



Rigorous Development of the Fixed Dead State Version of the Exergy Equation Suitable for Undergraduate Class Presentation and Coursework

Sheldon M. Jeter (Associate Professor)

Sheldon M. Jeter has mechanical engineering degrees from Clemson, the University of Florida, and Georgia Tech. He has been on the academic faculty at Georgia Tech since 1979 and will retire in August 2022. He has written over 250 refereed journal articles and conference papers and numerous research reports and other articles. He has supervised 16 Ph. D. graduates and numerous other research students. His research interests are thermodynamics, experimental engineering, heat and mass transfer, solar energy, and energy systems including concentrating solar power and other solar issues, building energy systems, and HVAC issues in health care facilities.

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School of Mechanical Engineering, Georgia Institute of Technology

Introduction

This paper presents a brief review of the background and then a detailed development of the version of the exergy equation most useful and interesting to mechanical engineering and indeed to thermal and energy systems engineering faculty. In presentation to undergraduates, the background information included herein can mostly be relegated to a quick review or even a posted reference. After this hopefully interesting but not crucial background, a concise and hopefully convincing development of the subject exergy equation, which can be called the Fixed (Composition) Exergy Equation or FEE is presented. This presentation is followed by a review of the theoretical and especially the pedagogical aspects of this presentation.

Background

The summary background presented herein is mostly for completeness and is primarily of interest to the faculty community and does not merit much class time. The ability of a substance or a system or heat to produce useful work is of obvious importance, and investigations of this issue began in the nineteenth century and continue. Numerous publications address the foundations and practice of this subject, which is much too extensive to more than nominally summarize here. It is well known that early investigators included several significant figures, most notably Gibbs, Gouy, and Stodola. Evans [1] and others address this history. Later in the twentieth century, the concept and application were addressed to practicing mechanical engineers perhaps earliest by Keenan in his highly regarded textbook [2] and in his later research literature [3]. Keenan used the term “availability” for the pertinent potential work ability of a fluid. This might have been a disadvantageous or even confusing choice of wording especially to engineers in industry. Later textbooks also adopted the “availability” name convention including popular texts by Wark [4], earlier work by Sonntag and Van Wylen [5], and especially Moran [6]. The latter work seems to have enhanced interest in applying these concepts among mechanical engineers with special regard to reactive systems. The more recently popular term “exergy”, one possible derivation of which may be taken to mean “external work”, is attributed to Rant [7] and has achieved general use and wide acceptance. Examples of worthwhile presentations of exergy include Bejan [8], Klein and Nellis [9] and, especially, later work by Sonntag, Borgnakke and Van Wylen [10].

All of these cited works address features of exergy (or earlier “availability”) and most of these develop some sort of exergy balance equation. It is the development of the exergy balance equation that is addressed in this paper. In the works cited, the exergy property is usually developed first, and then the exergy balance equation is typically developed by argument or synthesis often supported by physical considerations. The later development by Sonntag et al. [10] differs considerably from the earlier presentations in that the time rate of change of the exergy

stored in a control volume is defined and then expanded. Then the energy and entropy laws and mass conservation are introduced, and the resulting equation simplified. Undergraduates can surely appreciate and benefit from this approach. Indeed, their approach is almost purely mathematical and results in an unambiguous exergy equation with no additional physical arguments. However, an even simpler approach is possible as outlined in an upcoming section following a quick review of the concept of a “dead state” and the related “medium” or inert ambient surrounds of the system. Both of these concepts are fundamentally important in exergy theory and application.

Given the basic preparation needed to understand and appreciate the FEE, at least three approaches to its derivation are feasible (1) the typical textbook presentation which requires some heuristic justification of the dead state terms appearing in the FEE or (2) the apparently more rigorous substitution method of [10], (3) the even simpler derivation herein, a purely rigorous derivation that actually requires barely more classroom time than a mere statement of the exergy equation. The heuristic or shorthand derivation involves combining the time derivative CV energy and entropy equations and apparently rather arbitrarily introducing the dead state extensive properties into the time derivative term. The current alternative rigorous development relies instead on the always arbitrary definitions available for the reference properties for the entropy and enthalpy and recognizing the coupling of the internal energy and enthalpy. In this approach the expected dead state properties arise naturally, and the expected system and flow exergy terms also arise naturally. The result is an enhanced teaching and learning strategy that exemplifies a rigorous approach and emphasizes the scope and rigor of thermodynamics.

Overview of the Dead State Concept and Related Concept of the Medium

Any approach to exergy requires the consideration of (1) a so-called “dead state”, in which the system under consideration can generate no further useful work and (2) a so-called “medium” the inert surroundings, which can produce no useful work by internal interactions. As detailed in the Appendix, at least three dead states and related versions of the medium should be considered:

1. The Generalized Dead State (GDS) in which the system is allowed, at least in principle, to merge with and become identical to the matter in the medium. The medium is typically a gaseous atmosphere with constant intensive state, which is the GDS. The medium must contain the major compounds in the natural atmosphere plus the stable trace gases that together contain all the chemical elements represented in the system. For example, hydrocarbon fuels will not be considered as components of the GDS, but CO₂ and H₂O must be in the generalized medium to allow hydrocarbons such as CH₄ to exist in the system. The relevant form of the exergy equation for this GDS can be called the Generalized Exergy Equation (GEE). Some further discussion and examples of the GDS are given in the appendix.
2. The Restricted Dead State (RDS) in which the system is allowed to reach pressure and temperature equilibrium with the medium but not merge with the medium. The pertinent form of the exergy equation for this RDS can be called the Restricted Exergy Equation (REE). Even closed chemical and thermochemical energy (really exergy) storage systems

can be analyzed with respect to the REE as well as thermal systems such as adsorption chillers, in which the composition of the working fluid (always contained in the system) is changed by separation or dilution rather than by chemical reaction.

3. The Fixed Dead State (FDS, alternatively Frozen DS), which is a variation on the RDS in that the composition of the working fluid never changes. This is by far the DS of most interest to ME students and even most ME faculty. The pertinent form (or case) of the exergy equation for this RDS can be called the Fixed (Composition) Exergy Equation (FEE) for symmetry and to emphasize the “fixed composition” of the fluid in the system.

Junior or senior students in mechanical or related engineering interested in thermal systems should be aware of the FEE at least. It may be desirable to at least advise students of the existence of the GEE and REE but not overwhelm most of the students with these concerns too early in their education. Typical students should have finished the usual first or only semester thermodynamics course and be well aware of energy and entropy analysis and mass conservation. Appropriately, concern can be limited only to working or process fluids of fixed composition, for which the FDS is the applicable dead state. This FEE version appears to be the only version applied in typical undergraduate textbooks, and it is probably the only version widely needed by typical students and even practitioners in mechanical and related disciplines.

Overview of the Development of the FEE Equation

The simpler approach presented below has the important feature that neither the control volume exergy nor the stream or flow exergy properties are addressed or defined *a priori*. Rather, a simple combination of the energy and entropy equations is made. After which, the arbitrary nature of reference states of enthalpy and entropy is invoked and adjusted to generate the desired equation. It is proposed that this development presented herein may be especially satisfactory to some since (1) the well-known universally applicable energy and entropy equations are invoked without further physical argument or evidence and (2) the control volume and stream exergies arise naturally from the very few required steps.

As background to this presentation, note that it is useful to emphasize the existence of the “restriction” against combining with the surroundings. A further constraint is to exclude the possibility of chemical reactions or separations changing the composition of the fluid in the system. This version can be called the Fixed (Composition) Exergy Equation or FEE. This final version satisfied the needs of the vast majority of mechanical engineers in practice and even in research.

Narrative Details of the Development of the FEE

The balance of this paper is devoted to a rigorous derivation and presentation of the FEE. The result supports a brief presentation that can be conducted in class without an excessive investment in time or be readily packaged into a video presentation for student-paced self-study. The required steps are presented in detail subsequently, but the summary is very simple

- Draw a sufficiently generalized CV that is part of an overall system (a CM) kept separate from the medium and define the control surface (CS) and the necessary set of interactions with other CVs in the overall CM.

- Write the transient energy equation for the CV
- Redefine the reference state, for which zero values of the enthalpy and the entropy will be returned, so that the enthalpy is zero in the FDS
- Recognize that the redefinition of the enthalpy imposes a necessary merely algebraic reconsideration of the internal energy, a step crucial to the remarkably natural and unforced appearance of the System Exergy in the final resulting equation
- Split the work into (1) useful work that might be delivered to a receiver of work distinct from or “external” to the medium and (2) the boundary work expended on compressing and received on being compressed by the medium itself
- Reset the entropy so that, similarly to the enthalpy, it is zero at the FDS but with no further ramifications
- Multiply the entropy equation by the constant ambient temperature, necessary of course for unit consistency alone, and subtract from the energy equation.
- Recognize the rate of change of the System Exergy appears naturally without any arbitrary manipulation in the left-hand side time derivative and the Stream Exergy appears similarly naturally on the right-hand side along with the Thermal Exergy of heat, the useful boundary power, the non-boundary “net” power (usually shaft power), and the Rate of Exergy Destruction (the RED, otherwise called the Irreversibility)

Ultimately, this presentation should be a useful addition to an elementary or intermediate thermodynamics course or any thermal and energy systems engineering course. It is concise and internally complete and easily within the comprehension of engineering undergraduates.

The detailed but still concise presentation is in the next sections. The development begins, as all such thermodynamic applications should, with a sketch of a suitable simplified schematic, which is used to support the definition of the control volume (CV) and associated control surface (CS).

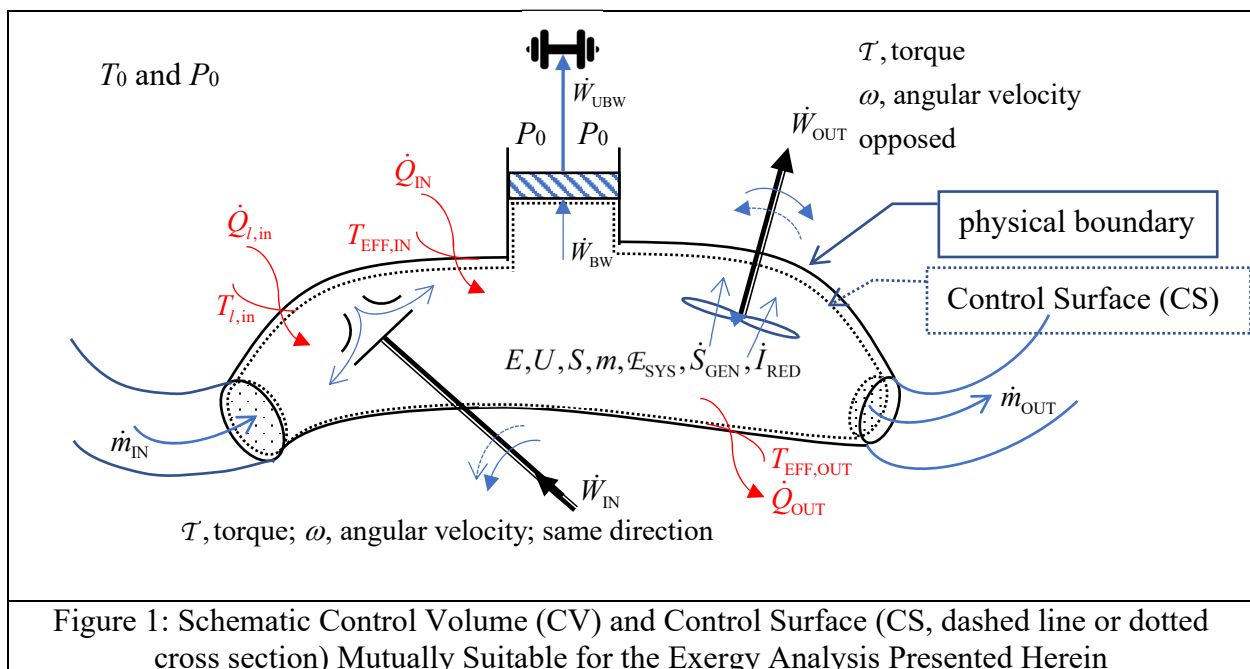


Figure 1: Schematic Control Volume (CV) and Control Surface (CS, dashed line or dotted cross section) Mutually Suitable for the Exergy Analysis Presented Herein

Details of the Mathematical Development:

Start the mathematical derivation of the exergy equation with the transient CV energy equation written using a conventional reference state, such as the liquid at the ice point in the ASME steam tables, for the enthalpy

$$\begin{aligned} \frac{dE'_{CV}}{dt} &= \frac{d(U' + E_K + E_P)_{CV}}{dt} \\ &= \sum_{i,in} (h' + e_K + e_P)_{i,in} \dot{m}_{i,in} - \sum_{e,exit} (h' + e_K + e_P)_{e,exit} \dot{m}_{e,exit} + \dot{Q}_{in} - \dot{W}_{net,out} - \dot{W}_{BW,out} \end{aligned} \quad (1)$$

or using the specific properties (possibly bulk averages) in the CV and around the CS one has:

$$\begin{aligned} \frac{dE'_{CV}}{dt} &= \frac{d(m(u' + e_K + e_P))_{CV}}{dt} \\ &= \sum_{i,in} (h' + e_K + e_P)_{i,in} \dot{m}_{i,in} - \sum_{e,exit} (h' + e_K + e_P)_{e,exit} \dot{m}_{e,exit} + \dot{Q}_{in} - \dot{W}_{net,out} - \dot{W}_{BW,out} \end{aligned} \quad (2)$$

Then replace the conventional enthalpy with the enthalpy written with respect to a new baseline, which will be the ambient temperature and pressure. These properties prevail at Fixed Dead State (FDS) when the fluid is at rest at ground elevation, in internal equilibrium, and at ambient temperature and pressure. In a classroom or similar presentation, one can comment to the effect that “the dead state is so important that it is preferred for the dead state to be the baseline for enthalpy and entropy”. The making this replacement, perhaps reminding undergraduates what is meant by a “replacement”, gives

$$h' \leftarrow h - h_0 \quad \text{where } h_0 = h(T_0, P_0) \quad (3)$$

Then the internal energy must, by definition, now be written, in the following equation, as

$$u' = h' - Pv = (h - h_0) - Pv = u + Pv - (u_0 + P_0 v_0) - Pv = u - u_0 - P_0 v_0 \quad (4)$$

Take note that the previous replacement is nothing more than the universal definition that relates internal energy and enthalpy. In the current context, this simple step is extremely important since the substitution above, in one step, introduces the dead state internal energy and one volumetric term that contribute critically to the natural appearance of the system exergy in the final result.

Recognize that while all of the shaft or even electrochemical or otherwise “net” work is useful work, some of the boundary work is uselessly expended on the environment while the remainder is useful boundary work (UBW)

$$\dot{W}_{BW} = \dot{W}_{UBW} + P_0 \frac{dV_{CV}}{dt} = \dot{W}_{UBW} + P_0 \frac{d(mv)_{CV}}{dt} \quad (5)$$

Introducing this expression for the BW gives

$$\frac{d(m(u - u_0 - P_0 v_0 + e_K + e_P))_{CV}}{dt} = \sum_{i,in} (h - h_0 + e_K + e_P)_{i,in} \dot{m}_{i,in} - \sum_{e,exit} (\dots)_{e,exit} \dot{m}_{e,exit} + \dot{Q}_{in} - \left(\dot{W}_{net,out} + \left(\dot{W}_{out}^{UBW} + P_0 \frac{d(mv)_{CV}}{dt} \right) \right) \quad (6)$$

Then rearranging gives

$$\frac{d(m(u - u_0 - P_0 v_0 + P_0 v + e_K + e_P))_{CV}}{dt} = \sum_{i,in} (h - h_0 + e_K + e_P)_{i,in} \dot{m}_{i,in} - \sum_{e,exit} (\dots)_{e,exit} \dot{m}_{e,exit} + \dot{Q}_{in} - \dot{W}_{net,out} - \dot{W}_{out}^{UBW} \quad (7)$$

and after simplifying and allowing for multiple heat inputs or outputs

$$\frac{d(m(u - u_0 + P_0(v - v_0) + e_K + e_P))_{CV}}{dt} = \sum_{i,in} (h - h_0 + e_K + e_P)_{i,in} \dot{m}_{i,in} - \sum_{e,exit} (h - h_0 + e_K + e_P)_{e,exit} \dot{m}_{e,exit} + \sum_k \dot{Q}_k - \dot{W}_{net,out} - \dot{W}_{out}^{UBW} \quad (8)$$

Similarly in the entropy equation, begin with the entropy defined with respect to a conventional reference

$$\frac{dS'_{CV}}{dt} = \frac{d(m s')_{CV}}{dt} = \sum_{i,in} s'_i \dot{m}_{i,in} - \sum_{e,exit} s'_e \dot{m}_{e,exit} + \sum_k \frac{\dot{Q}_{k,in}}{T_k} + \dot{S}_{gen} \quad (9)$$

Note that temperatures in the entropy equation above may apply to a simplistic one-dimensional heat transfer or a more realistic effective temperature. Then replace the conventional entropy with the entropy written with respect to the Fixed Dead State (FDS) at ambient temperature and pressure, so

$$s' \leftarrow s - s_0 \quad \text{where } s_0 = s(T_0, P_0) \quad (10)$$

and

$$\frac{dS'_{CV}}{dt} = \frac{d(m(s - s_0))_{CV}}{dt} = \sum_{i,in} (s - s_0)_i \dot{m}_{i,in} - \sum_{e,exit} (s - s_0)_e \dot{m}_{e,exit} + \sum_k \frac{\dot{Q}_{k,in}}{T_k} + \dot{S}_{gen} \quad (11)$$

Multiply the entropy equation by the ambient absolute temperature and subtract that product from the modified energy equation giving the following transient control volume FDS exergy equation

$$\frac{d\left(m\left(u-u_0+P_0\left(v-v_0\right)-T_0\left(s-s_0\right)+e_K+e_P\right)\right)_{CV}}{dt} = \sum_{i,\text{in}}\left(h-h_0-T_0\left(s-s_0\right)+e_K+e_P\right)_{i,\text{in}}\dot{m}_{i,\text{in}}-\sum_{e,\text{exit}}\left(\dots\right)_{e,\text{exit}}\dot{m}_{e,\text{exit}} \quad (12)$$

$$+\sum_k\dot{Q}_{k,\text{in}}\left(1-\frac{T_0}{T_k}\right)-\dot{W}_{\text{net out}}-\dot{W}_{\text{UBW out}}-T_0\dot{S}_{\text{gen}}$$

Note that the FDS terms occur naturally without any additional physical argument or need for further heuristic justification. Now for notational efficiency, write the exergy equation in terms of the system exergy (\mathcal{E}_{SYS}) or CV exergy, the stream exergy (e_x or informally as “ ex ”), and the rate of exergy destruction (RED) or “irreversibility” (\dot{I}_{RED}) as follows: [Author hint: for reader’s notes and coursework, note that Monotype Corsiva is readily available choice of a distinct script-like font for system exergy, which is very disparate from the Italic E for energy.]

$$\frac{d\left(\mathcal{E}_{\text{SYS}}\right)_{CV}}{dt} = \sum_{i,\text{in}}e_{x,i,\text{in}}\dot{m}_{i,\text{in}}-\sum_{e,\text{exit}}e_{x,e,\text{exit}}\dot{m}_{e,\text{exit}}+\sum_k\dot{Q}_{k,\text{in}}\left(1-\frac{T_0}{T_k}\right)-\dot{W}_{\text{net out}}-\dot{W}_{\text{UBW out}}-\dot{I} \quad (13)$$

Here the **system exergy** or CV exergy has the following formula derived independently by many researchers and authors.

$$\mathcal{E}_{\text{SYS}} = m\left(u-u_0+P_0\left(v-v_0\right)-T_0\left(s-s_0\right)+e_K+e_P\right)_{CV} = U-U_0+P_0\left(V-V_0\right)-T_0\left(S-S_0\right)+E_K+E_P \quad (14)$$

The system exergy is the maximum potential work that the mass currently in the CV could perform and deliver to a load or system external to the CV and the medium. Furthermore, the **stream exergy** (e_x , which is the maximum potential external work per unit mass transferred by a flowing fluid or other energy carrier medium is given by

$$e_x = h-h_0-T_0\left(s-s_0\right)+e_K+e_P \quad (15)$$

The system exergy is always equal to or greater than zero and is zero at the FDS. The stream exergy is usually positive and is zero when the fluid is in the FDS. Note that the fluid is at ambient T_0 and P_0 and at rest at the lowest accessible or ground elevation in any dead state.

This completes the development of the FEE equation in a style though to be completely devoid of any substantial physical considerations other than the basic equations for energy and entropy. This development, most significantly, shows exergy to be a natural consequence of universal thermodynamic principles rather than, perhaps, being shown as an application consistent with thermodynamics like many other less significant applications. It has a secondary benefit of reminding undergraduates that an arbitrary reference state can be defined for internal energy or for enthalpy but not for both independently. This version of the exergy equation is valid for all the applications normally encountered in undergraduate thermodynamics and energy systems

courses except for explicit combustion applications, and it works well even for combustion systems when heat inputs can be substituted for combustion. Indeed, all the usual and proposed internal combustion engine systems can be modeled as equivalent heat engines with this model. In classical mechanical engineering, the only systems needing a generalized exergy approach are probably air-conditioning with dehumidification, desalination, and air separations. The exergy equation for the generalized exergy and the restricted exergy can later be addressed and compared with this version, but it is likely best to defer this consideration to advanced courses.

Nomenclature	
E, U, V, S and U_0, V_0, S_0	Extensive Energy, Internal Energy, Volume and Entropy in the CV and corresponding properties in the FDS (sub-0)
$e, u, h, s,$ and u_0, h_0, s_0	Specific Properties in the CV or at the CS and in the FDS (indicated by subscript-0)
e_K and e_P ; and E_K and E_P	Kinetic and Potential Energies per mass and the extensive cases
E_{SYS}	Extensive System Exergy, see Equation 14
e_x	(mass) Specific Stream Exergy, see Equation 15
\dot{Q}_k and $T_{k(CS)}$	Heat Transfer Rate (input positive) and corresponding one-dimensional or effective CS Temperature
T_0 and P_0	Temperature and Pressure of the ambient inert atmosphere of the medium defining the FDS
$\dot{W}, \dot{W}_{net}, \dot{W}_{BW}, \dot{W}_{UBW}$	Power generally or generically, "net" Power (<i>i.e.</i> , non-boundary power, usually shaft or electrical), the total Boundary Power, and the Useful Boundary Power

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Appendix on the Dead States and the Related Exergy Equations

As background to this presentation, note that it is useful to recognize the existence of a generalized exergy equation (GEE) in which the overall system is a CV open to heat, work, and mass transfer with its surroundings. The surroundings must be assumed to be completely in internal equilibrium so that the surroundings cannot produce any useful work from any internal interaction. Typically, the surroundings are taken to be or to include an inert fluid atmosphere called the “medium”. (The choice of the commonplace word “medium” may also be unfortunate, so in classroom presentations an unambiguous phrase such as the “inert surroundings” or “inert fluid atmosphere” may be preferable.) This equation is generally applicable but is of most interest to researchers concerned with combustion systems and chemical processing systems. The latter have feedstock and/or fuel inputs and chemically different waste and product stream outputs.

If the material in the overall system is kept permanently separate from the medium, two special cases of the exergy equation are obvious. In one case the composition of the captive working fluid mixture is considered to be variable from place to place in the overall system. A simple everyday example of this case is a familiar electrochemical cell or “battery” of cells. (An example is the power supply for an annoying communication device surely, or unfortunately, in immediately possession of and in active use by every person in every classroom today, so it is easy to ask a class to present examples.) More complex examples include other closed system chemical energy (more pertinently “exergy”) storage systems. It is convenient to call this version the restricted exergy equation (REE) being “restricted” against combining with the surroundings. A further constraint is to exclude the possibility of chemical reactions or separations changing the composition of the fluid in the system. This version can be called the Fixed (Composition) Exergy Equation or FEE addressed herein. This final version satisfied the needs of the vast majority of mechanical engineers in practice and even in research.

The versions of the exergy equations are closely related and differ primarily with respect to the applicable “Dead State”, in which the matter in the thermodynamic system under consideration can perform no further useful work and therefore has zero exergy. In all dead states, the matter in the system has been brought to ambient pressure and temperature. For the Restricted Dead State (RDS) the system is explicitly kept separate from its surroundings; in contrast, for the ultimate or Generalized Dead State (GDS), the material in the system is allowed to blend and react with and ultimately become identical to the surroundings. When the system is kept separate from the

medium, the dead state is taken to exist when the material in the engineering system is at ambient temperature and pressure and, if capable of chemical or other change in composition, in internal chemical equilibrium as well. A common and important, but not always specifically identified, special case of the RDS can be called for convenience the “Fixed Dead State”. This FDS is the state in which the composition of the pertinent material in the system is uniform and constant never changing anywhere within the system. For most simpler mechanical engineering applications, the FDS is the pertinent dead state.

Importantly, this FDS case is applicable to the usual working fluids in closed heat engine, heat pump, refrigeration, fluid power, and similar systems. Such systems are often overall closed or control mass (CM) systems with components such as compressors, fans, and pumps or turbines, fluid motors, and power cylinders that are individual CV subsystems. It is hardly necessary to note that the control mass (CM) system is, of course, a trivial but important special case of the control volume. Obviously, there are two sets of applications for systems not exchanging matter with the medium: (1) cases in which the composition of the engineering system is constant and uniform throughout the system so that the FDS and FEE case applies and (2) cases such as electrochemical or thermochemical exergy storage systems with chemical or other composition changes within the overall system under consideration, in which the RDS and REE are pertinent.

In a presentation for undergraduates, it is recommended to point out that the alternative GDS case applies when the engineering system is open to the surrounding inert medium. The medium in its minimal form can be just the surrounding gaseous atmosphere. This gaseous atmosphere can conceivably be as simple as a hypothetical single component “dry air”, but more likely the simplest worthwhile medium is a mixture such as (1) “moist air” (water vapor and dry air) in HVAC and similar applications or (2) a slightly more complicated mixture of dry gases (nitrogen, oxygen, argon, carbon dioxide) and water vapor for air separation applications. For desalination systems the medium must include the liquid saline ocean in equilibrium with the saturated gaseous atmosphere. If more complex chemical processing applications are considered, an inert version of the solid crust of the earth must be included in the medium containing the most stable chemical versions of the ores or other inert feedstocks of interest. This case of the unrestricted version, which for convenience can be called the Generalized Exergy Equation, is not addressed herein but a streamlined and related presentation exists in a complementary publication, which is available on request from this author.