



The Generalized Exergy Equation: A Rigorous Development and Detailed Presentation Suitable for Presentation to Advanced Undergraduates and Beginning Graduate Students

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Introduction

Exergy is well known as the potential for a system or perhaps most often the material in a system to produce useful work in interaction with its surroundings, primarily or exclusively an atmosphere or medium, which is assumed to remain in equilibrium in this context. The generalized form of the exergy equation applies when the engineering system is ultimately open to the surrounding medium so that the matter in the system can merge with and react with and ultimately become identical with the constituents of the medium. The medium in its minimal form could be just the surrounding gaseous atmosphere. Most likely the simplest worthwhile and interesting medium is “moist air” (water vapor and dry air) in HVAC and similar applications or a slightly more complicated mixture of dry gases (nitrogen, oxygen, argon, carbon dioxide) and water vapor in combustion applications. For desalination systems, the medium must include the liquid saline ocean in equilibrium with the gaseous atmosphere. If more complex chemical processing applications are considered, an inert version of the crust of the earth must be included in the medium. The latter rather complex medium must contain the stable chemical versions of the ores or other inert feedstocks of interest that are in equilibrium with the gaseous atmosphere. A straightforward, if somewhat necessarily complicated, derivation of the unrestricted version of the control volume (CV) exergy equation is detailed in the herein. In literature or practice, this equation is episodically referred to distinctively as the “Generalized Exergy Equation” (GEE) or an equivalent name, so this convenient and descriptive terminology is adopted herein.

The history, general development, and application of the various formulations for exergy (also formerly known as “availability”) has been well reported and evaluated by authors including notably Evans [1], Haywood [2], and numerous other scholars and researchers. The aim of this article is not to contribute much new to the elementary understanding of generalized exergy, but to offer a classroom tested presentation suitable for adequately prepared mechanical engineering students. The resulting GEE is not new; however, some features and considerations are introduced herein that are (1) thought to be innovative for the presentation and proof of the GEE and (2) especially helpful to mechanical engineering graduate students who are almost always new to chemical thermodynamics and certainly not comfortable with this increasingly important aspect of the subject. There are several pedagogical aspects of this presentation that have been found useful in two courses each taught over several years that should be of interest and hopefully of use to this teaching community. These educational benefits will be detailed following the presentation.

The Dead States and Exergy

The nature of the applicable or assumed dead state is critical in exergy analyses. For the Restricted Exergy Equation, the system is kept separated from its surrounding, with the pertinent dead state being the Restricted Dead State (RDS) at ambient temperature and pressure. A commonly encountered special case of the RDS is the situation in which the composition of the matter, usually a fluid, is unchanged between the prevailing state and the dead state. This RDS can be called the

Fixed Dead State. A similar RDS is useful in this presentation such that the material in a control volume or at a control surface is frozen in composition and brought to dead state temperature and pressure. This dead state will be called the Frozen Dead State (FDS) herein. In contrast, for the GEE addressed herein, the ultimate or General Dead State (GDS) must primarily be considered. A typical textbook or heuristic presentation of the GEE involves the expected combination of the energy and exergy equations along with a somewhat challenging and superficially plausible introduction of the FDS properties. While the result is useful, there are logical and pedagogical deficiencies in this approach, specifically (1) it could be erroneously inferred from some presentations that the mole numbers of the components of the system are fixed, (2) the expected forms of the system and stream exergies do not appear naturally unless the FDS is arbitrarily introduced as an intermediate state, (3) the role of the FDS in distinguishing and quantifying the Chemical Exergy is not demonstrated, and (4) an equivalent form of the total exergy often seen in the literature and practice of chemically oriented disciplines is not encountered.

Development of the Generalized Exergy Equation

The alternative straightforward and rigorous development herein generates an equation governing the generalized exergy by introducing equalities involving the chemical potentials of the components of the system that prevail in the medium. Note of course, species, such as fuels, will not exist as independently defined components of the medium. In these cases, consideration of chemical equilibrium in the medium will lead to unambiguous formulation of the chemical potentials for such species. At this point a fully accurate and useful form of the GEE will have been generated. Nevertheless, this equation can be reformulated for mechanical engineering applications and expectations by introducing the FDS properties both in the CV and at the inlets and exits. The revised formulation splits the total exergy into the chemical exergy and the more familiar thermomechanical energy. The result is a highly adaptable and informative GEE, and the process generating this equation should be a significant teaching tool and learning experience that emphasizes the breath, simplicity, and rigorous nature of thermodynamics.

Concerning student preparation, students should be familiar with the elementary thermodynamic relations allowing change of composition, the chemical potential, the conditions for chemical equilibrium, and partial molar properties. These topics are normally covered in more advanced thermodynamics courses for mechanical engineers. References are readily available, and a concise reference is also available on request from this author. Please note that in the following an effort has been made to generate a presentation suitable for somewhat unsophisticated students; therefore, an effort is made to show all intermediate steps, even purely mathematical steps, and certainly all intermediate thermodynamic steps. This probably reduces the time needed for a student to absorb the presentation. The classroom presentation begins with a sketch of the physical system (a CV with all typical interactions), which is presented after the table of nomenclature. As usual the schematic, such as Figure 1, should show the control surface (CS) defining the control volume and the typical heat and work inputs. It is important to show possible boundary work (BW) and distinguish the useful BW (UBW) from the BW on the surrounding atmosphere by some artifice such as explicitly showing the UBW being delivered to something external to the medium such as the stylized weight in the figure. Non-boundary work, often called “net” work should be included such as forms of shaft work from flow or positive displacement machines. Furthermore, and importantly in this application, possible electrochemical work should definitely be shown as is done below by including a stylized representation of fuel cell or generic chemical cell in the CV.

Table of Nomenclature

E, U, V, S and $U_{FDS}, V_{FDS}, S_{FDS}, G_{FDS}$	Extensive Energy, Internal Energy, Volume and Entropy in the CV and corresponding properties and Gibbs property in the Frozen DS, the FDS
$e, u, h, s,$ and $u_{FDS}, h_{FDS}, s_{FDS}$	Specific Properties in the CV or at the CS and in the FDS (the FDS properties are 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
\mathcal{E}_{SYS}	Extensive System Exergy, see Equation Error! Reference source not found.
e_x	(mass) Specific Stream Exergy, see Equation Error! Reference source not found.
\hat{h}, \hat{s}	Molar enthalpy, entropy
$I_{(IRR)}, T_0 S_{GEN}$	Extensive Irreversibility and its definition
$m; \dot{m}_{IN}$	Mass in a CV; mass flow rate across a CS
\dot{Q}_k and $T_{k(CS)}$	Heat Transfer Rate (input positive) and corresponding one-dimensional or effective CS Temperature
S_{GEN}	Extensive entropy generation
\bar{H}_k, \bar{S}_k	Partial Molar Enthalpy, and PM Entropy; or PM Property (PMP) generally for any property shown by the extensive property symbol with overbar and relevant chemical species indicated by subscript
$T, P,$ and μ_k	Local or prevailing Temperature, Pressure, and Chemical Potential of component k in the CV or at the CS; absolute T and P assumed
$T_0, P_0,$ and μ_k^0	Temperature and Pressure in the ambient atmosphere or medium and the Chemical Potential of generic component k of the ambient inert atmosphere or medium defining the GDS
$\dot{W}, \dot{W}_{net}, \dot{W}_{BW}, \dot{W}_{UBW}, \dot{W}_{ECW}$	Power generally or generically, "net" Power (<i>i.e.</i> , non-boundary power, usually shaft or electrical), the total Boundary Power, Useful Boundary Power, and the Electrochemical Power
z_k	Mole fraction

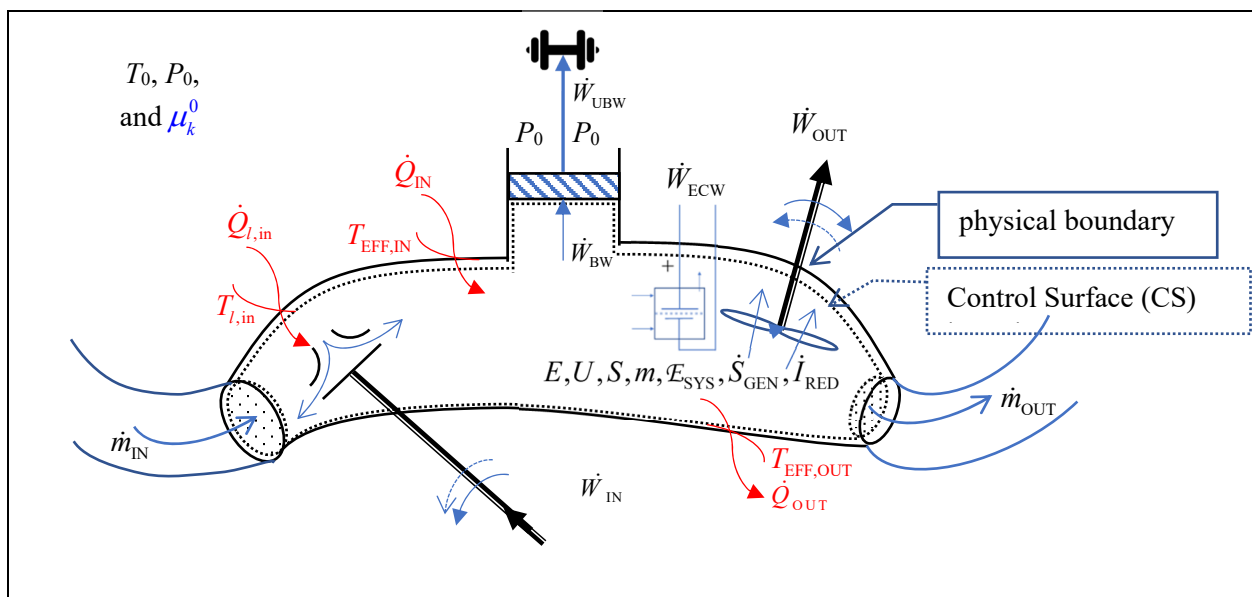


Figure 1: Schematic Control Volume (CV) and Control Surface (CS, dashed line or dotted cross section) Mutually Suitable for the Generalized Exergy Analysis Presented Herein

Begin the mathematical and logical development with the CV energy equation,

$$dE_{CV} + \delta W = \sum_{\substack{\text{ALL Q} \\ \text{INPUTS, } j}} \delta Q_j + \sum_{\text{ALL INLETS, } i} \delta m_{\text{INLET, } i} (h + e_K + e_P)_{\text{AT INLET, } i} \quad (1)$$

$$dE_{CV} + \delta W = \sum_{\text{IN}} \delta Q_j + \sum_{\text{IN}} \delta m_{\text{IN, } i} (h + e_K + e_P)_{\text{IN, } i}$$

and the CV entropy equation

$$dS_{CV} = \sum_{\text{IN}} \frac{\delta Q_j}{T_{CS, j}} + \sum_{\text{IN, } i} \delta m_{\text{IN, } i} s_{\text{IN, } i} + \delta S_{\text{GEN}} \quad (2)$$

Note that only the input streams (index = IN, i) are shown for simplicity and to save presentation space, and as usual these streams are considered to be one-dimensional. Similarly, the heat transfer terms are either one-dimensional or associated with an appropriate effective temperature. The individual student or practical analyst should include output streams (with negative algebraic signs) as needed. Execute the probably familiar and anticipated three starting steps (1) add and subtract $P_0 dV$ to the energy equation, (2) multiply the entropy equation by negative- T_0 , and (3) combine the two modified equations to give:

$$d(E_{CV} + P_0 V - T_0 S) + (\delta W - P_0 dV) = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{CS}} \right) + \sum_{\text{IN}} \left[\delta m_{\text{IN, } i} (h - T_0 s + e_K + e_P)_{\text{IN, } i} \right]_{\text{IN, } i} - T_0 \delta S_{\text{GEN}} \quad (3)$$

Here the summation over “IN” might span over several inputs (and/or outputs as needed). Recognize that the useful work is all the work of all types (especially now including electrochemical work) done by the CV less any boundary work merely expended on compressing the ambient medium without useful effect (i.e., work that cannot be delivered to an external recipient or “user” system), so

$$\delta W_U = \delta W - P_0 dV \quad (4)$$

Also recognize and define the lost work term as the exergy destruction or “irreversibility”, I , and identify it as

$$\delta I = T_0 \delta S_{\text{GEN}} \quad (5)$$

Rewrite the combined equation using this standard shorthand notation, and drop some redundant indices to give

$$d(E_{CV} + P_0 V - T_0 S) + \delta W_U = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{CS}} \right) + \sum_{\text{IN, } i} \delta m_{\text{IN}} (h - T_0 s + e_K + e_P)_{\text{IN, } i} - \delta I_{\text{(IRR)}} \quad (6)$$

Next switch the equation to molar fluid flow accounting using partial molar properties (PMPs) in the input stream. Students should be at least briefed on PMPs before this presentation. Note first that the extensive enthalpy entering the CV during a short time interval is

$$\delta H_{\text{IN},i} = \delta m_{\text{IN},i} h_{\text{IN},i} = \sum_k (\delta N_k \bar{H}_k)_{\text{IN},i} \quad (7)$$

A similar flux-related formula holds for the entropy, so the result is this basic combined-laws equation in terms of partial molar properties:

$$d(E_{\text{CV}} + P_0 V - T_0 S) + \delta W_U = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}} \right) + \sum_{\text{IN},i} \sum_k \delta N_k (\bar{H}_k - T_0 \bar{S}_k + M_k e_K + M_k e_P)_{\text{IN},i} - \delta I_{(\text{IRR})} \quad (8)$$

(Note carefully above the use of partial molar properties in representing the extensive properties.)

Here it is now necessary to sum over the several possible input ports ($i = 1$ to the number of inlets or exits) and also to sum over the possibly numerous ($k = 1$ to n_C) chemically distinct components in a mixed fluid flowing into (or out of) these ports. Herein n_C is number of components (e.g. O₂, N₂, CO₂, etc.). Note that M_k is the molar mass of component k , a multiplier needed to convert the kinetic and potential energies from their natural mass units to the molar basis.

Next introduce a finding to be developed based on conservation of the various chemical species or different elements and compounds. For each inert chemical species, entering (or leaving) the CV, a simple conservation equation may be written such as

$$dN_{k,\text{CV}} = \delta N_{k,\text{IN},i} \quad (9)$$

For reactive species, mole numbers can change due to chemical reaction(s) within the CV as well. Define a representative extent of reaction N_{ER} , for a reaction assumed to produce some component k , and write now in general

$$dN_{k,\text{CV}} = \delta N_{k,\text{IN},i} + \delta N_{\text{ER}} \nu_k \quad (10)$$

For a given reaction, the stoichiometric coefficients of the products (i. e. the components being produced by the reaction) are by convention taken to be positive, and the coefficients of the reactants (i. e. the components being consumed) are then necessarily negative. For example, note how the mole number for CO₂ in the CV can increase by (1) input of CO₂ with ambient air and (2) generation by combustion of a carbon-containing fuel.

Note in Equations (11) below that the differential “ d ” symbol is required on the left for the differential change in a **property** of the CV system since such a thermodynamic property is a

mathematical function of state. Also note that the process-dependent **infinitesimals** (with δ used for infinitesimal amount of a process dependent quantity) are used on the right for the process dependent flow input term and the reaction dependent term. For each species equation, it is acceptable to multiply the equation by the **constant** chemical potential of that species in the medium (superscript MED = superscript 0), where no intensive properties ever change, and write

$$\mu_k^{\text{MED}} dN_{k,\text{CV}} = \mu_k^0 dN_{k,\text{CV}} = \mu_k^0 (\delta N_{k,\text{IN},i} + \delta N_{\text{ER}} \nu_k) \quad (11)$$

When summed over all components involved in an individual reaction, the reaction dependent right-hand side can be simplified, and the reaction dependent terms actually eliminated. Note that for any given reaction, a sum of product and reactant terms can be identified that must have the general form

$$\sum_k (\mu_k^0 \nu_k) \delta N_{\text{ER}} = (-\mu_{\text{R}1}^0 \nu_{\text{R}1} - \mu_{\text{R}2}^0 \nu_{\text{R}2} - \dots + \mu_{\text{P}1}^0 \nu_{\text{P}1} + \dots) \delta N_{\text{ER}} \quad (12)$$

Note that the sum in parentheses is just the condition for chemical equilibrium. Consequently, (after grouping all the components involved in a particular reaction) the series in parentheses must always sum to zero when chemical equilibrium prevails. Now equilibrium (by basic principles and definition) is required to prevail in the medium, so applying the previous consideration to Equation (11) requires that all the terms that group together multiplying any δN_{ER} must sum to zero. This result eliminates all the reaction-based terms and requires that the developing equation simplifies to include only the accumulation and input terms. When equations like the differential accumulation Equation (11) are summed for all components and Equation (12) is applied to all the chemical reactions, the sum is simplified with all the terms related to every extent of reaction being eliminated.

After this simplification, the concise and important result is as follows,

$$\sum_k \mu_k^0 dN_{k,\text{CV}} = \sum_k \mu_k^0 \delta N_{k,\text{IN},i} \quad (13)$$

and this equation, based on conservation of chemical species, can be combined with the already combined energy and entropy equation to generate the generalized exergy equation. Now repeating Equation (8) for convenience in further developing the derivation gives:

$$d(E_{\text{CV}} + P_0 V - T_0 S) + \delta W_{\text{U}} = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}} \right) + \sum_{\text{IN}} \sum_k \delta N_k (\bar{H}_k - T_0 \bar{S}_k + M_k e_{\text{K}} + M_k e_{\text{P}})_{\text{IN},i} - \delta I_{(\text{IRR})} \quad (\text{copy of 8})$$

Note again that M_k is the molar mass of component k . Subtract from both sides the series summation of mole numbers weighted by the chemical potentials in the medium developed as Equation 13. These two equal sums, one on the LSH with $dN_{k,\text{CV}}$ and one on the RHS with the process dependent $\delta N_{k,\text{CV}}$, have been introduced below and are temporarily enclosed in square brackets just to aid identification. The intermediate result is

$$\begin{aligned}
& d\left(E_{CV} + P_0V - T_0S - \left[\sum_k \mu_k^0 N_{k,CV}\right]\right) + \delta W_U = \sum_{IN} \delta Q \left(1 - \frac{T_0}{T_{CS}}\right) \\
& + \sum_{IN} \left[\sum_k \delta N_k \left(\bar{H}_k - T_0\bar{S}_k + M_k e_K + M_k e_P\right)_{IN-i} - \left[\sum_k \mu_k^0 \delta N_{k,IN-i}\right] \right] - \delta I_{(IRR)}
\end{aligned} \tag{14}$$

or after slight simplification and dropping the unnecessary brackets

$$\begin{aligned}
& d\left(E_{CV} + P_0V - T_0S - \sum_k \mu_k^0 N_{k,CV}\right) + \delta W_U = \sum_{IN} \delta Q \left(1 - \frac{T_0}{T_{CS}}\right) \\
& + \sum_{IN} \left[\sum_k \delta N_{k,IN-i} \left(\bar{H}_k - T_0\bar{S}_k + M_k e_K + M_k e_P - \mu_k^0\right)_{IN-i} \right] - \delta I_{(IRR)}
\end{aligned} \tag{15}$$

Next, it may be desirable for mostly interpretive and pedagogical reasons to manipulate the properties so that differences in the extensive properties appear on the LHS side of an equation to be developed from Equation (15). This modification is done by introducing terms relating to what we can call the Frozen Dead State (FDS) properties. The FDS is at temperature and pressure of the ambient (absolutely or unrestricted) dead state but with the material “frozen” at the **same** composition as the prevailing physical state in the CV. Imagine capturing the fluid instantaneously in the CV and bringing it to the FDS conditions but with chemical reactions turned off or “frozen”. A schematic of first isolating the material in the CV and then bringing this isolated system into thermal and pressure equilibrium with the medium is illustrated in Figure 2 below. Note that in the top schematic in the figure the CV has been isolated from any previous interactions with any other engineering systems or components. Examples include sealing the inlet and outlet ports, stopping all flow machines, and stopping all heat transfer operations. Also note that the expansion piston has been pinned. Then allow the system to interact thermally and by expansion or contraction against the medium and to come into thermal and pressure equilibrium with the medium. This is the condition shown in the bottom schematic in Figure 2.

Recall that the FDS is “frozen” in the same composition as the actual instantaneous state but is at the temperature and pressure of the medium. In the FDS, the composition (expressed for example in terms of mole numbers) is by definition unchanged from the original composition that prevails instantaneously in the CV. In the FDS the extensive Gibbs property of this FDS fluid has the following representations (note use of PMP)

$$G_{FDS} = U_{FDS} + P_0V_{FDS} - T_0S_{FDS} = \sum_k N_{k,CV} \bar{G}_{k,FDS} = \sum_k N_{k,CV} \mu_{k,FDS}$$

Subtract the middle version and then add the last version of G_{FDS} within the differential on the left-hand side of the developing equation (note the color coding) giving

$$d\left(E_{\text{CV}} - U_{\text{FDS}} + P_0(V - V_{\text{FDS}}) - T_0(S - S_{\text{FDS}}) + \sum_k N_{k,\text{CV}}(\mu_{k,\text{FDS}} - \mu_k^0)\right) + \delta W_U = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}}\right) + \sum_{\text{IN}} \sum_k \delta N_k (\bar{H}_k - T_0 \bar{S}_k + M_k e_K + M_k e_P - \mu_k^0)_{\text{IN-}i} - \delta I_{(\text{IRR})} \quad (16)$$

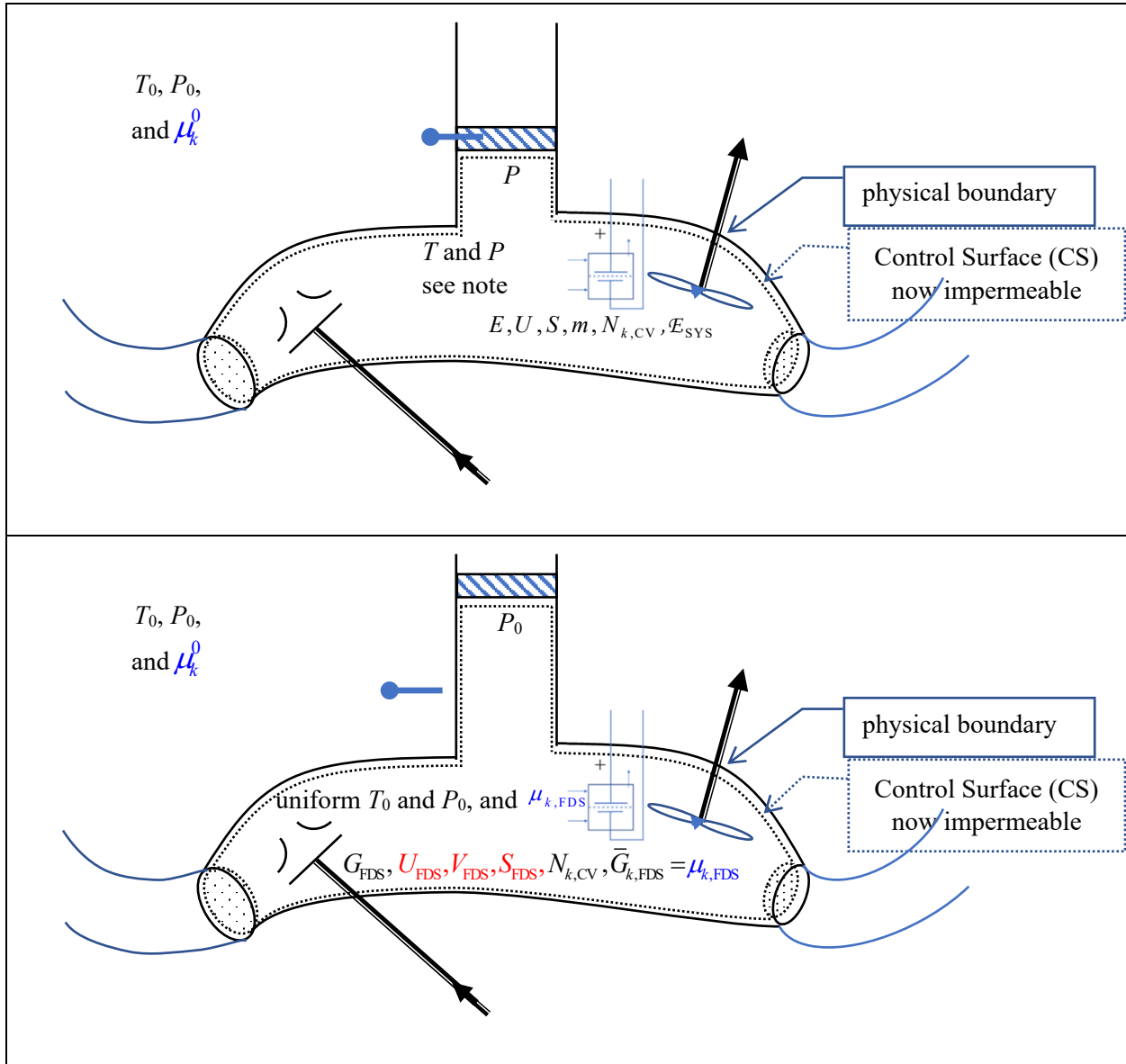


Figure 2: Schematic Control Volume (CV) and Control Surface (CS) with CS now made Impermeable. Top: CV hypothetically isolated in its instantaneous thermodynamic state
 Bottom: the isolated CV now evolved into the Frozen Dead State (FDS).
 Note: the intensive state is not necessarily uniform in the instantaneous state shown in the Top.

Recall that the FDS is “frozen” in the same composition as the actual instantaneous state, but it is at the temperature and pressure of the medium. In the FDS, the composition (expressed for

example in terms of intensive mole fractions and extensive mole numbers) is by definition unchanged from the original composition that prevails instantaneously in the CV. The temperature and pressure in the FDS are similarly well defined and equal of course to the properties of the medium. Consequently, the intensive and extensive state of the system in the FDS is well defined, and in particular the extensive Gibbs property of the system is well defined.

Consequently, in the FDS the extensive Gibbs property of this FDS system and fluid has the following representations (note use of PMP)

$$G_{\text{FDS}} = U_{\text{FDS}} + P_0 V_{\text{FDS}} - T_0 S_{\text{FDS}} = \sum_k N_{k,\text{CV}} \bar{G}_{k,\text{FDS}} = \sum_k N_{k,\text{CV}} \mu_{k,\text{FDS}}$$

Subtract the middle version and then add the last version of G_{FDS} within the differential on the left-hand side of the developing equation giving

$$d \left(E_{\text{CV}} - U_{\text{FDS}} + P_0 (V - V_{\text{FDS}}) - T_0 (S - S_{\text{FDS}}) + \sum_k N_{k,\text{CV}} (\mu_{k,\text{FDS}} - \mu_k^0) \right) + \delta W_{\text{U}} = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}} \right) + \sum_{\text{IN}} \sum_k \delta N_k (\bar{H}_k - T_0 \bar{S}_k + M_k e_{\text{K}} + M_k e_{\text{P}} - \mu_k^0)_{\text{IN-}i} - \delta I_{(\text{IRR})} \quad (16)$$

Next consider the fluid (or generally “material”) flow terms on the right. Conceptually, a small sample of the inlet fluid (or outlet fluid) could be captured just at the CS and taken (by change in temperature and pressure) to temperature and pressure conditions of the frozen FDS condition. The sample **when taken** would have the mole fractions or composition of the inlet or exit fluid at the CS and will keep this composition in its corresponding FDS. This condition is best identified as the FDS for inlet IN- i (or for exit, OUT- i). At this FDS condition, the enthalpy and entropy will be changed, but the composition will **not have changed**. Evaluating a distinct set of FDS properties for every inlet or exit probably appears to be a nuisance; however, the capabilities of a typical chemical process simulator make this task at least straightforward. The extensive Gibbs property of this hypothetical fluid, sampled at the CS and then brought to the FDS condition, could then be written as follows:

$$\delta G_{\text{HYP-CS}}(T_0, P_0) = \sum_k \delta N_{k,\text{CS}} (\bar{H}_{k,\text{FDS}} - T_0 \bar{S}_{k,\text{FDS}})_{\text{IN-}i} = \sum_k \delta N_{k,\text{CS}} (\mu_{k,\text{FDS}})_{\text{IN-}i} \quad (17.A)$$

so, after rearrangement we have for each stream of fluid

$$\sum_k \delta N_{k,\text{CS}} (\bar{H}_{k,\text{FDS}} - T_0 \bar{S}_{k,\text{FDS}})_{\text{IN-}i} - \sum_k \delta N_{k,\text{CS}} (\mu_{k,\text{FDS}})_{\text{IN-}i} = 0 \quad (17.B)$$

Subtract this identity equal to zero from the right-hand side of the exergy equation in the stream exergy term. Again noting the color coding to give.

$$\begin{aligned}
d\left(E_{\text{CV}} - U_{\text{FDS}} + P_0(V - V_{\text{FDS}}) - T_0(S - S_{\text{FDS}}) + \sum_k N_{k,\text{CV}}(\mu_{k,\text{FDS}} - \mu_k^0)\right) + \delta W_{\text{U}} = \\
\sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}}\right) + \\
\sum_{\text{IN}} \sum_k \delta N_k \left(\bar{H}_k - \bar{H}_{k,\text{FDS}} - T_0(\bar{S}_k - \bar{S}_{k,\text{FDS}}) + M_k e_{\text{K}} + M_k e_{\text{P}} + \mu_{k,\text{FDS}} - \mu_k^0\right)_{\text{IN}-i} - \delta I_{(\text{IRR})}
\end{aligned} \tag{18}$$

Next, combine the chemical potential terms on the RHS to give the following equation, which is the CV exergy equation enhanced to include the FDS properties effectively as reference states for the enthalpy, entropy, and chemical potential. The enhanced equation with FDS properties introduced is then

$$\begin{aligned}
d\left(E_{\text{CV}} - U_{\text{FDS}} + P_0(V - V_{\text{FDS}}) - T_0(S - S_{\text{FDS}}) + \sum_k N_{k,\text{CV}}(\mu_{k,\text{FDS}} - \mu_k^0)\right) + \delta W_{\text{U}} = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}}\right) + \\
\sum_{\text{IN}} \sum_k \delta N_k \left(\bar{H}_k - \bar{H}_{k,\text{FDS}} - T_0(\bar{S}_k - \bar{S}_{k,\text{FDS}}) + M_k e_{\text{K}} + M_k e_{\text{P}} + (\mu_{k,\text{FDS}} - \mu_k^0)\right)_{\text{IN}} - \delta I_{(\text{IRR})}
\end{aligned} \tag{19}$$

Note that the earlier elementary (and actually simpler) form without the complication of inserting the FDS properties may be more practical in some applications.

$$\begin{aligned}
d\left(E_{\text{CV}} + P_0V - T_0S - \sum_k \mu_k^0 N_{k,\text{CV}}\right) + \delta W_{\text{U}} = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}}\right) \\
+ \sum_{\text{IN}} \left[\sum_k \delta N_{k,\text{IN}} \left(\bar{H}_k - T_0\bar{S}_k + M_k e_{\text{K}} + M_k e_{\text{P}} - \mu_k^0\right)_{\text{IN}} \right] - \delta I_{(\text{IRR})}
\end{aligned} \tag{repeat of 15}$$

The coefficient of the infinitesimal mole numbers in the sum on the right of (15) or (19) is recognized as the generalized partial molar stream exergy of component k .

$$\begin{aligned}
\text{Partial Molar Stream Exergy} = \\
\bar{H}_k - T_0\bar{S}_k + M_k e_{\text{K}} + M_k e_{\text{P}} - \mu_k^0
\end{aligned} \tag{20.A}$$

or after inserting FDS properties, the alternative Partial Molar Stream Exergy =

$$\bar{H}_k - \bar{H}_{k,\text{FDS}} - T_0(\bar{S}_k - \bar{S}_{k,\text{FDS}}) + M_k e_{\text{K}} + M_k e_{\text{P}} + (\mu_{k,\text{FDS}} - \mu_k^0) \tag{20.B}$$

It may actually be handier to write this exergy in simple molar properties instead of partial molar (PM) properties. Note first that the partial molar properties on the right can be used to write the corresponding extensive properties. For example, consider specifically the extensive enthalpy entering the CV through a particular input port (“IN”). This extensive amount can be calculated by summing the partial molar properties entering there as shown and then recognizing that the molar enthalpy naturally results as seen next,

$$\delta H_{\text{IN}} = \sum_k \delta N_k \bar{H}_k = \delta N_{\text{IN}} \sum_k z_k \bar{H}_k = \delta N_{\text{IN}} \hat{h} \quad (20)$$

Note that z_k may be a preferred generic symbol for mole fractions since x_k and y_k are often reserved for the mole fractions in the liquid or vapor phases respectively. Note importantly that the mole fractions are the same in the instantaneous state and the FDS. Now the same type of summation and definition can be applied to the entropy in the stream, so

$$\delta S_{\text{IN}} = \sum_k \delta N_k \bar{S}_k = \delta N_{\text{IN}} \hat{s} \quad (21)$$

In this way, the extensive properties on the RHS may be written as molar properties evaluated at the inlet (IN, shown) or exit (EX, not shown) so that a more convenient form of Equation (15) is as follows:

$$\begin{aligned} d \left(E_{\text{CV}} + P_0 V - T_0 S - \sum_k \mu_k^0 N_{k,\text{CV}} \right) + \delta W_{\text{U}} = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}} \right) \\ + \sum_{\text{IN}} \delta N \left[\hat{h} - T_0 \hat{s} + \sum_k z_{k,\text{IN}} \left(M_k e_{\text{K}} + M_k e_{\text{P}} - \mu_k^0 \right)_{\text{IN}} \right] - \delta I_{(\text{IRR})} \end{aligned} \quad (22)$$

For temporary emphasis, the molar enthalpy (kJ/kmole) and entropy (kJ/kmole-K) terms on the RHS of Equation 22 are identified with the accent circumflex (or “hat”) as \hat{h} and \hat{s} . In actual practice, this distinction in symbols is probably unnecessary since we are unlikely to mix molar and mass-specific quantities in the same equation or even in the same project. The corresponding molar (not PMP) form of Equation (19) with FDS properties included is developed below, starting with a slight revision of Equation (19) to show the mole fractions

$$\begin{aligned} d \left(E_{\text{CV}} - U_{\text{FDS}} + P_0 (V - V_{\text{FDS}}) - T_0 (S - S_{\text{FDS}}) + \sum_k N_{k,\text{CV}} (\mu_{k,\text{FDS}} - \mu_k^0) \right) + \delta W_{\text{U}} = \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}} \right) + \\ \sum_{\text{IN}} \delta N_{\text{CS}} \sum_k z_k \left(\bar{H}_k - \bar{H}_{k,\text{FDS}} - T_0 (\bar{S}_k - \bar{S}_{k,\text{FDS}}) + M_k e_{\text{K}} + M_k e_{\text{P}} + (\mu_{k,\text{FDS}} - \mu_k^0) \right)_{\text{IN}} - \delta I_{(\text{RED})} \end{aligned} \quad (23.A)$$

Then after restating in terms of molar properties by performing the indicated multiplication

$$\begin{aligned} d \left(E_{\text{CV}} - U_{\text{FDS}} + P_0 (V - V_{\text{FDS}}) - T_0 (S - S_{\text{FDS}}) + \sum_k N_{k,\text{CV}} (\mu_{k,\text{FDS}} - \mu_k^0) \right) + \delta W_{\text{U}} = -\delta I_{(\text{RED})} \\ + \sum_{\text{IN}} \delta Q \left(1 - \frac{T_0}{T_{\text{CS}}} \right) + \\ \sum_{\text{ALL IN}} \delta N_{\text{CS}} \left[\hat{h}_{\text{IN}} - \hat{h}_{\text{FDS}} - T_0 (\hat{s}_{\text{IN}} - \hat{s}_{\text{FDS}}) + \sum_{\text{ALL } k} z_{k,\text{IN}} (\mu_k^{\text{FDS}} - \mu_k^0)_{\text{IN}} + \sum_k z_{k,\text{IN}} (M_k e_{\text{K}} + M_k e_{\text{P}})_{\text{IN}} \right] \end{aligned} \quad (23.B)$$

Either Equation (22) or (23) may be useful for some transient CV exergy analysis. In application, they are better restated as time derivative equations. The time derivative form of Equation (22) is

$$\begin{aligned} \frac{d}{dt} \left(E_{CV} + P_0 V - T_0 S - \sum_k \mu_k^0 N_{k,CV} \right) + \dot{W}_U = \sum_{IN} \dot{Q} \left(1 - \frac{T_0}{T_{CS}} \right) \\ + \sum_{IN} \dot{N} \left[\hat{h} - T_0 \hat{s} + \sum_k x_{k,IN} (M_k e_K + M_k e_P - \mu_k^0) \right]_{IN} - \dot{I}_{(RED)} \end{aligned} \quad (24)$$

and the time derivative form of Equation (23) is

$$\begin{aligned} \frac{d}{dt} \left(E_{CV} - U_{FDS} + P_0 (V - V_{FDS}) - T_0 (S - S_{FDS}) + \sum_k N_{k,CV} (\mu_{k,FDS} - \mu_k^0) \right) + \dot{W}_U = \\ \sum_{IN} \dot{Q} \left(1 - \frac{T_0}{T_{CS}} \right) + \\ \sum_{IN} \dot{N}_{CS} \left[\hat{h}_{IN} - \hat{h}_{FDS} - T_0 (\hat{s}_{IN} - \hat{s}_{FDS}) + \sum_k z_{k,IN} (\mu_k^{FDS} - \mu_k^0)_{IN} + \sum_k z_{k,IN} (M_k e_K + M_k e_P)_{IN} \right] - \dot{I}_{(RED)} \end{aligned} \quad (25)$$

As a word equation, either differential (actually or potentially integral-differential) equation may be restated as follows:

The rate of accumulation of system thermomechanical and chemical exergy plus the useful work output equals the net input rate of thermal exergy plus the next input rate of stream thermomechanical and chemical exergy less the exergy destruction rate.

Or in shorthand symbols, using script \mathcal{E} for extensive system exergies and thermal exergy and e_x for stream exergies:

$$d\mathcal{E}_T + \delta\mathcal{W}_U = d(\mathcal{E}_{TM} + \mathcal{E}_{CH}) + \delta\mathcal{W}_U = \sum_{IN} \delta\mathcal{E}_Q + \sum_{IN} \delta\mathcal{N}(e_{XTM} + e_{XCH})_{IN} - \delta\mathcal{I}_{(IRR)} \quad (26)$$

In Equation 26, (note use of the Frozen Dead State, FDS) the shorthand symbols stand for (1) the extensive thermomechanical and chemical (in parentheses) System Exergies, or

$$\begin{aligned} \mathcal{E}_T = \mathcal{E}_{TM} + (\mathcal{E}_{CH}) = \\ E_{CV} - U_{FDS} + P_0 (V - V_{FDS}) - T_0 (S - S_{FDS}) + \left(\sum_k N_{k,CV} (\mu_{k,FDS} - \mu_k^0) \right) \end{aligned} \quad (26.a)$$

or in the simpler form without reference to the FDS,

$$\mathcal{E}_T = E_{CV} + P_0 V - T_0 S - \sum_k \mu_k^0 N_{k,CV} \quad (26.a)$$

(2) the extensive Thermal Exergy input along with heat, or

$$\delta\mathcal{E}_Q = \sum_{IN} \delta\mathcal{Q} \left(1 - \frac{T_0}{T_{CS}} \right) \quad (26.b)$$

and (3) the molar Stream Exergy (separated into the thermomechanical and chemical components), or

$$(e_{\text{XTM}}) + (e_{\text{XCH}}) = \left(\hat{h} - \hat{h}_{\text{TDS}} - T_0 (\hat{s} - \hat{s}_{\text{FDS}}) + \sum_k z_k (M_k e_K + M_k e_P) \right) + \left(\sum_k z_k (\mu_{k,\text{FDS}} - \mu_k^0) \right) \quad (26.c)$$

This completes the derivation of the generalized CV exergy equation. This equation is still not much (or maybe not enough) used in mechanical engineering thermal systems analysis and design, but increased attention to innovation and efficiency in energy systems that involve composition changes coupled with interaction with the environment will surely increase mechanical engineering interest. Current and future examples include advanced combustion and carbon sequestration systems, biofuel production such as ethanol production, and numerous thermal processing applications of interest to mechanical engineers should promote its use.

Theoretical Considerations of some Significance

The development of the control volume Generalized Exergy Equation (GEE) has been shown to be a straightforward, if somewhat complex, application of three principles: (1 and 2) a combination of the CV energy and entropy equations resulting in the combined laws Equation 8 and (3) the conservation equations for chemical species in the forms of Equation 10. The energy and entropy laws are enhanced for this application by further combination with the conservation equations for chemical species in the forms of Equation 10. This combination is modified by some due considerations pertaining to the existence of chemical equilibrium in the medium, or inert surrounding atmosphere. Significantly, no new physical or chemical considerations at all are required allowing for a purely mathematical development. An especially appealing feature and result is that the terms involving chemical reactions in Equation 10 actually cancel themselves out identically during the development when consideration of chemical equilibrium in the medium is taken into account. This feature explains the somewhat puzzling absence of reaction related terms in the final equation. Another helpful feature is the introduction of the so-called Frozen Dead State. Consideration and application of this state facilitates the splitting of the exergy expressions into the thermomechanical and chemical parts, a feature found very appealing to most mechanical engineers. In teaching, these features alone should make this development at least of interest if not of use to classroom teachers of intermediate thermodynamics.

Pedagogical Considerations and Experience

Graduate students and advanced undergraduates in mechanical or related thermal systems engineering interested in advanced energy conversion and chemical process systems should be aware of the GEE in addition to the two forms of the REE. For background, such students should be well versed in energy and entropy analysis and mass conservation. In addition, some introduction to applied physical chemistry should be provided or required. In the author's experience, it is preferable use the ongoing course to provide or review the needed chemical thermodynamic theory, which is rather minimal. The required chemistry is mostly just familiar stoichiometry; however, a working knowledge of chemical equilibrium and an appreciation of the

chemical potential is also necessary. From a pedagogical view, the development of the GEE is a challenging but rewarding exercise in the integration of most of the principles of basic thermodynamics and elementary chemical thermodynamics. Knowledge and understanding of the GEE will be helpful in the thermodynamic analysis and, perhaps more importantly, the technoeconomic analysis of combustion and reaction systems, desalination and chemical process systems and even some advanced HVAC systems among other applications.

In classroom teaching, this development has been introduced much as presented herein to graduate students for several years, and most of the students appreciate both the results and the development. Some specific applications of some familiar and some less familiar thermodynamic concepts in this development have special pedagogical impact to mechanical engineering students as follow:

- Demonstration of the use of Partial Molar Properties (PMPs) especially in theoretical developments and demonstration of the conversion from PMPs to molar properties for further applications.
- A further demonstration of the utility of the Extent of Reaction to represent the generation or consumption of chemical species in chemical reactions. This demonstration reinforces the concept first encountered in chemical equilibrium studies.
- Providing several opportunities to point out the important disparity between the differentials of thermodynamic properties and the infinitesimals of process dependent quantities
- Demonstrating to all students the adaptability and efficiency of rigorous thermodynamic analysis to very practical problems best achieved by bypassing unnecessary assumptions
- Demonstrating the use of chemical equilibrium considerations in simplifying the equations for the conservation of various chemical species.

The development of this equation has been presented in basically the same form as given herein over several years. Consistently, all available informal student feedback and casual assessment has been at least minimally positive and sometimes enthusiastic. Most students have been able to successfully apply generalized exergy to such simple applications as air separation and evaluation of the rate of exergy destruction in uncontrolled combustion.

Conclusions

Ultimately, this presentation should be a useful addition to, or at least useful reference and background material for, an intermediate thermodynamics course or an advanced engineering course on thermal and combustion systems. Obviously, many interesting student research topics on exergy and exergy related systems already exist and new opportunities are being developed or announced almost every day. The future for exergy research and exergy related energy research is bright, and the GEE, perhaps further illustrated by the presentation herein, should be a useful tool in promising and interesting exergy related research.

References

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