

EXERGETICS

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Summary

This article will introduce the exergy concept and exergy methods, i.e. the study of exergetics. Exergy is a fundamental concept in the study of life support systems and resource use in society. Exergy provides increase knowledge and understanding of sustainable development and a basis of a new paradigm.

The exergy concept is gaining popularity, between scientist and engineers, as well as in the community at large. A scientific journal dedicated to exergy was recently launched, *The International Journal of Exergy*.

This article approaches exergy from a physical angle, which is different from what is done elsewhere in the EOLSS . Thus, I will here point out some of these differences, in order to minimize confusion. Exergy is defined as work, i.e. ordered motion or ability of work. This means that exergy is always positive.

Exergy is applied to different intensive quantities, e.g. temperature, pressure and chemical potential, however, it is not divided into physical or chemical exergy, as is done elsewhere . Since exergy of real processes is never balanced, this concept is not used here. The link between exergy and information theory is treated in this article. It should also be noted that different symbols are used to denote exergy in different articles.

1. The Exergy Concept

The exergy concept has its roots in the early work of what would later become thermodynamics. In 1824 N.L. Sadi Carnot stated that the extractable work of a heat engine is proportional to the temperature difference, which later led to the definition of the second law of thermodynamics. Willard Gibbs introduced the notion of available work, including the diffusion term, in 1873. He simply stated:

We will first observe that an expression of the form

$$-\varepsilon + T\eta - Pv + M_1m_1 + M_2m_2 \dots + M_nm_n \quad (1)$$

denotes the work obtainable by the formation (by a reversible process) of a body of which ε , η , v , m_1 , m_2, \dots, m_n are the energy, entropy, volume, and the quantities of the components, within a medium having the pressure P , the temperature T , and the potentials M_1 , M_2 , \dots , M_n . (The medium is taken to be so large that its properties are not sensibly altered in any part by the formation of the body).

This relation, i.e. Equation 1, originally referred to as Equation 54 in Gibbs' work, is in exact correspondence with the present definition of exergy. Exergy is thermodynamic potential; it is a general measure of "difference" or contrast.

Thus, two states must be defined i.e. the actual state and an equilibrium or a reference state, often defined by the environment. In 1953 the term exergy was first expressed by Z. Rant to denote "technical working capacity" (Rant 1956). In 1961 Tribus linked classical thermodynamics with information theory, through the entropy and exergy concepts.

In 1977 a concise theory of exergy was offered and exergy was introduced as a useful concept not only of engineering but also for resource accounting in order to reduce environmental destruction (Wall 1977). The term exergy is gaining in popularity and

gradually replacing terms such as availability, available energy, essergy, utilizable energy, work potential, available work, convertible energy, etc.

1.1 Thermodynamics and Thermostatistics

Thermodynamics provides the concepts of temperature T , pressure P , heat Q , and work W , internal energy U , entropy S and four laws of thermodynamics:

The zero law defines the concept of temperature.

The first law defines energy as a conserved quantity, i.e. added heat ΔQ is equal to the increase of internal energy ΔU and the extracted work ΔW .

$$\Delta Q = \Delta U + \Delta W \quad (2)$$

The extracted work is force times distances, or pressure times volume change, i.e. PdV . Pressure is an intensive variable that is independent of the amount of matter. Volume is an extensive quantity that obviously depends on the size of the matter.

$$dW = PdV \quad (3)$$

where V is the volume.

The second law defines the concept of entropy through heat:

$$dS \geq 0, dS_{reversible} = 0 \quad (4)$$

$$dQ = TdS \quad (5)$$

Analogous to Equation 3.

The third law defines the zero level of entropy.

Thermodynamics only treats reversible processes, i.e. processes with no direction, and systems in equilibrium states. Thus, dynamics is not treated and a more proper name is thermostatistics (Tribus 1961). Even so, thermodynamics remains one of the most successful pieces of physics, particularly in engineering.

1.2 Energy and Exergy

The first law, i.e. energy conservation, generally fails to identify losses of work and potential improvements or the effective use of resources, e.g. in an adiabatic throttling process. The second law of thermodynamics shows that, for some energy forms, only a part of energy is convertible to work, i.e. the exergy.

Thus, exergy is a very useful tool in engineering. Table 1 summarizes the main differences between energy and exergy, and the relations will be further explained below.

Energy	Exergy
The first law of thermodynamics	The second law of thermodynamics
Nothing disappears.	Everything disperses.
Energy is motion or ability to produce motion.	Exergy is work, i.e. ordered motion, or ability to produce work.
$\Delta Q = \Delta U + \Delta W$ (2 as above) Where: ΔQ Is the total heat supplied to the system, ΔU Is the total increase in the internal energy U of the system, ΔW Is the total increase in the external energy of the system or the total work done by the system.	$E = T_0 \Delta S^{\text{tot}}$ (6) Where: E is exergy, T_0 Is the temperature of the environment, ΔS^{tot} Is the change of the entropy of the total system S^{tot} , i.e. the system and the environment.
$U = mc^2$ (7) Energy U and matter m is “the same thing.” Everything is energy.	$E = k \ln 2 T_0 I$ (8) Exergy and information I is “the same thing.” Contrast is exergy.
Energy is always conserved, i.e. in balance; it can neither be produced nor consumed.	Exergy is only conserved in a reversible process, but partly consumed in an irreversible process, i.e. real processes. Thus, exergy is <i>never in balance</i> for real processes.
Energy is a measure of quantity.	Exergy is a measure of quantity and quality.

Table 1. Energy versus exergy

1.3 Calculation of Exergy

The exergy of a system is expressed by the formula

$$E = U + P_0 V - T_0 S - \sum_i \mu_{i0} n_i \quad (9)$$

where U , V , S and n_i denote extensive parameters of the system (energy, volume, entropy, and the number of moles of different chemical materials i) and P_0 , T_0 , and μ_{i0} are intensive parameters of the environment (pressure, temperature, and chemical potential). This expression is exactly what Gibbs stated in 1873, see Equation 1. The chemical potential μ_{i0} may be generalized to also include exergy from electromagnetic forces, stress, nuclear forces etc. This makes exergy the most general concept of work or ability of work.

By using colors to indicate to which system the quantities belong it is easier to see the particular character of this expression, see Figure 1. System A is indicated by green color and the environment A_0 by red. The environment is assumed to be much larger than the system, i.e. almost infinite in size.

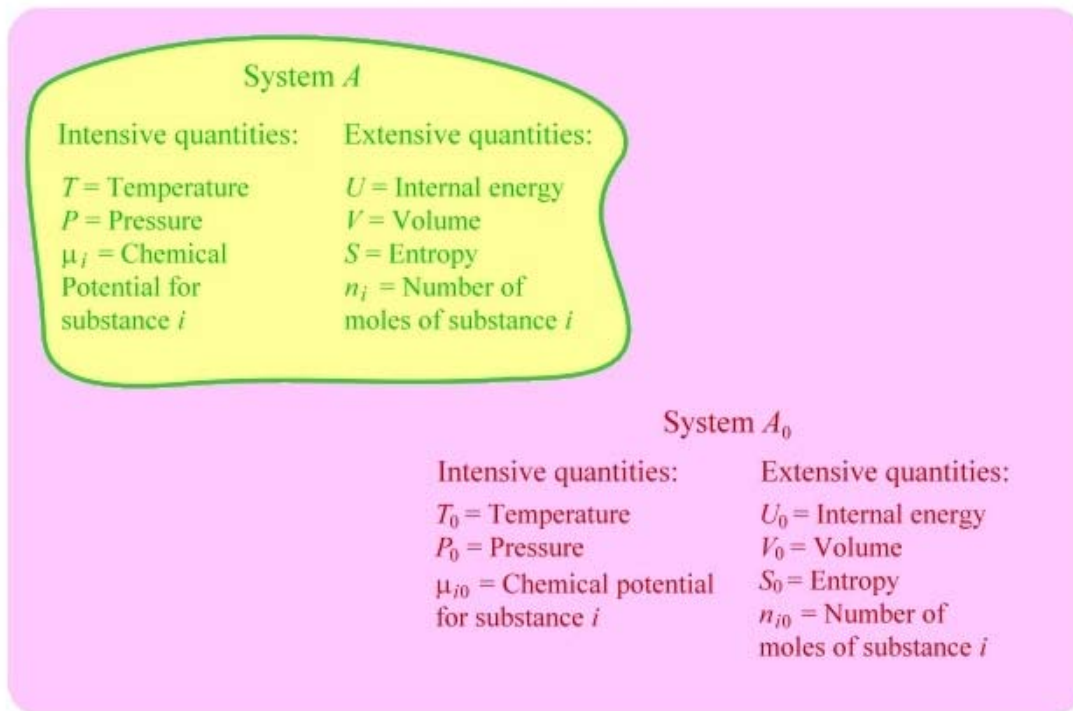


Figure 1. System A in a much larger environment A_0

What we have is actually a contrast described by the two systems A and A_0 , however, we have purposely chosen to assign one of these systems to be unchangeable. The reason is simply that by doing so we know the final state, i.e. the equilibrium state, when both systems have interacted in such a way that the contrast is exhausted. In the real world, the situation is often like this. The ambient is usually so immense that it may be regarded as unchangeable. Each system is described by intensive and extensive quantities. The intensive quantities are actual measures of the contrast, as the temperature T , the pressure P and the chemical potential μ for every substance i . These quantities are not affected by the size of the system, only by the level of contrast. The extensive quantities, on the other hand, are directly proportional to the size of the system. However, in recent times we have learned that human action, e.g. from combustion of fossil fuels, has an impact on the environment in terms of changing its intensive quantities, e.g. temperature and composition. By applying the colors presented in Figure 1 to Equation 9 above, this will now become:

$$E = U + P_0V - T_0S - \sum \mu_{i0}n_i \quad (9)$$

The following constituent parts: the external energy P_0V , energy as “ambient heat” T_0S and energy as “ambient substances” $\sum \mu_{i0}n_i$, are the product of an intensive quantity of the environment, i.e. of red color and an extensive quantity of the system, i.e. of green color. (Ambient heat and substances will be presented below). This is the expression of the available work from system A when it comes to equilibrium with the environment, system A_0 , i.e. when all contrasts have been transformed into work. The expression is built up of four different terms. These terms may be described accordingly: U is the energy carried within the system itself, part of this energy is

useless as work, i.e. exergy. The values for exergy are handled by the last two terms. P_0V is the work as a volume V that occupies a space of the environment of pressure P_0 . This is pure work. Thus by reducing the volume we could actually extract work. These two are positive contributions to the work. The internal energy unfortunately also carries two parts of useless energy or disorder, which has to be deducted. T_0S is the part of energy U , which is useless due to lack of order S , or heat at ambient temperature T_0 . Similarly, the last term is another useless part of the energy U . In this case as substances at ambient states. Obviously, these two terms are not in contrast to the environment, thus they are useless as work. The energy that is carried by substances can only be used “down to” the level that is given by the environment, cf. with the available potential energy of a waterfall or the carrying capacity of a ship, which is the total capacity minus the ballast.

In short exergy expresses the maximum available work, in this case with reference to the ambient, i.e. to what extent the contrast that is carried by the system could be used as work. Work and heat are concepts related to a process, i.e. that something is happening. They are not state variables. They are phenomena of time, i.e. the existence of time is necessary in order to experience these phenomena. When we say that work and heat is stored in a body, we actually mean that the ability to create work and heat is stored. What is stored is exergy as some form of contrast.

By using the so called Gibbs relation

$$U = ST - VP + \sum_i n_i \mu_i \quad (10)$$

we get the following expression

$$E = S(T - T_0) - V(P - P_0) + \sum_i n_i (\mu_i - \mu_{i,0}) \quad (11)$$

From which we see that E vanishes at equilibrium with the environment, i.e. when $T = T_0$, $P = P_0$, $\mu_i = \mu_{i,0}$. This is the same as to say that with no contrast there is no exergy and no potential of action.

Analogously, the exergy of a flow can be written as:

$$E = H - T_0S - \sum \mu_{i,0} n_i \quad (12)$$

Where H is the enthalpy.

Exergy is the most general expression of work. Other, less general expression of thermodynamic potentials, e.g. Gibbs and Helmholtz free energies and enthalpy, are just special cases of exergy as described in Table 2 (Wall, 1977). By comparing Equation 9 and the Equations of Table 2 we see that they generate the expression of exergy that is given by each specific thermodynamic potential. The cases also specify the conditions when these less general expression are applicable.

Case	$\Delta E = \Delta X$	Definition of X	Usually named
$\Delta n_i = 0, P = P_0, T = T_0$	$\Delta E = \Delta G$	$G = U + PV - TS$	Gibbs free energy
$\Delta n_i = 0, \Delta V = 0, T = T_0$	$\Delta E = \Delta F$	$F = U - TS$	Helmholz free energy
$\Delta n_i = 0, \Delta S = 0, P = P_0$	$\Delta E = \Delta H$	$H = U + PV$	Enthalpy

Table 2. Relations between differences in exergy and in other thermodynamic potentials.

1.4 Reference States

The major conceptual issue is the choice of reference state to which the chemical reactant under consideration is to be compared. Usually the standard state of each element is defined as its pure elementary state, such as C for carbon, O₂ for oxygen, N₂ for nitrogen, and so on. The pure elements are normally assigned zero values in Gibbs free energy.

Szargut et al. (1988) point out that the standard chemical exergies are calculated on the assumption the environment consists of a number of reference substances, one of each chemical element, with standard concentrations based on the average concentration in the natural environment. The reference substances selected fall into three groups, gaseous compounds of the atmosphere, solid substances from the lithosphere, and both ionic and nonionic substances from the oceans. It is claimed that the removal of the actual environment from the standard environment only occasionally introduces significant errors.

It should also be noticed that exergy may well be defined with reference to any other state, i.e. not necessarily a reference state. Thus, a locally defined environmental state is sometimes preferred (Wall 1977). However, such a definition will imply a less general applicability of its use.

1.5 Exergy and Work

Since exergy is defined as the maximum work potential, it is thus equivalent to exergy in every respect.

$$W = E - T_0 \Delta S \quad (13)$$

It is stated in the Second law that ΔS is always positive. From Equation 13 it is obvious that exergy gives an upper limit to the work that is extractable from the process. The maximal amount of work is achieved when ΔS is minimal.

1.6 Exergy of Pressure

Exergy is work, which is force F time distance S , i.e. FS or pressure P times volume V , PV . This is illustrated by the movement of a piston in a cylinder in Figure 2.

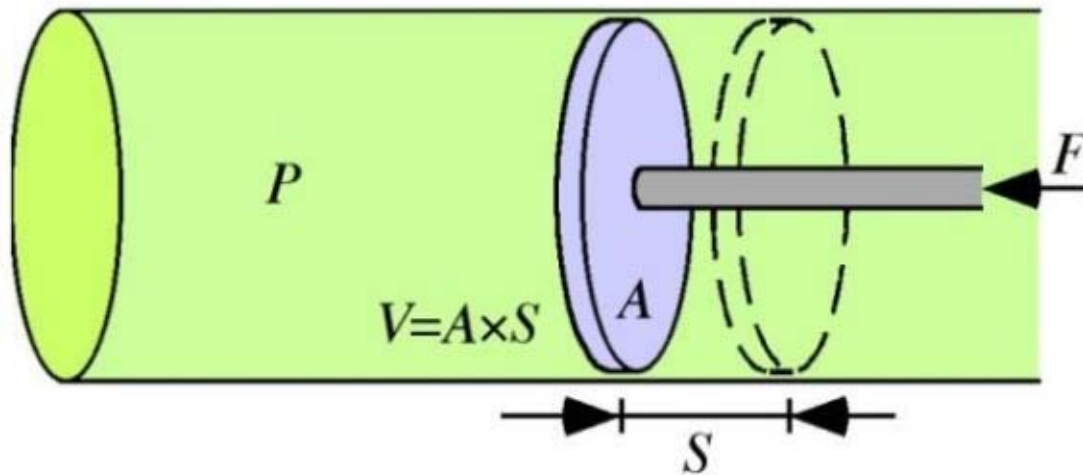


Figure 2. Pressure P is acting on a piston with area A that is moved the distance S by applying the force F .

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Biographical Sketch

Göran Wall is an independent researcher, specializing in exergy, sustainable development, and quality in education and management. He obtained his Ph.D. in 1986 and was appointed Associate Professor (Docent) in Physical Resource Theory at Chalmers University of Technology, Göteborg, Sweden, in 1995. Among his publications are more than forty papers in journals and international conference proceedings; for further information see home page: <http://www.exergy.se>