Exergy Concepts for Thermal Plant

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First of two papers on exergy techniques in thermal plant analysis

In this work the concepts applicable to a method of thermodynamic analysis known as exergy analysis are defined and discussed. Expressions are obtained for exergy components of a steady stream of matter and the relationship between the exergy of a steady stream of matter and that of a closed system is derived. The concept of the standard environment is introduced, its relationship to standard chemical exergy is established, and tables of standard chemical exergy of chemical elements are presented. An idealized model of an open system interacting with the standard environment is used to show the relationship between absolute availability function and exergy.

NOTATION

A_p	Piston area
b	Specific steady-flow availability function
g	Specific Gibbs function
Δg	Change in specific Gibbs function during a reaction
h	Enthalpy
Δh	Change in specific enthalpy
n	Number of moles of constituent
P	Absolute pressure
P_0	Absolute pressure of the environment
Q	Heat transfer
R	Ideal gas constant
s	Specific entropy
T	Thermodynamic temperature
T_0	Thermodynamic temperature of the environment
V	Volume
v	Specific volume
W	Work
W_x	Shaft work
x_p	Piston displacement
x_i	Mole fraction of substance i
E	Exergy
ε	Specific exergy
E^Q	Exergy transfer associated with heat transfer
Ξ	Stagnation exergy
ζ	Specific stagnation exergy

Subscripts

el	Relates to a chemical element
f	Relates to a reaction of formation
i	Identifies constituent of a mixture
j	Identifies a co-reactant
k	Identifies a product
M	Relates to a mixture
REV	Relates to a reversible process
1	Relates to the initial state
0	Relates to the state of restricted equilibrium with the environment
00	Relates to the state of unrestricted equilibrium with the environment

Superscripts

~	Indicates a molar quantity
0	Indicates a quantity in standard state
00	Relates to the state of unrestricted equilibrium with the standard environment

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1 INTRODUCTION

The techniques of analysis of thermal plant which are based on both the First and the Second Laws of Thermodynamics are generally known under the name of Availability Analysis and Exergy Analysis. It is the latter of the two techniques which will be the subject of this paper. Both the techniques make use of the concept of the work potential of different forms of energy rather than the energy itself which provides means for the calculation of the degradation of energy through irreversibility. These features of the techniques make them valuable in thermodynamic analyses aiming at the improvement of the efficiency of existing thermal plants through an adjustment of their operating parameters or in the design of efficient new thermal plants. Because of the current concern with the rapid depletion of the world non-renewable energy resources the advantages which these methods of analysis offer give them a new and enhanced relevance and importance.

Although the amount of electric power generated from nuclear fuels has been increasing steadily in recent years, the fossil fuels are still by far the most important source of energy, not only for power generation but also in chemical and metallurgical processes, space heating, transportation, etc. All of these applications involve chemical reactions of various kinds including reactions of combustion. It is therefore important that the method of analysis used should offer means of dealing, without undue complication, with the chemical aspects of energy conversion. The Exergy Analysis fulfills this requirement through the use of a system of environmental reference substances with respect to which, in their environmental states, standard exergies (work potentials) of commonly used chemical elements can be evaluated. Such a reference state is known as the state of unrestricted equilibrium with the environment and is equivalent to the state of thermal, mechanical, and chemical equilibrium combined. In the Availability Analysis the condition of chemical equilibrium in the reference state is not used and hence it has been called a state of restricted equilibrium with the environment. As a result, this technique

is not readily applicable to processes involving chemical reactions.

This work is intended as an up-to-date presentation of exergy concepts and techniques with the following particular objectives:

(1) To bring together exergy concepts developed in different parts of the world, with particular reference to the work carried out by Szargut and his co-workers (1, 2, 3), which is largely unknown in English language literature.
(2) To define clearly the principal quantities and concepts used in the technique and to offer suggestions for suitable terminology.
(3) To integrate these concepts into a practical method of thermodynamic analysis.
(4) To present tables of standard chemical exergy for chemical elements.
(5) To prepare groundwork for the next, related publication (4) concerned with the formulation of rational performance criteria and thermal plant analysis.

2 THE FUNDAMENTAL CONCEPTS

Exergy of a system is the amount of work obtainable when the system is brought to a state of unrestricted equilibrium (that is, thermal, mechanical, and chemical) with the environment by means of reversible processes involving thermal and chemical interaction only with the environment. As follows from this definition, exergy is a property of two states, the state of the system and the state of the environment. Its magnitude can be looked upon as a measure of the departure of the state of the system from that of the environment. This definition is quite general and can be applied to a variety of systems. In the present work the considerations will be mainly limited to systems made up of homogeneous fluids. Since the exergy of a stagnant fluid, as will be seen later, is different from that of a fluid moving at a steady rate, we shall restrict the use of the unqualified term 'exergy' to the latter. This is in accordance with the terminology generally adopted on the Continent of Europe and is justified by the fact that steady-flow quantities are of greater practical importance in engineering applications.

The two terms, environment and equilibrium, referred to in the definition of exergy require some clarification. Two types of equilibria are distinguished in this context.

3 RESTRICTED EQUILIBRIUM

This is the state when the system is in thermal and mechanical equilibrium with the environment. Under these conditions the temperature and the pressure of the system are equal to those of the environment, T_0 and P_0 respectively. In the case of restricted equilibrium the system is kept separate from the environment by a physical boundary to prevent mixing and chemical interaction with the environment. Because of this, the composition of the environment is of no interest and the state of the environment is adequately defined by its pressure and temperature. Therefore, in the case of restricted equilibrium the environment can be regarded as an infinitely large reservoir of thermal energy of zero grade, since its exergy is zero. The specification of the environmental pressure P_0 is necessary for the evaluation of the work done by the system on the environment when there is a change in the volume of the system.

4 UNRESTRICTED EQUILIBRIUM

This is the state when the system under consideration is in thermal, mechanical, and chemical equilibrium with the environment. Under these conditions the system should be made up entirely of common constituents of the environment in the thermodynamic states in which they exist freely in the environment. For this purpose the environment (i.e., the atmosphere, the seas, the oceans, and the crust of the earth) is assumed to consist of substances of low Gibbs function which are in thermodynamic equilibrium with each other. This implies that no work can be obtained from the interaction of various parts of the environment. Hence, in the case when we consider unrestricted equilibrium, the environment can be thought of as a reservoir of both zero grade thermal energy and zero grade substances. The real environment, as is well known, contains also pockets of high-grade thermal energy in the form of geothermal energy and high-grade substances such as fossil fuels, neither of which is in equilibrium, thermal or chemical, with the bulk of the environment. Hence, these must be looked upon as separate reservoirs of high-grade thermal energy and high-grade substances.

5 COMPONENTS OF EXERGY

If we exclude nuclear effects, magnetism, electricity, and surface tension, the exergy of a steady stream of a fluid can be divided into four main components. These are:

(1) Kinetic exergy, E_k. Since kinetic energy associated with the bulk velocity of a fluid is, under ideal conditions, fully convertible into mechanical work, kinetic energy is equal to kinetic exergy when the velocities are considered relative to the surface of the Earth.
(2) Potential exergy, E_p. For the same reason potential energy is equal to potential exergy, when the former is evaluated with respect to the sea level.
(3) Physical exergy, E_{ph}, is the work which is obtained by taking the system by means of reversible physical processes, from its initial state to the state of restricted equilibrium with the environment, i.e., to P_0, T_0.
(4) Chemical exergy, E_0, is the work which is obtained by taking the system by means of reversible processes, from the state of restricted equilibrium with the environment to unrestricted equilibrium with the environment. In general both chemical and physical processes are involved. The chemical processes are necessary to turn the substances initially making up the system into those present in the environment. The physical processes are necessary to adjust the concentrations and the physical states of the latter to those of the environment.

The name, chemical exergy, is justified on the grounds that in most cases the exergy is mainly due to energy released as a result of a chemical reaction and also since the magnitude of chemical exergy is determined from the condition of chemical equilibrium of the system with the environment. Putting the four terms together we have the exergy of a fluid in steady flow

$$E = E_k + E_p + E_{ph} + E_0 \qquad (1)$$

6 EXERGY OF A HOMOGENEOUS SUBSTANCE

The general principles underlying the evaluation of exergy of a substance in steady flow will be discussed making use of reversibly operating idealized devices so that, as the substance is brought, in stages, from its initial state to a state of unrestricted equilibrium with the environment, the work obtained in each stage is the maximum. The whole process takes place basically in three stages, each carried out in a separate module, as shown in Fig. 1. We shall assume, at this stage of the discussion, the substance to consist of a single chemical species.

Module A

The substance entering this module may, in general, possess in its initial state kinetic as well as potential energies. When leaving the module the kinetic and potential energies are zero and the substance is at the environmental pressure P_0 and temperature T_0, i.e., it is in a state of restricted equilibrium with the environment. Thus the reversible work delivered by this module is made up of kinetic, potential, and physical exergy. The reversible heat transfer with the environment per mole of the substance is given by

$$[(\tilde{Q}_0)_{REV}]_1^0 = T_0(\tilde{s}_0 - \tilde{s}_1) \qquad (2)$$

Substituting (2) in the steady flow energy equation for the module we obtain the reversible work delivered by the module, which by definition is equal to the change of exergy $(\tilde{\varepsilon}_1 - \tilde{\varepsilon}_0)$,

$$[(\tilde{W}_x)_{REV}]_1^0 = (\tilde{h}_1 - T_0\tilde{s}) - (\tilde{h}_0 - T_0\tilde{s}_0)$$
$$+ (\tilde{K}E)_1 + (\tilde{P}E)_1 \qquad (3)$$
$$\equiv \tilde{\varepsilon}_1 - \tilde{\varepsilon}_0$$

Denoting physical exergy by $\tilde{\varepsilon}_{ph}$, we can write

$$\tilde{\varepsilon}_{ph1} = (\tilde{h}_1 - T_0\tilde{s}) - (\tilde{h}_0 - T_0\tilde{s}_0) \qquad (4)$$

Hence

$$\tilde{\varepsilon}_1 - \tilde{\varepsilon}_0 = \tilde{\varepsilon}_{ph1} + (\tilde{K}E)_1 + (\tilde{P}E)_1 \qquad (5)$$

Module B

In the space of this module the substance undergoes a reversible reaction with some common constituents of the environment, called here co-reactants, to form products which are other common constituents of the environment. If, for example, the substance under consideration is methane the reaction is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$
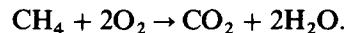
In this reaction oxygen is the co-reactant while carbon diodixe and water are products. All the three substances are common constituents of the environment. All the substances are delivered to the module and are removed from it at the environmental pressure P_0 and temperature T_0. The function of this module can be fulfilled by such idealized devices as the van't Hoff equilibrium box or a reversible fuel cell with, in either case, the necessary reversible isothermal compressors and expanders. The reversible work delivered by the module can be shown to be equal to the difference between the Gibbs function of the reactants and the products. Thus,

$$[(\tilde{W}_x)_{REV}]_{or}^{op} = \tilde{g}_0 - \left(\sum_k n_k \tilde{g}_{k0} - \sum_j n_j \tilde{g}_{j0} \right) = -\Delta\tilde{g}_0 \qquad (6)$$

where $\Delta\tilde{g}_0$ is the Gibbs function of the reaction.

Module C

The purpose of this module is to bring about an isothermal change of concentration of the environmental substances which are delivered to (co-reactants) and removed from (products) Module B. Module C consists of a number of cells equal to the number of environmental substances involved in the reaction. Each cell is equipped with suitable semi-permeable membranes to enable the required substances to be separated from the environmental mixture. The calculation of the reversible net work delivered by the cells requires the knowledge of the activities of the substances in their environmental states. In the case of *gaseous* environmental substances
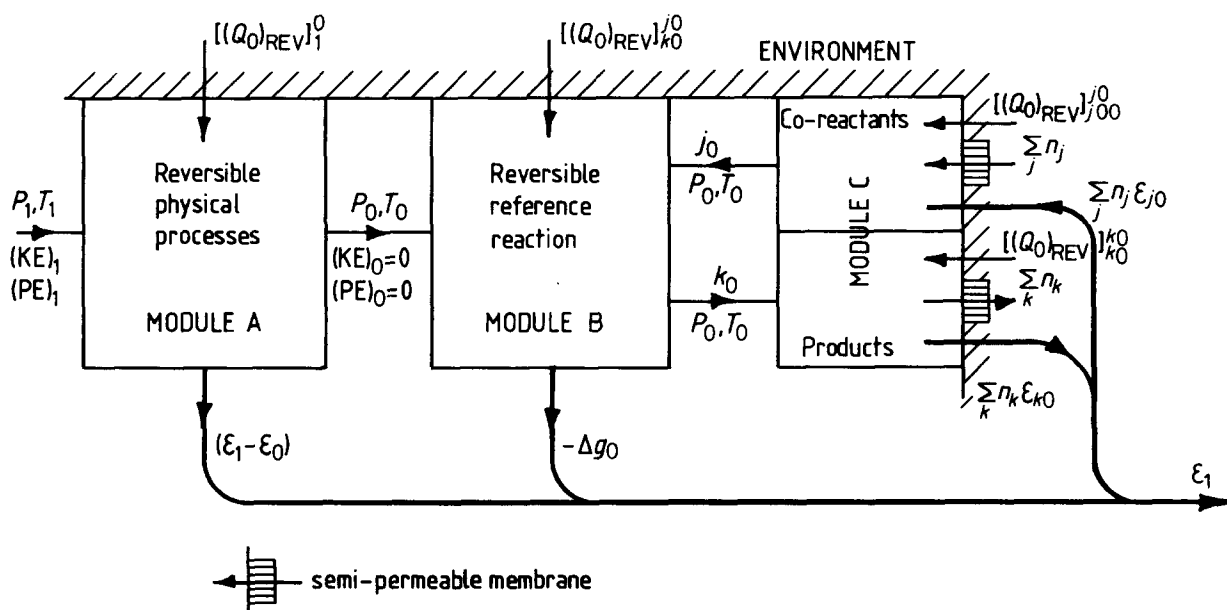

Fig. 1. An ideal device for determining the exergy of a homogenous substance of a single chemical species

the cells would consist of reversible isothermal compressors compressing the co-reactants from their environmental partial pressures P_{j00} to P_0 and reversible isothermal expanders expanding the products from P_0 to their environmental partial pressures P_{k00}. The reversible work of each cell is equal to the chemical exergy ε_{j0} of the particular environmental substance when at P_0 and T_0, or alternatively to the change in the Gibbs function associated with the isothermal change in concentration.

Thus we can express the total work absorbed by the cells handling the co-reactants as

$$[\tilde{W}_x)_{\text{REV}}]^{j0}_{j00} \equiv -\sum_j n_j \tilde{\varepsilon}_{j0}$$

$$= -\sum_j n_j (\tilde{g}_{j0} - \tilde{g}_{j00}) \qquad (7)$$

The work delivered by the cells handling the products is

$$[(\tilde{W}_x)_{\text{REV}}]^{k0}_{k00} \equiv \sum_k n_k \tilde{\varepsilon}_{k0}$$

$$= \sum_k n_k (\tilde{g}_{k0} - \tilde{g}_{k00}) \qquad (8)$$

In the case of the gaseous components of the atmosphere the reversible isothermal work terms given above can be put in the following form

$$[(\tilde{W}_x)_{\text{REV}}]^{j0}_{j00} = -\tilde{R}T_0 \sum_j n_j \ln \frac{P_0}{P_{j00}} \qquad (9)$$

$$[(\tilde{W}_x)_{\text{REV}}]^{k0}_{k00} = \tilde{R}T_0 \sum_k n_k \ln \frac{P_0}{P_{k00}} \qquad (10)$$

The net work delivered by modules B and C combined is equal, according to the definition, to the chemical exergy of the substance. Hence, we have

$$\tilde{\varepsilon}_0 = -\Delta\tilde{g}_0 - \sum_j n_j (\tilde{g}_{j0} - \tilde{g}_{j00})$$

$$+ \sum_k n_k (\tilde{g}_{k0} - \tilde{g}_{k00}) \qquad (11)$$

or

$$\tilde{\varepsilon}_0 = -\Delta\tilde{g}_0 - \sum_j n_j \tilde{\varepsilon}_{j0}$$

$$+ \sum_k n_k \tilde{\varepsilon}_{k0} \qquad (12)$$

In accordance with expression (1) and using expressions (3) and (11) we can write an expression for the molar exergy of the substance in its initial state 1 as

$$\tilde{\varepsilon}_1 = (\tilde{h}_1 - T_0\tilde{s}_1) - (\tilde{h}_0 - T_0\tilde{s}_0)$$

$$+ (\tilde{K}E)_1 + (\tilde{P}E)_1 \qquad (13)$$

$$- \Delta\tilde{g}_0 - \sum_j n_j \tilde{\varepsilon}_{j0} + \sum_k n_k \tilde{\varepsilon}_{k0}$$

It should be observed that in the case when the substance under consideration is a common constituent of the environment the work delivered by module B is zero. Also, since no co-reactants are required, the corresponding work term $\sum_j n_j \tilde{\varepsilon}_{j0}$ is zero. Thus for a common environmental substance of a single molecular species, the expression for exergy in state 1 reduces to the following form

$$\tilde{\varepsilon}_1 = (\tilde{h}_1 - T_0\tilde{s}_1) - (\tilde{h}_0 - T_0\tilde{s}_0) + \tilde{\varepsilon}_0 \qquad (14)$$

In this expression $\tilde{\varepsilon}_0$ represents the chemical exergy of such a substance which in this case is determined by the work derived from the reversible isothermal change in concentration carried out in a cell of module C.

7 EXERGY OF A MIXTURE OF IDEAL GASES

When the substance under consideration is a mixture of ideal gases, as may often be assumed in the case of gaseous fuels, the chemical exergy of the mixture can be determined from the chemical exergies of the constituents and the composition of the mixture. An ideal device which illustrates the procedure used (for a three-component mixture) is shown in Fig. 2. The mixture is supplied at a steady rate at the environmental pressure P_0 and temperature T_0. Each component is separated in
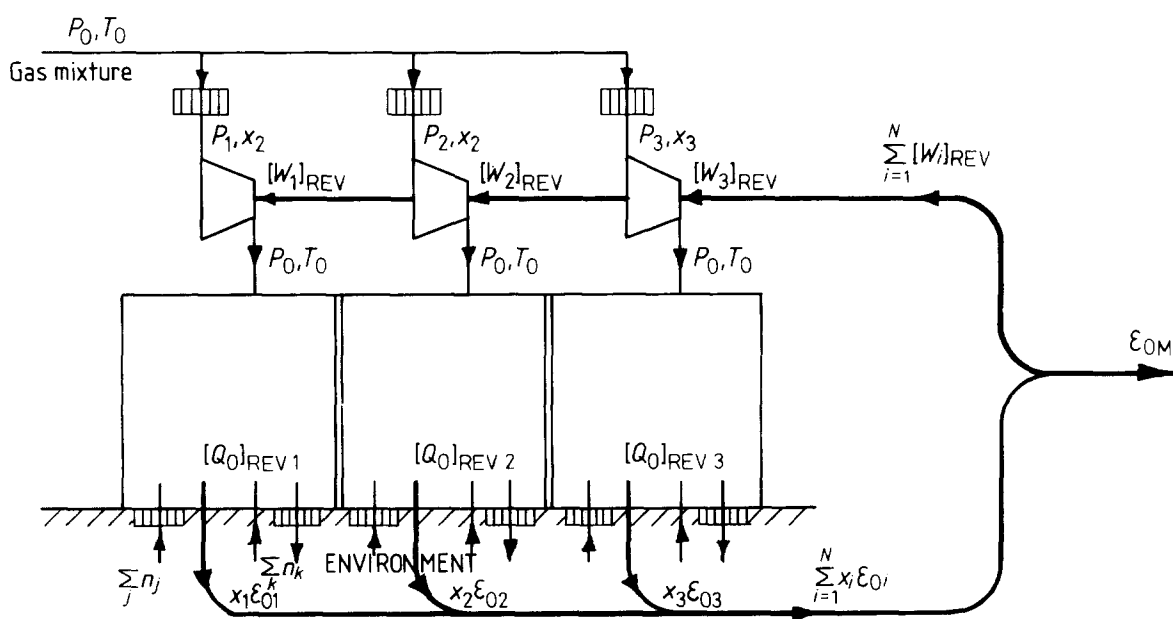

Fig. 2. An ideal device for determining the chemical exergy of a mixture of ideal gases

turn by means of a semi-permeable membrane whereupon it is compressed reversibly and isothermally from its partial pressure in the mixture P_i to P_0. The work of compression per mole of the substance is given by $\tilde{R}T_0 \sum_i x_i \ln x_i$. This work term may also be looked upon as the loss of potential work when the components of the mixture are mixed irreversibly to form the mixture. Subsequently the separated components at P_0 and T_0 are passed through modules, each of which corresponds to modules B and C of Fig. 1 combined, where their chemical exergies are evaluated. The total reversible work delivered by these modules is equal to the sum of the products of molar fractions and molar exergies of the constituents of the mixtures, i.e., $\sum_i x_i \tilde{\varepsilon}_{0i}$. Hence, the exergy of the mixture is given by the following expression

$$\tilde{\varepsilon}_{OM} = \sum_i x_i \tilde{\varepsilon}_{0i} + \tilde{R}T_0 \sum_i x_i \ln x_i \qquad (15)$$

8 EXERGY OF A FLUID IN A CLOSED SYSTEM

As stated in the Introduction the exergy of a fluid in steady flow has been taken as the fundamental quantity because of the importance of steady-flow processes in engineering applications, and consequently all the considerations so far have been limited to this quantity. By deriving a relationship between exergy of a fluid in steady flow and that of exergy in a closed system we can extend the applicability of these considerations to the latter quantity. This relationship will be derived by using an ideal device consisting of a horizontal frictionless, leakproof, and adiabatic piston and cylinder assembly shown in Fig. 3. The fluid enters the cylinder through a reversible diffuser so that the fluid velocity inside the cylinder can be made arbitrarily small by choosing the cylinder-to-pipe diameter ratio large enough. The piston which separates the fluid at pressure P from the environmental medium at pressure P_0 moves at a small steady velocity as the system is charged with the fluid. Subsequently, the supply is cut off and the fluid contained within the system boundary can be regarded as a closed system. If x_p is the displacement of the piston when a mole of the fluid enters the system, the corresponding reversible net work delivered by the system is

$$\tilde{W}_{REV} = (P - P_0)A_p x_p$$
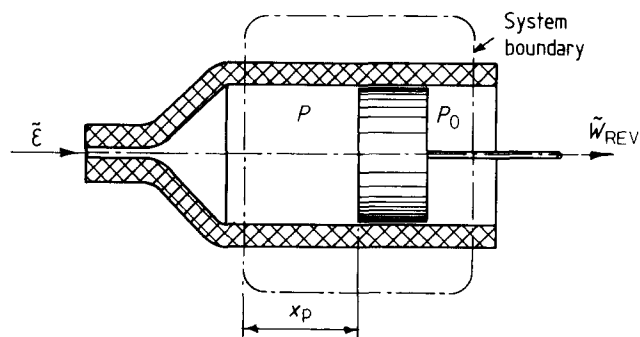$$= (P - P_0)\tilde{v} \qquad (16)$$

Fig. 3. An ideal device for determining the stagnation exergy of a fluid

where, A_p is the piston area and $\tilde{v}$ is the molar volume. It will be observed that the environmental medium displaced by the piston has zero exergy. Hence, in the absence of any irreversibilities, the exergy of the fluid inside the system boundary is equal to the exergy of the fluid delivered to the cylinder minus the work done by the system. Thus the exergy of a homogenous substance in a closed system is given by

$$\tilde{\zeta} = \tilde{\varepsilon} - \tilde{W}_{REV} \qquad (17)$$

or, using expression (16)

$$\tilde{\zeta} = \tilde{\varepsilon} - (P - P_0)\tilde{v} \qquad (18)$$

This quantity has been named by Evans (5) 'essergy', a name derived from 'essence of energy'. Haywood (6) proposed for it the name 'exergy of extraction and storage' which while being descriptive is rather long for a thermodynamic quantity. A somewhat shorter name of 'stagnant exergy' has been used by Rietman (7), although perhaps the version 'stagnation exergy' would be more appropriate in view of existing terms such as stagnation enthalpy or stagnation temperature. It is therefore proposed to adopt the name 'stagnation exergy' in this work. An interesting aspect of expression (18) is that it can be used to obtain the stagnation exergy of an evacuated vessel. When written for a closed system of volume V this expression takes the following form,

$$\Xi = E - (P - P_0)V \qquad (19)$$

Since in the case of vacuum we have $E = 0$ and $P = 0$, the stagnation exergy of an evacuated vessel of volume V is

$$\Xi_{VAC} = P_0 V \qquad (20)$$

This quantity may be looked upon as the reversible work obtainable when filling an evacuated vessel of volume V in an environment at pressure P_0.

9 STANDARD CHEMICAL EXERGY

The calculation of chemical exergy of a substance requires information regarding the concentration and the thermodynamic states in the environment of common environmental substances. The accuracy of this information will affect the accuracy of calculated irreversibilities in open systems arising from their interaction with the environment. The calculation of irreversibilities of closed systems will not be affected as long as one adopts for each chemical element one, and one only, common environmental substance containing this particular chemical element as its *reference substance*.

If the environment were in a state of perfect thermodynamic equilibrium, the choice of the particular system of reference substances would be immaterial. As this is not so, it is advantageous to adopt as reference substances the most common ones, since their concentration in the environment is known with a high degree of precision. By allocating zero exergy to the most common substances, the rare substances have positive exergies, which, incidentally, may be considered as an index of the value of these substances.

Because of the complexity of the calculations of chemical exergy, Szargut and his co-workers (1, 2, 3) introduced the concept of standard chemical exergy.

This is calculated on the assumption that the environmental pressure and temperature have standard values and the environment consists of a number of reference substances, one for each chemical element, with standard concentrations based on average concentration in the actual environment. The concept of the standard environment permits the calculations and tabulation of standard chemical exergies which greatly facilitates the drawing up of exergy balances and the computation of irreversibilities. It is found in many cases that the departures of the actual environment from the standard environment do not introduce significant errors, so that the standard values of chemical exergy have only occasionally to be corrected to obtain the actual values.

The general scheme for the calculation of chemical exergy is shown in Fig. 4. The main processes in the scheme occur at the standard environmental conditions which enables the relationship between the standard chemical exergy and chemical exergy to be established. The scheme shows the transformation of the substance, in five stages, through reversible processes from the initial state at T_0 and P_0 to a state of unrestricted equilibrium with the environment. In Stage 1 there is a change from the environmental pressure and temperature to the standard pressure and temperature. The work of this stage is small and has the opposite sign to that of the work of Stage 4. Since the two work terms approximately cancel each other, they can be neglected. During

Stage 2, a *standard reference reaction* takes place in which, besides the substance under consideration, the other substances are all reference substances, i.e., reference co-reactants and reference products. The processes taking place in Stage 2 are the same as those in Module B, described above, except that all the substances are delivered and removed at standard conditions rather than the actual environmental conditions. The heat interaction Q_{2a} is utilized in a reversible heat engine which operates between the temperatures T^0 and T_0 and produces work W_{2b}. This work is one of the correction terms used in the calculation of chemical exergy E_0 from standard chemical exergy E^0.

The reversible isothermal change of concentration of Stage 3 corresponds to the processes already described for Module C, except that in this case the substances are reference substances and are drawn from, and are rejected to the standard environment. The heat interaction Q_{3a} is utilized in a reversible heat engine and gives rise to the work W_{3b} which is another of the correction terms used in the calculation of E_0 from E^0.

The processes of Stage 2 and Stage 3, occurring within the confines of the open system boundary indicated in Fig. 4, give rise to the reversible work terms W_{2a} and W_{3a} respectively, the sum of which is a measure of the standard chemical exergy of the substance under consideration. Thus, we have

$$E^0 = W_{2a} + W_{3a} \qquad (21)$$

In Stage 4 we have a change of temperature and pressure of the reference substances in the standard environment. As stated above, the work W_4 cancels out with W_1.

In the last stage, Stage 5, there occurs a reversible isothermal change of concentration of the reference substances between the environment of standard chemical composition and the actual environment. The maximum work of this stage is mostly very small and besides, the data necessary to calculate it are most often lacking. Consequently, the work W_5 is normally omitted in the course of calculations.

From the scheme which has just been described one obtains the following formula for the chemical exergy of a substance:

$$E_0 = E^0 + (Q_{2a} + Q_{3a})\frac{T^0 - T_0}{T^0} + W_5 \qquad (22)$$

Given the standard molar enthalpy of the reaction, $\Delta \bar{h}^0$, of Stage 2, the molar chemical exergy of the substance can be written, subject to the simplifications explained above, in the following form

$$\tilde{\varepsilon}_0 = \frac{T_0}{T^0}\tilde{\varepsilon}^0 - \Delta \bar{h}^0 \frac{T^0 - T_0}{T^0} \qquad (23)$$

The reference substances selected by Szargut and his co-workers for the chemical elements fall into the following groups:

(1) Gaseous constituents of the atmosphere.
(2) Solid reference substances from the lithosphere.
(3) Ionic reference substances from the seas.
(4) Reference substances in molecular, non-ionized form from the seas.
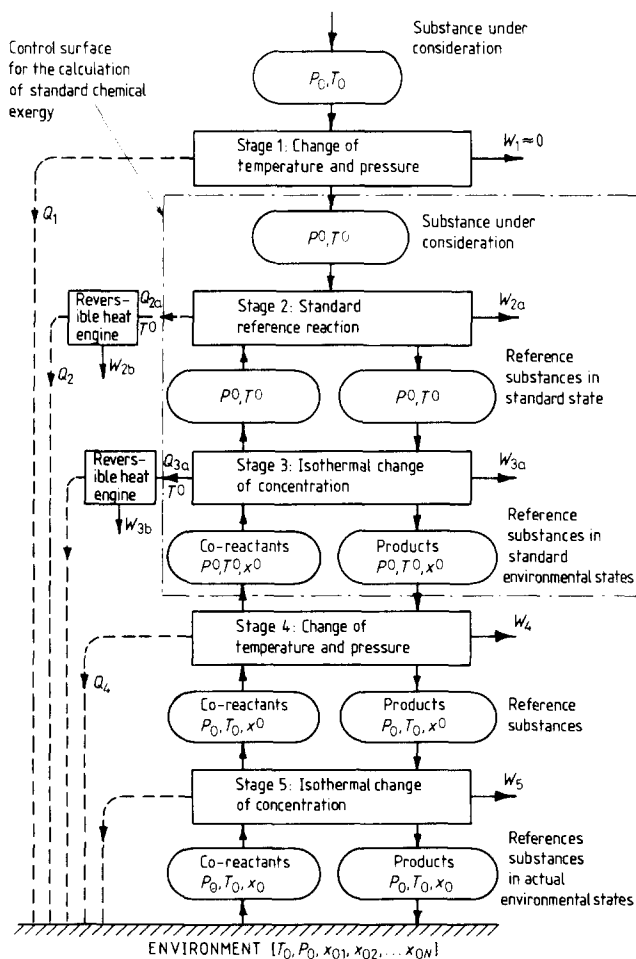

Fig. 4. Scheme for the calculation of chemical exergy

For a detailed description of the method of calculation of standard chemical exergies for the various chemical elements the reader is referred to the original publications (1, 2).

10 TABLES OF STANDARD CHEMICAL EXERGY

Because of the importance of atmospheric (gaseous) reference substances in combustion processes the scheme used in the calculation of their standard chemical exergies is shown in Table 1. As the molar composition of dry air is known quite precisely (column 3), it was only necessary to assume an average annual value of partial pressure of water vapour and the average annual value of the atmospheric pressure to obtain the partial pressures of the gaseous reference substances (column 4). In column 5 are the values of the standard chemical exergies of these reference substances. Since they can be treated as ideal gases, the standard chemical exergies are given by the reversible isothermal expansion work from the initial standard pressure P^0 and temperature T^0 to the standard partial pressure P_i^{00} of the particular reference substance in the atmosphere. In cases where the chemical elements, including those already considered in the environment, this work quantity is also equal to the standard chemical exergy of the chemical element. This is the case for all the elements listed in Table 1 except for carbon, hydrogen, and deuterium.

Table 2 gives the reference substances and the standard chemical exergies of some of the more important chemical elements, include those already considered in Table 1. With the aid of this table and the values of Gibbs function of formation of a chemical compound, the standard chemical exergy of the chemical compound can be calculated. In the case of a reversible chemical reaction of formation, exergy is conserved, and hence we can write, using molar quantities

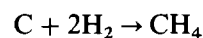$$\tilde{\varepsilon}^0 = \Delta \tilde{g}_f^0 + \Sigma E_{el}^0 \tag{24}$$

where
$\tilde{\varepsilon}^0$ standard chemical exergy of the chemical compound
$\Delta \tilde{g}_f^0$ standard Gibbs function of formation

E_{el}^0 standard chemical exergy of the constituent elements, per mole of the chemical compound

Example 1

Calculation of the standard chemical exergy of methane vapour. The reaction of formation is

$$C + 2H_2 \rightarrow CH_4$$

Hence, expression (24) becomes

$$\tilde{\varepsilon}_{CH_4(g)}^0 = \Delta \tilde{g}_{f CH_4(g)}^0 + \tilde{\varepsilon}_{C(s)}^0 + 2\tilde{\varepsilon}_{H_2(g)}^0$$

From (8), the Gibbs function of formation is

$$\Delta \tilde{g}_{f CH_4(g)}^0 = -50\,819 \text{ kJ/kmol}$$

From Table 2,

$$\tilde{\varepsilon}_{C(s)} = 410\,530 \text{ kJ/kmol}$$

$$\tilde{\varepsilon}_{H_2(g)} = 238\,350 \text{ kJ/kmol}$$

Substituting,

$$\tilde{\varepsilon}_{CH_4(g)}^0 = -50\,810 + 410\,530 + 2 \times 238\,350$$

$$= 836\,420 \text{ kJ/kmol}$$

Example 2

Calculation of the chemical exergy of methane vapour when the environmental temperature T_0 is $10°C$. From (8), the enthalpy of combustion of methane vapour when all the products are in gaseous phase is

$$\Delta \tilde{h}^0 = -802\,300 \text{ kJ/kmol}$$

Using expression (23) and the value of standard chemical exergy of methane calculated in Example 1, the chemical exergy of methane when $T_0 = 10°C$ is

$$\tilde{\varepsilon}_{0\ CH_4(g)} = 836\,420\frac{283\cdot15}{298\cdot15} + 802\,300\frac{15}{298\cdot15}$$

$$= 834\,703 \text{ kJ/kmol}$$

As will be observed, the difference between $\tilde{\varepsilon}^0$ and $\tilde{\varepsilon}_0$ is quite small amounting to only about 0·2 per cent.

Table 1

Chemical elements with gaseous reference substances
$T^0 = 298\cdot15$ K $P^0 = 1\cdot013\,25$ bar

| Chemical element | Reference substances | | | | Reference reaction |
	Chemical symbol	Mole fraction in dry air	Standard partial pressure in the environment P_i^{00}/bar	$-\tilde{R}T^0 \ln P_i^{00}/P^0$	
Ar	Ar	0·009 33	0·009 07	11 690	Ar → Ar
C	CO₂	0·000 3	0·000 294	20 170	C + O₂ → CO₂
D	D₂O g	—	0·000 001 37	33 500	D + ¼O₂ → ½D₂O
H	H₂O g	—	0·008 8	11 760	H + ¼O₂ → ½H₂O
He	He	0·000 005	0·000 004 9	30 360	He → He
Kr	Kr	0·000 001	0·000 000 98	34 320	Kr → Kr
N	N₂	0·780 3	0·758 3	720	N → ½N₂
Ne	Ne	0·000 018	0·000 017 7	27 150	Ne → Ne
O	O₂	0·209 9	0·204 0	3 970	O → ½O₂
Xe	Xe	0·000 000 09	0·000 000 088	40 300	Xe → Xe

Table 2

Standard molar chemical exergy of chemical elements
$T^0 = 298 \cdot 15$ K, $P^0 = 1 \cdot 013\,25$ bar

Chemical element	Standard state of the element	Reference substance	Standard molar chemical exergy of the element $\varepsilon^0/[\text{kJ/kmol}]$
Ag	s	Ag, aq	59 100
Al	s	Al_2SiO_5, s, silimanite	887 890
Ar	g	Ar, g	11 690
As	s	$HAsO_4^{--}$, i	477 040
Au	s	Au, aq	69 950
B	s	$H_2BO_3^-$, i	615 920
Ba	s, II	Ba^{++}, i	760 050
Bi	s	Bi_2O_3, s	271 370
Br_2	l	Br^-, i	91 770
C	s, graphite	CO_2, g	410 530
Ca	s, II	Ca^{++}, i	717 400
Cd	s	Cd^{++}, i	290 920
Cl_2	g	Cl^-, i	117 520
Co	s, III	Co^{++}, i	260 520
Cr	s	Cr_2O_3, s	538 610
Cs	s	Cs^+, i	408 530
Cu	s	Cu^{++}, i	134 400
D_2	g	D_2O, g	264 780
F_2	g	F^-, i	448 820
Fe	s	Fe_2O_3, s	377 740
H_2	g	H_2O, g	238 350
He	g	He, g	30 360
Hg	l	Hg, aq	66 010
I_2	s	IO_3^-, i	184 190
K	s	K^+, i	371 520
Kr	g	Kr, g	34 320
Li	s	Li^+, i	396 170
Mg	s	Mg^{++}, i	626 710
Mn	s, α, IV	MnO_2, s	483 240
Mo	s	MoO_3, s	715 540
N_2	g	N_2, g	720
Na	s	Na^+, i	343 830
Ne	g	Ne, g	27 150
Ni	s	Ni^{++}, i	252 800
O_2	g	O_2, g	3 970
P	s, white	HPO_4^{--}, i	859 600
Pb	s	Pb^{++}, i	226 940
Rb	s	Rb^+, i	398 800
S	s, rhombic	SO_4^{--}, i	598 850
Sb	s, III	Sb_2O_5, s	359 190
Se	s	SeO_4^{--}, i	326 960
Si	s	SiO_2, s	803 010
Sn	s, white	SnO_2, s	542 660
Sr	s	Sr^{++}, i	737 650
Ti	s, II	TiO_2, s, III rutile	876 000
U	s, III	UO_3, s	1 224 180
V	s	V_2O_5, s	725 880
W	s	WO_3, s	799 680
Xe	g	Xe, g	40 300
Zn	s	Zn^{++}, i	353 160

Key: s—solid, l—liquid, g—gaseous, i—ion, aq—in aqueous solution.

11 STANDARD ENVIRONMENT AS A SOURCE AND SINK OF REFERENCE SUBSTANCES AND ZERO-GRADE THERMAL ENERGY

It may be instructive to consider an open system undergoing a prescribed flow process whilst interacting thermally and chemically solely with the environment. The purpose of this exercise is to demonstrate the relationships existing between exergies of material streams, exergies of heat transfers, work transfer, irreversibility rate for the process, and the balance of reference substances participating in the secondary reactions inside the injection and extraction modules associated with the prescribed process. In this arrangement the process under consideration may be any real, steady-flow process of arbitrary complexity involving any substances and chemical reaction, but excluding nuclear reactions. As shown in Fig. 5, the actual environment has been replaced by injection and extraction modules and heat pumps interacting with the standard environment which becomes the sole source and sink of both matter and thermal energy as required by the prescribed process. Each stream of matter entering the control region is synthesized beforehand in reversible extraction modules from reference substances withdrawn from the standard environment. As each stream may, in general, consist of a mixture of a number of chemical compounds, each module must perform the function of the open system shown in Fig. 1.

The streams of matter leaving the control region are passed through similar modules operating in a reverse mode where matter is decomposed reversibly into reference substances which are then returned to the standard environment. The net reversible work delivered or absorbed by a module represents the exergy of the particular stream. The heat transfers at the temperatures required at the system boundary are provided in this arrangement by heat pumps or heat engines operating reversibly between the system boundary and the stan-dard environment. The work input or output E^Q represent the exergy of the heat transfers. When all the reversible work quantities associated with the supply and removal of matter and with the provision of the necessary heat transfers are summed up and added to the net shaft work of the system, the net work which has to be supplied from outside (say, from a mechanical energy reservoir) is equal to the irreversibility of the control region.

The arrangement described above will now be used to determine the relationship between molar exergy of a steady stream of matter, $\tilde{\varepsilon}$, and molar steady flow absolute availability function $\tilde{b} = (\tilde{h} - T^0\tilde{s})$ in which $\tilde{h}, \tilde{s}$, and T^0 have absolute values. The two quantities may be expressed in the following form

$$\tilde{\varepsilon} = \tilde{h} - T^0\tilde{s} - \left(\sum_k n_k \tilde{g}_k^{00} - \sum_j n_j \tilde{g}_j^{00}\right) \qquad (25)$$

$$\tilde{b} = \tilde{h} - T^0\tilde{s} - \left(\sum_k n_k \tilde{g}_k^{00} - \sum_j n_j \tilde{g}_j^{00}\right)$$
$$+ \left(\sum_k n_k \tilde{g}_k^{00} - \sum_j n_j \tilde{g}_j^{00}\right) \qquad (26)$$

Subtracting the two expressions we get

$$\tilde{b} = \tilde{\varepsilon} + \left(\sum_k n_k \tilde{g}_k^{00} - \sum_j n_j \tilde{g}_j^{00}\right) \qquad (27)$$

It will be observed from the above expression that the difference between the two quantities is a function of the molar quantities of the reference substances (co-reactants and products) required in the reference reaction of the substance under consideration and their environmental values of Gibbs function. Under steady-flow conditions the quantities of the different reference substances processed by the extraction modules and the injection modules are the same. Hence, it follows
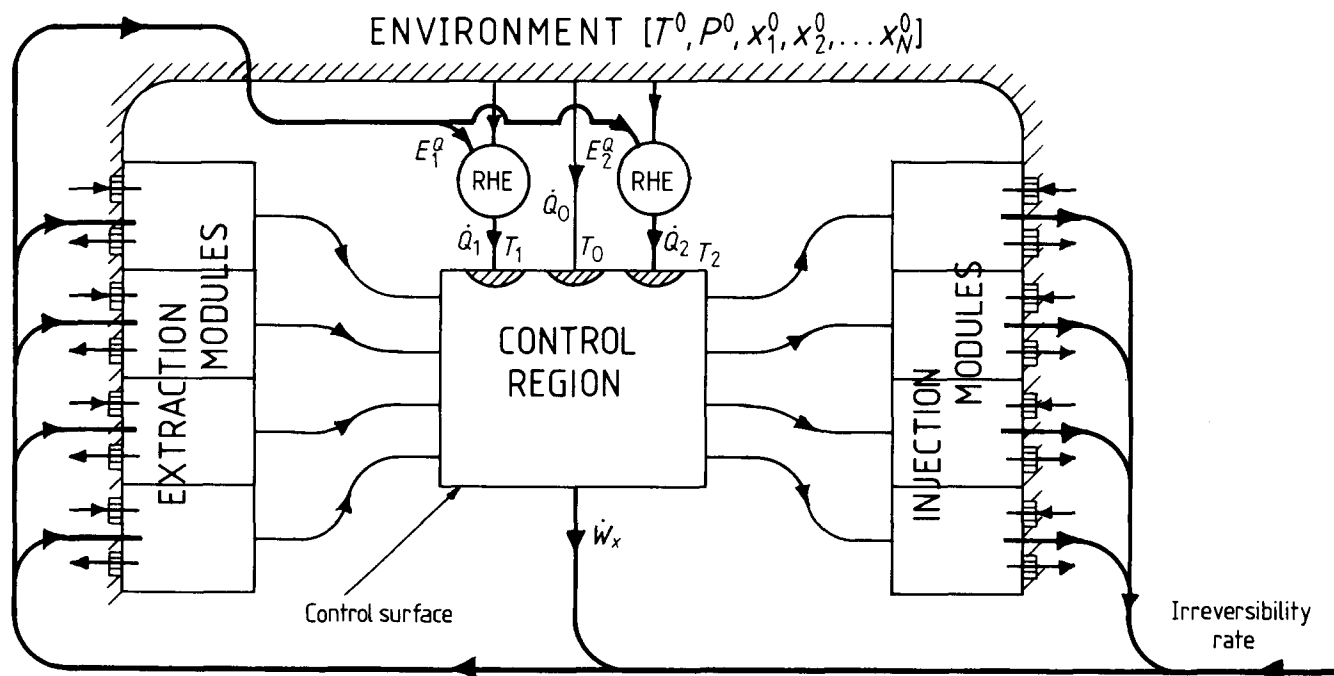

Fig. 5. An open system undergoing a steady flow process whilst interacting solely with the standard environment

that in an exergy balance the sum of the terms $(\sum_k n_k \tilde{g}_k^{00} - \sum_j n_j \tilde{g}_j^{00})$ for all the processes at the inlet to the control region will cancel with the sum of such terms for the outlet. This leads to the conclusion that the absolute values of the availability function may be used instead of exergy in an exergy balance. It must, however, be added that the use of exergy values (as defined in this work) is to be preferred to the absolute availability function, since the former has a clear physical significance whilst the latter has none in this context.

Similar arguments can be produced to show that the same relationship as in (27) holds for the absolute non-flow availability function and the stagnation exergy.

12 CONCLUSION

This work has presented an up-to-date review of the concepts of the exergy technique of thermodynamic analysis. The technique is an extension of an older and better-known technique which uses the availability function, but one which cannot so readily be applied to processes involving chemical reactions. Because of the ease with which the exergy concepts can be applied to chemical reactions, they are particularly valuable in the analysis of internal and external combustion power plants, fuel cells, and industrial chemical and metallurgical processes. Furthermore, since exergy takes common environmental substances as the reference substances, it is a natural measure of the work potential of a fuel and hence lends itself particularly to the formulation of various criteria of thermodynamic perfection. This topic will be discussed at some length in another publication (4).

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