. To the best of this author's knowledge, this requirement is fundamental to the derivation of exergy (Bejan 1998, ch. 5), and in this respect does not represent a requirement that is out of the ordinary for exergy. However, there appears to be important implications to the requirement, including that chemical exergy is essentially only formulated with respect to

concentration exergy. These implications will be explored further in section 6.3.1 as they do not represent specific problems with Eco-exergy, but rather with how exergy itself is formulated.

**Step 2 – Defining A, A<sub>o</sub>: the sum of the concentrations**

In the second step Jorgensen defines ‘A’ and ‘A<sub>o</sub>’, which are the summations of all the biomass in the ecosystem (A) and at equilibrium (A<sub>o</sub>) (Jorgensen 2006; Susani, Pulselli et al. 2006, ch. 3). The formulas for A and A<sub>o</sub> are shown in Equation (5.5):

$$A = \sum_i c_i, \quad A_o = \sum_i c_{i,o} \tag{5.5}$$

Apparently, the use of ‘A’ was proposed by Yuri Svirezhev (Svirezhev 2001).

One immediate problem defining A and A<sub>o</sub> as the sum of biomass is that the c<sub>i</sub>’s are concentrations. By this token, A and A<sub>o</sub> are concentrations as well. Furthermore, Jorgensen does not define whether the concentrations are mass concentrations or volume concentrations. It is likely that Jorgensen is using mass concentrations because the final units of Eco-exergy are with respect to mass (kJ per gram of organism). However, if A and A<sub>o</sub> are mass concentration, then they are both equal 1 (unity). To show how both A and A<sub>o</sub> would be 1 (unity), Table 4-1 outlines a theoretical system of five components whose total mass sums up to 100 kg. Since the concentration is measured in terms of mass (kg per kg), then the total concentration is simply the total mass divided by itself, and therefore the total concentration must be unity. The confusion regarding A and A<sub>o</sub> is once again a result of Jorgensen not properly defining terms.

**Table 4-1 - Sum of mass concentrations**

Component	Mass (kg)	Concentration (kg/kg)
Component 1	20	0.20
Component 2	10	0.10
Component 3	25	0.25
Component 4	15	0.15
Component 5	30	0.30
<b>Total</b>	<b>100</b>	<b>1.00</b>

**Step 3 – Converting concentrations to probabilities**

With A and A<sub>o</sub>, Jorgensen then defines the probability of a specific component, and this shown in Equation (5.6) (Jorgensen 2006, ch. 3; Susani, Pulselli et al. 2006):

$$p_i = \frac{c_i}{A} \quad p_i^{eq} = \frac{c_i^{eq}}{A_o} \quad (5.6)$$

Jorgensen then uses these probabilities and A and A<sub>o</sub> to eliminate the c<sub>i</sub>'s and c<sub>i</sub><sup>eq</sup>'s from Equation (5.4) (Jorgensen 2006, ch. 3; Susani, Pulselli et al. 2006). The results of this substitution are shown in Equation (5.7):

$$\begin{aligned} b &= RT^o \sum_c p_i A \ln \frac{p_i A}{p_i^{eq} A_o} = RT^o \sum_c A p_i \left( \ln \frac{p_i}{p_i^{eq}} + \ln \frac{A}{A_o} \right) \\ &= ART^o \left( \sum_c p_i \ln \frac{p_i}{p_i^{eq}} \right) + ART^o \ln \frac{A}{A_o} \sum_c p_i \end{aligned} \quad (5.7)$$

which can be shortened as the p<sub>i</sub>'s must sum to unity. This is shown in Equation (5.8)

$$b = ART^o \sum_{i=1}^n p_i \ln \frac{p_i}{p_i^{eq}} + ART^o \ln \frac{A}{A_o} \quad (5.8)$$

In Equation (5.8), if both A and A<sub>o</sub> are mass concentrations then the second term vanishes due to the ln(A/A<sub>o</sub>) factor.

At this point, there is still ambiguity as to what these concentrations and probabilities refer to. The basic Eco-exergy equation described in section 4.1.2 relates to organisms, yet the derivation so far still relates to chemicals and chemical concentrations. If Jorgensen were in fact describing organisms in these equations, then these equations would require further explanation and justification. The equations for chemical exergy (and thermodynamic equations in general) are derived under very specific limitations were not intended to describe organisms.

#### **Step 4 – Simplification of the exergy equation**

Jorgensen's following step is to claim that A and A<sub>o</sub> are approximately equal, and therefore the second term in Equation (5.8) may be ignored (Jorgensen 2001; Jorgensen 2006; Susani, Pulselli et al. 2006). On the other hand, Svirezhev argues this is not the case (Svirezhev 2001).

As mentioned in Step 3, if A and A<sub>o</sub> are mass concentrations, then they are indeed equal (and both equal to unity). However, if A and A<sub>o</sub> are not mass concentrations, and are instead volume concentrations, then Jorgensen's claim is unjustified. Once again, the difficulty in arguing definitively results from the concentrations not being defined.

While what follows in this paragraph is pure speculation, an attempt will be made to discuss how  $A$  and  $A_o$  may compare to one another if they are indeed volume concentrations. Since  $A_o$  is the concentration of  $A$  at maximum oxidation, they will be different if mass is permitted to enter the system, or if the volume has changed (changes in volume will not be discussed here). In general, based on Jorgensen's description of the reference environment being the same system, but at maximum oxidation, the question becomes primarily an issue of where the oxygen came from. If all the oxygen required for oxidation originates within the system then  $A$  would equal  $A_o$ . By contrast, if the oxygen originates from outside the system, such as the atmosphere, then the  $A$  and  $A_o$  would differ. A simple calculation of the oxidation of glucose into carbon dioxide and water shows a change in mass from 180 to 372 (in whatever units are chosen). However, in the situation of an external oxygen supply, the only way to neglect the second term is if the second term is negligible with respect to the first term, i.e. (Equation (5.9)):

$$\sum p_i \ln \frac{p_i}{p_{i,o}} \gg \ln \frac{A}{A_o} \quad (5.9)$$

To summarize, there are essentially three possible modes in which the second term of Equation (5.8) may be neglected: first, the concentrations are mass concentrations, in which case  $A$  and  $A_o$  are both unity; second, the concentrations are volume concentrations but system is closed to mass flow, and therefore,  $A$  and  $A_o$  are equal; third, the concentrations are volume concentrations and the system is open to mass flow, but the second term is negligible compared to the first, and therefore it may be neglected. However, as mentioned above, this is all purely speculative as the terms have not been properly defined.

In any event, to continue with the derivation, the second term of Equation (5.8) will be ignored, with the resulting equation shown in Equation (5.10):

$$b = ART^o \sum_{i=1}^n p_i \ln \frac{p_i}{p_i^{eq}} \quad (5.10)$$

### Step 5 – Removing the $p_i$ 's

With the simplified version of chemical exergy shown in Equation (5.10), Jorgensen then claims that since the a posteriori probabilities (the  $p_i$ 's) within the natural logarithm

are all known, they must be equal to 1 (unity) (Susani, Pulselli et al. 2006). The new equation is shown in Equation (5.11):

$$b = -ART \sum_{i=1}^n p_i \ln p_i^{eq} = -RT \sum_{i=1}^n c_i \ln p_i^{eq} \quad (5.11)$$

There are several problems with the jump from Equation (5.10) to (5.11). First, Jorgensen removes the  $p_i$ 's inside the natural logarithm, but chooses to keep the  $p_i$ 's outside. If the  $p_i$ 's are indeed equal to unity, then they must all be removed.

The second problem is more fundamental. One of the basic requirements of a probability distribution is that the probabilities of the individual states *sum* up to unity. Therefore it is impossible for every probability within the distribution to be equal to unity, unless the distribution contains only one possible state. With respect to system context, this implies that only one chemical species is present in the system, which is not the case here. The fact that the current concentrations are known (once again assuming concentration is properly defined), means only that values may be to the individual  $p_i$ 's with confidence. Therefore, it is incorrect for Jorgensen to claim the  $p_i$ 's are all equal to unity.

At this juncture, it would make sense to stop the derivation of Eco-exergy. Not only is there a great deal of ambiguity regarding the reference environment and the definition of terms (such as  $A$  and  $A_0$ ), there is also a specific flaw in the logic that has been made. However, to critique Eco-exergy as an entire concept, as well as to discuss the Eco-exergy approach to resource consumption, the derivation must continue.

### **Step 6 – Determining the $p_i^{eq}$ 's**

Using Equation (5.11), Jorgensen then argues that the probability of an ecosystem component to be found at equilibrium is at least the joint probability of finding the organic matter (detritus) ( $p_1$ ) multiplied by the probability of finding the correct composition of nucleotides that determine the biochemical processes in the organism ( $p_L$ ) (Jorgensen 2001; Jorgensen 2006 ch. 3; Susani, Pulselli et al. 2006). For the purpose of this derivation, this author assumes that Jorgensen likely meant that the probability was at *most* and not at *least* the joint probability, as the underlying purpose of the derivation is to value living systems based upon their improbability. The joint probability is shown in Equation (5.12):

$$P_i^{eq} = P_1 P_{L,i} \quad (5.12)$$

It is in this step, Jorgensen makes it clear that the components (the  $N_i$ 's,  $c_i$ 's and  $p_i$ 's) used in the derivation above are not in fact chemical species but rather organisms. This is an important clarification because it allows for reinterpretation of the derivation up to this point. As mentioned above, thermodynamic exergy is not valid for organisms, if only because there is no plausible interpretation of a concentration exergy for organisms. Despite the problems that result from the clarification, the derivation will continue.

### **Step 6a – Determining the $p_{L,i}$ s**

The first probability to discuss is the probability of the nucleotides ( $p_L$ ). This probability carries with it the very important metaphysical assumption that life is probabilistic. Effectively, Jorgensen is assuming that organisms with longer DNA strands (only counting non-nonsense genes) are less likely to be alive.

This author argues that it is extremely difficult to assign a probability to an event or system within the context of self-organizing systems, a class of systems that includes ecosystems and organisms (Kay 1984; Jorgensen 2006; Jorgensen 2007; Kay and Boyle 2008). An example of a self-organizing system is the Bénard convection cell (Schneider and Kay 1994; Schneider and Sagan 2005). Bénard set up a temperature gradient of 80° Celsius through a one-millimetre layer of whale oil. The convection cells that arose were in a structure involving “in excess of  $10^{23}$  molecules acting coherently” (Schneider and Kay 1994). The probability of  $10^{23}$  molecules randomly forming a Bénard cell is incredibly low. However, given the appropriate experimental conditions (temperature gradient), these cells will repeatedly form. In this respect, it is nonsensical to apply a probability to Bénard cell formations, because Bénard cells are not probabilistic events.

To further the Bénard example, Wicken argued that the probability of Cytochrome C being formed from random assembly over the entire life of the universe is so tiny that it is not worth mentioning (Wicken 1987). By the same token, the probability of an organism (or indeed a human) forming by random assembly within an inorganic soup would be even less noteworthy, and it seems nonsensical to assign a probability to the formation of organism. Furthermore, this author argues that applying a probabilistic interpretation of



life contradicts evolutionary theory and Jorgensen claims that Eco-exergy may even be a measure of evolution, as mentioned in section 4.1.1 (Jorgensen 2007).

From an entirely different perspective, Svirezhev argues that  $p_{eq}^i$ 's are zero because life cannot exist at thermodynamic equilibrium (Svirezhev 2001). Jorgensen counters by claiming that the  $p_{eq}^i$ 's are not zero, merely incredibly low (Jorgensen 2006). Svirezhev's argument is quite important because if he is correct then the exergy values of organisms would be infinite (due to the natural logarithm found in the concentration exergy).

Despite the arguments given above, the derivation will continue. The probability,  $p_L$ , is calculated based upon the number of nucleotides ( $a_i$ ), and the percentage of non-nonsense genes ( $1-g_i$ ), where  $g_i$  is the percentage of nonsense genes<sup>15</sup>. Since there are four possible nucleotides, the probability is shown in Equation (5.13).

$$p_{L,i} = 4^{-a_i(1-g_i)} \quad (5.13)$$

#### **Step 6b – Determining $p_1$**

The second probability from Equation (5.12) is  $p_1$ , the probability of finding detritus.  $P_1$  is based upon the chemical potential of detritus, which is approximately 18.7 kJ per gram (based on the heat of combustion) (Jorgensen, Nielsen et al. 1995; Jorgensen 2001; Jorgensen 2006; Susani, Pulselli et al. 2006).

To determine  $p_i$ , Jorgensen reorganizes Equation (5.3) to solve for  $c_1^{eq}$ , shown in Equation (5.14):

$$c_1^{eq} = c_1 e^{-\frac{u_1 - u_1^{eq}}{RT}} \quad (5.14)$$

Then using Equation (5.6) (the definition of  $A$  and  $A_0$ ) the probability of finding detritus at equilibrium is the concentration of detritus at equilibrium divided by  $A_0$ . However, Jorgensen claims that at equilibrium almost all compounds are inorganic (Jorgensen, Nielsen et al. 1995; Jorgensen 2006; Susani, Pulselli et al. 2006), and therefore,  $A_0$  can be approximated by  $c_0^{eq}$ , which is the concentration of all inorganic compounds.  $P_1$  then becomes what is shown in Equation (5.15):

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<sup>15</sup> It must be mentioned that this author's grasp of genetics is tenuous at best, and therefore only the underlying logic of the derivation is critiqued at this point, not the specifics.

$$p_1 = \frac{c_1^{eq}}{A_o} \approx \frac{c_1 e^{-\left(\frac{u_1 - u_1^{eq}}{RT}\right)}}{c_o^{eq}} \quad (5.15)$$

One point of note is that the chemical potential of detritus, 18.7 kJ per gram, (based on its heat of combustion) is not the equilibrium chemical potential but rather Szargut's defined reference state. The implications of this difference are unknown, but it may bear further investigation. A second point of note is that Jorgensen is essentially converting the heat of combustion of detritus into the probability of detritus occurring at equilibrium. While this interpretation of exergy may appear to be nonsense, it once again seems to be consistent within the formulation of exergy (once again, this will be discussed in section 6.3.1).

### Step 6c – Combining 6a and 6b

With  $p_1$  and the  $p_L$ 's known, the probabilities may be combined to form a new equation for exergy, shown in Equation (5.16):

$$b = -RT^o \sum_{i=1}^n c_i (\ln p_{L,i} + \ln p_1) \quad (5.16)$$

Jorgensen then substitutes  $p_1$  in Equation (5.16) for what is shown in Equation (5.15).

The result of the expansion is shown in Equation (5.17):

$$b = -RT^o \sum_{i=1}^n c_i \left[ \ln p_{L,i} - \left( \frac{u_1 - u_1^{eq}}{RT} \right) + \ln \frac{c_1}{c_o^{eq}} \right] \quad (5.17)$$

Jorgensen then assumes that  $\ln \frac{c_1}{c_o^{eq}}$  is negligible, and can be ignored. What this most recent assumptions implies is that either  $c_1$  is close in magnitude to  $c_o^{eq}$  (which seems unlikely, as according to Jorgensen  $c_o^{eq}$  is roughly equal to  $A_o$ ), or that  $\ln \frac{c_1}{c_o^{eq}}$  itself is negligible with respect to the other two terms. In either case, Jorgensen provides no theoretical or numerical justification for the assumption.

The new equation is shown in Equation (5.18), where the chemical potential of detritus has been removed from the summation, and  $p_i$  has been replaced using Equation (5.13).

$$b = (u_1 - u_1^{eq}) \sum_{i=1}^n c_i + RT^o \sum_{i=1}^n c_i a_i (1 - g_i) \ln 4 \quad (5.18)$$

Jorgensen then assumes an average enzyme molecular weight of  $10^5$  grams per mole (Jorgensen 2006). This assumption is necessary to numerically solve for R. However, this assumption essentially assumes that organisms are primarily composed of enzymes

because the individual items in the summation refer to organisms. Otherwise, Eco-exergy does not in fact refer to organisms, but rather enzymes (specifically DNA).

After substituting the chemical potential of detritus, setting the temperature to 300 Kelvin, moving the  $\ln 4$  outside of the second summation, and substituting for  $R$ , the end result is Equation (5.19), which is the ‘final’ Eco-exergy equation:

$$b \left( \frac{kJ}{g} \right) = 18.7 \sum_{i=1}^n c_i + 3.54 * 10^{-5} \sum_{i=2}^n c_i a_i (1 - g_i) \quad (5.19)$$

Where exergy is in units of kJ per gram of organism. It should be noted that although the  $c_i$ 's began as chemical concentrations, when Jorgensen switched from chemical concentrations to organisms (see Step 6), the  $c_i$ 's are in fact units of mass.

### Step 7 – The Eco-exergy of organisms

The final step in the derivation is to break apart the summation to solve for the Eco-exergy of an individual organism, shown in Equation (5.20):

$$b_i \left( \frac{kJ}{g} \right) = 18.7c_i + 3.54 * 10^{-5} c_i a_i (1 - g_i) \quad (5.20)$$

Jorgensen distinguishes the two parts to Equation (5.20) as being chemical exergy and biological exergy (Jorgensen 2006), or classical exergy and information exergy (Susani, Pulselli et al. 2006). It is at this point that Jorgensen introduces the  $\beta$  values, which is a dimensionless number relating the chemical to the biological (or classical to information) exergy. The formula for  $\beta$  is provided in Equation (5.21):

$$\beta_i = \frac{18.7c_i + 3.54 * 10^{-5} c_i a_i (1 - g_i)}{18.7c_i} = 1 + \frac{3.54 * 10^{-5} a_i (1 - g_i)}{18.7} \quad (5.21)$$

As can be seen from Equation (5.21), the  $\beta$  value of an organism is based entirely upon its gene length ( $a_i$ ) and percentage of non-nonsense genes ( $1-g_i$ ). Jorgensen provides tables of  $\beta$  values for different substances in several publications (Jorgensen, Ladegaard et al. 2005; Jorgensen 2006; Susani, Pulselli et al. 2006).

Finally, using  $\beta$  values, Equation (5.20) can be rewritten for the standard Eco-exergy equation of an organism, Equation (5.22).

$$b_i \left( \frac{kJ}{g} \right) = 18.7c_i \beta_i \quad (5.22)$$

Equation (5.22) is identical to Equation (5.1), given in section 4.1.2. This completes the derivation of Eco-exergy.

### 4.2.3 Eco-exergy derivation summary

To summarize the derivation of eco-exergy, the principle points and assumptions will be provided in Table 4-2, along with the step in which the assumption or point was made.

**Table 4-2 –Assumptions in the Eco-exergy derivation**

Location	Assumption
Section 4.2.1	Only chemical exergy is used. Temperature and pressure are 300 Kelvin and 1 atmosphere respectively.
Section 4.2.1	The reference environment is defined as the same system but at maximum oxidation (thermodynamic equilibrium), however the reference environment is not formulated.
Step 2	Switches from using concentrations ( $c_i$ 's) to masses (A) without justification.
Step 4	Incorrectly claims that if the system states are known, then all the a posteriori probabilities are equal to unity. Furthermore, selects to change only the $p_i$ 's inside the natural logarithm to unity and leave the $p_s$ outside as they are.
Step 6	Switches from calculating the chemical exergy of chemical components to the chemical exergy of organisms without justification, and then to the chemical exergy of enzymes; thereby invalidating previous derivation.
Step 6a	Defines a probability to life based on number of non-nonsense genes as well as the chemical potential of organic matter.
Step 6b	Uses the chemical potential of organic matter derived from a non-equilibrium reference state.
Step 6c	Assumes the dominant components (by mass) of an organism are enzymes.

### 4.2.4 Comments on the Eco-exergy derivation

Based on the derivation and comments presented above, Eco-exergy is not related to chemical exergy through any formal procedure. There are too many assumptions and missteps along the derivation. Similarly, as de Witt notes, it is difficult to see how the Eco-exergy of a substance can be liberated for useful work (de Witt 2005).

Jorgensen appears to be aware of the theoretical gaps between Eco-exergy and chemical exergy. In one publication, he states that Eco-exergy is not in fact true work potential, but rather “an operative system interpretation proportional to the available energy invested by ecosystem in building up its ‘structure’ (information and mass)” (Fonseca, Marques et al. 2000). Similarly, Jorgensen writes that due to “unavoidable approximations and hypotheses, [Eco-exergy] is more an index related to exergy than the ‘real’ exergy content” (Bastianoni, Nielsen et al. 2005). While the above statements are ambiguous, they appear to be admissions that Eco-exergy is not chemical exergy.

Despite the gaps in the derivation, the final equation does contain a chemical exergy factor, namely the chemical potential of organic matter multiplied by the mass of the organism. In essence, Eco-exergy is chemical exergy multiplied by a ‘complexity’ factor, where the complexity is based on the number of genes in the organism. This is shown in Equation (5.23).

$$b_i = [c_i * (\mu - \mu_o)_{\text{detritus}}] * \beta_i = (\text{chemical exergy}) * (\text{complexity}) \quad (5.23)$$

Whether the link between Eco-exergy and chemical exergy is fortuitous or by design, the optimal approach to view Eco-exergy is as a *defined* rather than *derived* concept.

### **4.3 Critiques of Eco-exergy**

Similar to the Exergy Replacement cost, Eco-exergy has not been previously critiqued in a formal manner (aside from de Witt 2005). However, Jorgensen’s admissions above that Eco-exergy is not the true exergy (section 4.2.4) imply that there has been some form of constructive criticism regarding Eco-exergy. This section will briefly outline some of the principle critiques of Eco-exergy as seen by this author.

#### **4.3.1 Misinterpretations of Eco-exergy**

The first critique of Eco-exergy is that there is ambiguity as to what Eco-exergy in fact measures. As mentioned above, Jorgensen relates Eco-exergy to measures of “organisms, complex biochemical compounds and [the] complex ecological network” (Jorgensen 2006). However, by examining Equations (5.22) (Eco-exergy of an organism) and (5.19) (total Eco-exergy), the following is noted:

1. The Eco-exergy of an organism is the chemical exergy of the organism (at 300 Kelvin and 1 atmosphere) multiplied by a complexity factor (what de Witt calls an amplification factor (de Witt 2005)). The Eco-exergy of an ecosystem is simply the sum of the Eco-exergies of the individual organisms.
2. All organisms contain the base factor of 18.7 kJ per gram, which Jorgensen claims is the chemical exergy of organic matter.

Point 1 indicates there is no direct connection between Eco-exergy and the ecological network. While Jorgensen claims that the contribution of the ecological network to Eco-exergy is likely negligible (Jorgensen 2006), the Eco-exergy formula is not even capable

of accounting for the ecological network (as ecological networks do not have DNA nor mass).

Point 2 indicates that the chemical exergy factor does not provide useful information when comparing different organisms or ecosystems, because all organisms have the same factor. Furthermore, since Eco-exergy is not a thermodynamic derived concept, it is not necessarily appropriate to compare Eco-exergy values with chemical exergy values (such as in Susani, Pulselli et al. 2006). If this is the case, then this author questions whether Eco-exergy should have any relation to exergy. In other words, if the salient aspects of Eco-exergy are the organism's mass (the  $c_i$ 's) and gene length (the  $\beta$  values), is there any benefit achieved by converting a  $c_i\beta_i$  equation into units of exergy? Furthermore, if there is no benefit to maintaining an exergy foundation to Eco-exergy, what are the impacts of this regarding Jorgensen's 4<sup>th</sup> law of thermodynamics?

It is interesting to interpret Eco-exergy within the ecological literature. For example, the 'Ecosystems Emerging' work of Jorgensen et al. describes the three steps of ecosystem growth, which are (Jorgensen, Patten et al. 2000; Jorgensen 2006):

1. Growth of the physical structure (*total organism biomass*)
2. Growth of the ecological network, including increased material and energy cycling
3. Growth of information, including more plants and animals with longer gene lengths (*the  $\beta$  values*)

In this respect, Eco-exergy appears to quantify the first and third growth forms into one equation. Furthermore, the Eco-exergy formula provides a hypothesis for how this optimization occurs (there are different equations that could relate  $c_i$  and  $\beta$ , as well as different equations to formulate  $\beta$ ). However, under this interpretation of Eco-exergy, there is no longer a direct link to thermodynamics, and one must once again question whether there is any reason to relate Eco-exergy to exergy.

#### **4.3.2 The importance of the $\beta$ -values**

A second critique of Eco-exergy as a defined concept is the importance Jorgensen gives to DNA length. As briefly mentioned above, there are other possible equations that could be formulated to combine an organism's mass and its gene length.

Table 4-3 compares the  $\beta$ -values of a human, rice, bacteria, and coal, and determines how many kilograms of rice, bacterial and coal are required to equal the Eco-exergy value of an 80 kg human. The  $\beta$ -values are derived from (Jorgensen 2006), and the chemical exergy of coal is taken to be 33 kJ per gram (Jorgensen 2006). As can be seen the  $\beta$ -value (gene length) is a dominant factor in Eco-exergy resource value.

**Table 4-3 –Mass of selected substances that equal the Eco-exergy of an 80 kg human**

Object	$\beta$ -value	Mass (kg)
Human	2173.0	80
Rice	275.0	630
Bacteria	8.5	20,500
Coal	1.0	101,000

**Source for  $\beta$ -values: (Jorgensen 2006, ch. 3)**

When the Eco-exergy approach to resource consumption is critiqued in the following section, this author will be argue that by assigning gene length such a dominating characteristic of resource value, Eco-exergy may in fact promote certain practices that are currently viewed as problematic.

#### **4.4 Limits to resource consumption**

While Eco-exergy has been applied primarily within the ecological sciences, Jorgensen has proposed it as a measure of sustainability. Jorgensen refers to the total Eco-exergy of the world as the ‘natural capital’, and claims that strong sustainability<sup>16</sup> requires maintaining or increasing the global value of Eco-exergy (natural capital) (Bastianoni, Nielsen et al. 2005). In other words, sustainability requires that Eco-exergy gained must exceed Eco-exergy lost (Jorgensen 2006). According to Jorgensen, there are several means by which natural capital can be increased or decreased, and these are summarized in Table 4-4 and Table 4-5.

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<sup>16</sup> Based on the work of Herman Daly

**Table 4-4 - Methods of decreasing Eco-exergy**

<b>Method of decreasing Eco-exergy</b>	<b>Measured by:</b>
Consumption of fossil fuels	Loss of work capacity and dispersion of gases
Deterioration of ecosystems	Total final Eco-exergy minus total initial Eco-exergy
Use of renewable resources	Annual consumption multiplied by Eco-exergy content
Depreciation of products	Not described
Dispersion of wastes	The concentration exergy

**Source: (adapted from Jorgensen 2006)**

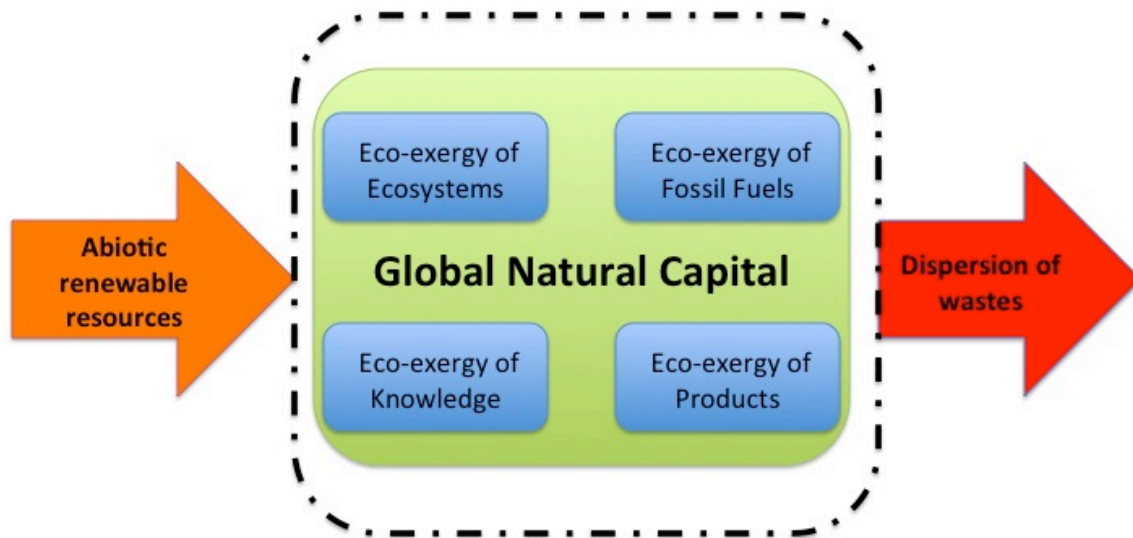
**Table 4-5 – Methods of increasing Eco-exergy**

<b>Method of increasing Eco-exergy</b>	<b>Measured by:</b>
Development of new products	Not described
Recovery of ecosystems	Total final Eco-exergy minus total initial Eco-exergy
Formation of renewable resources	Annual growth multiplied by Eco-exergy content
Repair of products	Not described
Increase of our knowledge	Not described

**Source: (adapted from Jorgensen 2006)**

There is some confusion regarding Jorgensen’s approach to how natural capital (global Eco-exergy) is measured. For example, some aspects of natural capital (namely ecosystems, products, fossil fuels and knowledge) are related to static values, while other aspects of natural capital (namely dispersion of wastes) appear to be more process oriented. Furthermore, the Eco-exergy of renewable resources includes biotic resources that should already be accounted for in the Eco-exergy of ecosystems. Figure 4-1 attempts to reconcile the confusion by including both process and static variables, and noting that many renewable resources (such as wind and solar exergy) are not included in the summation of global natural capital, but rather represents exergy inputs. Likely, the dispersion of wastes is better (but not perfectly) represented as an output from the global natural capital.





**Figure 4-1 - Eco-exergy approach to resource consumption**  
**Source: (adapted from Jorgensen 2006)**

As can be seen graphically in Figure 4-1, or described in Table 4-4 and Table 4-5, Jorgensen’s approach applies limits to resource consumption based on the stock of Eco-exergy, as opposed to the amount of incoming exergy (solar, lunar and deep Earth heat). While incoming exergy is implicitly necessary to maintain Eco-exergy stocks, there is no direct link between the two. In this respect, Jorgensen applies a black box approach to incoming exergy sources.

From an empirical perspective, promoting the increase in Eco-exergy is somewhat problematic, and depends a great deal upon scale. For example, in one study Jorgensen compared different farming practices, from industrial agriculture to very integrated Chinese agriculture (Jorgensen 2006). Of the six farming systems compared, industrial agriculture had the highest specific Eco-exergy, yet Jorgensen stated that industrial farming is very vulnerable and polluting. Furthermore, many of the valuable attributes of agriculture were related to the ecological network maintained within the agricultural system; none of which can be measured by Eco-exergy. In the end, Jorgensen concluded that Eco-exergy and specific Eco-exergy were not sufficient to measure sustainability (Jorgensen 2006, ch. 8).

A second related problem with Jorgensen's proposal for hard sustainability (and resource consumption) is that it amounts to comparisons and trade-offs between a thermodynamic concept (exergy) and a defined concept (Eco-exergy). It is in the area of the tradeoffs that the high value placed on gene length becomes salient. With reference to Table 4-3, if 101,000 kg of coal was consumed, but 630 kg of rice were grown, the net Eco-exergy would remain unchanged. What does that mean? It is interesting to note de Witt's argument that while producing information in the first place is expensive (hence high Eco-exergy values) copying the information is comparatively cheap (de Witt 2005). In this respect, part of the disjunction between coal combustion and rice growing may be that Eco-exergy value is based more upon evolution and history as measured by gene length (if gene length is in fact a proper measure of both). It may not be appropriate to compare an evolutionary value with a real-time process (such as the combustion of coal).

As a final critique, it is difficult to draw a link between Eco-exergy values, and incoming solar exergy. The link between Eco-exergy and solar exergy is quite important, as almost all of our global processes are driven by solar exergy (Jorgensen 2006).

#### **4.5 Conclusion**

Despite its current units of exergy, Eco-exergy is not a derived thermodynamic concept. Instead, Eco-exergy appears to be a defined concept that relates an organism's mass to its gene length, and does so in units of exergy. Furthermore, Eco-exergy appears biased towards gene length, and assumes that gene length is a measure of both evolution and complexity. Since Eco-exergy is not exergy, it is problematic to perform comparisons or tradeoffs between the two. A summary of Eco-exergy is provided in Table 4-6 below.

Jorgensen's approach to resource consumption provides no direct link between Eco-exergy and incoming exergy sources, as 'hard sustainability' is based on maintaining the global sum of Eco-exergy. In this respect, Eco-exergy places no direct upper limit to resource consumption.

Despite the critiques of Eco-exergy, this thesis makes no attempt to criticize the use of Eco-exergy for ecological modelling except to say that it appears doubtful that using

exergy provides useful information to Eco-exergy. As was mentioned in section 4.3.1, in the analysis of ecosystems and organisms, exergy is neither useful nor novel because all organisms are multiplied by the same exergy factor of 18.7 kJ per gram. Therefore, for the purpose of ecological modelling, no information would be lost by considering only the organism's mass and gene length. While Eco-exergy may be useful in ecological modelling, Jorgensen has not provided sufficient justification for applying Eco-exergy outside of ecological modelling.

Finally, Jorgensen's Eco-exergy does not appear to provide new or useful links between exergy and resource consumption. In this respect, further exploration of Eco-exergy as a measure of resource value, resource consumption or 'hard sustainability' must wait until the concept is more properly formulated.

**Table 4-6 - Summary of Eco-exergy**

Eco-Exergy- Summary	
Definition of resource value	<ul style="list-style-type: none"> <li>• The resource value of an organism is the multiplication of the chemical exergy of organic matter (18.7 kJ per gram) by the complexity of the organism (as measured by the gene length).</li> </ul>
Purpose of ecological organization	<ul style="list-style-type: none"> <li>• Ecosystems evolve to increase the storage of Eco-exergy.</li> </ul>
Exergy reference state	<ul style="list-style-type: none"> <li>• Exergy reference state not formally defined.</li> <li>• Claims to adopt an equilibrium reference state, but the chemical exergy of organic matter is based on Szargut's defined reference state.</li> </ul>
Assumptions	<ul style="list-style-type: none"> <li>• Assumes complexity of organisms is a function of gene length (length of non-nonsense genes).</li> <li>• Assumes Eco-exergy can be compared to standard chemical exergy.</li> </ul>
Limitations	<ul style="list-style-type: none"> <li>• Eco-exergy not derived from thermodynamic exergy, and consequently there is no link between Eco-exergy and exergy.</li> <li>• Eco-exergy can only be compared within organisms.</li> <li>• Eco-exergy built on an improper reference state formulation.</li> </ul>
Validation	<ul style="list-style-type: none"> <li>• Studies of different agricultural practices show that increase of Eco-exergy not well correlated to ecological organization (section 4.4).</li> </ul>
Approach to resource consumption	<ul style="list-style-type: none"> <li>• Proposes that hard sustainability requires maintaining the global natural capital, where the natural capital is measured by global Eco-exergy (Table 4-4 and Table 4-5). Consequently, assumes Eco-exergy may be cross-compared to other forms of exergy.</li> <li>• No link to incoming solar exergy.</li> </ul>
Usefulness and novelty of exergy within the approach	<ul style="list-style-type: none"> <li>• Based on limitations, Eco-exergy can only be used to compare different organisms and ecosystems.</li> <li>• Within organisms and ecological communities, all systems are multiplied by the same chemical exergy factor, therefore there is no new information provided by adopting units of energy.</li> </ul>
This author's proposed use	<ul style="list-style-type: none"> <li>• Eco-exergy should only be used for ecological modeling. Within ecological modeling, Eco-exergy would not to be an exergy-based indicator.</li> </ul>

## Chapter 5 – Emergy

This chapter will assess H.T. Odum's Emergy analysis, the third and final exergy-based approach to valuing resources and quantifying resource consumption. Odum developed Emergy analysis as a means of valuing values resources based on their embodied energy. Unlike Eco-exergy and the Exergy Replacement Cost, Emergy has been substantially critiqued (see, for instance Hau and Bakshi 2004), and Emergy proponents have spent a great deal of time rebutting critics (such as Odum 1995). While the important aspects of Emergy will be discussed, Emergy extends beyond the scope of this thesis. The reader is encouraged to consult the Emergy reference material, such as Odum's book on environmental accounting (Odum 1996) or the Emergy handbooks (Odum, Brown et al. 2000).

Emergy was conceived in the ecological sciences, but proponents claim it is applicable to all forms of systems, including natural systems, human systems, and the interface of natural and human systems (Ulgiati and Brown, 2001). Furthermore, proponents claim some of the underlying principles of Emergy analysis are universal principles applicable at all ranges of scales (Odum 1996 ch. 2; Jorgensen, Odum et al. 2004).

### 5.1.1 Emergy and resource value

According to Odum, the heat equivalent or exergy content of a resource does not relate to its value (Odum 1994 ch. 14; Brown, Odum et al. 1995). Instead, Odum proposes that resources have value based on their Emergy (Odum 1994 ch. 14), where:

*Emergy is the sum of all the direct and indirect energy use to make a service or product (Odum 1994; Odum 1996; Bastianoni, Marchettini et al. 2001)*

While any form of energy may be used as the universal measure of comparison, the Emergy group uses solar energy as the common currency, and therefore the operational definition of Emergy is (Odum 1996ch. 2).:

*Emergy is the sum of all the direct and indirect solar energy use to make a service or product*

The fundamental unit of Emergy is the solar emjoule, sej (Odum 1996).

According to the Emergy group, Emergy is a “universal measure of the real wealth of the work of nature and society made on a common basis” (Odum, Brown et al. 2000). Furthermore, Emergy flows are an indication of “what nature invested to make a resource available” (Bastianoni, Facchini et al. 2007). In this respect, Emergy is proposed as a supply-side, ecocentric, formulation of resource value.

There are several equivalent forms of the Emergy equation. The most basic equation for Emergy is Equation (5.1):

$$Em = Tr * B \quad (5.1)$$

Where  $Em$  is the Emergy of an item (in solar emjoules),  $Tr$  is the transformity (in solar emjoules per joule), and  $B$  is the non-flow chemical exergy<sup>17</sup> of the item (Bastianoni, Facchini et al. 2007). The transformity will be discussed in detail in section 5.3; it is essentially the unit Emergy of an item (product or service). Earlier formulations of Emergy used energy in place of exergy, and Emergy proponents have been criticized for their ambiguity towards whether Emergy is based on energy, exergy, or availability (Hau and Bakshi 2004). However, for the purpose of this thesis, the exergy formulation of Emergy will be adopted, as it is the more recent formulation (Bastianoni, Facchini et al. 2007). Furthermore, Emergy proponents claim that energy- and exergy-based Emergy are proportional (Bastianoni, Facchini et al. 2007), and this will be discussed in the following section.

The second equation form of Emergy accounts for the fact that Emergy is a network approach. The Emergy of a product is equal to the Emergy of the inputs, which are in turn equal to their respective transformities and non-flow chemical exergies, as shown in Equation (5.2):

$$Em_{out} = Em_{in} = \sum_i Em_{in,i} = \sum_i Tr_{in,i} B_{in,i} \quad (5.2)$$

A more in-depth approach to calculating Emergy is provided in chapter 6 of Odum’s ‘Environmental Accounting’ (Odum 1996).

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<sup>17</sup> While the qualifier used is non-flow chemical exergy, it must be noted that Emergy proponents simply call it ‘exergy’ (which could be a number of different types of exergy). In practice, however, they appear to be referring to non-flow chemical exergy.

### 5.1.2 The reference environment

While exergy is included in the calculation of Energy, no mention is made of the reference environment. Despite this lack of discussion, by combining Equations (5.1) and (5.2), the sensitivity of the transformity to the reference environment is somewhat more apparent, as is shown in Equation (5.3):

$$Tr_{out} = \frac{Em_{in}}{B_{out}} = \frac{\sum_i Tr_{in,i} B_{in,i}}{B_{out}} \quad (5.3)$$

Where  $B_{out}$  and the  $B_{in,i}$ 's depend on the choice of the reference environment.

As long as all the components of the system are organic (living creatures), then one could argue that  $B_{out}$  and the  $B_{in,i}$ 's would all have the same non-flow chemical exergy (the 18.7 kJ per gram provided by Jorgensen in Chapter 3), and therefore the transformity would not depend upon reference state formulation. However, once non-organic elements are included within the system (such as minerals), the transformity will be sensitive to reference state formulation, especially if the reference state allows for negative non-flow chemical exergy values (such as Szargut's defined reference state, discussed in Chapter 2). Therefore, since Energy is proposed for all forms of systems analysis, a proper discussion of the reference state is required.

The sensitivity of the transformity to the reference environment allows a better interpretation of Bastianoni et al.'s claim that exergy-based Energy only differs from energy-based Energy by a factor of 0.93 (Bastianoni, Facchini et al. 2007). The incoming solar exergy may indeed be 93 percent of the incoming solar energy, and this factor of 0.93 carries through to all items in a system, as shown in Equation (5.4):

$$Em(exergy)_{in} = 0.93 * Em(energy)_{in} \quad (5.4)$$

By combining Equation (5.4) with Equation (5.3), it is possible to determine the sensitivity, as shown by Equation (5.5):

$$\frac{Tr_{out}(exergy)}{Tr_{out}(energy)} = \frac{\frac{Em_{in}(exergy)}{B_{out}}}{\frac{Em_{in}(energy)}{B_{out}}} = \frac{Em_{in}(exergy)}{Em_{in}(energy)} * \frac{U_{out}}{B_{out}} = 0.93 * \frac{U_{out}}{B_{out}} \quad (5.5)$$

Where  $U_{out}$  is the energy of the item. As Equation (5.5) shows, the difference between the energy- and exergy-based Transformities are not simply a factor of 0.93, but rather

depend upon the difference between the energy and the exergy of the item (i.e., Chapter 1, Figure 1-1). Therefore, while exergy- and energy-based *Emergy* are proportional, the *transformities* are not.

## **5.2 *Emergy and ecological development***

Similar to Jorgensen's Eco-exergy, the formulation of Emergy is predicated upon an understanding of how systems self-organize. In the case of Emergy, Odum has proposed both a 4<sup>th</sup> and a 5<sup>th</sup> law of thermodynamics.

Odum's 4<sup>th</sup> law of thermodynamics is the one that is most well known in connection to Emergy, and is based on the work of Alfred Lotka. Lotka postulated that systems evolve to maximize useful power transformations. In other words, successful systems are those best able to capture and direct useful energy for their own purposes (Lotka 1922). Odum reformulated the maximum power principle to account for Emergy, by stating that systems self-organize to maximize empower (the capture and use of Emergy) (Brown and Herendeen 1996; Odum 1996). In Odum's words (Odum 1996):

*Prevailing systems are those whose designs maximize empower by reinforcing resource intake at the optimum efficiency.*

Odum argues that maximum power is ambiguous because it "might imply that transformations on a smaller scale with more energy but lower transformity prevail over those on the larger scale with higher transformity" (Odum 1996).

One corollary of the proposed 4<sup>th</sup> law is that the most efficient system at maximum empower will prevail (Odum 1994ch. 14). By this understanding, old ecological and biological systems are now operating at a maximum efficiency under the constraint of maximum power, (Odum 1994 ch. 14; Ulgiati, Brown et al. 1995).

Similar to Jorgensen's proposed 4<sup>th</sup> law, there are some difficulties with Odum's 4<sup>th</sup> law. The first difficulty is related to the discrepancy between maximum power and maximum empower. Despite Odum's claim that maximum power is an ambiguous term, there has been little detailed explanation as to the differences between the two, and Emergy



proponents often use maximum power and maximum empower interchangeably (see, for instance Odum 1995). Furthermore, Emery proponents recognize that maximum empower has still not been verified or demonstrated for complex systems (Hall 1995; Hammond 2007). Hammond claims that the validity of maximum empower is not necessarily critical to the formulation of Emery (Hammond 2007). However, maximum empower forms the basis for determining many of the Transformities (Odum 1996), and for this reasons seems quite deeply rooted in the formulation.

### **5.3 The transformity**

In this section some specific aspects of the transformity will be discussed. The transformity is defined as the amount of indirect and direct solar Emery required to produce one Joule of exergy of an item or process. The units of the transformity are solar Emery Joules per exergy Joule (sej/J).

Theoretically, the transformity of an item is a property of the system from which the item was produced, and an item may have different transformities depending upon which system produced it. However, Emery proponents have determined generic values of the transformity for various items (Brown and Arding 1991; Odum 1996), and these are the transformities used in Emery analysis (for example, see Bastianoni, Marchettini et al. 2001). Emery proponents justify using generic transformities by claiming that the maximum empower principle produces an optimum transformity (Ulgiati and Brown 2001), and by assuming that transformities do not differ too much for specific cases (Hau and Bakshi 2004). Therefore, while the transformity is by definition a property of the system producing the item, it is in practice an intrinsic property of the item itself.

One consequence of the Emery formulation is that the transformity of a product is always larger than the weighted average transformity of the inputs, where the weighted average transformity is shown in Equation (5.6).

$$Tr_{in,ave} = \frac{\sum_i Tr_{in,i} B_{in,i}}{\sum_i B_{in,i}} \quad (5.6)$$

To show how the output transformity is always larger than the average weighted input, Equation (5.6) is combined with Equation (5.3), the results of which are shown in Equation (5.7).

$$Tr_{out} = \frac{Tr_{in,ave} \sum_i B_{in,i}}{B_{out}} = Tr_{in,ave} \left( \frac{\sum_i B_{in,i}}{B_{out}} \right) \quad (5.7)$$

Since exergy is destroyed in all real energy transformations, the bracketed term in Equation (5.7) is always greater than one, and hence the transformity increases with each energy transformation step. Odum claims that the transformity tends to increase exponentially with the number of energy transformation steps, forming a so-called energy hierarchy, and this claim is codified as a 5<sup>th</sup> law of thermodynamics (Odum 1996). Energy hierarchies will not be discussed in depth in this thesis.

The Emergy group refers to the transformity as the quality of the energy (Brown, Odum et al. 2004; Hau and Bakshi 2004; Hau and Bakshi 2004; Sciubba and Ulgiati 2005). Interpreting the transformity as energy quality is a direct reference to the proposition that thermodynamic value is based on the Emergy of an item, with the transformity essentially defined as the unit Emergy of that item.

### 5.3.1 Problems with the transformity, efficiency, and value

There appears to be confusion as to whether the transformity of an item represents resource value, efficiency, or both. According to Emergy proponents, and as mentioned in section 5.1.1, thermodynamic (resource) value is based upon the Emergy of an item (Odum 1996 ch. 2; Bastianoni, Marchettini et al. 2001). Since the transformity is the unit Emergy of the item, it is essentially the specific value of the item. By equating the transformity to value, one must question what this value means? For example, does something with twice the transformity contain twice the value?

Aside from being a measure of value, the transformity is also a measure of the efficiency of the production of an item. According to Emergy proponents, the lower the transformity, the more efficiently the item is produced (Odum 1996). Emergy proponents claim that over time natural systems tend to reduce the transformity (increase the

efficiency) as much as possible while still maintaining maximum empower (Ulgiati, Brown et al. 1995; Brown and Herendeen 1996; Bastianoni, Marchettini et al. 2001).

The situation created by these two interpretations of the transformity is one where value is negatively correlated to efficiency: the more efficiently an item is produced the less value it has. Since Odum claims humans systems are less efficient at producing items than natural systems (Odum 1996 ch. 14), are human items therefore more valuable?

A second problem that arises is that associating the transformity with efficiency is a teleological argument. An efficiency calculation must always be with respect to a certain goal; otherwise the calculation is nonsense. For example, one may choose to calculate how efficient a wood stove is at air conditioning, but this would be absurd because a wood stove is not designed for that function. By the same token, calculating the efficiency at which an ecosystem produces a given item contains the assumption that the goal of the ecosystem is the production of that given item. There is no part of the maximum empower principle that assigns such a goal to ecosystems.

One might argue that whatever it is that ecosystems do, they happen to do better over time. By this token, the transformity of an item, whatever it may be, will tend to lower in time as ecosystems do whatever they do better. However, at the same time as ecosystems are becoming more 'efficient', they also tend to increase the number of interconnections between components, and this is well documented in the ecological modelling community. The research concerning these connections is the subject of ecological information theory (such as Rutledge, Basore et al. 1976; Kay 1984; Ulanowicz, Goerner et al. 2008, among others). As the number of interconnections between elements in an ecosystem increase, so too would the transformity. In other words, a loosely connected young ecosystem may not be efficient, but each item is almost linearly connected to the incoming solar energy. By contrast, as the ecosystem develops, it may get better at what it does, but each item is now dependent on so many more interconnected links, and this would increase the transformity.

There is far more to the story concerning connectivity in ecosystems. However, for the purposes of this argument, it is hopefully clear that the relationship between the transformity, maximum empower, efficiency, and resource value may be confusing at times, and should ideally be redefined. The reason for this appears to be that the transformity is a single indicator that attempts to account for two different ecological tendencies (if not more): *the tendency to increase efficiency over time, and the tendency to increase interconnections over time.*

One option to redefine the transformity is to sever the links between the transformity and the maximum empower principle. The transformity essentially becomes a macroscopic bookkeeping item with no association to any understanding of how systems organize. Furthermore, the two-tendency underpinning of the transformity is packaged into a single term that loses all underlying meaning. Despite the loss of theoretical grounding associated with severing the links between maximum empower and the transformity, this is essentially the proposal of Hau and Bakshi with their Ecological Cumulative Exergy Consumption (Hau and Bakshi 2004; Hau and Bakshi 2004).

A second, less drastic, option is to redefine the relationship between maximum empower and the transformity. Such a project would likely require a significant reformulation of Emergy analysis, and is beyond the scope of this thesis.

#### **5.4 General critiques of Emergy**

As has been previously mentioned, Emergy has been critiqued many times over the years. Some of the criticism is related to the basic formulation of Emergy, while others are based upon the extension of Emergy into economic systems and sustainability. To avoid rewriting old arguments, the reader is encouraged to read the review article by Hau and Bakshi (Hau and Bakshi 2004). However, the major themes of the article are summarized in Table 5-1.

**Table 5-1 - Hau and Bakshi critique summary**

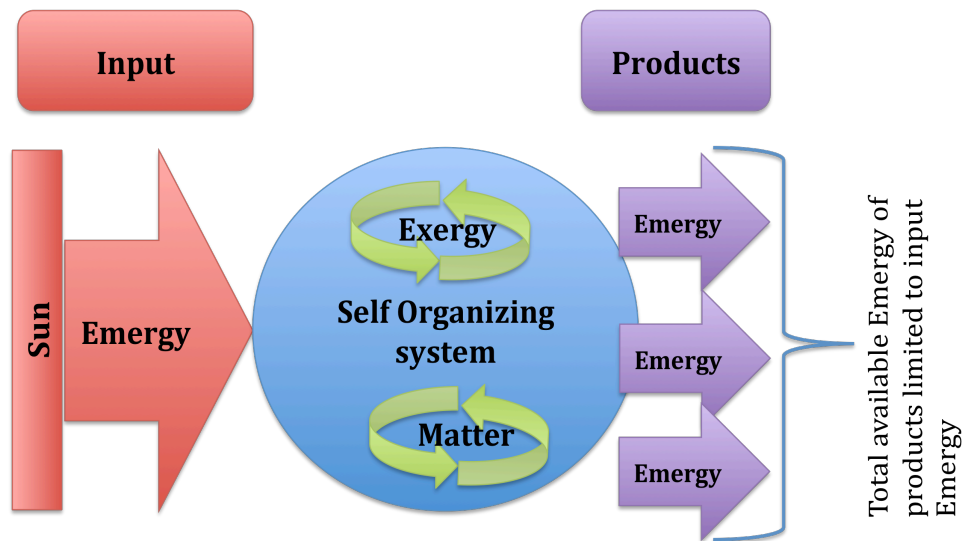
Theme	Critique
Economics	<ul style="list-style-type: none"> <li>•Emergy focuses on supply side, ignores human preference and demand and cannot capture the value of products to humans (i.e. two paintings may have similar Emergies, but be of different values.</li> </ul>
Maximum empower	<ul style="list-style-type: none"> <li>•While some biological systems have been shown to maximize power, this principle is not necessarily universal.</li> <li>•The behaviour of complex systems cannot be described via a single indicator.</li> </ul>
Thermodynamic concepts	<ul style="list-style-type: none"> <li>•Odum applies a different understanding of energy quality. For example, he claims that Emergy accounts for energy quality, while other thermodynamic quantities, such as exergy do not.</li> <li>•There is confusion and inconsistency about ‘B’ in the formula: it may be exergy, availability, or energy.</li> </ul>
Working with time scales	<ul style="list-style-type: none"> <li>•There is confusion as to how time scales should be included in Emergy.</li> <li>•Odum does not distinguish between Emergy of storage and Emergy required to make storage available. For example, fossil fuels are evaluated on the Emergy required to concentrate the resources in the oil.</li> </ul>
Global Emergy equivalence	<ul style="list-style-type: none"> <li>•To determine solar equivalence of tidal and earth energy flows requires many assumptions, most notably maximum empower.</li> </ul>
Quantification	<ul style="list-style-type: none"> <li>•There is uncertainty in Emergy calculations. For example, the Emergy of natural gas is determined by comparing the efficiency of natural gas relative to coal.</li> </ul>
Allocation	<ul style="list-style-type: none"> <li>•Emergy algebra is confusing and very sensitive to the level of knowledge about the system.</li> <li>•Emergy suffers from allocation problems similar to lifecycle methodologies.</li> </ul>

**Source: (adapted from Hau and Bakshi 2004)**

As is shown in Table 5-1, many of the problems associated with Emergy analysis are operational in nature, including problems with: allocation, quantification, scale and the determination of global Emergy. The relationship to other thermodynamic variables was briefly discussed in section 5.1.1. The link between Emergy and economics will not be discussed in this thesis as it is out of the scope of the research program.

## 5.5 Limits to resource consumption

Since Emergy measures the amount of solar energy required to produce an item or resource, by its very definition Emergy appears to be a good candidate for quantifying resource consumption. In this respect, Emergy proponents claim that sustainability involves using less Emergy to produce a unit or product (Bastianoni, Marchettini et al. 2001). Interpreted literally, Emergy sets an upper limit on the amount of solar Emergy that may be consumed, and this is simply the total solar Emergy striking the Earth. This literal interpretation is shown in Figure 5-1.



**Figure 5-1 - Emergy approach to resource consumption (literal interpretation)**

Despite the simplicity of the literal interpretation of Emergy, there are several operational problems that prevent this approach from being used. As mentioned in section 5.3.1 above, self-organizing systems do not organize to produce just one product, and in fact do not organize for the explicit production of any product. In this respect, there are many products that can be produced from the same Emergy simultaneously. This problem is largely a problem of allocation and double counting (as mentioned in Table 5-1). While Odum developed a set of Emergy algebra rules to avoid double-counting (Odum 1996 ch. 6), the problem remains that there is no direct link between incoming solar Emergy and the amount of Emergy that may be sustainably consumed on Earth.

Despite the problems with allocation and double counting, there is a second possible reason why Emergy proponents do not propose a literal interpretation of Emergy:

Emergy is conserved and is building up on the Earth. The fact that Emergy is conserved in all processes is a consequence of the basic formulation, such as what is shown in Equation (5.2), and shown again:

$$Em_{out} = Em_{in} = \sum_i Em_{in,i} = \sum_i Tr_{in,i} B_{in,i}$$

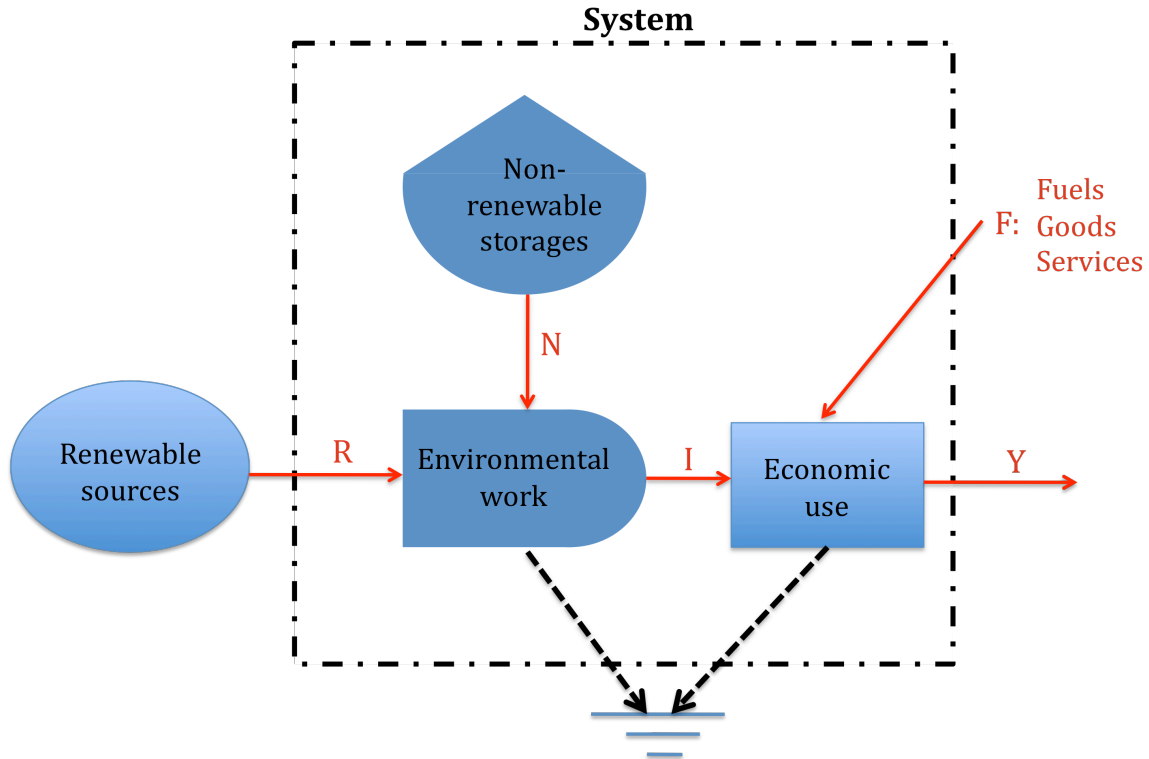
In every energy transformation, the Emergy of the products is equal to the Emergy of the inputs even though both exergy and energy (and availability) are lost in the form of dissipated energy (heat). In fact, if Emergy were not conserved, then there would be no method of calculating transformities. The conservation of Emergy creates a great deal of confusion, and to the best of this author's knowledge, Emergy proponents do not address the issue. However, a literal interpretation of Emergy conservation implies that the world is increasing its Emergy supply every second.

In practice, Emergy appears to be modelled as a flow-through approach, where the world receives a certain amount of Emergy, and this is lost through the consumption of resources. However, the basic definition of Emergy appears to deny the flow-through approach. The consequences of Emergy conservation are potentially far reaching, and many are likely beyond the appreciation and scope of this research program. However, the fact that the Emergy content of the Earth is continuously increasing implies that the basic formulation of Emergy (constantly increasing Emergy supply) is counterproductive to addressing problems of resource consumption (constantly decreasing resources).

### **5.5.1 The Emergy indicators**

Instead of the literal interpretation, Emergy proponents have proposed to relate Emergy to sustainability and resource consumption through Emergy indicators and ratios of sustainability. There are several key ratios proposed by Emergy proponents, including: Emergy yield ratio, Emergy loading ratio, and Emergy sustainability index (Ulgiati, Odum et al. 1994; Ulgiati, Brown et al. 1995; Odum 1996). For brevity, only Emergy yield ratio will be discussed to elucidate some of the problems encountered with the operationalizing of Emergy via the ratios.

Most of the Emergy indicators, including Emergy Yield Ratio are based on the simplified Emergy diagram, shown in Figure 5-2:



**Figure 5-2 - Emergy Figure for Ratios**  
**Source: (adapted from Ulgiati and Brown 2001)**

In Figure 5-2, the solid arrows (R, N, I, F, and Y) are Emergy flows, in units of solar Emjoules. By contrast, the two dashed arrows represent dissipated energy flows (zero exergy) to a heat sink, and these flows have no Emergy. The specific flows are (in units of solar Emergy) are described in Table 5-2:

**Table 5-2 – Emergy flows for the Emergy ratios**

Flow	Definition
R	Input Emergy from local renewable sources
N	Input Emergy from local non-renewable sources (storages)
I	Combined Emergy from renewable and non-renewable sources. $I = R + N$
F	Input Emergy from the economy in to form of fuels, goods, and services
Y	Output Emergy from the system $Y = I + F = R + N + F$

**Source: adapted from (Ulgiati and Brown 2001)**



According to proponents, the Energy yield ratio is a consequence of the maximum Empower principle, and is defined as (Ulgiati, Brown et al. 1995):

*The Energy yield ratio is the ratio of yield from a process to the costs of obtaining the yield where costs (inputs) and yields are evaluated in Energy terms.*

*The Energy yield ratio may be a measure of sustainability.*

The equation form of the Energy yield ratio is shown in Equation (5.8):

$$EYR = \frac{Y}{F} = \frac{N + R + F}{F} = 1 + \frac{N + R}{F} \quad (5.8)$$

The minimum value of the Energy yield ratio is 1, and this occurs when there are no renewable (R) or non-renewable (N) Energy inputs to a process. According to Energy proponents, “the closer the ratio is to unity, the less sustainable a process is” (Ulgiati, Brown et al. 1995).

The essential two points mentioned about the Energy Yield Ratio that were mentioned above are

1. The Energy yield ratio is a result of the maximum empower principle.
2. The closer the ratio is to unity, the less sustainability a process is (and presumably vice versa).

That the Energy yield ratio is a result of maximum power implies that systems (as depicted in Figure 5-2) evolve to maximize empower, where empower is the sum of all Energy inputs to the system. Based on the flows of Figure 5-2, the formula for maximum empower is shown in Equation (5.9):

$$Empower = N + R + F \quad (5.9)$$

Furthermore, based on point 2, and the equation for Energy loading ratio (Equation (5.8)), one can deduce that more sustainable processes would have a high Energy yield ratio, which correlates to a high (N+R) to F ratio, as this is the only manner in which the Energy yield ratio can increase. This is shown in Equation (5.10):

$$N + R \gg F \quad (5.10)$$

Literally combining points 1 and 2, via Equations (5.9) and (5.10), one deduces that the most sustainable method to maximize empower is simply to consume as many local renewable and non-renewable resources, shown in Equation (5.11):

$$\textit{Sustainability} = \text{maximize}(\text{EYR}) = \text{maximize}(N + R) \quad (5.11)$$

It is unlikely the Emergy group would recommend maximizing the consumption of natural resources (both renewable and non-renewable) for the purposes of increasing sustainability. Unfortunately, this appears to be a pitfall of using such ratios, and this author would argue that the Emergy ratios are fundamentally opposed to the maximum empower principle. The reason for this contradiction is that the ratios are developed to limit Emergy consumption (empower flow) and lower transformities, while the two laws essentially state that systems self-organize to states of higher empower flow and higher transformities.

At this point, it is difficult to state whether or not exergy-based Emergy can set any hard limits on resource consumption, and if so, whether these limits are due to using exergy. However, there appears to be a disjunction between the very definition of Emergy (which appears to set literal limits to resource consumption) and the quantification of resource consumption via the Emergy ratios. More research in this regard is needed.

## **5.6 Conclusion**

Several critiques of Emergy have been discussed above, and this section will attempt to summarize the critiques into a coherent package. A summary of Emergy is provided in Table 5-3 below.

Many of the problems of Emergy relate to the operationalizing of Emergy, as shown by Hau and Bakshi's critique (Table 5-1). However, by coupling the problems operationalizing Emergy with the issue that Emergy is constantly accumulating on the Earth, this author tentatively concludes that, in and of itself, Emergy cannot quantify resource consumption.

Second, the characteristics of complex self-organizing systems are likely not well measured using simple ratios. The contradiction of the Emergy yield ratio (section 5.5.1) and the dual nature of the transformity appear to be two manifestations of the problems encountered in reduction. At the heart of the problem is that self-organizing systems are

not reducible to their component parts (Boyle and Kay 2008; Kay and Boyle 2008) and involve internal contradiction (Funtowicz and Ravetz 2008), and this makes it difficult to characterize them by simple equations and ratios. Emergy proponents appear to be aware of the challenge as they have recently discussed Emergy within the realm of Post-Normal Science<sup>18</sup> (Sciubba and Ulgiati 2005). Due to the problem of reduction, Odum's 4<sup>th</sup> and 5<sup>th</sup> laws are perhaps most appropriate as a heuristic for understanding self-organizing systems. For example, the transformity is likely more useful for placing items within an energy hierarchy than assigning a value or efficiency to the item.

At this point there is uncertainty as to how using exergy instead of energy impacts the formulation of Emergy. The reason for this is that Emergy proponents have not been clear about the B term in Emergy (Hau and Bakshi 2004), and no one appears to have examined the issue to any depth. While Bastianoni et al. claim the only difference between energy- and exergy-based Emergy is a factor of 0.93 (Bastianoni, Facchini et al. 2007), this is likely not the case as was discussed in section 5.1.2.

There does not appear to be any gain from using exergy as opposed to energy, as many of the problems with Emergy listed in Table 5-1 are unrelated to exergy. The only problem directly addressed by using exergy is what term multiplies the transformity to determine the Emergy (the B term). For the most part, using exergy as opposed to energy creates a whole new set of problems with respect to reference state formulations and the usefulness of exergy (vis-à-vis the Exergy Replacement Cost). This author questions whether it is worthwhile for Emergy proponents to adopt exergy as the energy carrier of Emergy. Regardless of what thermodynamic concept is ultimately chosen, Emergy proponents need to critically and openly reassess the impacts of the B term on the understanding of Emergy.

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<sup>18</sup> Post-Normal science is often described as science where the stakes are high and the certainty is low. See, for instance Ravetz, J. R. (2006). "Post-Normal Science and the complexity of transitions towards sustainability." *Ecological Complexity* 3(4): 275-284.

Despite the problems of Emergy, there is a vast body of knowledge underpinning Emergy that includes thermodynamics and systems modelling (for example, Odum 1994; Odum 1996). Furthermore, the systems approach of Emergy allows for other indicators to be used as well, such as the Ascendency principle of professor Ulanowicz (Ulanowicz 1980; Christensen 1994). Another advantage of Emergy is that the methodology attempts to bridge the gap between natural and human systems. The attempt to synthesize between human and natural systems is gaining ground, and forms an underlying principle to both ecological engineering and industrial ecology (Connelly and Koshland 2001; Nielsen 2007; Gosselin 2008). This area may prove very fruitful for future research.

**Table 5-3 - Summary of Emergy**

<b>Emergy- Summary</b>	
Definition of thermodynamic value	<ul style="list-style-type: none"> <li>• The thermodynamic value of an item the amount of direct and indirect solar energy required to produce the item.</li> </ul>
Purpose of ecological organization	<ul style="list-style-type: none"> <li>• Ecosystems evolve to maximize solar energy utilization.</li> </ul>
Exergy reference state	<ul style="list-style-type: none"> <li>• Exergy reference state not formally defined.</li> </ul>
Assumptions	<ul style="list-style-type: none"> <li>• Assumes that self-organizing systems are organized to produce a specific, item, and that there is an optimal efficiency at which this item is produced.</li> <li>• Assumes efficiencies (Transformities) for many geological processes.</li> <li>• Assumes that only difference between exergy- and energy-based Emergy is a factor of 0.93.</li> </ul>
Limitations	<ul style="list-style-type: none"> <li>• Impossible to properly account for all solar Emergy due to issues of double counting and allocation.</li> </ul>
Approach to resource consumption	<ul style="list-style-type: none"> <li>• Divides resources in categories of (renewable / non-renewable, local / imported) and proposes a set of Emergy sustainability ratios.</li> </ul>
Validation	<ul style="list-style-type: none"> <li>• Emergy ratios lead to contradictions with the purpose of ecological organization.</li> <li>• Unlike exergy, which can be destroyed, and energy, which is conserved, Emergy can only build up on the Earth. Emergy proponents have not discussed how this relates to resource consumption, or Emergy in general.</li> </ul>
Usefulness and novelty of exergy within the approach	<ul style="list-style-type: none"> <li>• There is no adequate discussion of the implications of adopting exergy-based Emergy.</li> <li>• Exergy-based Emergy may not be beneficial to Emergy methodology due to problems with exergy theory itself.</li> </ul>
This author's proposed use	<ul style="list-style-type: none"> <li>• Emergy may be best used as a heuristic, or set of guiding principles, to better understand self-organizing systems.</li> </ul>

## Chapter 6 – Synthesis and Conclusions

As mentioned in Chapter 1, the objective of this thesis is to establish the utility and limitations of using exergy as a resource consumption metric, and to investigate what role exergy may play in resource consumption decision-making. Once again, exergy is a thermodynamic measure of energy quality, or ability to perform useful work.

In this final chapter, the author will attempt to synthesize the major arguments from the previous five chapters. The chapter will begin by discussing the limitations of the exergy-based resource consumption methodologies. Following that, in an attempt to explain why exergy may not be an appropriate thermodynamic resource consumption metric, the derivation of exergy will be explored.

### **6.1 Resource consumption methodologies**

In Chapters 3, 4, and 5, three different resource consumption methodologies of varying degrees of comprehensiveness were discussed: Exergy Replacement Cost, Eco-exergy, and Emergy. Despite the variations in comprehensiveness, there are some common themes that may be drawn concerning exergy as a resource consumption metric, and these themes will be discussed in this section.

#### **6.1.1 Removing exergy from the methodologies**

In the conclusions of Chapters 3, 4, and 5, a proposed use of each resource consumption methodology was provided. The proposed uses are summarized in Table 6-1.

**Table 6-1 - Proposed use of the methodologies**

<b>Methodology</b>	<b>Proposed use</b>
Exergy Replacement Cost	Categorizing (and potentially in the future predicting) the amount of work required to refine mineral deposits.
Eco-exergy	One set of indicators for ecological modelling.
Emergy	Heuristic (or set of guiding principles) to better understand self-organizing systems. May link different types of self-organizing systems.

Exergy is not directly applied in any of the proposed uses provided above, primarily because exergy does not appear to be a relevant characteristic of both resources in

general, and non-work producing resources in particular. Equally important, while proponents of the methodologies claim to be exergy-dependent, they are not applying exergy in the manner in which it is formally defined in section 1.1.1. To further this line of reasoning, section 6.3 will re-examine the very derivation of exergy to assess whether the inherent limitations of the derivation prevent exergy from being a salient characteristic of resources. For example, the reference environment formulations do not appear to be adequately robust or consistent when applied in an item-specific (as opposed to systems-based) manner.

Despite the limitations due to the derivation of exergy, there are also specific reasons for excluding exergy from each methodology. These specific reasons are summarized in Table 6-2.

**Table 6-2 – Reasons for excluding exergy**

Methodology	Reasons
Exergy Replacement Cost	<ul style="list-style-type: none"> <li>• Disjunction between the theoretical (state-property) and empirical (lifecycle) replacement costs indicates that exergy theory may not be salient.</li> <li>• Lack of definition of terms (i.e. thermodynamically dead planet, entropic plant, etc) and confusion regarding what the reference environment actually represents (mine, nature, entropic planet?) makes it difficult to apply exergy in a consistent manner.</li> </ul>
Eco-exergy	<ul style="list-style-type: none"> <li>• Not properly derived from thermodynamic principles.</li> <li>• Within ecological modeling, exergy is not necessary because all organisms carry the same factor of 18.7 kJ per gram. Using exergy becomes simply a matter of preferred units.</li> </ul>
Emergy	<ul style="list-style-type: none"> <li>• Lacks clarity regarding B (exergy) term multiplying the Transformity.</li> <li>• Lacks a sensitivity analysis regarding the impact of using exergy.</li> <li>• As a heuristic to understand self-organizing systems, exergy may not be necessary and may in fact detract from Emergy theory.</li> </ul>

From a different perspective, Ulgiati et al. argue that no single indicator (such as exergy) is sufficient to adequately describe resource consumption; other non-cross-comparable indicators are also necessary (Ulgiati, Raugei et al. 2006). For example, the Ecosystem Approach methodology proposes using exergy, material, and information as the salient resource inputs to a system (Kay, Boyle et al. 1999; Kay and Boyle 2008). However, in the Ecosystem Approach, there are no specific rules for quantifying resource consumption; resource consumption is largely case-specific, and it is difficult and likely incorrect to draw universal rules from specific cases.

### **6.1.2 Conflict between being comprehensive and being consistent**

One topic that bears much further discussion and research is whether there is a relationship between the comprehensiveness of a resource consumption methodology and the amount of internal contradiction contained within the methodology. This section will briefly outline the discussion, but leaves this mainly as a topic for future research.

Exergy Replacement Cost is the most limited of the three methodologies. The approach is primarily a bookkeeping method where biological and geochemical processes are black-boxed, only the available exergy is determined, and ecological self-organization is ignored. As a resource consumption methodology, Exergy Replacement Cost does not suffer from internal contradictions.

Eco-exergy is more comprehensive than the Exergy Replacement Cost, and attempts to value both living and non-living resources. The type of internal contradiction suffered by Eco-exergy is exemplified by Jorgensen's assessment of agricultural systems (section 4.4) where the least sustainable system has the highest Eco-exergy. In effect, Jorgensen's proposed 4<sup>th</sup> law of thermodynamics leads to internal contradiction for some small-scale applications, and perhaps for larger scale applications as well (more data is required to make a stronger claim).

Emergy is the most comprehensive of the three methodologies. Emergy applies to all systems (biotic, abiotic, industrial, etc.) and attempts to understand the dynamics of self-organization. Emergy also suffers from a great deal of internal contradiction with respect to resource consumption: the transformity simultaneously measures efficiency and value, and negatively correlates the two; and the Emergy ratios, when literally interpreted, state that sustainable resource consumption requires maximizing the consumption of both renewable and non-renewable resources.

One potential reason why more comprehensive methodologies are more prone to suffering internal contradiction is that the resource consumption methodologies are attempting to reduce and describe systems that are inherently irreducible (Boyle and Kay

2008; Kay and Boyle 2008). Perhaps more comprehensive resource consumption methodologies are simply more likely to encounter internal contradictions, or create their own contradictions in the process of reduction. As mentioned above, this is not a final conclusion, but rather a question for future research.

### **6.1.3 The next step in resource consumption methodologies**

This author notes that all three of the resource consumption methodologies discussed in this thesis propose a larger scope than what is proposed in Table 6-1. Effectively, Table 6-1 argues that none of the methodologies are universal.

In the opinion of this author, the most important step needed to move forward is to have a clear discussion on the limitations and scope of the current and future methodologies. Table 6-1 represents one potential area of application for each methodology, but there may be other applications. Whatever is proposed for the different methodologies, the methodologies should be treated as working hypotheses, rather than assuming they are correctly applied.

## **6.2 Exergy as a characteristic of a resource**

This section will attempt to codify the important problems elucidated regarding exergy. While each subsection will address a specific issue regarding exergy, there will necessarily be some overlap, as not every characteristic of exergy may be reduced and isolated. This section is the bridge between the discussion of the resource consumption methodologies above, and a discussion of the derivation of exergy that will follow in section 6.3.

### **6.2.1 How exergy is context sensitive but blind to perspective**

The first issue concerning exergy is that while exergy is sensitive to context (it measures thermodynamic distance from equilibrium) it is blind to perspective. This section will discuss four perspectives, exergy as either: (1) harmful or helpful; (2) organizing or disorganizing; (3) a restricted or unrestricted measure of potential useful work; and (4) a system-based or item-specific tool.



In Chapter 1, exergy was introduced both as a measure of resource value (explored in this thesis) and as a measure of waste impact (Chapter 1, section 1.2.2). The mere fact that exergy can describe both resources and wastes in different terms (one has value, the other causes harm), requires that different perspectives are adopted to interpret the same thermodynamic measurement.

As a second example along the same theme, both Jorgensen's and Odum's proposed 4<sup>th</sup> laws of thermodynamics require that the exergy (or Emergy) captured by a system promotes self-organization. However, exergy may be added to a self-organizing system and cause disorganization rather than promote self-organization. Furthermore, whether exergy is harmful or helpful is not always a question of what type of exergy is added (i.e. adding solar versus nuclear exergy to an ecosystem), but may also relate to the manner in which the exergy is added (too much solar exergy can burn an organism).

Rosen attempts to address the harmful/helpful perspectives of exergy by arguing that the difference is whether the exergy is constrained or not (Rosen and Dincer 1997; Dincer and Rosen 1999; Rosen 2002; Rosen, Dincer et al. 2008). According to Rosen (Rosen 2002):

*“Most resources found in the environment are constrained and are by virtue of their exergy of value, while unconstrained emissions of exergy are free to impact in an uncontrolled manner on the environment.”*

While Rosen's approach to perspective has some intuitive appeal, it appears to be incomplete. For example, sunlight, water, and wind, are three vital, but unconstrained, resources. In this respect, the perspective required to discern harmful from helpful exergy is not merely a matter of constraint.

A third method by which perspectives enters the exergy discussion is via restrictions imposed upon exergy. All of the methodologies discussed in this thesis place restrictions upon exergy. One form of restriction is the choice of which exergy forms are relevant. For example, the primary form of exergy discussed in this thesis is non-flow chemical exergy, which ignores all manner of flow exergy, as well as nuclear, solar, thermo-

mechanical, kinetic and potential exergy. Furthermore, the different reference environment methodologies had to contend with the inclusion or omission of blocked energy pathways (for example, see section 2.1.1).

A fourth example of exergy perspectives is the conceptual shift from exergy as a systems-based analysis tool to exergy as an item-specific analysis tool. This perspective question was addressed in section 1.4.3 and still represents a source of confusion and ambiguity.

The problem with exergy being blind to perspective is that many of the important aspects of exergy analysis are choices among different perspectives. In many respects, exergy only has meaning within a given perspective, but there has been very little discussion regarding the different perspectives taken on exergy. Ideally, this thesis will promote future dialogue about the conceptual frameworks and perspectives of exergy.

### **6.2.2 How exergy is not an appropriate measure of resource quality**

The second issue regarding exergy, and one that lies at the heart of this thesis is whether exergy in fact represents a measure of resource quality. Chapter 1 (section 1.1.4) presented the primary argument for adopting exergy as measure of resource consumption: energy and mass are both conserved, while exergy is not. Under this perspective, the salient aspect of resource consumption is the loss of quality of the resource, and this quality is measured by exergy. This argument underlay the thesis, as it provided justification for examining the three exergy-based resource consumption methodologies.

While it is difficult at times to distinguish between limitations in exergy and limitations in the resource consumption methodologies, the k-values determined by the Exergoecology group (in section 3.2.2) help expose a fundamental problem of applying exergy as a universal measure of resource value: exergy may not be applicable for all types of resources. If exergy is not always applicable to the measure of consumption, then the fundamental argument must be revisited.

The key to understanding the primary argument hinges on the definition of quality. Exergy measures the quality of energy of a system where:

*the quality of energy is related to the amount of useful work that can be obtained by bringing the system into equilibrium with its reference environment.*

For work-producing resources such as fossil fuels or biomass, exergy is possibly an appropriate measure of how much work can be extracted from these resources. However, for non work-producing resources such as minerals, the quality of the resource is not necessarily the amount of useful work that can be extracted from the resource because useful work is not a salient characteristic of a mineral resource. This is likely why exergy is such a poor indicator for mineral resources.

The Exergoecology group's lifecycle Replacement Cost essentially has no link to exergy. The lifecycle Replacement Cost is effectively a measure of how much work is required to refine a mineral. While mineral refining requires work, exergy is once again likely not the defining characteristic of mineral upgrading; if only because mineral processing requires useful work regardless of whether one is going from the mineral deposit to the pure state, or from the pure state to the mineral deposit. In many respects, the k-values of Chapter 3 (section 3.2.2) provide the first true empirical test of whether or not the exergy definition of quality is salient for non work-producing systems, with the results indicating that exergy is not salient.

### **6.2.3 Moving forward with exergy as a measure of resources**

In the opinion of this author, there should be no further application of exergy as a measure of resources until the fundamental problems of perspective and quality are addressed. For the most part, neither quality nor perspective relate to the specific item being measured by exergy, but rather the context in which the item is placed.

One possible explanation for the problems associated with exergy as a measure of resources relates to the confusion of the exergy reference environment. If the reference environment is modelled to mimic the world outside, then it is not a properly defined reference environment and the exergy values are suspect. By contrast, if the reference environment is properly defined, then there is no reason why the exergy values will have any relation to the real world. Similarly if the exergy reference environment is modelled as infinitely large and universal, then exergy is no longer context sensitive. However, if

the reference environment is localized, then the exergy values may no longer be generalized. The conflicting properties of the reference environment are crucial to the proper application of exergy.

### **6.3 Revisiting the derivation of exergy**

While quality and perspective are both critical to application of exergy, neither of these characteristics engenders much exploration into the very derivation of exergy. This section will briefly explore some defining characteristics of the derivation of exergy to argue that some of the problems of applying exergy are based upon the fundamental formulation. The first step in this exploration is a brief discussion of the concentration exergy. Following that, some key assumptions of the exergy derivation will be discussed.

#### **6.3.1 Problems with the derivation of the concentration exergy**

One of the arguments alluded to several times in this thesis is that the concentration exergy may be potentially irrelevant. This section will attempt to argue against using the concentration exergy, both as a measure of exergy in general, and exergy as applied to valuing resources.

The derivation of the concentration exergy is interesting because, to the best of this author's knowledge, the concentration exergy is always derived in a reverse manner via the Guoy-Studola theorem mentioned in section 1.1.2.3 and shown again in equation form:

$$B_{\text{destroyed}} = T^o S_{\text{gen}}$$

To quote Çengel, Çerçi and Wood (1999):

*From a thermodynamic point of view, work potential is wasted (or exergy is destroyed) during any process that occurs irreversibly, such as mixing, and this wasted work potential is proportional to the entropy generation and the absolute temperature of the environment. The exergy destroyed represents the work that would be produced if the mixing process occurred reversibly.*

Çengel, Çerçi and Wood then go on to say (1999):

*The beauty of working with reversible processes is that we can work with the process that we feel most comfortable with, and then apply the results to the reverse process by simply reversing the directions of the interactions.*

The important aspects of the quotes above are the obvious reference to the Guoy-Studola theorem (entropy generated multiplied by the absolute temperature), and the assumption that mixing may be reversibly performed. With these assumptions, calculating entropy generated in mixing allows exergy to be determined via the Guoy-Studola theorem.

The final qualifier needed before deriving the concentration exergy is that the assumptions of ideal solutions (based upon ideal gases) and constant temperature and constant pressure are required. These assumptions are made by Çengel, Çerçi and Wood (Çengel, Çerçi et al. 1999) as well as the Exergoecology group (Szargut 2005; Valero 2008) and appear to be quite common within exergy theory as a whole, mainly due to the requirements of reversibility and for simplicity of calculations.

By using the Guoy-Studola theorem, and assuming ideal gases, the derivation of the concentration exergy is simple. For an ideal gas, at constant temperature and pressure the entropy produced in mixing is related to the change in volume as shown in Equation (6.1)

$$s_{gen} = R \ln \frac{V_{tot}}{V_1} \quad (6.1)$$

Where  $V_1$  is the original volume of the ideal gas, and  $V_{tot}$  is the total volume of the mixing chamber (final volume of the ideal gas).

For ideal gases at constant temperature and pressure, the change in volume from a pure state to a mixture, is measured by the inverse of the mole fraction, as shown in Equation (6.2)

$$S_{gen,i} = -n_i R \ln x_i \quad (6.2)$$

where  $x_i$  is the mole fraction of the ideal gas in the mixture, and  $n_i$  is the number of moles of gas  $i$ .  $x_i$  is related to the volumes by Equation (6.3):

$$x_i = \frac{V_i}{V_{tot}} \quad (6.3)$$

Finally, using the Guoy-Studola theorem, the exergy lost (which is assumed equal to the concentration exergy) is simply the entropy generated multiplied by the absolute temperature, shown in Equation (6.4):

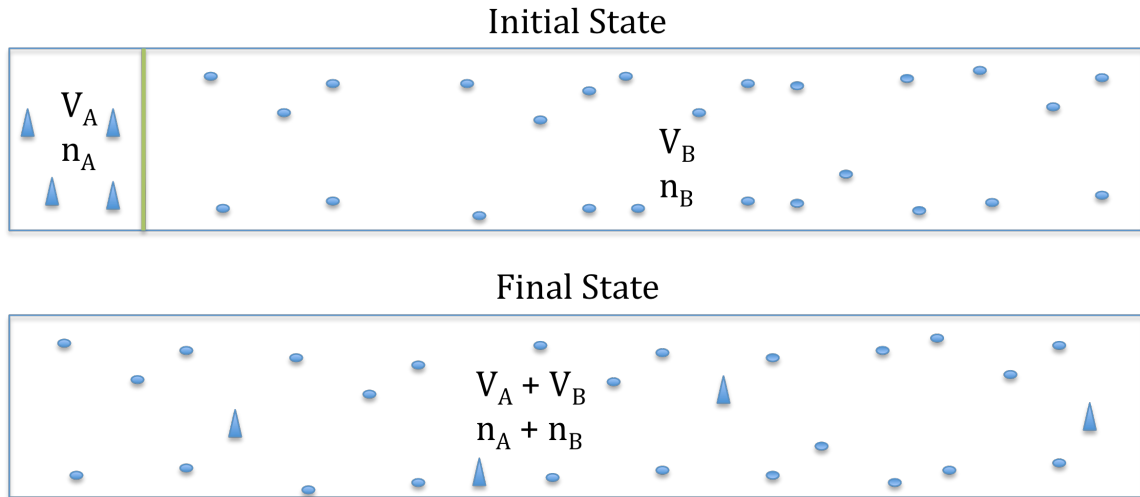
$$B_i = T^o S_{gen,i} = -n_i R T^o \ln x_i \quad (6.4)$$

The concentration exergy shown in Equation (6.4) forms the basis of exergy as applied to resource value.

The first problem with simply applying the concentration exergy, and the Guoy-Studola theorem as a whole, is that the Guoy-Studola theorem ignores the requirements placed on the reference environment. With respect to the concentration exergy, when ideal gases (at the same temperature and pressure) mix, there is no change in temperature or pressure because no work is produced. The entropy generated is calculated purely based upon changes in mole fractions, and the system is effectively isolated from the environment (in that there is no transfer of matter, heat, or work between the system and the environment). By applying the Guoy-Studola theorem in a constant temperature and pressure process, the only manner in which work can be obtained from the system is by heat transfer from the reference environment.

By examining Equation (6.4) above, it is possible to develop a thought experiment involving the concentration exergy in a manner that is almost nonsensical. The thought experiment that follows is related to the Gibbs Paradox. Despite being well over 100 years old, the Gibbs Paradox appears to still be an ongoing topic of discussion among theoretical physicists (for example, see Jaynes 1992; Lin 1996; Maslov 2008).

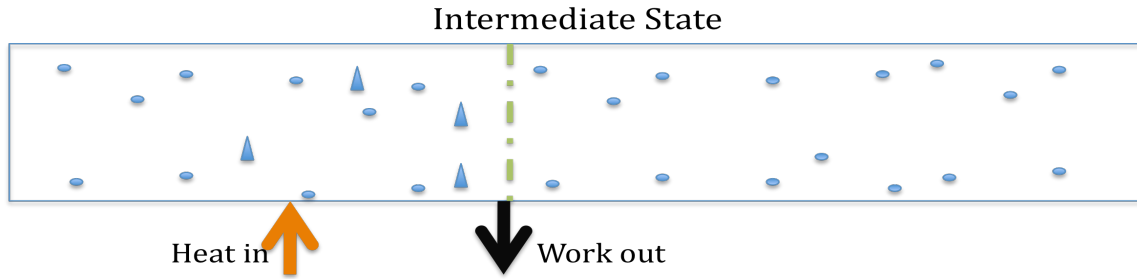
The experiment involves a minute volume ( $V_A$ ) of ideal gas A at temperature  $T^o$ , and pressure  $P^o$  separated from a large volume ( $V_B$ ) of ideal gas B at the same temperature and pressure.  $V_B \gg V_A$ , such that  $x_A$  (the final molar concentration, or partial pressure of the ideal gas A) is negligible. The initial and final end states of the example are shown in Figure 6-1.



**Figure 6-1 - Initial and final states of ideal gas mixing**

To extract useful work from the mixing process requires both a source of heat from the environment, and the existence of ‘semi-permeable’ membranes: a membrane that blocks the passage of the substance of choice and allows all other substances through. In Figure 6-1 there are two different ideal gases, and therefore there could be two different semi-permeable membranes (one for each ideal gas). For simplicity, only one semi-permeable membrane will be applied in this example, and it will be used to extract work from the expansion of ideal gas A.

The semi-permeable membrane is placed at the barrier between the two ideal gases, and as the barrier is removed, ideal gas A (the triangles) slowly pushes the semi-permeable membrane to the right, producing work via expansion. As ideal gas A produces work, heat is transferred from the reference environment to the ideal gas so as to maintain a constant temperature ( $T^0$ ). It must be noted that the molecules of ideal gas B (the dots) pass freely through the semi-permeable membrane. The working of the semi-permeable membrane is shown in Figure 6-2, where the semi-permeable membrane is depicted as a dashed line.



**Figure 6-2 - Intermediate state of mixing process**

Based upon the equation for the concentration exergy, Equation (6.4), the work that may be extracted by use of the semi-permeable membrane is shown in Equation (6.5):

$$Work = -n_A RT^o \ln x_i = n_A RT^o \ln \frac{V_{tot}}{V_1} = n_A RT^o \ln \frac{V_1 + V_2}{V_1} \quad (6.5)$$

This work increases as  $V_2$  increases (since  $x_1$  decreases as  $V_2$  increases). In the limit as  $V_2$  approaches infinity the work that may be extracted approaches infinity.

The thought experiment above is, of course, nonsense, but it appears to be consistent with the interpretation of the concentration exergy. Both the existence of a semi-permeable membrane, as well as the ability of this membrane to extract work (and infinite work as well) as an ideal gas expands towards infinite volume are effectively pure theoretical constructions. Furthermore, to extract the infinite work requires infinite heat transfer from the reference environment<sup>19</sup>. However, the existence of a semi-permeable membrane also underlies the derivation of exergy (Bejan 1998, ch. 5), and this will be discussed in the following section.

### **6.3.2 Problems with the derivation of exergy**

While the critique of the concentration exergy mentioned several times in the thesis (and discussed above) often focuses upon the relevance of concentration exergy for non work-producing systems (such as mineral deposits), the relevance of the concentration exergy is also important for exergy theory as a whole. The reason the concentration exergy is so

<sup>19</sup> It is interesting to note that the reference environment appears to be theoretically capable of providing infinite heat transfer without changing temperature (this author originally assumed the reference environment would lower in temperature). This apparently ‘magical’ ability of the reference environment is due to different types of infinity (similar to how the Cantor sets exhibit different types of infinity).



important for exergy theory is that it appears that chemical exergy is derived solely based upon the concentration exergy. To explain this dependence on the concentration exergy, key points of Bejan's (Bejan 1998, ch. 5) derivation of non-flow exergy will be quoted.

Bejan describes the system as a mixture containing  $N_1, N_2, \dots, N_n$  moles of  $n$  constituents. According to Bejan, "the initial *equilibrium*<sup>20</sup> state of the system is characterized by the temperature ( $T$ ), pressure ( $P$ ), and  $n$  chemical potentials ( $\mu_1, \mu_2, \dots, \mu_n$ ) which differ from the corresponding intensities of the environment ( $T_0, P_0, \mu_{0,1}, \mu_{0,2}, \dots, \mu_{0,n}$ )" (Bejan 1998, ch. 5).

Bejan approaches the derivation of non-flow exergy by posing the question (Bejan 1998, ch. 5): "What is the maximum useful work that could be produced as the system and the environment reach equilibrium?" This maximum useful work is related to temperature and pressure differences between system and environment, and (more important for this thesis) differences in chemical potentials between system and environment. According to Bejan (Bejan 1998, ch. 5), "these [mole] numbers change as each of the  $n$  constituents diffuses through its own *semi-permeable*<sup>21</sup> membrane that makes up the system-environment boundary."

At this point it is possible to draw some potentially surprising conclusions regarding the derivation of exergy, and the subsequent consequences for the application of exergy. The conclusions are based upon the following requirements of non-flow exergy:

1. Both the system and the reference environment are in a state of internal equilibrium, as mentioned in the first Bejan quote. Rosen and Dincer (Rosen and Dincer 1999) also confirm that the environment is in internal stable equilibrium, as mentioned in section 2.4.4.
2. For every chemical species, there exists a semi-permeable membrane, as mentioned in the second Bejan quote.

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<sup>20</sup> Equilibrium is italicized by this author for emphasis.

<sup>21</sup> Semipermeable is italicized by this author for emphasis. It was also changed into a compound word (Bejan uses semipermeable) to maintain consistency with the text.

3. Every chemical species present in the system is also present in the reference environment. Without this requirement, a chemical species would have infinite exergy as it expanded into the reference environment.

The first tentative conclusion to be drawn from the points above is that non-flow exergy cannot quantify any chemical reaction between chemical species. The reason for this is that any net chemical reaction is a non-equilibrium situation and this violates the first requirement above. One might argue that in determining the exergy of a fossil fuel (for example), the ‘system’ is the fossil fuel, and the ‘environment’ is the atmosphere (composed of oxygen, nitrogen, etc). However, this description of system and environment violates the third requirement of non-flow exergy, namely that every component in the ‘system’ is present in the ‘environment’, because otherwise the non-flow exergy would be infinite.

The second conclusion, which follows from the first, is that the only manner by which work can be extracted from the chemical difference between the system and the environment is via the concentration exergy. Furthermore, to obtain the work from the concentration exergy requires (and assumes) the existence of semi-permeable membranes.

Based on the two tentative conclusions above, it appears that what many authors claim to be exergy may in fact be a different thermodynamic concept. Furthermore, the very derivation of exergy appears to limit it both in scope and relevance.

### **6.3.3 Moving forward with exergy**

The two conclusions about non-flow exergy introduced above require a reinterpretation of the meaning and teaching of exergy. The three key problems of exergy appear to be the infinite size of the reference environment, the inability for exergy to characterize both systems and reference environments that are not in internal equilibrium, and the inability of exergy to characterize chemical reactions.

In this author's personal experience, exergy is taught primarily within the realm of combustion-based (i.e., chemical reaction based) power generation. For instance, many of Rosen's examples of the benefits of exergy analysis relate to coal-fired power plants in Ontario (Rosen and Dincer 1997; Rosen 2002; Dincer and Rosen 2007, ch. 3; Rosen, Dincer et al. 2008). However, it appears that the non-flow exergy of coal may not be defined because it violates the conditions of the derivation (as mentioned in section 6.3.2 above).

As a derived concept, exergy does not appear suitable to quantify work potential from chemical reactions, and in this respect, some other thermodynamic concept may be necessary. Furthermore, by applying a more appropriate theory to discuss chemical reactions, there is the potential for greater insight.

#### **6.4 Conflicts between the three levels**

Over the course of this thesis, several problems with applying exergy as a measure of resource value have been introduced. Furthermore, some fundamental problems with resource consumption methodologies themselves were proposed as the beginning of this chapter. There are effectively three levels of problems that have been discussed in this thesis: (1) the resource consumption methodology level; (2) the use of exergy within the resource consumption methodology; and (3) the relevance of exergy as a derived concept. While the discussion within each level is important, there is also some interesting synergy that emerges by looking between levels. This section will briefly explore one such synergy.

As mentioned above in section 6.3 above, exergy appears to only be derived based upon the concentration exergy, and therefore would have no meaning with regard to chemical reactions. Furthermore, the concentration exergy derivation requires that work be produced via a semi-permeable membrane, a mechanism that is essentially a theoretical construct. In this respect, the derivation of exergy produces a concept that is limited in scope to differences in chemical concentrations.

At the level of applying exergy to resource consumption, the situation presented is entirely different. In section 6.2.2, this author argued that valuing non work-producing resources by their concentration exergy was meaningless because the *quality* of non work-producing resources was not measured with respect to how much work can be extracted from them. By contrast, work producing resources (such as fossil fuels) are perhaps better measured by exergy because one of their defining characteristics is how much useful work can be extracted from them.

Only by looking at the two levels combined can the problem of using exergy be appreciated. Exergy is derived based upon concentration exergy, but this very same concentration exergy is used to value non work-producing resources in a manner that appears to be irrelevant. By contrast, the work producing resources seem to be meaningless in terms of exergy because chemical reactions are not defined through exergy. In other words, exergy appears to be incapable of measuring what it should measure (work producing resources), and is not a relevant characteristic of what it can measure (concentration exergy of non work-producing resources).

There are other examples of exergy problems that emerge from different scales. For example, ideal gas assumptions may simplify calculations at the derivation level, but they do so at the expense of appropriately characterising resources. Furthermore, the formulation of the reference environment must contend with either being a properly derived reference environment that in no way resembles the natural environment, or a more realistically based reference environment that violates the basic derivation of exergy. These multi-level problems appear to pose serious problems for the applicability of exergy.

## **6.5 Summary**

In an attempt to establish the utility and limitations of exergy, this thesis has produced many conclusions, some tentative, other firms. This section attempts to very briefly summarize the major findings of the thesis.

The principle argument for applying exergy as a resource consumption metric hinges upon the assumption that exergy is a salient characteristic of resources. In other words, exergy proponents assume that exergy measures the quality of the resource. Despite this assumption, none of the three resource consumption methodologies assessed in this thesis apply exergy in the manner which it is formally defined in section 1.1.1, and derived in section 6.3. Furthermore, this author proposes that exergy be removed from the resource consumption methodologies because it is not appropriately applied, for the three reasons that are provided below.

The first reason preventing the appropriate application of exergy is that there is a conflict between requirements and assumptions at the exergy derivation level with the requirements and assumptions at the resource valuation level. For example, the exergy reference environment is modelled as an infinitely large system in internal chemical equilibrium, and this reference environment is in no way comparable to the real world outside. The result is tension is a tradeoff between determining exergies that are relevant, or exergies that are properly defined (with the understanding that improperly defined exergies may also be irrelevant). This problem is applicable to all three methodologies, but most notably the Exergy Replacement Cost.

A second example of the disjunction between the derivation and valuation levels is the manner in which non-flow chemical exergy is determined. The formal derivation of chemical exergy only includes the concentration exergy (which this author argues is only a theoretical construct and is not relevant), whereas the valuation of resources is most often concerned with chemical reactions (such as combustion). Furthermore, in situations where a resource may be valued for its concentration (such as mineral resources) exergy is not useful because there resources are not work producing. As was

mentioned above in section 6.4, exergy appears to be incapable of measuring what it should measure (work producing resources), and is not a relevant characteristic of what it can measure (concentration exergy of non work-producing resources). This problem is once again quite pertinent for the Exergy Replacement Cost. However, it is also noteworthy that Eco-exergy attempts to use concentration exergies more explicitly, but does so by adopting a probabilistic approach to life.

The second reason that prevents the appropriate application of exergy towards resources is that exergy proponents have not validated the use of exergy. For example, Energy proponents do not appear to have re-examined Energy to determine how adopting exergy may change the methodology. In general, the argument connecting exergy to resource quality appears to have been accepted as a law rather than being understood as a theory.

The third reason preventing the appropriate application of exergy towards resources is that exergy proponents have not adequately addressed the different perspectives related to exergy. In section 6.2.1, four different perspectives of exergy were introduced, including: (1) exergy as either harmful or helpful; (2) exergy as either organizing or disorganizing; (3) exergy as either a restricted or unrestricted measure of potential useful work; and (4) exergy as either a system-based or item-specific tool. These perspectives (and there may be others) are critical to determine the manner in which exergy is applied, and the insight gained from the application. None of these perspectives have been adequately addressed, with the result being that exergy may be applied in many different ways depending on the preference of the proponent. Such subjective application of exergy makes the concept less coherent and consistent.

For the three reasons provided above, the argument relating exergy to resource value must be tentatively rejected until further justification and self-reflexive research is provided.

## **6.6 Final thoughts**

To conclude, exergy analysis appears to be a concept still lacking theoretical grounding. In this respect, what it intuitively thought to be exergy might in fact not be, due to the very formulation of the concept. While not a categorical claim, this author must conclude that non-flow chemical exergy is not a universal thermodynamic measure of resource value or resource consumption. The fundamental problem may be in the attempt to produce a unifying theory.

In the opinion of this author, the relevance of exergy to its many applications (ecology, systems theory, lifecycle assessments, power production etc) depends on how well exergy proponents can reassess the theory. In some instances exergy may be abandoned in lieu of a different conceptual framework.

Many of the important problems regarding the application of exergy result from conflicts that emerge at different theoretical levels (i.e.: the derivation of exergy, the connection between exergy and resources, and the resource consumption methodologies). To fully understand the tension between these levels requires a holistic approach to resources, and such approach appears to be currently lacking.

There are several impacts that may hopefully arise from this thesis. First, by showing the weaknesses in the exergy conceptual framework, a new thermodynamic conceptual framework may be formulated. The importance of a new conceptual framework is that it may allow insight into the world that exergy is blind to, because of the very assumptions made in the derivation of exergy.

A second potential impact is that if the results of this thesis are fully appreciated, then researchers will no longer apply exergy analysis in a manner that provides one-way legitimacy to their research. In other words, every application of exergy (or some new thermodynamic concept) should be viewed as a method of informing research based on the exergy conceptual framework *and* a simultaneous test of the exergy framework itself. This reflexive application of exergy is lacking in many publications, where for the most

part exergy is assumed valid, and any conflict does not reflect on the relevance of exergy. The end result of this one-way legitimacy is that a great deal of potential insight is lost.

Despite all the problems related to resource consumption methodologies and exergy, there is a need to understand energy flows in the world. At this point the door is still open for some fresh new ideas; both to reinterpret what is already known, and to provide meaning for what isn't.



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