

1. Introduction: The exergy concept

The idea of available energy dates back to the last century, when it was first understood by the French engineer Sadi Carnot for the specialized case of heat engines. In the next decades the concept of available work was further developed theoretically, especially by Herman Helmholtz and J. Willard Gibbs. It has been applied to many kinds of processes, for different purposes, under several different names: availability, available work, essergy, physical information X but only recently a standard definition has been formulated and the name *exergy* definitely adopted [Rant 1956; Gyftopoulos *et al* 1974; Wall 1977; Szargut *et al* 1988]. However, for the purposes of this study it is sufficient to present only the essential features of the theory.

An adequate definition of exergy is the following: "Exergy is the amount of work obtainable when some matter is brought to a state of thermodynamic 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]. In short, exergy is an extensive non-conservative variable which synthesizes in a concise and useful expression both the first and second law of thermodynamics. It is definable and computable (in principle) for any substance, or system, with respect to the real environment in which the system is located and/or operates.

In principle, four different types of exergy B can be identified. These are denoted, respectively, as kinetic, potential, physical and chemical exergy, viz.

$$B = B_k + B_p + B_{ph} + B_{ch}$$

Kinetic and potential exergy have the same meaning as the corresponding energy terms. Kinetic exergy is relevant for analyzing a flywheel or turbine. Potential exergy is relevant for electrical or hydraulic systems. But these two terms can safely be neglected for purposes of analyzing most common industrial processes. Physical exergy is the work obtainable by taking a substance through reversible physical processes from its initial state (temperature T , pressure p) to the state determined by the temperature T_0 and the pressure p_0 of the environment [Szargut *et al* 1988]. Physical exergy assumes an important role for purposes of optimization of thermal and mechanical processes, including heat engines and power plants. But it is of secondary importance when attention is focused on very large scale systems, such as chemical and metallurgical processes at the industry level. In this case chemical exergy plays a major role for purposes of resource accounting and environmental analyses.

Chemical exergy is the work that can be obtained by a substance having the parameters T_0 and p_0 to a state of thermodynamic equilibrium with the datum level components of the environment [Szargut *et al* 1988]. It has two components: a component associated with chemical reactions occurring in isolation and a component associated with the diffusion of reaction products into the surroundings.

All the foregoing definitions stress the importance of defining a reference state, or system, when calculating both physical and chemical exergy. As a matter of fact, the exergy function is a measure of the difference between two states, namely the state of the "target" system and that of its surroundings (or, more precisely, the ultimate state of the combined system + surroundings, after they have reached mutual equilibrium). In short, exergy cannot be calculated without defining appropriate parameters for the environment where the target system operates, in terms of temperature, pressure and chemical composition.

The importance of defining the parameters for the common environment emerges clearly when we consider the analytical expressions for exergy. They also show that exergy is a measure of the thermodynamic "distance" of the target system from equilibrium. Another way of saying this is that exergy is a measure of the "distinguishability" of the target system from its

environment. These statements follow from the fact that exergy vanishes when the target system under consideration has the same thermodynamic state as the environment.

In general, for a closed system with temperature T , pressure p , entropy S , and volume V , exergy can be written as:

$$(1) \quad B = S(T - T_o) - V(p - p_o) + \sum N_i (\mu_i - \mu_{io})$$

where N_i is the number of moles of the i^{th} system and μ_i is its chemical potential. The subscript o refers to the final state of equilibrium of the system *plus* the environment, combined together. Again, the exergy of a flow crossing the system boundaries of an open system can be written as the sum of three terms:

$$(2) \quad B = H - H_o - T_o(S - S_o) - \sum \mu_i (N_i - N_{io})$$

where the letter H stands for enthalpy. The third term of these expressions takes account of the contribution due to the chemical transformation of the system.

In both of these expressions is straightforward to recognize how the choice of the reference state affects the value of the function B . For the purpose of calculating physical exergy, this choice does not represent a major problem, as it is relatively easy to define an appropriate level for pressure and temperature of the environment, namely ambient atmospheric temperature and pressure. This is not the case for calculation of chemical exergy. The latter step requires knowledge of the detailed average chemical composition of the reaction products and the environmental sink with which the system interacts.

In this context, considerable efforts have been undertaken by a number of authors. One possible approach would be to assume, as the reference level, the average chemical composition of the earth's crust after reaching an hypothetical (calculated) equilibrium with the atmosphere and oceans [Ahrendts 1980]. However, the results vary dramatically according to the depth of the crustal layer that is assumed to be equilibrated. A more practical generic solution has been proposed by Szargut *et al* [1988]. This approach recognizes that the three main sinks X atmosphere, oceans and crust X are not in equilibrium with each other, but assumes that the reaction products in any given case must go to one of the three, depending on whether they are volatile (to air), soluble in water (to oceans) or neither (to earth's crust). They calculate standard chemical exergy for a number of chemical compounds and pure elements. The latter procedure has been adopted and extended in several later works [Ayres & Martinàs 1995; Ayres *et al* 1995, 1998; Ayres & Ayres 1996] and its results have been also used in the present study.