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On Exact and Local Polytropic Processes: Etymology, Modeling, and Requisites

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Abstract

This preprint concerns polytropic processes, a fundamental process type in engineering thermodynamics. An etymology is presented for the term, and the ties to its usefulness are identified. The seemingly new support concept of 'logical' thermodynamic process, as well as the seemingly new working concept of 'exact' polytropic process, and a statement for 'local' polytropic process, are herein provided. The proposition of employing local polytropic processes as computational discrete elements for generic engineering thermodynamics process modeling is made. Finally, theoretical requisites for a process to be an exact polytropic one, including the deduction of the most general equation of state of the underlying substance, subject to $u:u(T)$, are discussed beyond a reference.

Keywords

Thermodynamics — Polytropic Processes — Logical Processes — Etymology

Remarks

Provides *etymology* for the 'polytropic' term — Defines *logical thermodynamic process* — Defines *exact polytropic process* — Presents a statement for *local polytropic process* — Defines theoretical *requisites* for exact polytropic process

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1. Introduction

Many equilibrium engineering thermodynamics processes are taken to follow a polytropic relationship,

$$Pv^n = \mathsf{c} = \text{const.}, \tag{1}$$

in which P is the system pressure, usually in kPa, v is the system specific volume, usually in $\mathrm{m^3/kg}$, and n is the dimensionless polytropic exponent [13]—which, for a '1–2' process, with initial and final end states labeled as '1' and '2', can also be written in terms of end state properties, as $P_1 v_1^n = P_2 v_2^n$, which also sets the particular value of the c constant.

Some mainstream thermodynamics textbooks introduce polytropic processes in the context of closed system boundary work, as a $P:P(v)$ relationship to plug into the boundary work integral, which contains a $P\,dv$ integrand [13, 10, 12]. In such texts, the polytropic relationship is frequently said to find support in measurements, while no specific theoretical derivation is presented at the point of introduction.

On the other hand, other texts [7, 4, 8] include derivations that lead to a polytropic process, or at least to an isentropic version of it, in which the exponent n has a determined value.

Moreover, Bejan [4, p. 175] indicates that a constant Pv^n relation only holds *locally* if the process is such that n is a function of either P, v, or both.

A paper due to Christians [6] discusses the topic from a perspective of teaching polytropic processes themselves, placing emphasis on the *heat-to-work transfer ratio*—named by that author as "energy transfer ratio"—and how its constancy not only yields, but constitutes a prerequisite for a process to be polytropic, besides, naturally, the constancy of the caloric properties of the working pure substance.

Starting with an *etymological* presentation of polytropic processes, this work proposes and develops the concepts of *exact polytropic* and *local polytropic* processes, as well as the supporting concept of *logical thermodynamic* processes, and presents theory-derived *requisites* for a process to be exactly polytropic beyond reference [6]. Moreover, local polytropic processes are proposed as discrete building blocks for general engineering thermodynamics *process modeling*.

2. Etymology of the 'Polytropic' Term

The 'polytropic' term has its etymology (origin) in the Greek language. This author's sources on Greek are mostly based on modern romance languages, such as French [5, 2] and his native Portuguese [9]; therefore, the etymology herein brought forth will include intermediate French terms.

The word 'polytropic' stems from the Greek word 'πολύτροπος' that itself is composed of two Greek words: (i) 'πολύς'[1], and (ii) 'τρόπος'.

The Greek adjective 'πολύς' includes meanings such as ≪ abondant, nombreux, vaste ≫ [5], i.e., abundant, numerous, vast [3, 1]. The Greek noun 'τρόπος' includes meanings such as ≪ manière, façon, mode ≫ [2], i.e., manner, way, fashion, and mode [3, 1]—hence, meaning: numerous forms, or many ways.

The composed Greek noun 'πολύτροπος' is also lexical, and includes figurative meanings such as ≪ souple, habile, industrieux ≫ [2], i.e., flexible, adaptive, able, laborious [1]; as well as meanings such as ≪ versatilité, très divers, très varié ≫ [2], i.e., versatility, very diverse, a great variety—thus indicating the *wide-range* of processes that it is capable of representing.

In fact, from a mathematical standpoint, Equation (1), there are really infinitely many allowable (possible) values for the real polytropic exponent n and for the c constant; thence, uncountably many processes departing from uncountably many initial states. It is this kind of flexibility that is encoded in the etymology of the process name.

3. Exact and Local Polytropic Processes

3.1 Logical Processes

In equilibrium engineering thermodynamics, a *process*—more properly a quasi-static or quasi-equilibrium one—is defined in terms of changes from a certain equilibrium state of a system to another [13], with process *path* being the (infinite) sequence of (quasi-)equilibrium states visited by the system during the process. A process can be referred to by its path, with implicit or explicit end states.

It is worth noting that no constraints are stated for the end states of a process in its definition. This allows for the needed flexibility in describing the variety of transformations systems and control volumes can undergo in engineering thermodynamics.

This lack of end state constraints in the definition of a process allows them to be splitted into multiple, successive 'sub-processes' that still fit the definition of a process, as well as to merge multiple successive ones together into 'super-processes' that also fit the definition of a process. This ability is extremely useful in grouping and splitting systems and control volumes along with their underlying processes—a common practice in engineering thermodynamics.

However, in order to make the intended distinction between proposed 'exact' and 'local' polytropic processes, additional constraints need to be made to process end states. Thus, the following defines a *logical thermodynamic process*, which is a thermodynamic process with constrained end states. In context, i.e., in thermodynamics texts, what's defined next can be simply called a 'logical process':

Definition 1 (logical process)**.** *A logical process is one in which its stated defining conditions, which determines all of the allowed interactions or property relations for the underlying system or control volume, uniformly and continually apply to the entirety of its path from—but not earlier than—its initial state until—but not later than—its end state.*

Therefore, for a simple compressible system—one admitting only work and heat interactions—either stated heat and work interactions, or system property specifications, or combinations of the two, define possible logical processes.

Moreover, the stated defining conditions of a logical process can also carry a 'logical' qualifier, as to make it

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[1] The lexical form of Greek adjectives is the nominative, singular, masculine. The nominative, singular, *neuter* of 'πολύς' is 'πολύ'.

explicit they're being used in the definition of a logical process, as in the 'logical conditions,' or 'defining logical conditions' expressions. Furthermore, the conditions themselves can carry the 'logical' qualifier, for the same purpose.

Example 1. *The well-known air-standard ideal Diesel power cycle, illustrated on Figure 1, with 'intake' state (of lowest temperature and pressure and maximum specific volume) labeled as '1', can be divided in different ways using only logical processes. One such division is: (i) 'logical isentropic compression', ($\Delta s = 0 \therefore Q = 0$, $W < 0$), (ii) 'logical isobaric heating', ($Q > 0$, $\Delta P = 0 \therefore W > 0$), (iii) 'logical isentropic expansion', ($\Delta s = 0 \therefore Q = 0$, $W > 0$), and (iv) 'logical isochoric cooling', ($Q < 0$, $\Delta v = 0 \therefore W = 0$), which correspond, respectively, to the '1–2', '2–3', '3–4', and '4–1' processes, i.e., to the canonical processes for this cycle, excluding sub-processes thereof. Another possible division is: (a) 'logical isentropic compression', ($\Delta s = 0 \therefore Q = 0$, $W < 0$), (b) 'logical no-heat-removal expansion', ($Q \geqslant 0$, $W > 0$), and (c) 'logical isochoric cooling', ($Q < 0$, $\Delta v = 0 \therefore W = 0$), which correspond, respectively, to the '1–2', '2–4' (through '3'), and '4–1' processes, excluding sub-processes thereof, since these encompass the farthermost end states that uniformly and continually match the stated defining logical conditions (a), (b), and (c).*

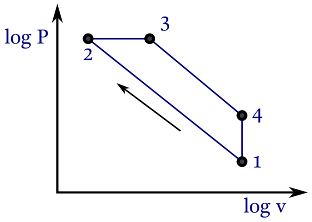

Figure 1. Air-standard ideal Diesel cycle in $\log P \times \log v$ coordinates, in support for the Example 1.

3.2 Exact Polytropic Processes

One is now in a position to define *exact polytropic processes*:

Definition 2 (exact polytropic process)**.** *An exact polytropic process is a logical process in which either (i) a polytropic relation $Pv^n = const.$, with a unique polytropic exponent n, or (ii) an isochoric logical condition, can be its sole logical defining condition, provided that no state in its path is visited more than once or serves simultaneously as initial and final end states in a given execution.*

It is worth noting that isochoric processes are equivalent to polytropic processes with $n \to \pm\infty$ between stated end states. Definition 2 accounts for the isochoric process non-unique polytropic exponent by explicitly including it as a valid exact polytropic process.

Lemma 1. *Any logical process defined by a single polytropic relation with a unique polytropic exponent, with non-identical end states can only be an exact polytropic process in the absence of reversals in its path.*

Proof. Let a logical process $\mathscr{P}_{1,2}$ be defined by a single polytropic relation with a unique polytropic exponent n, with non-identical end states '1' and '2' that contains a set of reversal states 'r_i', with $\{i \in \mathbb{Z} | i \geqslant 1\}$ in its path.

Without loss of generality, let further $P_{r_1} < P_1$, if $n \neq 0$, i.e., an initially pressure-decreasing process—since the following argument can be otherwise flipped, or laid out in either direction in v, for non-zero n:

Let state 'ε', defined as $(P_\varepsilon, v_\varepsilon)$, belong to the path of a sub-process $\mathscr{P}_{1,r_1}$ of the original logical process $\mathscr{P}_{1,2}$, so that

$$P_\varepsilon - P_{r_1} = \Delta P \to 0. \tag{2}$$

Since 'ε' $\in \mathscr{P}_{1,r_1} \in \mathscr{P}_{1,2}$, it follows from the definition of $\mathscr{P}_{1,2}$:

$$P_\varepsilon v_\varepsilon^n = P_1 v_1^n = P_{r_1} v_{r_1}^n. \tag{3}$$

Since at 'r_1', the process experiments a reversal, thus proceeding with increasing pressures. Let state 'ζ', defined as (P_ζ, v_ζ), belong to the path of a sub-process $\mathscr{P}_{r_1,2}$ of the original logical process $\mathscr{P}_{1,2}$, so that

$$P_\zeta \equiv P_\varepsilon = \lim_{\Delta P \to 0} P_{r_1} + \Delta P, \tag{4}$$

so that process $\mathscr{P}_{r_1,2}$ is guaranteed to contain state 'ζ', since state 'r_1' is a reversal one, rather than a stopping one, therefore: 'ζ' $\in \mathscr{P}_{r_1,2} \in \mathscr{P}_{1,2}$, implying:

$$P_\zeta v_\zeta^n = P_{r_1} v_{r_1}^n = P_\varepsilon v_\varepsilon^n \quad \text{(by Eq. (3))} \quad \rightharpoondown \tag{5}$$

$$P_\varepsilon v_\zeta^n = P_\varepsilon v_\varepsilon^n \quad \rightharpoondown \tag{6}$$

$$v_\zeta^n = v_\varepsilon^n \quad \rightharpoondown \tag{7}$$

$$v_\zeta = v_\varepsilon. \tag{8}$$

From Eqs. (4) and (8), one has states 'ε' and 'ζ' being identical: 'ε' $\equiv$ 'ζ', with 'ε' $\in \mathscr{P}_{1,2}$ and 'ζ' $\in \mathscr{P}_{1,2}$.

Therefore, by the exact polytropic process definition, Definition 2, logical process $\mathscr{P}_{1,2}$ cannot be an exact polytropic process, since there is at least one state—state 'ε'—that is visited more than once in a given execution. ☐

Remarks. Given that the polytropic exponent is unique, any reversal would cause the underlying system or control volume to re-visit states already covered, thus violating the exact polytropic process definition. ☐

Theorem 1 (Cycle)**.** *No cycle is an exact polytropic process.*

Proof. The defining feature of a cycle of same end states directly violates the restriction of no same initial and end states for an exact polytropic process. □

Remarks. Even if a cycle can be collapsed down as to be described in terms of a single polytropic process, such as an ideal Diesel cycle with fuel cut ratio $r_c \equiv v_3/v_2 = 1$, the fact that such a cycle must invariably make at least one reversal, as to cycle back to previous states, Lemma 1 would constitute a second reason to disqualify the cycle as a (single) exact polytropic process. □

For an exact polytropic process, one has, between its end states extrema:

$$Pv^n = c_1 = \text{const.} \qquad \rightharpoondown \tag{9}$$

$$\log(Pv^n) = \log(c_1) \equiv c_2 \qquad \rightharpoondown \tag{10}$$

$$\log P + n \log v = c_2 \qquad \rightharpoondown \tag{11}$$

$$\log P = -n \log v + c_2. \tag{12}$$

Equation (12) is an affine relationship between $\log P$ and $\log v$—a line segment that links the process end states extrema—in which the polytropic exponent n figures as the negative of the line segment slope.

Figure 1 is drawn in $\log P \times \log v$ coordinates, and depicts one line segment between each adjacent labeled state pairs '1–2', '2–3', '3–4', and '4–1', in which all labeled states are extrema of each line segment, and there are no reversals. Therefore, all such processes, enumerated on Example 1 with roman numerals (i)–(iv), are exact polytropic ones.

3.3 Local Polytropic Processes

Figure 2 illustrates a process that plots as a curved segment in $\log P \times \log v$ coordinates. Basic derivative knowledge allows us to think of such process as one with a continuously variable slope in double logarithmic $P \times v$ coordinates, which, allied to the conclusions drawn from Equation (12), as one with a polytropic-like relationship with continuously varying exponent n.

Attempting to *exactly* represent the process as a set of straight line segments would result in an infinite set of segments, with each one being of vanishing length—hence, having same end states. The definition of exact polytropic processes excludes all processes in such a set from being exact polytropic ones; thus, the following Lemma:

Lemma 2 (continuously curved process)**.** *A process whose path is continuously curved in* $\log P \times \log v$ *coordinates has no exact polytropic sub-process segments.*

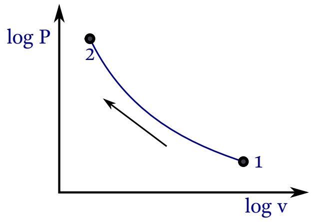

Figure 2. A process displaying a curve in logarithmic $P \times v$ coordinates.

If, however, one allows for approximations, as is common practice in engineering, the curved process can be represented by an increasing but finite amount of line segments with decreasing amounts of deviation (errors). The beginning of such a process, in which the amount of line segments is doubled at each step, is depicted, with a shift in v for the sake of improved visualization, on Figure 3.

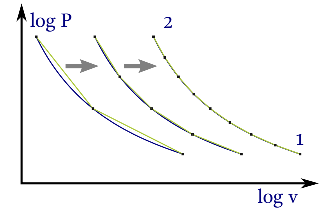

Figure 3. Successive approximations to the curved process, in dark blue solid line, by means of 2, 4, and 8 straight line segment sub-processes, in dark yellow solid lines, in $\log P \times \log v$ coordinates (shifted in v for easier visualization)

The rationale behind such approximation process is in support of the following definition:

Definition 3 (local polytropic process)**.** *A local polytropic process is a polytropic process that approximates or models a subset of or another process to within suitable error intervals, while sharing common end states with it.*

Regarding envisioned capabilities of local polytropic processes in the context of equilibrium thermodynamics, one herein states:

Conjecture 1 (general approximability)**.** *Any continuous, quasi-equilibrium process set can be approximated or modeled, to within finite error intervals, by a finite set of local polytropic processes.*

Remarks. It is worth noting that all equilibrium thermodynamic *cycles* can be trivially subdivided into the process set stated on the general approximability conjecture, since (sub-)process end states can be arbitrarily placed within the larger cycle path. □

The rationale behind the general approximability conjecture is the very definition of local polytropic process, stated on Definition 3.

Numerical methods in engineering typically employ a form of discretization of the underlying quantities. Numerical schemes geared towards solving equilibrium engineering thermodynamic cycles and processes may also apply the concept to *processes*.

Proposition 1 (process modeling)**.** *It is proposed that local polytropic processes, as herein defined, to be employed as discrete building blocks for general equilibrium engineering thermodynamics process modeling.*

A validated model description published by the author before the present formalization, has successfully employed the proposed strategy in solving Finite-Time Heat-Addition (FTHA) air-standard Otto cycles, using local polytropic processes as computational elements [11].

Since unsteady, non-instantaneous addition of heat in an Otto cycle invariably leads to simultaneous heat and work interactions and result in non-trivial thermodynamic processes, even under quasi-equilibrium hypotheses, study [11] concluded that a set of discrete polytropic subprocesses was the theoretical tool to provide the needed generality in the model formulation, and thus, inspired the current formulations.

4. Requisites for Exact Polytropic Processes

One can show that the polytropic relation, Equation (1), is the solution of

$$\frac{dP}{P} = -n\frac{dv}{v}, \tag{13}$$

with n not a function of either P or v:

$$\begin{aligned}
\int \frac{dP}{P} &= -n \int \frac{dv}{v} && \rightharpoondown && (14)\\
\log P + \mathsf{c}_1 &= -n \log v + \mathsf{c}_2 && \rightharpoondown && (15)\\
\log P &= -n \log v + \mathsf{c}_3 && \rightharpoondown && (16)\\
\log P + n \log v &= \mathsf{c}_3 && \rightharpoondown && (17)\\
Pv^n &= e^{\mathsf{c}_3} \equiv \mathsf{c}, && && (18)
\end{aligned}$$

thus recovering Equation (1).

The work of Christians [6] shows that internally reversible processes in closed systems with a calorically perfect gas with a $Pv = ZRT$ equation of state with constant compressibility factor Z assuming negligible changes in system kinetic and potential energies, absence of chemical reactions, and constant energy transfer ratio,

$$K \equiv \frac{\delta q}{\delta w}, \tag{19}$$

yield a polytropic relation between P and v with a constant exponent $n = (1-\gamma)K + \gamma$. In this work, K is also referred to as *heat-to-work transfer ratio*.

The employed $Pv = ZRT$ equation of state is indicative of real gases; however, the constant Z assumption narrows down the scope of the result. This prompts the question of whether this finding is actually only applicable to ideal gases, for which $Z = 1$, or whether other constants work.

The energy balance equation for a closed unreactive system reads, in the intensive differential form, as

$$\delta q - \delta w = du + de_k + de_p, \tag{20}$$

where δq and δw are the differential heat and work interactions, following the historical thermodynamic sign convention of positive heat interactions being into the system and positive work interactions being out of the system; u is the system specific internal energy, with e_k and e_p being the system specific kinetic and potential (macroscopic) energies, respectively. Neglecting the variation of the system macroscopic energy forms, simplifies Equation (20), giving:

$$\begin{aligned}
\delta q - \delta w &= du, && \rightharpoondown && (21)\\
(K-1)\delta w &= du, && && (22)
\end{aligned}$$

in which Equation (19) is used.

At this point, reference [6] replaces du by $c_v dT$—where c_v and c_p are the constant-volume and constant-pressure specific heats, respectively—in order to be able to arrive at a polytropic relation between P and v, and continues the analysis with a $Pv = ZRT$ equation of state with the assumption of constant Z.

Shortly after, the ZR term is replaced by $(c_p - c_v)$, which can recover an ideal gas result if Z is further restricted to 1. His analysis seems to request the adoption of an ideal gas model, rather than a real gas one, as the $ZR = (c_p - c_v)$ relation cannot hold in general for a real gas. Take, for instance, the close vicinity of the critical state, predictable by a real gas model, in which $c_p \to +\infty$, even if approached from the monophase region, while all other quantities remain finite, indicating the $ZR = (c_p - c_v)$ relation is subject to arbitrarily large errors in the real gas model domain.

Moreover, from the perspective of real gas model, constant Z in general must be based either on (i) negligible reduced pressure, temperature, and specific volume variations in the process—recall the generalized compressibility chart [13]—or on (ii) the substance being in the ideal gas limit during the entirety of the process.

Following reference [6], du is replaced by $c_v\,dT$, yielding a $u\!:\!u(T)$-only substance, whose property relations are investigated. In the following, it is theoretically demonstrated that $Z\!:\!Z(v)$ for such a substance—a useful intermediate result—among other outcomes.

4.1 Substance Equation of State Yielding $u\!:\!u(T)$

For $u\!:\!u(T)$ to hold, one must have:

$$\left(\frac{\partial u}{\partial i}\right)_T = 0. \tag{23}$$

for *any* choice of property i other than T.

Perhaps the easiest way of deriving the outcomes of Eq. (23) is by rewriting it in terms of Bridgman's relations [4], which are expressed in terms of a peculiar notation. Therefore, rewriting Eq. (23) in Bridgman's notation yields

$$\frac{(\partial u)_T}{(\partial i)_T} \equiv \left(\frac{\partial u}{\partial i}\right)_T = 0 \quad \rightharpoondown \quad (\partial u)_T = 0. \tag{24}$$

It is worth noting than the $\equiv$ sign on Eq. (24) indicates the definition of the *ratio* between Bridgman's primitives $(\partial u)_T$ and $(\partial i)_T$ in terms of $(\partial u/\partial i)_T$, rather than the other way around.

Bridgman's relations are tabulated expressions for its *individual primitives* in terms of thermodynamic properties that are easily obtainable from physical measurements [4], which makes them ingeniously useful.

Bridgman's peculiar notation allowed Eq. (23) to be expressed in terms of Bridgman's $(\partial u)_T$ primitive only, thus eliminating the role of Bridgman's $(\partial i)_T$ primitive, *irrespective of the choice of property* i. This greatly simplifies the analysis of Eq. (23)'s outcomes.

From reference [4], one has

$$(\partial u)_T = v(\beta T - \kappa P) = 0 \qquad \rightharpoondown \tag{25}$$

$$\beta T = \kappa P, \tag{26}$$

where β is the *volumetric coefficient of thermal expansion*, or the *volume expansivity* [4], or the *coefficient of volume expansion* [7], and κ is the *isothermal compressibility* [4], also denoted by some authors as κ_T, as to distinguish it from the isentropic compressibility, κ_s [7].

Put differently, Eqs. (23)–(26) indicate that any substance for which $\beta T = \kappa P$ will have $u\!:\!u(T)$ only.

Eq. (27) brings forth definitions of β and κ:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P, \quad \text{and} \quad \kappa \equiv \frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T. \tag{27}$$

Plugging in Eq. (27) on Eq. (26) and using the cyclic relationship,

$$-1 = \left(\frac{\partial j}{\partial i}\right)_\ell \left(\frac{\partial \ell}{\partial j}\right)_i \left(\frac{\partial i}{\partial \ell}\right)_j, \tag{28}$$

gives, after some manipulation,

$$\left(\frac{\partial T}{\partial P}\right)_v = \frac{T}{P} \qquad \rightharpoondown \tag{29}$$

$$\left(\frac{\partial T}{T}\right)_v = \left(\frac{\partial P}{P}\right)_v \qquad \rightharpoondown \tag{30}$$

$$T = \mathsf{f}(v)P, \tag{31}$$

with $\mathsf{f}(v)$ arising from the partial integrations. Therefore, this result expresses a substance in which $T \propto P$ at constant volume. Letting $\mathsf{f}(v) \equiv f(v)/R$, yields

$$Pf(v) = RT, \tag{32}$$

with $f\!:\!f(v)$ being an arbitrary function of v only. If this equation of state is represented as $Pv = ZRT$, then $Z = v/f(v)$, as previously announced. Equation (32) is the most general equation of state for a substance that has $u\!:\!u(T)$, and consequently $du = c_v\,dT$.

4.2 Specific Heats of a $u\!:\!u(T)$ Substance

Writing $s\!:\!s(T,v)$ and differentiating, with $du = T\,ds - P\,dv$ and the Maxwell relation based on the Helmholtz energy, $(\partial s/\partial v)_T = (\partial P/\partial T)_v$, one arrives at

$$ds = \frac{c_v}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_v dv. \tag{33}$$

Writing $s\!:\!s(T,P)$ and differentiating, with $dh = T\,ds + v\,dP$ and the Maxwell relation based on the Gibbs energy, $(\partial s/\partial P)_T = -(\partial v/\partial T)_P$, one arrives at

$$ds = \frac{c_p}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_P dP. \tag{34}$$

Equating the cross derivatives from the dT and dv (or dP) coefficients on Eqs. (33) and (34), yields [13]:

$$\left(\frac{\partial c_v}{\partial v}\right)_T = +T\left(\frac{\partial^2 P}{\partial T^2}\right)_v, \quad \text{and} \tag{35}$$

$$\left(\frac{\partial c_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P. \tag{36}$$

Eqs. (35) and (36) are to be used in determining whether the specific heats of a substance with equation of state given by Eq. (32) are functions of other thermodynamic properties.

Therefore, from Eq. (32), one has:

$$P = \frac{RT}{f(v)} \qquad \rightharpoondown \tag{37}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{f(v)} \qquad \rightharpoondown \tag{38}$$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0. \tag{39}$$

Therefore, $(\partial c_v/\partial v)_T = 0$ making $c_v : c_v(T)$ at best for a Eq. (32) substance.

Let

$$\mathsf{g}(v) \equiv f(v)/v. \tag{40}$$

then, from Eq. (32), one has:

$$v = \frac{RT}{P\mathsf{g}(v)} \qquad \rightharpoondown \tag{41}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P\mathsf{g}(v)} \qquad \rightharpoondown \tag{42}$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0. \tag{43}$$

Therefore, $(\partial c_P/\partial P)_T = 0$ making $c_P : c_P(T)$ at best for a Eq. (32) substance. Moreover, since

$$\gamma \equiv \frac{c_p}{c_v}, \tag{44}$$

one also has $\gamma : \gamma(T)$ at best for this substance.

The textbook expression for dh is [13]:

$$dh = \left(\frac{\partial h}{\partial P}\right)_T dT + \left(\frac{\partial h}{\partial T}\right)_P dP \tag{45}$$

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP. \tag{46}$$

From Eq. (42), the $(\partial h/\partial T)_P$ term can be written as

$$\left(\frac{\partial h}{\partial T}\right)_P = v - T\left(\frac{\partial v}{\partial T}\right)_P \qquad \rightharpoondown \tag{47}$$

$$\left(\frac{\partial h}{\partial T}\right)_P = v - \frac{RT}{P\mathsf{g}(v)} \qquad \rightharpoondown \tag{48}$$

$$\left(\frac{\partial h}{\partial T}\right)_P = v - v = 0, \tag{49}$$

thus making $h : h(T)$ for an unreactive substance with $Pf(v) = RT$ equation of state.

The findings of this subsection are thus summarized in an already proven theorem:

Theorem 2 ($u : u(T)$ unreactive substance)**.** *An unreactive substance for which $u : u(T)$, necessarily has $c_v : c_v(T)$, $c_P : c_P(T)$, and $\gamma : \gamma(T)$ at best, and also $h : h(T)$. Moreover, it has a $Pf(v) = RT$ equation of state, with $f(v)$ being an arbitrary function of v.*

4.3 Energy Balance with a $u : u(T)$ Model

Plugging in $du = c_v dT$ on Eq. (22) and differentiating Eq. (32) will make a dT appear on both equations. Equating the common dT leads to

$$dT = \frac{K-1}{c_v} P dv = \frac{Pf'(v)dv + f(v)dP}{R}, \tag{50}$$

where $f'(v) \equiv df/dv$.

The goal now is to write Eq. (50) in the form of Eq. (13), with constant n, which yields

$$\frac{dP}{P} = -[f'(v) + (1-K)(\gamma - 1)]\frac{dv}{f(v)} \qquad \rightharpoondown \tag{51}$$

$$\frac{dP}{P} = -\frac{f'(v) + (1-K)(\gamma-1)}{\mathsf{g}(v)}\frac{dv}{v}, \tag{52}$$

in which $\mathsf{g}(v)$ is defined by Eq. (40). By inspection, the polytropic exponent is identified as:

$$n \equiv \frac{f'(v) + (1-K)(\gamma-1)}{\mathsf{g}(v)} \qquad \rightharpoondown \tag{53}$$

$$n = \frac{vf'(v)}{f(v)} + (1-K)[\gamma(T) - 1]\frac{v}{f(v)}. \tag{54}$$

The constancy of n depends on the constancy of all of Eq. (54) terms. Enforcing this condition upon the first term leads to the following ODE:

$$\frac{v}{f}\frac{df}{dv} = \mathsf{c}_1 \qquad \rightharpoondown \tag{55}$$

$$\frac{df}{f} = \mathsf{c}_1\frac{dv}{v} \qquad \rightharpoondown \tag{56}$$

$$f(v) = v^{\mathsf{c}_1} + \mathsf{c}_2. \tag{57}$$

The second term of Eq. (54) contains v and T functions. Enforcing constancy separately in v terms yields:

$$\frac{v}{f(v)} = \mathsf{c}_3 \qquad \rightharpoondown \tag{58}$$

$$\frac{v}{v^{\mathsf{c}_1} + \mathsf{c}_2} = \mathsf{c}_3, \tag{59}$$

which yields $\mathsf{c}_1 = 1$, $\mathsf{c}_2 = 0$, with $\mathsf{c}_3 = 1$ being the only possibility for constancy in v terms. This result finally fixes the substance equation of state by fixing $f(v)$ as

$$f(v) = v. \tag{60}$$

Consequently, the $Pf(v) = RT$ equation of state, with $f(v) = v$, *exactly recovers the ideal gas equation of state*, which reads

$$Pv = RT. \tag{61}$$

Moreover, the constancy of the $(1-K)[\gamma(T)-1]$ term must account for the fact that K is defined only in terms of *process energy interactions*, Eq. (19), while $\gamma(T)$ is defined only in terms of system *substance properties*, Eq. (44). Therefore, the analysis is two-fold:

(i) For interactions that yield a constant value of K, as assumed on reference [6], one must have constant $\gamma(T) = 1 + R/c_v(T)$, for an ideal gas, which requires constancy in c_v, which, in turn, also means constancy in c_p, since $c_p = c_v + R$ for ideal gases.

(ii) For Eq. (54)'s second term constancy, with $v/f(v) = 1$, interactions must be made system temperature dependent, i.e., $K:K(T)$, resulting in $[1-K(T)] \propto c_v(T)$, which is hardly practical and is left as a note.

Plugging the results back in Eq. (54), yields the value of the resulting polytropic exponent:

$$n = 1 + (1-K)(\gamma-1) = \gamma + K(1-\gamma), \tag{62}$$

which is in agreement with Christian's results [6].

This section's outcomes are the base for the following, 'K-polytropic', theorem:

Theorem 3 (K-polytropic)**.** *Internally reversible processes in constant-specific-heat unreactive closed systems with negligible kinetic and potential energy changes and constant heat-to-work ratio interactions, K, are exact polytropic processes only if the substance is an ideal gas.*

Therefore, the K-polytropic theorem answers the question herein raised in light of Christian's work [6], that the constant-Z, $u:u(T)$ real gas working substance yielding an exact polytropic process under a reversible, constant-K process in a closed system, needs to be further narrow down to an ideal gas, i.e., one for which $Z = 1$.

5. Summary and Conclusions

This work has concerned itself with polytropic processes. An *etymology* of the 'polytropic' term that relates to its mathematical possibilities has been given on Section 2.

The concept of a *logical thermodynamic process*, idealized by the author as a process with restricted end states, has been laid out by Definition 1. With logical process, or logical conditions, processes and associated end states can be uniquely referred to. Example 1 works out the concept on an ideal, air-standard Diesel cycle.

The concept of *exact polytropic process*, idealized by the author as being both logical, polytropic, and non-reversing, see Lemma 1, has been laid out in Section 3.2. A 'Cycle' theorem relating to exact polytropic processes, Theorem 1, is provided. The way towards local polytropic process is paved with the discussion of processes with continuously curved paths in double logarithmic $P \times v$ coordinates, see Lemma 2.

A definition of *local polytropic process*, formulated by the author—although the concept of process relations applying locally is found in previous literature, as, for instance, in [4, p. 175]—that explicitly mentions the purpose of approximation of another process, is provided by Definition 3 in Section 3.3.

By means of the Conjecture 1, it is claimed that finitely many local polytropic process can be used to model *any* given equilibrium thermodynamics process or cycle to within finite errors, which leads to Proposition 1, of equilibrium thermodynamics numerical schemes to use them as discrete building blocks for general process modeling.

A validated model description that employs discrete local polytropic processes as building blocks in general process modeling [11], which has been published by the author before the present formalization of concepts, is referenced in Section 3.3 as a successful case in implementing Proposition 1.

In Section 4, a statement that under certain conditions a gas with $u:u(T)$ and a $Pv = ZRT$ equation of state with constant Z displays a constant exponent polytropic process, found in [6], is investigated using thermodynamic property relations, seeking theoretical requisites for the occurrence of exact polytropic processes.

Section 4.1 shows that a $u:u(T)$ substance must have a $Z:Z(v)$. Moreover, Section 4.2 determines whether c_v, c_p, γ, and h of the $u:u(T)$ substance depend on properties other than T. The findings are summarized in Theorem 2.

It is finally concluded, in Section 4.3, that the most general $u:u(T)$ substance to yield an exact polytropic process under constant heat-to-work transfer ratio is, in fact, an ideal gas—see Theorem 3.

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To YHWH God be the glory!

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