

Thermo-Mechanical Exergy of a Substance in Cold Applications Approaching Absolute Zero

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ABSTRACT

In this work, we consider the thermo-mechanical exergy of a substance for cold applications, even as it approaches absolute zero. This is relevant for cold-service applications such as refrigeration, liquefied natural gas, air separation, and liquid hydrogen. We demonstrate how the optimization formulation for the determination of exergy is the most suitable way for process systems engineers to think about exergy. We provide an illustrative example by computing thermo-mechanical exergy of neon approaching absolute zero. We also discuss how this result relates with the Third Law of Thermodynamics, both how it is used to compute thermo-mechanical exergy, but also what it implies about the validity of the results and the equations used to compute them.

Keywords: Exergy, thermo-mechanical exergy, absolute zero, neon, low temperature

1. INTRODUCTION

Exergy is a thermodynamic property of matter and energy which describes both the quantity and the quality of an energy source by combining the First and Second Laws of Thermodynamics. It is quite useful in the design of chemical process systems, especially energy conversion systems common in chemical engineering. Exergy as a metric helps in identifying process bottlenecks, improving system efficiency, making prudent design decisions, understanding energy quality, and as an approximation for value or cost. As a result, it is increasingly popular as a systems analysis tool in scientific research, with exergy analyses considered in over 2500 journal articles published in 2022 alone (Figure 1), growing exponentially at about 14% per year.

1.1 General Definition

Although there are several competing definitions for exergy, the Moran *et al.* [1] definition is the most useful, the most general, and the easiest to understand for chemical engineering purposes. Our emphasis is in bold, and the definition is quoted as:

Definition 1. (Definition of Exergy)

Exergy is the **maximum** theoretical work obtainable from an overall system consisting of a

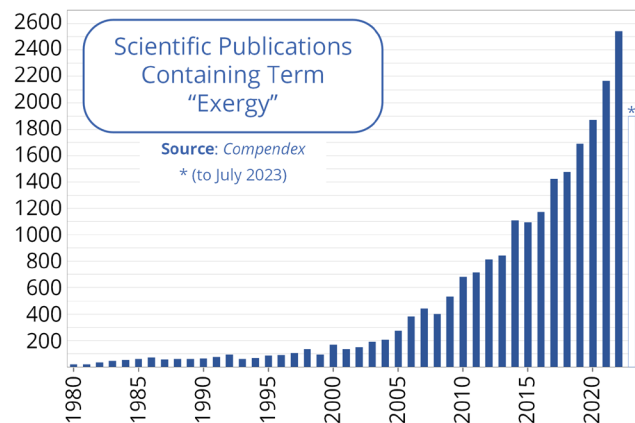


Figure 1. Scientific publications involving exergy

system and the environment as the system comes into equilibrium with the environment (passes to the dead state). [1]

This describes exergy generally, for all kinds of systems, and considering all forms of energy that contribute to the calculation of exergy. For the process systems engineer, it is convenient and useful to understand this definition in terms of an optimization problem [2]:

$$e = \max_P w \quad (1)$$

where e is the exergy of the system, \mathcal{P} is a process that brings the system into equilibrium with its environment within the set of all such processes \mathbb{P} such that $\mathcal{P} \in \mathbb{P}$, and w is work that is produced by \mathcal{P} . Process engineers understand optimization, and so it makes sense then to understand exergy in the form of an optimization problem. In plain language, it means that one way to compute the exergy is to find a process \mathcal{P} that produces the absolute most amount of work possible, exploiting everything possible that can be exploited, using perfect, reversible, and lossless process steps. \mathcal{P} does not have to be unique; many processes could do this in theory. This concept is general and applies to all forms of exergy.

1.2 Thermo-mechanical exergy

In this work, we consider only the specific thermo-mechanical exergy (e^{tm}) of substances (noting that photons are not considered substances for this analysis), which includes the contribution of temperature, pressure, and phase of a substance. It does not consider exergy arising from chemical composition of that substance, atomic energy, motion, height, electrostatic charge, stress, strain, or other forms of energy.

As shown in [2], the following equation is one solution to the optimization problem of eq. (1) for the case of the thermo-mechanical exergy of a substance at state 1 (e_1^{tm}) relative to environmental reference state 0:

$$e_1^{tm} = |h_1 - h_*| + (h_* - h_0) - T_0(s_1 - s_0) \quad (2)$$

where h and s are the specific enthalpy and specific entropy (on a per mass or per mole basis) of a substance at state 0, *, or 1 [1, 2]. State 0 describes the surrounding environment, typically chosen by the person doing the analysis to be at about 1 atm and between 15–25°C for systems on the surface of the earth. State * is an intermediate state at pressure $p_* = p_0$ and $s_* = s_1$, such that the work required/produced from isentropic pressure change between state 1 and * is $|h_1 - h_*|$, and the work required/produced from an isobaric reversible heat pump/reversible heat engine between state 0 and * is $(h_* - h_0) - T_0(s_1 - s_0)$. Eq. (2) uses the so-called “flow exergy” form, which is exergy for systems in which mass can be exchanged with the environment. As discussed previously [3], eq. (1) differs from the classical thermo-mechanical exergy expression below ambient pressure. The classical form of thermo-mechanical exergy has historically been expressed as [4]:

$$e_1^{tm} = (h_1 - h_0) - T_0(s_1 - s_0) \quad (3)$$

Note that eq. (2) reduces to eq. (3) for $p_1 \geq p_0$. However, our previous work [2] showed that eq. (3) is inaccurate for $p_1 < p_0$ because it does not solve the optimization problem in eq. (1). In short, it arises from a theoretical model that is not general enough and constrains the problem to a suboptimal solution. As a result, if eq. (3) is

used for $p_1 < p_0$ it can result in too-low or even negative values of e_1^{tm} , which is not meaningful.

In this work, we address a much-neglected aspect of thermo-mechanical exergy of a substance, namely, its behaviour as the temperature of a substance approaches absolute zero. We discuss considerations relating to the Third Law of Thermodynamics and the Unattainability Principle regarding absolute zero. We provide a proof that e_1^{tm} is finite as $T_1 \rightarrow 0\text{ K}$ that is general for all pressures. This work also contains enthalpy-pressure-exergy and temperature-exergy diagrams of neon, with the latter being first quantified values approaching absolute zero in the literature to the best of the author’s knowledge.

2. e_1^{tm} AS TEMPERATURE APPROACHES ABSOLUTE ZERO

2.1 The Third Law of Thermodynamics

The Third Law of Thermodynamics deals with the thermodynamic properties of matter as it approaches absolute zero. A modern definition is “that any process cannot reach absolute zero temperature in a finite number of steps and within a finite time” [5]. This leads to several useful corollaries.

Corollary 1

The absolute entropy of a substance in thermal equilibrium, which is the total entropy of a system, tends toward zero, from above, as temperature approaches 0 K.

This is a rephrasing of the description in [6]. The exception to this rule is if the substance has a degenerate ground state at absolute zero; but nevertheless, the absolute entropy (s^{abs}) would still be finite and zero in nearly all cases, and if not, very small [7]. This leads to a second corollary, directly quoted here:

Corollary 2

The heat capacity of a substance tends toward zero, from above, as temperature approaches 0 K. [7]

A simple explanation is that a substance at absolute zero cannot have any heat capacity. If it were to absorb even the slightest bit of energy, such as from a single photon collision, the temperature of the substance must increase. Otherwise, by definition, it would not have been at absolute zero in the first place. However, since it is incredibly difficult to experimentally measure heat capacity near absolute zero, models and extrapolations are needed [6].

2.2 e_1^{tm} of a substance is finite as $T \rightarrow 0\text{ K}$

In this section, it should be noted that this proof

applies only to the thermo-mechanical exergy of substances, not matter generally, nor exergy generally.

2.2.1 Enthalpy

We start with eq. (3) because it is easier to follow, noting that this equation is valid for $p_1 \geq p_0$. We first note that h_0 , T_0 , and s_0 are fixed environmental reference conditions and of course finite. Therefore, to show that e_1^{tm} is finite, we need only to show that h_1 and s_1 are finite as $T_1 \rightarrow 0 K$. h_1 for any pure substance is:

$$h_1 = h_{ref} + \int_{T_{ref}}^{T_1} C_p(T) dT \quad (4)$$

Where T_{ref} is some arbitrarily chosen temperature at the thermodynamic reference state such that h_{ref} is defined (usually to be 0) at $T = T_{ref}$. In this formulation, the heat capacity equation $C_p(T)$ applies to the same pressure as state 1. It is important to note that the thermodynamic reference state here need not be the same as the environmental reference state. For convenience, write the equations such that the chosen reference state is at the same phase as at absolute zero (such that we do not have to consider latent heats as $T \rightarrow 0 K$).

In the limit as $T_1 \rightarrow 0 K$, eq. (4) becomes:

$$h_{0K} = h_{ref} + \int_{T_{ref}}^{0K} C_p(T) dT \quad (5)$$

Note the integral term evaluates to a negative number for any thermodynamic reference temperature $T_{ref} > 0 K$. $C_p(T)$ is finite at any T and approaches zero in the limit as $T \rightarrow 0 K$ by Corollary 2. As a result, the integral term must be finite as well, and so must be the enthalpy.

2.2.2 Entropy

Corollary 1 does not imply that $s_1 \rightarrow 0$ because s_1 is not the absolute entropy, it is the thermodynamic entropy relative to the thermodynamic reference state. However, the absolute entropy s^{abs} , which is the entropy calculated on an absolute scale, and the specific entropy s , which is the entropy calculated relative to a reference condition, are easily related by a constant:

$$s_1^{\text{abs}} - s_{ref}^{\text{abs}} = s_1 - s_{ref} \quad (6)$$

The thermodynamic reference entropy s_{ref} is defined to be zero at some $T_{ref} \geq 0 K$, with a corresponding absolute reference entropy equal to $s_{ref}^{\text{abs}} = s_{0K}^{\text{abs}} + \int_{0K}^{T_{ref}} \frac{C_p(T)}{T} dT$. s_{0K}^{abs} is usually zero (but at least non-negative) and finite (corollary 1) and $\int_{0K}^{T_{ref}} \frac{C_p(T)}{T} dT$ is non-negative and finite (corollary 2), so s_{ref}^{abs} is non-negative and finite. By eq. (6) s_1 is finite and usually negative as $T_1 \rightarrow 0K$ unless the reference condition chosen is absolute zero.

2.2.3 Exergy

Since h_1 and s_1 are finite as $T_1 \rightarrow 0 K$, and h_0 , T_0 , and s_0 are known and constant, e_1^{tm} is also finite as $T_1 \rightarrow 0K$

(so far shown only for the $p_1 \geq p_0$ case). Moreover, since exergy can never be negative [2], e_1^{tm} is always positive and finite, except at the environmental reference state, where it is zero. Modifications to this analysis to include enthalpy or entropy terms considering phase change or multiple species do not change the result that the exergy must be finite at absolute zero.

2.2.4 When $p_1 < p_0$

For sub-ambient pressures as $T_1 \rightarrow 0 K$, $h_1 \leq h_* \leq h_0$. Since h_0 and h_1 are finite, h_* is always bounded between them. Therefore, e_1^{tm} in eq. (1) is always finite in the limit as $T_1 \rightarrow 0 K$, at any pressure.

2.2.5 Remarks

Petela [8] presented a similar proof that e_1^{tm} is finite as $T_1 \rightarrow 0 K$, but the proof required that the $C_p(T)$ equation had a particular form ($C_p(T) = mT^3$). It also used eq. (3) and so did not apply to pressures below p_0 . In fact, the author used weak language concerning eq. 3, declaring that e_1^{tm} “**might** be expressed as [eq. (3)]” (emphasis ours) [8]. This kind of language is strangely common in the exergy literature when referring to eq. (3), and perhaps indicates a general uneasiness when using it. Therefore the above proof is stronger and applies to all pressures.

It is also interesting to note also that for a pure substance, $\left(\frac{\partial s}{\partial p}\right)_h < 0$ and $\left(\frac{\partial s}{\partial p}\right)_h$ tends toward zero from above as $T_1 \rightarrow 0 K$. This is visually apparent as nearly vertical iso-entropy lines on a pressure-enthalpy diagram below atmospheric pressure and at low temperature, as shown repeatedly in [3], and also evident on the example for neon in Figure 2, discussed in the next section. As a result, $h_* \rightarrow h_1$ from above as $T_1 \rightarrow 0K$. So, eq. (2) tends toward to eq. (3) as $T_1 \rightarrow 0 K$ at low pressures.

3. EXAMPLE WITH NEON

Neon is a noble gas used as a cryogenic refrigerant, especially in refrigerant blends, at temperatures potentially down to its normal boiling point near 27 K (-300°C) [9, 10]. It also forms diverse crystalline structures below its fusion point (near 24.5 K). As temperatures approach absolute zero, many different crystalline configurations have been observed or predicted using quantum mechanics-based modelling approaches. For example, as solid neon is cooled, it can in theory undergo many transitions between crystalline configurations, including core melting. This can cause the heat capacity curves to be non-monotonic in the solid region, but they still tend toward zero as temperature approaches absolute zero [11].

A pressure-enthalpy-exergy diagram of fluid-phase neon is shown in Figure 2. The enthalpy, entropy, phase, and temperature lines were computed using CoolProp [12]. The iso-exergy lines are computed using eq. (2) with

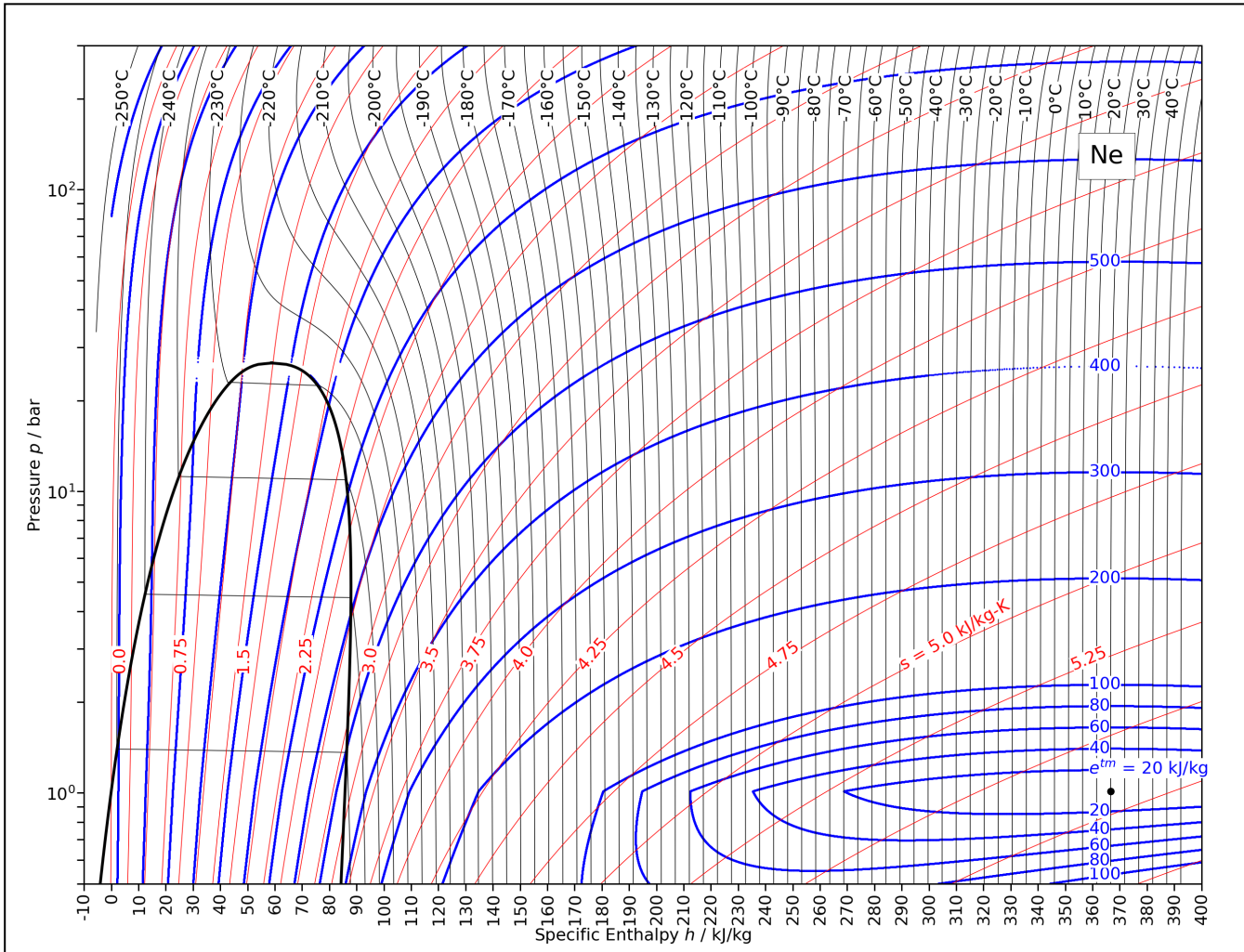


Figure 2: Pressure-enthalpy-exergy diagram of neon using eq. (2) for cold applications. This diagram applies to fluid phases only within model limits. Closed circle (•): Environmental reference state at $T_0 = 25^\circ\text{C}$, $p_0 = 1.01325$ bar. Blue lines (—): e^{tm} in kJ/kg. Red lines (—): specific entropy in kJ/kg-K. Black lines (—): temperature in $^\circ\text{C}$.

an environmental reference state of $(T_0, p_0) = (25^\circ\text{C}, 1.01325 \text{ bar})$. e_1^{tm} increases as neon gets colder or as the pressure deviates (above or below) the reference pressure. Due to the limits of the model used [12], the figure cannot be extended below -250°C .

3.1 Heat Capacity Curves for Crystalline Neon

To produce a meaningful thermo-mechanical exergy curve for neon down to absolute zero, we used experimentally determined [13] heat capacity values for ^{20}Ne and ^{22}Ne from 3 to 23 K, which are only slightly different. Recent statistical moment method computations explain these curves well, showing that heat capacity should smoothly approach zero as temperature approaches zero [14] (see also Corollary 2).

Therefore, we used the average experimental heat capacity of the ^{20}Ne and ^{22}Ne isotopes to represent the solid phase neon more generally for the purposes of diagram construction. We then constructed a simple model

valid between $0 < T < 23 \text{ K}$:

$$C_{p,Ne}(T) = 2.3246 T^2 + 5.1511 T \tag{7}$$

where the heat capacity of bulk crystalline neon $C_{p,Ne}$ is in J/kg-K. We note that it is an extrapolation to use this curve below 3 K but it evaluates to zero at 0 K and follows the quadratic-like trend in that region predicted by the statistical moment method models [14]. The resulting curve is shown in Figure 3.

We chose to use the as-reported experimentally determined values of h [13] as a function of temperature in the 3 K to 23 K region because of the known effect of core melting and various transitions on the heat capacity function [11] which are not reflected in eq. (7). However, eq. (7) was used to estimate the entropy from 0 K to 23 K analytically. The enthalpy of fusion at 1.01325 bar was taken to be 16.259 kJ/kg [15] which when using a melting point of 24.56 K for that pressure gives an entropy of fusion of 0.662 kJ/kg-K. All entropy and enthalpy

calculations above the melting point were performed using an equation of state for neon as computed by [12].

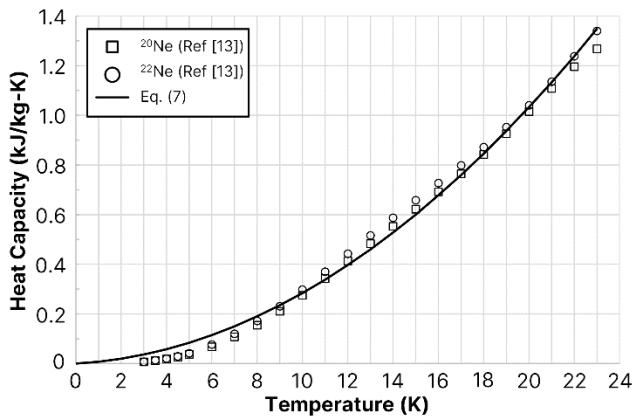


Figure 3. The heat capacity model for solid neon used in computing thermo-mechanical exergy at very low temperatures. Black lines (—): model. Circle: (○) Experimental data for ²²Ne. Square: (□) Experimental data for ²⁰Ne. Data from [13].

The final temperature-exergy diagram, computed using eq. (2), is shown in Figure 4. Four lines are shown for four selected pressures: one at the reference

pressure p_0 (1.01325 bar), one below the reference pressure (0.8 bar), one above it (8 bar) but below the critical point of neon, and one above (40 bar) the critical point. Thermo-mechanical exergy was only computed below the melting point for the 1.01325 bar pressure case since heat of fusion data were only available at that pressure, even though it is expected to be very similar at other pressures. Thermo-mechanical exergy could only be calculated for the gas phase for the 0.8 bar state due to limitations in the equation of state model.

4. DISCUSSION

4.1 Qualitative Assessment

As temperature moves down from T_0 , decreasing toward the melting point, all four pressure lines curve smoothly upward, forming a convex shape. For the subcritical pressure lines, this ends upon reaching the two-phase region, where it jumps sharply upward, reflecting the heat of condensation. The supercritical pressure case does not experience a jump; instead, the slope of the exergy curve transitions to something concave, with a less steep slope, closely matching the liquid curves for the 1.01325 bar and 8 bar cases in both quantity and slope. The liquid phase region is small for the atmospheric

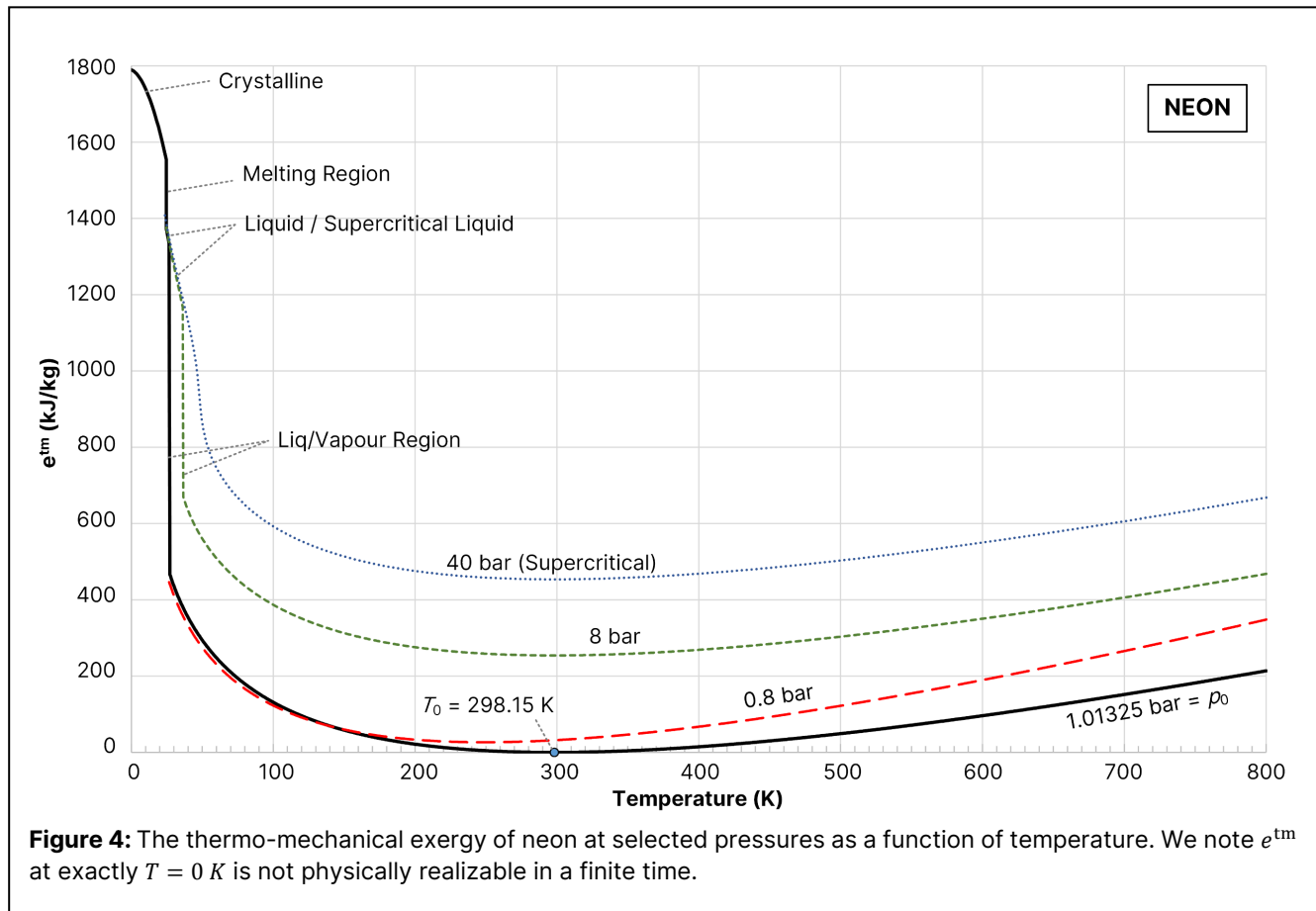


Figure 4: The thermo-mechanical exergy of neon at selected pressures as a function of temperature. We note e^{tm} at exactly $T = 0 K$ is not physically realizable in a finite time.

pressure case (only about 2.5 K). Essentially, the lines for the compressible fluids all collapse onto each other as they transition into the crystalline phases. As noted previously, this is because $\lim_{T \rightarrow 0K} \frac{\partial s}{\partial p} \rightarrow 0$.

In the crystalline region, exergy continues to increase as $T \rightarrow 0K$ but with decreasing slope as the heat capacity is likewise approaching zero. The final estimate for thermo-mechanical exergy approaching absolute zero for neon at atmospheric pressure relative to 25°C and 1.01325 bar reference conditions is 1,790 kJ/kg. It should be noted that it does not make sense to speak of e_1^{tm} at 0 K exactly because it is unreachable in practice.

Finally, there is an open argument as to whether the “flow” form of thermo-mechanical exergy (eq. (2)) or the “closed” form of thermo-mechanical exergy is the more useful choice to describe the exergy of a substance for chemical process systems engineers for use as an analysis tool. The closed form is:

$$e_1^{tm} = (u_1 - u_0) + p_0(v_1 - v_0) - T_0(s_1 - s_0) \quad (8)$$

where u and v are the specific internal energy and specific volume, respectively. The closed form and flow forms differ by a term $v_1(p_1 - p_0)$ sometimes called the “flow work” [1], which is work associated with the substance flowing into the environment and/or the boundary of the system expanding or contracting. However, for $p_1 = p_0$, this term is zero, making the flow and closed forms identical. Moreover, because there is very little influence of pressure on exergy in the crystalline state, the e_1^{tm} values calculated by eqs. (2), (3), and (8) converge to the same trajectory as $T_1 \rightarrow 0K$.

4.2 Comparison to Literature Predictions

Although Figure 4 is the first such quantitative diagram in the open literature that we can find, it is interesting to compare against two previous hypothetical sketches of what such a diagram would look like. Figure 5 shows two previously published curves from two previous works, for an arbitrary substance.

In Figure 5 (top), e_1^{tm} in the vacuum pressure ($p < p_0$) case is sometimes negative, in contrast to Figure 4 where $e_1^{tm} > 0$ always. This is because that work [4] assumes the form of eq. (3) to compute e_1^{tm} , which as shown previously cannot be correct precisely because it can result in negative values [2]. It is also interesting to note that the thermo-mechanical exergy of the vacuum pressure case in Figure 5 (top) has the same qualitative shape as the high-pressure case, whereas in Figure 4, the slope of the line in the vacuum pressure case increases more quickly as temperature increases, while the $p \geq p_0$ cases have very similar slopes at all temperatures as T increases. As discussed in [2], the behaviour shown in Figure 4 is because the mechanics of mass exchange with the environment for systems above atmospheric pressure are different than those for systems below it. Also,

Figure 5 (top) does not consider phase change, nor does it account for the switch to a concave shape as $T \rightarrow 0K$.

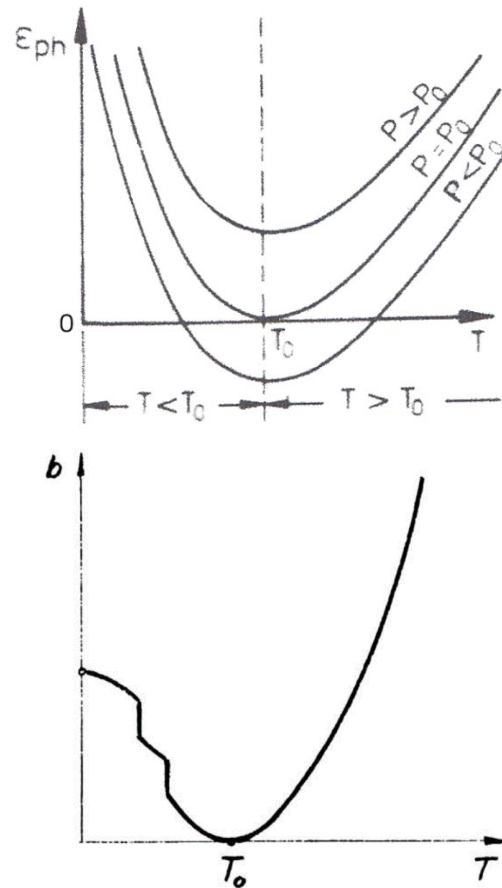


Figure 5: Two hypothesized sketches of e_1^{tm} as a function of T and p in previous works. Top: Reprinted from Kotas [4] with digital enhancements. Bottom: Reprinted from Petela [8] with digital enhancements, noting the open circle at $T = 0K$. Note that ϵ_{ph} and b in the sketches are equivalent to our notation e_1^{tm} .

Figure 5 (bottom) [8] shows a more accurate prediction below T_0 . However, in Figure 5 (bottom) e_1^{tm} increases very quickly as T increases above T_0 , rapidly overtaking the maximum cold e_1^{tm} at $T \rightarrow 0K$. In the final result of Figure 4, e_1^{tm} for neon grows very quickly as $T \rightarrow 0K$ and far more slowly as T increases above T_0 . This prediction in Figure 5 is curious. It arises because that work assumes that heat capacity near 0 K is cubic ($C_p(T) = kT^3$ for some constant k), which is quite reasonable—in fact we considered a cubic version of eq. (7) and achieved almost identical results. However, in making the drawing, it assumes that $C_p(T) = kT^3$ for all T , with no balancing factors of lower order terms, which is not reasonable. Thus in the drawing of Figure 5 (bottom), $e_1^{tm}(T)$ is quartic ($\sim T^4$) and this term dominates. This was thought to be correct because the exergy of heat radiation also grows $\sim T^4$ above T_0 and follows a very similar shape to

Figure 5 (bottom) except without the jumps due to phase change, and so it was thought to be justified by analogy. However, the real example of Figure 4 shows that this is not the case.

4.3 e^{tm} in cryogenic applications and relationship to the Unattainability Principle

Figure 4 is useful because it shows a clear upper bound on thermo-mechanical exergy of neon as temperature approaches absolute zero. In the context of the definition of exergy, this is the thermodynamically limited maximum work that could be produced by very cold substances **from thermo-mechanical processes**. However, there are some key points for discussion.

It is well known that the processes which produce the maximum theoretical work in eq. (1) must be reversible [1] and in fact, some theorists have gone so far as to require reversibility in the very definition of exergy itself [16]. From the optimization perspective, this means the optimization problem formulation for exergy can be posed in the reverse [2]:

$$e = \min_Q w \quad (9)$$

where Q is a process that brings the system **from** equilibrium with its environment **to** the state of interest within the set of all such processes \mathbb{Q} such that $Q \in \mathbb{Q}$, and w is work that is required by Q . By computing a finite value for e^{tm} as a substance approaches absolute zero, this implies that this is the **minimum** amount of work that must be consumed in order to bring a substance to absolute zero, which would be finite.

However, consider the Principle of Unattainability, which Kieu [17] words as “cooling any system to absolute zero temperature in a finite number of steps and within a finite time is physically impossible by any procedure, no matter how idealized the procedure.” Razek [18] states that “it is impossible to cool, using finite resources, any finite quantum system below a certain minimal temperature T_{min} .” This is a stronger claim because it means that not only is absolute zero unattainable, but for quantum systems at least, there are temperatures above 0 K that are also unattainable. Shargut and Brodyanskii [19] reject the application of eq. (3) “in the region close to” absolute zero as being meaningless (and therefore by extension also rejecting the more general form eq. (2) or the closed form eq. (8) as noted in section 4.1) precisely because it yields something not infinite. They claim this violates the Third Law of Thermodynamics (which may not be strictly equal to the Unattainability Principle [17], discussed later).

How then can we interpret these apparent contradictions? How useful is the computed value of e_1^{tm} in cryogenic applications? First, it should be noted that the Third Law was used both in the proof of the finiteness of e_1^{tm} approaching absolute zero (namely that the absolute entropy of a substance is zero at absolute zero) and in its

computation (that the heat capacity of a substance must be zero at absolute zero), not only in this work but also through alternative approaches in [8]. So, the Third Law itself cannot imply infinite exergy.

Second, when considering the definition of exergy and its subsequent optimization formulations, there is no constraint that the theoretical process that produces the maximum work requires **finite** time. In fact, it is theoretically possible to cool a substance to absolute zero using finite energy in an infinite amount of time [18, 20]. In optimization terms, the process Q which solves eq. (9) takes infinite time but results in a finite w . In fact, some recent work provides an interesting proof that the Third Law and the Principle of Unattainability are not strictly identical, and therefore the “possibility, logically and physically speaking, of attainability of absolute zero...by non-adiabatic means” remains [17]. So perhaps the solution Q is non-adiabatic. However, we note that there is ongoing disagreement in the equivalency of the Third Law and the Principle of Unattainability.

Finally, there is a more existential issue, namely that definition 1 applies to exergy generally, not thermo-mechanical exergy specifically. This distinction is important. Most process systems engineers find it very practical to decompose exergy into various types that can be summed together to get a final exergy value, using a variety of different taxonomies to do this [3]. For example, the exergy owing to chemical potential (molecular bonds and concentration differences), height above a reference point (potential energy due to gravity), kinetic energy of motion, temperature, pressure, and phase, are conceptually decomposable in many real applications. However, it has also been shown that these different kinds of exergies are strongly interlinked, and such decompositions are not applicable in many cases. For example, the exergy associated with phase (e.g. saturated vapour vs. saturated liquid) is not isolatable because it affects both thermo-mechanical and chemical exergy [3]. Marmolejo-Correa [21, 22] also showed that even the decomposition into temperature and pressure-based contributions was not meaningful because the solutions to eq. (1) are not unique, so it is not possible to take any given thermo-mechanical exergy and uniquely describe it as the sum of a temperature and a pressure component. Therefore, the quantification of exergy at absolute zero in general outside of thermo-mechanical contributions remains an open problem. Nevertheless, the practicality of computing e_1^{tm} down to absolute zero remains because it is a good and meaningful descriptor, useful in the analysis of real cryogenic processes that considers the First, Second, **and** Third Laws of Thermodynamics.

5. CONCLUSIONS

Using neon as an illustrative example, we

demonstrated how the thermo-mechanical exergy of substances changes due to the impacts of pressure and phase across subcritical gas, subcritical liquid, supercritical fluid, and crystalline phases as temperature decreases toward absolute zero. Although pressure impacts exergy in the gas phase, it has almost no impact on substances in compressed phases. For example, liquid and supercritical liquid phases at the same temperature have virtually indistinguishable thermo-mechanical exergies. Furthermore, contrary to previous predictions, calculations using real data for neon shows that e_1^{tm} grows much more slowly as temperature increases away from T_0 than it does as temperature decreases away from T_0 .

For practicing engineers, the general form of thermo-mechanical exergy in eq. (2) can be used even for very cold situations. The most common applications in chemical process systems engineering are in assessing the quality and performance of refrigeration systems, organic Rankine cycles, and in work recovery from stored very cold substances, such as in the regasification of liquified natural gas or liquid hydrogen.

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