METHODS

Energy limits on recycling

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Abstract

Increasing efficiency of resource use is a major ecological-economics goal. Opportunities for large efficiency increases have been found in every area carefully investigated. What are the limits? Energy analysis offers powerful insights. Ayres has argued that, even with unlimited available energy, over time it becomes necessary to have ever-more dilute waste reservoirs. If correct, this would significantly limit the potential of a hypothetical sustainable spaceship, and of a ‘spaceship economy’. However, we know the world is self-contained and long lived, and that stable laboratory microcosms have been built. Thus, this assertion appears to violate reality. I argue that the alleged problem does not exist. Given available energy, there is no concentration limit on sustainability. My result is consistent with the work of Georgescu-Roegen and others. I estimate some numerical examples to show that present systems are extremely far from theoretical limits. For a long time to come, there will be vast opportunities to improve efficiency. The paper includes a classification schema for recycling based on chemical bonding and thermodynamic considerations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

If the society toward which we are developing is not to be a nightmare of exhaustion, we must use the interlude of the present era to develop a new technology which is based on a circular flow of materials such that the only sources of man’s provisions will be his own waste products. (Boulding, 1980)

The ‘spaceship earth’ metaphor of Boulding (1980, 1993a,b) provides a perspective encouraging husbanding of resources and recycling. Boulding conceptualized economies in terms of stocks and flows. To Boulding, a society that overly values throughput relative to stocks errs. The primary goal is to have a house, a shirt, or shoes, not their production. Flow is important primarily in the context of basic life-support. Survival requires flow of air and food. Boulding recognized that many biological/ecological resources are irreplaceable at any cost. He recognized that most physical re
sources are replaceable, given enough available energy.

The ‘spaceship earth’ metaphor appeals to ecologists, ecological economists and industrial ecologists. The metaphor provides wonderful imagery for the emerging field of industrial ecology, a field that takes as its goal the task of operating industrial systems with minimal external by-products (for example, Lifset, 1997; Lowenthal and Kastenberg, 1998; Moolensar and Lexmond, 1999; Rejeski, 1999). Industrial ecology is, in effect, the design of engineered subsystems that lead to reduced resource use, reduced emissions, and reduced environmental impact.

We live in a world focused on throughput. From an ecological-economic perspective, Kenneth Boulding’s focus on stocks rather than flows is a sound direction. However, so long as resources are used, it is incumbent upon us to use them effectively. Recycling is a key to this. However, while the directions are clear enough, details are inevitably murky. The futurist Willis Harmon expressed the need for modesty:

It is difficult for any of us to fully comprehend what is undoubtedly true: If the basic assumptions underlying modern society are indeed shifting in the way we have suggested, it follows that society will, only a few generations from now, be as different from modern industrial society as that is from society of the Middle Ages. Furthermore, it will be different in ways that we can only vaguely intuit, just as a Renaissance futurist would have had a hard time trying to describe modern society. (Harmon, 1988, p. 168)

While we cannot know how future societies will evolve, fundamental principles, especially conservation laws, impose limits. My focus here is on fundamental limits to recycling. I conclude that, if energy is available, the theoretical limit is minute. My analysis is inspired by an important article by Ayres (1999) in which he argues that theoretical considerations may in principle require large ‘waste baskets’ on idealized spaceships. While I disagree with his conclusion, I confirm that he has set the right agenda and asked the right questions.

2. How much recycling is theoretically possible?

From a physics perspective, recycling is best viewed in terms of energy. The primary considerations are energy conservation thermodynamics. These principles place limits on the usability of energy, and allow estimates of the minimum energy required for particular processes (Fermi, 1936; Davidson, 1962).

In the context of ecological economics, it is useful to note a recurring factor: Nicholas Georgescu-Roegen’s proposal of a ‘fourth law of thermodynamics’ (Georgescu-Roegen, 1971, 1980). This ‘law’ asserts the impossibility of complete recycling. This controversial proposal continues to provide intellectual stimulus. The idea underlies the suggestion by Ayres (1999) that theoretical limits to recycling exist. As he put it: “One can only wonder whether an interstellar spaceship capable of internally recycling all resources would have to be so large that most of its mass would have to be inactive by design”. Much of this paper explores thermodynamic arguments that show that Ayres’ conclusion is not persuasive.

3. Principles

My reasoning derives from energy and thermodynamic considerations. Ecological economists have long recognized the importance of this type of approach (Georgescu-Roegen, 1980; Mayumi, 1990; O’Connor, 1991, 1994; Biancardi et al., 1993; Ehrlich et al., 1993) The heart of recycling is the separation of components. All objects (natural, biological, or man-made) are constructed from atoms and bound by chemical or nuclear forces. The meaning of ‘bound’ is that energy is required to take things apart (to break chemical bonds). The inverse is also true: energy is released in the formation of compounds. A consequence of the first law of thermodynamics, conservation of energy, is that chemical and nuclear reactions are

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1 There have been many efforts to relate thermodynamics to economic considerations (for example, Mayumi, 1990; O’Connor, 1991, 1994; Biancardi et al., 1993).
ideally fully reversible. Precisely the amount of energy released when a bond is created must be added to take it apart.

Irreversibility, which inevitably occurs in practical processes, arises from disorder. Thermodynamics is the science of disorder. Limits on energy requirements for recycling can thus be reduced to analysis of energy and thermodynamics. The power of energy analysis is well illustrated with two examples from outside the recycling area. These examples provide context for the recycling analysis that follows.

3.1. Example 1. First law of thermodynamics: minimum energy to drive a car around a closed path

The theoretical limiting energy required to move a vehicle over a closed path is zero. This surprising conclusion may be understood as follows. Suppose the car is driven up a hill. The work done against gravity is $W = mgh$, where $m$ is the car mass, $g$ is the acceleration of gravity, and $h$ is the height. The work done to raise the car can, in principle, be recovered as the car descends the hill. There are many irreversible energy losses, but none of these are constrained by theoretical limits. For example, frictional loss in bearings can in principle be made arbitrarily small. Energy losses due to air drag can, in principle, be made arbitrarily small as by aerodynamic design and by moving the vehicle slowly. One can envisage linear-motor propelled, magnetically levitated trains operating in a vacuum, using minute amounts of energy compared with any existing transportation system. Perhaps the best example of the principle is found in a satellite, which moves in a vacuum and requires no energy input whatsoever.

3.2. Example 2. Second law of thermodynamics: ideal efficiency of a heat pump

The efficiency of a heat engine can be no greater than a limiting value established by the Carnot cycle. We use a more subtle illustration — a heat pump. Heat pumps are designed to move energy from a high temperature to a low temperature. Examples are air conditioners and refrigerators. Heat pumps are constrained by the second law of thermodynamics. The heat that can be moved to a cool reservoir (e.g. an air-conditioned house) from a warm one (typically outside air) is proportional to the external work (or power) input. The amount of heat, $Q$, that can be moved by an amount $W$ of external work (e.g. supplied by a motor) is constrained by an inequality.

$$Q \leq \frac{T_h}{T_h - T_c} \times W$$  \hspace{1cm} (1)

where $T_h$ is the absolute temperature of the hot reservoir (the outside) and $T_c$ is the temperature of the cold reservoir (the room from which energy is to be pumped (removed)). Equality applies in the ideal case, which is a limit and cannot be achieved in practice.

The beauty of this example is that it is both simple and surprising. The surprising result is that the ‘efficiency’ of the heat pump (the amount of energy pumped per unit external work input) increases as the temperature difference between the outside and the inside decreases. The efficiency of an ideal heat pump is exactly the inverse of the Carnot efficiency for a heat engine. Practical heat pumps are rated in terms of a ‘coefficient of performance’, which is a measure of their performance relative to this thermodynamically limiting value.

Fundamental principles allow one to calculate the ideal or best conceivable performance. Practical systems can then be assessed relative to the ideal. In the next section, we apply this idea to two simple but important recycling examples.

4. Recycling

The key to recycling is to make as much use as possible of order that exists in anything being recycled. Materials should be thought of in terms of ‘building blocks’. One should keep the largest
building-blocks that one can. If one is recycling a car, it makes sense to take out the copper wire and not allow it to mix with the iron of the engine and frame. The separated copper and iron can readily be refabricated. In contrast, alloys of iron and copper have poor properties and are difficult to separate.

This deep principle of recycling is entirely familiar to ecologists. Ecologists know how important it is to keep ecosystems intact. Once dismantled, they are at best difficult and usually impossible to reassemble.

The most difficult recycling problem occurs when building blocks are randomly distributed. Work is required to establish order. The problem is the same as separating different gases. The limiting case is ideal gases with no binding energy. In the next section, we analyze this case. I show later that the energy per atom (or per building block) required for separation increases as the system becomes more and more dilute. This means that recycling is easier if concentrations of desirable substances can be maintained at a high level.

Numerically, it turns out that, for atomic-scale building blocks the minimum energy per atom required for separation, even for very dilute gases, is small in comparison with typical chemical binding energies. The vast majority of current technologies are far from the limits. Theoretical calculations are, nevertheless, useful to provide benchmarks to measure how well one is doing. Design of any proposed self-sustaining spaceship should clearly benchmark against limiting calculations.

5. Energy of separation

The most difficult recycling challenge is the separation of randomly intermixed particles. This problem can best be approached through an ‘entropy of mixing’ calculation. While this is the most general approach, it is not particularly transparent. An energy-based calculation is more readily understandable.

Consider two perfect gases. By definition, perfect gases do not interact. Placed in a container, each distributes itself throughout the entire volume. To separate them, each must be compressed into a portion of the total container. As they are compressed, their pressures increase. In equilibrium, after compression, the pressures of the two gases must be equal. An impermeable membrane separating them experiences no force. This calculation is presented in Appendix A. The energy reduction when the two gases are mixed (which, except for sign, is identical to the energy that must be supplied to separate them) is (Appendix A):

\[ W = nRT \times \left[ x_1 \times \ln(x_1) + (1 - x_1) \times \ln(1 - x_1) \right] \]

where \( x_1 \) and \( x_2 = 1 - x_1 \) are the number fractions of molecules 1 and 2, \( \ln(x) \) denotes the natural logarithm of \( x \), \( R = 8.32 \text{ J/mol/K} \) is the gas constant, and \( T \) is the absolute temperature. At room temperature, 300 K, the energy is about 2500 J/mol, or (in atomic scale units) \( \sim 1/40 \text{ eV/atom} \).

This expression results directly from the work of compression of two ideal gases obeying Dalton’s law, which states that the pressure exerted by a mixture of gases is equal to the sum of the partial pressures of all the components. Real gases can deviate from Dalton’s law, but the approximation is adequate for the ‘order of magnitude’ estimates of interest here.

For low concentrations \( (x_1 < 1) \) the energy per mole associated with mixing is approximately:

\[ w = \frac{W}{n_1} \sim RT[\ln(x_1) + 1] \]

This may be written in dimensionless form as

\[ Z = \frac{W}{n_1 \times RT} = [\ln(x_1) + 1] \]

Eq. (4) is plotted in Fig. 1 for low molar concentrations. The energy associated with mixing can, at low concentrations, be somewhat larger than thermal energies, but is modest relative to typical chemical binding energies.

My idea that the ideal energy for recycling is small can be illustrated with examples from two very different domains: separating uranium from sea-water and separating helium from the earth’s atmosphere. Since currently available resources are far more concentrated than these sources, the
example is of theoretical interest only at this time. The value of the calculation is that it shows the theoretical separation energies to be so low that both uranium and helium could, in principle, be extracted at a cost that would only marginally impact practical applications such as electricity from uranium fusion or helium for welding.

5.1. Example 1: uranium in ocean water

The concentration of uranium in ocean water is about 3 parts per billion (Uranium Information Center, 1999). From Eq. (3), the minimum work required to separate one atom of uranium from seawater is about 0.5 eV. This energy is minute as compared with the energy release from nuclear fission of about 200 MeV. Thus, the separation process could be exceedingly inefficient and yet still yield a large net energy gain in fission energy technologies.

Practical experiments confirm this conclusion. Hiraoka (1994) has used a polymer absorbent to concentrate uranium from ocean water. He estimates that, at commercial scale, the process could produce uranium at about 34 000 yen/kg uranium ( ~ $300/kg). This would amount to about 11.8 yen (~ $0.001) per kilowatt hour (kwh), a small fraction of the several cents per kwh total cost of generating electricity in reactors.

Uranium ore from rocks contains up 2% uranium and uranium from ore bodies currently sells for far less than the cost of extraction from seawater. Hence, such extraction is of no commercial interest today.

Because the uranium content of sea water is extremely small, enormous amounts of water would have to be moved. The cost of moving so much water would be substantial. It is also likely that the environmental disruption associated with moving so much water would be considerable. At the present time, the example is of pedagogical rather than practical interest.

5.2. Example 2: helium in the atmosphere

The earth’s atmosphere contains about 700 000 billion cubic feet (~ 2.3 × 10^{13} m^3), an enormous quantity relative to annual use by society. The concentration is minute (0.0005%). Currently, commercial helium is extracted from certain natural gas reservoirs containing far higher concentrations (typically ~ 0.3% helium). Despite the low atmospheric concentration, the theoretical energy requirement for extraction is modest. A typical helium tank sold in the US contains 244 cubic feet (~ 8 m^3) of helium. Using Eq. (1), extraction of this amount of helium from the atmosphere would require about 5 million joules. This amount of energy from natural gas costs less than $1, and amounts to less than 1% of the selling price of a tank of helium gas (~ $100).

The American Physical Society (Dunn et al., 1996) calculated that recovery of the 3.2 billion cubic feet (~ 10^9 m^3) of helium used in commerce by the United States would require about 5% of total US energy. This is a factor of about 50 000 larger than the theoretical limit already calculated. Since there has never been any need to extract helium from air in commercial quantities, attention has never been given to achieving high efficiency. Should air extraction become necessary, it is clear that attention to efficiency would increase enormously.

The helium example is particularly interesting in that it shows how low theoretical limits can be compared with practical engineering, and suggests the possibility of enormous improvement should...
incentive appear. The literature of industrial engineering and efficiency engineering contains many examples of the successful search for major improvements. The ‘factor X’ debate provides a particularly helpful focus for this theme (Reijnders, 1998; Hawken et al., 1999).

6. Reservoirs

The presented analysis shows that the separation energy requirement per mole of a valued substance increases at low dilution. This means that it is best to run recycling systems at as high a concentration as possible. In this section, I approach the problem slightly differently, using the framework discussed by Ayres (1999). The analysis is described in words in the text. The mathematical details are presented in Appendix B. The example is for the simplest possible recycling system. This system consists of two components, a critical resource (CR) and a matrix material (M). These substances may be located in either an ‘in-service’ container or a ‘waste’ container. A recycling system removes material from the waste container for processing. Material concentrated in the critical resource is returned to the in-service container and reject material goes to the waste container. The separation process is imperfect. The output of the recycling system contains a fraction \( f(CR) \) of the critical resource. In the ideal case of (perfect separation), \( f(CR) = 1 \). The recycled stream is contaminated by a fraction \( f(M) \) of the matrix material. Material not returned to the in-service reservoir goes back to the waste reservoir. In the ideal case, none of the desired material is returned to the waste stream, so \( f(M) = 0 \).

Equation A4 (Appendix B) shows that, in equilibrium, the concentration of the critical resource in the in-service container is related to that in the waste container. The concentration ratio between the two containers is equal to the recycle efficiency for the critical resource \( f(CR) \) divided by the recycle efficiency for the matrix material \( f(M) \):

\[
\text{Concentration (in-service)} = \left[ \frac{f(CR)}{f(M)} \right] \times \text{concentration (waste)}
\]

In an ideal system, the critical resource is recycled with 100% efficiency. Thus, \( f(CR) = 1 \) while \( f(M) = 0 \). In this case, the recycler allows no matrix material to re-enter the in-service container. The in-service container therefore contains no impurities, and the waste container contains none of the critical material. A specified concentration of in-service material can be obtained by suitable choice of the three parameters on the right-hand side of the equation. If the concentration in the waste container is to be kept small, then the recycler must operate with high efficiency (high ratio of \( f(CR)/f(M) \)). As already argued, however, even exceedingly dilute waste streams can be concentrated with modest energy. There is no requirement that the waste container be large.

The discussion can be extended in a number of directions. Recycling can include multiple stages and can be designed with special subunits for processing particular chemical forms. Processes can use waste from one process as input to others. Technology also provides many means to reduce process leakage.

Design can eliminate or minimize dangerous or difficult-to-handle substances. Chlorine, for example, is a commonplace industrial feedstock that is dangerous to handle and if released to the environment can have serious consequences for humans and biota. At high concentrations, chlorine can damage respiratory tracts; at low concentrations, it damages the protective ozone layer. These adverse consequences have provided incentives not only for technical controls to minimize release, but also for new product design to provide needed services with greatly reduced or without chlorine.

All processes are inefficient and leak to some degree. Thus materials must be replaced. Sound systems design will do its best to limit loss and to control the places where lost material goes. Resources, e.g. energy, spent in resource recovery are resources not spent elsewhere (Van Berkel et al., 1997).

Ecologists and industrial ecologists recognize that the very idea of ‘waste container’ can be misleading. Just as ‘beauty is in the eye of the beholder’, so is it true that what is ‘waste’ to me may be feedstock to you. Indeed, some of the
most elegant examples of recycling have arisen from conscious efforts to design waste streams from one process so they can serve as feedstock to another (Socolow and Thomas, 1997).

7. Recycling classification

This section introduces a conceptual framework for thinking about recycling. The goal is to present a ‘schema’, not to offer recipes. The basic ideas underlying the approach are the centrality of sensitivity to chemical bonding energy and thermodynamics. Sound system design should focus on keeping the largest possible reusable ‘chunks’ in any stream, and should seek to maintain the highest possible concentrations in all feedstocks. This approach minimizes the work (and the cost) of recycling.

All useful substances, both man-made and natural, are ordered. Chemical compounds are carefully constructed to have specific structures. Manufactured items such as cars, computers, shirts and shoes have a high degree of order. Biological systems are the most ordered of all. A sound recycling program must give the study of order the highest priority.

The goal of any process designed to maximize recycling must be to maintain existing order, and to introduce new order. Thermodynamics is the study of order and disorder. Accordingly, thermodynamics provides the best framework for a general discussion of recycling.

Two principles provide the framework for conceptualizing any recycling question.
1. Concentrated materials require less energy and are easier to recycle than dilute materials. It is good strategy to separate materials and not allow them to mix and become dilute.
2. Ordered systems are easier to recycle than disordered systems. The energy associated with chemical bonds can, in principle, be recovered through reversible (non-entropy-creating) processes. Disorder places limits on reversibility. Increasing order requires inputs of energy (more precisely, available energy) in order to decrease entropy in the subsystem of interest.

Examples of ordered flow are water in a channel or river, and flow of electrons in a wire. Ordered flow may be conceptualized as a thermal system at infinite temperature. The reason electrical energy is a high-quality energy source is its effectively infinite temperature. Water flow is also effectively at infinite temperature, which is the reason that hydro-power plants can convert mechanical energy of flow to electricity at first law of thermodynamics efficiencies approaching 100%.

Recyclability can be conceptualized in three categories: (a) chunk size, (b) concentration, and (c) bonding. Multiple considerations and multiple objectives are necessarily involved. This multiple characteristic means that no unique ranking is possible. The ranking system presented in Table 1 is to provide insight and guidance.

I illustrate these concepts with several examples: (a) motor vehicle wiring; (b) steel scrap mixed with other waste; (c) used motor oil; (d) helium; (e) uranium ore; (f) agricultural runoff to rivers; and (g) end-of-pipe waste to rivers.

### Table 1

<table>
<thead>
<tr>
<th>Recyclability</th>
<th>Easier</th>
<th>Harder</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chunk size</td>
<td>Big</td>
<td>Small</td>
</tr>
<tr>
<td>2. Concentration of critical components</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>3. Bonding energy ratio (intra-component/intra-component)</td>
<td>Tight bonding</td>
<td>Loose bonding</td>
</tr>
</tbody>
</table>

7.1. Chunk size

The key idea here is that ordered systems are more valuable than unordered systems. Situations are common in which ordered systems are embedded within disordered systems. Motor vehicle wiring is generally made of copper wire. Under old practices, entire vehicles were melted down. This mixed the copper with steel, thereby degrading the quality of the steel and making the copper inaccessible. Modern practice uses removable wiring assemblies. The copper can be recycled with minimal contamination, and the steel is no longer...
contaminated. The wire harness constitutes a macroscopic 'chunk'. Steel scrap mixed with other waste (e.g. aluminum cans) can be magnetically separated with low energy cost. The aluminum can be separated with eddy current or flotation techniques. The 'chunks' in this case are tightly bound pieces of steel or aluminum, loosely coupled to each other. Macroscopic separation is generally preferable to microscopic separation. The reason is that there is less mixing of subclasses of materials, thereby reducing the need for separation at the atomic or molecular level.

7.2. Concentration

The higher the concentration, the easier the recycling. As already discussed for helium and uranium, the energy per mole of the desired substance required for concentration from a mixed gas increases as concentration decreases. In practice, low concentrations require moving large amounts of host material, thereby costing energy due to viscous forces, etc. Dumping of materials into waterways decreases concentration and complicates recycling. Agricultural runoff is a generally non-point-source and is very difficult to deal with. Waste appearing at pipe-ends is relatively concentrated and should be dealt with prior to dumping into a river. A polluted river joining a less polluted river leads to lower pollutant concentration in the merged river. The general guideline is: when possible, do not dilute.

7.3. Bonding

A definition of an ordered subsystem is that it is tightly bound internally, and distinguishable from its environment. A goal of recycling should be to separate the ordered subsystems. The motor vehicle wiring harness is bonded to the vehicle loosely, except for connections and hold-downs. These tight bonds are designed so they can be easily broken in the recycling process. Aluminum cans and steel scrap are tightly bonded internally, but pieces are usually weakly bonded to each other.

8. Observations

This paper has focused on recycling. However, viewed in the large, it is not the difficulty of concentrating dilute materials that matters most. It is rather that what is waste from one perspective can be a critical resource to another part of the system. For example, the atmosphere and the oceans have long been used by humans as dumps, yet they are critical parts of our life-support system and we pay heavily when we allow them to become contaminated. What is waste to one part of the system is feedstuff to another. We must learn how to keep pollution levels low enough as not to cause damage to any system that depends on it. The latter is a key issue for global warming. From an ecological perspective, there is little exaggeration to assert that there is no such thing as a waste stream.

Sound system design should seek to contain materials to the maximum extent feasible, and to minimize waste streams. This criterion can be met by tight containment associated with highly efficient recycling systems taking their feed at the highest-concentration points available. When substances released to general pools (e.g. atmosphere, lakes, oceans) remain at low concentrations, they are difficult to recover but do no harm. As concentrations increase, harm inevitably occurs (e.g. pesticide water contamination and CO₂ greenhouse contamination), but the higher concentrations can, to a degree, simplify removal or reprocessing. There are no ‘in principle’ reasons why waste reservoirs need be large.

Biological and ecological resources often fall into a qualitatively different category from non-biological resources. They cannot be manufactured. Once lost, a species is gone forever. Humanity must be careful not to allow arrogance about our ability to recycle to distract attention from our inability to recreate biological and ecological elements of our life-support system. This limitation is crucially important on earth. It is a critical management consideration for any sustainable spacecraft, including spaceship earth.
Appendix A

Thermodynamics provides a lower limit on the amount of energy required for recycling. This lower limit is often discussed in terms of the ‘entropy of mixing’ of two gases. Entropy analysis is of broad applicability, but the concepts are far less intuitive than energy analysis. The Second Law of Thermodynamics places important constraints on what is and is not possible. We are interested in the limits of recycling. That is, we want to understand what is possible in order to provide benchmarks against which practical recycling techniques may be measured.

Modern research on the Second Law of Thermodynamics reaffirms the high place in the pantheon of knowledge accorded it by Albert Einstein, who wrote: “A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of its basic concepts, it will never be overthrown” (quoted in Lieb and Yngvason, 2000). Lieb and Yngvason (2000) describe an entirely new way of looking at the Second Law. The approach focuses on comparison of states, with entropy appearing as a key variable and temperature emerging in a natural way as a derived concept. The approach avoids statistical mechanical models. Thermodynamic reasoning regarding recycling is as fundamental as is energy analysis in work on energy efficiency.

Our goal here is to establish limits. We find it useful to frame recycling in energy terms via an elementary energy analysis for a perfect gas. (Fermi, 1936; Davidson, 1962, p. 60).

The molecules of a perfect gas do not interact. The pressure produced by two perfect gases in a container is thus the sum of the pressures that each would produce alone (Dalton’s Law). Consider two gases at the same pressure but in separate containers. Place the container in an isothermal bath so it can absorb or reject heat. Because the pressures are equal, an impenetrable barrier separating the two gases will experience no force. Now remove the barrier. Each gas expands to fill the entire region. As the gases expand, they do work. This work appears as heat, which flows into the surrounding bath. After expansion, the system of two gases has a lower energy.

The work of compression to separate the two mixed gases is calculated as follows. The perfect gas law is \( PV = nRT \), where \( T \) is constant, \( R \) is the gas constant (8.2 J/mol) and \( n \) is the number of moles.

A.1. Initial state: both gases occupy volume \( V \)

\[ V_1({\text{initial}}) = V_2({\text{initial}}) = V({\text{initial}}) \]

The partial pressures differ, and are given by:

\[ P_1({\text{initial}}) = n_1 \times \frac{RT}{V} \]
\[ P_2({\text{initial}}) = n_2 \times \frac{RT}{V} \]

A.2. Final state: both gases are at the same pressure

\[ P_1({\text{final}}) = P_2({\text{final}}) = P({\text{final}}) \]
\[ V_1({\text{final}}) = n_1 \times \frac{RT}{P_1({\text{final}})} \]
\[ V_2({\text{final}}) = n_2 \times \frac{RT}{P_2({\text{final}})} \]

The molecular fraction of the first gas is

\[ x_1 = \frac{n_1}{n_1 + n_2} \]

The molecular fraction of the second gas is

\[ x_2 = \frac{n_2}{n_1 + n_2} = 1 - x_1 \]

The final pressure is

\[ P({\text{final}}) = n_1 \times \frac{kT}{[V_1({\text{final}})]} = n_2 \times \frac{RT}{[V_2({\text{final}})]} = n_2 \times \frac{RT}{[V - V_1({\text{final}})]} \]

Using the molecular fractions \( x_1 \) and \( x_2 \), the volumes of the two components are:
The work done on the first and second gases is $W_1$ and $W_2$. The total work of separation is $W = W_1 + W_2$:

$$W = W_1 + W_2 = \int (n_1 \times RT/V_1) \, dT$$

$$+ \int (n_2 \times RT/V_2) \, dT$$

$$= RT \{ n_1 \times \ln[V_1(\text{final})/V] + n_2 \times \ln[V_2(\text{final})/V] \}$$

$$= nRT \{ x_1 \times \ln(x_1) + x_2 \times \ln(x_2) \}$$

$$= nRT \{ x_1 \times \ln(x_1) + (1 - x_1) \times \ln(1 - x_1) \}$$

(A1)

The work per mole of gas 1 is $w = W/n_1$

$$w = W/n_1 = RT \{ \ln(x_1) + [(1 - x_1)/x_1] \}$$

$$\times \ln(1 - x_1)$$

(A2)

This calculation is for a perfect gas compressed reversibly. If the process is irreversible, additional work may be required.

For low concentration, $x_1 \ll 1$, $\ln(1 - x_1) \approx -x_1$, and the work per mole (Eq. (A2)) reduces to:

$$W \sim RT \{ \ln(x_1) + 1 \}$$

For an isothermal reversible process, the entropy change is given by $S = \text{work}/T$. This yields the standard expression for entropy of mixing, which is valid even for irreversible processes:

$$S = nR \{ x_1 \times \ln(x_1) + (1 - x_1) \times \ln(1 - x_1) \}$$

(A3)

### Appendix B

This example is the simple two-reservoir recycling model presented by Ayres (1999). The notation has been slightly changed for clarity. The system, shown in Fig. 2, consists of two materials, two reservoirs, and a materials recovery (recycling) unit.

The materials consist of a critical resource (CR) and a matrix material (M). These materials flow from an in-service reservoir (in-service) to a wastebasket reservoir (waste).

The masses $M_{CR}$ and $M_M$ of the resource and matrix materials in the in-service reservoir are: $M_{CR}(\text{in-service})$ and $M_M(\text{in-service})$. The concentration of the critical resource of the in-service reservoir is:

$$\text{Concentration(in-service)} = M_{CR}(\text{in-service})/M_M(\text{in-service})$$

The waste reservoir contains masses $M_{CR}(\text{waste})$ and $M_M(\text{waste})$. The waste concentration is:

$$\text{Concentration(waste)} = M_{CR}(\text{waste})/M_M(\text{waste})$$

Both the critical resource and the matrix material flows from the active to the inactive reservoir. The critical resource flows at a rate $d(CR)$ (per s). The mass flow of the critical resource is $d(CR) \times M_{CR}(\text{in-service})$. The matrix material flows at a rate $d(M)$ (per s) so the total mass flow is $d(M) \times M_M(\text{in-service})$.

Material flows from the waste container to the recovery unit at rate $w$ (per s). The rates of flow of both the critical resource and the matrix material are identical. The mass flow of the critical resource is $w \times M_{CR}(\text{waste})$. The mass flow of the matrix material is $w \times M_M(\text{waste})$.

The recovery unit has less than 100% efficiency. Of every unit of critical resource flowing in, a fraction $f(CR)$ is transferred to the (in-service) stock and the remainder $1 - f(CR)$ is returned to the waste reservoir. Ideally, $f(CR) = 1$.

Fig. 2. Flow with imperfect recycling in a two-component system consisting of a critical resource (CR) and a matrix material (M). See Ayres (1999) and Appendix B.
Similarly, a fraction \( f(M) \) of the matrix flows from the recovery unit to the in-service reservoir, the remaining fraction \( 1 - f(M) \) returning to the waste reservoir. Ideally, \( f(M) = 0 \).

These equations may be solved dynamically, either analytically or using a computer technique such as STELLA (for example, Ford, 1999) For the special case where the system is linear, the response to a step change in a stock is exponential and approaches to a new equilibrium.

In steady-state, mass must balance for both the critical resource \( CR \) and the matrix \( M \).

For the critical resource \( CR \), the mass balance equation is:

\[
dM_{\text{CR}(\text{in-service})} = f(\text{CR}) \times w \times M_{\text{CR}(\text{waste})}
\]

For the matrix material \( M_M \), the mass balance equation is:

\[
dM_{M\text{(in-service)}} = f(M) \times w \times M_{M\text{(waste)}}
\]

The ratio of the critical resource \( [CR] \) concentration in the in-service container to that in the waste container is found to equal the ratio of the recycle efficiency for the critical resource divided by the recycle efficiency for the matrix material:

\[
\frac{\text{Concentration(\text{in-service})}}{\text{Concentration(\text{waste})}} = \frac{f(\text{CR})}{f(M)} \quad (A4)
\]

The choice of recycle technology drives the ratio of the concentrations of the critical resource in the in-service and the waste reservoirs. There is no term involving the concentration of the critical resource in either reservoir.

References


Rejeski, D., 1999. Learning before doing: simulation and

