

**ECO-THERMODYNAMICS: EXERGY  
AND LIFE CYCLE ANALYSIS**

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# **ECO-THERMODYNAMICS: EXERGY AND LIFE CYCLE ANALYSIS**

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## **Abstract**

This paper argues that thermodynamics offers a means of accounting both for resources and wastes in a systematic and uniform way. Unfortunately, the proposed measure has been called by several different names, including *available work*, *availability*, *exergy*, *essergy*, *potential entropy*, and *physical information (pi potential)*, by different authors, in different countries and for different purposes. At bottom, however, exergy is a measure of distance from thermodynamic equilibrium. It is not a conserved quantity (like energy) but it is possible to construct an exergy balance for any energy or materials transformation process, accounting for inputs, process losses, useful products and wastes. The essential unity underlying the various independent definitions and research efforts has not been recognized until recently. Most of the basic data has been compiled, and has been published in the scientific literature. Unfortunately, because it was done mainly in the context of design optimization in mechanical, chemical and metallurgical engineering, the relevant publications are not very accessible to non specialists.

The new feature of the present work is to extend the applications of exergy analysis into the realm of resource and waste accounting, and to present the results in an integrated analytical framework, namely life cycle analysis (LCA). To do this for a non-specialist audience requires considerable background explanation. This is done in Part I (sections 1 through 6). Applications and examples are discussed in subsequent sections (part II). The paper concludes that the proposed measure (which we call *exergy* hereafter) is indeed feasible for general statistical use, both as a measure of resource stocks and flows, and as a measure of waste emissions and potential for causing environmental harm.

# PART I

## 1. Introduction: Why Thermodynamics Is So Difficult

Thermodynamics is the branch of science dealing with the phenomenon of physical (and chemical) equilibrium and the extraction of "useful work" from the processes of equilibration in systems. It is important to other branches of science, from geology to biology and ecology to economics and social science, because it deals with the available (transformable) component of energy stocks and flows. Energy is the basic currency of physical events. The laws of thermodynamics are therefore fundamental to all actions, all reactions, all occurrences, indeed everything that changes or "happens" in the universe. In a sense, thermodynamics is the science of change as regards material substances, from the molecular scale to the planetary scale (or even beyond).

Thermodynamics has been a difficult subject to learn and understand — and correspondingly difficult to teach — for at least three reasons. The first relates to its particular history. The second reason has to do with complexity. It has been convenient, for various purposes, to define a surprisingly large number of different thermodynamic variables, each of which is particularly convenient for one class of applications. Thus, several different derivations of most of the basic thermodynamic equations exist, based on different variables and even different assumptions. Some of these variables have been defined and used in several different ways in different countries (and some of the definitions in the literature are actually faulty).

A further difficulty for most students is that much of thermodynamics was developed originally to explain a set of relationships that apply only to an idealized and unrealistic situation, namely for *reversible* processes. Finally, all formulations of thermodynamics involve a number of variables that are *unobservable*. They are abstractions, defined from other variables (often also unobservable), with no obvious or direct link to experience. To make matter worse, some of these non-observable abstractions are defined only in special cases.

I do not mean to imply that the difference between an observable variable and a non-observable (i.e. constructed) variable is a fundamental one. The direct link to human experience is unimportant as far as the theory goes. However, it is a great help to a student of any subject to have some intuitive understanding of the variables being used. This is relatively easy when the variable interacts directly with one of the human senses (like pressure, temperature or color) or can be measured in some straightforward way (like mass or volume). Conversely, if the variables cannot easily be understood in terms of everyday experience, it is very difficult to explain their relationships except in terms of mathematical relationships with other variables. Examples of such abstract variables include enthalpy, entropy, internal energy, Helmholtz free energy, Gibbs free energy and exergy. The latter variable is the main subject of this paper. Nor is the distinction unambiguous. There are "in-between" cases. Heat and work are both intermediate cases, being both abstract and yet somehow familiar.

Before proceeding to the main subject of the paper, therefore, it is worthwhile spending a little effort on explaining and interpreting the variables.

## 2. The Variables of Thermodynamics

Every thermodynamic system is characterized by two *kinds* of variables. *Extensive* variables are functions of the size of the system. Obvious examples are volume  $V$ , particle number  $N$ , or mass  $M$ . There are several others, such as internal energy  $U$ , heat  $Q$ , and entropy  $S$ , which will be discussed later. But extensive variables have the property that when two systems — say A and B — are combined, their extensive variables are simply added together. In other words, the volume of the combined system is the sum of the individual volumes, the mass of the combined system is the sum of their individual masses, and so on.

The second kind of variable is known as *intensive*. An intensive variable is a local property of the system that is independent of its size or magnitude. It may be the ratio of two extensive variables. For instance, density  $d$  is the ratio of mass  $M$  to volume  $V$ :

$$d = M/V \quad (1)$$

However, intensive variables are also definable for systems that are not internally equilibrated. Thus, the local density of such a system might differ from the ratio  $M/V$ , which then refers only to the average density. Other intensive variables include temperature  $T$ , and pressure  $p$ . The main point here is that when two thermodynamic systems are combined, their intensive variables do not simply add together. The temperature of a two systems combined together (after they reach equilibrium) is not the sum of their individual temperatures, but rather it is a mass-weighted average. The density of A + B is the ratio of the sum of the masses to the sum of the volumes, and so on for other intensive variables.

As mentioned above, volume and weight (or mass) are accessible to the senses (i.e. observable) and easy to measure. Thus, density (equation 1) is also fairly straightforward to calculate. Temperature  $T$  and pressure  $p$  are also both accessible to the human senses (the inner ear, in the case of pressure). Temperature is commonly measured by simple analog thermometers. Similarly, atmospheric pressure is measured by analog barometers. These instruments have been in everyday use for hundreds of years. In these two cases it is fairly easy to understand the thermodynamic measure by extrapolation from experience.

On the other hand "heat" is a much less straightforward concept. It cannot be sensed directly, as can temperature. It can be measured (by a specialized device called a calorimeter), but calorimeters are not found in every household and most people have never seen such a thing. It is difficult for the average person to make a clear conceptual distinction between the temperature of a source of heat, a quantity of heat, and a flow of heat. It is often the latter that we are really thinking of, when, for instance, we speak of "heating" a house or a kettle of water. Work (or mechanical work) is another difficult case. In thermodynamics it is said that a system "does work" on another system. When work is done on a system it changes in one or more of several ways: the system may be compressed and heated at the same time, it may acquire kinetic energy of motion, it may acquire gravitational potential energy, it may acquire electromagnetic potential energy or it may be heated by friction. In all of these cases work converted to another form of energy. Usually work is done by a machine or engine — sometimes called a "prime mover".

Energy, while seemingly familiar, is an even more difficult and abstract concept to grasp. It is not directly accessible to the human senses, and it cannot be measured directly (i.e. there is no such thing as an "energy-meter"). Though we use the term "energy" constantly, we use it so loosely that it conveys no precise meaning. What most people think of as energy (as in the "energy industry", or "the children have no energy this morning") is actually something else. Properly speaking, it is usually *exergy* (see below) rather than energy

that people are usually thinking of. But energy — in contrast to exergy — is possibly the most fundamental variable of all, partly because it is the subject of a conservation rule known as the "First Law" of thermodynamics.

### 3. Energy and the First Law

Many of the commonly used thermodynamic variables (heat, work, enthalpy, etc.) are actually forms of energy. Much of thermodynamics is concerned with the conditions and limits on interconversion from one form to another. The most fundamental constraint on conversion, known as the "Second Law" is discussed in the next section.

The First Law says that energy is *conserved*, meaning that the total energy "content" of any isolated system can never be increased or decreased. Energy can only be converted from one form to another. But this notion is much less straightforward than it seems to be. Its meaning is clear enough in the case of a pendulum, or a planet circling the sun in an elliptical orbit. There are two kinds of energy in either of these cases, namely *potential energy* associated with the body's position with respect to an external force field (e.g. gravity) and *kinetic energy* of motion with respect to a fixed frame of reference.

A third and fourth kind of energy, *heat* and *mechanical work* were recognized in the 18th century, as steam engines first appeared on the scene. Heat is clearly related to temperature; as heat is added to a system (e.g. a kettle of water or a bar of iron), the temperature rises.<sup>1</sup> But, while one speaks of the "heat content" or "heat capacity" of a body, what can actually be measured is the flow of heat from one body to another. This is the first example of a fundamental characteristic of thermodynamics: with regard to forms of energy, it is almost always only the changes that can be measured, rather than the absolute quantities.

It was also observed in the 18th century that, in most cases, chemical reactions either generate or absorb heat. That is, they are either *exothermic* or *endothermic*. This suggested another form of energy associated with thermodynamic systems, namely "chemical energy". A chemical energy term, called *enthalpy* is needed to balance the accounts in any process involving chemical reactions.

But by the 19th century it had become clear that any macroscopic body (solid, liquid or gas) really consists of a system, or assembly of microscopic particles — atoms, molecules — interacting with each other. Once again, there is kinetic energy or relative motion to consider, but there is also energy associated with rotational and vibrational motions of molecules. At the macro-scale this kinetic energy becomes *internal energy*. In addition, the particles may, of course, interact with an external force field (such as gravity), although this sort of interaction is usually unimportant and can be neglected.<sup>2</sup>

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<sup>1</sup> Except during a phase change. When heat is added to a kettle of *boiling* water the temperature remains constant as the liquid water gradually vaporizes to steam.

<sup>2</sup> Also, real particles exert molecular forces on each other. These forces give rise to another sort of potential energy, whenever two molecules are close enough together to "feel" each other. This is known as the Van der Waals potential, for its discoverer. The Van der Waals potential, which arises from electromagnetic (dipole, quadrupole, etc.) forces at the atomic level, tends to be weakly attractive at short distances and strongly repulsive at still shorter distances. The combination of vibrational and rotational energy states and Van der Waals potentials explains why gases consisting of real molecules do not behave like idealized gases of electrically neutral point particles.

Finally, when molecules of several species are mixed together they may react with each other chemically, thereby changing the molecular composition of the assembly. To take the simplest case, suppose molecular oxygen and molecular hydrogen are mixed together. Then, in principle, two hydrogen molecules can combine with each oxygen molecule to form two water molecules with a release of heat.<sup>3</sup>

The reaction of oxygen and hydrogen to form water is *exothermic* (i.e. the reaction releases heat) and is therefore self-sustaining. There are other important examples of reactions that are *endothermic* (i.e. requiring heat inputs). For instance the synthesis of ammonia from atmospheric nitrogen and hydrogen is highly endothermic. It only occurs at high temperatures and pressures, in the presence of a catalyst.

Mechanical work, or simply work, can be conceptualized as motion against a resistance, such as pressure, gravity, or friction. Clearly rowing a boat, plowing a field, raising a bucket of water from a well, operating a bellows or grinding the surface of a piece of metal all have this in common. All are "work". Work can always be converted into heat with 100% efficiency, but not *vice versa*. Heat can be converted into work, but only within limits. The essential "one-way-ness" of this conversion is the subject of the Second Law, discussed below.

The energy conservation law could not be established empirically until all the various forms of energy were included. To include them, they had to be defined and measured. For this reason, the First Law was not clearly formulated until the 1840's (J. R. Mayer, J. Joule, W. Thomson). Einstein "completed" the formulation of the first law in the first decade of this century by noting the equivalence of mass and energy, with all its surprising implications. However, for present purposes, we can ignore the possibility of converting mass into energy (or *vice versa*) except in the special case of nuclear power.

## 4. Entropy and the Second Law

As noted above, the conversion of mechanical work into heat is straightforward, but in the reverse direction — from heat into work — the conversion is subject to fundamental limits. The so-called "Second Law" of thermodynamics — also known as the "entropy law" — was first understood (but expressed in an obscure way, to be sure) in 1824, by the French engineer N. S. Carnot. It resulted from his attempt to find a general expression for the maximum amount of work that can be done by a heat engine. (Heat engines are nothing else but devices for converting heat into work). Carnot observed: "For a heat engine operating in cycles to perform mechanical work, we must use two bodies at different temperatures". He went on to derive an expression for the maximum amount of work that could be extracted by an idealized heat engine operating through expansion and compression, taking heat from a high temperature source and dumping waste heat into a low temperature sink. This expression is

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<sup>3</sup> In practice, the oxygen molecule must first be dissociated into its component oxygen atoms. Then, each of these atoms may combine with a hydrogen molecule (or, more likely, with two dissociated hydrogen atoms). Energy is needed to dissociate the relatively unreactive molecules into their reactive atomic components. This is, essentially, the energy needed to "ignite" the reaction. Then, the energy released (as heat) by the recombination of oxygen and hydrogen atoms into water molecules is enough to dissociate more oxygen and hydrogen molecules, thus keeping the chain reaction going until all the oxygen or all the hydrogen is used up, whichever occurs first.

$$\epsilon = (T_s - T_0) / T_s \quad (2)$$

i.e. the ratio of the temperature difference between source and sink to the absolute temperature of the source. It is known as the Carnot efficiency. Since this is a maximum, all "real" heat engines necessarily operate at lower efficiencies.

The Carnot limit has an implication: that high temperature heat is more "available" (for conversion into mechanical work) than low temperature heat. Moreover, it is possible to "convert" high temperature heat into low temperature heat (thereby generating some mechanical work), the only way to convert low temperature heat into high temperature heat would be to expend mechanical work.<sup>4</sup> In other words, the conversion is essentially uni-directional.

However, while Carnot's insight has belatedly been recognized as the fundamental discovery, it did not immediately lead on to the concept of entropy. The first mathematical formulation of the second law did not occur until 1865 (R. Clausius). Clausius introduced a new variable  $S$  called entropy. The definition of entropy given by Clausius (familiar to generations of first or second year students of physics and mechanical engineering) involves a so-called path integral over of the expression  $dS = dQ/T$ , where  $dQ$  is an incremental heat flow and  $T$  is absolute temperature. The entropy law, in Clausius' version is:  $dS > 0$  for any path that is not reversible. (In the special case of a reversible process  $dS = 0$ .) As a practical matter there are no reversible processes, but for purposes of discussion and exposition they are a convenient fiction.

It is not surprising that the Clausius definition of entropy has almost no operational value or intuitive content. Since any closed system must eventually reach a static equilibrium state in which all forces are balanced and "nothing happens or can happen", it follows that such a state also corresponds to maximum entropy. The implication is that increasing entropy marks the approach to thermodynamic equilibrium, which is irreversible.

In short, there is a maximization principle here. Thermodynamic equilibrium for an isolated system corresponds to maximum entropy  $S$ . However, the entropy of an isolated system is neither easy to determine (it cannot be measured directly) nor very interesting, as such. What is more interesting is the equilibration *process*. This can best be considered in terms of a more complex situation: that of a subsystem embedded in a larger system (its "surroundings") and the two systems approach a mutual equilibrium. It is important to bear in mind that the final equilibrium will differ from both. In some cases this matters. However, for most cases of interest to us the "surroundings" may be considered to a good approximation as infinite, with infinite capacity to do or receive heat, work, or chemical species. (Later we will consider examples in which the "surroundings" are the atmosphere, the ocean, or the earth's crust).

Instead of defining the entropy variable first, and then showing that this function would necessarily increase during any real (i.e. irreversible) process, the mathematician Carathéodory took a different approach. He showed (1909) that a necessary consequence of the property of irreversibility *per se* is the existence of a non-decreasing function of the state variables. That function can be interpreted as entropy. This approach enables us to view the

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<sup>4</sup> As a practical matter it is necessary to define the sink. On earth, the ambient temperature (of the ocean or the atmosphere) is the most convenient choice. It has an average temperature of about 300 K. No heat *engine* can operate with a heat source below this temperature. However a heat *pump*, using mechanical work supplied by an external source, can extract heat from a source at less than ambient temperature and dispose of it at a temperature at or above ambient. A refrigerator is a specialized heat pump.

difference between current and final entropy as a measure of the distance from the current state to final equilibrium. This difference is proportional to the variable we wish to discuss in detail, namely *exergy*.

Why is the entropy concept so hard to grasp? The Clausius approach is nearly incomprehensible for anyone not familiar with abstract descriptions of heat engines, and it is not intuitively obvious how it applies to non-cyclic phenomena. The Carathéodory derivation is elegant, but it is totally incomprehensible to a non-mathematician. Perhaps due, in part to its difficult history, entropy has been endowed with a kind of mystical quality. Clausius himself used the evocative phrase "heat-death of the universe" to describe the ultimate thermodynamic equilibrium state. The cosmologist Sir Arthur Eddington labelled it "time's arrow", referring to the coincidence between the direction of time, the increase of entropy in the universe and the irreversible approach to that ultimate equilibrium.

Finally, entropy is essentially non-observable: there is no such thing as an "entropy-meter". Nor is there any straightforward cookbook formula for calculating the absolute entropy of real systems from observables.<sup>5</sup> As in the case of most thermodynamic variables, there are only formulae for calculating entropy *differences* from other measurable variables. However; we return to this later.

However, there is one more topic that needs to be addressed briefly first.

## 5. Thermodynamic Potentials

There are several other specialized thermodynamic variables that reflect the fact that thermodynamic systems can *act* (perform mechanical work) on other systems and, conversely, can *be acted on* (have work performed on them) by other systems. There are four basic mechanisms for such action, viz. expansion/compression, heating/cooling, diffusion and chemical transformation. These can occur (at least in our imagination) separately and sequentially, as when one variable changes while others remain constant. The so-called thermodynamic potentials, defined later, define the maximum useful work that can be extracted from a system under various conditions.

Those who have studied mechanical engineering will recognize that there is a variety of possible cycles for a heat engine.<sup>6</sup> Such cycles are typically analyzed in terms of sequences of idealized steps where one "driving" variable, such as (steam) pressure or (cylinder) volume, follows a prescribed path while another variable such as (condenser) temperature) is held constant. The law of energy conservation provides an absolute condition that must be

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<sup>5</sup> The statistical definition of entropy introduced by Boltzmann, is equally obscure and lacking in intuitional value. Boltzmann and Maxwell introduced the idea of a large assembly of  $N$  identical objects, each of which could be in any one of several allowed energy states, subject to total energy  $E$  being conserved. For a system of  $N$  identical particles, Boltzmann's definition was equivalent to  $S = -k \sum f_i \ln f_i$ , where  $k$  is a constant and  $f_i$  is the fraction of all the  $N$  objects in the  $i$ th microstate. The sum is taken over all microstates. But there is no practical way to observe the  $f_i$ . They can only be computed in certain highly idealized situations, mainly for gases

<sup>6</sup> Examples of true heat engine cycles include the Rankine (steam) cycle, the Erickson (air) cycle, and the Stirling cycle. The Carnot cycle is physically unrealizable, but it represents the theoretical maximum of efficiency. The so-called Otto and Diesel "cycles" (applicable to combustion engines), along with fuel cells, are not subject to the Carnot limit because they are not true cycles. They are, however, subject to other thermodynamic constraints.

satisfied. All other variables are then fully determined.

It was pointed out above that entropy is maximized at equilibrium. This fact can be used to formulate a maximization principle for determining the dynamic *path* to equilibrium from any given starting point, as defined by state variables. Such maximization principles have long been used for this purpose in mechanics. A certain function can be defined (known as Hamiltonian or Lagrangian in mechanics) that has two characteristics (i) it is either a minimum or a maximum when the system reaches equilibrium and (ii) the set of differential equations that result from setting the partial derivatives with respect to all state variables and time equal to zero (the mini/maxi-mization condition) define the trajectory of each state variable over time. The question arises: are there analogous functions for thermodynamics? If so, what are they?<sup>7</sup> It turns out there are such quantities.

One important case arises when the subsystem is closed with respect to matter transfer but not thermally isolated. (Think of it as being enclosed by an impermeable elastic rubber balloon). If the internal and external pressures are equal (and constant), allowing chemical composition and temperature to vary, the path to equilibrium corresponds to minimum enthalpy  $H$ . The variable was introduced by Gibbs:

$$H = U + pV \quad (3)$$

where  $U$  is the internal energy. For purposes of interpretation, when a chemical process occurs there is a change in the enthalpy of the reactants, corresponding to either release or absorption of heat. Roughly, enthalpy can be thought of as chemical energy. For fuels, the change in enthalpy is exactly the heat of combustion. This quantity, together with some others (including Gibbs free energy of formation, discussed below) is tabulated for a large number of compounds in standard references.<sup>8</sup>

However, if we hold temperature  $T$  fixed, letting the pressure vary, allowing chemical reactions and letting the rubber balloon to be a perfect conductor of heat but impermeable to molecules, the final equilibrium corresponds to the minimum of another quantity, called the Helmholtz free energy:

$$F = U - TS \quad (4)$$

Finally, holding both pressure and temperature constant, but allowing chemical reactions and letting the heat of reaction (but not the reactants themselves) pass through the membrane, the path to final equilibrium corresponds to minimum Gibbs free energy of formation:

<sup>7</sup>A number of years ago, the mathematician Garrett Birkhoff proved that, for every physical theory, there is corresponding variational principle i.e. a minimization (or maximization) process [Birkhoff 1944]. In mechanics, the quantities to be mini(maxi)mized are either Hamiltonians or Lagrangians. These are generalized expressions with dimensions of energy but also including physical constraints expressed in the form  $F(x,y) = 0$ , with non-zero coefficients (Lagrange multipliers) that have physical interpretations. Finding the equations of motion of a mechanical system is essentially reduced to finding the appropriate Hamiltonian (or Lagrangian) and differentiating it with respect to the canonical variables.

<sup>8</sup> See, for instance, Robert H. Perry & Cecil H. Chilton eds. *The Chemical Engineer's Handbook* 5th Ed. McGraw-Hill, N.Y. or the David R. Lide ed. *Handbook of Chemistry and Physics* 74th ed. CRC Press, Boca Raton Fla. Further references can be found in the latter, especially M. W. Chase *et al* *JANAF Thermochemical Tables 3rd ed. J. Phys. Chem. Ref. Data* 14 Supp. 1 1985 and DIPR *Data Compilation of Pure Compound Properties* Design Institute for Physical Properties Data, American Institute of Chemical Engineers, 1987.

$$G = U + pV - TS = H - TS \quad (5)$$

The Gibbs free energy of formation of a compound is important for what follows. It is the energy absorbed (+ sign) or released (- sign) when the compound is formed from its pure constituents, either in atomic or molecular form, whichever is preferred by nature. For instance, the Gibbs free energy of formation of carbon dioxide, per mole, is the heat energy *released* when a mole of pure carbon (C) combines with a mole of molecular oxygen (O<sub>2</sub>), namely -394.4 kJ/gm. Conversely, to form nitric oxide (NO) 86.7 kJ/gm of energy must be *absorbed*. The signs are conventional.

The "equations of motion" for the path to equilibrium, in all these cases, are found by partially differentiating the potential ( $H$ ,  $F$ ,  $G$ ) with respect to all variables, except those constrained to be constant. All of these potentials are defined only for closed systems that are internally in equilibrium. They define the maximum amount of work that can be done by the system on its surroundings (or *vice versa*) subject to the specified constraint.

## 6. Exergy

What if chemical reactions are allowed and no special constraints are imposed on the path to equilibrium? The maximum amount of work that can be done by (or on) a subsystem, without constraining any variable, has been variously called *availability*, *available work*, *exergy*, *essergy* (for "essence of energy"), *distinguishability* (by at least one author) *potential entropy* and *physical information* or *pi-potential*. Surprising as it may seem, it was not obvious until recently that all of these names really referred to the same thing, or effectively so.<sup>9</sup> Hereafter we use the most common European terminology, *exergy*, for which the letter  $B$  is usually adopted.

The notion of available work, including the diffusion term, was first introduced by Willard Gibbs in 1878 [Gibbs 1948]. The theory has been developed sporadically, e.g. [Gouy 1889; Jouget 1907; Keenan 1951; Evans 1969; Riekert 1974; Szargut *et al* 1988]. Applications have been presented for the internal combustion (gas) engine by Stodola [Stodola 1898], by Darrieus and Keenan for flow processes in steam turbines [Darrieus 1930; Keenan 1932], by Rant for the Solvay process for synthesizing sodium carbonate [Rant 1951] and by Glansdorff for air conditioning systems [Glansdorff 1957]. The notion of exergy efficiency, as a tool for process design optimization, has been attributed to Denbigh [Denbigh 1956]. Exergy (under various names) has been discussed in textbooks since 1935, e.g. [Bosnjakovic 1935; Keenan 1948].

Evidently exergy  $B$  is only defined — and non-vanishing — for a system that is not in final equilibrium with its surroundings. By definition, exergy vanishes in equilibrium. It is effectively a measure of *distance from equilibrium*, indeed, it is the most general such measure [Evans 1969]. There are several equivalent expressions, including:

$$B = (G - G_p) - T_0(S_f - S_d) \quad (6)$$

$$B = H - H_f - T_0(S - S_p) - T_0(S_f - S_d) \quad (7)$$

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<sup>9</sup> Potential entropy and physical information content (with units of entropy) are equivalent to each other; they are both equal to exergy divided by the ambient temperature,  $T_0$ .

and

$$B = U - U_f + p_o(V - V_f) - T_o(S - S_f) - T_o(S_f - S_d) \quad (8)$$

where the subscript *o* refers to the standard temperature and pressure (e.g. of the atmosphere) and the subscript *f* refers to the thermal equilibrium state of the system *plus* the environment. Note that there are two entropic terms in these expressions. The first represents the entropy change as the system reaches thermal equilibrium (*p*, *T*) with the environment, while leaving the "rubber balloon" of reaction products intact. The second represents the entropy change as the balloon breaks and the reaction products diffuse into the environment. In the final (diffusion) term in equations (6-8) the subscript *d* refers to the final state of the combined systems after they become indistinguishable in terms of chemical composition.

Consider the thermal equilibration stage of the equilibration process first. By assumption, we have an elastic but impermeable "balloon" full of hot (or possible, cold) gas. The gas may or may not consist of reaction products. If the reaction products are hotter than their surroundings, they expand and push the surroundings out of the way. This is a way of doing work on the environment. As the balloon expands, it cools. When the temperature and pressure on both sides of the balloon membrane become equal, no more work can be done. Conversely, if the contents of the balloon are cold, the environment does the work on the balloon.

Obviously, we can replace the elastic balloon by a piston in a rigid cylinder. The hot gas expands against the piston. *Voilà*, we have the essentials of a heat engine. How much work can be extracted from such an engine? Carnot gave the answer in 1824. The maximum work that can be done by thermal equilibration depends *only* on the temperature differential between the system and the environment. (In textbooks, the environment is described as an infinite heat reservoir). It requires that the heat transfer be carried out reversibly (at an infinitesimal rate). The result is, essentially,

$$B = \epsilon Q, \text{ or } B/Q = \epsilon \quad (9)$$

where *Q* is the heat "content" of the balloon (or the cylinder, in the case of the heat engine), usually equal to the heat of combustion, while  $\epsilon$  is a simple function of the temperature of the source given previously by equation (2). Thus, the exergy content of steam at 200 °C, is only about 40% of its heat content, whereas at 400 °C, the exergy content rises to about 60%.

Since work can also be extracted from a cold body by operating the "engine" in reverse, the function  $\epsilon$  can be extended into temperature regions below ambient. This extended function (equation 2) is shown in *Figure 1*. The exergy "content" of a very cold body obviously exceeds its heat content, since heat is taken from the environment. This is because the work is done not *by* the body, but *on* it.

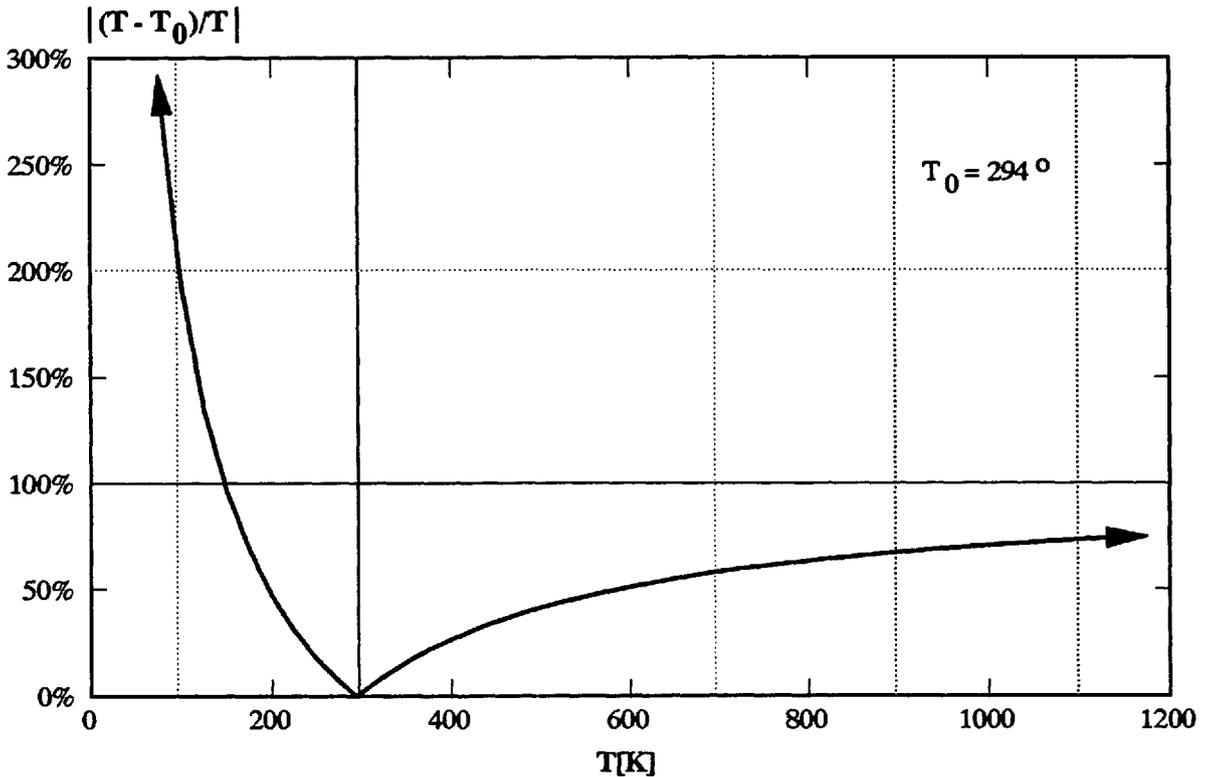


Figure 1: Quality factor  $v_c$  of heat as a function of its temperature

This diffusion term represents "work" that is done on the environment and is therefore theoretically recoverable, though not recoverable in practice.<sup>10</sup> For instance, when carbon dioxide is produced in a combustion process it has a pressure close to atmospheric; but by the time it is totally diffused into the atmosphere it has also effectively been decompressed (i.e. expanded) by a factor of 4000. In so doing, it has done work. Thus, diffusion does represent a real loss of exergy (and information), or an increase in the entropy of the system-plus-environment.

The general diffusion term was first defined by Gibbs [e.g. Gibbs 1948] as follows:

$$-T_0(S_f - S_d) = \sum_i n_i (\gamma_{fi} - \gamma_{di}) \tag{10}$$

where  $\gamma_{fi}$  is the chemical potential of the  $i$ th species in the final equilibrium state prior to diffusion and  $\gamma_{di}$  is the chemical potential after diffusion. For a clear discussion see [Carnahan *et al* 1975, pp. 35-46]. (Incidentally, this is another case of confusing terminology, since the term "chemical potential" is no longer used and there are no tabulations of it in standard reference works under that name. However, it is simply the Gibbs free energy per mole).

The diffusion term can be adequately approximated in most cases by the so-called ideal gas approximation

$$-T_0(S_d - S_f) = RT_0 \sum_i n_i \ln(x_{fi}/x_{di}) \tag{11}$$

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<sup>10</sup> When we discuss "exergy efficiency" (or "second law" efficiency) of resource usage, in a later section, this term will generally be neglected.

where  $R$  is the gas constant (Avogadro's number),  $T_0$  is the standard temperature (usually taken to be 298.15 °K)  $x_{\beta}$  is the mole fraction in the equilibrium state *before* diffusion and  $x_{\beta}$  is the mole fraction in the equilibrium state *after* diffusion. The ratio of mole fractions in equation (11) is the same as the ratio of partial pressures.

In practice, diffusion occurs into one of two possible "sinks": the atmosphere or the ocean. With regard to chemical species not found in the natural atmosphere, the logarithmic divergence in equation (9) would introduce a spurious infinity. This could be "defined" away, as in [Carnahan *et al* 1975] by introducing an arbitrary cutoff value for dilution, based on the argument that even at this level, the diffusion term contributes much less than typical heats of combustion, for instance.<sup>11</sup>

A more refined approach would be to postulate a further reaction within the atmosphere or ocean that finally reduces the reactants to the final "reference" forms wherein they are found in nature. For instance, HCl does not exist in equilibrium in the natural environment. If it is emitted from a chemical reaction, a further reaction must be postulated that finally leaves the chlorine in the form of sodium chloride (NaCl), or chlorine ion (Cl<sup>-</sup>), which are the forms in which chlorine is found in the ocean. A consistent and practical procedure for dealing with this problem has been worked out by Szargut, Morris and Steward [Szargut *et al* 1988, Chapter 2]. We discuss it in more detail hereafter.

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<sup>11</sup> Specifically, dilution to 1 ppm would contribute 13.8 RT<sub>0</sub> to B.

## PART II

### 7. Toward Practical Applications: Introduction

As noted in the previous section, exergy is a general measure of "distance from equilibrium". It has also been interpreted as "available" energy [Keenan 1948], "the capacity to do work" [Rant 1956], and the "transformable or convertible component of energy" [Rant 1964].<sup>12</sup> Tribus and co-workers preferred the term *essergy* (for "essence of energy"), and emphasized the relationship with information theory [Tribus 1961; Tribus & McIrvine 1971].<sup>13</sup> Exergy can also be equated to "potential entropy", i.e. the ultimate entropy increase in the system-plus-environment as the system finally reaches thermodynamic equilibrium [Ayres & Martinàs 1993, 1995]. In the case of a waste residual, this can be regarded as the potential for doing harm to the environment by driving undesirable and uncontrollable reactions with components of the environment.

In general, exergy is an extensive variable, with the same units as energy. All materials have a definable and calculable exergy-content, with respect to a defined environment. The exergy content of a natural resource input to the economy can be interpreted as a general measure of its potential "usefulness". The notion of exergy efficiency, comparing theoretical with actual exergy use for a process, is an important tool for process design optimization. On the other hand, the exergy-content of a waste residual can be interpreted as its potential for doing harm by driving uncontrolled reactions in the environment. We note, especially, that exergy can drive physical processes as well as chemical reactions.

### 8. Reference States for Chemical Exergy Calculations

Exergy has been defined as "the maximum decrease in the function  $B$  as the system (body) proceeds toward equilibrium with its environment" (usually taken to be the atmosphere in early analyses) [e.g. Gyftopoulos *et al* 1974, p. 11]. Riekert defined exergy as "the shaft work or electrical energy necessary to produce a material in its specified state from materials common in the environment, in a reversible way, heat being exchanged with the environment at temperature  $T_0$ " [Riekert 1974]. Szargut defines it as "the amount of work obtainable when some matter is brought into a state of thermo-dynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above mentioned components of nature" [Szargut *et al* 1988 p. 7]. In both the these last two definitions, which are equivalent, reference is made to common *components* of the environment, meaning the components of the atmosphere, the ocean and the earth's crust.

Hereafter we use the treatment of Szargut [Szargut *et al* 1988]. In principle one can

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<sup>12</sup> The latter definition is not acceptable, however, because it mis-characterizes the case where exergy is non-zero but energy is transferred *from* the environment (i.e. the case of a heat pump) [Szargut *et al* 1988 pp.8,9].

<sup>13</sup> The quantity  $B$ , divided by standard temperature, can be interpreted as the physical information (or "pi-potential") embodied in a material, differentiating it from the environment [Ayres & Miller 1980; Ayres 1988, 1994].

subdivide exergy into four contributing parts: viz.

$$B = B_k + B_p + B_{ph} + B_{ch} \quad (12)$$

where  $B_k$  is the *kinetic* exergy (reflecting the velocity of a flow),  $B_p$  is the (gravitational or electro-magnetic) *potential* exergy,  $B_{ph}$  is the *physical* exergy in Szargut's terminology (we would prefer to call it the *thermal* exergy) and  $B_{ch}$  is the *chemical* exergy. The *physical* exergy  $B_{ph}$  is the work obtainable by taking the system through reversible physical processes — compression, expansion and heat exchange — to the temperature and pressure of the environment. It is, in effect, the work that could be extracted from an idealized (reversible) heat engine operating between the system and its surrounding environment. The *chemical* exergy,  $B_{ch}$ , is the work obtainable by taking a subsystem with the same temperature and pressure as the environment reversibly to the same chemical composition of the environment.

Note that kinetic and potential exergy terms can be neglected, for our purposes, if we assume that all material and energy transformations of economic and ecological interest occur at constant altitude, in the absence of electromagnetic fields, and at zero velocity, relative to the earth's surface. The third term, physical (i.e. thermal) exergy, can also be treated very simply, based on equation (9) above, for our purposes. Physical exergy changes are relevant mainly for analyzing the performance of heat engines, refrigeration systems and the like. These systems are of great economic importance, but for our purposes only their gross *efficiency* aspects need be considered. (This topic is considered in a later section).

The chemical exergy includes both reaction and diffusion terms. For resource and waste residual accounting purposes, only chemical exergy need be considered. Hereafter, the unitalicized capital letter  $B_i$  will be used to refer to the chemical exergy of the  $i$ th chemical species, viz.  $B_i = B_{ch,i}$  to avoid unduly complicated notation.

The major conceptual issue in the calculation of chemical exergy is the choice of *reference state* to which the chemical reactant under consideration is to be compared. In the chemical and engineering literature the standard state of each element is defined as its pure elementary state (i.e. C for carbon,  $O_2$  for oxygen,  $N_2$  for nitrogen,  $H_2$  for hydrogen, and so on). The pure elements are normally assigned zero values of the Gibbs free energy of formation. The enthalpy of formation and Gibbs free energy of formation for all other compounds are defined as the energy required to form the compound from its pure components, or the negative of the heat generated or work done, respectively by taking the substance via a reversible path back to those pure components. By convention, if the reaction to form the compound is exothermic (i.e. generates heat) then the enthalpy and Gibbs free energy of reaction are negative, and conversely. The enthalpy of air oxidation is equivalent to the heat of combustion. These are internally consistent definitions, but not particularly convenient for calculation.

The problem is that in the real world, reactions generally do not leave elements in their pure states (as defined above). Thus every exergy calculation, in principle, involves two stages: (1) calculation of the exergy difference between the starting compound and the pure elements of which it is formed and (2) calculation of the exergy difference between the pure states and the common substances in the environment. The environment, for this purpose, must be either the atmosphere, the ocean or the earth's crust (down to some level to be determined later). For purposes of exergy efficiency estimates at the aggregate industry level, it is satisfactory in many cases to consider only the atmosphere as the environment for processes involving fuel combustion. Other processes, such as metallurgical reduction from ore, are broken into sub-processes and approximated as closed cycles without explicit

reference to the environment. In effect, the reference states are combustion products and metal oxides.

A practical illustration of this *ad hoc* approach to exergy calculation was given by Keenan, Gyftopoulos and Hatsopoulos [Keenan *et al* 1973]. This was followed by a pioneering thermo-economic study of opportunities for energy conservation in several industries (steel, aluminum, petroleum refining, paper, copper and cement), carried out for the Ford Foundation Energy Project [Gyftopoulos *et al* 1974].<sup>14</sup> The Ford Foundation study did not explicitly address the issue of reference states, although the authors must have done so implicitly in the calculations.

A slightly more sophisticated study of seven industries (steel, copper, aluminum, glass, rubber, plastics and paper) that did address this question explicitly, though not entirely consistently, was conducted by Hall *et al* at Battelle Memorial Laboratories for the U.S. Federal Energy Administration [Hall *et al* 1975]. In the latter work, modified values of the enthalpies and Gibbs free energies were computed by redefining the "zero enthalpy" state. In the case of fuels, hydrocarbons and organic materials, the zero state for oxygen continues to be oxygen, but the zero state for carbon and hydrogen respectively was taken to be the appropriate combustion product (e.g. CO<sub>2</sub> and H<sub>2</sub>O).

The modified enthalpies (and Gibbs energies) were calculated for hydrocarbons and organics by simply adding the (negative) values of heats of combustion to the tabulated values. In a number of other cases (e.g. iron, aluminum, silicon) the most oxidized forms (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) were chosen as the standard, and the negative value of the enthalpies of formation of those compounds were added to the standard values of all their compounds. Where this procedure was not applicable, the compound with the most negative tabulated value of enthalpy of formation was selected as the zero point, and the modified enthalpies and Gibbs energies of other compounds were increased by this amount.

Unfortunately, there are some elements for which this *ad hoc* technique becomes ill-defined or leads to inconsistent results and cannot easily be applied. Chlorine is an example. Hall *et al* did not follow their own rule; in the chapter on pulp and paper they chose the zero value of chlorine to be Cl<sub>2</sub>, which is problematic, since chlorine is very energy intensive. Nitrogen compounds are another case in point. The most oxidized form of nitrogen (N<sub>2</sub>O<sub>5</sub>) is the one with the most negative value of standard enthalpy of formation. But, fortunately for life on the planet, atmospheric nitrogen does not combine spontaneously with atmospheric oxygen to form nitric acid, which would be the theoretical thermodynamic equilibrium state.

What we want to calculate instead is the enthalpy (and from it the Gibbs free energy) of formation/devolution *not* from pure elemental form, but from the form in which the element is "commonly" found in nature. Exergy can then be computed simply and directly. To distinguish the recalculated enthalpy and exergy values from those tabulated in standard reference books, Szargut has introduced the terms "enthalpy of devaluation"<sup>15</sup> and "standard chemical exergy" [Szargut *et al* 1988, chapter 2]. Gibbs free energy is tabulated in some references, but exergy is not. Szargut essentially proposes that his calculations (described hereafter) be adopted as the appropriate standard.

It must be emphasized that the exergy value, in given units, should be calculated once

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<sup>14</sup> In this study the term exergy was not used. It was called "available work", using the terminology of Keenan.

<sup>15</sup> We prefer the term "devolution" in place of "devaluation".

for all. The problem, up to now, has been the difficulty of assigning appropriate "zero" levels for the calculation. This is a conceptual problem for the following reason: The earth itself, and the three major environmental "sinks" we have to consider (atmosphere, hydrosphere, lithosphere) are not actually in thermodynamic equilibrium, either internally, or with each other. The atmosphere is the most nearly in equilibrium, although it contains highly variable amounts of water vapor and the two chief constituents, oxygen and nitrogen, should theoretically react with each other to form oxides of nitrogen. Luckily, molecular nitrogen is quite stable. Hence, the oxidation reaction occurs so slowly at atmospheric pressure and temperature that other (biologically catalyzed) denitrification reactions are able to compensate by replenishing the nitrogen [Ayres *et al* 1994]. In fact, the earth is best characterized as a quasi-stable self-organized system (with important biochemical elements) that is far from thermodynamic equilibrium. It is maintained in its quasi-stable state by a constant influx of exergy from the sun.

The exergy calculation involves three steps. The first is to select the appropriate zero level. This is taken to be a particular chemical compound in an environmental sink where that element is "most likely" to end up after it undergoes all thermodynamically favored reactions. This is very straightforward for combustion products, but less so for compounds of metals, halogens and other elements. The second step, is to identify a "standard" chemical reaction for each element leading to the selected final chemical form (i.e. the selected "common constituent" of one of the environmental media). This enables the calculations of enthalpy and Gibbs free energy changes. The third step is to estimate the molar concentration of that compound in the specified environmental sink (atmosphere, ocean, earth's crust) and compute the diffusion contribution to the chemical exergy. Only the first step involves any conceptual difficulties, discussed below; the second step is elementary chemistry, while the third step is trivial, once the concentration data has been compiled. In this regard, only seawater offers any difficulties.

As regards the atmosphere, its composition is well known [e.g. Szargut *et al* 1988, *Table 2.4*] and it can be regarded as the "sink" for nine elements whose reference states are gaseous molecular species (not including water). These are H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, C (as CO<sub>2</sub>), and the five inert gases. The diffusion term in equations (6-8) is easily calculated using equation (11). For the ocean, 31 elements can be identified in seawater with plausible reference species, mostly ionic in nature [Szargut *et al* 1988 *Table 2.6*]. Of these 31, 4 elements (Co, Mg, Mn, P) must be discarded because of apparent inconsistencies (e.g. negative calculated exergies, using measured concentrations in seawater).<sup>16</sup> These inconsistencies arise for various reasons we need not discuss in detail.

There are at least 13 elements (including the 4 elements mentioned above), that must be linked to solid reference species in the earth's crust. These elements are Al, Co, Cr, Fe, Mg, Mn, P, Sb, Si, Sn, Ti, U, V. Here things get complicated for several reasons, but mostly because the composition of the lithosphere varies with depth. Thus the "dead state" of final equilibrium depends on how deep the interacting layer of the earth's crust is assumed to be. For instance, detailed analysis by Ahrendts has been done for assumed interaction depths of 1, 10, 100 and 1000 meters [Ahrendts 1977, 1980]. The implications are drastically different. This is mainly because atmospheric nitrogen as well as carbon and sulfur trapped in the

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<sup>16</sup> This problem also arises for calcium, sodium and potassium nitrates. However, in this case the result is not inconsistent with chemistry. The atmospheric components oxygen and nitrogen are kinetically — not thermodynamically — blocked from reacting with each other.

earth's crust would eventually combine with atmospheric oxygen, forming nitrates, carbonates and sulfates. For instance, if the top 100 meters of the earth's crust were allowed to reach chemical equilibrium with the atmosphere and the ocean, the atmospheric CO<sub>2</sub> level would be 15 times higher than at present while atmospheric oxygen would be almost entirely combined with nitrogen as nitrates and nitric acid dissolved in seawater (ibid). It follows chemical exergy calculations, not only for elements with solid reference species, are highly dependent on assumptions.

To avoid the apparent ambiguity it is necessary to adopt some convention. The convention clearly must exclude the theoretical possibility of mutual interaction between the components of the atmosphere, the ocean and the lithosphere. These environmental media must be assumed to interact only at their mutual boundaries, as at present. Otherwise they remain distinct. The key point is that the composition of the lithosphere (as well as the atmosphere and the hydrosphere) must be assumed to remain as they are at present, not as they might be after some theoretical mixing and chemical equilibration process.

What must we choose as solid reference species? The real lithosphere is extremely complex, with numerous compounds and solid solutions of each element. A further simplification is needed. The guidepost for selection is that the chosen reference species must have zero effective chemical exergy by definition. In effect, they cannot drive further reactions of any kind. They are not "resources". *Thus, it is sufficient to identify commonplace and chemically unreactive species.* (This is essentially the procedure advocated by Hall *et al* [Hall *et al* 1975], mentioned above, except that is applied specifically to the lithosphere). All of these are oxides, carbonates, sulfates, or silicates. Szargut has constructed an idealized model lithosphere for computational purposes, using these species. Using this idealized model the diffusion term in equations (6-8) can be calculated using the approximation equation (11). It is argued that the results are not sensitive to the details of the model. That is, to modify the specific choices in the idealized model would have little consequence as regards the results. See [Szargut *et al* 1988, Table 2.8 and pp. 67 et seq].

A composite list of 400 industrially important compounds is given in *Table 1* of the Appendix. Where available Szargut's values for exergy have been used. Other sources in different units have been converted and, where only the standard Gibbs free energy of formation was known, the exergy was calculated using equation 13 below. The reference values as calculated by Szargut for the elements used in these compounds are also listed.

Without presenting the derivation in full, it is sufficient for our purposes to present the main result. It is that the standard chemical exergy, per mole, of any pure *compound* involving these elements can now be computed by means of a simple formula, viz.

$$B = G + \sum_j n_j B_j \quad (13)$$

where  $G$  is the standard Gibbs free energy of formation of the compound, the  $n_j$  are molar fractions of the  $j$ th element and the index  $j$  runs over the elements in the compound. Using values of  $G$  from standard references, together with  $B_j$  values from Szargut *et al*, we have calculated the chemical exergies of a large number of pure compounds. The results are given in Appendix Table 1, which also presents those exergies already computed by Szargut.

To calculate the chemical exergies of mixtures and composite materials, such as ores and alloys, it is only necessary to have detailed composition data.

## 9. Exergy as a Measure of Resource Flows and Reserves

Being *the* measure of potential work embodied in a material — whether it be a fuel, a food or a material used for other purposes — makes exergy a more natural choice for a common measure of resource quantity than either mass or energy. Unfortunately, it has not yet achieved this role. For historical reasons, another thermodynamic variable, the heat of combustion, has been used for this purpose, under the incorrect and misleading title "energy". Evidently this measure is not applicable to non-fuel resources at all.

The importance of potential work (i.e. exergy) as a *factor of production* was not clearly understood among economists, for many years. This was probably partly because of the semantic confusion between "labor" and "work". In ordinary language (which colors thought) the two words were — and are — used more or less synonymously. The difference has become progressively clearer since animals, and later, machines, took over most of the activities involving physical strength or power and the role of human workers came to be understood more clearly as design, planning, supervision, inspection and monitoring [Ayres 1987, 1994]. In other words, human workers (except in rare cases) are not valued for jobs that horses or steam engines could do just as well, but rather for physical dexterity and information processing skills, especially including sensory and mental abilities.

Whether for this reason, or others, "energy" was recognized for the first time in the 1970's as a distinct factor of production (i.e. distinct from labor and capital).<sup>17</sup> The addition of material flows to the group was almost an afterthought. At any rate, macro-economists now tend to distinguish four factors of production (capital, K; labor, L; energy, E; materials, M), as against only the first two (capital and labor) as recently as the 1960's. Indeed, production functions of the modern sort are generally called KLEM functions, reflecting the equal status of the four factors. We suggest, below, that the two factors E, M can and should be combined into a single factor, namely Exergy.

The identification of energy — really heat of combustion — (rather than exergy) as the "fundamental currency" for industrial activity goes back to the 1950's. The first attempt to construct a consistent set of energy accounts for the U.S. was a chapter by R. Widgery in a book entitled *Energy Sources - The Wealth of the World* [Ayres & Scarlott 1952, Chapter 21]. The 1952 book was seminal; it was written during the deliberations of President Truman's Commission on Resources and America's Future (the so-called Paley Commission), to which its authors contributed. This led to the creation in 1952 of Resources For the Future Inc., a non-profit research institute funded by the Ford Foundation. RFF subsequently carried out a number of major landmark studies of resource availability, including *Scarcity & Growth* [Barnett & Morse 1962], *Energy in the American Economy, 1850-1975* [Schurr & Netschert 1960] and *Resources in America's Future* [Landsberg *et al* 1963].

Since that time the energy-as-resource literature has expanded to enormous proportions, both in the U.S. and worldwide. In most of this literature, the term "energy" has been used rather carelessly, to say the least. The energy accounting scheme initiated by Widgery in 1952 reduces all fuels to their equivalent heat-of-combustion value and allocates them among uses, such as transportation, manufacturing, farming and household use. This is done, both for primary fuels (coal, oil, natural gas) and after conversion to other secondary forms, including electric power generation. The loss of heating value during secondary conversion, especially electric power generation, is noted, but not discussed in depth. Losses in the conversion of "finished fuels" to final services are scarcely mentioned, still less

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<sup>17</sup> See, for instance, [Allen *et al* 1976; Allen 1979].

quantified. Standard energy accounting methodology still uses the same basic scheme. The format of the 1952 accounts is essentially the same as the format of the energy balances for OECD countries published annually by the International Energy Agency (IEA) in Paris.

The importance of the Second Law of thermodynamics — hence the distinction between energy and exergy — was, and still is, completely ignored in the standard accounting methodology. (This methodology has recently been criticized by IASA [Nakićenović *et al* 1996]). Resource economists had certainly noticed the fact that ore grades were declining, on the average. This was particularly noticeable in the case of copper ores. Economic theory suggests that the highest grade ores should be mined first, which seems to accord with practice [Herfindahl 1967]. But, although geologists have long known that there is an inverse relationship between ore grade and identifiable reserves (more ore at lower grades), it is also a fact that lower grade ores require more energy to process, *ceteris paribus*. This suggests that raw material costs should increase over time. The empirical work of Barnett & Morse, cited above, did not confirm this hypothesis, however. On the contrary, raw material prices over the previous century had showed a consistent long-term pattern of decrease. Subsequent work confirms that these trends (except in the case of wood products) continued at least until the mid 1970's [Smith 1979], and probably through the 1980's as well. This strongly implies that technological improvements in exploration, extraction, beneficiation, and refining have, so far, more than compensated for declines in resource quality. In any case, concerns about ore grade/quality did not seem to justify the incorporation of quality measures in the resource accounting system.

One of the first economists to emphasize the importance of resource quality was Nicholas Georgescu-Roegen [Georgescu-Roegen 1971]. He based his argument, not on empirical data, but on fundamental theory, notably the Second Law of thermodynamics. He forcefully pointed out what should have been obvious, namely that the economic system depends on the use of enormous quantities of low entropy raw materials (e.g. fossil fuels), which are converted by combustion into high entropy combustion products. In short, the economic system is built around the use of resource stocks equivalent to a storehouse of "negative entropy" accumulated by natural processes over hundreds of millions of years. This stock of "negentropy" would be exhausted, at present rates of consumption, in a few hundred years at most. (Indeed, Georgescu-Roegen went beyond the classical theory, in that he asserted a "Fourth Law", to the effect that "matter" becomes unavailable independently of energy.

Concerns about resource depletion achieved more widespread recognition in theoretical economics during the mid-1970's, largely in response to the Club of Rome sponsored study on "Limits to Growth" [Meadows *et al* 1972] and the resulting controversy. Economists responded with a burst of publications dealing for the most part with "optimal depletion" policies under a variety of assumptions and conditions.<sup>18</sup> However, the prevailing view among economists was (and still is) that resource depletion *per se* is not a serious threat, because technological progress and capital accumulation would automatically compensate for the loss of natural capital due to depletion.

Meanwhile energy analysis proceeded independently and in a different direction. Prompted by the peaking of domestic U.S. petroleum production in 1969 and the subsequent

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<sup>18</sup> For a good summary of the current thinking, including citations, see Robert Solow's address to the American Economic Association, on assuming the presidency, entitled "The economics of resources or the resources of economics" [Solow 1974]. See also [Dasgupta & Heal 1979].

sharp rise in imports, the U.S. government and various interest groups (not least, the electric power industry and the petroleum industry), sponsored a series of commissions and reports on future energy demand and the adequacy of energy supplies.<sup>19</sup> The nuclear power industry (backed by the Atomic Energy Commission and its supporters in Congress) foresaw a supply crisis and a major growth opportunity. On the other hand, a number of analysts, notably Amory Lovins, saw a need and an opportunity for increased energy conservation [Lovins 1977; Lovins *et al* 1982].

A further development from the concern with respect to the potential for energy conservation was a series of sectoral engineering-oriented studies focussed on energy efficiency. It quickly became obvious that the interest groups on the "supply" side of the controversy were claiming a need for continued investment in production capacity based on assumptions of a tight relationship between GDP and energy consumption (the famous E/GDP curve) which, in turn, depended on an implicit assumption derived from the energy accounting methodology itself.<sup>20</sup> As noted above, the official accounting methodology took note of energy losses in conversion *only* on the supply side. Finished fuels delivered to "end users" were, at first, assumed to be consumed with optimal (i.e. near perfect) efficiency. Losses within user sectors were ignored because end-uses themselves were not carefully defined, still less measured, by the either the energy industry or its regulatory bodies.

The first explicit public admission of energy (exergy) losses elsewhere in the system was a report initially prepared by Livermore National Laboratories for the Joint Committee on Atomic Energy of the U.S. Congress. It was repackaged as a Committee Report and circulated widely [Bridges 1973]. In this publication the notion of "useful" energy was introduced. It was assumed, essentially without discussion, that the ratios of Useful energy to Energy Input were 33% for the electric power sector, 25% for the transportation sector, 50% for manufacturing and 80%(!) for households. Overall, the ratio of "Useful Energy" to Energy Input for the economy as a whole, based on these assumptions, turned out to be close over 50%. Admittedly, these ratios were not explicitly defined as "efficiencies", but the reader/viewer could scarcely avoid this implication. A further (but also unstated) implication was that remaining opportunities for energy conservation could not be very great since the system was already converting raw fuels into "useful" forms so efficiently.

The broader scientific and engineering community finally took notice of the problem. Thermodynamic analysis of energy conversion systems became interesting to theoreticians again, for the first time in many years. The methodology for efficiency calculation, in particular, was re-examined. The American Physical Society sponsored a landmark summer study in 1974 which led to an influential report, entitled "Efficient Use of Energy: A Physics Perspective" [Carnahan *et al* 1975]. The Report defined availability (i.e. exergy), and presented a large number of calculations of exergy losses for different processes and activities. It also clarified many previously murky questions — such as how to calculate the real

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<sup>19</sup> For instance: *U.S. Energy Outlook* (National Petroleum Council, 1972); *The Nation's Energy Future* (U.S. Atomic Energy Commission, 1973); *Exploring Energy Choices* (Ford Foundation Energy Policy Project, 1974); *Nuclear Power: Issues and Choices* (Ford Foundation and MITRE Corp, 1977); *Energy: The Next Twenty Years* (Ford Foundation and Resources for the Future, Inc. 1979).

<sup>20</sup> It is interesting that several of these studies were initiated *before* the oil crisis of 1973-74. The most comprehensive, by far, was the Ford Foundation's Energy Project, which led to a series of book publications, including the pathbreaking study of exergy-efficiency in industry [Gyftopoulos *et al* 1974]. For a more complete summary of the conservation vs. growth debate and citations of the early literature, see [Ayres 1992].

efficiency of refrigeration equipment and heat pumps — and introduced the important distinction between "First Law" efficiency (i.e. "useful" output/input) and "Second Law" efficiency. The former is easier to calculate, but extremely misleading in many cases. The latter, defined as "minimum theoretical available energy input/actual available energy input", is a far more informative measure of the potential for future improvement.

The first attempt to estimate exergy (i.e. second-law) efficiency for the U.S. economy as a whole, based largely on the results of the APS summer study, concluded that the current mix of final services could theoretically be delivered using only around 2.5%-3% of the exergy actually being used [Ayres & Narkus-Kramer 1976]. In effect, the analysis concluded that 97% of the exergy input was being wasted. This result implied a very large potential for conservation, in complete disagreement with conventional estimates at the time (which typically allowed for a potential gain of 15-20%, at most). This analysis was later updated and revised, reflecting a modest improvement during the interim (to about 3%-3.5%) [Ayres 1989]. A similar study was subsequently conducted for Austria [Bodda *et al* 1991]. It was later extrapolated to the global level, with comparable results.

The first systematic attempt to use exergy as a general measure of all resources, including renewables (food and forest products) and mineral ores, was conducted in Sweden [Wall 1977, 1986]. Later Wall applied this approach to Japan [Wall 1990] and Italy [Wall *et al* 1994; Sciubba 1995]. Several other national studies to estimate energy and/or exergy efficiency for a wide range of countries have been published recently, e.g. Canada [Rosen 1992], Brazil [Schaeffer & Wirtshafter 1992]; OECD countries [Nakićenović 1993], and Turkey [Ozdogan & Arikol 1995].

Wall's work, and its successors, focussed mainly on the conversion of "primary" exergy into "useful" exergy (e.g. space heating, hot water, mechanical energy). These analyses are incomplete insofar as they implicitly assume that "useful" exergy is equivalent to final services. In fact, this is not so. Indeed, "useful energy" tends to be used quite inefficiently (e.g. due to poor insulation, wasteful use of transport vehicles, etc.) Data is sketchy but, taking into account the missing last step in the conversion chain, namely the efficiency of generating final services from useful exergy, it is clear that the overall second-law efficiency of modern economies is only a few percent, consistent with the earlier estimates by Ayres & Narkus-Kramer [op cit 1976; also Ayres 1989]. In sharp contrast to most estimates in the 1970's, Gilli, Nakićenović and Kurz now argue forcefully that the theoretical potential for improvement might be as great as 20-fold [Nakićenović *et al* 1996]. On the global scale, Nakićenović *et al* now estimate that primary to useful energy efficiency is around 30% while exergy efficiency is about 10% (*ibid*); however, in this estimate end-use efficiency is not fully considered.

Unfortunately, all of the above-mentioned studies were carried out at a very aggregated level. Among them, only Wall considered non-fuel resources such as forest products and iron ore, and he did not attempt to incorporate sophisticated calculations of the exergy content of non-fuel materials and materials losses at various stages of processing. (Nor did he deal with the problem of end-uses, mentioned above.) Nevertheless, Wall's work was path-breaking, in that it suggested for the first time a common way of measuring stocks and flows of all natural resources.

Using the computational tools and data base developed by engineers and chemists (summarized in Part I of this document), it would now be a fairly straightforward exercise to implement a more complete exergy accounting system. This system would serve as a resource accounting framework, covering both stocks and flows of fuels, agricultural and forest products, and other industrial materials. It would provide a natural basis for assessing

the efficacy of resource use and identifying policy tradeoffs and cost effective opportunities for conservation. As discussed below, it would also provide a natural means of including waste flows and pollution in the same comprehensive framework.

## 10. Exergy as a Measure of Waste Residuals and Potential for Harm

As emphasized in the previous section, exergy is not only a natural measure of the resource *inputs* to an economic system. It is also a measure of the material *outputs*. If 90% or 95% of the exergy inputs are "wasted", what happens to this exergy? Exergy is lost in all processes, mostly — but not entirely — as low temperature heat. Low temperature heat is rarely damaging to the environment.<sup>21</sup> But some exergy is lost in the form of chemically or physically reactive materials. We would like to know what environmental processes this lost exergy might drive? What harm — if any — may result? The last question is a very deep one, but the first step, we argue, is to quantify the residual emissions themselves, in common units of exergy.

Here, it is vital to recall that exergy is not a conserved quantity like mass or energy. Thus, all mass extracted from the earth's crust must either be added to anthropogenic stocks (e.g. structures) or eventually discarded as wastes. On the other hand, since mass is conserved, the goal of "zero emissions" that is often proposed by environmentalists is physically impossible, at least if wastes and emissions are to be measured in terms of mass. One can only attempt to reduce the overall consumption of materials (mass), and make sure that it is as harmless as possible when discarded.

However, this is not the case for exergy. On the contrary, the exergy content of a physical waste stream is typically much less than the exergy content of the inputs. The more efficient the process (in the second law, or exergetic sense), the less exergy is embodied in the materials that must be discarded. There is no reason *in principle* why the exergy content of material wastes could not be reduced arbitrarily near to zero. But before considering ways and means of reducing the waste exergy embodied in materials, we need ways to measure and/or estimate it.

To calculate the exergy content of waste materials, in practice, there are two approaches. Ideally they should be used together for mutual verification. The first approach requires a detailed knowledge of the chemical composition of the waste stream. Once this is known, the calculation of exergy proceeds component by component according to the scheme outlined in Part I and summarized in equation (13). Here the difficulty is obvious: for many chemical and metallurgical processes it is difficult to obtain reliable data on the chemical composition of the wastes. Nevertheless, the composition of the waste stream can be estimated approximately, in many cases, if the basic chemical reactions, temperatures, pressures and yields are known. Indeed, commercially available software suitable for use in a desktop computer is capable of making such calculations at minimal cost [Ayres 1995; Wolfgang & Ayres 1995].

The second, alternative approach involves using the exergy balance equation:

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<sup>21</sup> The case of warm water discharged from the condensers of steam power plants may be an exception, in some cases. It does alter the local ecosystem. On the other hand, this is not necessarily harmful. For example, warm (but clean) water discharges from power plants and pulp mills into the estuaries of several rivers in the southeastern U.S. have actually extended the range of the dugong, a rare marine mammal that was formerly restricted to Florida, where its survival was severely threatened.

$$B_{in} = B_{product} + \Delta B_{process} + B_{waste} \quad (14)$$

which can be rewritten

$$B_{waste} = B_{in} - B_{product} - \Delta B_{process}$$

Evidently, in this case it is only necessary to know the composition of the process inputs (including utilities) and that of the main products. Then it is possible to estimate the exergy loss (or gain) in the process. The exergies of process inputs and product outputs are computed, as before, using (11), when Gibbs free energies of formation are known.

A practical difficulty is that Gibbs free energies of formation are not available (at least published) for more than a few hundred chemicals. This forces us to use some crude approximations, in some cases. Where Gibbs energies are not available, it is often easier to estimate exergy directly. Three examples are worth noting.

(1) In the case of process utilities, it is sufficient to know that the exergy content of electricity is essentially 100% of its energy content. In the case of other fuels, the exergy content is very close to the heat of combustion, with two (usually small) adjustments. One adjustment is for the fact that part of the combustion products of any hydrocarbon consists of water vapor, and some allowance must be made for the fact that water vapor (i.e. steam) is not an ideal gas. Steam can do work as it expands, but it cannot expand further when its temperatures reaches its condensation point (e.g. 100° C at normal atmospheric pressure).

The other adjustment is for the fact that combustion temperatures are not infinite. The exergy content of combustion gases is the work that could be done by an ideal gas of that temperature through a Carnot engine. (See *Figure 1*). For most fuels, combustion temperatures are fairly high, typically at least 2500° C. At this temperature the efficiency factor  $\epsilon$  approaches 90%. However, it is significantly less for fuels that are not completely dry, such as wood. However for process steam, which is rather common in industry, the temperature adjustment is even more critical. At a typical steam temperature of 600°K, (around 300°C) the Carnot efficiency is approximately 50%, whence the exergy content of the steam is 50% of its enthalpy content. This approximation is usually adequate, since the uncertainty in the utility input exergy translates *only* into some uncertainty — rarely more than a few percent) in the exergy loss in the process, not the exergy content of the waste residuals.

(2) In the case of chlorinated hydrocarbons, only a few Gibbs energies have been published, whence exact exergy values can only be computed for a few such compounds. However, it is sometimes possible to interpolate or extrapolate from a well-defined series. For instance, exact values (of both) are known for ethane (C<sub>2</sub>H<sub>6</sub>) and for both mono- and dichlorinated ethanes. Using this data, presented as a series, it is possible to estimate the corresponding values for 1,1,1 trichloroethane, for which there are no published values. The results are shown below.

compound	formula	Gibbs free energy/gm	exergy/gm
ethane	C <sub>2</sub> H <sub>6</sub>	-31.9	49.78
monochloroethane	C <sub>2</sub> H <sub>5</sub> Cl	-59.3	21.91
dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-73.4	13.57
trichloroethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	-82.(est)	9.28 (est)

The actual method of extrapolation can be as simple as graphing and curve-fitting. In practice, we adopted a numerical method, the details of which need not be spelled out here. To verify the method, we tested the same procedure on chlorinated ethylenes, for which there is a corresponding series. The results were quite satisfactory for our purposes.

(3) In the case of polymers (including PVC), we could find no published values of the Gibbs energy. We did, however, find a source that gave exergy values per unit mass for several polymers together with their corresponding monomers [Hall *et al* 1975]. The results are presented below:

$$\begin{aligned}
 B_{PVC} &= 0.933 B_{VCM} \\
 B_{PS} &= 0.997 B_S \\
 B_{LDPE} &= 0.965 B_E \\
 B_{HDPE} &= 0.919 B_E
 \end{aligned}$$

where the indices PS and S refer to polystyrene and styrene, respectively, while LDPE and HDPE refer to low density and high density polyethylene; E refers to ethylene.

To demonstrate the complete procedure, two examples are presented hereafter. *Figure 2* shows a well-known unit process for chlorine production in terms of mass and exergy flows. Exergy values in kJ per kilogram of chlorine, have been calculated for every input and output stream. Minor flows have been included, here, because of their important contribution to the waste exergy. It is vitally important to distinguish *waste* exergy from *lost* exergy, which literally disappears. (Remember, exergy is not conserved). In the case of the chlorine process, which is highly endothermic, input materials (salt, water) have very little exergy. The main source on the input side is electric power. Non-waste output products, totalling 7027 kJ, account for about a third (33%) of the total inputs. Of this, however, 3113 kJ is hydrogen, which is actually recovered and burned for process heat. (It is the source of heat for the steam). Exergy embodied in waste materials account for only 1.2% of total exergy inputs. The remainder of the input exergy is lost in the electrolysis process. Full details of this process are given in *Table 4* (Appendix).

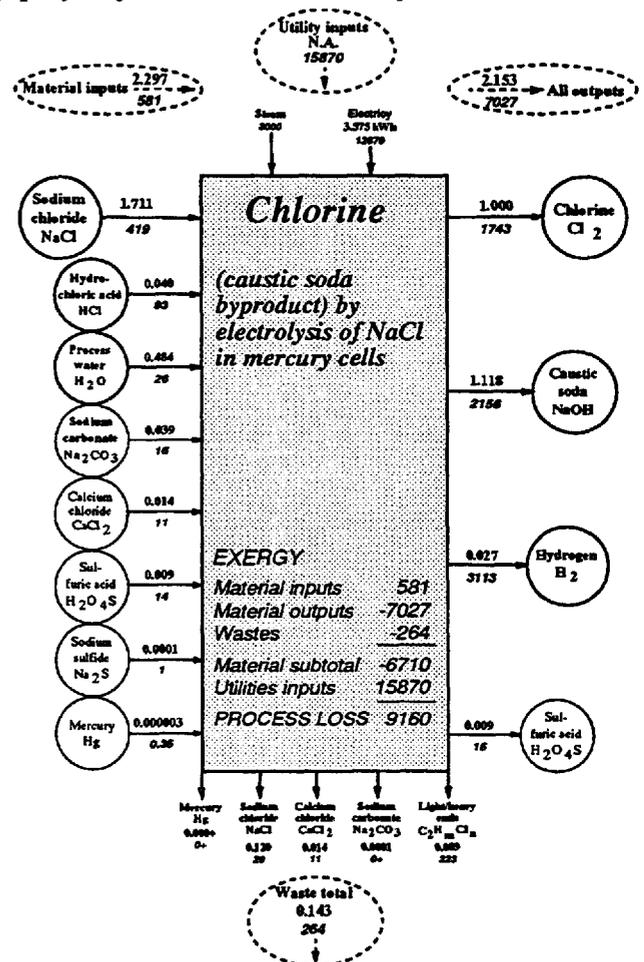


Figure 2: Sample unit process: Chlorine, kJ per kg

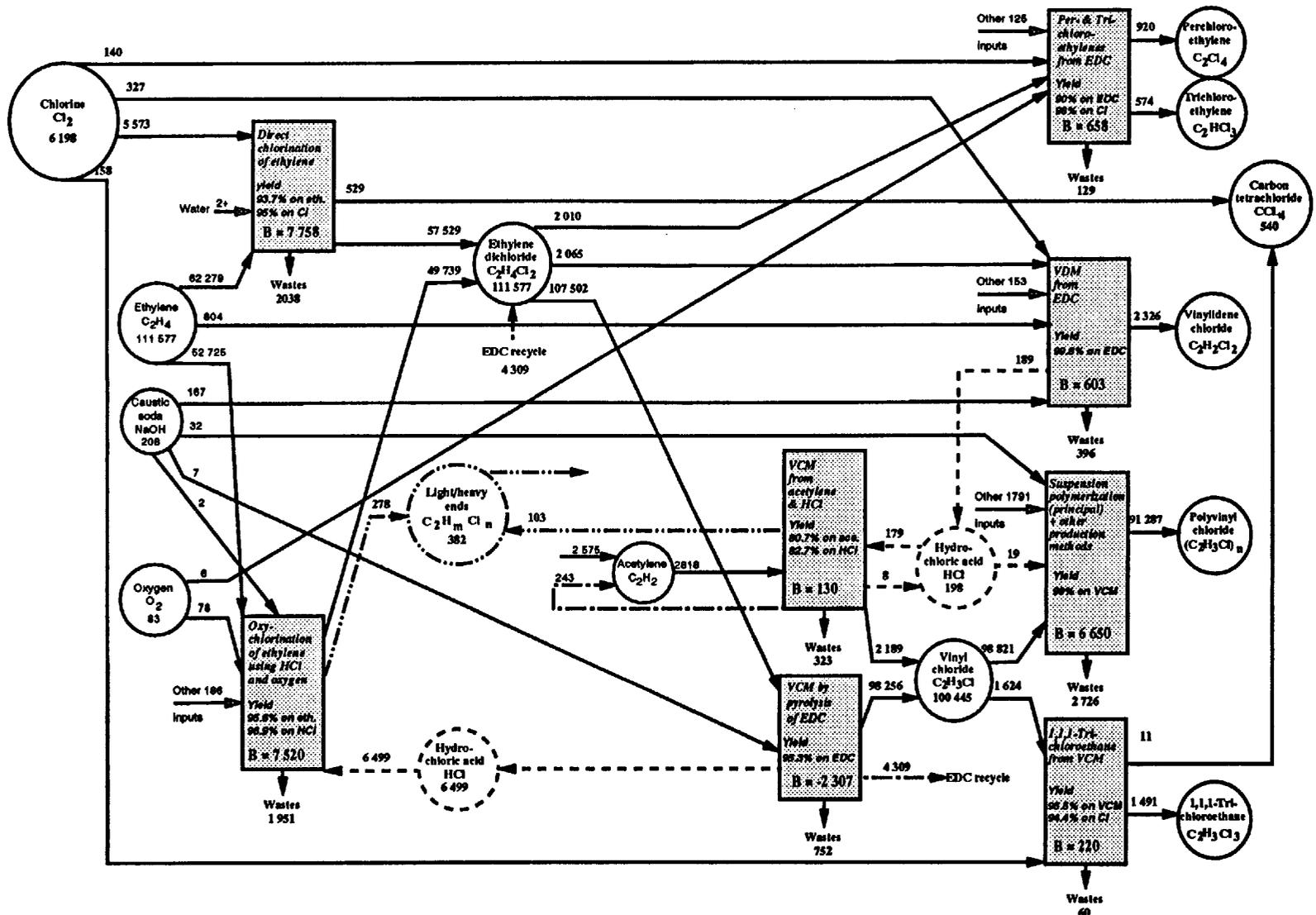
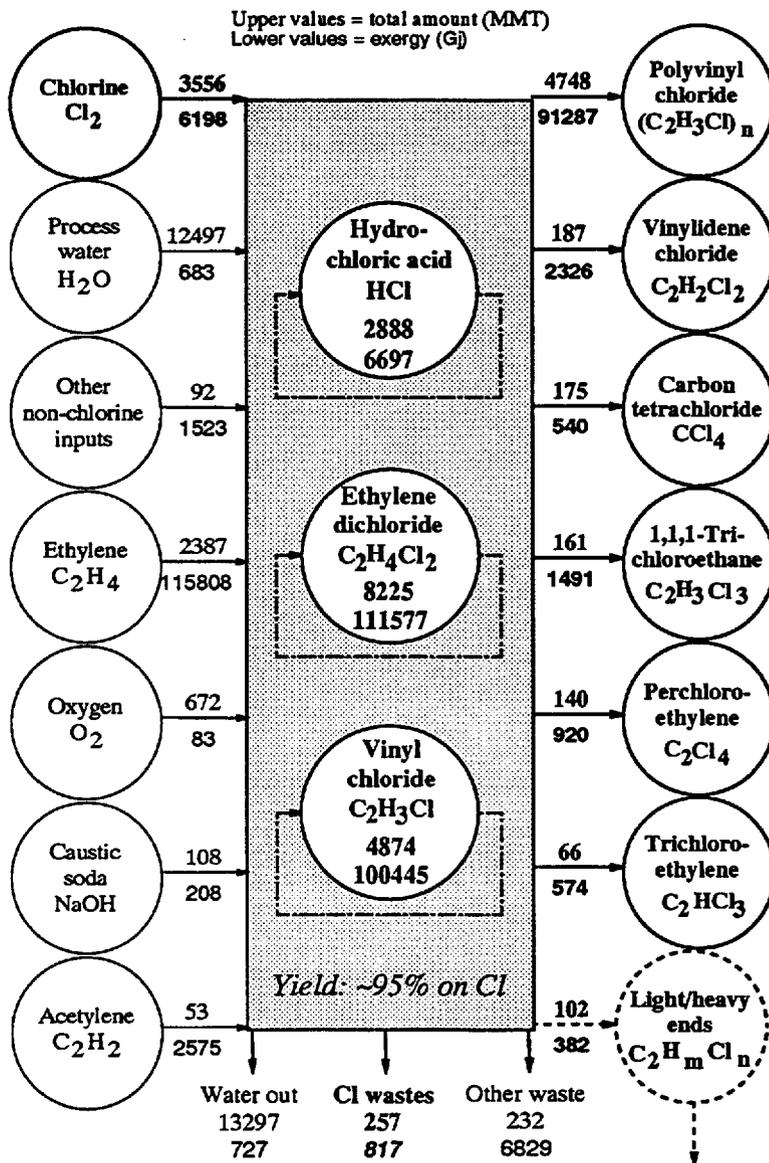


Figure 3: Exergy in the production of PVC & other byproducts (chlorination of ethylene): Western Europe 1992 (gigaJoules)

A much more complex case is illustrated in *Figure 3* (See Appendix *Tables 2 & 3* for details). Here the whole chain of actual processes used in Europe from chlorine to PVC and its co-products (including trichloroethane) is taken into account. Numbers are all in units of millions of kJ, or gigajoules gJ. All the numbers adjacent to lines refer to exergy being conveyed from one process to another, while the numbers in the circles refer to annual production of that material. The boxes, which are processes, generally have more than one input and more than one output. (Utilities, in this case, have been ignored). Only one of the eight processes is endothermic: pyrolysis of EDC. The others are exothermic and, effectively, "self energizing".

The sum total of material-embodied input exergies (not including utilities) for the whole chain is 346,090 gJ, or 346.1 terajoules (TJ), shown in *Figure 4*. The exergy embodied in output products (mainly

PVC) was 316,483 gJ. The exergy embodied in material waste streams for the system as a whole was 8376 gJ or only about 0.22% of the embodied inputs, exclusive of utilities. The exergy efficiency of the process chain cannot be calculated from the data shown, because process exergy has not been calculated. Both could be calculated immediately with the additional data on fuels and electricity used in the eight individual processes.



*Figure 4: Mass & Exergy Summary for production of PVC & other byproducts of the chlorination of ethylene in Western Europe 1992*

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## Appendix: Data

The sources for Table 1 are as follows:

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**Table 1: Exergy of Some Selected Chemicals**

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY kJ/mol</i>	<i>State</i>	<i>GFORM kJ/mol</i>	<i>Weight mole</i>	<i>REF</i>
<b>ELEMENTS</b>							
Al	Aluminum	Al	888.40		289.40	26.98	SZAR
B	Boron	B	628.50		521.00	10.81	SZAR
Ba	Barium	Ba	747.70		146.00	137.34	SZAR
Br	Bromine	Br <sub>2</sub>	101.20		82.40	79.90	SZAR
C	Carbon	C	410.26		671.30	12.01	SZAR
Ca	Calcium	Ca	712.40		144.00	40.08	SZAR
Cl	Chlorine	Cl <sub>2</sub>	87.10	123.60	105.30	35.45	SZAR
Cr	Chromium	Cr	544.30		351.80	52.00	SZAR
Cu	Copper	Cu	134.20		297.70	63.55	SZAR
F	Fluorine	F <sub>2</sub>	466.30		62.30	19.00	SZAR
Fe	Iron	Fe	376.40		370.70	55.85	SZAR
H	Hydrogen	H <sub>2</sub>	331.30	236.10	203.30	1.01	SZAR
Hg	Mercury	Hg	115.00		31.80	200.59	SZAR
I	Iodine	I <sub>2</sub>	174.70		70.20	126.90	SZAR
K	Potassium	K	366.60		60.50	39.10	SZAR
Mg	Magnesium	Mg	633.80		112.50	24.31	SZAR
Mn	Manganese	Mn	482.30		238.50	54.94	SZAR
Mo	Molybdenum	Mo	730.30		612.50	95.94	SZAR

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> <i>kJ/mol</i>	<i>State</i>	<i>GFORM</i> <i>kJ/mol</i>	<i>Weight</i> <i>mole</i>	<i>REF</i>
N	Nitrogen	N2	0.72		455.50	14.01	SZAR
Na	Sodium	Na	336.60		77.00	22.99	SZAR
O	Oxygen	O2	233.70	3.97	231.70	16.00	SZAR
P	Phosphorus	P	875.80	863.60	280.10	30.97	SZAR
Pb	Lead	Pb	232.80		162.20	207.19	SZAR
S	Sulfur	S	609.60		236.70	32.06	SZAR
Sb	Antimony	Sb	435.80		222.10	121.75	SZAR
Si	Silicon	Si	854.60		405.50	28.09	SZAR
Ti	Titanium	Ti	906.90		428.40	47.90	SZAR
Zn	Zinc	Zn	339.20		94.80	65.37	SZAR

**INORGANIC COMPOUNDS: In order by alphabetized element, then name**

AlCl3	Aluminum chloride (aq,600)	AlCl3	445.00	S	-628.80	133.34	CRC
AlNaO2	Sodium aluminate	NaAlO2	151.70	S	-1077.27	81.97	SZAR
Al2O12S3	Aluminum sulfate (aq)	Al2(SO4)3	535.23	S	-3094.19	342.15	CEH
Al2O3	Aluminum oxide (corundum)	Al2O3	200.46	S	-1582.30	101.96	CRC
B2H6	Diborane	B2H6	873.28	G	-1092.02	27.67	CEH
BaCl2	Barium chloride (aq,300)	BaCl2	60.90	S	-810.40	208.25	CRC
BaCO3	Barium carbonate (witherite)	BaCO3	26.32	S	-1137.60	197.35	CRC
BaO4S	Barium sulfate	BaSO4	3.04	S	-1362.20	233.40	CRC
BaS	Barium sulfide	BaS	901.30	S	-456.00	169.40	CRC
BCl3	Boron trichloride	BCl3	426.50	L	-387.40	117.17	CRC
BF3	Boron fluoride	BF3	208.55	G	-1119.40	67.81	CRC
BH3O3	Boric acid	B(OH)3	28.80	S	-959.81	61.83	CEH
Br2Ca	Calcium bromide	CaBr2	150.00	S	-663.60	199.89	CRC
BrH	Hydrogen Bromide (aq,400)	HBr	65.81	L	-102.84	80.91	CEH
BrK	Potassium bromide (aq,400)	KBr	36.50	S	-380.70	119.01	CRC
BrNa	Sodium bromide (aq,400)	NaBr	210.10	G	-177.10	102.89	CRC
BrNaO3	Sodium bromate	NaBrO3	150.56	S	-242.60	150.89	CRC
CaCl2	Calcium chloride (aq)	CaCl2	87.20	S	-748.80	110.99	CRC
CaF2	Calcium fluoride	CaF2	73.71	S	-1104.99	78.08	CEH
CaH2O2	Calcium hydroxide (aq,800)	Ca(OH)2	54.97	S	-897.50	74.09	CRC

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
CaO	Calcium oxide	CaO	111.09	S	-603.30	56.08	CRC
CCaO3	Calcium carbonate (calcite)	CaCO3	-0.49	S	-1129.10	100.09	CRC
CCIN	Cyanogen Chloride	CCIN	603.42	G	131.00	61.47	CRC
CCl2F2	Dichlorodifluoromethane	CCl2F2	560.76	G	-439.40	120.91	CRC
CCl2O	Carbonyl chloride	COCl2	330.95	G	-204.90	98.92	CRC
CCl3F	Trichlorofluoromethane	CCl3F	592.01	L	-236.80	137.37	CRC
CCl4	Carbon tetrachloride	CCl4	473.10	L	-184.36	153.82	SZAR
CK2O3	Potassium carbonate (aq,400)	K2CO3	85.92	S	-1063.50	138.21	CRC
CNNa	Sodium cyanide (aq,200)	NaCN	670.82	S	-76.40	49.01	CRC
CNa2O3	Sodium carbonate (aq,1000)	Na2CO3	45.02	S	-1044.40	105.99	CRC
CO	Carbon monoxide	CO	275.05	G	-137.20	28.01	CRC
CO2	Carbon dioxide	CO2	19.83	G	-394.40	44.01	CRC
COS	Carbonyl Sulfide	COS	852.65	G	-169.20	60.07	CRC
CS2	Carbon disulfide	CS2	1694.06	L	64.60	76.14	CRC
CSi	Silicon carbide (cubic)	SiC	1202.06	S	-62.80	40.10	CRC
ClFO3	Perchloryl Fluoride	ClO3F	349.11	G	48.20	102.45	CRC
ClH	Hydrogen chloride (aq,400)	HCl	84.55	G	-95.30	36.46	CRC
ClH4N	Ammonium chloride	NH4Cl	331.46	S	-202.90	53.49	CRC
ClHO	Hydrochlorous acid (aq,400)	HOCl	101.88	L	-79.96	52.46	CEH
ClHO4	Perchloric acid (aq,660)	HClO4	143.02	L	-44.77	100.46	CEH
ClK	Potassium chloride (aq,400)	KCl	19.90	S	-408.50	74.56	CRC
ClNO	Nitrosyl chloride	ClNO	130.25	G	66.10	65.46	CRC
ClNa	Sodium chloride (aq,400)	NaCl	14.30	S	-384.10	58.44	CRC
ClNaO3	Sodium chlorate (aq,400)	NaClO3	142.06	S	-262.30	106.44	CRC
ClNaO4	Sodium perchlorate (aq,476)	NaClO4	151.44	S	-254.90	122.44	CRC
ClO2	Chlorine dioxide	ClO2	186.27	G	120.50	67.45	CRC
Cl2Cu	Cupric chloride	CuCl2	82.10	S	-175.70	134.45	CRC
Cl2O2S	Sulfuryl Chloride	SO2Cl2	423.12	L	-314.05	134.97	CEH
Cl2OS	Thionyl chloride	SOCl2	536.89	G	-198.30	118.97	CRC
Cl2S2	Sulfur monochloride	S2Cl2	1318.11	L	-24.69	135.03	CEH
Cl3HSi	Trichlorosilane	SiHCl3	675.55	L	-482.50	135.45	CRC
Cl3OP	Phosphorus oxychloride	POCl3	542.39	L	-520.80	153.33	CRC
Cl3P	Phosphorus trichloride	Cl3P	788.90	L	-272.30	137.33	CRC
Cl4Si	Silicon tetrachloride	Cl4Si	482.00	L	-619.80	169.90	CRC

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
Cl5P	Phosphorus pentachloride	PCl5	879.80	G	-305.00	208.24	CRC
Cr2O3	Chromium oxide	Cr2O3	36.46	S	-1058.10	151.99	CRC
CuO	Cupric oxide	CuO	6.49	S	-129.70	79.55	CRC
Cu2O	Cuprous oxide	Cu2O	124.39	S	-146.00	79.55	CRC
FH	Hydrogen fluoride	HF	75.80	G	-275.40	20.01	CRC
F4Si	Silicon Tetrafluoride	SiF4	280.96	G	-1506.24	104.08	CEH
F6S	Sulfur Hexafluoride	SF6	1016.89	G	-991.61	146.05	CEH
Fe2O3	Ferric oxide	Fe2O3	16.56	S	-742.20	159.69	CRC
FeS2	Pyrites	FeS2	1428.70	S	-166.90	119.98	CRC
HI	Hydrogen iodide (aq,400)	HI	153.73	L	-51.67	127.91	CEH
HNO3	Nitric acid	HNO3	43.67	L	-80.70	63.01	CRC
HNaO	Sodium hydroxide (aq,400)	NaOH	77.14	S	-379.50	40.00	CRC
H2O	Water	H2O	0.99	L	-237.10	18.02	CRC
H2O2	Hydrogen peroxide (aq,200)	H2O2	134.47	G	-105.60	34.01	CRC
H2O4S	Sulfuric acid	H2SO4	163.64	L	-690.00	98.08	CRC
H2S	Hydrogen sulfide	H2S	812.30	G	-33.40	34.08	CRC
H3N	Ammonia	NH3	338.11	G	-16.40	17.03	CRC
H3O4P	Phosphoric acid (aq,400)	H3PO4	113.59	S	-1124.30	98.00	CRC
H3P	Phosphine	PH3	1243.35	G	13.40	34.00	CRC
H4N2	Hydrazine	N2H4	622.22	L	149.30	32.05	CRC
H4Si	Silane	SiH4	1383.70	G	56.90	32.12	CRC
H6Si2	Disilane	Si2H6	2544.80	G	127.30	62.22	CRC
IK	Potassium iodide (aq,500)	KI	129.05	S	-324.90	166.01	CRC
INa	Sodium iodide (aq,inf)	NaI	137.85	S	-286.10	149.89	CRC
MgO	Magnesium oxide	MgO	66.49	S	-569.30	40.31	CRC
MnO2	Manganese oxide	MnO2	21.17	S	-465.10	86.94	CRC
NO	Nitric oxide	NO	89.03	G	86.69	30.01	CEH
NO2	Nitrogen dioxide	NO2	55.63	G	51.30	46.01	CRC
N2O	Nitrous oxide	N2O	106.91	G	104.20	44.01	CRC
N2O3	Nitrogen Trioxide	N2O3	146.18	G	139.50	76.01	CRC
N2O4	Nitrogen Tetroxide	N2O4	106.56	G	97.90	92.01	CRC
N2O5	Nitrogen Pentoxide	N2O5	125.75	G	115.10	108.01	CRC
Na2O	Sodium oxide	Na2O	299.69	S	-375.50	61.98	CRC
Na2S	Sodium sulfide (aq,400)	Na2S	933.00	S	-349.80	78.04	CRC

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
OPb	Lead monoxide	PbO	46.89	S	-187.90	223.19	CRC
OPb	Litharge	PbO	46.89	S	-187.90	223.19	CRC
OPb	Yellow lead oxide	PbO	46.89	S	-187.90	223.19	CRC
OZn	Zinc oxide	ZnO	20.69	S	-320.50	81.37	CRC
O2S	Sulfur dioxide	SO2	313.47	G	-300.10	64.06	CRC
O2Si	Silicon dioxide	SiO2	2.28	S	-856.29	60.08	CRC
O2Ti	Titanium dioxide	TiO2	22.07	S	-888.80	79.90	CRC
O2Zr	Zirconium oxide	ZrO2	-1038.83	S	-1042.80	123.22	CRC
O3	Ozone	O3	169.16	G	163.20	48.00	CRC
O3S	Sulfur trioxide	SO3	244.46	G	-371.10	80.06	CRC
O5V2	Vanadium Pentoxide	V2O5	-1409.58	S	-1419.50	181.88	CRC
SZn	Zinc sulfide (sphalerite)	ZnS	747.50	S	-201.30	97.43	CRC

**PURE HYDROCARBONS - in order by C, then H, then name**

CH4	Methane	CH4	832.16	G	-50.30	16.04	CRC
C2H2	Acetylene	C2H2	1267.32	G	210.70	26.04	CRC
C2H4	Ethylene	C2H4	1361.12	G	68.40	28.05	CRC
C2H6	Ethane	C2H6	1496.92	G	-31.90	30.07	CRC
C3H4	methyl acetylene	CH3C=CH	1896.75	G	193.77	40.07	CEH
C3H4	propadiene	C3H4	1523.80	G	-179.18	40.07	SZAR
C3H6	Cyclopropane	C3H6	2043.20	G	104.12	42.08	SZAR
C3H6	Propylene	C3H6	2001.69	G	62.61	42.08	CEH
C3H8	Propane	C3H8	2151.69	G	-23.49	44.10	CEH
C4H6	1-Butyne	C4H6	2552.35	G	203.01	54.09	CEH
C4H6	2-Butyne	C4H6	2536.47	G	187.13	54.09	CEH
C4H6	1,3-Butadiene	C4H6	2500.38	G	151.04	54.09	MAR
C4H8	1-butene	C4H8	2657.48	G	72.04	56.11	CEH
C4H8	1-butylene	C4H8	2659.70	G	74.26	56.11	SZAR
C4H8	2-methyl-2-propene	C4H8	2646.42	G	60.98	56.11	CEH
C4H8	cis-2-butene	C4H8	2652.41	G	66.97	56.11	CEH
C4H8	cyclobutane	C4H8	2516.20	G	-69.24	56.11	SZAR
C4H8	trans-2-butene	C4H8	2649.55	G	64.11	56.11	CEH
C4H10	Isobutane	C4H10	2803.57	G	-17.97	58.12	CEH

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
C4H10	n-Butane	C4H10	2805.83	G	-15.71	58.12	CEH
C5H8	1-Pentyne	C5H8	3205.61	G	209.91	68.12	CEH
C5H8	2-Pentyne	C5H8	3189.88	G	194.18	68.12	CEH
C5H8	3-Methyl-1-Butyne	C5H8	3201.22	G	205.52	68.12	CEH
C5H8	pentadiene	C5H8	2914.80	G	-80.90	68.12	SZAR
C5H10	1-Pentene	C5H10	3310.40	G	78.60	70.14	CEH
C5H10	2-Methyl-1-Butene	C5H10	3296.69	G	64.89	70.14	CEH
C5H10	2-Methyl-2-Butene	C5H10	3291.49	G	59.69	70.14	CEH
C5H10	3-Methyl-1-Butene	C5H10	3306.58	G	74.78	70.14	CEH
C5H10	cis-2-Pentene	C5H10	3303.65	G	71.85	70.14	CEH
C5H10	Cyclopentane	C5H10	3268.20	L	36.40	70.14	CEH
C5H10	trans-2-Pentene	C5H10	3301.15	G	69.35	70.14	CEH
C5H12	2,2-Dimethyl Propane	C5H12	3452.67	G	-15.23	72.15	CEH
C5H12	2-Methyl Butane	C5H12	3452.88	L	-15.02	72.15	CEH
C5H12	n-Pentane	C5H12	3458.65	L	-9.25	72.15	CEH
C6H6	benzene	C6H6	3299.52	G	129.66	78.11	CEH
C6H6	Benzol	C6H6	3294.36	L	124.50	78.11	MAR
C6H10	1-Hexyne	C6H10	3865.10	G	223.04	82.15	SZAR
C6H12	1-hexylene	C6H12	3967.90	L	89.74	84.16	SZAR
C6H12	Cyclohexane	C6H12	3904.90	L	26.74	84.16	CEH
C6H12	Methyl Cyclopentane	C6H12	3909.67	L	31.51	84.16	CEH
C6H12	Hexahydrobenzene	(CH <sub>2</sub> ) <sub>6</sub>	3877.87	G	-0.29	84.16	MAR
C6H14	2,2-dimethylbutane	C6H14	4102.21	L	-12.05	86.18	CEH
C6H14	2,3-dimethylbutane	C6H14	4108.24	L	-6.02	86.18	CEH
C6H14	2-methylpentane	C6H14	4107.02	L	-7.24	86.18	CEH
C6H14	3-methylpentane	C6H14	4109.57	L	-4.69	86.18	CEH
C6H14	n-hexane	C6H14	4110.45	L	-3.81	86.18	CEH
C7H8	Toluene	C7H8	3938.51	L	122.29	92.14	CEH
C7H8	Methylbenzene	C6H5CH3	3938.52	L	122.30	92.14	MAR
C7H14	1-Heptene	C7H14	4604.60	L	80.08	98.19	SZAR
C7H14	Ethylcyclopentane	C7H14	4561.51	L	36.99	98.19	CEH
C7H14	Methyl Cyclohexane	C7H14	4551.80	G	27.28	98.19	CEH
C7H16	2,2,3-trimethylbutane	C7H16	4758.82	L	-1.80	100.21	CEH
C7H16	2,2-dimethylpentane	C7H16	4756.10	L	-4.52	100.21	CEH

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
C7H16	2,3-dimethylpentane	C7H16	4755.31	L	-5.31	100.21	CEH
C7H16	2,4-dimethylpentane	C7H16	4758.57	L	-2.05	100.21	CEH
C7H16	2-methylhexane	C7H16	4758.65	L	-1.97	100.21	CEH
C7H16	3,3-diemthylpentane	C7H16	4757.73	L	-2.89	100.21	CEH
C7H16	3-ethylpentane	C7H16	4765.06	L	4.44	100.21	CEH
C7H16	3-methylhexane	C7H16	4758.99	L	-1.63	100.21	CEH
C7H16	n-heptane	C7H16	4762.38	L	1.76	100.21	CEH
C8H10	Ethylbenzene	C8H10	4582.30	L	119.72	106.17	CEH
C8H10	m-xylene	C8H10	4570.23	L	107.65	106.17	CEH
C8H10	o-xylene	C8H10	4572.91	L	110.33	106.17	CEH
C8H10	p-xylene	C8H10	4572.66	L	110.08	106.17	CEH
C8H10	Xylene	C6H4(CH3)2	4581.45	G	118.87	106.17	MAR
C8H16	Ethylcyclohexane	C8H16	5200.00	L	29.12	112.22	CEH
C8H18	2,2,3,3-tetramethylbutane	C8H18	5427.40	G	20.42	114.23	CEH
C8H18	2,2,3-trimethylpentane	C8H18	5416.27	L	9.29	114.23	CEH
C8H18	2,2,4-trimethylpentane	C8H18	5413.30	L	6.32	114.23	CEH
C8H18	2,2-dimethylhexane	C8H18	5403.97	L	-3.01	114.23	CEH
C8H18	2,3,3-trimethylpentane	C8H18	5417.61	L	10.63	114.23	CEH
C8H18	2,3,4-trimethylpentane	C8H18	5416.77	L	9.79	114.23	CEH
C8H18	2,3-dimethylhexane	C8H18	5416.06	L	9.08	114.23	CEH
C8H18	2,4-dimethylhexane	C8H18	5410.70	L	3.72	114.23	CEH
C8H18	2,5-dimethylhexane	C8H18	5409.45	L	2.47	114.23	CEH
C8H18	2-methylpheptane	C8H18	5410.83	L	3.85	114.23	CEH
C8H18	2-methyl-3-ethylpentane	C8H18	5419.66	L	12.68	114.23	CEH
C8H18	3,3-dimethylhexane	C8H18	5412.13	L	5.15	114.23	CEH
C8H18	3,4-dimethylhexane	C8H18	5418.95	L	11.97	114.23	CEH
C8H18	3-ethylhexane	C8H18	5414.51	L	7.53	114.23	CEH
C8H18	3-methylpheptane	C8H18	5411.67	L	4.69	114.23	CEH
C8H18	3-methyl-3-ethylpentane	C8H18	5418.23	L	11.25	114.23	CEH
C8H18	4-methylpheptane	C8H18	5414.76	L	7.78	114.23	CEH
C8H18	n-octane	CH3(CH2)6CH3	5414.39	L	7.41	114.23	CEH
C9H12	1,2,3-trimethylbenzne	C9H12	5216.38	L	107.44	120.20	CEH
C9H12	1,2,4-trimethylbenzne	C9H12	5211.29	L	102.35	120.20	CEH
C9H12	1,3,5-trimethylbenzne	C9H12	5212.84	L	103.90	120.20	CEH

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
C9H12	1-methyl-2-Ethylbenzene	C9H12	5225.98	L	117.04	120.20	CEH
C9H12	1-methyl-3-ethylbenzene	C9H12	5221.81	L	112.87	120.20	CEH
C9H12	1-methyl-4-ethylbenzene	C9H12	5222.08	L	113.14	120.20	CEH
C9H12	isopropylbenzene	C9H12	5233.24	L	124.30	120.20	CEH
C9H12	n-propylbenzene	C9H12	5232.79	L	123.85	120.20	CEH
C9H12	Cumene	C6H5CH(CH3)2	5233.20	L	124.26	120.20	MAR
C9H18	n-Propylcyclohexane	C9H18	5857.70	L	40.46	126.24	SZAR
C9H20	n-Nonane	C9H20	6064.90	L	11.56	128.26	SZAR
C10H8	Naphthalene	C10H8	5255.00	S	208.00	128.18	SZAR
C10H14	1,2,4,5-Tetramethylbenzene	(CH3)4C6H2	5880.00	S	124.70	134.22	SZAR
C10H14	n-Butylbenzene	C6H5C4H9	5892.00	L	136.70	134.22	SZAR
C10H20	n-Butylcyclohexane	C10H20	6511.50	L	47.90	140.27	SZAR
C10H22	n-Decane	C10H22	6716.80	L	17.10	142.29	SZAR
C11H10	2-Methylnaphthalene	C11H10	5881.40	S	188.04	142.20	SZAR
C11H16	pentamethylbenzene	C6H(CH3)5	6516.00	S	114.34	148.25	SZAR
C11H24	n-Undecane	C11H24	7376.90	L	30.84	156.31	SZAR
C12H18	hexamethylbenzene	C6(CH3)6	7171.00	S	122.98	162.28	SZAR
C12H26	n-Dodecane	C12H26	8029.40	L	36.98	170.34	SZAR
C13H28	n-Tridecane	C13H28	8682.00	L	43.22	184.37	SZAR
C14H10	Anthracene	C14H10	7218.10	S	293.96	178.24	SZAR
C14H10	Phenanthrene	C14H10	7201.80	S	277.66	178.24	SZAR
C14H14	1,1-Diphenylethane	C14H14	7665.90	S	269.56	182.27	SZAR
C14H30	n-Tetradecane	C14H30	9334.50	L	49.36	198.40	SZAR
C15H32	n-Pentadecane	C15H32	9984.80	L	53.30	212.42	SZAR
C16H26	n-Decylbenzene	C16H26	9700.80	L	67.34	218.39	SZAR
C16H34	n-Hexadecane	C16H34	10639.70	L	61.84	226.45	SZAR
C18H38	n-Octadecane	C18H38	11937.40	S	66.82	254.50	SZAR
C19H16	Triphenylmethane	(C6H5)3CH	10109.20	S	425.46	244.34	SZAR

## ORGANIC COMPOUNDS - in order by name

C2Cl4F2	1,1,1,2-tetrachloro-2,2-difluoroethane	C2Cl4F2	1127.02	G	-407.00	203.83	CRC
C2Cl4H2	1,1,2,2-Tetrachloroethane	C2H2Cl4	1218.26	G	-85.56	167.85	MAR
C2Cl2H4	1,1-Dichloroethane	C2H4Cl2	1343.23	L	-73.09	98.96	MAR

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY kJ/mol</i>	<i>State</i>	<i>GFORM kJ/mol</i>	<i>Weight mole</i>	<i>REF</i>
C2Cl2H2	1,1-Dichloroethylene	C2H2Cl2	1204.32	L	24.10	96.94	CRC
C2H8N2	1,1-Dimethylhydrazine	(CH3)2NNH2	1972.04	L	206.40	60.10	CRC
C6Cl3H3	1,2,4-Trichlorobenzene	C6H3Cl3	3063.87	G	62.76	181.45	MAR
C2Cl2H4	1,2-Dichloroethane	C2H4Cl2	1342.52	L	-73.80	98.96	CRC
C2ClF2H	1-chloro-2,2-difluoroethylene	C2HClF2	1177.57	G	-289.10	98.48	CRC
C7H16O	1-Heptanol	C7H16O	4619.20	L	-143.41	116.20	SZAR
C6H14O	1-Hexanol	C6H14O	3961.10	L	-155.15	102.18	SZAR
C5H12S	1-Pentanethiol (amyl mercaptan)	C5H12S	4091.30	L	13.80	104.22	SZAR
C4H10O	2-Butanol	C4H10O	2672.86	G	-150.67	74.12	MAR
C8H18O	2-Ethylhexanol	C8H18O	5304.37	L	-104.60	130.23	MAR
C4H10S	2-methylpropyl mercaptan	C4H10S	3434.30	L	3.16	90.19	SZAR
C5H12O	2-Methyl-1-Butanol	C5H12O	3093.33	L	-376.56	88.15	MAR
C5H12O	2-Methyl-2-Butanol	C5H12O	3275.70	L	-194.19	88.15	SZAR
C5H12O	3-Methyl-1-Butanol (amyl alcohol)	CH3CHCH3CH2CH2OH	3311.70	L	-158.19	88.15	SZAR
C2H4O	Acetaldehyde	CH3CHO	1161.91	G	-132.80	44.05	CRC
C2H4O2	Acetic acid	CH3CO2H	906.79	L	-389.90	60.05	CRC
C4H6O3	Acetic anhydride	C4H6O3	1845.89	L	-509.40	102.09	CEH
C3H6O	Acetone	CH3COCH3	1785.59	L	-155.48	58.08	CEH
C2H3N	Acetonitrile	CH3CN	1252.23	L	77.20	41.05	CRC
C2ClH3O	Acetyl Chloride	C2H3ClO	1030.46	L	-208.00	78.50	CRC
C3H4O	Acrolein	C3H4O	1637.31	L	-67.66	56.06	CEH
C3H3N	Acrylonitrile	C3H3N	1780.60	G	195.31	53.06	MAR
C6H10O4	Adipic acid	C6H10O4	2908.72	L	-741.28	146.14	CEH
C6H8N2	Adiponitrile	C6H8N2	3635.25	L	228.57	108.14	CEH
C7ClH7	Alpha-chlorotoluene	C6H5CH2Cl	3843.65	L	83.68	126.59	MAR
C6H12O6	alpha-d-galactose	C6H12O6	2928.80	S	-961.27	180.16	SZAR
C2H7NO2	Ammonium Acetate (a1,400)	NH4C2H3O2	1198.24	L	-452.96	77.08	CEH
CH5NO3	Ammonium bicarbonate	NH4HCO3	340.93	S	-665.90	79.06	CRC
C2H8N2O4	Ammonium Oxalate (aq)	(NH4)2C2O4	952.68	L	-820.90	124.10	CEH
C6H7N	Aniline	C6H7N	3281.27	G	-7.00	93.13	CRC
C7H6O	Benzaldehyde	C7H6O	3591.48	L	9.37	106.13	CEH
C7H6O2	Benzoic acid	C7H6O2	3343.50	S	-240.59	122.12	SZAR
C7H8O	Benzyl Alcohol	C7H8O	3795.80	L	-22.41	108.14	SZAR
C7ClH7	Benzyl chloride	C7H7Cl	3901.22	L	141.25	126.59	MAR

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY kJ/mol</i>	<i>State</i>	<i>GFORM kJ/mol</i>	<i>Weight mole</i>	<i>REF</i>
C4H10S	butyl mercaptan	C4H10S	3438.70	L	7.56	90.19	SZAR
C4H11N	Butylamine	C4H9NH2	3020.91	G	80.96	73.14	CEH
C4H8O	Butyraldehyde (Butanal)	CH3CH2CH2CHO	2280.99	G	-306.44	72.11	CEH
C4H8O2	butyric acid	C4H8O2	2215.80	L	-373.61	88.11	SZAR
C6H6O	Carbolic acid	C6H5OH	3138.96	L	-32.89	94.11	MAR
C2ClH3O	Chloroacetaldehyde	C2H3ClO	1029.26	L	-209.20	78.50	MAR
C6ClH5	Chlorobenzene	C6H5Cl	3202.81	G	89.20	112.56	MAR
C2ClH3	chloroethylene	CH2=CHCl	1290.07	G	53.60	62.50	CRC
CCl3H	Chloroform (trichloromethane)	CHCl3	640.01	L	-73.70	119.38	CRC
C2ClF3	Chlorotrifluoroethylene	C2ClF3	1057.97	G	-523.80	116.47	CRC
C2Cl2H2	cis-1,2-Dichloroethylene	C2H2Cl2	1204.57	G	24.35	96.94	MAR
C7H8O	cresol	C7H8O	3763.10	G	-55.10	108.14	CEH
CH2N2	Cyanamide	H2NCN	748.25	S	101.17	42.04	CEH
C2N2	Cyanogen	C2N2	1118.39	G	297.15	52.04	CEH
C6H12O	Cyclohexanol	C6H12O	3750.80	L	-129.35	100.16	SZAR
C5H10O	cyclopentanol	C5H9OH	3109.70	L	-124.09	86.13	SZAR
C2Cl3HO	Dichloroacetyl Chloride	C2HCl3O	919.73	L	-206.23	147.39	MAR
C4H10O	Diethyl Ether	C4H10O	2707.42	L	-116.11	74.12	CEH
C4H10S	diethyl sulfide	C4H10S	3446.30	L	15.16	90.19	SZAR
CH2I2	Diiodomethane	CH2I2	911.46	L	90.40	267.84	CRC
C4H4O2	Diketene	C4H4O2	1908.01	L	-209.20	84.08	MAR
C2H6O	Dimethyl Ether	C2H6O	1418.21	G	-112.60	46.07	CRC
C2H6S	Dimethyl sulfide	C2H6S	2145.40	L	6.98	62.13	SZAR
C2H6OS	Dimethyl sulfoxide	C2H6OS	2040.51	L	-99.90	78.13	CRC
C2H7N	Dimethylamine	C2H7N	1717.23	L	70.00	45.08	CRC
C2H6S	Ethanethiol (ethyl mercaptan)	C2H5SH	2132.92	L	-5.50	62.13	CRC
C2H6O	Ethanol	CH3CH2OH	1356.01	L	-174.80	46.07	CRC
C2H7NO	Ethanolamine	H2NCH2CH2OH	1764.28	L	115.06	61.08	CEH
C4H10O	Ether	C2H5OC2H5	2661.06	L	-162.46	74.12	CEH
C4H8O2	Ethyl acetate	C4H8O2	2270.97	L	-318.44	88.11	CEH
BrC2H5	Ethyl Bromide (bromoethane)	C2H5Br	1435.57	L	-25.80	108.97	CRC
C2ClH5	Ethyl chloride (chloroethane)	C2H5Cl	1413.27	L	-59.30	64.52	CRC
C2H5I	Ethyl Iodide (Iodoethane)	CH3CH2I	1512.82	L	14.70	155.97	CRC
C5H10O2	Ethyl Propionate	C5H10O2	2904.56	L	-331.21	102.13	CEH

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> kJ/mol	<i>State</i>	<i>GFORM</i> kJ/mol	<i>Weight</i> mole	<i>REF</i>
C2H7N	Ethylamine	C2H7N	1683.53	G	36.30	45.08	CRC
C4H10S2	ethylbutyl disulfide	C4H10S2	4055.40	L	14.66	122.25	SZAR
C2H6O2	Ethylene glycol	C2H6O2	1212.97	L	-319.82	62.07	CEH
C2H4O	Ethylene oxide	C2H4O	1281.71	G	-13.00	44.05	CRC
C2H8N2	Ethylenediamine	H2NCH2CH2NH2	1891.16	L	125.52	60.10	MAR
CH2O	Formaldehyde	CH2O	545.85	G	-102.50	30.03	CRC
CH3NO	Formamide	CH3NO	613.62	G	-153.13	45.04	CEH
CH2O2	Formic acid	HCO2H	288.93	L	-361.40	46.03	CRC
C4H4O4	Fumaric acid	C4H4O4	1471.50	S	-649.68	116.07	SZAR
C4H4O	Furan	C4H4O	2118.20	L	2.98	68.08	SZAR
C5H6O2	Furfuryl Alcohol	C5H6O2	2687.70	L	-75.87	98.10	SZAR
C3H8O3	Glycerine	CH2CHCH2OHOHOH	1704.08	L	-477.06	92.10	MAR
C3H8O3	Glycerol	C3H8O3	1705.62	L	-475.51	92.10	CEH
C2H4O3	Glycolic (hydroxacetic) Acid	HOCH2COOH	773.29	L	-525.38	76.05	CEH
C6H16N2	Hexamethylenediamine	C6H16N2	4472.04	G	120.96	116.21	CEH
C6H13N	Hexamethyleneimine	C6H13N	4117.24	L	120.67	99.18	CEH
CHN	Hydrogen cyanide	CHN	653.67	L	125.00	27.03	CRC
C4H10O	Isobutanol	(CH3)2CHCH2OH	2658.84	L	-164.68	74.12	CEH
C4H8O	Isobutyraldehyde	C4H8O	2463.30	L	-124.13	72.11	SZAR
C2H3N	Isocyanomethane (ethanenitrile)	C2H3N	1334.53	L	159.50	41.05	CRC
C3H8O	Isopropanol	CH3CHOHCH3	2003.57	L	-173.59	60.10	MAR
C3H8S	Isopropyl Mercaptan (methylethyl sulfide)	(CH3)2CHSH	2795.00	L	10.22	76.16	SZAR
C2H2O	Ketene	C2H2O	1002.87	L	-55.73	42.04	CEH
C6H12O6	l-sorbose	C6H12O6	2939.00	S	-951.07	180.16	SZAR
C4H4O4	Maleic Acid	C4H4O4	1495.70	S	-625.48	116.07	SZAR
C4H2O3	Maleic anhydride	C4H2O3	1506.54	S	-376.56	98.06	MAR
C3H6N6	Melamine	C3N3(NH2)3	2111.95	L	170.71	126.12	CEH
CH4S	Methanethiol (methyl mercaptan)	CH4S	1484.36	L	-7.70	48.11	CRC
CH4O	Methanol	CH4O	717.85	L	-166.60	32.04	CRC
C4H6O2	Methyl acrylate	C4H6O2	2110.09	L	-243.22	86.09	CEH
BrCH3	Methyl bromide (bromoethane)	CH3Br	788.71	G	-26.30	94.94	CRC
C4H8O	Methyl ethyl ketone (2-butanone)	CH3CH3COCH3	2432.60	L	-154.83	72.11	SZAR
C2H4O2	Methyl formate	HCO2CH3	997.41	L	-299.28	60.05	CEH
CH6N2	Methyl Hydrazine	CH6N2	1299.28	L	180.00	46.07	CRC

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY kJ/mol</i>	<i>State</i>	<i>GFORM kJ/mol</i>	<i>Weight mole</i>	<i>REF</i>
C6H12O	Methyl isobutyl ketone	C6H12O	3762.99	G	-117.15	100.16	MAR
CH5N	Methylamine	CH5N	1028.48	G	27.61	31.06	CEH
CCl2H2	Methylene chloride	CH2Cl2	699.67	L	-70.29	84.93	MAR
C4H10S	methylpropyl sulfide	C4H10S	3442.60	L	11.46	90.19	SZAR
CClH3	Monochloromethane	CH3Cl	763.32	L	-62.89	50.49	MAR
C6Cl2H4	m-Dichlorobenzene	C6H4Cl2	3135.94	G	78.58	147.00	MAR
C7H9N	m-Toluidine (methyl aniline)	C7H9N	4100.03	G	165.40	107.16	CRC
C6H5NO2	Nitrobenzene	C6H5NO2	3202.37	L	146.23	123.11	MAR
CH3NO2	Nitromethane	CH3NO2	754.34	L	-14.40	61.04	CRC
C4H10O	n-Butanol	C4H10O	2654.62	L	-168.91	74.12	CEH
C3H8O	n-propanol	CH3CH2CH2OH	2010.47	L	-166.69	60.10	CEH
C2H2O4	oxalic acid (aq,300)	C2H2O4	371.52	L	-693.04	90.04	CEH
C6Cl2H4	o-Dichlorobenzene	C6H4Cl2	3140.04	G	82.68	147.00	MAR
C7H9N	o-Toluidine (methyl aniline)	C7H9N	4102.23	G	167.60	107.16	CRC
C2Cl4	Perchloroethylene	CCl2=CCl2	1088.22	L	20.50	165.83	MAR
C6H6O	Phenol	C6H6O	3125.74	L	-46.11	94.11	CEH
C8H6O4	Phthalic Acid	C8H6O4	3412.60	S	-585.72	166.13	SZAR
C8H4O3	Phthalic anhydride	C8H4O3	3434.80	S	-325.44	148.12	SZAR
C2H3KO2	Potassium acetate (aq,400)	KC2H3O2	889.48	L	-655.76	98.15	CEH
CHKO3	Potassium bicarbonate	KHCO3	37.37	S	-863.50	100.12	CRC
C3H8O	Propanol-2	CH3CHOHCH3	1998.60	L	-178.57	60.10	SZAR
C3H6O	propionaldehyde	CH2CH2O	1798.98	G	-142.09	58.08	CEH
C3H6O2	Propionic Acid	C3H6O2	1559.59	L	-383.46	74.08	CEH
C6H10O3	Propionic Anhydride	C6H10O3	3172.46	L	-475.55	130.14	CEH
C3H8S	propyl mercaptan	CH3CH2CH2SH	2794.70	L	9.92	76.16	SZAR
C3H9N	Propylamine	C3H7NH2	2353.76	G	60.17	59.11	CEH
C3H8O2	Propylene glycol	CH3CHOHCH2OH	1802.59	L	-376.56	76.10	MAR
C3H6O	Propylene oxide	C3H6O	1914.33	L	-26.74	58.08	MAR
C6Cl2H4	p-Dichlorobenzene	C6H4Cl2	3134.51	G	77.15	147.00	MAR
C8H8O	p-toluic aldehyde	C8H8O	4232.52	L	4.06	120.15	CEH
C7H9N	p-Toluidine ( methyl aniline)	C7H9N	4102.33	G	167.70	107.16	CRC
C7H6O3	Salicylic acid	HOC6H4CO2H	3151.20	S	-434.88	138.12	SZAR
C2H3NaO2	Sodium acetate	NaC2H3O2	908.04	S	-607.20	82.03	CRC
CHNaO3	Sodium bicarbonate (aq)	NaHCO3	19.87	S	-851.00	84.01	CRC

<i>Elements</i>	<i>NAME</i>	<i>FORMULA</i>	<i>EXERGY</i> <i>kJ/mol</i>	<i>State</i>	<i>GFORM</i> <i>kJ/mol</i>	<i>Weight</i> <i>mole</i>	<i>REF</i>
C6H14O6	Sorbitol	C6H14O6	3204.80	S	-921.37	182.17	SZAR
C4H6O4	Succinic acid	C4H6O4	1609.40	S	-747.88	118.09	SZAR
C2Cl4	Tetrachloroethylene	C2Cl4	1070.72	L	3.00	165.83	CRC
C4H12Si	Tetramethylsilane	C4H12Si	3812.24	L	-100.00	88.23	CRC
C4H4S	Thiophene	C4H4S	2847.00	L	124.16	84.14	SZAR
C6H6S	thiophenol (mercaptobenzene)	C6H5SH	3916.10	L	136.64	110.18	SZAR
CH4N2S	Thiourea (aq)	NH4CNS	1511.19	L	18.41	76.12	CEH
C7H10N2	Toluenediamine	C7H10N2	4011.20	L	-41.84	122.17	MAR
C2Cl2H2	trans-1,2-Dichloroethylene	C2H2Cl2	1207.52	L	27.30	96.94	CRC
Br3CH	Tribromomethane	CHBr3	675.11	L	-5.00	252.73	CRC
C2Cl4O	Trichloroacetyl Chloride	C2Cl4O	860.51	G	-209.20	181.83	MAR
C2Cl3H3	Trichloroethane	CH3CCl3	1282.58	L	-77.49	133.41	MAR
C2Cl3H	Trichloroethylene	C2HCl3	1143.84	G	19.87	131.39	MAR
CH4N2O	Urea	CH4N2O	688.02	S	-197.14	60.06	CEH
BrC2H3	Vinyl Bromide	CH2=CHBr	1307.07	G	81.80	106.95	CRC
C2ClH3	Vinyl chloride monomer	CH2=CHCl	1287.97	G	51.50	62.50	KO
C2Cl2H2	Vinylidene chloride	CCl2=(CH2)	1205.32	G	25.10	96.94	KO

**Table 2: Detailed processes: PVC chain (chlorination of ethylene)  
Unit processes & values for Western European production in 1992**

		<i>Unit Process</i>			<i>Europe 1992</i>		
		<i>Mass grams</i>	<i>Cl content grams</i>	<i>Exergy kiloJ</i>	<i>Mass MMT</i>	<i>Cl content MMT</i>	<i>Exergy gigaJ</i>
<b>Ethylene dichloride by direct chlorination</b>							
	YIELD 93.7%on ethylene, 95% on Cl				Input Cl=		3197
Ethylene-in	C2H4	0.303		14.686	1284		62279
Chlorine-in	Cl2	0.754	0.754	1.314	3197	3197	5573
Water-in	H2O	0.010		0.001	42		2.3
Ethylene dichloride-prod	C2Cl2H4	-1.000	-0.717	-13.566	-4241	-3038	-57529
Carbon tetrachloride-byprod	CCl4	-0.041	-0.037	-0.125	-172	-159	-529
other-waste	~C7H17	-0.016		-0.480	-68		-2035
Water-waste	H2O	-0.010		-0.001	-42		-2.3
	<b>PROCESS SUMMARY</b>						
	Inputs	1.067	0.754	16.001	4523	3197	67854
	Outputs	-1.041	-0.754	-13.691	4413	-3197	-58058
	Recycles						
	Wastes	-0.026		-0.481	-110		-2038
	Net	0	0	1.829	0	0	7758
<b>Ethylene dichloride by oxychlorination</b>							
	YIELD 95.6%on ethylene, 96.9% on HCl				Use HCl=process C= (EDC=)		3666.37
Ethylene-in	C2H4	0.296		14.381	1087		52725
Hydrochloric acid-in	ClH	0.764	0.743	1.773	2803	2725	6499
Oxygen-in	O2	0.171		0.021	626		78
Alkylbenzene(avg)-in	C12H14	0.0003		0.013	1.1		
Ammonia-in	H3N	0.002		0.036	6.6		130
Caustic soda-in	HNaO	0.0003		0.001	1.1		2.1
Water-in	H2O	0.030		0.002	110		6.0
Ethylene dichloride-prod	C2Cl2H4	-1.000	-0.717	-13.566	-3666	-2627	-49739
Ends- byproduct	CCl4	-0.025	-0.023	-0.076	-91	-83	-278
Sodium chloride-waste	ClNa	-0.0004	-0.0003	-0.0001	-1.6	-0.97	-0.39
Ammonium chloride-waste	ClH4N	-0.006	-0.004	-0.035	-21	-14	-128
Cl-waste (total)		-0.006	-0.004	-0.035	-22	-15	-128
other-waste	~C10H17	-0.011		-0.485	-40		-1779
Water-waste	H2O	-0.222		-0.012	-816		-45
	<b>PROCESS SUMMARY</b>						
	Inputs	1.264	0.743	16.225	4634	2725	59488
	Outputs	-1.025	-0.739	-13.642	-3757	-2710	-50017
	Recycles						
	Wastes	-0.239	-0.004	-0.532	-877	-15	-1951
	Net	0	0	2.051	0	0	7520

		Unit Process			Europe 1992		
		Mass grams	Cl content grams	Exergy kiloJ	Mass MMT	Cl content MMT	Exergy gigaJ
<b>VCM from Acetylene &amp; Hydrogen Chloride</b>							
YIELD 80.7% on ethylene, 82.&% on HCl				Balance HCl with processes A&H			
Acetylene-in	C2H2	0.545		26.534	58		2818
Hydrochloric acid-in	ClH	0.725	0.705	1.682	77	75	179
Mercuric chloride*-in	Cl2Hg	0.001	0.0003	0.001	0.11	0.03	0.05
Vinyl chloride-prod	C2ClH3	-1.000	-0.567	-20.608	-106	-60	-2189
Hydrochloric acid-byprod	ClH	-0.034	-0.033	-0.078	-3.6	-3.5	-8.3
Acetylene-recycle	C2H2	-0.047		-2.292	-5.0		-243
1,1-Dichloroethylene-byprod ends	C2Cl2H2	-0.0004	-0.0003	-0.004	-0.04	-0.03	-0.47
cis-1,2-Dichloroethylene-byprod ends	C2Cl2H2	-0.002	-0.001	-0.020	-0.17	-0.13	-2.1
1,1,1,2-Tetrachloroethane*-byprod ends	C2Cl4H2	-0.001	-0.001	-0.007	-0.10	-0.08	-0.71
1,1,1-Trichloroethane*-byprod ends	C2Cl3H3	-0.101	-0.080	-0.936	-11	-8.5	-99
Carbon tetrachloride-byprod ends	CCl4	-0.002	-0.002	-0.005	-0.18	-0.16	-0.55
Ends- byproduct (total)	C?Cl?H?	-0.105	-0.084	-0.973	-11	-8.9	-103
Ethylene-waste	C2H4	-0.030		-1.436	-3.1		-152
Acetylene-waste	C2H2	-0.027		-1.334	-2.9		-142
Carbon, activated-waste	C	-0.001		-0.030	-0.09		-3.2
Other-waste (total)	??	-0.057		-2.769	-6.1		-294
1,1-Dichloroethylene-waste ends	C2Cl2H2	-0.0001	-0.0001	-0.001	-0.01	-0.01	-0.12
cis-1,2-Dichloroethylene-waste ends	C2Cl2H2	-0.0004	-0.0003	-0.005	-0.04	-0.03	-0.53
1,1,1,2-Tetrachloroethane*-waste ends	C2Cl4H2	-0.0002	-0.0002	-0.002	-0.02	-0.02	-0.18
1,1,1-Trichloroethane*-waste ends	C2Cl3H3	-0.025	-0.020	-0.234	-2.7	-2.1	-25
Carbon tetrachloride-waste ends	CCl4	-0.0004	-0.0004	-0.001	-0.04	-0.04	-0.14
Mercuric chloride*-waste	Cl2Hg	-0.001	-0.0003	-0.001	-0.11	-0.03	-0.05
Cl-waste (total)	Cl??	-0.027	-0.021	-0.244	-2.9	-2.3	-26
PROCESS SUMMARY							
	Inputs	1.272	0.706	28.216	135	75	2997
	Outputs	-1.139	-0.684	-21.659	-121	-73	-2300
	Recycles	-0.047		-2.292	-5.0		-243
	Wastes	-0.085	-0.021	-3.043	-9.1	-2.3	-323
	Net	0	0	1.223	0	0	130
<b>VCM by Pyrolysis of EDC</b>							
YIELD on EDC= 95.3%				Orig Cl in= 3197			
				VCM out= 4767.901			
Ethylene dichloride-in	C2Cl2H4	1.662	1.191	22.547	7924	5678	107502
Caustic soda-in	HNaO	0.001		0.002	3.8		7.3
Vinyl chloride-prod	C2ClH3	-1.000	-0.567	-20.608	-4768	-2705	-98256
Hydrochloric acid-byprod	ClH	-0.588	-0.572	-1.363	-2803	-2725	-6499
Ethylene dichloride-recycle	C2Cl2H4	-0.067	-0.048	-0.904	-318	-228	-4309
Acetylene-waste	C2H2	-0.002		-0.089	-8.7		-426
Ethylene dichloride-waste	C2Cl2H4	-0.005	-0.004	-0.068	-24	-17	-325
Sodium chloride-waste	ClNa	-0.001	-0.001	-0.0003	-5.5	-3.3	-1.3
Cl-waste (total)		-0.006	-0.004	-0.068	-29	-21	-327
Water-waste	H2O	-0.0004		-0.00002	-1.7		-0.09
PROCESS SUMMARY							
	Inputs	1.663	1.191	22.549	7928	5678	107510
	Outputs	-1.588	-1.139	-21.971	-7570	-5430	-104755
	Recycles	-0.067	-0.048	-0.904	-318	-228	-4309
	Wastes	-0.008	-0.004	-0.158	-40	-21	-752
	Net	0	0	-0.484	0	0	-2307

		Unit Process			Europe 1992		
		Mass grams	Cl content grams	Exergy kiloJ	Mass MMT	Cl content MMT	Exergy gigaJ
<b>PVC by suspension polymerization</b>							
	YIELD on VCM=	99.0%			Cl from VCM=(3197-G)=		4748
Vinyl chloride-in	C2ClH3	1.010	0.573	20.814	4795	2720	98821
Caustic soda-in	HNaO	0.004		0.007	17		32
Hydrochloric acid-in	ClH	0.002	0.002	0.004	8.1	7.9	19
Water-in	H2O	2.600		0.142	12344		675
Other chemicals*	??	0.016		0.235	74		1116
Polyvinyl chloride*-prod	C2ClH3	-1.000	-0.567	-19.227	-4748	-2693	-91287
Carbon tetrachloride-waste	CCl4	-0.005	-0.004	-0.014	-22	-20	-66
Sodium chloride-waste	ClNa	-0.005	-0.003	-0.001	-25	-15	-6.0
Cl-waste (total)	Cl?	-0.010	-0.007	-0.015	-46	-35	-72
Butadiene (1,3-butadiene)-waste	C4H6	-0.004		-0.182	-19		-862
Other chemicals*-waste	C?H?	-0.016		-0.235	-74		-1116
Other-waste (total)	??	-0.020		-0.417	-93		-1978
Water-waste	H2O	-2.602		-0.142	-12352		-675
<b>PROCESS SUMMARY</b>							
	Inputs	3.631	0.575	21.202	17239	2728	100663
	Outputs	-1.000	-0.567	-19.227	-4768	-2693	-91287
	Recycles						
	Wastes	-2.631	-0.007	-0.574	-12471	-35	-2726
	Net	0	0	1.401	0	0	6650
<b>Vinylidene chloride from EDC</b>							
	YIELD on EDC=	99.8%			use Cl in=		187.849
Ethylene-in	C2H4	0.089		4.299	17		804
Chlorine-in	Cl2	1.004	1.004	1.750	188	188	327
Ethylene dichloride-in	C2Cl2H4	0.814	0.583	11.036	152	109	2065
Caustic soda-in	HNaO	0.462		0.890	86		167
Di-n-propylamine*-in	C4H15N	0.020		0.808	3.8		151
Hydroquinone*-in	C6H6O2	0.0003		0.010	0.06		1.8
Vinylidene chloride-prod	C2Cl2H2	-1.000	-0.731	-12.433	-187	-137	-2326
Hydrochloric acid-byprod	ClH	-0.436	-0.424	-1.011	-82	-79	-189
Hydroquinone*-recycle	C6H6O2	-0.0003		-0.010	-0.06		-1.8
Ethylene dichloride-waste	C2Cl2H4	-0.002	-0.001	-0.022	-0.30	-0.22	-4.1
1,1,2-Trichloroethane*-waste	C2Cl3H3	-0.027	-0.021	-0.248	-5.0	-4.0	-46
Sodium chloride-waste	ClNa	-0.674	-0.409	-0.165	-126	-77	-31
Cl-waste (total)	Cl?	-0.703	-0.432	-0.435	-131	-81	-81
Di-n-propylamine*-waste	C4H15N	-0.020		-0.808	-3.8		-151
Mixed hydrocarbons*	C?H?	-0.021		-0.864	-3.9		-162
Other-waste (total)	??	-0.041		-1.672	-7.7		-313
Water-waste	H2O	-0.208		-0.011	-39		-2.1
<b>PROCESS SUMMARY</b>							
	Inputs	2.388	1.587	18.793	447	297	3516
	Outputs	-1.436	-1.155	-13.444	-269	-216	-2515
	Recycles	-0.0003		-0.010	-0.06		-1.8
	Wastes	-0.952	-0.432	-2.118	-178	-81	-396
	Net	0	0	3.221	0	0	603

		Unit Process			Europe 1992		
		Mass	Cl content	Exergy	Mass	Cl content	Exergy
		grams	grams	kiloJ	MMT	MMT	gigaJ
<b>Unit Per/Tri-Chloroethylene from EDC &amp; Cl</b>							
YIELD 90% on EDC, 97.7% on Cl				from Per/Tri=	140.257		65.904
Ethylene dichloride-in	C2Cl2H4	0.786	0.563	10.667	148	106	2010
Chlorine-in	Cl2	0.323	0.323	0.563	80	80	140
Oxygen-in	O2	0.221		0.027	46		5.6
Ammonia-in	H3N	0.031		0.608	6.3		125
Perchloroethylene-prod	C2Cl4	-0.291	-0.249	-1.911	-140	-120	-920
Trichloroethylene-prod	C2Cl3H	-0.709	-0.574	-6.171	-66	-53	-574
Ammonium chloride-waste	ClH4N	-0.096	-0.064	-0.596	-20	-13	-123
Water-waste	H2O	-0.221		-0.012	-46		-2.5
Carbon Dioxide-waste	CO2	-0.043		-0.020	-8.9		-4.0
PROCESS SUMMARY							
	Inputs	1.361	0.887	11.865	280	186	2281
	Outputs	-1.000	-0.823	-8.082	-206	-173	-1494
	Recycles						
	Wastes	-0.361	-0.064	-0.628	-74	-13	-129
	Net	0	0	3.156	0	0	658
<b>1-1-1-Trichloroethane from vinyl chloride</b>							
YIELD 96.5% on VCM, 94.4% on Cl						Out =	161
Vinyl chloride-in	C2ClH3	0.491	0.278	10.109	79	45	1624
Chlorine-in	Cl2	0.563	0.563	0.981	90	90	158
1,1,1-Trichloroethane-prod	C2Cl3H3	-1.000	-0.797	-9.280	-161	-128	-1491
Carbon tetrachloride-byprod	CCl4	-0.022	-0.020	-0.067	-3.5	-3.2	-11
1,1-Dichloroethane-waste	C2Cl2H4	-0.026	-0.019	-0.356	-4.2	-3.0	-57
Carbon tetrachloride-waste	CCl4	-0.005	-0.005	-0.017	-0.9	-0.80	-2.7
Cl-waste (total)	Cl?	-0.032	-0.024	-0.373	-5.1	-3.8	-60
PROCESS SUMMARY							
	Inputs	1.053	0.841	11.091	169	135	1782
	Outputs	-1.022	-0.817	-9.347	-164	-131	-1501
	Recycles						
	Wastes	-0.032	-0.024	-0.373	-5.1	-3.8	-60
	Net	0	0	1.371	0	0	220

\* indicates that the exergy unit value for this chemical was derived by analogy with others of similar chemical formula or from other similarities and ratios as discussed in the text rather than from the standard sources or formulae.

**Table 3: Summary: Materials Flows in PVC Production by Chlorination of Ethylene  
Western European production in 1992**

		Mass MMT	Cl content MMT	Exergy gJ
1,1,1-Trichloroethane-prod	C2Cl3H3	-161		2818
Acetylene-in	C2H2	58		-243
Acetylene-recycle	C2H2	-5	-162	-540
ACETYLENE-NET	C2H2	53		2575
CARBON TETRACHLORIDE-BYPROD	CCl4	-175		208
CAUSTIC SODA-IN	HNaO	108	3556	6198
CHLORINE-IN	Cl2	3556	-170	-817
CL-WASTE	Cl?	-257	-92	-382
ENDS- BYPRODUCT	CCl4	-102	5893	111577
ETHYLENE DICHLORIDE-IN	C2Cl2H4	8225	-5665	-107268
ETHYLENE DICHLORIDE-PROD	C2Cl2H4	-7907	-228	-4309
Ethylene dichloride-recycle	C2Cl2H4	-318		115808
ETHYLENE-IN	C2H4	2387	2808	6697
HYDROCHLORIC ACID-byprod	ClH	-2888	-2808	-6697
HYDROCHLORIC ACID-IN	ClH	2888	0.03	1523
OTHER-IN	??	92		-6829
OTHER-WASTE	??	-232		83
OXYGEN-IN	O2	672	2765	100445
Perchloroethylene-prod	C2Cl4	-140	-2765	-100445
Polyvinyl chloride-prod	C2ClH3	-4748		683
Trichloroethylene-prod	C2Cl3H	-66		-727
VINYL CHLORIDE-IN	C2ClH3	4874	-128	-1491
VINYL CHLORIDE-PROD	C2ClH3	-4874	-120	-920
Vinylidene chloride-prod	C2Cl2H2	-187	-2693	-91287
WATER-IN	H2O	12497	-53	-574
WATER-WASTE	H2O	-13297	-137	-2326

**Table 4: Chlorine unit process**

		Mass grams	Cl content grams	Exergy kJ
Sodium chloride-in	ClNa	1.711	1.038	419
Sulfuric acid-in	H2O4S	0.009		14
Calcium chloride-in	CaCl2	0.014	0.009	11
Sodium carbonate-in	Na2CO3	0.039		16
Hydrochloric acid-in	ClH	0.040	0.039	93
Sodium sulfide-in	Na2S	0.0001		1.3
Water-in	H2O	0.484		26
Chlorine-prod	Cl2	-1.000	-1.000	-1743
Caustic soda-byprod	HNaO	-1.118		-2156
Sulfuric acid-byprod	H2O4S	-0.009		-15
Hydrogen-byprod	H2	-0.027		-3113
Sodium chloride-waste	ClNa	-0.120	-0.073	-29
Calcium chloride-waste	CaCl2	-0.014	-0.009	-11
Sodium carbonate-waste	Na2CO3	-0.0001		-0.04
ends-waste	C?Cl?H?	-0.009	-0.004	-223
SUMMARY	Inputs	2.297	1.086	581
	Outputs	-2.153	-1.000	-7027
	Recycles			0
	Wastes	-0.143	-0.086	-264
	Process	0	0	-6710