

Chapter 2

Exergy Concept and Determination

Abstract Exergy is the cornerstone of exergetic and thermoeconomic analyses. This chapter explains what exergy is and how to calculate it for matter, heat, and work flows. The calculations depend on the information available, but it is easy to obtain at least an approximation. The example case is used briefly (normal text) and in detailed form (grey boxes).

2.1 Introduction

The exergy of a portion of matter is equal to the maximum useful work obtainable when taken from its given state to the thermodynamic equilibrium with the environment, without intervention rather than its own and the one of the environment [7]. Such a final state of equilibrium is known as dead state. From another point of view, the exergy can be considered as a measure of the existing disequilibrium between the considered matter and the environment.

To be able to carry out exergy calculations, it is necessary to define a reasonable idealized model for the environment, which is taken as reference, since the exergy will always depend on the system's and environment's states. It is also essential to analyse the diverse possibilities of reaching the dead state of equilibrium with the environment, following the restrictions imposed on the different analysed systems.

The exergy of every energy flow (matter flow, heat, work,...) can be calculated with the methods shown in this chapter, as it is explained. A very important point will be the analysis of the destruction of exergy due to the inevitable irreversibility of real processes.

2.2 Environment and Dead State

From a theoretical standpoint, the environment must be in thermodynamic equilibrium, and therefore with no usable energy, but in fact it is not, as its intensive properties vary from place to place and from time to time. Owing to a high activation

energy, many reactions—thermodynamically spontaneous—that lead to thermodynamic equilibrium are kinetically blocked. A very important and noticeable case is that of molecular nitrogen contained in atmospheric air and dissolved in oceanic waters. In presence of oxygen or water, the dissolved gaseous nitric acid in the atmosphere, and the dissolved nitrate ion in seawater, are more stable. The free enthalpies of formation of nitric acid and of nitrates are negative, and therefore their formation reactions are spontaneous. The energetic barrier that stops them is the rupture of the triple bond of the nitrogen molecule, which has an activation energy of almost $1\,000\text{ kJ mol}^{-1}$. At ordinary temperatures, the reaction speeds are practically zero. To produce them, really high temperatures are needed, which can be given in combustion processes or in atmospheric electric discharges. Owing to this—as we shall see promptly—atmospheric nitrogen is used as a reference substance and not as a proper stable compound.

In fact, the usable energy of the natural environment is not null, since useful work would be possible to obtain if it evolves towards thermodynamic equilibrium. Therefore, it is vital to compromise in the formulation of a model that approximates the real ambient environment and is thermodynamically acceptable. A conventional stable reference environment (SRE) is established, normally at $T_o = 298.15\text{ K}$ ($25\text{ }^{\circ}\text{C}$) and $p_o = 1\text{ atm}$ (1.013 bar), due to the fact that most of the thermodynamic properties are tabulated at this T_o, p_o [16].

The calculation of thermodynamic properties of substances requires a clear and unambiguous characterization of thermodynamic states. The normal or standard state of a certain substance at a generic temperature T is defined as the most stable pure form of that component at this temperature and at a normal pressure of 1 atm, which is usually the SRE one (called AER in the MHB software [11]).

The values of the properties in the *standard state* are distinguished with the superscript $^{\circ}$. The basic data tabulation is usually done at the conventional temperature of $25\text{ }^{\circ}\text{C}$, equivalent to 298.15 K , called *normal temperature*, usually being that of the SRE. The normal state at 298.15 K is commonly called the *normal state*, leaving the explicit indication of the temperature for those who take a different one.

This is the reason why the subscript $^{\circ}$ has been used in this text to identify a temperature of $25\text{ }^{\circ}\text{C}$ and a pressure of 1 atm for the SRE.

Chemically the SRE is formed by diverse existent reference substances in the natural environment, to which null exergy is assigned and possesses the following properties:

- Approximates as much as possible to thermodynamic equilibrium.
- Reproduces reality reasonably.
- Is large enough so that its exchanges of matter and energy with systems under study do not alter significantly its intensive properties (temperature, pressure and chemical potential).

The SRE is used as a common reference level for exergy determination. In any case, this is indispensable to ensure consistent calculations. When the system under study reaches complete thermodynamic equilibrium with the environment, it

is assumed that it is already in the dead state. In this state, pressure, temperature and chemical potential of the system are equal to that of the environment.

Closed systems cannot achieve total equilibrium with the environment, as matter exchanges, which are probably needed to reach chemical equilibrium, are not allowed. In this case, a state of physical or restricted equilibrium is achieved, in which only pressure and temperature match, which we will know as environmental state.

The natural environment can be considered to be made up of three subsystems that, strictly speaking, are not entirely in thermodynamic equilibrium, neither in internal equilibrium nor between themselves. These are the following:

- *Atmosphere*: Saturated humid air, in equilibrium with liquid water. Provides reference substances: oxygen, nitrogen, as well as the other gases that make up the air including CO_2 , which is the reference substance for carbon.
- *Hydrosphere*: Saturated liquid water (H_2O), which is a reference substance for hydrogen.
- *Lithosphere*: The reference substances are selected from those most abundant and of lowest value, existing in the solid crust. For example, for sulphur and calcium, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcite (CaCO_3) are respectively taken.

This SRE model closely approximates the real environment, and therefore conserves most of the existing imbalances in it. For example, for nitrogen, the reference substance chosen is the one in the atmosphere, resulting in normal negative exergy for sodium, potassium and calcium nitrates.

2.3 Physical Exergy

The physical exergy b_{ph} is the maximum useful work obtained by passing the unit of mass of a substance of the generic state (T, p) to the environmental (T_o, p_o) state through purely physical processes [1, 3, 17]. Thus, if kinetic and potential energy are not taken into consideration, according to Eq. 2.1, the physical exergy b_{ph} can be determined with the enthalpy and entropy values of the stream (characterized by its composition), both at the generic state, and the environmental state temperatures and pressures.

$$b_{\text{ph}} = [h(T, p) - h(T_o, p_o)] - T_o [s(T, p) - s(T_o, p_o)] \quad (2.1)$$

For the determination of physical exergy, always using (2.1), there are two methods that can be used, based on the data available. The *direct method* involves the direct use of the values of enthalpy and entropy, which shall be known, (i.e. with the simulation of the process). Whenever there exists reliable entropy and enthalpy data in terms of temperature and pressure, its direct input is preferable, to achieve more accurate results with less effort.

As the $h(T_o, p_o)$ and $s(T_o, p_o)$ are the values of enthalpy and entropy at T_o, p_o , they will be referred to in the text as h_o and s_o . If the values are not known, then they can be estimated to obtain an approximate value of the physical exergy, also using (2.1).

2.3.1 Direct Method

If data concerning enthalpy and entropy in terms of temperature and pressure is available, Eq. 2.1 provides the values of physical exergy. When analysing facilities, all the streams with equal composition have the same h_o and s_o values [8].

In the simulation used the enthalpy and entropy data is given, but it is simple to obtain the specific values of enthalpy and entropy in thermo-physical equilibrium (same T and p) of the SRE [9].

Firstly, all the streams of equal composition are identified with the same first three digits, as shown in Figs. 1.2 and 1.3. Streams with equal composition, can only be differentiated amongst themselves in terms of the temperature, pressure and mass flow of each stream, but all of them will have the same thermodynamic intensive properties if the same temperature and pressure is given to them, as it will happen at T_o , p_o .

Secondly, as shown in Figs. 1.2 and 1.3, for each different stream composition in the simulation, there has been added a pair of streams joined by a heater, one entering and the other one exiting the heater. The purpose is to give the incoming stream the chemical composition of the fluid, in order to obtain in the exiting stream the thermodynamic intensive properties of every stream with the same composition at T_o , p_o . Thus, the incoming stream is identified with letter Z, the exiting stream with the letters SRE, and the heater with the letters SRE, all of them followed by the same three digits identifying streams of identical composition.

Due to the existence of six different compositions or fluids in the case analysed, streams beginning with: 931, 941, 951, 961, 971, 981, six streams have been brought to the stable reference state using the streams: Z931, Z941, Z951, Z961, Z971 and Z981. The data of the currents analyzed (931, 941, 951, 961, 971, 981) can be directly introduced in the Z streams (Z931, Z941, Z951, Z961, Z971, Z981) or transferred to them by using specific functions in Aspen Plus®. The mass flow chosen in these currents does not matter as only specific values of enthalpy and entropy in the SRE are going to be used, being the same for the current that has the same composition.

The “Z-streams” are used as inputs of the heaters: SRE931, SRE941, SRE951, SRE961, SRE971, SRE981, followed by the outgoing streams, named exactly the same as the heaters constituting their source: SRE931, SRE941, SRE951, SRE961, SRE971. The input streams of these heaters are only used to receive the chemical input data of each stream from the simulation.

The heaters are configured to give their exiting streams the temperature and pressure of the SRE: T_o , p_o . Thus, the exiting streams have the chemical composition of each stream of the process at the temperature and pressure of the SRE, providing the thermodynamic intensive properties needed to calculate the physical exergy (see Sect. 2.3.1).

With the method explained, the $h(T_o, p_o)$ and $s(T_o, p_o)$ values of every stream correspond to the specific enthalpy and entropy values calculated by the simulator for the stream identified with the letters SRE, followed by the three digits identifying the same composition.

Table 2.1 Data selection for the physical exergy calculation of E914 streams from the data obtained in the simulation

| Streams | 93103 | 93104 | SRE931 | 94106 | 94107 | SRE941 |
|--------------------------------|-----------|------------|------------|-------------|-------------|-------------|
| \dot{n} | 1.48 | 1.48 | | 0.47 | 0.47 | |
| \dot{m} | 42.08 | 42.08 | | 8.20 | 8.20 | |
| T [°C] | 500.00 | 442.47 | | 255.66 | 350.00 | |
| p [bar] | 1.06 | 1.06 | | 115.00 | 115.00 | |
| x | 1.00 | 1.00 | | 1.00 | 1.00 | |
| \tilde{h} | -9 966.81 | -11 826.94 | -25 985.90 | -118 100.00 | -112 270.00 | -143 310.00 |
| h | -349.54 | -414.77 | -911.33 | -6 782.92 | -6 448.21 | -8 230.68 |
| \tilde{s} | 32 660.97 | 30 161.05 | -554.96 | -97 622.99 | -87 439.36 | -137 110.00 |
| s | 1 145.42 | 1 057.75 | -19.46 | -5 606.94 | -5 022.04 | -7 874.61 |
| Mole frac | | | | | | |
| H ₂ O | 0.0550 | 0.0550 | 0.0550 | 0.3865 | 0.3865 | 0.3865 |
| NH ₃ | 0.0000 | 0.0000 | 0.0000 | 0.6135 | 0.6135 | 0.6135 |
| CO ₂ | 0.0288 | 0.0288 | 0.0288 | 0.0000 | 0.0000 | 0.0000 |
| CH ₄ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C ₂ H ₆ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C ₃ H ₈ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C ₄ H ₁₀ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C ₅ H ₁₂ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| O ₂ | 0.1479 | 0.1479 | 0.1479 | 0.0000 | 0.0000 | 0.0000 |
| N ₂ | 0.7683 | 0.7683 | 0.7683 | 0.0000 | 0.0000 | 0.0000 |

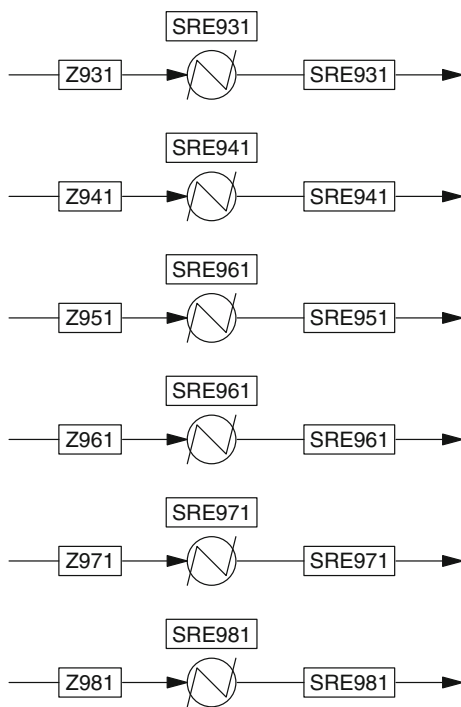
For a piece of equipment with no chemical processes (reactions, separation or mixtures of substances), only the physical exergy of the streams needs to be calculated, because the composition of the incoming and outgoing streams is identical.

In the case under study, the heat exchanger E914 is an example of a piece of equipment without chemical processes. This piece of equipment can be seen in different ways:

- In a material vision, streams 93103 and 94106 enter and streams 93104 and 94107 exit the heat exchanger.
- In an energetic vision, fluid 931 losses temperature and enthalpy, giving it to the heat exchanger, where the fluid 941 increases its temperature and enthalpy. If the heat exchanger is well insulated it can be said that the energy given by one fluid is completely received by the other.
- Finally, in an exergetic vision, the fluid 931 gives exergy to the heat exchanger, which is used to increase the exergy of stream 941, but only partially. The exergy given by fluid 931 is higher than the exergy received by stream 941, which means that some of the exergy has been destroyed inside the equipment, in a non-recoverable way.

For the calculation of the physical exergy of the aforesaid streams, the SRE streams with the same composition have to be considered: SRE931 and SRE941. Upon

Fig. 2.1 Simulation of the SRE using Aspen Plus®



completion of the simulation, the mass and molar flow data is obtained, as well as the enthalpy and entropy in terms of pressure and temperature, so it is possible to directly calculate the exergy of the streams under analysis. Table 2.1 shows the data from the above mentioned, obtained from the simulation. The specific values of the SRE stream: SRE941, provides the values of h_o and s_o for streams 94106 and 94107, as all of them share the same fluid composition 941. The same happens with streams 93103, 93104 and SRE931 (Fig. 2.1).

The calculation of the exergy of the streams using (2.1), gives the specific physical exergy in a mass base b . This calculation can also be realized in a molar base. In either case, the resulting value must be multiplied by the mass or molar flows respectively, to obtain the value of \dot{B}_{ph} provided in Table 2.2.

As shown in Table 2.2, the use of either base (molar or mass) offers very similar values (Tables 2.3 and 2.4 show an explanation of the content of each row and the calculations done in WB1001).

The calculations for the whole process are very similar. With the aid of the stream identification used and the workbook functions, they are quite easy to do. The calculations have been performed in the sheet BCorrM from WB1011 (Annex A). In this sheet, firstly, a selection is realized from the data contained in the m, w, Q sheets from WB1001:

Table 2.2 Physical exergy of E914 streams

| Streams | 93103 | 93104 | 94106 | 94107 |
|----------------|-----------|-----------|-----------|-----------|
| \dot{m} | 42.08 | 42.08 | 8.20 | 8.20 |
| $h - h_o$ | 561.79 | 496.56 | 1447.76 | 1782.47 |
| $s - s_o$ | 1.16 | 1.08 | 2.27 | 2.85 |
| b_{ph} | 214.48 | 175.38 | 771.66 | 931.98 |
| \dot{B}_{ph} | 9 025.33 | 7 380.20 | 6 328.62 | 7 643.51 |
| n | 1.48 | 1.48 | 0.47 | 0.47 |
| $h - h_o$ | 16 019.09 | 14 158.96 | 25 210.00 | 31 040.00 |
| $s - s_o$ | 33.22 | 30.72 | 39.49 | 49.67 |
| b_{ph} | 6 115.76 | 5 000.98 | 13 436.95 | 16 230.70 |
| \dot{B}_{ph} | 9 025.33 | 7 380.20 | 6 329.36 | 7 645.33 |
| Difference | | | | |
| Absolute [kW] | 0.00 | 0.00 | 0.74 | 1.82 |
| Relative [%] | 0.00 | 0.00 | 0.01 | 0.02 |

Table 2.3 Identification of content and row in WB1001

| Row | Content |
|-------|--|
| 1 | Stream identification |
| 2 | Equipment where the streams enters |
| 3 | Equipment from which the streams come from |
| 4 | Temperature |
| 5 | Pressure |
| 6 | Mass flow |
| 7 | Enthalpy given by the simulator |
| 10 | Specific enthalpy |
| 11 | Specific entropy |
| 21 | Molecular weight |
| 22–32 | Composition of the streams in molar fraction |

Several calculations are made and added to this sheet to enable a quick vision of all the thermodynamic stream data of interest.

The 29 matter streams of the case occupy columns A to AD. Columns AE to AJ are occupied with the information of the six SRE streams: SRE931, SRE941, SRE951, SRE961, SRE971, SRE981, providing with their specific enthalpy (row 10) and specific entropy (row 11) data, h_o and s_o values of all the

Table 2.4 Example of calculations done and shown in WB1001

| Row | Content |
|-----|--|
| 8 | Positive enthalpy. This row is the specific positive enthalpy times the mass flow. The calculation is: row 17 \times row 6 |
| 9 | Total exergy of the stream |
| 12 | Specific enthalpy at T_o , p_o (h_o). Data read from the specific enthalpy (row 10) of the corresponding SRE stream |
| 13 | Specific entropy at T_o , p_o (s_o). Data read from the specific enthalpy (row 11) of the corresponding SRE stream |
| 14 | Specific enthalpy difference between the stream state and the T_o , p_o value: row 10 – row 12 |
| 15 | Specific entropy difference between the stream T , p and the T_o , p_o value: row 11 – row 13 |
| 16 | Specific high heating value, calculated for each stream making use of the data composition and the tabulated HHV of the substances present in the simulation |
| 17 | Specific positive enthalpy. This row is added to obtain positive values of enthalpy. The value contained is the difference between the enthalpy given by the simulator (row 7) and H_o , summed all it with the HHV. The calculation is: row 14 + row 16 |
| 18 | Specific physical exergy (b_{ph}). Calculated according to Eq. 2.1, where $T_o = 298.15$ K. The calculation is: (row 14 – 298.15 \times row 15) |
| 19 | Specific chemical exergy (b_{ch}). Calculated according to Eq. 2.24 |
| 20 | Specific total exergy (b) |

Table 2.5 High heating values of the substances present in the simulation

| Substance | HHV |
|--------------------------------|-----------|
| H ₂ O | 0 |
| NH ₃ | 382 800 |
| CO ₂ | 0 |
| CH ₄ | 890 700 |
| C ₂ H ₆ | 1 560 700 |
| C ₃ H ₈ | 2 219 200 |
| C ₄ H ₁₀ | 2 877 500 |
| C ₅ H ₁₂ | 3 535 400 |
| O ₂ | 0 |
| N ₂ | 0 |

streams with same composition. As it can be shown, the molar composition (rows 22 and below) are identical between the streams with the same first 3 numbers in their names, so for this task an excel function can be used, that compares them and search for the adequate values in rows 10 and 11 of the corresponding SRE stream (this is not done in the workbook).

As the HHV of the streams depends exclusively in the composition of the streams and the HHV values of the substances (see Table 2.5), the HHV obtained for each SRE stream is also the HHV value for all the streams with same composition. Thus, in the range AE16 : AJ16, the value of the specific HHV (in kJ kmol^{-1}) of the fluids has been calculated, making use of the composition (rows 23–32) and the HHV of the substances in the same order, available in rows 33–42 (in kJ kmol^{-1}).

2.3.2 Indirect Method

In the case that the enthalpy and entropy data is unavailable, the enthalpy and entropy differences of Eq. 2.1 must be formulated for the specific substance under study. Considering the two particular cases that occur more frequently, depending on whether it involves an incompressible substance or an ideal gas.

2.3.2.1 Incompressible Condensed Substance (Pure or Homogeneous Mixture)

The enthalpy and the entropy term must be calculated. As for the enthalpy, upon developing s in terms of T and p , Eq. 2.2 remains:

$$\begin{aligned} dh &= T \left[\left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp \right] + v dp \\ &= T \left(\frac{\partial s}{\partial T} \right)_p dT + \left[v + T \left(\frac{\partial s}{\partial p} \right)_T \right] dp \end{aligned} \quad (2.2)$$

As the last member expresses dh in terms of dT and dp , the coefficient of its first term must be equal to the specific heat at constant pressure c_p [1]. Additionally applying Maxwell's formula to the $\left(\frac{\partial s}{\partial p} \right)_T$ of the second term, it gives (2.3):

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (2.3)$$

For a condensed body, $\left(\frac{\partial v}{\partial T} \right)_p$ can be neglected, so that very approximately in this case, the following is verified:

$$dh = c_p dT + v dp \quad (2.4)$$

The entropic term is deduced to be in general:

$$ds = \frac{1}{T}dh - \frac{v}{T}dp \quad (2.5)$$

Applying (2.4) obtained by applying Maxwell's function to a condensed body in (2.3):

$$ds = c_p \frac{dT}{T} \quad (2.6)$$

Integrating both expressions between the states (T_o, p_o) and (T, p) and expressing c_p in terms of T , the following dimensionless polynomial, named a "NASA polynomial", is obtained for the molar heat \tilde{c}_p :

$$\frac{\tilde{c}_p^o(T)}{\tilde{R}} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \quad (2.7)$$

where \tilde{R} is the gas constant, and a_1, \dots, a_5 are constants corresponding to the considered substance. There are different data bases for these coefficients and their validity interval for diverse substances.

Specific heat \tilde{c}_p is easily computed with the following expression:

$$c_p = \frac{\tilde{c}_p}{M} \quad (2.8)$$

M represents the *molar mass* of the substance. In small enough temperature intervals, c_p can be considered constant; in these cases the physical exergy can be calculated roughly as follows:

$$b_{ph} = c_p (T - T_o) - T_o c_p \ln \frac{T}{T_o} + v(p - p_o) \quad (2.9)$$

In general, this expression provides enough approximation for small temperature and pressure intervals.

2.3.2.2 Ideal Gaseous Substance (Pure or of Constant Composition)

The enthalpy of an ideal gas only depends on its temperature so that the enthalpy increase is simply:

$$h - h_o = \int_{T_o}^T c_p dT \quad (2.10)$$

As for the entropy, it is expressed through (2.11), where R is the gas constant:

$$s - s_o = \int_{T_o}^T c_p \frac{dT}{T} - R \int_{p_o}^p \frac{dp}{p} = \int_{T_o}^T c_p \frac{dT}{T} - R \ln \frac{p}{p_o} \quad (2.11)$$

If c_p is considered to be constant, the physical exergy can be expressed by (2.12):

$$b_{ph} = c_p (T - T_o) - T_o c_p \ln \frac{T}{T_o} + RT_o \ln \frac{p}{p_o} \quad (2.12)$$

If the gaseous substance is liquid at T_o, p_o (in the SRE), then the enthalpy of vaporization Δh_{vap} must be added to Eq. 2.10, and the corresponding term $\frac{\Delta h_{\text{vap}}}{T_{\text{vap}}}$ must be added to Eq. 2.11. If the gaseous substance is a subcooled liquid in the SRE then, the enthalpy and entropy increases from (T_o, p_o) to the boiling point must be added, following the Sect. 2.3.2.1 procedure, then the vaporization shall be considered, and finally the Eqs. 2.10 and 2.11 for the gaseous temperature and pressure increases shall be considered. Due to the Hess law, in this case, the path followed from the (T_o, p_o) to reach the final state at (T, p) of the streams are all equivalent. Nevertheless, special attention should be given to the vaporization stage, as the values of Δh_{vap} and T_{vap} depend on the pressure of the boiling point selected.

2.4 Chemical Exergy

Chemical exergy is the maximum useful energy which would be attained by passing from the environmental state to the dead state, by means of chemical processes with reactants and products at the environmental temperature and pressure, when the stream composition is not in chemical equilibrium with the environment.

If the substance of a stream is present in the environment but in a partial pressure greater than the one it has in the environment, some work can still be done in the expansion of this component. For example, if a stream composed exclusively of CO_2 at (T_o, p_o) , is considered, the stream has no physical exergy, but as CO_2 is only a small fraction of the air composition (0.035 %), the pressure decrease of the stream from p_o to the partial pressure of CO_2 in the environment, can theoretically produce work, and this will also be called chemical exergy, although no chemical reaction is produced.

If the chemical exergy of any of the substances of the process is unknown (not available in tables), they can be determined through two methods:

- General Method: calculating the chemical exergy of the chemical elements which constitute the substance and the free energy of formation of the substance.

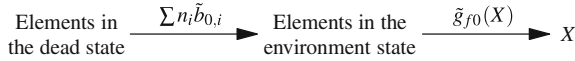


Fig. 2.2 Formation process of a substance from its elements in the dead state

- **Alternative Method:** when the substance is not found in the SRE but is stoichiometrically linked to substances contained in the SRE and only to them.

In any case, once the chemical exergy of all the components is calculated, the chemical exergy of the stream can be calculated, according to the instructions given in Sect. 2.5.3.

2.5 Chemical Exergy of Substances

2.5.1 General Method

We will consider a compound X , formed by various elements whose chemical exergy $\tilde{b}_{0,i}$ is known. Evidently, the chemical exergy of X will be equal to the minimum useful work required to form it from its elements in the dead state, through the process shown in Fig. 2.2, where $\tilde{g}_{f0}(X)$ represents the free energy of formation of X , supposing that the normal state is the same as the environmental one:

Therefore, the total is equivalent to the chemical exergy of X , as follows:

$$\tilde{b}_{ch}(X) = \sum n_i \tilde{b}_{ch,i}(\text{elems.}) + \tilde{g}_{f0}(X) \quad (2.13)$$

CO_2 can be found in streams 93103 and 93104. Although its normal chemical exergy is tabulated, this method will be applied to calculate it as an example. According to Eq. 2.14, the chemical exergy of CO_2 can be written as:

$$\tilde{b}_{ch}(\text{CO}_2) = \tilde{b}_{ch}(\text{C}) + \tilde{b}_{ch}(\text{O}_2) + \tilde{g}_{f0}(\text{CO}_2) \quad (2.14)$$

Using the values of normalized chemical exergy, as well as of free energy, the following result is obtained:

$$\tilde{b}_{ch}(\text{CO}_2) = 410\,820 + 4\,000 - 394\,400 = 20\,420 \text{ kJ kmol}^{-1} \quad (2.15)$$

The difference with the tabulated value is of 1.5%, this being considered acceptable.

2.5.2 Alternative Method

This method will be used in the cases in which the substance cannot be found in the SRE, but is stoichiometrically linked to substances only from the SRE. Assuming that the reaction that links them is written in the standard form where the negative coefficients v_i correspond to the positive reactants and the positive ones to the reaction products:

$$\sum_{\forall i} v_i C_i = 0 \quad (2.16)$$

For this reaction at T_o and p_o (2.17) is verified, which represents $-W_{u,\max.}$, which is the minimum useful work required for a reaction to take place.

$$\Delta B_{\text{react.}} = \sum_{\forall i} v_i \tilde{b}_{ch,i} \quad (2.17)$$

Equation (2.18) is also verified, where $\tilde{g}_{f0,i}$ represents the standard free energy of formation of the generic substance at T_o and p_o .

$$-W_{u,\max.} = \Delta G_{\text{react.}} = \sum_{\forall i} v_i \tilde{g}_{f0,i} \quad (2.18)$$

Therefore, from expressions (2.17) and (2.18) the following expression can be written:

$$\sum_{\forall i} v_i (\tilde{b}_{ch,i} - \tilde{g}_{f0,i}) = 0. \quad (2.19)$$

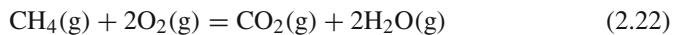
If substance j does not belong to the SRE and its chemical exergy is the one to be calculated, (2.19) can be written as (2.20)

$$v_j (\tilde{b}_{ch,j} - \tilde{g}_{f0,j}) + \sum_{i \neq j} v_i (\tilde{b}_{ch,i} - \tilde{g}_{f0,i}) = 0. \quad (2.20)$$

Reordering (2.20), the sought chemical exergy is determined with (2.21).

$$\tilde{b}_{ch,j} = \tilde{g}_{f0,j} - \frac{1}{v_j} \sum_{i \neq j} v_i (\tilde{b}_{ch,i} - \tilde{g}_{f0,i}) \quad (2.21)$$

We will apply (2.21) to the case of CH_4 , it does not belong to the SRE but verifies reaction (2.22) which links it to SRE substances:



From the equation of reaction (2.22) and the data tables, the information in Table 2.6 is obtained.

Table 2.6 Chemical exergy and standard free energy of formation

| Substance | ν_i | $\tilde{g}_{fo,i}$ | $\tilde{b}_{ch,i}$ |
|------------------|---------|--------------------|--------------------|
| CH ₄ | -1 | -50 757 | ? |
| O ₂ | -2 | 0 | 3 970 |
| CO ₂ | +1 | -394 364 | 20 140 |
| H ₂ O | +2 | -237 141 | 3 120 |

Table 2.7 Chemical exergy of the substances present in the simulation

| Substance | \tilde{b}_{ch} |
|--------------------------------|------------------|
| H ₂ O | 3 120 |
| NH ₃ | 341 250 |
| CO ₂ | 20 140 |
| CH ₄ | 836 510 |
| C ₂ H ₆ | 1 504 360 |
| C ₃ H ₈ | 2 163 190 |
| C ₄ H ₁₀ | 2 818 930 |
| C ₂ H ₁₂ | 3 477 050 |
| O ₂ | 3 970 |
| N ₂ | 720 |

With the help of (2.21) we can write (2.23).

$$\begin{aligned} \tilde{b}_{ch}(\text{CH}_4) = & -50\,757 - (1/-1)[-2(3\,970 - 0) + 1(20\,140 + 394\,364) \\ & + 2(3\,120 + 237\,141)] = 836\,329 \text{ kJ kmol}^{-1} \end{aligned} \quad (2.23)$$

This result compared with data contained in other databases has an error of 0.02 %. This method is very useful for fuels whose chemical exergy is not available in tables.

Unlike the case of physical exergy, the data necessary for the calculation of chemical exergy cannot be directly obtained from the performed simulation, from which the data relative to the composition of the different streams will be used. The normalized chemical exergy per mole of the components of the streams is obtained through the process described in Sect. 2.5.1 obtaining the value of the chemical exergy of the different components at 1 atm and 298.15 K in Table 2.7.

2.5.3 Chemical Exergy of a Stream

Once the chemical exergy of all the substances present in the process is known, the chemical exergy of the streams can be evaluated. As the specific chemical exergy depends exclusively on the composition of the streams, it can be calculated only once per composition.

For the calculation of the chemical exergy of a stream, the chemical exergy of its components and their molar fraction must be known. The components of the streams which are part of the SRE, and several others can be found tabulated in [12, 14, 15].

Table 2.8 Specific and total chemical exergy of E914 streams

| Streams | 93103 | 93104 | 94106 | 94107 |
|----------------|----------|----------|-----------|-----------|
| \dot{m} | 42.08 | 42.08 | 8.20 | 8.20 |
| b_{ch} | 66.37 | 66.37 | 12 094.44 | 12 094.44 |
| \dot{B}_{ch} | 2 792.75 | 2 792.75 | 2 792.75 | 2 792.75 |

In this case, the chemical exergy of the stream is calculated as [4]:

$$\tilde{b}_{ch} = \sum x_i \tilde{b}_{ch,i} \quad (2.24)$$

It is important to point out that in other publications [7], the formula given for the chemical exergy determination is slightly different. For both gas mixtures and ideal liquid solutions, formula (2.25) is applied:

$$\tilde{b}_{ch} = \sum x_i \tilde{b}_{ch,i} + \tilde{R}T_o \sum x_i \ln x_i \quad (2.25)$$

The difference between both equations is $\tilde{R}T_o \sum x_i \ln x_i$, which account for the exergy destroyed ($\ln x_i$ is always negative) due to the mixing of the different components of the stream (it can be called *mixture exergy*). As can be seen in comparison with the term $RT_o \ln \frac{p}{p_o}$ for the physical exergy (2.12), this term corresponds to $s - s_o$, and comes from the consideration of the partial pressure of each component in the numerator; which is $x_i p_o$ in the SRE according to Dalton's Law. The use of (2.24) or (2.25) depends on the pressure used in (2.12). If the partial pressure of each component is used in (2.12), or the entropy used is the entropy of the stream, then the mixing effect is already considered, and therefore the appropriate equation is (2.24), in any other case Eq. 2.25 must be used.

This expresses the chemical exergy of the mixture in terms of its components and of its composition [16]. Upon obtaining the exergy of the components that form the streams under analysis as well as its compositions attained from the simulation, the chemical exergy of the different streams that affect E914 can be obtained. Table 2.8 shows the acquired results, both unit chemical exergy and each stream's chemical exergy:

This method has been used to obtain the chemical exergy of the six different compositions present in the case analyzed, present in the SRE streams.

In the worksheet BCoRRM of the workbook WB1011 the chemical exergy of the substances present in the composition are written in the range AE43 : AE52 in kJ kmol^{-1} . With these values, the chemical compositions given in rows 23–32, and the molecular weight available in row 21, the specific chemical exergy is calculated, for each SRE stream, in the range AE19 : AJ19, applying Eq. 2.24 (which gives the result in kJ kmol^{-1}) divided by the molecular

weight [kg kmol^{-1}] given in row 21 (to obtain the value in kJ kg^{-1} instead of kJ kmol^{-1}). As all the streams in the simulation have the same composition as that of one of the SRE streams, the specific calculated values are used for all of them, filling row 19.

2.5.4 Chemical Exergy of a Fuel Stream

The determination of the chemical exergy of a fuel is a particular case of the calculation of the chemical exergy of a stream, of great interest in the analysis of industrial facilities.

If the methods already described cannot be used, an approximate determination of the specific chemical exergy of industrial fuels can be easily carried out through empirical coefficients f_l and f_h , which relate it to the lower or higher heating values (2.26), where LHV and HHV respectively represent the lower and higher heating values.

$$b_{\text{ch}} = f_l \cdot \text{LHV} = f_h \cdot \text{HHV} \quad (2.26)$$

This can be done because solid and liquid fuels have usually exergy values similar to the HHV, and gaseous fuels have values very similar to the LHV, so the empirical coefficients are numbers close to 1.

2.6 Total Exergy of a Matter Stream

The calculation of total exergy is usually reduced to the sum of the chemical and physical exergy, including only in specific cases, the kinetic and potential exergy (the energy and exergy values are the same).

2.6.1 Exergy of an Ideal Gas Mixture

The calculation of total exergy can be accomplished via two equivalent methods:

1. Calculating the chemical exergy $\tilde{b}_{\text{ch}}(T_o, p_o)$ of the mixture in environmental state through (2.25). Physical exergy, $\tilde{b}_{\text{ph}}(T, p)$ is then calculated with (2.12), referring to the unit of substance of the mixture, using the average \tilde{c}_p of the mixture. Finally, the total exergy $\tilde{b}(T, p)$ of the mixture, is obtained through the addition of $\tilde{b}_{\text{ch}}(T_o, p_o)$ and $\tilde{b}_{\text{ph}}(T, p)$.

Table 2.9 Total, chemical and physical exergy of E914 streams

| Streams | 93103 | 93104 | 94106 | 94107 |
|----------------|-----------|-----------|------------|------------|
| \dot{m} | 42.08 | 42.08 | 8.20 | 8.20 |
| $h - h_o$ | 561.79 | 496.56 | 1 447.76 | 1 782.47 |
| $s - s_o$ | 1.16 | 1.08 | 2.27 | 2.85 |
| b_{ph} | 214.48 | 175.38 | 771.66 | 931.98 |
| \dot{B}_{ph} | 9 025.33 | 7 380.20 | 6 328.62 | 7 643.51 |
| b_{ch} | 66.37 | 66.37 | 12 094.44 | 12 094.44 |
| \dot{B}_{ch} | 2 792.75 | 2 792.75 | 99 190.74 | 99 190.74 |
| b | 280.85 | 241.75 | 12 866.10 | 13 026.42 |
| \dot{B} | 11 818.08 | 10 172.95 | 105 519.36 | 106 834.25 |

2. The $\tilde{b}_{ph,i}(T, p_i)$ of each gas is calculated with (2.12) and to it its chemical exergy is added $\tilde{b}_{ch,i}(T_o, p_o)$ to achieve the total exergy $\tilde{b}_i(T, p_i)$. The molar exergy of the mixture is obtained as (2.27):

$$\tilde{b}(T, p) = \sum x_i \tilde{b}_i(T, p_i) \quad (2.27)$$

Table 2.9 shows the total exergy, as well as the exergy value of each component. As the $s - s_o$ of the entire stream takes into consideration the mixture effect, the chemical exergy is given by (2.24).

Exactly the same procedure has been followed in the case analysed (WB1011), the specific total exergy of the matter stream is calculated in row 20 of sheet BCorrM, adding up the physical and chemical exergies (rows 18 and 19 respectively).

2.6.2 Exergy of an Ideal Liquid Solution

The same procedure applied in Sect. 2.6.1 for a mixture of ideal gases should be followed. The chemical exergy can be calculated by applying (2.25), and the physical exergy can be calculated applying (2.9) per mole and with the average \tilde{c}_v of the solution. This average of the solution can be calculated applying (2.28):

$$\tilde{c}_v = \frac{d\tilde{u}}{dT} = \sum_i x_i \tilde{c}_{v,i} \quad (2.28)$$

Finally, the total exergy $\tilde{b}(T, p)$ of the mixture is obtained through the addition of $b_{ch}(T_o, p_o)$ and $b_{ph}(T, p)$.

2.7 Exergy of Non-Matter Streams

2.7.1 Exergy of Work

Since exergy is defined as the maximum work potential, a work interaction in energy terms is equivalent in exergy terms. Therefore, the exergy content of a work flow is the amount of work of the flow [18]:

$$\dot{B}_W = \dot{W} \quad (2.29)$$

2.7.2 Exergy of Electricity

As electrical energy (active power) can be fully converted in work, the exergy content of electricity is equivalent to the energy content of work and therefore the energy content of the electrical flow. It can be therefore considered as a particular case of the exergy of a work stream [2]:

$$\dot{B}_W = \dot{W}_e \quad (2.30)$$

2.7.3 Exergy of Heat Flows

The exergy content of a heat flow \dot{Q} at a temperature T is of [13]:

$$\dot{B}_q = \left(1 - \frac{T_o}{T}\right) \dot{Q} \quad (2.31)$$

This means that for the same heat flow, the exergy content is lower when the temperature T is nearer T_o . If $T < T_o$, the exergy flow is opposite to the heat flow, and therefore all heat flow input at a lower temperature than the ambient temperature is equivalent to an exergy output. This exergy output is higher as the temperature in which the heat transmission occurs is lower. This is especially important in cryogenic facilities, where a small heat leakage that is incoming from the ambient to the system, can be responsible of high exergy leakages [6].

2.7.4 Exergy of Solar Radiation

Energy emission of a blackbody is σT^4 in W/m^2 where σ is the Stefan-Boltzmann coefficient. This exergy is the equivalent energy transferred to a sink at $T = 0 \text{ K}$.

In this case the Carnot efficiency cannot be used to calculate the exergy of the solar radiation flux σT^4 at a temperature T , as a heat sink at the same temperature is considered [5, 19]. If an infinite amount of Carnot engines producing the maximum amount of work are imagined, all of them working between a heat source at T_i absorbing radiation $T_i + dT_i$ and emitting radiation at T_i , the maximum amount of work is [19]:

$$W_{\max} = \int_{T_i=T_o}^{T_i=T} 4\sigma T_i^3 dT \left(1 - \frac{T_o}{T_i}\right) = \sigma(T^4 - T_o^4) - \frac{4}{3}T_o\sigma(T^3 - T_o^3) \quad (2.32)$$

Being the maximum efficiency relative to the radiation energy [10]:

$$\eta_{\max} = \frac{W_{\max}}{\sigma T^4} = 1 - \frac{4T_o}{3T} + \frac{1}{3} \left(\frac{T_o}{T}\right)^4 \quad (2.33)$$

Its value is always smaller than the Carnot efficiency $(1 - \frac{T_o}{T})$.

For practical purposes, the exergy of solar radiation can be calculated as the exergy of a heat source at $T = 6000$ K applying Carnot's efficiency [5]. Additionally, as a first approach, the solar radiation exergy can be considered equivalent to its energy (due to uncertainties in solar insolation data, blackbody deviations, etc.).

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