"WASTE POTENTIAL ENTROPY: THE ULTIMATE ECOTOXIC?"

by

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WASTE POTENTIAL ENTROPY: 
THE ULTIMATE ECOTOXIC?

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Abstract

We explore some economic implications of three simple ideas. These are as follows: (1) all resource flows and all economic goods and services can be characterized as stocks or flows of "useful" embodied information, (2) the economy is an information processor, in the sense that large quantities of low grade "physical" information are converted, by intention, into smaller quantities of higher grade "morphological" and "symbolic" information and (3) the most general pollutant is the physical information in the waste. Production, in the economic system, is the conversion of low economic value information-content raw materials into high economic value information-content goods and services.

We point out in this paper that entropy generated in the creation of economic goods or services is not a priori damaging to the environment. Entropy, as such, is not pollution, although it is generated by the consumption of non-renewable natural resources. What is dangerous to the environment is the emission of material fluxes (i.e. waste streams) that are not in thermodynamic equilibrium with the environmental systems into which they are emitted. Temperature or pressure differentials are unimportant. By far the most dangerous aspect of disequilibrium is differential physico-chemical composition, between the waste stream and the environmental medium into which it is emitted. Such differentials constitute potential entropy increase.

Eco-toxicity is, in effect, the potential of such entropic differentials for driving uncontrolled processes that threatens the stability of organisms, ecosystems and the environment as a whole. The most vulnerable environmental media are the atmosphere and the terrestrial biosphere. Thus the highest priorities for environmental policy must be to protect these two systems, above all, from unwarranted anthropogenic disturbance. A general criterion for environmental sustainability is proposed. The implications for economic and environmental policy are discussed briefly.
The Economy as an Information Processor

The first major point we wish to make in the present paper is that the economic system is, in essence, a system for processing and reducing information. All factors of production, including technological knowledge, can be regarded as forms of "condensed" or "embodied" forms of information (Figure 1). Information is used in a technical sense, based on notions introduced by Hartley [Hartley 1928], elaborated by Shannon [Shannon 1948], and further developed by Brillouin and Tribus [Brillouin 1949, 1950, 1951, 1953; Tribus 1961, 1979] and others. Basically, all forms of information can be regarded as measures of "uncertainty" (Shannon) or "distinguishability" (Tribus).

Solar radiation is information rich because it is highly distinguishable (in terms of equivalent 'black-body' temperature) from the low temperature background radiation. High quality metal ores contain information because their composition is highly distinguishable from the surrounding earth's crust. Purified metals contain even more information for the same reason. And so on.

Both resource inputs and outputs of the production process (e.g. GNP), and all factors of production (capital, labor) can also be thought of as forms of condensed information.

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1 Some features of the present framework were previously suggested in earlier publications, notably [Ayres 1978], [Ayres & Nair 1984], and especially [Ayres 1994].
tion, although the relevant reference systems must be carefully defined, as will be seen later. These stocks and flows of information can be measured, in principle, in terms of a common unit, "bits". We can also identify technical knowledge as a more refined (i.e. reduced) form of information. Not all information is knowledge, but all knowledge is information. "Useful", in this context, merely means that it contributes to the production of useful goods and services.

In fact, it requires no great leap of the imagination, at this point, to interpret physical capital stock as knowledge (i.e. useful information) embodied in material form. Similarly, various skill levels of labor can readily be interpreted as knowledge embodied in human workers. When capital equipment depreciates due to 'wear and tear', the (useful) information content embodied in its design (form and function), are gradually lost. As a cutting tool loses its physical edge, its distinguishability is obviously decreased, as is its economic productivity.

The interpretation of capital and labor as embodiments of knowledge does not alter the desirability of taking into account the fact that the economic system also depends on a continuing flow of available energy (or essergy). Available energy (essergy) is the "ultimate" resource, in the same sense that all other material resources can be extracted from the earth's crust, in principle, if enough energy is available. Energy (essergy) flux from the sun is, of course, the ultimate source of all localized negentropic (information) accumulation on the earth. This being so, that the solar energy flux is, in effect, a flux of information. Similarly, the earth's store of fossil fuels can be regarded as a stock of information. Some of the latter can be captured and embodied by biological and/or technological processes in other (even more condensed) forms, such as capital goods or products.

Some material products are entirely consumed or dissipated in some subsequent process. Presumably this adds value to the next product (or service) in the chain. But final goods themselves (other than food) are not actually consumed. They produce services for some period of time, before they "wear out". The final service may be transportation, housing, heating, illumination, entertainment, security or whatever. But we argue that, in every case, the service as received by the consumer can be regarded as information.

If all forms of embodied and disembodied information were mutually substitutable and inter-convertible, the ratio of aggregate outputs (e.g. GNP) to aggregate resource inputs (both measured in 'bits') would be a natural generalized measure of the state of technology at a given time. However, the real situation is somewhat more complicated. The information embodied in a mineral ore can only be defined in terms of its distinguishability from its surrounding matrix (e.g. the earth's crust, or some local geological subregion). A sample of liquid or gas is distinguishable, by similar arguments, from the oceans or the atmosphere. Needless to say, the processes of ore concentration, smelting and refining increase the distinguishability of the concentrated material from its surroundings; in this sense, information has been added to the system. However, this added information had to be created somehow. In general, it results from a mechanical action (such as centrifuging or filtration) and/or a chemical
reaction that recombines the elements using heat energy from fuel and air. The latter is "free" but the former is itself a mineral product; moreover, the reduction/refining process yields unwanted materials — gangue, slag — in inverse proportion to the grade of the ore. These reaction products and/or unwanted materials are left behind as wastes.

The micro-scale compositional and structural information embodied in finished high-value material (and the "waste" information embodied in unwanted materials, such as combustion products) can be calculated by conventional thermodynamic methods. But the thermodynamic calculation yields a numerical result in units of energy/temperature per unit mass (joules/degree-mole). This can be converted to 'bits' per unit mass by first defining information as an entropy difference times the proportionality factor \(1/(k_B \log 2)\), where \(k_B\) is the Boltzmann's constant.

However, materials processing in modern industrial economics constitutes a relatively small share of value-added. The later stages in the value-added chain are quite different in nature from the extraction, concentration, smelting/refining and energy-conversion stages. They consist largely of processes that modify the macro-scale \textit{shape} of the material, by cutting, trimming, deforming, joining and/or assembly into complex structures or artifacts. Increasingly, these artifacts are themselves carriers of higher (more condensed) forms of information, namely symbols (printing, numbers) and images.

Each manufacturing operation in the value-added chain beyond the finished materials stage adds macro-scale "morphological" information to each workpiece. In the case of a computer chip, a magnetic tape, a printed page, or a photograph, the morphological information also carries symbolic significance. As in the materials processing stages, there are usually some material wastes associated with the process. A high value product like a computer chip may be the end result of a series of intermediate process steps that generates material wastes in quantities significantly greater than the mass of the finished product. However, these wastes result from process inefficiencies. In principle, they could be eliminated by perfecting the processing steps.

There are also losses of "pure" morphological (including digital) information to be considered, as for instance, when the contents of a computer memory are wiped clean.\(^2\) These losses, too, generate entropy. Morphological information can also be measured, in principle, in 'bits'. [Ayres 1987]. But, while the morphological information embodied in a macro-scale shape may have very large economic value, it is

\(^2\) A type of information that is largely lost in the productive process itself can be called 'control information'. This is information consumed during the manufacturing process for a variety of purposes, including controlling machines or (in the case of workers) for controlling the body motions of the workers. The latter is supplied largely by the sensory organs of the workers, especially the eyes. Process control information is also provided by mechanical and electronic sensors, such as TV scanners or photo-cells. This information is often processed by computers and reduced before being used for decision purposes. Much control information is wasted in the sense that it is not embodied in the product, and the process could theoretically proceed in the absence of (much of) it. Nor does lost control information have any first order effects on the environment.
quantitatively insignificant (in 'bits') compared to the physical information embodied in material composition and structure. From the economic point of view, one cannot safely assume that different kinds of information have comparable value per bit. In short, the information-content of different constituents of the economic system cannot be aggregated. Morphological and/or symbolic information cannot be arithmetically added to or subtracted from the physical information associated with the micro-scale physico-chemical composition of a material. Some conversion factor is needed.

From the environmental standpoint (to a first approximation, at least) only the loss of information associated with material composition/structure need be considered. This 'potential entropy' has the potential for driving uncontrolled environmental processes.

We emphasize an important point: the assertion that all economic quantities can be considered as forms of information and measured in 'bits' does not imply cross-substitutability. (By the same token, all materials can be measured in mass units, but a unit mass of computer chips or vitamin B-12 has very different value than a unit mass of iron ore or gravel). There are several different kinds of information. The different kinds of information stocks and flows can (and do) have radically different valuations in monetary units (e.g dollars). The two kinds of units (information and money) need not coincide, any more than the relative prices of two materials necessarily coincide with their relative masses. The traditional objective of economic activity continues to be the maximization of output, in value terms. However, we suggest that this maximization must be subject to a constraint on the output of potential entropy associated with waste and discarded materials.

Thermodynamics and Economics

Twenty years ago the apparent relevance of thermodynamics to environmental economics was two-fold. The first law of thermodynamics (conservation of mass-energy) is the basis of the materials-balance principle. Applying this principle to environmental economics led to the important insight that the total mass of wastes produced by an economic system must essentially be equal to the mass of raw materials extracted (or harvested) from the earth. Trivial as this observation may appear in retrospect, it had an inescapable corollary: that the potential for environmental harm increases in direct proportion to the intensity of economic activity (at least, in the sense of material production and consumption). Moreover, because of this linkage, environmental externalities cannot be dismissed as marginal or unusual. On the contrary, these problems are inherent and pervasive [Boulding 1966; Ayres & Kneese 1969; Kneese et al 1970].

The second law of thermodynamics states that, entropy always increases in an isolated system as it approaches thermodynamic equilibrium. This approach to equilibrium is characterized by the gradual decrease and eventual disappearance of gradients. Thus, temperature and pressure differentials tend to vanish, "order" is gradually replaced by "disorder" and everything tends toward a state of homogeneity. In effect, high quality mineral fuels and ores in the ground can be regarded as stocks
In effect, economic processes are always accompanied by entropy production. It seems to follow that, to maximize human welfare over the long run, a strategy of minimization of entropy production should be adopted. This viewpoint was elaborated by Georgescu-Roegen [Georgescu-Roegen 1971, 1977, 1979, 1979a]. It is still widely accepted by environmental economists. For example, Herman Daly writes "The sources become depleted and the sinks fill up and become polluted. The entropy law is supremely relevant because it says that sinks cannot serve as sources" [Daly 1992]. Here again, we disagree. Daly's statement is only true as regards energy itself, however. Sinks can indeed be sources of materials, if sufficient free energy is available to drive the processes of separation. The sun will be an adequate source of energy for the next several billion years.

Since the early 1970's, as it happens, a more sophisticated view of thermodynamics itself has gradually emerged, thanks largely to the pioneering work of Ilya Prigogine and his co-workers. The older formulation is still valid for isolated systems close to equilibrium. However, the older formulation failed to give sufficient weight to the fact that the systems we live in and deal with every day are neither isolated nor close to thermodynamic equilibrium. The fundamentally new insight of Prigogine et al. is that self-organized systems — including all living organisms, and the biosphere as a whole — can only exist in thermodynamic disequilibrium [e.g. Nicolis & Prigogine 1977; Prigogine 1989]. The key to self-organization, in short, is not minimization of entropy production, at all. On the contrary, it is dissipation of free energy from an external source. In fact, dissipative systems may actually maximize local entropy production (although entropy continues to increase in the universe as a whole). This changes the conventional picture so much that we can safely describe it as a new paradigm.

The negative aspect of entropy, which was noticed in the 19th century and has had by far the most influence on other disciplines, has been the implication of approaching universal homogenization: the so-called "heat death of the universe". In economics, Georgescu-Roegen's prescription for human economic development strategy was essentially based on this negative interpretation of the second law, even though the usual formulation is only valid for isolated systems4.

However, there is another face to the second law, implicit in Prigogine's work on non-equilibrium thermodynamics. It is, in effect, that entropy is actually the source of order and structure, in the sense that increasing "order" — or "embodied structural

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3 A self-organized system can be characterized as a stable spatial arrangement of material fluxes and a cyclic sequence of chemical reactions, driven by a continuing flux of free energy from some external source. Such a system tends to endure in time as long as the energy flux continues.

4 In fact, apart from laboratory artifacts, the only isolated system we know of is the universe as a whole.
"information" — is a necessary requisite of a dissipative system (such as the earth) far away from thermodynamic equilibrium [Prigogine, 1989].

There is another way to think about the positive aspect of entropy, which (like much else) we owe to Boulding [Boulding 1981]. In the older paradigm, entropy is a measure of the extent to which "available useful work" or "availability", "essergy" or "exergy" is depleted. (These terms are defined later). Whenever the chemical energy stored in a fuel is released by combustion, it is converted into heat. The ability of this heat to perform "useful" (i.e. mechanical) work is degraded as the heat is dissipated and the temperature declines toward the ambient level. In effect, the "useful" component of the energy is converted into a "non-useful" or "unavailable" component. This is accompanied by increasing entropy.

But, of course it follows that all "availability" (or essergy, or exergy) is also a potential source of future entropy increase. By the same token, the difference between the actual entropy of an existing system that is not in equilibrium, and its future entropy (after final equilibration with the environment), is a measure of its potential for doing future work or driving future processes. This simple insight, which also seems trivial when stated as above, has interesting and non-trivial environmental consequences. Suppose an industrial process is less efficient than it could be. Suppose there are material wastes that contain "unexpended" potential entropy that was not needed, and was not used, to drive the process under examination. These wastes (not to mention consumption wastes) are dissipated into the environment. Of course, some entropy of mixing is generated by the dissipation itself. But, more important, the waste material (by assumption) still has reactive potential, i.e. potential to drive environmental processes.

As we noted earlier, it is not only unutilized exergy (i.e. waste heat or unburned fuel) that can drive undesired environmental processes in a non-equilibrium situation. On the contrary, it is far more likely to be the insertion of unfamiliar chemical species (i.e. chemical potentials) in delicately balanced biological cycles that can cause trouble. At the micro-scale, very small amounts of some chemicals are enough to disrupt life processes. In fact, we have a general label for such disruptive chemicals: toxins. The first point we wish to emphasize in this paper is that unexpended potential entropy increase has the potential for disruption of delicately balanced dissipative structures, far from equilibrium. For this reason, unexpended essergy or exergy — potential entropy increase — can be regarded as a potential for causing environmental harm.

**Definition of the Measure**

Discarded physical information, or potential entropy, can therefore be a measure to evaluate the potential human impact on the environment. We introduce the terminology "waste II-potential", hereafter, to emphasize that it is not a measure of actual harm done. The logical framework for the introduction of this potential is the existence of a localized subsystem (a production or consumption activity, or even a product) embedded within a larger and more encompassing system that we call "the local..."
The end-state for the localized subsystem is defined as the state our sub-system would eventually reach when it becomes indistinguishable from its local environment or surroundings. (We do not characterize the environment itself as being in thermodynamic equilibrium. This is important, because the earth system is not in thermodynamic equilibrium with the universe, but is maintained in a steady state by the constant influx of solar energy).

As noted above, the general measure of information $H = S_o - S$ has already been proposed by Shannon, Brillouin, Tribus and others. The possible environmental significance of entropy has also been suggested in somewhat vague terms by various writers, starting with Georgescu-Roegen, but without a clear definition of the reference state, or a useable prescription for calculation. We define II-potential as stock of physical information, namely the difference between the actual entropy of a (sub)system and its final entropy, after it reaches equilibrium with — or becomes indistinguishable from — its local environment [Martinás & Ayres 1993]. More precisely, let:

$$\Pi = S_o - S$$  \hspace{1cm} (1)

The anthropic subsystem under our conceptual microscope — perhaps a machine or engine, a process, an industrial plant, or even a city — will be denoted $X$ hereafter. Thus $X$, together with its "local" environment, which could be a valley, a watershed, a lake, a continent or the earth as a whole, is assumed to constitute a distinct combination system $XY$. In turn, $XY$ is embedded in a still larger meta-system $XY'$, and that in a still larger one $XY'Y''$, and so on like Russian dolls. Everything is embedded in a "supersystem", namely the universe itself, $Z$. The undisturbed environment $Y$, perhaps the whole earth, is a stable but non-equilibrium system maintained by a constant flux of free energy from outside. It also radiates thermal energy into space. However, these steady-state fluxes do not reflect any process of thermal equilibration between $X$ and $Y$ within the earth system. However, $X$ is small compared to $Y$, so this equilibration can be neglected for purposes of the following derivation.

The combination $XY$ (e.g. the anthropic system embedded in the earth, as defined above) can be assumed to conserve energy. That is, energy influx from the sun is balanced by energy loss, as infra-red radiation, to the rest of the universe $Z$. It follows that the steady-state entropy $S_o$ of $Y$, the undisturbed earth-system is also constant. On the other hand, the second law implies that $S$ (the actual entropy of the

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5 This is true even if "the environment" itself is not in a state of thermodynamic equilibrium, but is a system maintained in steady state by an external free energy flux. It is enough that the environment can be locally characterized (on average) by well-defined values of thermodynamic variables, such as temperature, pressure, density, chemical composition, and so on. Obviously the earth's surface consists of a multiplicity of such environments. Some with very sharply defined boundaries (such as the sea-air, sea-land or land-air interfaces); others are differentiated by almost imperceptible gradients.
disequilibrium combination XY) is *increasing*, the increase in unit time is called entropy production $\sigma$. The two statements together imply that the entropy difference $\Pi$ is *decreasing*. It further follows that, if $\Pi = 0$, there can be no further localized equilibration process taking place. In this case the system XY is already indistinguishable from Y. Just as in a true thermodynamic equilibrium, "nothing happens, or can happen" thereafter. Nevertheless the energy influx from the sun is a $\Pi$-potential flux, $J_\Pi$. It is this flux which drives every process — natural or anthropogenic — on the earth.

There is a balance equation for the $\Pi$-potential. It is as follows:

$$\frac{d\Pi}{dt} = J_\Pi - \sigma \quad (2)$$

The steady-state condition is $J_\Pi = \sigma$. In words, a steady-state earth implies that the annual entropy generation by *all* processes on the earth must equal the rate of influx of $\Pi$-potential, from the sun. If the rate of entropy generation on earth exceeds the annual influx of $\Pi$-potential, it means the earth-system is "running down" by losing physical information (i.e. order and structure). If the annual influx exceeds the annual entropy production, the reverse is happening: the physical information content (order and structure) is increasing.

Undoubtedly the physical information ($\Pi$-potential) embodied in the biosphere had been increasing, on the average, since the origin of life on earth. This is reflected in the complexity of ecosystems, in biodiversity, in the maintenance of "dissipative structures" like the carbon cycle and the nitrogen cycle that are far from thermodynamic equilibrium, and in the accumulation of reserves of elemental carbon, sulfur, oxygen, and nitrogen that embody large amounts of natural capital.

Human activity has converted a significant quantity of this stock of accumulated natural capital ($\Pi$-potential) into what we call "useful work". In the process, humans have created a different form of capital. Some economists have argued, in effect, that human-created capital more than compensates for natural resources that have been consumed. This is strongly disputed by many ecologists and others with a broader view of what natural capital really is. We (the authors) advocate the broader view.

Sustainability is a notion that has been very vexing to economists. From a thermodynamics perspective, the criterion for sustainability would seem to be fairly simple to state: the earth system is sustainable if the average rate of entropy production $\sigma$ does not exceed (though it may be equal to) the average rate of influx of $\Pi$-potential $J_\Pi$ from the sun — which is the only sustainable source. Sustainability may not require an absolutely steady state (except in some average sense), but a steady-state must be the minimum objective for environmental policy. (A more far-sighted policy objective would be to reduce the annual entropy generation of human activity sufficiently to permit some rebuilding of the depleted stock of biospheric $\Pi$-potential).
The foregoing statement in terms of II-potential is still rather abstract. In order to give it operational significance, the crucial element is the interpretation of "environment". The earth system Y is not itself in true thermodynamic equilibrium with the universe U. A strict application of conventional thermodynamic rules implies that the "environment" can only be the whole Universe. With this interpretation the II-potential would be meaningless. Fortunately, for the majority of real problems it is possible to identify a meaningful local environment, namely some subset of Y. For our purposes the environment is that part of Y which is in direct contact with the anthropic subsystem X. Typically, we are talking about the (lower) atmosphere, surface waters, soils, or biota. In the present investigation we consider only those changes in the local environment that are directly attributable to interactions with the human-created subsystem X.

It is worthwhile to note that the combination XY (subsystem + environment) need not be thermodynamically isolated, or even closed. It is sufficient that the interaction with the remaining part of the Universe Z is by means of constant, balanced fluxes of energy.\(^6\)

**Interpretation of II-potential**

For a thermodynamic characterization of the system, one has to know its extensive variables, namely the internal energy, \(U\), volume, \(V\), and mole numbers \(N_i\). The theory of thermodynamics states that, for every equilibrium state there exists a corresponding equilibrium entropy value, viz.

\[
S = S(U,V,N) \tag{3}
\]

To summarize the thermodynamic relationships between entropy and II-potential, we have plotted the equilibrium relationship between entropy (\(S\)) and internal energy (\(U\)) for an isolated thermodynamic system (Figure 2), under the condition that the other extensive variables (e.g. \(V, N\)) are fixed. (The picture is also valid for the more general case where \(V\) and \(N\) can vary, but the representation is more complicated, being multi-dimensional). The curve is concave (monotonically increasing with decreasing slope). The slope is the inverse temperature:

\[
\frac{\partial S}{\partial U} = \frac{1}{T} > 0 \tag{4}
\]

\(^6\) Matter fluxes are not theoretically excluded, though in the earth system, such fluxes appear insignificant.
Since temperature is positive, by definition, its inverse is always positive.\(^7\)

This equilibrium curve divides S-U space into two parts. Under the curve are the possible non-equilibrium states, while above the curve is a region we might characterize (in the spirit of Koopmans) as "the land of Cockaigne": i.e a region that cannot be reached from a possible state.\(^8\) The Second Law states that, if we are in state C in an isolated system, then only the BC points can be reached by an adiabatic process (no heat transfer). This is because an isolated system can neither gain nor lose energy, so the internal energy \((U_A)\) is fixed. For adiabatic processes and \(U = \) constant, only vertical upward motion in S-U space is possible. If one starts from state C, then the maximum entropy change is \(S(B) - S(C)\). This distance is the information content (or distinguishability) and also the \(\Pi\)-potential for an isolated system.

The Second Law can now be restated as follows: transformation processes can occur if (and only if) there is a non-zero potential for change, viz. \(\Pi > 0\). In an isolated system that is internally in equilibrium \(\Pi\) cannot increase. On the contrary, in any real process in an isolated system \(\Pi\) always decreases: \(d\Pi/dt < 0\). (One can define an idealized extreme case, mostly for the sake of mathematical convenience, such that \(d\Pi/dt = 0\)). Rudolph Clausius introduced the word entropy, where *tropy* in Greek

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\(^{7}\)The systems with negative absolute temperature do not have economic significance.

\(^{8}\)This is rather analogous to the constraint against travelling backward in time.
means 'transformation' or 'change' [Clausius 1865]. With this meaning $S(C)$ is the measure of the magnitude of past transformations, which have already occurred. By contrast, the difference $S(B) - S(C)$ measures the magnitude of potential future transformations. With this in mind, we call it II-potential.

The connection of II-potential with the 'usefulness' of an anthropic system — its ability to do mechanical work — can also be seen from Figure 2. Here the horizontal line of constant entropy represents the trajectory of reversible (quasi-static, adiabatic) processes. If we relax the reversibility condition any trajectory starting from a non-equilibrium point $C$, as before, and tending monotonically upward corresponds to an adiabatic process. Trajectories to the left of the vertical segment $CB$ represent processes such that the anthropic sub-system does work on its surroundings. Trajectories to the right of the vertical segment represent processes such that the surroundings do work on the sub-system. The length of the horizontal segment $CD$ (reversible processes) represents the maximum amount of useful work the system can do on its surroundings ($W = U_D - U_A > 0$).

Suppose we draw the hypotenuse $DB$. It can be seen that its slope is the ratio $BC/DC$. This must be equal to the actual slope at some point along the curve $DB$. Thus the length of the horizontal leg of the right triangle $(DBC)$ is proportional to the length of the vertical leg divided by the slope of the hypotenuse. But the slope is a constant with the dimensions of temperature $T$. The actual temperature corresponds to some intermediate point between $D$ and $B$ where the slopes are parallel, viz.

$$B = T \Pi$$

where $T(B) > T > T(D)$.

In the special (but important) case where the external environment is so large that its equilibrium state is essentially unaffected by the disturbance created by the equilibration of the system in question, the situation is simpler. The inequalities above can become equalities in the limit viz. $T(B) = T(D) = T_0$, where $T_0$ is the ambient temperature of the local environment. In this case, the maximum work that can be extracted from the system is called the "essergy". We emphasize that essergy is only defined for a system in relation to its environment, i.e. when both the subsystem and the environment are well-defined. In some cases this is not possible. However, whenever the essergy is actually defined, it is proportional to the II-potential.
a. The equilibrium state of a sub-system is characterized by the minimum value of one of these functions. If the sub-system is closed, with constant entropy, the internal energy $U$ is a minimum. If the temperature $T$ is fixed the equilibrium corresponds to minimum Helmholtz free energy $F$. If pressure $p$ is constant, then the equilibrium corresponds to minimum enthalpy $H$. Finally, if $T$ and $p$ are both held constant, then the equilibrium corresponds to minimum Gibbs free energy $G$.

b. The potential functions are characteristics of the sub-system. They measure the work needed to be done on the system to take it from equilibrium state 1 at temperature $T_1$ to equilibrium state 2 at temperature $T_2$. The maximum work that can be done by the sub-system (such as in an engine) is given by the difference between the initial and final values of the relevant potential, namely:

$$W = F(2) - F(1)$$

(6)

In most practical applications the environment of the sub-system is "large", and it remains unaffected by the system. The initial and final temperature, pressure and chemical potential of the environment are $T_o$, $p_o$, and $\mu_{io}$, respectively.

Like internal energy, the classical thermodynamic potentials above have absolute values defined completely by the internal state of the system under consideration and independent of its surroundings. One can, of course, compare the state of the system under different conditions (constraints) keeping one or more of the variables fixed and allowing others to vary. This can be done either for an isolated system, or for a system in thermal, mechanical or even chemical contact with the external environment. The internal equilibrium condition for the system in each case corresponds to minimizing one of the classical potentials. These relationships hold regardless of the state of the external environment. (Nothing whatever is implied about the state of the external environment, beyond its mere existence and its ability to transfer heat, pressure or chemical species in or out). This is obviously a very idealized picture.

The last two sentences are not applicable to essergy, because essergy is only defined for a system in relation to its external environment. Essergy can be thought of as a more general thermodynamic potential in one particular sense. $H$, $F$ and $G$ are defined only for equilibrium states of the system, and from them it is possible to determine the maximum work the system can do (or which can be done to the system) under specific constraints. By contrast, essergy measures the maximum available work that can be extracted from a system and its environment jointly, as the system approaches equilibrium with its environment. The system is characterized by a set of (non-independent) variables $E$, $V$, $N$, $S$ while the environment is characterized by $T_o$, $p_o$, $\mu_{io}$. Here the system in question is not necessarily in internal equilibrium. A function
The last two sentences are not applicable to essergy, because essergy is only defined for a system in relation to its external environment. Essergy can be thought of as a more general thermodynamic potential in one particular sense. H, F and G are defined only for equilibrium states of the system, and from them it is possible to determine the maximum work the system can do (or which can be done to the system) under specific constraints. By contrast, essergy measures the maximum available work that can be extracted from a system and its environment jointly, as the system approaches equilibrium with its environment. The system is characterized by a set of (non-independent) variables \( E, V, N_i, S \) while the environment is characterized by \( T_o, p_o, \mu_{io} \). Here the system in question is not necessarily in internal equilibrium. A function \( \Phi \) similar to essergy was proposed in the last century by both Maxwell and Gouy [Jouget 1909].

\[
\Phi = E + p_o V - T_o S \tag{7}
\]

A generalization of (7) was introduced by R.B.Evans who coined the name "essergy" (for "essence of energy").\(^{10}\) The essergy for a sub-system with energy \( E \), volume \( V \), entropy \( S \) and mole number \( N \), in relation to an environment characterized by \( T_o, p_o, \) and \( N_{io} \) was defined as follows:

\[
B = E - T_o S + p_o V - \sum_i \mu_{io} N_i \tag{8}
\]

This form is not particularly convenient for practical calculations, however. We now return to our main theme.

**Calculation of the \( \Pi \)-potential**

By definition \( \Pi \)-potential of a sub-system is the entropy difference between two states of nature, the initial state and an ultimate state after the sub-system has equilibrated with its environment, viz.

\[^{10}\] The name "exergy" (German: "Exergie") is sometimes erroneously confused with "essergy". It was proposed by Z. Rant in 1953 in Lindau, and was first used by German power and refrigeration plant engineers. The exergy per kg of a process stream is defined as:

\[
\text{Exergy} = H - H_o + T_o(S-S_o)
\]

where \( H \) is the enthalpy. Like essergy, exergy is only defined for a system in relation with its external environment, but chemical interactions are excluded. It essentially defines the maximum work that can be done by a system by means of temperature and pressure alone. (In practice, it is applied to steam or a refrigerant fluid).
\[ \Pi = (S_{\text{system}} + S_{\text{env}})_o - (S_{\text{system}} + S_{\text{env}}) \quad (9) \]

Assuming the initial and final states are not "too" far apart, it is convenient to carry out a Taylor-series expansion in the differences of the different variables:

\[ S_e(E_{eo} + \Delta E, V_{eo} + \Delta V, \ldots) = S_{eo}(E_{eo}, V_{eo}, \ldots) + \left( \frac{\partial S_{eo}}{\partial E} \right) \Delta E + \ldots + \frac{1}{2} \left( \frac{\partial^2 S_{eo}}{\partial E^2} \right) \Delta E^2 + \ldots \quad (10) \]

ii) Only the first one of the second order terms is displayed explicitly. The others are similar in structure. Here the subscript symbols are: index e for environment and o for the long run equilibrium. Thus, the long-run equilibrium value of energy of the environment is \( E_{eo} \) and the initial value is \( E = E_{eo} + \Delta E \). Similarly, the entropy of the system:

\[ S_s(E_{so} - \Delta E, V_{so} - \Delta V, \ldots) = S_{so}(E_{so}, V_{so}, \ldots) - \left( \frac{\partial S_{so}}{\partial E} \right) \Delta E + \frac{1}{2} \left( \frac{\partial^2 S_{so}}{\partial E^2} \right) \Delta E^2 + \ldots \quad (11) \]

The subscript s refers to the sub-system. The sub-system's final equilibrium energy is \( E_{so} \), while the initial energy is \( E_{eo} - \Delta E \). The first order terms in the Taylor expansion cancel each other out because

\[ \frac{\partial S_{eo}}{\partial E} = \frac{\partial S_{so}}{\partial E} = \frac{1}{T_o} \quad (12) \]

The second order term from equation (9) can now be rewritten:

\[ \frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E} \left( \frac{1}{T} \right) = - \frac{1}{T^2} \frac{\partial T}{\partial E} = - \frac{1}{T^2 C_V} \quad (13) \]

where
\[ C_v = \frac{\partial E}{\partial T} \] (14)

is the specific heat at constant volume. The energetic term in the \( \Pi \)-potential is:

\[ \Pi_E = \frac{1}{2T^2C_{ve}}(\Delta E)^2 + \frac{1}{2T^2C_{se}}(\Delta E)^2 \] (15)

The first term is negligible if the environment is much larger than the sub-system, since in this case \( C_{ve} \gg C_{se} \).

Similar arguments can be given for the other equilibration processes. The general form for all the second-order terms can symbolically written as:

\[ \Pi = \sum_{i,k} g_{ik} \Delta X_i \Delta X_k \] (16)

where \( g_{ik} \) is the symbol for the (negative) second derivative of entropy with respect to extensive variables \( X_i \) and \( X_k \),

\[ g_{ik} = -\frac{\partial^2 S}{\partial X_i \partial X_k} \] (17)

From equation (12) it follows that \( g_{11} = 1/(T^2C_v) \). The matrix \( g \) defines the deviation of the intensive variables \( Y \) from their equilibrium value, whence.

\[ \Delta Y_k = -\sum_i g_{ik} \Delta X_k \] (18)

The \( \Pi \)-potential can be rewritten.

\[ \Pi = \sum_i \Delta Y_i \Delta X_i \] (19)
Here all the calculations were made (implicitly) for the case of a "small" sub-system in a "large" environment, such that the latter is unaffected by the former. It is straightforward to generalize for the case where the environment is finite and the impacts are mutual. Actually, the second order changes in the environment also appeared explicitly in equation (14) above. If, in a reasonably large environment, there are several systems to consider, then the total Π-potential is the sum of several components with different physical interpretations:

\[ Π = \sum_α Π_α \]  \hspace{2cm} (20)

The final result is that the Π-potential can be considered to be the sum of contributions from three sources: (i) thermal interactions (heat flow), (ii) mechanical interactions (pressure changes), and (iii) physico-chemical interactions (diffusion & mixing, molecular recombination). If need be, electric, magnetic and other forces can also be taken into account. Let us consider them individually:

(i) Thermal interactions involving heat flow:

\[ Π_{therm} = -\frac{1}{2} \Delta \left( \frac{1}{T} \right) \Delta E = \frac{1}{2T_o^2} \Delta T \Delta E \]  \hspace{2cm} (21)

By definition of the heat capacity, \( C_v \) we can say that \( \Delta E = C_v(T_o - T) \), whence

\[ Π_{therm} = C \left( \frac{T_o - T}{T_o} \right)^2 \]  \hspace{2cm} (22)

(ii) Mechanical interactions involving compression:

\[ Π_{mech} = -\frac{1}{2} \Delta \left( \frac{\rho}{T} \right) \Delta V = -\frac{1}{2T_o} \Delta \rho \Delta V \]  \hspace{2cm} (23)

Introducing the compressibility: \( K = - (\Delta V/\nu)(\rho/\Delta \rho) \), (23) can be rewritten
\[ \Pi_{mech} = \frac{1}{2} \left( \frac{\kappa V}{T_o} \right) \left( p_o - p \right)^2 \]  

(iii) Chemical reactions and diffusion:

\[ \Pi_{chem} = \sum_i \frac{\mu_{i,o}}{T_o} N_{env,i,o} + \sum_i \frac{\mu_{i,o}}{T_{i,o}} N_{s,i,o} - \sum_i \frac{\mu_{i,o}}{T_{i,o}} N_{env,i} - \sum_i \frac{\mu_i}{T} N_{s,i} \]  

where the first and third terms in (25) can be combined

\[ \sum_i \frac{\mu_{i,o}}{T_{i,o}} N_{env,i,o} - \sum_i \frac{\mu_{i,o}}{T_{i,o}} N_{env,i} = \sum_i \frac{\mu_{i,o}}{T_{i,o}} \Delta N_{env,i} \]  

The second and fourth terms in (25) can be recombined by adding and subtracting a term containing the mole numbers \( N^* \) of reaction products:

\[ \sum_i \frac{\mu_{i,o}}{T_{i,o}} N_{s,i,o} - \sum_i \frac{\mu_i}{T} N_{s,i} = \sum_i \frac{\mu_{i,o}}{T_{i,o}} N_{s,i,o} - \sum_i \frac{\mu_i}{T} N^*_{s,i} - \sum_i \mu_i N_{s,i} \]  

Thus, the last pair of terms taken together refers to entropic changes resulting from chemical reactions only. They can be rewritten in terms of the Gibbs potential (essentially, the heat of formation) for the chemical reactions that occur:

\[ \Pi_{reaction} = \sum_i \frac{\mu_i}{T} N^*_{s,i} - \sum_i \frac{\mu_i}{T} N_{s,i} = \frac{\Delta G}{T_o} \]  

On the other hand, the first two terms in (24) together with the environment term (23) yields the entropy change resulting from diffusion and mixing:

\[ \Pi_{mixing} = \sum_i \frac{\mu_{i,o}}{T_o} \Delta N_{env,i,o} + \sum_i \frac{\mu_{i,o}}{T_o} N_{s,i,o} - \sum_i \frac{\mu_i}{T} N^*_{s,i} = \sum_i \left( \frac{\mu_{i,o}}{T_o} - \frac{\mu_i}{T} \right) (N_{i,o} - N^*_{s,i}) \]  

The final result, substituting (27) and (28) into (22) is:
\[ \Pi_{ch} = \frac{\Delta G}{T_o} + \sum_i \left( \frac{\mu_i}{T_o} - \frac{\mu_i^*}{T} \right)(N_{io} - N_{io}^*) \]  

There are two limiting cases where the mixing term can be simplified considerably and expressed in terms of the concentration values \( c_i = N_i / \Sigma N_i \), in an ideal gas approximation where \( \mu = RT \log c_i \), \( R \) being the ideal gas constant (8.3 Joules/K):

**Case A:** Suppose \( c_i \approx c_{io} \). Then in the ideal gas approximation, \( N_{s,io} = Vc_{io} \) and \( N_{s,i} = Vc_i \), whence it follows that

\[ \frac{\Delta \left( \frac{\mu}{T} \right)}{c} = R \frac{\Delta c}{c} \]  

This, in turn, yields

\[ \Pi_{mixing} = \sum_i R \frac{V(c_{io} - c_i)^2}{c_{io}} \]  

**Case B:** Suppose that \( c_i \approx 1 \), and \( c_{io} > 1 \).

\[ \Pi_{mixing} = - \sum_i RN \log c_{io} \]  

As a practical matter, the problem of computing anthropogenic changes in \( \Pi \)-potential can be simplified enormously by a simple observation. It is, simply, that the thermal term (i) and the mechanical term (ii) are insignificant in relation to natural (i.e. non-anthropogenic) fluxes of solar radiation on the earth's surface and natural material fluxes in the atmosphere and oceans (winds and ocean currents), respectively. It is only the third term (iii), consisting of chemical reaction potential and mixing (equation 30) that is not quantitatively insignificant. In practice, only the chemical reaction (Gibbs) potential (equation 28) is really important.

A further word of explanation is helpful at this point. The Gibbs potential is a well known quantity to chemists and thermodynamicists. It is tabulated for many substances, and can be found in many reference books. However, what is normally tabulated for a molecular substance is the so-called Gibbs "free energy of formation" which is the energy that would be required to break up the molecule into its component atoms. In other words, the Gibbs potential is defined with respect to a reference state that is physically rather artificial.
We are concerned with computing the Gibbs potential change when a waste stream consisting of some collection of molecules finally reaches local thermodynamic (i.e. chemical) equilibrium with its surroundings — in other words, when all reactions that are thermodynamically favored have finally occurred. The end result, of course, is another collection of different, less reactive molecules with different Gibbs potentials (as defined in terms of the artificial reference state). So, to calculate the differential Gibbs potential in equation 28, it is necessary to know the final equilibrium state — meaning, the final chemical combination — that will be reached.

This last step is the only difficult part of the analysis. It is difficult only because we are necessarily concerned with a localized chemical equilibrium, with respect to a larger system (the earth, the atmosphere, etc.) that is itself not in true thermodynamic equilibrium, but is really a dissipative structure in a quasi-steady state. To illustrate the difficulty (without offering a solution) consider the case of chlorine. It is not found in elemental form in nature. It is produced by electrolysis of sodium chloride. Some of the chlorine that is produced is converted to hydrochloric acid that eventually combines with sodium hydroxide to produce sodium chloride once again. The Gibbs potential of the end product, in this case, is the same as that of the starting point, and the only global change is that fossil fuel has been burned to produce heat (and entropy) to generate electricity to drive the electrolysis of salt.

However quite a lot of the chlorine that is produced does not recombine (at least on a short time scale) with sodium hydroxide. This is the chlorine that combines, instead, with organic molecules, in PVC and so on. What is the long-term fate of these chlorine molecules? This is the sort of question that must be addressed. (We leave it for a later paper). Once the final state is known (or, more accurately, hypothesized) the calculation itself becomes comparatively trivial.

Implications for Sustainability

To summarize the discussion up to this point, the economic system can be considered to be a kind of information processor. It converts materials with low value and information content into materials with high value and information content. In so doing, waste materials with physical information content are discarded. The potential for environmental harm attributable to such wastes depends on their information content. This can be interpreted as the magnitude of the "distance" from equilibrium with the local environment. Thus, as waste materials approach local equilibrium with the environment, the potential for future entropy generation — or II-potential — is a measure of their potential for driving uncontrolled chemical or physical processes in environmental systems. Eco-toxicity is nothing more nor less than environmental disturbance. Thus, potential entropy can be regarded as a measure of the a priori probability of eco-toxicity.

To avoid confusion, we emphasize the words "a priori potential". The II-potential of a waste stream is a zeroth order approximation to the probability of harm. It is the best measure only in the case where nothing else is known. It is not an adequate predictor.
of the actual damage that will be done by given pollutants. For example, it would not be a reliable measure of the actual toxicity of a given waste stream to a particular biological species. (Biochemists and toxicologists are still far from being able to predict the toxicity of a chemical from its structure). Nor would \Pi\text{-potential} be a reliable predictor of the effect of chlorocarbons, for instance, on the stratospheric ozone layer. In this case it is the detailed kinetics of atmospheric nitrogen and chlorine chemistry that matter. Even though the properties of the molecular species (all relatively simple ones) have been studied in laboratories for many years, the most sophisticated computer models are still unable to simulate the phenomenon with great precision. The "ozone hole" was completely unexpected, even though scientists had been modelling the chemistry of the stratosphere for a number of years.

Despite the foregoing caveat, we believe that there is a very useful role for the \Pi\text{-potential} in policy analysis. While it is too simplistic to be an adequate predictor of specific damages from specific pollutants, it is quite reasonable to postulate that the aggregate damage potential of human economic activity is proportional to the total \Pi\text{-potential} of aggregated waste emissions. We have previously suggested a criterion for sustainability (equation 2 above), namely that the average annual production of entropy by all natural processes plus human activities should be equal to the annual influx of \Pi\text{-potential} \(J_{\Pi}\) from the sun. This is a global criterion, but it has regional and sectoral implications.

These \Pi\text{-potentials} must be calculated in practice, to be of any value for policy. The computational problems are not unreasonably difficult, in many cases, given sufficient data. There are some problem areas, to be sure. Examples will be discussed in subsequent papers. However, several points can be made immediately. First, on the earth's surface neither thermal nor mechanical components of entropy generation are significant in most cases.

Second, since the potential for environmental harm depends on the differences between the chemical composition of the discarded materials and the composition of the environmental sink into which they are discharged, there is significant potential for matching wastes with localities. For instance, saline waste streams obviously do less damage if introduced into the ocean, than if they are discharged into fresh water. Similarly, mine wastes do less damage if they are restored to the same locations and strata from which they were removed.

Third, from simple mass-flow rate considerations, it is obvious that waste discharges will do much less harm if introduced into the deep ocean or into properly constructed landfills, old mines or other deep cavities in the earth (where the equilibration process can be extremely slow), than if they are discharged into the atmosphere or anywhere directly accessible to terrestrial biota.

A final point seems well worth emphasis: potential entropy (\Pi\text{-potential}) can be calculated for specific products in the "life cycle" sense. This is so because every material, and every mass flux have a computable \Pi\text{-potential}. Different processes to
produce a given product are already routinely compared in terms of "net energy", which is usually based on enthalpy or "heat of combustion". It would be comparatively easy to use Gibbs potentials instead. (While the heat of combustion is often a fair approximation to Gibbs potential, there are many cases where it is not). Such calculations would be objective and quite precise, given reasonably accurate process information.

For economic policy, a further implication can be drawn. It has long been conventional wisdom among environmental economists that the key to eco-sustainability is to "get the prices right". But how? Markets are effective devices for allocating resources when a number of conditions are met. One of the key conditions is that all of the relevant attributes of the goods and services being exchanged are fully known to all the parties, so that they can be taken into consideration in transactional decisions. It is not unreasonable, for example, for buyers and sellers of land to take into account attributes that they can sense directly, such as accessibility, air quality (in terms of odors and smoke) and view. It is much more difficult for people to make rational decisions about attributes they cannot sense and evaluate directly, such as long-term exposure to some toxic chemical. It is precisely for this reason that such risks are sometimes grossly exaggerated in the media and in the public mind.

At any rate, it is inherently difficult to incorporate "hidden" (i.e. indirect) attributes, or risks, associated with consumer products in their prices. Effluent taxes have often been advocated, but how should they be computed? One of the virtues of life cycle analysis (assuming it is done right) would be that such indirect effects could at least be brought to the attention of consumers, or of government officials. In principle, it would then be possible for governments to use taxes (which are, in any case, needed to raise revenue) as a way of shifting prices to better reflect these indirect effects.

Carbon taxes, energy taxes and even water taxes have been advocated in this spirit. For instance, an energy tax would be justified to the extent that indirect energy use is a reasonable proxy for potential environmental harm. We argue that II-potential, (or, at least, Gibbs potential) is a better proxy. It satisfies the basic requirement for a tax base. That is to say, products could be taxed, in theory, on the basis of their life-cycle potential entropy. This sort of tax would be — we believe — theoretically superior to water taxes, carbon taxes, energy taxes or other possible "effluent taxes" that have been proposed.

References


Waste Potential Entropy: The Ultimate Ecotoxic


