

A unified deduction of the expressions of exergy and flow exergy

Enzo Zanchini 

Department of Industrial Engineering, University of Bologna, Bologna, Italy

E-mail: enzo.zanchini@unibo.it

Received 29 December 2022, revised 12 May 2023

Accepted for publication 1 June 2023

Published 29 June 2023



CrossMark

Abstract

Exergy analysis is a branch of thermodynamics receiving an increasing interest in the scientific literature and in didactic presentations. Exergy represents the maximum useful work obtainable by a system that can interact with a reference environment. There exist two exergy functions: exergy, which refers to a collection of matter contained within the reference environment; flow exergy, which refers to a collection of matter flowing in a pipe, that can interact with the environment and diffuse into it. The usual derivations of the expressions of exergy and flow exergy are either complicated or not general. Moreover, two separate derivations are necessary, due to the different conceptual schemes employed in the definitions of these properties. As a consequence, the expressions of exergy and flow exergy are often reported without a derivation in didactic treatises. In this paper, we provide a simple and general unified deduction of the expressions of exergy and flow exergy. Moreover, we show that the logical scheme proposed, based on the concept of useful energy of a system contained in a pressure field, allows a simpler deduction and a deeper interpretation of the energy balance equation for a control volume in a steady state. Finally, in order to complete the didactic treatment, we rewrite the expression of the molar exergy of a pure substance at ambient temperature and pressure in a form applicable to reactive substances, and we present an application of this form.

Keywords: thermodynamics, exergy, flow exergy, unified deduction

(Some figures may appear in colour only in the online journal)



Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](https://creativecommons.org/licenses/by/4.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

1. Introduction

In order to reduce the environmental impact of the use of fossil fuels, two ways are fundamental. One way is the development of technologies based on the use of renewable energy sources, such as wind, solar, geothermal and nuclear energy sources. The other way is improving the efficiency in the conversion of energy from the source to the utilization. A correct initial step towards learning how to design an efficient energy conversion system is to understand that not only the amount of energy used to obtain a result is important, but also the quality of that amount of energy. Mechanical energy is the highest-quality energy because an amount of mechanical energy can be easily transformed into the same amount of any other form of energy. Thermal energy is all the more valuable the higher its temperature is. It cannot be transformed completely into work; a part of it must be rejected to a lower-temperature thermal reservoir.

The key concept to compare correctly amounts of different kinds of energy is the concept of exergy.

Exergy can be defined as follows. Consider a system composed of three subsystems: a collection of matter, that we call system A ; the environment of A , schematized as a reference thermal reservoir R^0 , with constant values of temperature, T_0 , pressure p_0 , and chemical potentials, μ_{i0} ; a cyclic device, X , namely an auxiliary system that performs thermodynamic cycles and is employed to transfer heat between A and R^0 , and work between A and a suitable mechanical apparatus. System A can exchange energy, volume and matter with R^0 , but the total volume of AR^0 is constant. We call exergy of A , in a state A_1 , the maximum work that can be obtained in an adiabatic process of the composite system AR^0X , with initial state A_1 .

An alternative configuration of the composite system AR^0X is as follows. The collection of matter A is not contained in R^0 but flows from the inlet to the outlet section a fixed region of space, called control volume, that remains in a stationary state. System A can exchange energy and matter with R^0 , and the volume of R^0 is constant. We call the flow exergy of A , in a state A_1 , the maximum useful work that can be obtained in an adiabatic process of the composite system AR^0X , with initial state A_1 . The useful work differs from the total work because it does not include the work exchanged by A with the fluid that precedes the inlet section and with the fluid that follows the outlet section of the control volume. The concept of useful work will be sharpened in section 2.

For both exergy and flow exergy, in order to extract all the possible work, the initial state A_1 must be changed to a final state such that the system has the same temperature, pressure and chemical potentials as R^0 , i.e. is in complete thermodynamic equilibrium with R^0 . Contrary to energy, exergy is not conserved for an isolated system: it decreases due to the entropy production caused by irreversibilities.

The branch of thermodynamics that deals with the evaluation of the property exergy (or flow exergy) and with the analysis of the exergy (or flow exergy) destruction caused by irreversibilities is called exergy analysis. It is now recognized as an important branch of thermodynamics, aimed at the optimal use of energy resources in technological processes. Many scientific papers presenting results of exergy analysis appear every year in the literature. They concern, for instance, combined cycle power plants [1–4], steam Rankine cycles [5–8], organic Rankine cycles [9–12], refrigeration cycles [13–16], thermal and PV solar systems [17–20], fuel cells [21–24], heat exchangers [25–28]. Review papers on the exergy analysis of combined cycle power plants [29], steam power plants [30], solar energy applications [31], fuel cells [32], and heat exchangers [33] are available. In parallel with the growth of the scientific literature on this topic, the education on exergy evaluation and exergy analysis is developing. Courses on exergy analysis are present in many universities, and wide

treatises on exergy analysis have been published [34–36]. In this framework, studies aimed at improving the didactic presentations of the expressions of exergy and flow exergy and of the methods to evaluate these properties for different systems appear as interesting.

Some authors [34–37] define exergy as the sum of different parts, namely kinetic exergy, potential exergy, physical exergy and chemical exergy. The kinetic exergy and the potential exergy are, respectively, the kinetic energy with respect to a reference system united with the Earth's surface, E_k , and the gravitational potential energy with respect to a selected reference level, E_p . If kinetic energy and potential energy are nonvanishing, they are obviously parts of the exergy, because they are already forms of mechanical energy.

The physical exergy of system A is the maximum amount of work that can be obtained by an adiabatic process of the composite system AR^0X described before, if A is closed, no chemical reaction takes place, and the pressure and temperature of A are changed to the pressure p_0 and the temperature T_0 of R^0 . The chemical exergy of system A is the maximum amount of work that can be obtained by an adiabatic process of AR^0X , if A is open, chemical reactions can take place, and the state of A is changed from the state with pressure p_0 and temperature T_0 mentioned above to a state with pressure p_0 and temperature T_0 in which the chemical potentials of the constituents of A are equal to those of the same constituents in R^0 . In this final state, the matter of A is indistinguishable from that of R^0 , and it is possible to think that all the matter of A has been transferred to R^0 .

Other authors [38–40] prefer not to employ the concepts of physical and chemical exergy, and to derive, either by steps [38, 39] or directly [40], the expressions of the total exergy and of the total flow exergy of the system. These expressions reduce to those of physical exergy and physical flow exergy if A is closed and no reaction takes place. In this paper, after a brief survey of the literature on the definition of exergy, we present a direct deduction of a slightly generalized expression of the total exergy, that contains those of exergy and of flow exergy as special cases.

Brzustowski and Golem [38] derive from the basic principles of thermodynamics the following expressions of the exergy, Ξ , and the flow exergy, Ψ , of a collection of matter with r constituents

$$\Xi = U - T_0S + p_0V - \sum_{i=1}^r \mu_{i0}n_i, \quad (1)$$

$$\Psi = H - T_0S - \sum_{i=1}^r \mu_{i0}n_i. \quad (2)$$

Equations (1) and (2) refer to a collection of matter, hereafter called system A , that either is in a stable equilibrium state or is composed of subsystems in stable equilibrium states. Clearly, if A has kinetic energy and/or potential energy, these terms must be added to the exergy and to the flow exergy. In equations (1) and (2), U , S , V , H and n_i are the internal energy, the entropy, the volume, the enthalpy and the number of moles of the i th constituent of A , T_0 and p_0 are the temperature and the pressure of the environment of A , R^0 , and μ_{i0} is the chemical potential of the i th constituent of A , evaluated in R^0 . Both for exergy and flow exergy, the deduction is performed in two parts: first, the system is brought from its initial state to a stable equilibrium state with $p = p_0$ and $T = T_0$ called by the authors dead state, then, it is brought to its final state, in mutual stable equilibrium with the environment. The deduction is correct, but rather long. Moreover, it is not quite complete. In fact, the authors evaluate the maximum work obtainable in the process from the dead state to the final equilibrium state as the decrease in the Gibbs free energy of the system but do not prove the equality between maximum work and decrease in Gibbs free energy in that process.

Kotas [38] presents a rather complex scheme for evaluating exergy and flow exergy, where the fluid is supposed to pass through three modules: module A, where the fluid is brought by a physical process to a stable equilibrium state with $p = p_0$ and $T = T_0$, called by the author constrained equilibrium state; module B, where the fluid undergoes a chemical reaction with some common constituents of the environment; module C, where the reaction products diffuse to the environment and unconstrained equilibrium with the environment is reached. The author does not obtain equations (1) and (2), because he considers only substances that react with the environment. In this case, equations (1) and (2) need further development, because the values of μ_{i0} are not known.

Expressions of the decrease in exergy and flow exergy of a system A that undergoes a change of state $A_1 \rightarrow A_2$ are derived by Gyftopoulos and Beretta [39]. The derived expressions agree with equations (1) and (2) and are obtained in three steps. First, the authors assume that system A can exchange neither volume nor matter with R^0 ; then, they assume that A can exchange volume, but not matter; finally, they assume that A can exchange both volume and matter with R^0 , and obtain the complete expressions of $\Xi_1 - \Xi_2$ and of $\Psi_1 - \Psi_2$. In the deduction, the authors assume that no reaction occurs in the composite system AR^0 . Rigorous deductions of equations (1) and (2), where chemical reactions are considered, are presented by Zanchini and Terlizzese [40].

Szargut [34] suggests to evaluate the flow exergy of a substance flowing through a fixed boundary as the sum of the kinetic exergy, the potential exergy, the physical exergy and the chemical exergy, i.e. by the expression

$$\Psi = E_k + E_p + \Psi_{\text{ph}} + \Psi_{\text{ch}}, \quad (3)$$

where E_k is the kinetic exergy, E_p is the potential exergy, Ψ_{ph} and Ψ_{ch} are the physical flow exergy and the chemical flow exergy, respectively. The author reports the following expression of Ψ_{ph}

$$\Psi_{\text{ph}} = H - H_0 - T_0(S - S_0), \quad (4)$$

where H and S are the system enthalpy and entropy, $H_0 = H(T_0, p_0)$ and $S_0 = S(T_0, p_0)$ are the system enthalpy and the system entropy in the stable equilibrium state with $p = p_0$ and $T = T_0$ having the same chemical composition as the initial state. No deduction of equation (4) from the basic principles of thermodynamics is presented in [34]. Similarly, the author reports without deduction some expressions for the calculation of Ψ_{ch} , and the relation between the flow exergy, Ψ , and the exergy Ξ

$$\Psi = \Xi + V(p - p_0), \quad (5)$$

where V is the system volume.

Sala Lizarraga and Picallo-Perez [35] present exergy as the sum of kinetic, potential, physical and chemical exergy and focus on the non-obvious parts, namely physical and chemical exergy. They derive the expressions of the physical flow exergy, equation (4), and of the physical exergy of a closed system contained in R^0 ,

$$\Xi_{\text{ph}} = U - U_0 - T_0(S - S_0) + p_0(V - V_0), \quad (6)$$

by energy and entropy balances. They define chemical exergy as the maximum useful work that can be obtained when the state of the system is changed from (T_0, p_0) to complete mutual equilibrium with the environment, and prove that the maximum useful work equals the decrease in Gibbs free energy of the system. They do not propose compact expressions of the total exergy and flow exergy of the system.

Dincer and Rosen [36] report, without deduction, expressions of exergy and flow exergy written as sums of physical exergy, or physical flow exergy, chemical exergy, kinetic exergy and potential exergy. In the case of vanishing kinetic and potential energy, the sums yield the following expressions of exergy and flow exergy:

$$\Xi = U - U_0 - T_0(S - S_0) + p_0(V - V_0) + \sum_{i=1}^r [\mu_i(T_0, p_0) - \mu_{i0}]n_i, \quad (7)$$

$$\Psi = H - H_0 - T_0(S - S_0) + \sum_{i=1}^r [\mu_i(T_0, p_0) - \mu_{i0}]n_i. \quad (8)$$

In equations (7) and (8): T_0 and p_0 are the temperature and the pressure of the reference environment R^0 ; μ_{i0} is the chemical potential of the i th constituent of the system in the state of complete mutual equilibrium with R^0 ; U , S , V , and H are the internal energy, the entropy, the volume and the enthalpy of the system in its initial state; U_0 , S_0 , V_0 , H_0 , $\mu_i(T_0, p_0)$ are the internal energy, the entropy, the volume, the enthalpy and the chemical potential of the i th constituent of the system in the state (T_0, p_0) of constrained mutual equilibrium with R^0 , that is reached from the initial state without matter exchange or chemical reactions. The terms preceding the summation correspond to the physical exergy in equation (7) and to the physical flow exergy in equation (8). Although written in a different form, equations (7) and (8) agree with equations (1) and (2). In fact, equation (7) can be written, for instance, as

$$\Xi = U - T_0S + p_0V - \sum_{i=1}^r \mu_{i0}n_i - \left[U_0 - T_0S_0 + p_0V_0 - \sum_{i=1}^r \mu_i(T_0, p_0)n_i \right], \quad (9)$$

where the term in square brackets is vanishing, on account of the Euler equation.

Since recent and wide treatises on exergy analysis, such as [34] and [36], report the expressions of exergy and flow exergy without derivations, it is reasonable to argue that the available derivations of these expressions are not completely satisfactory for didactic use. Indeed, most derivations are either complicated or not completely general. The simplest ones [39] do not consider the possibility of chemical reactions. Moreover, at least two separated derivations for Ξ and Ψ are necessary if the usual schemes are adopted. Several authors [35, 39] prefer to introduce gradually the concepts of exergy and flow exergy, starting from the simplest cases and presenting a separate derivation for each case. Although this can be a good teaching method, a simple and general unified deduction of the expressions of Ξ and Ψ can be interesting for postgraduate programmes in Energy Physics and Energy Engineering, either as an alternative to traditional procedures, or as a synthetic complement. A conceptual scheme that allows a unified deduction of the expressions of Ξ and Ψ has been proposed in [41]. However, this reference has not been written for didactic purposes and employs a rather difficult axiomatic language. Here, the same method is proposed in a simplified form, suitable for didactic presentations. Moreover, it is shown that the logical scheme employed, based on the concept of useful energy of a system in a pressure field, allows a simpler proof and a clearer interpretation of the energy balance equation for a control volume in a steady state.

2. Useful energy of a system in a pressure field

Consider a close system A embedded in an external pressure field $p_e(x, y, z)$, and a process $A_1 \rightarrow A_2$ of A in which the region of space occupied by A changes from V_1 to V_2 . The energy balance equation for the process is

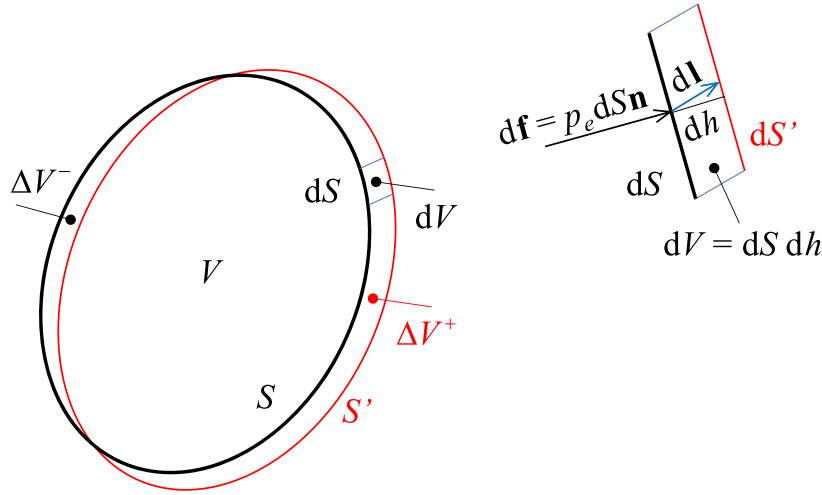


Figure 1. Work performed against the external pressure field for an infinitesimal deformation of the external surface of A .

$$E_2^A - E_1^A = Q - W, \tag{10}$$

where E^A is the energy of A , Q is the quantity of heat absorbed by A and W is the work performed by A . A part of the work W is performed unavoidably against the external pressure field, and cannot be collected as a useful result. The remaining part of the work, which is performed against the other external forces, will be called useful work, denoted by W_u . Thus, for any process of A , one has

$$W = W_u + W_{pe}, \tag{11}$$

where W_{pe} is the work performed against the external pressure field $p_e(x, y, z)$.

Let us clarify the meaning of useful work by means of a simple example. Consider a gas, A , contained in a vertical cylinder whose top is a frictionless moving piston, with area S . The gas performs a quasistatic expansion with constant pressure p , from volume V_1 to volume V_2 , i.e. from the level z_1 to the level z_2 of the surface between the gas and piston. The expansion work $W = p(V_2 - V_1) = pS(z_2 - z_1)$ is used to raise a weight. If the external pressure is vanishing, the gas rises a weight with mass m such that $pS = mg$, where g is the gravitational acceleration, and the whole work $W = pS(z_2 - z_1) = mg(z_2 - z_1)$ is transformed into the desired effect, namely into the potential energy of the weight. If the external pressure is $p_0 > 0$, a part of the pressure p of the gas is balanced by p_0 , and the mass m' of the weight that can be lifted is given by $(p - p_0)S = m'g$. Thus, only the part $(p - p_0)S(z_2 - z_1) = m'g(z_2 - z_1)$ of the work W is transformed into the desired effect, namely into the potential energy of the weight. This part is called useful work, denoted by W_u .

The substitution of equation (11) in equation (10) yields

$$E_2^A - E_1^A = Q - W_u - W_{pe}. \tag{12}$$

It is easily proved that

$$W_{pe} = \int_{V_2} p_e dV - \int_{V_1} p_e dV. \tag{13}$$

In fact, let V be the region of space occupied by A at an instant of time t , and let S be the external surface of V . As illustrated in figure 1, in an infinitely short time interval, dt , the

external surface of A displaces from S to S' . Consider an infinitely small element dS of S , in the neighborhood of a point \mathbf{P} , that undergoes an infinitely small displacement $d\mathbf{l}$. The force that must be exerted on dS in order to balance the external pressure p_e is $d\mathbf{f} = p_e dS \mathbf{n}$, where \mathbf{n} is the unit outward normal to S in \mathbf{P} . The work performed against the external pressure to produce the displacement $d\mathbf{l}$ of dS is

$$\delta W' = p_e dS \mathbf{n} \cdot d\mathbf{l} = \pm p_e dS dh = \pm p_e dV, \quad (14)$$

where dh is the height of the prism between dS and dS' , dV is the volume of the prism, the sign $+$ holds if $d\mathbf{l}$ has the same direction as the outward normal, \mathbf{n} , so that dV is gained by A , and the sign—holds in the opposite case, i.e. when dV is lost by A . If one considers the integral over S of the infinitesimal work quantities $\delta W'$, and denotes by ΔV^+ the sum of the volume elements gained by A and by ΔV^- the sum of the volume elements lost by A , one obtains, for the whole infinitesimal displacement of S

$$\delta W = \int_S \delta W' = \int_{\Delta V^+} p_e dV - \int_{\Delta V^-} p_e dV. \quad (15)$$

If one now considers the sequence of the infinitesimal deformations of S that yield the displacement of A from V_1 to V_2 , one obtains equation (13).

By substituting equation (13) in equation (12), one gets

$$E_2^A + \int_{V_2} p_e dV - \left(E_1^A + \int_{V_1} p_e dV \right) = Q - W_u. \quad (16)$$

We call useful energy of a system A embedded in an external pressure field $p_e(x, y, z)$ the quantity

$$E_u = E + \int_V p_e dV. \quad (17)$$

By this symbol, we write equation (16) in the form

$$E_{u2}^A - E_{u1}^A = Q - W_u. \quad (18)$$

For a system composed of simple subsystems, each in stable equilibrium except for a motion of the whole subsystem in a uniform gravity field, the useful energy can be expressed as

$$E_u = E_k + E_p + U + \int_V p_e dV, \quad (19)$$

where E_k is the kinetic energy, E_p is the gravitational potential energy, and U is the internal energy, namely the sum of the internal energies of the subsystems.

An interesting special case occurs when, in every state considered, the external pressure surrounding the system is uniform and equal to the pressure p of the system. In this case, equation (19) becomes

$$E_u = E_k + E_p + U + pV = E_k + E_p + H, \quad (20)$$

where H is the system enthalpy.

Equations (18) and (20) yield directly the energy balance equation for control volume in a steady state, crossed by a fluid flow. The only effect of the process, in a time interval $\Delta\tau$ equal to the inverse of the mass flow rate, is as follows: the unit mass of fluid is transferred from the inlet section 1, to the outlet section 2, with production of the useful work w_u and exchange of the heat quantity q . For the process $1 \rightarrow 2$ of the unit mass of the fluid, equations (18) and (20) yield the well-known equation

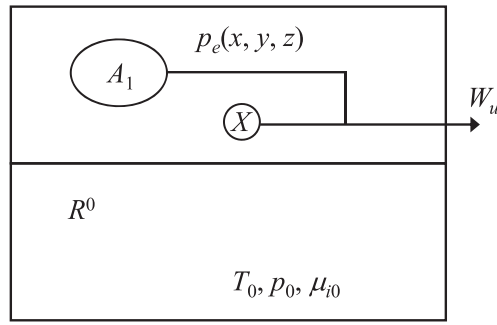


Figure 2. Scheme for the definition of generalized exergy.

$$e_{k2} - e_{k1} + e_{p2} - e_{k1} + h_2 - h_1 = q - w_u, \quad (21)$$

where lowercase letters denote quantities referred to the unit mass.

Consider now a process $A_1 \rightarrow A_2$ of a closed system A , such that the change in kinetic and potential energy is vanishing, no useful work is performed, and in the states A_1 and A_2 the external pressure p_e is uniform and equal to the pressure p of A . Equations (18) and (20) yield

$$H_2 - H_1 = Q. \quad (22)$$

Equation (22) is often derived in textbooks with the unnecessary assumptions that the process of A is quasistatic and at constant pressure. There is no need for the process to be quasistatic, and for the final pressure to be equal to the initial one.

3. Generalized exergy

In this section, we state a slightly generalized definition of exergy, which we call generalized exergy, and derive its expression. Generalized exergy includes exergy, flow exergy and all the other known availability functions as special cases.

Consider a system A , embedded in an external pressure field $p_e(x, y, z)$, that is open and can interact with an open reference thermal reservoir R^0 , with the aid of a cyclic device, X , as is represented in figure 2. System A can exchange energy and matter with R^0 ; the latter contains all the constituents of A and crosses only stable equilibrium states with fixed volume, temperature, T_0 , pressure, p_0 , and chemical potentials, μ_{i0} . We call the generalized exergy of A in any state A_1 , denoted by Ξ_{g1} , the maximum useful work that can be obtained by an adiabatic process of the composite system AXR^0 , starting from the initial state A_1 .

Clearly, the maximum useful work can be obtained when all the matter of A is transferred to R^0 , i.e. when the final state of A is such that the system has vanishing mole numbers and volume. In this condition, only the system R^0 remains available, in a stable equilibrium state with a fixed volume, and no more useful work can be obtained, on account of the impossibility of a perpetual motion machine of the second kind. We will denote by A_0 the end state of A , by R_1^0 and R_2^0 the initial and the final state of R^0 , and will determine the expression of Ξ_{g1} .

On account of equation (18), the useful work obtained in an adiabatic process of AXR^0 with the change of state $A_1 \rightarrow A_0$ of A is equal to the decrease in useful energy of the composite system AR^0 . Since the useful energy of A in the final state A_0 is vanishing, one has

$$W_u = E_{u1}^A + U_1^{R^0} - U_2^{R^0}. \quad (23)$$

The Gibbs equation for R^0 , which has constant volume and constant values of T_0 , p_0 , and μ_{i0} , yields

$$U_1^{R^0} - U_2^{R^0} = T_0(S_1^{R^0} - S_2^{R^0}) + \sum_{i=1}^r \mu_{i0}(n_{i1}^{R^0} - n_{i2}^{R^0}), \quad (24)$$

where S^{R^0} and $n_i^{R^0}$ are the entropy and the number of moles of the i th constituent of R^0 . By substituting equation (24) in equation (23), one gets

$$W_u = E_{u1}^A + T_0(S_1^{R^0} - S_2^{R^0}) + \sum_{i=1}^r \mu_{i0}(n_{i1}^{R^0} - n_{i2}^{R^0}). \quad (25)$$

Assume, provisionally, that no chemical reaction occurs in the whole system AXR^0 . Then one has, for each constituent

$$n_{i1}^{R^0} - n_{i2}^{R^0} = -(n_{i1}^A - n_{i0}^A) = -n_{i1}^A, \quad (26)$$

so that

$$\sum_{i=1}^r \mu_{i0}(n_{i1}^{R^0} - n_{i2}^{R^0}) = -\sum_{i=1}^r \mu_{i0}n_{i1}^A. \quad (27)$$

The principle of entropy nondecrease yields, for every adiabatic process $A_1R_1^0 \rightarrow A_0R_2^0$ of AXR^0 ,

$$S_2^{R^0} - S_1^{R^0} + S_0^A - S_1^A = S_{\text{irr}}, \quad (28)$$

where $S_{\text{irr}} \geq 0$ is the entropy production in the process. Since $S_0^A = 0$, equation (28) yields

$$T_0(S_1^{R^0} - S_2^{R^0}) = -T_0S_1^A - T_0S_{\text{irr}}. \quad (29)$$

By substituting equations (27) and (29) in equation (25), one obtains

$$W_u = E_{u1}^A - T_0S_1^A - \sum_{i=1}^r \mu_{i0}n_{i1}^A - T_0S_{\text{irr}}. \quad (30)$$

Clearly, the maximum useful work, Ξ_{g1} , is obtained in every reversible adiabatic process $A_1 \rightarrow A_0$ of AXR^0 , where $S_{\text{irr}} = 0$, and is given by

$$\Xi_{g1} = E_{u1}^A - T_0S_1^A - \sum_{i=1}^r \mu_{i0}n_{i1}^A. \quad (31)$$

We prove now that equation (31) holds even if any chemical reaction occurs in AXR^0 . Suppose that a chemical reaction with stoichiometric coefficients ν_i occurs in AXR^0 and involves all the constituents, with nonvanishing or with vanishing values of ν_i . The changes in mole numbers for AR^0 are given by

$$(n_{i2} - n_{i1})^{AR^0} = \nu_i \varepsilon, \quad (32)$$

where ε is the reaction coordinate. Equation (32) can be rewritten as

$$\nu_i = \frac{(n_{i2} - n_{i1})^{AR^0}}{\varepsilon}. \quad (33)$$

The condition of chemical equilibrium in R^0 yields

$$\sum_{i=1}^r \nu_i \mu_{i0} = 0. \quad (34)$$

By substituting equation (33) in equation (34), one obtains

$$\sum_{i=1}^r \mu_{i0} (n_{i1} - n_{i2})^{AR^0} = 0, \quad (35)$$

i.e. by recalling that the final state of A has been denoted by the subscript 0 and has vanishing mole numbers

$$\sum_{i=1}^r \mu_{i0} (n_{i1} - n_{i2})^{R^0} = -\sum_{i=1}^r \mu_{i0} (n_{i1} - n_{i0})^A = -\sum_{i=1}^r \mu_{i0} n_{i1}^A. \quad (36)$$

Since equation (36) coincides with equation (27), equation (31) still holds.

If system A is composed of simple subsystems, each in stable equilibrium except for a motion of the whole subsystem in a uniform gravity field, equation (19) holds, and equation (31) yields, for every state of A

$$\Xi_g = E_k^A + E_p^A + U^A + \int_{V^A} p_e dV - T_0 S^A - \sum_{i=1}^r \mu_{i0} n_i^A. \quad (37)$$

Since E_k and E_p are obvious parts of Ξ_g , whenever they are nonvanishing, we will use in the following the simpler notation

$$\Xi_g = U + \int_V p_e dV - T_0 S - \sum_{i=1}^r \mu_{i0} n_i, \quad (38)$$

where it is understood that the properties without the subscript 0 refer to system A .

4. Special cases: exergy, Keenan's availability function, physical exergy, available energy, flow exergy, flow availability and physical flow exergy

In this short section, we show that the exergy function given by equation (38) includes as special cases all the known availability functions.

If the external pressure field is uniform, and has a value equal to the pressure p_0 of R^0 , equation (38) yields the usual expression of exergy, namely

$$\Xi = U + p_0 V - T_0 S - \sum_{i=1}^r \mu_{i0} n_i. \quad (39)$$

If, in addition, system A is closed, the summation term in equation (24), that yields the summation term in equations (31), (38) and (39) is vanishing, because there are no changes in the mole numbers of R^0 . Thus, the exergy of a closed system is given by

$$\Xi = U + p_0 V - T_0 S = \Phi, \quad (40)$$

where the function $\Phi = U + p_0 V - T_0 S$ is often called Keenan's availability function. Therefore, if a closed system A and undergoes a change of state $A_1 \rightarrow A_2$, its decrease in exergy is given by

$$\Xi_1 - \Xi_2 = \Phi_1 - \Phi_2 = U_1 - U_2 + p_0(V_1 - V_2) - T_0(S_1 - S_2). \quad (41)$$

Equation (41) holds even if chemical reactions take place in A because no assumption on the existence of chemical reactions is needed to obtain equation (40). If the state A_2 has pressure p_0 and temperature T_0 and is denoted by the subscript 0, and no chemical reaction occurs, the right-hand side of equation (41) coincides with that of equation (6) and yields the physical exergy.

If system A is closed and undergoes a change of state $A_1 \rightarrow A_2$, the volume of A does not change or the external pressure field is vanishing, equation (40) yields

$$\Xi_1 - \Xi_2 = U_1 - U_2 - T_0(S_1 - S_2) = \Omega_1 - \Omega_2, \quad (42)$$

where the function $\Omega = U - T_0S$ is often called available energy. Like equation (41), equation (42) holds even if chemical reactions take place in A .

If the external pressure field is uniform in the region of space occupied by A , and its value is equal to the pressure p of A , equation (38) yields the usual expression of flow exergy, namely

$$\Psi = H - T_0S - \sum_{i=1}^r \mu_{i0}n_i. \quad (43)$$

If, in addition, system A is closed, the summation term does not appear in equation (43), so that the flow exergy becomes

$$\Psi = H - T_0S = X. \quad (44)$$

Therefore, if a closed system A in steady flow undergoes a change of state $A_1 \rightarrow A_2$, its decrease in flow exergy is given by

$$\Psi_1 - \Psi_2 = X_1 - X_2 = H_1 - H_2 - T_0(S_1 - S_2), \quad (45)$$

where the function $X = H - T_0S$ is usually called flow availability. Equation (45) holds even if chemical reactions take place in A . If the state A_2 has pressure p_0 and temperature T_0 , and is denoted by the subscript 0, and no chemical reaction occurs, the right-hand side of equation (45) coincides with that of equation (4) and yields the physical flow exergy.

5. Molar exergy and molar flow exergy of a pure substance at T_0, p_0

For one mole of a pure substance, equations (39) and (43) yield

$$\xi = u + p_0v - T_0s - \mu_0, \quad (46)$$

$$\psi = h - T_0s - \mu_0, \quad (47)$$

where the lowercase letters ξ, ψ, u, v, s , and h denote the molar properties, and μ_0 is the chemical potential of the substance under exam in the reference thermal reservoir, R^0 . The basic point is to determine ξ and ψ for $T = T_0$ and $p = p_0$. In fact, values for different temperatures and pressures can be then determined by the standard methods of thermodynamics, through the relations

$$\begin{aligned} \xi(T, p) - \xi(T_0, p_0) &= u(T, p) - u(T_0, p_0) \\ &\quad - T_0[s(T, p) - s(T_0, p_0)] + p_0[v(T, p) - v(T_0, p_0)], \end{aligned} \quad (48)$$

$$\psi(T, p) - \psi(T_0, p_0) = h(T, p) - h(T_0, p_0) - T_0[s(T, p) - s(T_0, p_0)]. \quad (49)$$

Therefore, in this section we illustrate how to determine the molar exergy and the molar flow exergy of a pure substance at $T = T_0$ and $p = p_0$. If $p = p_0$, exergy and flow exergy coincide. We will refer to the molar exergy, ξ , and we will select the atmosphere in thermodynamic equilibrium as the reference thermal reservoir.

Consider, first, a pure substance, A , that is nonreactive with atmospheric gases. For one mole of A , at $T = T_0$ and $p = p_0$, equation (46) yields

$$\xi_A(T_0, p_0) = g_A(T_0, p_0) - \mu_{A0} = \mu_A(T_0, p_0) - \mu_A(T_0, p_{A0}), \quad (50)$$

where we have used the equality between the molar Gibbs free energy, g_A , and the chemical potential, μ_A , and we have specified that the chemical potential of a gas A in the atmosphere, μ_{A0} , is equal to the chemical potential of A at T_0 and at the partial pressure p_{A0} of A in the atmosphere.

For a nonreactive substance A , the value of p_{A0} is known and $\xi_A(T_0, p_0)$ can be easily determined. For instance, if A is an ideal gas, by considering that $\mu_A = g_A = h_A - T_0 s_A$ and that h_A depends only on temperature, one has

$$\xi_A(T_0, p_0) = -T_0[s_A(T_0, p_0) - s_A(T_0, p_{A0})] = RT_0 \ln\left(\frac{p_0}{p_{A0}}\right) = RT_0 \ln\left(\frac{1}{y_{A0}}\right), \quad (51)$$

where R is the universal gas constant, $R \approx 8.314\,46\text{ J (mol K)}^{-1}$, and y_{A0} is the molar fraction of gas A in the atmosphere.

Consider now a pure substance, F , such as a fuel, that is reactive with atmospheric gases. For one mole of F , at $T = T_0$ and $p = p_0$, equation (46) yields, in analogy with equation (50)

$$\xi_F(T_0, p_0) = g_F(T_0, p_0) - \mu_{F0} = \mu_F(T_0, p_0) - \mu_F(T_0, p_{F0}). \quad (52)$$

This time, however, the value of the partial pressure p_{F0} is not known. Even if measured values of the molar fractions of some gaseous fuels in the atmosphere are available, these values do not correspond to a true stable equilibrium state of the atmosphere, and cannot be used in equation (52). Therefore, equation (52) requires further processing.

If we denote by ν_i the stoichiometric coefficients of the reaction of F with atmospheric gases, and by p_{i0} the partial pressures in the atmosphere, the condition of chemical equilibrium in R^0 yields

$$\sum_i \nu_i \mu_i(T_0, p_{i0}) = 0, \quad (53)$$

i.e.

$$\nu_F \mu_F(T_0, p_{F0}) = -\sum_{i \neq F} \nu_i \mu_i(T_0, p_{i0}). \quad (54)$$

By substituting equation (54), divided by ν_F , in equation (52), one gets

$$\xi_F(T_0, p_0) = \mu_F(T_0, p_0) + \sum_{i \neq F} \frac{\nu_i}{\nu_F} \mu_i(T_0, p_{i0}). \quad (55)$$

Multiplying equation (55) by ν_F , and replacing $\mu_F(T_0, p_0)$ and $\mu_i(T_0, p_{i0})$ with $g_F(T_0, p_0)$ and $g_i(T_0, p_{i0})$, one obtains

$$\nu_F \xi_F(T_0, p_0) = \nu_F g_F(T_0, p_0) + \sum_{i \neq F} \nu_i g_i(T_0, p_{i0}). \quad (56)$$

Since both reactants and reaction products are ideal gases in the atmosphere, one has

$$g_i(T_0, p_{i0}) = g_i(T_0, p_0) + RT_0 \ln \frac{p_{i0}}{p_0}. \quad (57)$$

By substituting equation (57) in equation (56), one gets

$$\nu_F \xi_F(T_0, p_0) = \nu_F g_F(T_0, p_0) + \sum_{i \neq F} \nu_i g_i(T_0, p_0) + RT_0 \sum_{i \neq F} \nu_i \ln \frac{p_{i0}}{p_0} \quad (58)$$

The sum of the first two terms of the right-hand side of equation (58) is the Gibbs free energy of reaction, ΔG^0 . Therefore, dividing equation (58) by ν_F one obtains

$$\xi_F(T_0, p_0) = \frac{\Delta G^0}{\nu_F} + \frac{RT_0}{\nu_F} \sum_{i \neq F} \nu_i \ln \frac{p_{i0}}{p_0}. \quad (59)$$

Equation (59) is the form of equation (52) suitable to evaluate the molar exergy of a substance, F , that reacts with atmospheric gases.

As an example, let us calculate the molar exergy of hydrogen, H_2 , when both H_2 and the atmosphere are at the standard conditions $T_0 = 298.15$ K and $p_0 = 1.01325$ bar, and the relative humidity of the atmosphere is 0.5. For H_2 , the combustion reaction is



so that $\nu_F = -1$ and equation (59) becomes

$$\xi_{H_2}(T_0, p_0) = -\Delta G_0^0 + RT_0 \sum_{i \neq F} \nu_i \ln \frac{p_0}{p_{i0}} = -\Delta G_0^0 + RT_0 \sum_{i \neq F} \nu_i \ln \frac{1}{y_{i0}}, \quad (61)$$

where ΔG_0^0 denotes the standard Gibbs free energy of reaction, and y_{i0} denotes the molar fraction in the atmosphere of the i th substance that takes part to the reaction. The first term, $-\Delta G_0^0$, can be calculated as [39]

$$-\Delta G_0^0 = -(\Delta g_{0f,H_2O}^0 - \Delta g_{0f,H_2}^0 - 0.5 \Delta g_{0f,O_2}^0) = -\Delta g_{0f,H_2O}^0, \quad (62)$$

where $\Delta g_{0f,H_2}^0$ and $\Delta g_{0f,O_2}^0$ are the standard molar Gibbs free energies of formation of H_2 and of O_2 , that are vanishing, and $\Delta g_{0f,H_2O}^0$ is the standard molar Gibbs free energy of formation of water. Since water is vapor in the final state of mutual equilibrium with the atmosphere, we assume that, after the reaction, water is a metastable state of ideal gas at T_0, p_0 . So, we have

$$-\Delta G_0^0 = -\Delta g_{0f,H_2O}^0 = 228.582 \text{ kJ}. \quad (63)$$

The numerical value can be found in CRC Handbook of Chemistry and Physics [42], or in NIST-JANAF Thermochemical Tables [43].

The second term in the right-hand side of equation (61) is

$$RT_0 \left(\ln \frac{1}{y_{H_2O}} - \frac{1}{2} \ln \frac{1}{y_{O_2}} \right). \quad (64)$$

According to the US standard atmosphere 1976 [42], the molar fraction of O_2 at sea level, for dry air, is 0.209476. By updating this value to take into account the present molar fraction of CO_2 , which we assume equal to 0.000417, one obtains for O_2 the molar fraction 0.209454. The partial pressure of H_2O at saturation, for $T_0 = 298.15$ K, is 0.031699 bar [44]. Thus, for relative humidity 0.5, the partial pressure of H_2O is 0.0158495 bar, and the molar fraction for $p_0 = 1.01325$ bar is $y_{H_2O} = 0.015642$. Finally, by updating the molar fraction of O_2 to take into account the water vapor, one obtains, $y_{O_2} = 0.206178$. Thus, equation (64) yields

$$RT_0 \left(\ln \frac{1}{y_{H_2O}} - \frac{1}{2} \ln \frac{1}{y_{O_2}} \right) = 8.350 \text{ kJ/(mol of } H_2). \quad (65)$$

Equations (61), (63) and (65) yield

$$\xi_{H_2}(T_0, p_0) = 228.582 + 8.350 = 236.932 \text{ kJ mol}^{-1}. \quad (66)$$

As an example of evaluation of the molar exergy of an ideal gas nonreactive with the atmosphere, let us calculate the molar exergy of oxygen at $T_0 = 298.15$ K and $p_0 = 1.01325$ bar, with relative humidity of the atmosphere 0.5. By applying equation (51), with

$y_{\text{O}_2} = 0.206178$, one finds

$$\xi_{\text{O}_2}(T_0, p_0) = RT_0 \ln\left(\frac{1}{y_{\text{O}_2}}\right) = 3.9143 \text{ kJ mol}^{-1}. \quad (67)$$

6. Conclusion

A unified deduction of the expressions of exergy and flow exergy has been presented, suitable for didactic presentations in postgraduate programmes in Energy Physics and Energy Engineering. The proposed derivation yields a broader exergy function, that includes the usual functions exergy and flow exergy as special cases, and is based on the concept of useful energy of a system in an external pressure field. Moreover, it has been shown that this concept allows a straightforward deduction and a deeper interpretation of two widely employed thermodynamic equations: the energy balance equation for a control volume in steady state; the equality between enthalpy change and heat received in a process of a closed system that exchanges work only with the external pressure, if the latter is equal to the pressure of the system in the initial and in the final state. Finally, the expression of the molar exergy of a pure substance at ambient temperature and pressure has been rewritten in a form applicable to reactive substances.

Data availability statement

No new data were created or analysed in this study.

Conflicts of interest

The author has no conflicts to disclose.

ORCID iDs

Enzo Zanchini  <https://orcid.org/0000-0002-2165-3743>

References

- [1] Reddy B W and Mohamed K 2007 Exergy analysis of a natural gas fired combined cycle power generation unit *Int. J. Exergy* **4** 180–96
- [2] Lee H Y and Kim K H 2015 Energy and exergy analyses of a combined power cycle using the organic Rankine cycle and the cold energy of liquefied natural gas *Entropy* **17** 6412–32
- [3] Tang Y, Chong C T, Li J, Ng J H and Herraiz L 2021 Exergy analysis of a natural gas-fired gas turbine combined cycle power plant with post-combustion carbon capture *Chem. Eng. Trans.* **83** 529–34
- [4] Altarawneh O R, Alsarayreh A A, Al-Falahat A M, Al-Kheetan M J and Alrwashdeh S S 2022 Energy and exergy analyses for a combined cycle power plant in Jordan *Case Studies Thermal Eng.* **31** 101852
- [5] Aljundi I H 2009 Energy and exergy analysis of a steam power plant in Jordan *Appl. Therm. Eng.* **29** 324–8

- [6] Elahifar S, Assareh E and Nedaei M 2018 Exergy analysis and optimization of the Rankine cycle in steam power plants using the firefly algorithm *Mech. Industry* **19** 505
- [7] Elhelw M, Al Dahma K S and Attia A H 2019 Utilizing exergy analysis in studying the performance of steam power plant at two different operation mode *Appl. Therm. Eng.* **150** 285–93
- [8] Shamet O, Ahmed R and Abdalla K N 2021 Energy and exergy analysis of a steam power plant in Sudan *African J. Eng. Technol.* **1** 1
- [9] Sun W, Yue X and Wang Y 2017 Exergy efficiency analysis of ORC (Organic Rankine Cycle) and ORC-based combined cycles driven by low-temperature waste heat *Energy Conversion Management* **135** 63–73
- [10] Liao G, Jiaqiang E, Zhang F, Chen J and Leng E 2020 Advanced exergy analysis for Organic Rankine Cycle-based layout to recover waste heat of flue gas *Appl. Energy* **266** 114891
- [11] Liu G, Wang Q, Xu J and Miao Z 2021 Exergy analysis of two-stage organic rankine cycle power generation system *Entropy* **23** 43
- [12] Elahi A E, Mahmud T, Alam M, Hossain J and Biswas B N 2022 Exergy analysis of organic Rankine cycle for waste heat recovery using low GWP refrigerants *Int. J. Thermo fluids* **16** 100243
- [13] Taleghani S T, Sorin M and Poncet S 2019 Analysis and optimization of exergy flows inside a transcritical CO₂ ejector for refrigeration, air conditioning and heat pump cycles *Energies* **12** 1686
- [14] Ebale L O, Nakavoua A H V and Gomat L J P 2020 Exergetic analysis of a refrigeration system with mechanical vapors compression *Energy Power Eng.* **12** 490–8
- [15] Voloshchuk V, Gullo P, Nikiforovich E and Buyak N 2021 Simulation and exergy analysis of a refrigeration system using an open-source web-based interactive tool—comparison of the conventional approach and a novel one for avoidable exergy destruction estimation *Appl. Sci.* **11** 11535
- [16] Aized T, Rashid M, Riaz F, Hamza A, Nabi H Z, Sultan M, Ashraf W M and Krzywanski J 2022 Energy and exergy analysis of vapor compression refrigeration system with low-Gwp refrigerants *Energies* **15** 7246
- [17] Kallio S and Siroux M 2020 Energy analysis and exergy optimization of photovoltaic-thermal collector *Energies* **13** 5106
- [18] Çiftçi E, Khanlari A, Sözen A, Aitaç I and Tuncer A D 2021 Energy and exergy analysis of photovoltaic thermal (PVT) system used in solar drier: a numerical and experimental investigation *Renew. Energy* **180** 410–23
- [19] Indira S S, Vaithilingam C A, Narasingamurthi K, Sivasubramanian R, Chong K K and Saidur R 2022 Mathematical modelling, performance evaluation and exergy analysis of a hybrid photovoltaic/thermal-solar thermoelectric system integrated with compound parabolic concentrator and parabolic trough concentrator *Appl. Energy* **320** 119294
- [20] Lentswe K, Mawire A and Owusu P 2022 Experimental energetic and exergetic performance of a combined solar cooking and thermal energy storage system *Energies* **15** 8334
- [21] Wang Z, Fan W and Zhang G 2017 Comparison of the exergy efficiency of four power generation systems from methane using fuel cells *RSC Adv.* **7** 39391
- [22] Machmoudi S M S, Sarabchi N, Yari M and Rosen M A 2019 Exergy and exergoeconomic analyses of a combined power producing system including a proton exchange membrane fuel cell and an organic rankine cycle *Sustainability* **11** 3264
- [23] Montazerinejad H, Fakhimi E, Ghandehariun S and Ahmadi P 2022 Advanced exergy analysis of a PEM fuel cell with hydrogen energy storage integrated with organic Rankine cycle for electricity generation *Sustain. Energy Technol. Assess.* **51** 101885
- [24] Bui T, Kim J S, Lee D K, Ahn K Y and Lee S M 2022 Tri-generation system configuration selection based on energy and exergy analyses *Energies* **15** 7958
- [25] Mehdizadeh-Fard M and Pourfayaz F 2019 Advanced exergy analysis of heat exchanger network in a complex natural gas refinery *J. Cleaner Prod.* **206** 670–87
- [26] Al-Abbas A H, Mohammed A A and Hassoon A S 2021 Exergy analysis of shell and helical coil heat exchanger and design optimization *Heat Mass Transfer* **57** 797–806
- [27] Mehdizadeh-Fard M, Pourfayaz F and Maleki A 2021 Exergy analysis of multiple heat exchanger networks: an approach based on the irreversibility distribution ratio *Energy Rep.* **7** 174–93

- [28] Hosseinizadeh S E, Majidi S, Goharkhah M and Jahangiri A 2021 Energy and exergy analysis of ferrofluid flow in a triple tube heat exchanger under the influence of an external magnetic field *Thermal Sci. Eng. Progress* **25** 101019
- [29] Ibrahim T K, Mohammed M K, Awad O I, Abdalla A N, Basrawi F, Mohammed M N, Najafi G and Mamat R 2018 A comprehensive review on the exergy analysis of combined cycle power plants *Renew. Sustain. Energy Rev.* **90** 835–50
- [30] Khaleel O J, Ismail F B, Ibrahim T K and bin Abu Hassan S H 2022 Energy and exergy analysis of the steam power plants: a comprehensive review on the classification, development, improvements, and configurations *Ain Shams Eng. J.* **13** 101640
- [31] Saidur R, Boroumandjazi G, Mekhlif S and Jameel M 2012 Exergy analysis of solar energy applications *Renew. Sustain. Energy Rev.* **16** 350–6
- [32] Arshad A, Ali H M, Habib A, Bashir M A, Jabbar M and Yan Y 2019 Energy and exergy analysis of fuel cells *Thermal Science Eng. Progress* **9** 308–21
- [33] Rashidi M M, Mahariq I, Nazari M A, Accouche O and Bhatti M M 2022 Comprehensive review on exergy analysis of shell and tube heat exchangers *J. Therm. Anal. Calorim.* **147** 12301–11
- [34] Szargut J 2005 *Exergy Method—Technical and Ecological Applications* (Southampton UK: WIT Press)
- [35] Sala Lizarraga J, Ma P and Picallo-Perez A 2020 *Exergy Analysis and Thermoeconomics of Buildings—Design and Analysis for Sustainable Energy Systems* (Amsterdam: Elsevier)
- [36] Dincer I and Rosen M A 2021 *Exergy—Energy, Environment and Sustainable Development* (Amsterdam: Elsevier)
- [37] Kotas T J 1980 Exergy concepts for thermal plant *Int. J. Heat Fluid Flow* **2** 105–14
- [38] Brzustowski T A and Golem P J 1976–1977 Second-law analysis of energy processes: I. Exergy—an introduction *Trans. CSME* **4** 209–18
- [39] Gyftopoulos E P and Beretta G P 2005 *Thermodynamics: Foundations and Applications* (New York: Dover)
- [40] Zanchini E and Terlizzese T 2009 Molar exergy and flow exergy of pure chemical fuels *Energy* **34** 1246–59
- [41] Zanchini E 2015 A more general exergy function and its application to the definition of exergy efficiency *Energy* **87** 352–60
- [42] Rumble J R 2022 *CRC Handbook of Chemistry and Physics* (Taylor & Francis, Boca Raton, FL: CRC Press) 103rd edn(Internet Version)
- [43] NIST-JANAF Thermochemical Tables <https://janaf.nist.gov/>
- [44] NIST Chemistry WebBook, SRD 69, Thermophysical Properties of Fluid Systems, <https://webbook.nist.gov/chemistry/fluid/>