Thermodynamics and Recycling, A Review

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Abstract—**Thermodynamics provides a value system and rules for evaluating separation and recycling systems. After a brief development to calculate the minimum work required to separate an ideal mixture, we review what thermodynamics has to say about four questions: 1) What gets recycled? 2) What gets lost? 3) What gets saved? and 4) How can we improve the system.**

Index Terms— **Recycling, Thermodynamics, Materials Separations**

I. INTRODUCTION

Recycling is generally thought of as an attempt to close a material loop with an additional input of energy. That is, by nature's own model, discarded mixed materials are restored to their original pure condition for re-use. Economically minded people recycle when the value of the reclaimed materials exceeds the cost to capture and restore them. Ecologically minded people recycle to conserve resources (or so they hope). Often the two do not agree. The main difference between these two points of view is the value system employed. Thermodynamics presents an alternative value system which can bring new understanding and insights to the issues of recycling. It can account for the restoration and loss of resources in a rigorous way. Furthermore, it is often the case that certain "scaling effects" suggested by thermodynamics often agree closely with observations of economic behavior.

Here we review briefly what Thermodynamics says about four important recycling questions: 1) What gets recycled?, 2) What gets lost?, 3) What gets saved? and 4) How can we improve the system? First we review briefly a thermodynamic analysis of an ideal material separation system.

II. A THERMODYNAMIC MODEL OF SEPARATION

The basic notion that materials are degraded as they are mixed and dispersed, and that something of value is lost in this process can be stated rigorously using thermodynamic principles. Additionally, thermodynamics can calculate the minimum amount of work required to separate a mixture and to restore the original value of the materials. The two problems are related. The development presented here applies to the separation of an ideal two component molecular mixture into it's pure components. Ideal mixtures include ideal gas mixtures and ideal solutions, but not necessarily many of the material separation situations that occur in recycling, material extraction and material purification. These cases may deviate from ideal mixtures because of specific interactions between dissimilar molecules, such as volume effects and heat effects, or because the mixtures are not actually molecular mixtures. Never the less, the ideal mixture result can provide guidance, for example, by suggesting scaling effects that could apply to many situations including non-ideal processes. An introduction to the thermodynamics of mixing and separation can be found in the text by Cengel and Boles [1]. The development here follows the lead of Gyftopoulos and Beretta [2].

Consider the open system shown in Fig. 1. A mixture denoted by "12" at temperature T_0 and pressure p_0 enters on the left and the pure components "1" and "2", also at T_0 and p_0, exit on the right. Each stream has enthalpy *"H"* (measured in Joules, J) and entropy *"S"* (measured in J/°K) which will be denoted by their subscripts. The system has a work input *W* and can exchange heat Q with the surroundings at temperature T_o. One can then write the rate balance equations (shown by the dot over each variable that changes with time) for constituents, energy and entropy as given below.

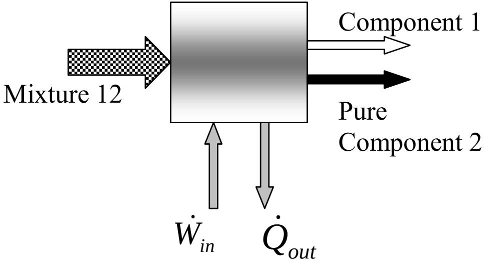

Fig 1 An ideal separation process

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$$\frac{dN_{i,sys}}{dt} = \dot{N}_{i,in} - \dot{N}_{i,out} \quad i = 1,2 \tag{1}$$

$$\frac{dE}{dt} = -\dot{Q}_{out} + \dot{W}_{in} + \dot{H}_{12} - \dot{H}_1 - \dot{H}_2 \tag{2}$$

$$\frac{dS}{dt} = -\frac{\dot{Q}_{out}}{T_0} + \dot{S}_{12} - \dot{S}_1 - \dot{S}_2 + \dot{S}_{irr} \tag{3}$$

Where N_i are in moles, and “S_{irr}“ is the entropy production. This term allows us to write (3) as a balance even though entropy is not conserved. Assuming steady state and eliminating the heat rate *Q dot* between (2) and (3) yields an expression for the work rate for separation.

$$\dot{W}_{in} = ((\dot{H}_1 + \dot{H}_2) - \dot{H}_{12}) - T_o((\dot{S}_1 + \dot{S}_2) - \dot{S}_{12}) + T_o\dot{S}_{irr} \tag{4}$$

The mass balance is implied because the terms in (4) are all extensive. This result can also be written using the molar intensive forms of the thermodynamic properties (denoted by lower case font) as,

$$\dot{W}_{in} = -\dot{N}_{12}(\Delta h_{mix} - T_0\Delta s_{mix}) + T_0\dot{S}_{irr} \tag{5}$$

or,

$$\dot{W}_{in} = -\dot{N}_{12}\Delta g_{mix} + T_0\dot{S}_{irr} \tag{6}$$

Where $\Delta h_{mix} = (h_{12} - x_1h_1 - x_2 h_2)$ and $\Delta s_{mix} = (s_{12} - x_1s_1 - x_2s_2)$, and x_1 and x_2 are mole fractions, (N_1 / N_{12} *and* N_2 / N_{12} respectively), with $N_{12} = N_1 + N_2$. And recognizing the term within the double brackets in (5) as the intensive form of the Gibbs Free Energy of Mixing, i.e., $\Delta g_{mix} = \Delta h_{mix} - T_0\,\Delta s_{mix}$.

We can now obtain an expression for the minimum work of separation per mole of mixture by letting $\dot{S}_{irr} = 0$ This gives the minimum rate of work as

$$\dot{W}_{min} = -\dot{N}_{12}\Delta g_{mix} \tag{7}$$

and the minimum work as

$$w_{min} = \frac{\dot{W}_{min}}{\dot{N}_{12}} = -\Delta g_{mix} \tag{8}$$

That is, the minimum work of separation is negative the Gibbs Free Energy of mixing. When two substances spontaneously mix, the Gibbs Free Energy of mixing is negative. So the minimum work required to separate these is the positive value of Δg_{mix}. Loses in the system i.e., $\dot{S}_{irr} > 0$, will make the work required even larger. If we consider the reverse problem, the one of mixing two pure streams, this could be accomplished without any work input provided $\Delta g_{mix} < 0$ (A common enough occurrence for many systems). Now the irreversible loss upon mixing is

$$T_0\dot{S}_{irr} = -\dot{N}_{12}\Delta g_{mix} \tag{9}$$

That is, the irreversible loss upon spontaneous mixing is the same as the minimum work for separation. Compare with (7). (Note the sign change when you write the material flows in the opposite direction.)

For an ideal mixture the enthalpy of mixing is zero, i.e., $\Delta h_{mix} = 0$. Hence the minimum work for separation becomes

$$w_{min} = T_0\Delta s_{mix}. \tag{10}$$

The mixing entropy Δs_{mix} can be calculated from the case of mixing ideal gases, or from a statistical interpretation of entropy and Boltzmann’s equation, with the same result.

$$w_{\min} = -T_0 R\sum_{i=1}^{n} x_i \ln x_i \tag{11}$$

This is the general result for a mole of mixture with “n” constituents, x_i is the mole fraction of the “i^{th}” constituent, and R is the universal gas constant, 8.314J/mole°K.

When there are only two components in the mixture, as is the case in Fig. 1, the result, for the work required per mole of mixture, then is

$$w_{\min} = -T_0 R(x\ln x + (1-x)\ln(1-x)) \tag{12}$$

Here the mole fraction of component 1 is x and for component 2 it is $(1 - x)$. This equation is symmetric, giving the largest work when $x = ½$ (at $T_o = 298.2$ °K, this is 1.7 kJ/mole of mixture) and, at the end points ($x = 0, 1$) the work is zero. Equation (11) can be further manipulated to give the work required to extract one mole of the material “1” from a mixture at a constant mole concentration “x”, (see [1]) as

$$w_{\min,1} = T_0 R(\ln\frac{1}{x}) \tag{13}$$

This equation is monotonically increasing as one tries to extract “1” at more and more dilute concentrations. In fact, in the limit as x → 0, the term ln(1/x) goes to infinity. This means the work to extract a valuable material from a dilute mixture increases without bounds as the solution becomes more and more dilute. Or put another way, the work to extract the last bit of impurity from an ultra pure material also increases without bounds as the purity requirement increases. These general behaviors have been commonly observed for many different materials extraction and purification processes, both for ideal and non-ideal mixtures. See for example, Krishnan et al in this Proceedings [3].

III. WHAT GETS RECYCLED?

Although recycling can be modified and even mandated by policy, the rules of the game are often essentially economic. When non-economic policy is put into place, the people who pay for the shortfall may push back which acts to reduce these instances. At the same time it is usually the case that the economic analysis is incomplete. Few economic analyses fully account for the social costs of not recycling, and it is usually the case that these social costs are not well known, and can well be beyond the purview of the payers. Thermodynamics can not solve these problems, but it has found utility as a conceptual representation of the costs and difficulty to separate and reclaim materials. In particular, entropic measures, either from Thermodynamics or from Information Theory have served well as surrogates for a) separations from dilute solutions, and b) separations from concentrated multi component solutions.

In the first case, it has been found empirically that for many materials under widely differing circumstances that are produced by extraction from a dilute solution (including gases, liquids and solids) that log (price) or in some cases log (cost) is proportional to log (1/concentration). This phenomenon has been documented in the so-called "Sherwood Plot" [4], [5], [6], [7], [8], [9]. Reference [10] for example, gives a very comprehensive and up to date version of this plot. See Figure 1. Referring to (10) this suggests that log (price or cost) scales like the minimum work of extraction.

In the second case, we have examined many different cases of product recycling where the resulting material mixtures are made up of many different components and have found clear evidence that the cost of separating these mixtures scales as the minimum work of separation as given in (11), [11]. In this work however, entropy, H, is obtained from Information Theory and is measured in bits. See Figure 2.

In both cases, the cost of separation appears to follow an analogy with thermodynamics. The interpretation of Figures 1 and 2 is similar; materials mixtures found above and to the left of the appropriate diagonal line in the figure are profitable to separate, while those below and to the right are unprofitable. In these empirical interpretations it is almost always the case that the concentrations are plotted as mass fractions and not mole fractions based primarily on convenience.

IV. WHAT GETS LOST?

Recycling is an imperfect process and some fraction of discarded materials will, under practical constraints, not get recycled. The first and sometimes largest loss is from the dispersive use of materials. This increases collection and separation effort and is portrayed clearly in the Sherwood Plot. For example, metals dispersed in ores with concentrations in the range of 0.1 – 1.0 ppm must have values on the order of gold to be economically recaptured.

Thermodynamics can also enable us to calculate what gets lost in the separation process. For example, once we know the minimum work of separation as given by equations (8), (9), and (10) above, we can compare this with the actual energy input required to separate the materials and calculate the efficiency of this process. See Table below.

TABLE I
ESTIMATED EFFICIENCIES OF SEPARATION PROCESSES

Materials	**Separation Process**	**Efficiency**	**Ref.**
Propane/ propylene	Distillation	2% $(-\Delta g_{mix}/Q)$	[12]
Various metallic ores	Mining and milling	0.3% $(-\Delta g_{mix}/E)$	[5]
Hexane/ polybutadiene	Steam vaporization	0.1% $(-\Delta g_{mix}/Q)$	[13]
CO_2/ combustion gas	amine stripping	3.6% $(-\Delta g_{mix}/Q)$	[14]

As can be seen these separation processes which cover many different materials and methods are quite inefficient. In fact, in a review of separation technologies, King states that most separation processes "use more than 50 times as much energy as is thermodynamically required to perform the separation" [7].

V. WHAT GETS SAVED?

In spite of the high losses one sustains in material separation and recycling processes, the effort is often well worth it. From an economic point of view, this assertion can be proven by the existence of profitable separation and recycling systems. At the same time it should be noted that not all recycling efforts are profitable [15], [16]. From an energy and/or environmental point of view, one way to test this assertion is by conducting a life cycle analysis. These kinds of analyses generally confirm the widely held notion that recycling saves energy (or exergy) and reduces impacts on the environment when compared to other end-of-life options [17] & [18]. Often these favorable results are due to some measure of reuse potential, such as the potential ability to displace virgin production [17], or the available energy stored in these materials as exergy [18]. For example, Chapman gives the following energy requirements for secondary metals production (recycling) as a percent of primary production (virgin) as: 28% steel, 14% copper, 6% aluminum, 39% zinc, 23% lead, and 33% titanium [5]. These numbers depend upon technology and input materials, but in a general sense reflect that significant savings are the usual case.

VI. HOW TO OPTIMIZE THE SYSTEM?

Systems cannot be optimized if they cannot be quantitatively characterized. Thermodynamics provide tools and a value system for doing this. In the recycling arena, several researchers have provided thermodynamic frameworks for characterizing recycling systems both at the grand scale, largely by analogy, and at the molecular scale for specified material systems, where rigorous thermodynamic methods apply [9], [11], [18], [19], [20], [21].

In general this area is just being developed as recycling grows in importance, and new developments and applications can be expected. For example, there are several efforts that address the application of various entropic metrics for characterizing and optimizing recycling and other end-of-life processes. These include entropy measures to optimize copper recovery [22], Shannon Information measures to optimize solid waste incineration [23], and Exergy Analysis to optimize metal recovery [21]. We have developed Bayesian models for materials separation which can be used in conjunction with various entropic models for recycling systems optimization [24]. In addition, it should be noted that recycling systems have several features in common with energy systems, (in particular multiple product outputs and intermediate streams with poorly defined market values) which suggest that various methodologies called "thermoeconomics" and "exergoeconomics", which have already been developed could, with appropriate modification, be applied to the optimization of recycling systems [25], [26], [27].

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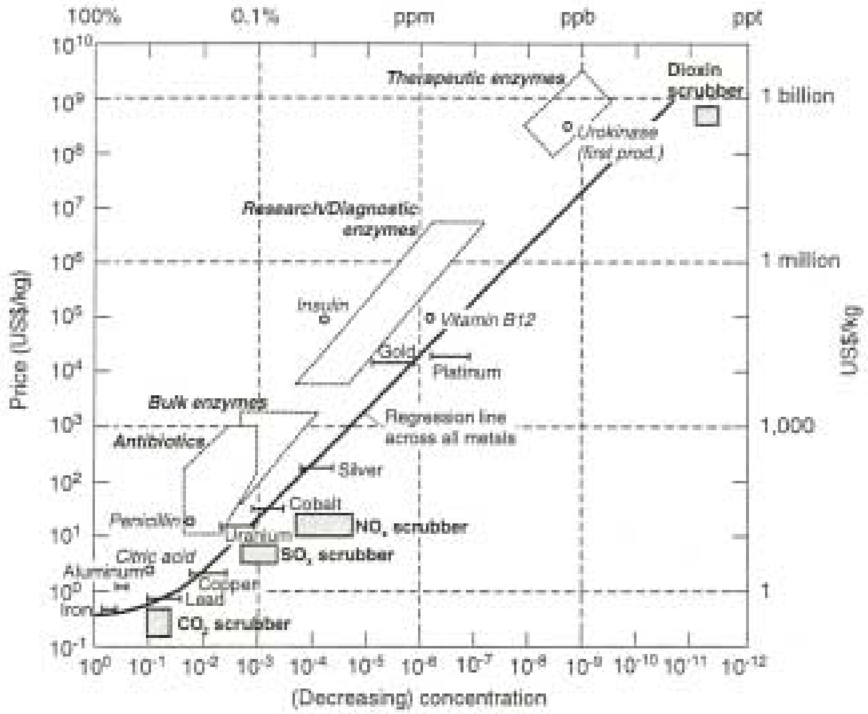

Figure 1: Sherwood plot showing the relationship between the concentration of a target material in a feed stream and the market value of (or cost to remove) the target material. Ref [10].

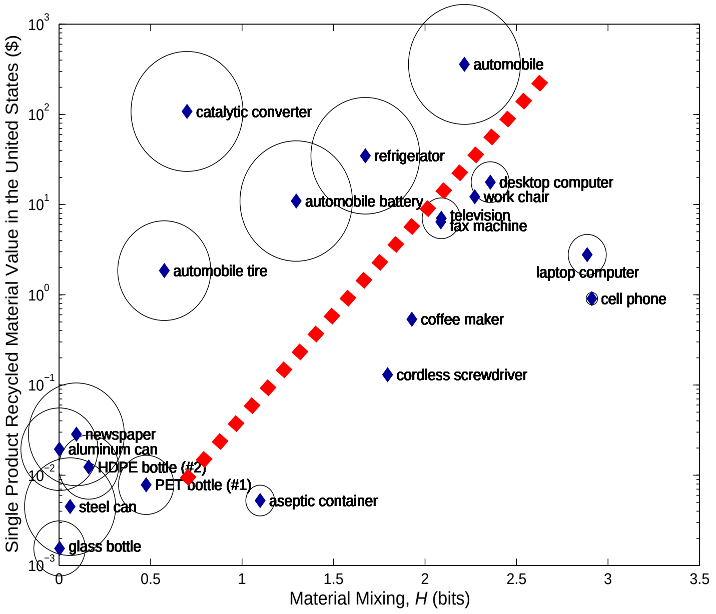

Figure 2 Single product recycled material values ($\Sigma m_i k_i$) and material mixing entropy (H) with recycling rates (indicated by the area of the circles) for 20 products in the US. The "apparent recycling boundary" is shown as a dashed line, see [11].