

Thermo-mechanical exergy of a substance below environmental pressure

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ABSTRACT

In this work, we demonstrate why classical thermo-mechanical exergy functions are incorrect below the environmental reference pressure, since they result in too-small or even negative values. We present new derivations for thermo-mechanical exergy for fluids at any temperature or pressure above or below the environmental reference temperature and pressure. We then present new pressure-enthalpy-exergy diagrams of real chemicals to visually demonstrate the results.

Keywords: Exergy, thermo-mechanical exergy, low pressure, thermodynamics

1. INTRODUCTION

Exergy is a thermodynamic metric of matter or energy which is useful for describing its energetic value in terms of both quantity (according to the 1st law of thermodynamics) and quality (according to the 2nd law of thermodynamics). Although several definitions of exergy have been proposed, the definition of Moran *et al.* (p372) [1] is the most general (emphasis ours):

Definition 1. (Definition of Exergy)

Exergy is the **maximum** theoretical work obtainable from an overall system consisting of a system and the environment as the system comes into equilibrium with the environment (passes to the dead state).

Since there are many kinds of exergy, it is quite useful to break down exergy into various kinds and classifications. Many taxonomies for this have been proposed, but for this work we use the taxonomy of Deng *et al.* [2], illustrated in simple form in Figure 1.

This paper only considers the thermo-mechanical exergy of fluids. Thermo-mechanical exergy is the exergy associated with pressure, temperature, and phase of a substance¹. It does not include chemical exergy (associated with chemical bonds and phase), exergy of height (potential) or motion

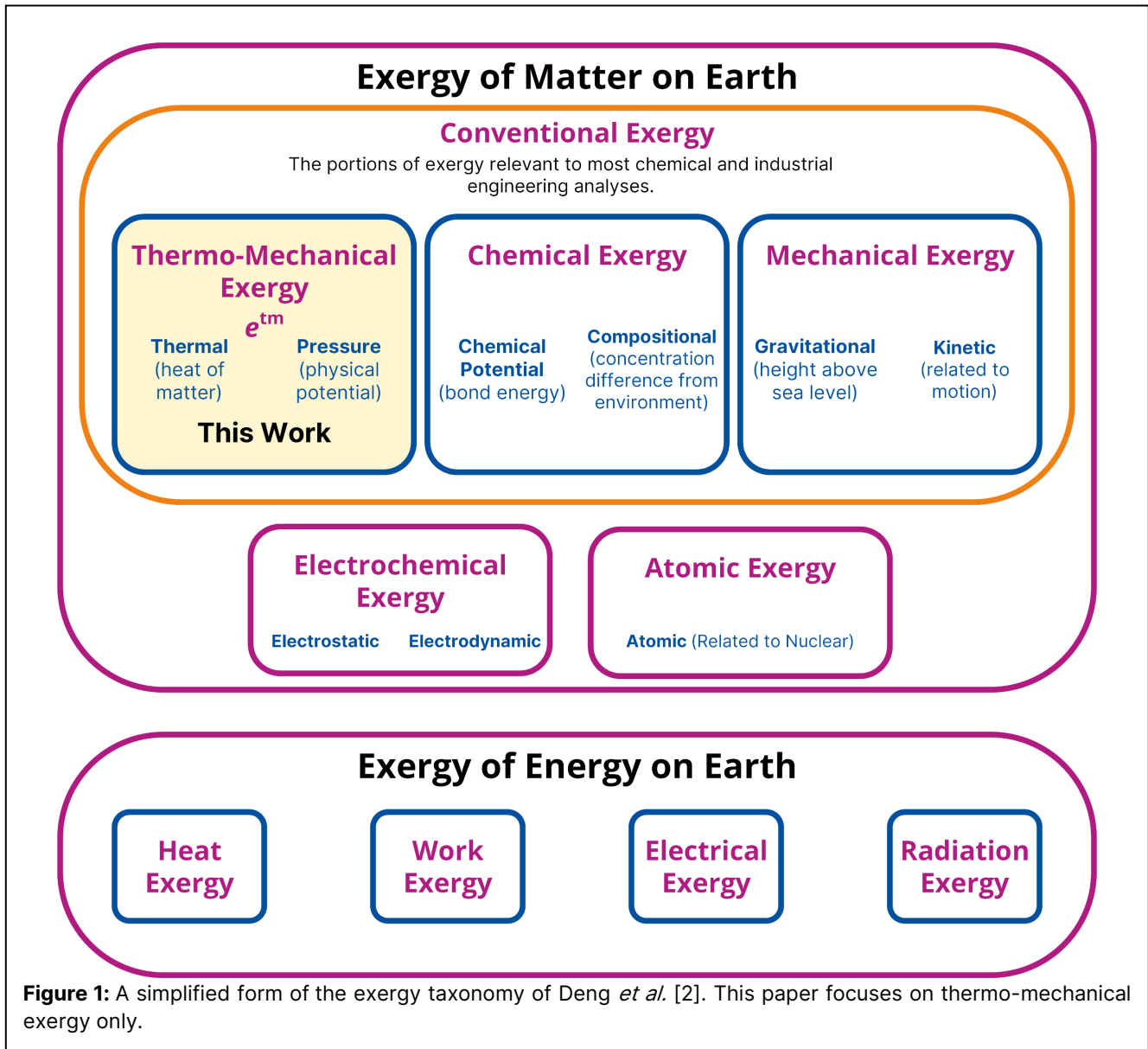
(kinetic), electrostatic / electrodynamic exergy, or atomic/nuclear exergy.

Some works decompose thermo-mechanical exergy into a temperature contribution and a pressure contribution, however, this is done for convenience; it has no fundamental basis. In addition, such a decomposition is not strictly correct in general because it neglects phase change and mixed-phases (e.g. vapor-liquid), but the sentiment is easy to follow. Instead, thermo-mechanical exergy (e^{tm}) is better generalized in terms of how a material's enthalpy and entropy differ from its enthalpy and entropy at the environmental state. The environmental reference state 0 is defined as (T_0, p_0) , which is the environmental reference temperature and pressure. Many classical texts have derived the equation for thermo-mechanical exergy (e^{tm}) of a substance as [3]:

$$e^{tm} = (h_1 - h_0) - T_0(s_1 - s_0) \quad (1)$$

where h is the specific enthalpy (we use kJ/kg in this work), s is the specific entropy (kJ/kg-K), and T is temperature (K). Subscript 0 indicates the temperature, enthalpy, or entropy of the substance at the environmental reference state, and subscript 1 indicates the enthalpy or entropy of the substance in its actual state. In this work, we will show that Eq. (1) is invalid below the environmental pressure. For

¹ Phase affects also other forms of exergy, like chemical exergy, but that is not within the scope of this paper.



this paper, we use environmental reference conditions (T_0, p_0) of (298.15 K, 1.01325 bar).

Eq. 1 is used widely in the literature for thermo-mechanical exergy in industrial, chemical, and mechanical systems analysis. It is often referred to as the specific flow exergy because it is the most appropriate form for flowing systems and arises naturally from general flow balances. However, McGovern noted that what has been labeled flow exergy in the literature is perhaps better described as “the sum of the exergy...of the **substance**...and the exergy transfer corresponding to a work interaction at a boundary” (emphasis ours) [4]. Thus it is not strictly limited to flowing systems.

However, as we will show, if $p_1 < p_0$, Eq. 1 will result in too-small values. In fact, it will result in a negative value for exergy when $(h_1 - h_0) < T_0(s_1 -$

$s_0)$. Very little has been published on sub-environmental pressures for Eq. 1 in the open literature. The few works that address it sometimes incorrectly conclude that any negative value resulting from Eq. 1 implies that e^{tm} can sometimes be negative.

In this paper, we demonstrate that (1) Eq. 1 is incorrect when $p_1 < p_0$; (2) we use an optimization approach to rederive e^{tm} for cases when $p_1 < p_0$ and show that this new equation is always positive; (3) we illustrate these findings visually with real chemicals by introducing a new pressure-enthalpy-exergy diagram. The resulting general form of the equation is very useful for practicing engineers.

2. THE CLASSICAL THERMO-MECHANICAL EXERGY EQUATION

2.1 Fundamental Principles of Exergy

We can rewrite Definition 1 as an optimization problem, as follows:

$$e^{\text{tm}} = \max_{\mathcal{P}} w \quad (2)$$

Here, $\mathcal{P} \in \mathbb{P}$ is a process within the set of all possible processes \mathbb{P} that bring the substance into equilibrium with its environment while producing work w (here expressed in specific form, or kJ per kg of substance). As currently defined, there is no restriction on the number of \mathcal{P} that are solutions to Eq. 2, and in fact there may be an infinite number of solutions as will be discussed later.

Theorem 1. Reversibility at Solution

The \mathcal{P} that produces the maximum w **must be a reversible process.**

This is a well-known thermodynamic result shown in other sources [1] and taken as true in this work. A reversible process has by its definition no thermodynamic losses (irreversibilities). This obviously means maximum work production or minimum work consumption for processes involving mechanical energy (work). In fact, other definitions of exergy go so far as to incorporate this result into the definition itself, such as that of Szargut [5] (emphasis ours):

Definition 2. (Alternative Definition of Exergy)

Exergy is the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of its surrounding nature by means of **reversible processes**, involving interaction only with the above mentioned components of nature.

However, it should be noted that Definition 1 is more general because it does not assume reversibility of \mathcal{P} , and so we use Definition 1 in this work. Definition 2 is still useful, but has led to some misinterpretations and misapplications which will be noted later. Both definitions rely on the assumption that the “environment” or “surrounding nature” is an infinite reservoir of mass and energy at (T_0, p_0) .

Although inelegant, it is technically possible to solve the optimization problem in Eq. 2 through guess-and-check on \mathcal{P} : propose a process \mathcal{P} ,

compute the work that results, and keep guessing new \mathcal{P} until it has somehow been determined that no \mathcal{P} that produces a larger w could exist. With this approach, each valid \mathcal{P} results in a valid lower bound on e^{tm} .

2.2 Exergy can Never be Negative

It is clear then that the thermo-mechanical exergy of a substance can never be negative, as noted by Moran et al. (p375) [1]. This is because it is always possible to propose a trivial process \mathcal{P} that does zero work but brings the substance into equilibrium with its environment by simply exposing the substance (at any temperature and pressure) to the environment and leaving it for infinite time. Because the environment is infinite, the substance will necessarily equilibrate to (T_0, p_0) and the environmental temperature and pressure remain unchanged. Obviously this process does zero work and is not reversible². However, because of Eq. 2, zero is therefore a lower bound on e^{tm} .

2.3 Reversibility Implications

Because \mathcal{P} is reversible at the solution to Eq. 2., the exergy is not only the maximum amount of work that can be obtained while bringing the substance into equilibrium with its environment, it is also the **minimum** theoretical work **required** to take the substance from its environment to the state of interest. For thermo-mechanical exergy, this means we are concerned only with taking the substance at state 0 (h_0, s_0) to new conditions of interest at state 1 (h_1, s_1) ³. Eq. 2 can be rewritten equivalently:

$$e^{\text{tm}} = \min_{\mathcal{Q}} w \quad (3)$$

where $\mathcal{Q} \in \mathbb{Q}$ is a process within the set of all possible processes \mathbb{Q} that bring the substance from state 0 to state 1 while consuming work w . Since all \mathcal{P}_i that are solutions of Eq. 2 are reversible, we can easily state:

Corollary 1

For each process \mathcal{P}_i that solves Eq. 2, let the reverse process be called \mathcal{Q}_i . Then all \mathcal{Q}_i are solutions to Eq. 3, and all solutions to Eq. 2 and all solutions to Eq. 3 result in the same e^{tm} .

This is simple but important. It means that e^{tm} can never be zero except at state 0, it must always

² Except for the trivial case where the substance already is at environmental conditions, in which case its thermo-mechanical exergy is 0 and it is reversible because there is no process to reverse.

³ Note we are using enthalpy and entropy pairs to describe the state so that we can include phase change intrinsically.

be positive everywhere away from state 0. If this were not true, it means it would be theoretically possible to *spontaneously* bring the substance from state 0 to state 1 *without the consumption of work*. This, however, cannot be true because then we would be able to construct a perpetual motion machine, violating the 2nd Law of Thermodynamics, as will be discussed later.

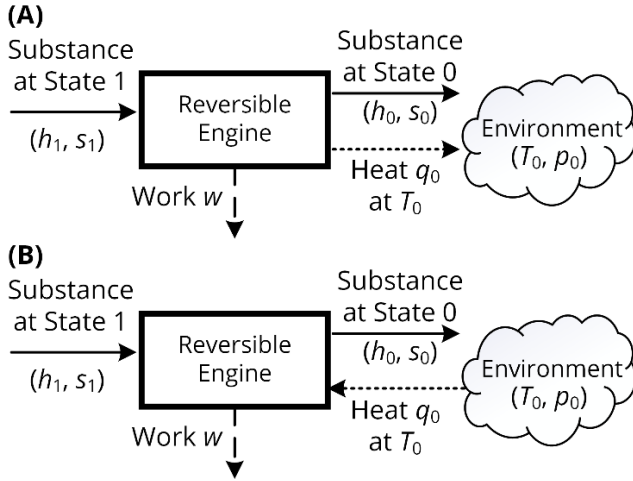


Figure 2. Process flow diagrams for computing Eq. 1. (A) when the reversible engine is such that it has waste heat to reject to the environment; (B) when the reversible engine consumes heat from the environment.

2.4 Derivation of Eq. 1

The derivation of Eq. 1 is well-known and summarized here briefly. Consider Figure 2A, which shows a generic hypothetical reversible engine \mathcal{P} that can produce work w while bringing a substance from state 1 to state 0. Figure 2A is valid for situations in which the substance at state 1 is hot enough such that there is sufficient heat above T_0 to produce work and reject heat to the environment at T_0 .

The steady-state energy balance for Figure 2A is shown below, written in the form Accumulation equals Input minus Output plus Generation:

$$0 = h_1 - (h_0 + q_0 + w) + 0 \quad (4)$$

where q_0 is the heat transferred to the environment (in terms of kJ per kg of the substance of interest). By noting that the entropy of heat q_0 at temperature T_0 is q_0/T_0 and that the entropy of work is zero, the corresponding steady-state entropy balance in the form Accumulation equals Input minus Output plus Generation using the model in Figure 2A is:

$$0 = s_1 - \left(s_0 + \frac{q_0}{T_0}\right) + s_{gen} \quad (5)$$

where s_{gen} is the entropy generated by the process. When the process is reversible, $s_{gen} = 0$, since reversible processes do not generate entropy by definition. Therefore, one can solve Eq. 5 for q_0 and substitute that into Eq. 4, and arrive at:

$$w = (h_1 - h_0) - T_0(s_1 - s_0) \quad (6)$$

However, because we are only considering a reversible process, by Theorem 1, $e^{tm} = w$ and therefore we arrive at Eq. 1.

The same procedure can be performed for “cold” exergy, considering Figure 2B. Other examples include cases in which T_1 might be somewhat above T_0 , but p_1 is well above p_0 . The energy and entropy balances for Figure 2B become:

$$0 = (h_1 + q_0) - (h_0 + w) + 0 \quad (7)$$

$$0 = \left(s_1 + \frac{q_0}{T_0}\right) - s_0 + s_{gen} \quad (8)$$

Repeating the procedure by solving for q_0 in Eq. 8 and substituting into Eq. 7 again results in Eq. 1 for reversible processes where $s_{gen} = 0$. Note that alternatively, one can simply use only Figure 2A and use a sign convention on q_0 instead of using arrows. All approaches result in Eq. 1 and are valid for the model shown in Figure 2. This derivation in various forms is well known and further explanations can be found in textbooks like Moran *et al.* (p388) [1] and Deng *et al.* (p13) [2].

2.5 Non-uniqueness of \mathcal{P}

The derivation for Eq. 1 does not require actually knowing what kind of reversible engine that is used. However, many have preferred to think about breaking the process \mathcal{P} down into two subprocesses in series, \mathcal{P}_{1*} followed by \mathcal{P}_{*0} , where \mathcal{P}_{1*} is a process where the substance moves from state 1 to some intermediate state $*$, and \mathcal{P}_{*0} is a process where the substance moves from state $*$ to state 0. In addition, it is obvious and commonly understood that if \mathcal{P} is reversible then the subprocesses are also reversible, and vice versa:

Corollary 2

Let \mathcal{P}_{AB} be a process going from state A to state B such that \mathcal{P}_{AB} can be broken down into two processes in series $\mathcal{P}_{A*} \rightarrow \mathcal{P}_{*B}$ through some intermediate state $*$. \mathcal{P}_{AB} is reversible $\Leftrightarrow \mathcal{P}_{A*}$ and \mathcal{P}_{*B} are both reversible.

Corollary 2 can be applied recursively to further break down the subprocesses.

This corollary is commonly used in the

literature to help in the computation of e^{tm} using Eq 2. For example, one common approach is to propose a \mathcal{P} consisting of two steps, a thermal step \mathcal{P}_{1*} followed by a pressure change step \mathcal{P}_{*0} . Very commonly, the \mathcal{P}_{1*} chosen is a Reversible Heat Engine (RHE), also called a Carnot Engine, which moves the substance from state 1 (T_1, p_1) to state * at (T_0, p_1) while producing work. Then \mathcal{P}_{*0} moves the substance from state * to state 0 (T_0, p_0) through isothermal expansion. This has led to a commonly used conceptual framework where e^{tm} can be *fundamentally decomposed* into thermal and mechanical (pressure) based components [6-10].

However, Marmolejo-Correa [11, 12] demonstrated⁴ that this is misleading, because one can simply choose * to be (T_1, p_0) instead, giving different processes for \mathcal{P}_{1*} and \mathcal{P}_{*0} , each producing a different value of work for each subprocess, but yet still arriving at the same total e^{tm} . In fact,

Marmolejo-Correa showed that for any * that does not cause subprocesses to cross T_0 , and even for $T_1 < T_0$:

$$-\Delta e_{1*}^{tm} = (h_1 - h_*) - T_0(s_1 - s_*) \quad (9)$$

$$-\Delta e_{*0}^{tm} = (h_* - h_0) - T_0(s_* - s_0) \quad (10)$$

$$e_1^{tm} = -\Delta e_{1*}^{tm} - \Delta e_{*0}^{tm} \quad (11)$$

such that Δe_{1*}^{tm} and Δe_{*0}^{tm} are the change in thermo-mechanical exergy of the substance during \mathcal{P}_{1*} and \mathcal{P}_{*0} respectively. By substituting Eq. 9 and Eq. 10 into Eq. 11, the * terms cancel, simply resulting in Eq. 1 for any reversible \mathcal{P} . Therefore, the thermal component and the pressure component are ambiguously defined. This shows that thermo-mechanical exergy can certainly be split into thermal and mechanical components as a conceptual or computational aid, but this decomposition is not fundamental.

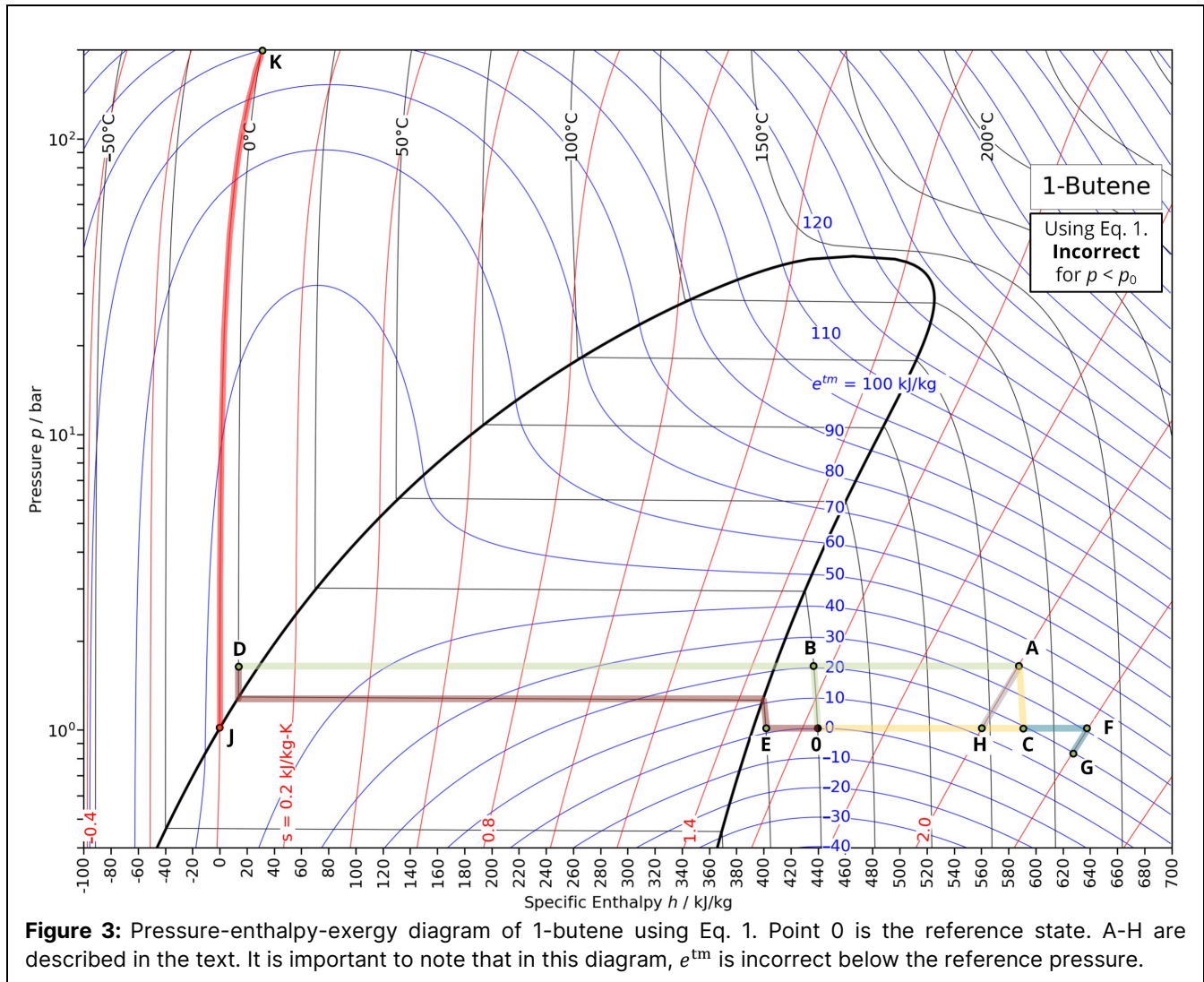


Figure 3: Pressure-enthalpy-exergy diagram of 1-butene using Eq. 1. Point 0 is the reference state. A-H are described in the text. It is important to note that in this diagram, e^{tm} is incorrect below the reference pressure.

⁴ See p34 in reference [12]

Remark 1

Marmolejo-Correa's result [11, 12] is only valid if Eq. 1 is valid since Eq. 9 and Eq. 10 assume that Eq. 1 is a valid way of computing Δe^{tm} between any two states. We will challenge this later.

2.6 Alternative Thermo-Mechanical Exergy Equation

An alternative expression for thermo-mechanical exergy has been derived for closed systems (see for example Moran *et al.* [1] p372, while neglecting the kinetic and potential energy terms not related to thermo-mechanical exergy, or McGovern [4]):

$$e^{\text{tm}} = (u_1 - u_0) + p_0(v_1 - v_0) - T_0(s_1 - s_0) \quad (12)$$

where u is specific internal energy (in kJ/kg) and v is the specific volume (in daL/kg, noting that 1 daL-bar = 1 kJ). Since $h = u + pv$ by definition, this can be rearranged:

$$e^{\text{tm}} = (u_1 + p_0v_1) - h_0 - T_0(s_1 - s_0) \quad (13)$$

Thus, Eq. 13 is equivalent to Eq. 1 if and only if $p_1 = p_0$. When $p_1 = p_0$, thermo-mechanical exergy is restricted to thermal exergy only, and can be computed using an RHE model that evaluates to the same value as computed by either Eq. 1 or Eq. 13 along p_0 . This is a well known result. Therefore we take the following as true:

Theorem 2. e^{tm} at p_0

Eq. 1 accurately computes e^{tm} of a substance at any h_1 if $p_1 = p_0$.

At other pressures, Eq. 1 and Eq. 13 produce very different quantities. Their difference (the right hand side of Eq. 1 minus the right hand side of Eq. 13) is $v_1(p_1 - p_0)$. This term is often called either the "flow work" when used in the context of flows [1] or "work interaction at a boundary" [4] more generally or in other contexts, such as boundary expansion or contraction (even for non-flowing systems).

The question considered in this paper therefore is which form (Eq. 1 or 13) should be chosen to describe the specific thermo-mechanical exergy of a substance itself. Both forms compute e^{tm} as a function of independent intensive state variables (h_1, s_1, u_1, v_1) and the reference state (h_0, s_0, u_0, T_0, p_0) which is constant. Either could be applied to a

substance in a general sense as a function of its state variables without further context as to how that substance exists in a part of some larger system.

The choice between the two depends on the definition of thermo-mechanical exergy itself. For example McGovern uses the following definition (emphasis ours) [4]:

Definition 3 (Alternate definition of thermo-mechanical exergy)

The thermomechanical exergy of any system is defined as the maximum useful work (assuming that any exergy associated with potential energy or kinetic energy remains unchanged) that could be produced by any interaction of the system with the specified reference environment **under the constraint that the system remains closed during any such interaction.**

The constraint in this definition is a key element: forcing the system to remain closed to the environment results in Eq. 13, and not having the constraint results in Eq. 1 as it is traditionally used.

As noted in Moran p.387, the Eq. 1 form is "most useful for engineering analyses" [1], and indeed our observation is that the large majority of the systems exergy analysis literature uses the Eq. 1 form. This is because most real systems of interest are not closed, and so the constraint in Definition 3 is not suitable.

That begs the question: which definition is the right one to use for computing the thermo-mechanical exergy of *substances* as a function of state, independent of application? We argue that Definition 3 is the wrong form because constraining a substance to closed systems is too limiting and impractical. Definition 1 is the preferred, more general form. According to Definition 1, exergy is the maximum amount of work a system *could* produce, which is stated as an optimization problem in Eq. 2. When seen in this context, the "system" is the substance plus any hypothetical process \mathcal{P} that brings the substance into equilibrium and is an optimal solution to Eq. 2, whether flowing or not. The e^{tm} computed is, for all intents and purposes, the specific thermo-mechanical exergy of the substance itself.

As will be discussed later, for substances at pressures other than p_0 , it is trivial to find practical processes \mathcal{P} that produce more work from a substance than the value of e^{tm} computed by Eq. 13 if the process were allowed to interact with the environment through boundary work interactions such

as compression, expansion, or mass flowing to/from the environment. Compression, expansion, or mass flowing to/from the environment are present in many real industrial applications, and so excluding them by using Eq. 13 does not seem useful. However, Eq. 1 is still incorrect below the environmental reference pressure, as discussed next.

2.7 Eq. 1 Fails Below the Reference Pressure

Figure 3 shows a pressure-enthalpy-exergy diagram (PHE) for 1-butene using Eq. 1. The figure shows the phase envelope and isometric lines for temperature, entropy, and thermo-mechanical exergy, with exergy computed using Eq. 1. State functions relating h , s , T , and p were computed using the CoolProp package in Python [13] and the equation of state for 1-butene given by Lemmon and Ihmel's [14].

In Figure 3, point 0 is the reference state ($h_0 = 439.7$ kJ/kg, $s_0 = 1.64$ kJ/kg-K). Consider point A. Marmolejo-Correa's work [12] showed that one can compute the e^{tm} at A by first computing the exergy change at constant pressure by moving from A to B reversibly, and then compute the exergy change at constant temperature by moving to point 0 reversibly (process $\mathcal{P}_{A0} = \mathcal{P}_{AB} \rightarrow \mathcal{P}_{B0}$). Marmolejo-Correa showed that this is equivalent to $\mathcal{P}_{A0} = \mathcal{P}_{AC} \rightarrow \mathcal{P}_{C0}$ by doing the reversible isothermal pressure change first, followed by the reversible isobaric temperature change. Similarly, she showed that this applies to point D which has a lower temperature than T_0 . Again, Marmolejo-Correa showed that one could choose two paths, DB0 or DE0 to get the same exergy value. However, her work did not consider pressures below the reference pressure.

Figure 3 is based on Eq. 1, which clearly fails for $p < p_0$. First, there is a large region where e^{tm} is zero or negative, which is impossible as noted in Section 2.2. Everything on or below the $e^{\text{tm}} = 0$ line, which occurs whenever $(h_1 - h_0) \leq T_0(s_1 - s_0)$, violates this principle and must be wrong.

Second, even the positive values below p_0 are too small. Consider point G ($s_G = 2.2$ kJ/kg-K, $h_G = 627.3$ kJ/kg), which on this plot has $e^{\text{tm}} = 20.0$ kJ/kg. It is quite easy to show that this value is not the true solution to Eq. 2 because one can propose a process $\mathcal{P}_{G0} = \mathcal{P}_{GF} \rightarrow \mathcal{P}_{F0}$ that generates more than 20 kJ/kg of work. This proposed process consists of isentropic compression of 1-butene from point G to F ($s_F = s_G$, $p_F = p_0$, and $h_F = 638.6$ kJ/kg), using the environment as the source of work, followed by isobaric cooling from F to 0. One simple

device to accomplish this might be to place the substance at state G inside of a movable piston-cylinder apparatus with a turbine attached such that it can produce shaft work. The atmospheric pressure p_0 is higher than the pressure p_G , so the environment will push the piston down, compressing the substance isentropically (adiabatically and reversibly) until it reaches p_0 , producing work w as it does. The work is easily computed by the enthalpy difference between G and F ($w = h_F - h_G$) which is 11.3 kJ/kg.

Now at point F, the substance in the piston-cylinder is at p_0 but at a higher temperature T_F . More work could be produced using the substance as a heat source to power an RHE in process \mathcal{P}_{F0} . The reversible work for that step would be computed by Theorem 2, which is $(h_F - h_0) - T_0(s_F - s_0) = 31.3$ kJ/kg. Therefore, the proposed machine should be able to produce $11.3 + 31.3 = 42.6$ kJ/kg of work total. Even an irreversible, imperfect machine should be able to produce more than 20 kJ/kg. So clearly, the exergy numbers calculated by Eq. 1 are incorrect below the reference pressure by using arguments from Eq. 2.

Kotas [3] considered a similar situation, but for a point in the low-pressure region where Eq. 1 is negative. There, Kotas proposed a very similar machine to our previous example (the GFO process), with isentropic compression of a substance at low pressure followed by an RHE. However, he erred by determining that the compression step would *consume* external work, offset by work produced in the RHE step, resulting in a negative exergy value since the isentropic compression step had a higher w than the w of the RHE in his example. This approach is essentially to apply Eqs. 9 and 10 naively, resulting in the direct application of Eq. 1. The text incorrectly concluded that negative exergies therefore can exist. It is easy to see why though; this seems at first to be in line with Definition 2 of exergy, since after all, both proposed steps in his machine are in fact reversible. Though technically correct, the particular language of Definition 2 is likely the source of confusion because it defines exergy as the "work obtainable" and thus only *implies* that it is the maximum work attainable, rather than using a stronger statement like "maximum theoretical work" in Definition 1. In the end, the Kotas example clearly does not solve the more basic Definition 1 as expressed explicitly in Eq. 2.

If Eq. 1 is derived from the abstract fundamental energy and entropy balances shown in Figure 2,

to be correct by Theorem 2), bringing the total work to 40.0 kJ/kg for this machine, far greater than the about 17 kJ/kg predicted by Eq. 13. In fact, 40.0 kJ/kg is the same exergy predicted by Eq. 1, implying that Eq. 1 is likely correct for point A given Theorem 2.

Although not shown for brevity, a similar check of the low-pressure region shows Eqs. 1 and 13 to be under-estimates as well. This means that both Eq. 1 and Eq. 13 are incorrect below p_0 .

Therefore, the closed form of thermo-mechanical exergy (Eq. 13) is not an appropriate choice for computing the thermo-mechanical exergy of **substances** at any pressure except at the reference pressure. Similarly, the specific-flow exergy form (Eq. 1) is also not appropriate for pressures below the reference pressure. This is addressed next.

3. THERMO-MECHANICAL EXERGY AT ALL PRESSURES

3.1 Derivation

We now derive a new equation for e^{tm} based on Definition 1 expressed in the optimization form of Eq. 3. We could use Eq. 2 equivalently, but our experience has shown that the Eq. 3 approach is easier to follow. To find e^{tm} of a substance at point 1 (e_1^{tm}) at any temperature, pressure, or phase, we propose the following process:

$$Q_{01} = Q_{0*} \rightarrow Q_{*1} \quad (14)$$

where Q_{01} is broken into two subprocesses through an intermediate point *. Point * is selected such that it is at state (p_0, s_1) .

The subprocess Q_{0*} that requires the minimum work is very well known: an RHE run in reverse (*i.e.* a reversible heat pump, or RHP) that performs isobaric enthalpy change (including both temperature and phase change if necessary). The subprocess Q_{*1} that requires the minimum work is also very well known: an isentropic compression performed in a piston-cylinder arrangement by pushing the piston down or an isentropic expansion for lowering the pressure below p_0 , by pulling the piston up. For example, to arrive at point A in either Figure 3 or 4, one could follow the path OHA, where H is the intermediate point *.

If we select those two reversible pathways (Q_{0*} and Q_{*1}), then by Corollary 2 we know that Q_{01} is reversible since both of the subprocesses are reversible. Furthermore, because those two subprocesses require the minimum work and Q_{01} is

reversible, process Q_{01} also requires the minimum work to get from point 0 to point 1. Then we know by Corollary 1 that the total work required for process Q_{01} is a solution to Eq. 3 and therefore equal to e_1^{tm} .

To be sure, there are many other pathways and approaches that could be proposed instead. However, by Corollary 1, a single pathway is sufficient.

For pathway 0* (for example, paths OH or OE in Figures 3 and 4), the work required using subprocess Q_{0*} is equal to its exergy change. Since this is an RHP, by Theorem 2, this is simply:

$$\Delta e_{0*}^{\text{tm}} = -w_{0*} = (h_* - h_0) - T_0(s_* - s_0) \quad (15)$$

Since we are choosing * to be at the state (p_0, s_1) , we can simplify Eq. 15:

$$\Delta e_{0*}^{\text{tm}} = -w_{0*} = (h_* - h_0) - T_0(s_1 - s_0) \quad (16)$$

For pathway *1 (for example, paths HA or FG in Figures 3 and 4), the work required using subprocess Q_{*1} is equal to its exergy change. Since this is isentropic expansion or compression, this is simply:

$$\Delta e_{*1}^{\text{tm}} = |h_1 - h_*| \quad (17)$$

The absolute value is important to make it general to both expansion and compression away from p_0 . For example, for the reversible pathway HA, the enthalpy difference $h_A - h_H$ (or $h_1 - h_*$) is the minimum work required. For the reversible pathway FG, the minimum work required is $h_F - h_G$ (or $h_* - h_1$) which equals $|h_G - h_F|$ (or $|h_1 - h_*|$).

Noting that $\Delta e_{0*}^{\text{tm}} = -\Delta e_{*0}^{\text{tm}}$ and $\Delta e_{*1}^{\text{tm}} = -\Delta e_{1*}^{\text{tm}}$, we can then combine Eqs. 11, 16 and 17 for process Q_{01} and compute the total thermo-mechanical exergy at state 1:

$$e_1^{\text{tm}} = |h_1 - h_*| + (h_* - h_0) - T_0(s_1 - s_0) \quad (18)$$

where $h_* = h(p_0, s_1)$.

3.2 Discussion

Note that when $p_1 \geq p_0$, $|h_1 - h_*| = h_1 - h_*$ since $h_1 \geq h_*$ for all states 1 at or above the reference pressure. Thus Eq. 18 reduces to Eq. 1 for all $p_1 \geq p_0$. Eq. 18 was not derived from the general energy and entropy balances of Figure 2. It only relies on Theorem 2, which is the computation of exergy for a reversible heat engine at the reference pressure agreed upon by both Eq. 1 and Eq. 13. This is important because it means that Eq. 1 is correct for all $p_1 > p_0$. Eq. 13 underestimates exergy in these cases because we can always propose a process P_{10} that is the reverse of process Q_{01} of Eq. 14,

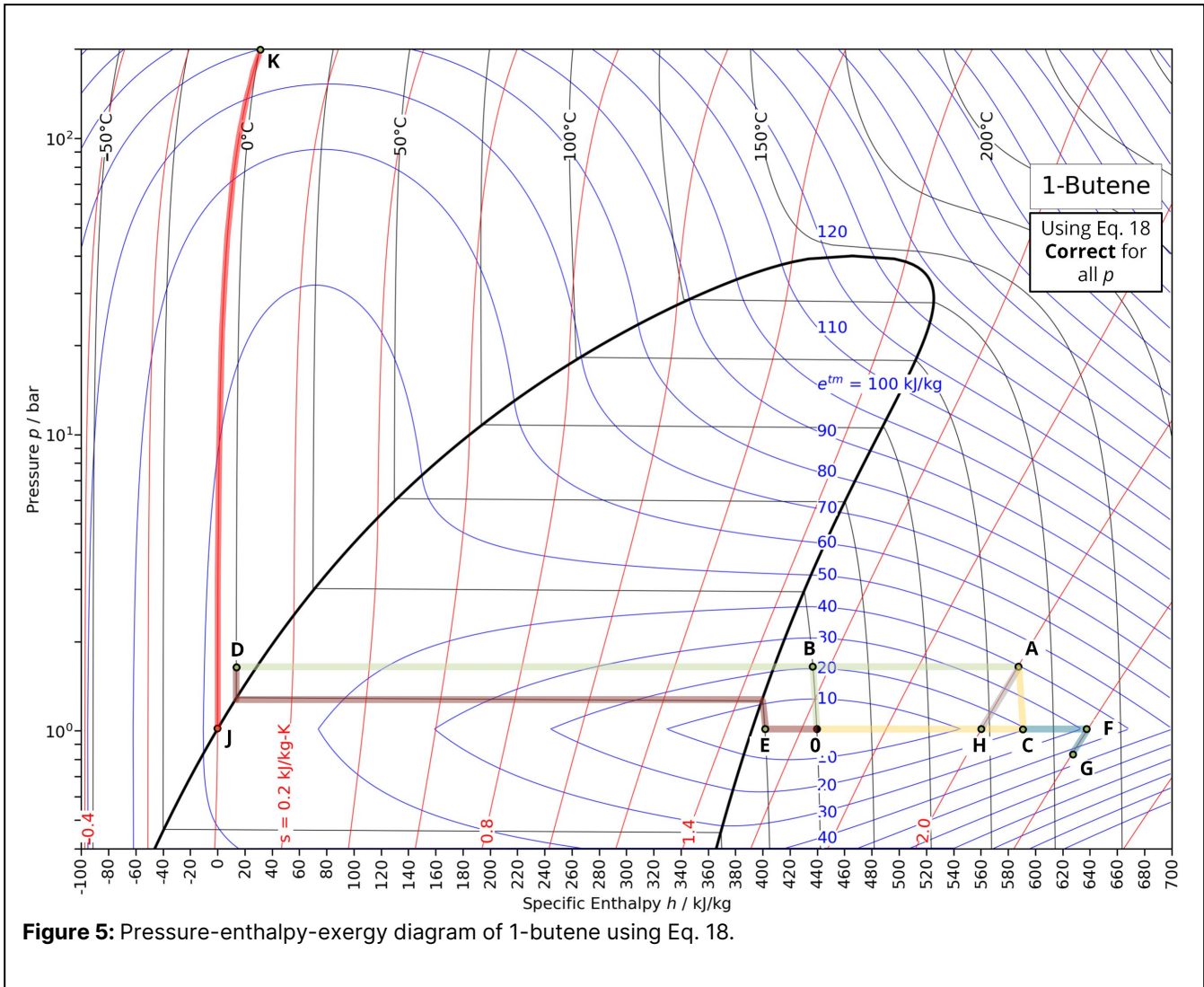


Figure 5: Pressure-enthalpy-exergy diagram of 1-butene using Eq. 18.

which would produce at least as much work as Eq. 1 and is always higher than the value computed by Eq. 13.

Below atmospheric pressure, $|h_1 - h_*| = h_* - h_1$, such as path FG in Figures 3 and 4. This is the work required to perform process Q_{FG} , which is to expand the fluid isentropically against the surrounding environment. For example, a substance could be in a piston-cylinder device at state F and then work would be required to pull the piston up to state G, such that the fluid is now at a lower pressure and temperature because of its expansion. This means Eq. 18 could be rewritten:

$$e_1^{tm} = \begin{cases} (h_1 - h_0) - T_0(s_1 - s_0) & p_1 \geq p_0 \\ ((2h_* - h_1 - h_0) - T_0(s_1 - s_0)) & p_1 \leq p_0 \end{cases} \quad (19)$$

By recognizing that process Q_{FG} requires the consumption of work to reduce the pressure of a substance below p_0 , it is easy to see that its reverse, P_{GF} , should produce work by the same amount. The mistake of Kotas [3] noted in Section 2.7 was, for

all intents and purposes, equivalent to computing $\Delta e_{*1}^{tm} = h_1 - h_*$ instead of $\Delta e_{*1}^{tm} = |h_1 - h_*|$. The erroneous result is Eq. 1 at low pressures, leading to negative exergies.

In another example, Szargut *et al.*'s classical book (p25) [15] provides an example using the closed form (Eq. 13) for ideal gas air at reduced pressure ($p_1 = 0.3$ bar, $T_1 = T_0 = 290$ K, $p_0 = 1$ bar), resulting in a positive e^{tm} of 94 kJ/kg. However, this value is too small, since from Eq. 18 (using a real equation of state [16]) the value should be 139 kJ/kg. The difference is not explained by Szargut's assumption of ideal gas equation of state (we determined that using the rigorous equation of state for air resulted in only a 0.01 kJ/kg differential in e^{tm}). It is ultimately explained by a difference in the boundary work term.

Figure 5 shows the final PHE diagram for 1-butene using Eq. 18. Here, exergy is everywhere positive. All points above p_0 have e^{tm} equivalent to Eq.

1, all points below p_0 have e^{tm} greater than from Eq. 13, and all points at p_0 are equal to both Eq. 1 and Eq. 13. They are characteristically different from the lines in Figures 3 and 4 in two key ways.

First, the lines in Figure 5 are non-smooth at p_0 with respect to Δp , which is a direct consequence of the absolute value in Eq. 18. This is important because the absolute value ensures that exergy always increases along a path of constant entropy as p moves away from p_0 . In other words:

$$\left. \frac{\partial e^{tm}}{\partial p} \right|_s \begin{cases} < 0, p < p_0 \\ \text{undefined}, p = p_0 \\ > 0, p > p_0 \end{cases} \quad (20)$$

Conceptually this makes sense, as we move isentropically away from the environmental reference pressure, e^{tm} should always increase. It should always require work to do this kind of operation. One can see that this fails for Eq. 1 in Figure 3 below p_0 because as we move down along an isentropic line, exergy decreases in general, which does not make sense. For that part of Figure 3, $\left. \frac{\partial e^{tm}}{\partial p} \right|_s < 0$ as p moves away from p_0 toward zero.

Second, in Figure 4 for Eq. 13, one can see that as we move away above atmospheric pressure along an isentropic line in the liquid and supercritical liquid phases, $\left. \frac{\partial e^{tm}}{\partial p} \right|_s \approx 0$ as p goes away from p_0 towards infinity. In other words, e^{tm} never increases (or increases trivially little) as pressure increases for isentropic compression. This would imply that it essentially requires zero work to pump liquids to extremely high pressure with a perfect pump, or that the work is so small that it could be neglected. For example, consider the point J at $s_j = 0$ kJ/kg-K, $h_j = 0$ kJ/kg, $p_j = 1$ bar (a saturated liquid) in Figure 4. Follow the isentropic red line up to point K at $p_K = 200$ bar and $T_K = 0.3^\circ\text{C}$ (the x-axis boundary at the top), which would be a reversible compression with a perfectly efficient reversible pump. The energy required is the enthalpy difference $h_K - h_j$, or 31.4 kJ/kg of work, which means the exergy should be 31.4 kJ/kg larger than it was as a saturated liquid in any practical context. However, it is not; the exergy of K is only slightly higher than that of J as computed by Eq. 13 ($e_j^{TM} = 48.7$ kJ/kg and $e_K^{TM} = 49.0$ kJ/kg). This clearly cannot be correct, otherwise we could pump liquids for almost free in practice. The same operation in Figure 5 reflects the expected 31.4 kJ/kg increase in exergy (using Eq. 18, $e_j^{TM} = 48.7$ kJ/kg and $e_K^{TM} = 80.1$ kJ/kg). So Eq. 13 is

clearly not a good representation of thermo-mechanical exergy of a substance in this region since there is no meaningful difference in exergy between a normal liquid and a supercritical one at the same entropy.

One other observation of interest is that Eqs. 1, 13, and 18 also converge toward agreement with each other in the liquid phase region at sub-ambient pressures and temperatures. For example, the lines for $e^{tm} = 60$ and 70 kJ/kg in Figures 3, 4, and 5 all are essentially the same in the small region on the lower left of the figures where $p < p_0$ and $h < 60$ kJ/kg.

The isoexergy lines are all almost vertical in this region because the isentropic lines are also almost vertical. This means that $|h_1 - h_*| \rightarrow 0$ there and so the difference between Eq. 1 and Eq. 18 also approaches zero, but from opposite sides. Thus the work associated with boundary interactions in this region approaches zero.

3.3 Non-smoothness Analogy with Thermal Exergy of Heat

It is important to point out that the non-smoothness of thermo-mechanical exergy of a substance when passing the reference pressure p_0 is analogous to a much more familiar and widely accepted concept. Figure 6 shows the thermal exergy of heat (not a substance) E^{th} relative to the amount of heat Q as a function of temperature T , according to the well-known equation of thermal exergy [11]:

$$\frac{E^{th}}{Q} = \begin{cases} 1 - \frac{T_0}{T}, T \geq T_0 \\ \frac{T_0}{T} - 1, T \leq T_0 \end{cases} \quad (21)$$

Eq. 21 contains a non-smoothness when passing the reference point (at T_0) because the fundamental mechanisms of heat transfer are different above and below T_0 . Above T_0 , heat at T flows from the heat source to the environment. Below T_0 , heat at T_0 flows from the environment to the heat sink. It is not unexpected then that the thermo-mechanical exergy of a **substance** should also show non-smoothness about the reference point in Eq. 18 because the fundamental mechanisms for energy transfer between the substance and the environment are different above and below p_0 .

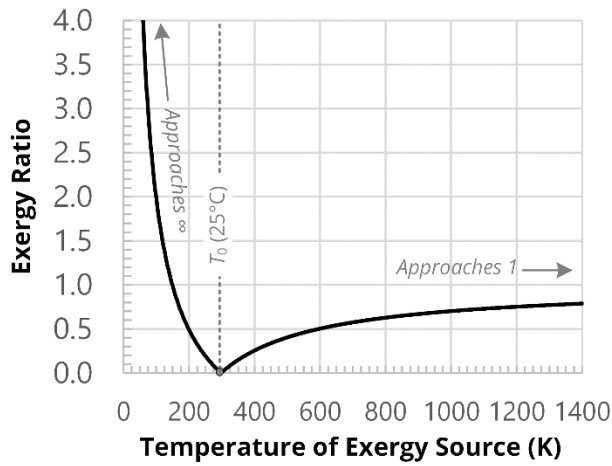


Figure 6: Thermal exergy of heat (not substances) using Eq. 21. The exergy ratio is $\frac{E^{th}}{Q}$ in Eq. 21.

3.4 An Example with a Normal Liquid

Figure 7 shows a PHE diagram of R113 (1,1,2-

trichloro-1,2,2-trifluoroethane, a normal liquid) generated using Eq. 18 and the equation of state of Marx *et al.* [17]. For this normal liquid example, the reference state is in the liquid (left) side of the phase envelope, which results in a characteristically different shape from the normal gas example in Figure 5.

In Figure 7, the iso-exergy lines are much more convex in nature, especially in the lower enthalpy, high pressure regions of the diagram. However, the shapes formed by the iso-exergy lines are still not completely convex, as can be seen most easily in the area where iso-exergy lines cross the phase envelope above the reference pressure. The non-smooth nature of the iso-exergy lines at the reference pressure is also evident in this example as well. Similarly, the nearly vertical iso-exergy lines in the low pressure, low temperature liquid region remain a characteristic, since the isentropic lines are also nearly vertical.

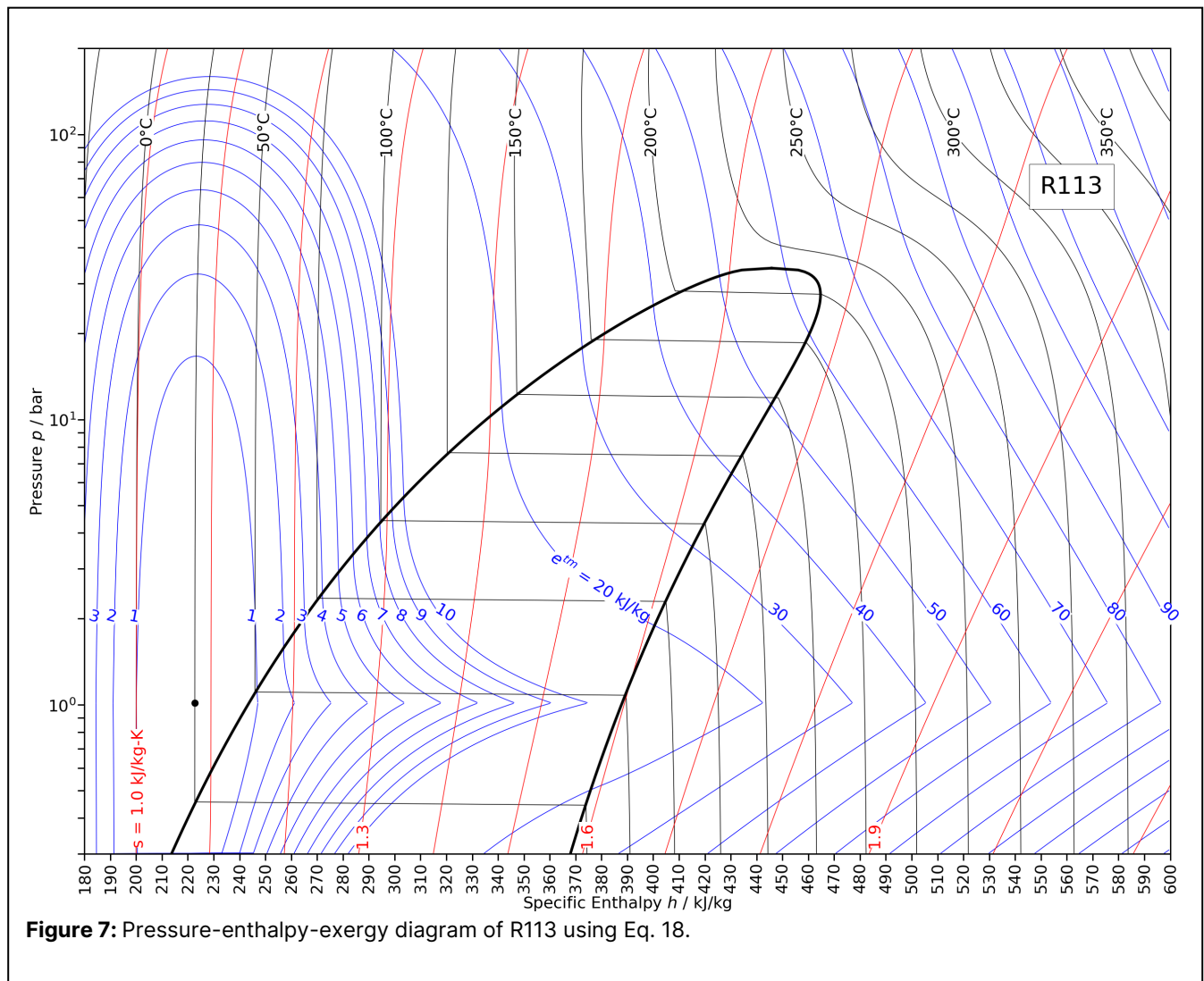


Figure 7: Pressure-enthalpy-exergy diagram of R113 using Eq. 18.

3.5 Further Examples

Although not shown for brevity, we also found that the characteristics shown in this work for 1-butene and R113 are the same for 25 other real chemicals, including water, air, and many normal liquids and normal gases. We did not find a single counter example for any real chemical. Pressure-enthalpy-exergy diagrams for these can be found in Deng *et al.* [2].

3.6 Other choices of p_0

Because Eq. 18 is general, it holds for any p_0 regardless of its value. Whether the analyst has chosen a p_0 that is correct for the analysis at hand is a different matter. For example, if analyzing substances on the surface of Mars, or in case-specific systems where there is a huge low-pressure reservoir that effectively serves as the environmental sink for analysis purposes and not the actual planetary environment on which it sits, the analyst should choose an appropriate p_0 lower than 1 atmosphere. The selection of appropriate reference conditions is always an important part of any exergy analysis.

3.7 Accuracy of Calculations

Like Eqs. 1 or 13, the accuracy of the exergy value computed in Eq. 18 is limited to the accuracy of the model or method used to compute the underlying enthalpies and entropies of a substance at any given state. For this work, the accuracy of Figures 5 and 7 are therefore limited to the accuracy of the equation of state models developed in references [14] and [17] respectively as implemented by CoolProps [13]. For the 1-butene case, Lemmon *et al.* [14] compared the equation of state to 52 different experimental data sets measuring densities, heat capacities, vapour pressures, heats of vaporization, and other properties, and found an average absolute deviation between model and experiment of less than 1% in most cases for the applicable pressure ranges used in this work. Span and Wagner [18] compared the equation of state in [17] to 16 different experimental data sets in a variety of categories and found average absolute deviations between model and experiment to be less than 0.6% in all cases, with most being below 0.2%.

CONCLUSIONS

The new equation for thermo-mechanical exergy e^{tm} derived in Eq. 18 should be used for fluids

in general, flowing or not, at all temperatures and pressures. It reduces to the classical Eq. 1 when $p_1 \geq p_0$. Since the vast majority of exergy analysis applications occur at or above environmental pressure, this means that most previous work using Eq. 1 is correct. However, any previous calculations using Eq. 1 below p_0 are underestimates of e^{tm} and should be recalculated by adding $2(h_* - h_1)$ to the previously computed value to get the new exergy value using Eq. 18. $2(h_* - h_1)$ is simply the difference between Eq. 1 and Eq. 18 when $p_1 < p_0$. Note that this is only applicable if the reference conditions are the same.

The results here are significant because they resolve the inconsistencies in formulas and interpretations found in the literature, many of them in widely used textbooks. Our more general equation relies only on the most basic form of the exergy definition and the portions of exergy calculations in which the literature is in complete agreement. This is in contrast to the classical “flow exergy” form which is derived from an incomplete model that allows potential energy (pressure) from the substance to be released to the surroundings (when $p > p_0$), but not the reverse direction. In other words, it fails below the reference pressure because it then fails to satisfy Definition 1.

Because Eq. 2 is an optimization problem, the only way Eq. 18 cannot be the correct solution at any p is if one could find a process $\mathcal{P} \in \mathbb{P}$ that produces more work to go from state 1 to 0 than the value computed by Eq. 18 (without violating the laws of thermodynamics). Conversely, one could disprove Eq. 18 by finding a process $\mathcal{Q} \in \mathbb{Q}$ that requires less work to go from state 0 to state 1 than the value computed by Eq. 18. However, as explained in Section 3.1, Eq. 18 should be the global optimal solution to Eq. 2 or Eq. 3 and thus Eq. 18 computes the true thermo-mechanical exergy for a substance. Even if someone could find a process \mathcal{P} that produces more work than the value computed by Eq. 18, the conclusion that the “flow exergy” form of thermo-mechanical exergy (Eq. 1) below the reference pressure is incorrect would remain unchanged.

For future work, it would be interesting to confirm Eq. 18 below the reference pressure by using a generalized optimal process synthesis approach in which Eq. 2 is solved using mathematical programming algorithms to provable global optimality (within convergence tolerances). For example, it should be possible to use formal superstructure

optimization approaches in which a large number of possible processes (but still a subset of \mathbb{P}) is considered that would arrive at the same values as Eq. 18, but not higher. A more difficult but more powerful approach would be to somehow include all \mathbb{P} in the decision space (which is infinite) into the mathematical programming formulation.

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NOMENCLATURE

e	specific exergy (in kJ/kg)
E	exergy (in kJ)
h	specific enthalpy (in kJ/kg)
p	pressure (in bar)
q	heat (in kJ/kg) relative to substance of interest
Q	heat (in kJ)
\mathcal{P}, \mathcal{Q}	a thermo-mechanical process. We use \mathcal{P} to distinguish processes that produce work from processes \mathcal{Q} that consume work.
\mathbb{P}	the set of all thermo-mechanical processes that bring a substance from state 1 into equilibrium with its environment at state 0.
\mathbb{Q}	the set of all thermo-mechanical processes that bring a substance from the environmental state 0 to state 1.
s	specific entropy (in kJ/kg-K)
T	temperature (in K)
u	specific internal energy (in kJ/kg)
v	specific volume (in daL/kg = kJ/bar-kg)
w	specific work (in kJ/kg)

Subscripts and Superscripts

0	at the reference state
1	at a state of interest
*	at some intermediate state
i	an index
gen	generated
tm	thermo-mechanical
work	work

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