

Absolute Reference Values of the Real Gas

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Abstract

With his publication in 1873 [1] J. W. Gibbs formulated the thermodynamic theory. It describes almost all macroscopically observed properties of matter and could also describe all phenomena if only the free energy $U - ST$ were explicitly known numerically. The thermodynamic uniqueness of the free energy obviously depends on that of the internal energy U and the entropy S , which in both cases Gibbs had been unable to specify. This uncertainty, lasting more than 100 years, was not eliminated either by Nernst's hypothesis $S = 0$ at $T = 0$. This was not achieved till the advent of additional proof of the thermodynamic relation $U = 0$ at $T = T_c$. It is noteworthy that from purely thermodynamic consideration of intensive and extensive quantities it is possible to derive both Gibbs's formulations of entropy and internal energy and their now established absolute reference values. Further proofs of the vanishing value of the internal energy at the critical point emanate from the fact that in the case of the saturated fluid both the internal energy and its phase-specific components can be represented as functions of the evaporation energy. Combining the differential expressions in Gibbs's equation for the internal energy, $d(\mu/T)/d(1/T)$ and $d(p/T)/d(1/T)$, to a new variable $d(\mu/T)/d(p/T)$ leads to a volume equation with the lower limit v_c as boundary condition. By means of a variable transformation one obtains a functional equation for the sum of two dimensionless variables, each of them being related to an identical form of local interaction forces between fluid particles, but the different particle densities in the vapor and liquid spaces produce different interaction effects. The same functional equation also appears in another context relating to the internal energy. The solution of this equation can be given in analytic form and has been published [2] [3]. Using the solutions emerging in different sets of problems, one can calculate absolutely the internal energy as a function of temperature-dependent, phase-specific volumes and vapor pressure.

Keywords

Entropy Reference Value $S(M, V, 0) = 0$, Internal Energy Reference Value

$$U(M, V, T_c) = 0, \text{ Critical Volume } V = M \cdot \left[d(\mu/T) / d(p/T) \right]_c, \text{ Two-Phase Equilibrium } -M(u_v - u_l)(0) \leq ST + M\mu = M \left[v_v + v_l - (v_v - v_l) / \ln(v_v/v_l) \right] \cdot d(p/T) / d(1/T) + V dp / dT \cdot T = U + Vp \leq Vp \leq Vp_c, \text{ Chemical Potential Negative, } M\mu(T) \leq M\mu(0) = U(M, V, 0) = M \cdot \left[-(u_v - u_l)(0) \right] < 0.$$

1. Introduction

The purpose of this paper is to show that Gibbs's theory [1] contains intrinsically "natural" reference values of entropy and internal energy that are reciprocal and thus represent thermodynamic reference values [4]. Nevertheless, it was and is still accepted till the recent past that the value of the internal energy of the real gas cannot be given absolutely, e.g. [5] [6]. Instead, the calculation of entropy and internal energy could be based on a so-called fiducial reference value [7]. To put an end to the diversity of individually, arbitrarily chosen fiducial values, it was decided at conferences in the 1950s to assign the values of entropy and internal energy (or enthalpy) of a liquid at the triple point the reference values zero, which in any case the Nernst hypothesis contradicts. On this basis mathematically complex equations were put forward, but an analysis (see **Appendix**) shows that they contain thermodynamic inconsistencies. These then yielded incorrect thermodynamic data published for a large number of gases, e.g. [8]-[15]. None of these skeleton tables presents data on the chemical potential, which could have been derived from the differences $h_{v,l} - s_{v,l}T$. A paper that specifically investigates calculation of the chemical potential of the generally accepted conference agreements comes to the surprising conclusion that the chemical potential increases as the temperature [16]. This result cannot, however, account for daily observation that flow of freely-moving matter occurs from cold to warm regions [17]. One has to take the consequence from the numerous thermodynamic discrepancies ensuing from calculating entropy and internal energy from the assumptions mentioned, $s_l(T_t) = 0$ and $u_l(T_t) = 0$ (or $h_l(T_t) = 0$). Here, too, as so often in the history of physics, one has to abandon a trusted hypothesis. Here it is the assumption of the naive addition of fiducial constants to thermodynamic fundamental quantities.

The paper shows four possible ways of finding directly the thermodynamic reference values of entropy and internal energy and thus comply with the correct treatment of real properties of matter called for by Gibbs. First there is the possibility of studying the characteristic features of intensive and extensive quantities in order to describe thermodynamically the real properties of matter. A second investigation deals with the question what follows from representation of the internal energy of the fluid as a function of the evaporation energy. The third possibility is concerned with solution of a functional equation for the sum of two dimensionless variables, the one referring to the local interaction potential of fluid particles in the vapor space and the other to that in the liquid.

The functional equation emerges from the original equation for the internal energy and has been solved [3]. The functional equation is, on the other hand, also encountered when one represents the particular phase-specific internal energy as a function of the evaporation or condensation energy. It has of course the same (physically unique) solution and allows the internal energy to be explicitly calculated as an absolutely determined temperature function of the measurable quantities: phase-specific volumes and vapor pressure [2].

2. Intensive and Extensive Quantities of the Saturated Fluid

The homogeneity of the fluid allows its macroscopic properties to be described by intensive and extensive quantities.

The intensive quantities are the temperature T , vapor pressure p and chemical potential μ ; vapor pressure and chemical potential are pure temperature functions below the critical point of the fluid. With the finite critical values p_c and $d^{n-1}p/dT_c^{n-1} > d^n p/dT_c^n$ ($n=1,2,3,\dots$) the ϵ -expansion of p to second order yields

$$\begin{aligned}
 0 \leq T \leq T_c, \quad 0 \leq \epsilon = 1 - T/T_c \leq 1, \\
 0 \leq p = p_c - \frac{dp}{dT}|_c T_c \epsilon + \frac{1}{2} \frac{d^2 p}{dT^2}|_c T_c^2 \epsilon^2 \leq p_c, \\
 0 \leq \frac{dp}{dT} = \frac{dp}{dT}|_c - \frac{d^2 p}{dT^2}|_c T_c \epsilon + \frac{1}{2} \frac{d^3 p}{dT^3}|_c T_c^2 \epsilon^2 \leq \frac{dp}{dT}|_c, \\
 0 \leq \frac{d^2 p}{dT^2} = \frac{d^2 p}{dT^2}|_c - \frac{d^3 p}{dT^3}|_c T_c \epsilon + \dots \leq \frac{d^2 p}{dT^2}|_c, \\
 \frac{d(p/T)}{d(1/T)} = p - \frac{dp}{dT} T \leq 0, \quad \frac{d}{dT} \frac{d(p/T)}{d(1/T)} = -\frac{d^2 p}{dT^2} T \leq 0. \tag{1.1}
 \end{aligned}$$

For $T \geq 0$ the vapor pressure is a positive and convexly curved temperature function increasing with T from 0 to p_c . Also the temperature derivatives increase with T from $d^n p/dT^n(0) = 0$ to finite values $d^n p/dT^n(T_c)$ (where $n=1,2,\dots$). In contrast, the chemical potential is a negative and concavely curved temperature function decreasing with T . With the finite critical values μ_c and $d\mu/dT_c$, and, on the other hand, the divergent terms $d^n \mu/dT_c^n$ ($n=2,3,\dots$) an ϵ -expansion of μ is not possible:

$$\begin{aligned}
 0 > \mu \geq \mu_c, \quad 0 \geq \frac{d\mu}{dT} \geq \frac{d\mu}{dT}|_c, \quad 0 \geq \frac{d^2 \mu}{dT^2} \geq \frac{d^2 \mu}{dT^2}|_c \rightarrow -\infty, \tag{1.2} \\
 0 > \frac{d(\mu/T)}{d(1/T)} \geq \frac{d(\mu/T)}{d(1/T)}|_c, \quad 0 \leq \frac{d}{dT} \frac{d(\mu/T)}{d(1/T)} = -\frac{d^2 \mu}{dT^2} T < -\frac{d^2 \mu}{dT^2}|_c T_c \rightarrow +\infty, \\
 0 > \frac{\mu}{p} > \frac{\mu}{p}|_c, \quad 0 > \frac{d\mu}{dp} > \frac{d\mu}{dp}|_c, \quad 0 < \frac{d^2 \mu}{dp^2} < \frac{d^2 \mu}{dp^2}|_c, \quad 0 < \frac{d(\mu/T)}{d(p/T)} \leq \frac{d(\mu/T)}{d(p/T)}|_c.
 \end{aligned}$$

Thermodynamics treats the quantity X as an extensive quantity, which means that X is proportional to the fluid mass M . The validity of the relation $X = xM$ leads to x having the property of additivity and ensures its uniqueness. At

temperatures below the critical point the fluid mass M in the volume V is additively composed of the vapor mass M_v and the condensed mass M_l in the sub-volumes V_v and V_l ; $M = M_v + M_l$ in $V = V_v + V_l$. The same applies to other extensive quantities such as the entropy S , internal energy U , enthalpy H , free energy F , and heat capacity C . Denoting such quantities by X and $X_{v,l}$ and the corresponding mass-specific quantities by $x = X/M$ and $x_{v,l} = X_{v,l}/M_{v,l}$, one obtains the following definitions:

$$\begin{aligned} M &= M_v + M_l, & X &= X_v + X_l, & X &= \{V, S, U, H, F, C\}, \\ x &= X/M, & x_{v,l} &= X_{v,l}/M_{v,l}, & x &= \{v, s, u, h, f, c\}. \end{aligned} \quad (1.3)$$

It is worth mentioning that the temperature variation of the ratio of the differences $(x - x_l)$ and $(x_v - x)$ of quantities such as the volume, entropy, internal energy, enthalpy, free energy, and specific heat is the same and equal to that of the ratio of vapor to condensed masses, viz.

$$0 \leq \frac{M_v}{M_l} = \frac{v - v_l}{v_v - v} = \frac{s - s_l}{s_v - s} = \frac{u - u_l}{u_v - u} = \frac{h - h_l}{h_v - h} = \frac{f - f_l}{f_v - f} = \frac{c - c_l}{c_v - c} \leq 1, \quad (1.4)$$

where the equality signs are valid for $T = 0$ and $T = T_c$, respectively. From Equation (1.4) one arrives at the interdependence of two extensive quantities x and y and their phase-specific values $x_{v,l}$ and $y_{v,l}$ in the following form:

$$x(y_l - y_v) + y(x_v - x_l) - x_v y_l + x_l y_v = 0. \quad (1.5)$$

This relationship can also be deduced from the correlations $x = (M_v/M) \cdot x_v + (M_l/M) \cdot x_l$ and $y = (M_v/M) \cdot y_v + (M_l/M) \cdot y_l$ with $(M_v/M) + (M_l/M) = 1$.

The decomposition of mass M into M_v and M_l below the critical point occurs within limits and is given by

$$0 \leq \frac{M_v}{M} = \frac{v - v_l}{v_v - v} \leq \frac{1}{2} \leq \frac{M_l}{M} = \frac{v_v - v}{v_v - v_l} \leq 1. \quad (1.6)$$

While the mass-specific quantity x constitutes an average of the quantity X in V in relation to the total mass M and is thus a function of T and V/M , the mass- and phase-specific quantity x_v describes the quantity X_v in the volume V_v and is related to the vapor mass M_v , and the quantity x_l describes X_l in V_l and is related to M_l . The quantities $x_{v,l}$ then give thermodynamic information on the masses $M_{v,l}$ in $V_{v,l}$, which are subject to equal values of temperature T , vapor pressure $p = p(T)$ and chemical potential $\mu = \mu(T)$ in V , and different density values v_v^{-1} in V_v and v_l^{-1} in V_l . Since the densities of the vapor and condensate in V_v and V_l are functions of the temperature alone, the quantities $x_{v,l}$ in $V_{v,l}$ are likewise pure temperature functions. As v_v is different to v_l for $T < T_c$, the value x_v is different to x_l for $T < T_c$, and as v_v and v_l are equal to the critical value v_c at the critical point (T_c, p_c, μ_c) , the values x_v and x_l are equal to the critical value x_c at (T_c, v_c) . The information from x_v and x_l implicitly contains all particle interactions that can be expressed in terms of various imaginable types of descriptions of thermodynamic properties.

If a thermodynamic quantity is represented in its domain of definition $[T, v]$ by a thermodynamic function $x(T, v)$, a thermodynamic quantity is always an absolute quantity. For example, the physics of the real gas operates in the temperature range $[0, T_c]$ in the limits

$$0 = S(0, M, V) < S(T, M, V) < S(T_c, M, V) = [Vp_c - M\mu_c]/T_c \text{ and} \\ -M(u_v - u_l)(0) = U(0, M, V) < U(T, M, V) < U(T_c, M, V) = 0.$$

The critical value x_c of the quantity $x = \{v, s, u, f\}$ is finite. In fact, when x_v approaches the finite value x_c from below, then x_l approaches x_c from above and vice versa; in any case, one has $x_v(T_c) - x_l(T_c) = 0$. The approach is determined by $\lim_{T \rightarrow T_c} (dx_v(T)/dT) = -\lim_{T \rightarrow T_c} (dx_l(T)/dT)$. The ratio value of $x_v(T)/x_l(T)$ at the critical point is then different for the two possible cases of equal or opposite sign of $x_v(T)$ and $x_l(T)$. One has

$$x_v(T_c) = x_l(T_c) \neq 0, \quad x_v(T_c)/x_l(T_c) = +1 \text{ for } x_v(T)/x_l(T) > 0, \\ x_v(T_c) = x_l(T_c) = 0, \quad x_v(T_c)/x_l(T_c) = -1 \text{ for } x_v(T)/x_l(T) < 0. \tag{1.7}$$

The relations of the first line of (1.7) are valid for the quantities $x = \{v, s, f\}$.

The consequence from relations (1.7) for the quantity $x = u$ shall be investigated. It can be stated that the vapor energy U_v at low temperatures is positive since vapor particles are so far apart that their (negative) interaction potentials are vanishingly small in comparison with their (positive) thermal energies. At low temperatures one thus has $u_v = U_v/M_v > 0$. Under these conditions the evaporation energy $(u_v - u_l)M$ is very much larger than U_v . From $(u_v - u_l)M \gg U_v$ one obtains $(u_v - u_l) \gg U_v/M = u_v M_v/M$ or, with $M_v/M \leq 1/2$, $(u_v - u_l) > u_v > u_v/2 > u_v M_v/M \geq 0$. This gives an estimate of the mass-specific energy u_l in the form of $u_l = u_v - (u_v - u_l) \leq 0$, i.e. the vapor energy u_v is not negative and the condensate energy u_l is not positive. The second line of relations (1.7) then states $u_c = 0$. This yields the important results,

$$u_l(T) \leq 0 \leq u_v(T), \quad u_l(T_c) = 0 = u_v(T_c), \quad u_v(T_c)/u_l(T_c) = -1. \tag{1.8}$$

From Equations (1.3) one obtains the thermodynamic relation of the mean fluid quantity x (which is a function of T and v) to the phase-specific quantities $x_{v,l}$ (which are pure temperature functions) as follows:

$$x(T, v) = \frac{M_v}{M}(T, v)x_v(T) + \frac{M_l}{M}(T, v)x_l(T) = x_v - \frac{M_l}{M}(x_v - x_l) \\ = x_l + \frac{M_v}{M}(x_v - x_l) = \frac{v - v_l}{v_v - v_l}x_v + \frac{v_v - v}{v_v - v_l}x_l \\ = x_v - \frac{v_v - v}{v_v - v_l}(x_v - x_l) = x_l + \frac{v - v_l}{v_v - v_l}(x_v - x_l). \tag{1.9}$$

Differentiation of $x(T, v)$ with respect to v at fixed T yields the coefficient of isothermal phase transition,

$$\left(\frac{\partial x}{\partial v}\right)_T = \frac{x_v - x_l}{v_v - v_l}. \tag{1.10}$$

Thus the fluid quantity $x(T, v_c)$ can be expressed in terms of $x_{v,l}$, $v_{v,l}$, v_c , and $(\partial x/\partial v)_T$:

$$x(T, v_c) = x_{v,l}(T) - (v_{v,l}(T) - v_c)(\partial x/\partial v)_T. \quad (1.11)$$

If the saturated fluid does not have the critical volume v_c but the volume v , the following conversion has to be made:

$$x(T, v) = x(T, v_c) - (v_c - v)(\partial x/\partial v)_T = x_{v,l} - (v_{v,l} - v)(\partial x/\partial v)_T. \quad (1.12)$$

At $T = T_c$ the fluid takes the critical volume v_c . From Equation (1.9) it is immediately obvious that the critical values $x(T_c, v_c)$, $x_v(T_c)$, $x_l(T_c)$, and the zero-point values $x(0, v)$ and $x_l(0)$ are respectively equal,

$$x(T_c, v_c) = x_v(T_c) = x_l(T_c) = x_c, \quad x(0, v) = x_l(0), \quad (1.13)$$

and from Equation (1.10) it follows that

$$\begin{aligned} x_l(T) < x(T, v) < x_v(T) & \text{ if } (\partial x/\partial v)_T > 0, \\ x_l(T) > x(T, v) > x_v(T) & \text{ if } (\partial x/\partial v)_T < 0. \end{aligned} \quad (1.14)$$

In the theory it is not only the difference of the phase-specific quantities x_v and x_l , *i.e.*

$$x_v - x_l = (v_v - v_l)(\partial x(T, v)/\partial v)_T, \quad (1.15)$$

that is of importance, but also their sum

$(x_v + x_l) = 2x(T, v) + (v_v + v_l - 2v)(\partial x(T, v)/\partial v)_T$. Since $(v_v + v_l - 2v)/(v_v - v_l) = ([v_v - v] - [v - v_l])/(v_v - v_l) = M_l/M - M_v/M \geq 0$, one has

$$x_v + x_l = 2x + (x_v - x_l)(M_l/M - M_v/M). \quad (1.16)$$

The sign of the function $(x_v + x_l)$ will subsequently be of interest. It is the same as that of the function $(x_v - x_l)$ if the product function $(x_v + x_l)(x_v - x_l)$ has a positive sign, while the signs of $(x_v + x_l)$ and $(x_v - x_l)$ are opposite if

$(x_v + x_l)(x_v - x_l) = 2x(x_v - x_l) + (x_v - x_l)^2(M_l/M - M_v/M)$ is negative. The latter can be the case if either the product function $x(x_v - x_l)$ or the difference $(x_v^2 - x_l^2)$ is negative (see Equations (1.25) and (1.26) below). At the critical point one has $(x_v + x_l)(T_c) = 2x(T_c, v_c)$ and at absolute zero $(x_v + x_l)(0) = 2x(0, v) + (x_v - x_l)(0)$ and $x_v(0) = x(0, v) + (x_v - x_l)(0)$; for the vapor-phase quantity x_v one then obtains

$$x_v(T_c) = 2x(T_c, v_c) - x_l(T_c), \quad x_v(0) = x(0, v) + (x_v - x_l)(0). \quad (1.17)$$

The critical mean fluid value $x(T_c, v_c)$ is thus equal to the mean of the phase-specific critical values $\frac{1}{2}[x_v(T_c) + x_l(T_c)]$ and, if the fluid value $x(0, v)$ at absolute zero is given by the condensation energy value $-(x_v - x_l)(0)$, the vapor value $x_v(0)$ vanishes, *i.e.* it holds, for example, that $x_v(0) = 0$.

At this place the quantum state of the Bose-Einstein condensation should be noticed. In contrast to the thermodynamic temperature absolute zero the lowest temperature available is the transition temperature

$T_{tr} = (\hbar^2/mk) \cdot (2\pi/e^{5/3}) \cdot n^{2/3} > 0$, where $\hbar = h/2\pi$ is the Planck constant, k the Boltzmann constant, m the particle mass and n the particle density in the condensate. The atomic densities achieved in experiments range from 10^{-14} to 10^{-15} cm^{-3} and transition temperatures from 100 nK to a few μK [18]. The internal energy of the dilute gas is positive for $T > T_{tr}$ and vanishes at $T = T_{tr}$, whereas that of the condensate is negative [19].

2.1. Interdependence of Extensive and Intensive Quantities

Since the two-phase equilibrium can be described by extensive as well by intensive quantities, an interdependence between these quantities exists. Thermodynamics yields for the quotients $(x_v - x_l)/(v_v - v_l)$ of the particular quantities $x = \{f, s, u, c\}$ the well-known vapor pressure relations,

$$\begin{aligned} \left(\frac{\partial f}{\partial v}\right)_T &= \frac{f_v - f_l}{v_v - v_l} = -p \leq 0, & \left(\frac{\partial s}{\partial v}\right)_T &= \frac{s_v - s_l}{v_v - v_l} = \frac{dp}{dT} \geq 0, \\ \left(\frac{\partial u}{\partial v}\right)_T &= \frac{u_v - u_l}{v_v - v_l} = -\frac{d(p/T)}{d(1/T)} \geq 0, & \left(\frac{\partial c}{\partial v}\right)_T &= \frac{c_v - c_l}{v_v - v_l} = \frac{d^2 p}{dT^2} T \geq 0. \end{aligned} \tag{1.18}$$

Correspondingly, for the quotients $(x_v v_l - x_l v_v)/(v_v - v_l)$ the chemical potential relations are

$$\begin{aligned} \frac{f_v v_l - f_l v_v}{v_v - v_l} &= -\mu > 0, & \frac{s_v v_l - s_l v_v}{v_v - v_l} &= \frac{d\mu}{dT} \leq 0, \\ \frac{u_v v_l - u_l v_v}{v_v - v_l} &= -\frac{d(\mu/T)}{d(1/T)} > 0, & \frac{c_v v_l - c_l v_v}{v_v - v_l} &= \frac{d^2 \mu}{dT^2} T \leq 0. \end{aligned} \tag{1.19}$$

Equations (1.18) and (1.19) allow one to define volume functions $(x_v v_l - x_l v_v)/(x_v - x_l)$, which can be represented in different ways:

$$\begin{aligned} \frac{x_v v_l - x_l v_v}{x_v - x_l} &= v_v + v_l - \frac{x_v v_v - x_l v_l}{x_v - x_l} = v_l + \frac{v_v - v_l}{1 - x_v/x_l} \\ &= v_v - \frac{v_v - v_l}{1 - x_l/x_v} = \frac{v_v + v_l}{2} - \frac{v_v - v_l}{2} \frac{x_v + x_l}{x_v - x_l}. \end{aligned} \tag{1.20}$$

In evaluating the critical value of a volume function (1.20) one should give heed, in respect of Equations (1.7) in the case $x_v(T_c)/x_l(T_c) = 1$, to whether a finite limiting value exists; in the case $x_v(T_c)/x_l(T_c) = -1$ the limiting value is v_c . Hence the result is:

$$\frac{u_v v_l - u_l v_v}{u_v - u_l}(T_c) = \frac{d(\mu/T)}{d(p/T)}(T_c) = v_c. \tag{1.21}$$

With $x_{v,l} = \{f_{v,l}, s_{v,l}, u_{v,l}, c_{v,l}\}$ one obtains

$$\frac{\mu}{p} = \frac{f_v v_l - f_l v_v}{f_v - f_l} < 0, \quad \frac{d\mu}{dp} = \frac{s_v v_l - s_l v_v}{s_v - s_l} < 0, \tag{1.22}$$

$$\frac{d(\mu/T)}{d(p/T)} = \frac{u_v v_l - u_l v_v}{u_v - u_l} > 0, \quad \frac{d^2 \mu / d^2 p}{dT^2} = \frac{c_v v_l - c_l v_v}{c_v - c_l} < 0.$$

From Equations (1.22) it immediately follows that the critical value is finite for $x = \{f, s, u\}$ and divergent for $x = c$.

2.2. Entropy and Internal Energy Relations

According to relation (1.5), the interdependence of volume and entropy is $v(s_l - s_v) + s(v_v - v_l) - v_v s_l + v_l s_v = 0$. Taking relations (1.18) and (1.19) into account, viz. $(s_v - s_l) = (v_v - v_l) \cdot dp/dT$ and $(v_v s_l - v_l s_v) / (v_v - v_l) = -d\mu/dT$, this can be transformed to $0 \leq -\frac{d\mu}{dT} = \frac{s_l v_v - v_l s_v}{v_v - v_l} = s - v \frac{dp}{dT}$. Thus one gets Gibbs's entropy relations, including the thermodynamic reference value 0:

$$0 \leq v \frac{dp}{dT} \leq -\frac{d\mu}{dT} + v \frac{dp}{dT} = s(v, T), \quad (1.23)$$

$$0 \leq s_l(T), \quad s_{v,l}(T) = -\frac{d\mu}{dT} + v_{v,l} \frac{dp}{dT} = s(v, T) + [v_{v,l}(T) - v] \frac{dp}{dT}.$$

The value $s(v, T)$ is the sum of the terms $v \cdot dp/dT \geq 0$ and $(-d\mu/dT) \geq 0$ and is positive for $T > 0$ and vanishes for $T = 0$. The same is valid for the phase-specific entropy $s_l(T)$; and since $0 < v_l(T) \leq v(T_c) = v_c \leq v_v(T)$ one obtains the following sequences

$$0 \leq s_l(T) \leq s(v_c, T) \leq s(v_c, T_c) = s_c \leq s_v(T). \quad (1.24)$$

The interdependence of volume and internal energy is

$$v(u_l - u_v) + u(v_v - v_l) - v_v u_l + v_l u_v = 0, \text{ which with}$$

$$(u_v - u_l) = -(v_v - v_l) \cdot d(p/T)/d(1/T) \text{ and}$$

$(v_v u_l - v_l u_v) / (v_v - v_l) = -d(\mu/T)/d(1/T)$ gives Gibbs's internal energy relations and with respect to relation (1.21) the thermodynamic reference value 0:

$$u(v, T) = \frac{d(\mu/T)}{d(1/T)} - v \frac{d(p/T)}{d(1/T)} \leq \frac{d(\mu/T)}{d(1/T)}(T_c) - v_c \frac{d(p/T)}{d(1/T)}(T_c) \leq 0, \quad (1.25)$$

$$u_{v,l}(T) = \frac{d(\mu/T)}{d(1/T)} - v_{v,l}(T) \frac{d(p/T)}{d(1/T)} = u(v, T) - [v_{v,l}(T) - v] \frac{d(p/T)}{d(1/T)}.$$

For $0 \leq T \leq T_c$ the value $u(v, T)$ is the sum of the negative term $d(\mu/T)/d(1/T)$ and the positive term $(-v \cdot d(p/T)/d(1/T))$, where it holds that $d(\mu/T)/d(1/T) - v \cdot d(p/T)/d(1/T) \leq 0$ and therefore $u(v, T)$ is not positive. Furthermore, the phase-specific internal energies obey the relations $(u_v - u_l) = -(v_v - v_l) d(p/T)/d(1/T) \geq 0$ and $(u_v + u_l) \leq 0$; the last relation follows from $(u_v + u_l)(u_v - u_l) = (u_v^2 - u_l^2) = -2(v_v - v_l) [d(p/T)/d(1/T)]^2 \cdot [d(\mu/T)/d(1/T) - (v_v + v_l)/2] \leq 0$ since $d(\mu/T)/d(1/T) - (v_v + v_l)/2 \geq 0$. Hence one gets

$$(u_v - u_l) \geq 0 \text{ and } (u_v + u_l) \leq 0, \quad (1.26)$$

$$-(u_v - u_l) \leq u_l \leq u \leq (u_v + u_l) \leq u_c = 0 \leq u_v \leq (u_v - u_l). \quad (1.27)$$

The relations $(u_v + u_l) = 2u_v - (u_v - u_l) \leq 0$ and

$-(u_v + u_l) = -2u_l - (u_v - u_l) \geq 0$ lead to the limits of the energies $u_{v,l}$ in relation to the transient energies $\pm(u_v - u_l)$:

$$0 \leq \frac{u_v}{u_v - u_l} \leq \frac{1}{2} \leq \frac{u_l}{-(u_v - u_l)} \leq 1. \tag{1.28}$$

In other words: For $0 < T < T_c$ the vapor internal energy u_v is positive and always lower than half the evaporation energy, $u_v \leq \frac{1}{2}(u_v - u_l)$, and the liquid internal energy u_l is negative and lower than half the condensation energy, $u_l \leq \frac{1}{2}[-(u_v - u_l)]$. The critical values of the entropy are obtained from the relations $s_c T_c = v_c p_c - \mu_c = (v_c \cdot dp/dT - d\mu/dT)_c \cdot T_c$, yielding

$$\begin{aligned} s(v_c, T_c) &= v_c \frac{dp}{dT}_c - \frac{d\mu}{dT}_c = v_c \frac{p_c}{T_c} - \frac{\mu_c}{T_c} \\ &= \frac{1}{2} \left[v_c \left(\frac{p}{T} + \frac{dp}{dT} \right)_c - \left(\frac{\mu}{T} + \frac{d\mu}{dT} \right)_c \right] = -\frac{f_c}{T_c} > 0. \end{aligned} \tag{1.29}$$

Because $0 \leq c(v, T) = du(v, T)/dT = T \cdot ds(v, T)/dT$, the functions $u(v, T)$ and $s(v, T)$ increase monotonically with increasing T , and so the critical values present the maximum internal energy and entropy of the saturated fluid.

The interdependence of entropy and internal energy is calculated from the equation $s(u_l - u_v) + u(s_v - s_l) - s_v u_l + s_l u_v = 0$ and leads to the following identities and estimates:

$$s = u \frac{s_v - s_l}{u_v - u_l} + \frac{u_v s_l - u_l s_v}{u_v - u_l} \geq 0, \quad u = s \frac{u_v - u_l}{s_v - s_l} + \frac{s_v u_l - s_l u_v}{s_v - s_l} \leq 0. \tag{1.30}$$

The estimates follow from $[u_v M_v/M + u_l M_l/M] \cdot [s_v - s_l] + [M_v/M + M_l/M] \cdot [u_v s_l - u_l s_v] \geq 0$ (where the equality sign is valid for $T = 0$) and $[s_v M_v/M + s_l M_l/M] \cdot [u_v - u_l] + [M_v/M + M_l/M] \cdot [s_v u_l - s_l u_v] \leq 0$ (where the equality sign is valid for $T = T_c$).

The two obviously equivalent Equations (1.30) present the opportunity for proving the correctness of the reference data mentioned in Equations (1.8), (1.13), (1.17), (1.21) and (1.27). For example, it follows from $s(v_c, 0) = 0$ that $u(v_c, 0) = \mu(0) = u_l(0) = -(u_v - u_l)(0)$ with $u_v(0) = 0$ and from $s(v_c, T_c) = -d\mu/dT_c + v_c dp/dT_c$ that $u(v_c, T_c) = 0$. The data mentioned are thus reciprocal to one another. These data are thermodynamic reference values.

2.3. Heat Capacity Relations

The measurable heat capacity is defined by

$$c(v, T) = \frac{du(v, T)}{dT} = \frac{ds(v, T)}{dT} T = s(v, T) + \frac{ds(v, T)}{dT} T + \frac{df(v, T)}{dT}. \tag{1.31}$$

Calculation of the specific heat capacities requires the temperature derivatives of the quantities given in Equations (1.23) and (1.25). Taking into consideration Equations (3.1)-(3.3) below, the heat capacity relations are

$$c(T, v) = \frac{d}{dT} \left[\left[v_v + v_l - v - \frac{v_v - v_l}{\ln(v_v/v_l)} \right] \frac{d(p/T)}{d(1/T)} \right] = -\frac{d^2\mu}{dT^2} T + v \frac{d^2p}{dT^2} T \geq 0, \quad (1.32)$$

$$c_{v,l}(T) = c(T, v) + (v_{v,l} - v) (\partial c(T, v) / \partial v)_T = -\frac{d^2\mu}{dT^2} T + v_{v,l} \frac{d^2p}{dT^2} T \geq 0.$$

As the values of $c(T, v)$, $s(T, v)$, and d^2p/dT^2 vanish at absolute zero, those of $(-d\mu/dT)$ and $(-d^2\mu/dT^2)$ also vanish there according to Equations (1.18) and (1.19). And as the value $d^2\mu/dT^2$ diverges at the critical point, the fluid heat capacity and the specific heat capacities also diverge there: $c(T_c, v) = c_l(T_c) = c_v(T_c) \rightarrow +\infty$.

Further expressions for the heat capacity and temperature derivatives of internal energies can be given as follows:

$$\begin{aligned} \frac{du(v, T)}{dT} = c(v, T) &= c_v \frac{v - v_l}{v_v - v_l} + c_l \frac{v_v - v}{v_v - v_l} \\ &= \left[\frac{du_v}{dT} + \frac{dv_v}{dT} \frac{d(p/T)}{d(1/T)} \right] \frac{v - v_l}{v_v - v_l} + \left[\frac{du_l}{dT} + \frac{dv_l}{dT} \frac{d(p/T)}{d(1/T)} \right] \frac{v_v - v}{v_v - v_l}, \end{aligned} \quad (1.33)$$

$$\begin{aligned} \frac{du_{v,l}}{dT} &= -T \frac{d^2\mu}{dT^2} + v_{v,l} T \frac{d^2p}{dT^2} - \frac{dv_{v,l}}{dT} \frac{d(p/T)}{d(1/T)} \\ &= c(v, T) + (v_{v,l} - v) \frac{c_v - c_l}{v_v - v_l} + \frac{dv_{v,l}}{dT} \frac{u_v - u_l}{v_v - v_l} \end{aligned} \quad (1.34)$$

$$\begin{aligned} &= c_v \frac{v - v_l}{v_v - v_l} + c_l \frac{v_v - v}{v_v - v_l} + (v_{v,l} - v) \frac{c_v - c_l}{v_v - v_l} + \frac{dv_{v,l}}{dT} \frac{u_v - u_l}{v_v - v_l} \\ &= c_{v,l} + \frac{dv_{v,l}}{dT} \frac{u_v - u_l}{v_v - v_l} = c_{v,l} - \frac{dv_{v,l}}{dT} \frac{d(p/T)}{d(1/T)}, \end{aligned}$$

$$\begin{aligned} \frac{d(u_v - u_l)}{dT} &= (c_v - c_l) + \frac{d(v_v - v_l)}{dT} \frac{u_v - u_l}{v_v - v_l} \\ &= (v_v - v_l) \frac{d^2p}{dT^2} T - \frac{d(v_v - v_l)}{dT} \frac{d(p/T)}{d(1/T)}, \end{aligned}$$

$$\frac{d(u_v + u_l)}{dT} = -2 \frac{d^2\mu}{dT^2} T + (v_v + v_l) \frac{d^2p}{dT^2} T - \frac{d(v_v + v_l)}{dT} \frac{d(p/T)}{d(1/T)} > 0. \quad (1.35)$$

It holds that

$$\begin{aligned} -(u_v - u_l)(0) = u_l(0) = u(0) = (u_v + u_l)(0) &< u_l(T) < u(T) < (u_v + u_l)(T) < u(T_c) \\ &= (u_v + u_l)(T_c) = 0 \end{aligned}$$

and for $0 < T < T_c$ that

$$(u_v + u_l) - u = \left[\frac{v_v - v_l}{\ln(v_v/v_l)} - v_c \right] \left[-\frac{d(p/T)}{d(1/T)} \right] > 0. \quad (1.36)$$

In order to show that $(u_v + u_l)$ is a convexly curved temperature function, one has to prove that $d^2(u_v + u_l)/dT^2 > 0$ or that the straight line $u(0)(1 - T/T_c)$ is above $(u_v + u_l)$. The condition of convexity for $(u_v + u_l)$ then reads $(u_v + u_l) \leq u(0)(1 - T/T_c)$, which can be transformed to

$$0 \leq u_v(T) + u_l(T) - u_l(0) \leq -u_l(0) \cdot T/T_c. \quad (1.37)$$

Indeed, for $T > 0$ the terms in Equation (1.37) are positive since $u_v(T) > 0$ and $u_l(T) > u_l(0)$, which meets the condition mentioned. Likewise, the function $(u_v - u_l)(T)$ is concavely curved when its values are above the straight line $-u(0)(1 - T/T_c)$, which means that $(u_v - u_l)(T) \geq -u(0)(1 - T/T_c)$. Division by $-u(0) = (u_v - u_l)(0) > 0$ gives the correct relations $1 \geq (u_v - u_l)(T)/(u_v - u_l)(0) \geq (1 - T/T_c) \geq 0$ and thus confirms that the condition for concavity of $(u_v - u_l)$ is met.

From $c_{v,l} = du_{v,l}/dT - (u_v - u_l)/(v_v - v_l) \cdot dv_{v,l}/dT$ and $(u_v - u_l)/(v_v - v_l) = -d(p/T)/d(1/T)$ it follows that

$$\begin{aligned} \frac{c_v - c_l}{u_v - u_l} &= \frac{d \ln[(u_v - u_l)/(v_v - v_l)]}{dT} \\ &= \frac{d \ln[-d(p/T)/d(1/T)]}{dT} = -\frac{d(1/T)}{d(p/T)} \frac{d^2 p}{dT^2} T. \end{aligned} \tag{1.38}$$

It is of interest to take $T = 0$ in entropy and heat capacity relations. This is immediately possible in the case of the entropy because Nernst's theorem states that the entropy vanishes at absolute zero, where only the condensed phase exists, and increases with the temperature:

$$s(0, v) = s_l(0) = 0, \quad (\partial s(T, v)/\partial T)_v = c(T, v)/T > 0. \tag{1.39}$$

For $0 \leq T \leq T_c$ one thus gets

$$0 = s(0, v) = s_l(0) < s_l(T) < s(T, v) < s(T_c, v) = s_l(T_c) = s_v(T_c) < s_v(T). \tag{1.40}$$

Similarly, in the case of the heat capacity one gets for $0 \leq T < T_c$

$$0 = c(0, v) = c_l(0) < c_l(T) < c(T, v) < c_v(T). \tag{1.41}$$

The temperature derivatives of the chemical potential function $(-d\mu/dT)$ and the phase-specific entropies $s_{v,l}$ can be determined from measurements of $c(T, v)$, $v_{v,l}(T)$ and $p(T)$ since

$$\begin{aligned} -\frac{d^2 \mu}{dT^2} &= \frac{c(T, v)}{T} - v \frac{d^2 p}{dT^2} > 0, \\ \frac{ds_{v,l}}{dT} &= \frac{c(T, v)}{T} + (v_{v,l} - v) \frac{d^2 p}{dT^2} + \frac{dv_{v,l}}{dT} \frac{dp}{dT}. \end{aligned} \tag{1.42}$$

With the result $(-d\mu/dT) > 0$ one obtains from Equations (1.23) the relations

$$s_l - v_l \frac{dp}{dT} = s_v - v_v \frac{dp}{dT} = s - v \frac{dp}{dT} = -\frac{d\mu}{dT} > 0. \tag{1.43}$$

These state that the entropy values are always positive and greater than the product of the volumes and vapor pressure coefficient. From relations (1.43), in turn, one can derive the following relations:

$$\frac{s_l}{v_l} > \frac{s}{v} > \frac{s_v}{v_v} > \frac{dp}{dT} > 0. \tag{1.44}$$

Temperature properties of the phase-specific heats are similarly derived. With the result $(-d^2 \mu/dT^2) > 0$ one obtains from Equations (1.32) the relations

$$c_l - v_l \frac{d^2 p}{dT^2} T = c - v \frac{d^2 p}{dT^2} T = c_v - v_v \frac{d^2 p}{dT^2} T = -\frac{d^2 \mu}{dT^2} T > 0, \quad (1.45)$$

from which in turn the relations

$$\frac{c_l}{v_l} > \frac{c}{v} > \frac{c_v}{v_v} > \frac{d^2 p}{dT^2} > 0 \quad (1.46)$$

can be derived. Experimental verification of $C_V/V = c/v > d^2 p/dT^2 \cdot T$ also proves confirmation of $(-d^2 \mu/dT^2) > 0$.

2.4. Chemical Potential Relations

The identities

$$\frac{x_v y_l - x_l y_v}{y_v - y_l} = -x_{v,l} + y_{v,l} \left(\frac{\partial x}{\partial y} \right)_T, \quad (1.47)$$

$$\frac{d}{dT} \frac{x_v y_l - x_l y_v}{y_v - y_l} = -\frac{dx_{v,l}}{dT} + \frac{dy_{v,l}}{dT} \left(\frac{\partial x}{\partial y} \right)_T + y_{v,l} \frac{d}{dT} \left(\frac{\partial x}{\partial y} \right)_T$$

are now used to put the chemical potential functions in explicit form as energy functions:

$$\begin{aligned} \mu &= f_{v,l} + v_{v,l} p = u_{v,l} - s_{v,l} T + v_{v,l} p < 0, \\ \frac{d\mu}{dT} &= -s_{v,l} + v_{v,l} \frac{dp}{dT} = \frac{df_{v,l}}{dT} + \frac{dv_{v,l}}{dT} p + v_{v,l} \frac{dp}{dT} < 0, \\ \frac{d(\mu/T)}{d(1/T)} &= u_{v,l} + v_{v,l} \frac{d(p/T)}{d(1/T)} = \frac{d(f_{v,l}/T)}{d(1/T)} - \frac{dv_{v,l}}{dT} T p + v_{v,l} \frac{d(p/T)}{d(1/T)} < 0, \\ \frac{d^2 \mu}{dT^2} &= -\frac{c_{v,l}}{T} + v_{v,l} \frac{d^2 p}{dT^2} = -\frac{ds_{v,l}}{dT} + \frac{dv_{v,l}}{dT} \frac{dp}{dT} + v_{v,l} \frac{d^2 p}{dT^2} < 0. \end{aligned} \quad (1.48)$$

The relations state that μ is a negative, concavely curved function, decreasing with increasing T . For μ as a function of measurable quantities see Equations (3.15) and (3.16) below.

3. Internal Fluid Energy as a Function of the Condensation Energy

It can be shown that the fluid energy $u(T, v)$ can be expressed in terms of the condensation energy $[-(u_v - u_l)]$:

$$\begin{aligned} u &= \frac{d(\mu/T)}{d(1/T)} - v \frac{d(p/T)}{d(1/T)} = \frac{d(p/T)}{d(1/T)} \left[\frac{d(\mu/T)}{d(p/T)} - v \right] \\ &= \frac{-(u_v - u_l)}{v_v - v_l} \left[\frac{u_v v_l - u_l v_v}{u_v - u_l} - v \right] \\ &= -(u_v - u_l) \left[\frac{v_l - v}{v_v - v_l} - \frac{u_l}{u_v - u_l} \right] \\ &= -(u_v - u_l) \left[\frac{v_v - v}{v_v - v_l} - \frac{u_v}{u_v - u_l} \right]. \end{aligned} \quad (2.1)$$

Since the temperature coefficients $(v - v_l)/(v_v - v_l)$ and $(v_v - v)/(v_v - v_l)$

are represented by M_v/M and M_l/M , respectively, the mass distributions $M_v/M=0$ and $M_l/M=1$ at $T=0$ give the three relations $u(0)=u_l(0)$, $u(0)=-(u_v-u_l)(0)+u_v(0)$, $u(0)=-(u_v-u_l)(0)$, and the distributions $M_v/M=M_l/M=1/2$ at $T=T_c$ give the three relations $u(T_c)=(u_v-u_l)(T_c)/2+u_l(T_c)$, $u(T_c)=-(u_v-u_l)(T_c)/2+u_v(T_c)$, $u(T_c)=u_v(T_c)/2+u_l(T_c)/2$. One thus obtains the following characteristic thermodynamic reference values, which are valid for every gas:

$$u(0)=u_l(0)=-(u_v-u_l)(0), u_v(0)=0, u(T_c)=u_l(T_c)=u_v(T_c)=0. \quad (2.2)$$

4. Internal Fluid Energy as an Expression of Measurable Quantities

Endeavors to publish data of the functions $u(v_c, T)$ and $u_{v,l}(T)$ are prominent in the current literature. The energy equations can be written in the form

$$u(v_c, T) = \left[\frac{d(\mu/T)}{d(p/T)} - v_c \right] \frac{d(p/T)}{d(1/T)} \leq 0, \quad u_{v,l}(T) = \left[\frac{d(\mu/T)}{d(p/T)} - v_{v,l} \right] \frac{d(p/T)}{d(1/T)}. \quad (3.1)$$

According to Equations (1.20)-(1.22) the differential quotient $d(\mu/T)/d(p/T)$ is a positive volume quantity monotonically decreasing with increasing T from high values $v_v(T)$ near absolute zero to the lowest value v_c at the critical point. The expression of measurable volumes $v_v(T)$ and $v_l(T)$ instead of $d(\mu/T)/d(p/T)$ as published in (2015) [3] reads:

$$\frac{d(\mu/T)}{d(p/T)} = v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)}. \quad (3.2)$$

It is symmetric in the variables and linear in both v_v and v_l and at the critical point it yields v_c . Then inserting the solution (3.2) in the internal energy Equations (3.1) yields the results

$$u(T, v_c) = \left[\frac{v_v - v_l}{\ln(v_v/v_l)} - v_v - v_v + v_c \right] \cdot \left[-\frac{d(p/T)}{d(1/T)} \right] \leq 0, \quad (3.3)$$

$$u_{v,l}(T) = \left[\frac{v_v - v_l}{\ln(v_v/v_l)} - v_{l,v} \right] \cdot \left[-\frac{d(p/T)}{d(1/T)} \right].$$

These equations state that the internal energies can be expressed in terms of the measurable quantities, phase-specific volumes and vapor pressure, and are given by absolute figures; in particular, it holds that $u_v(T_c)=u_l(T_c)=0$ since $(v_v - v_l)/\ln(v_v/v_l) = v_c$ and $v_v = v_l = v_c$ at $T = T_c$.

If the functions u_v and u_l are expressed as dependent on the volume ratio $z = v_v/v_l$, one obtains for the energy ratios $u_v/(u_v - u_l)$ and $-u_l/(u_v - u_l)$ according to Equations (1.28) the following relations:

$$0 \leq \frac{u_v}{u_v - u_l} = \frac{1}{\ln z} - \frac{1}{z-1} \leq \frac{1}{2} \quad \text{for } 0 \leq T \leq T_c \quad \text{and} \quad z = \frac{v_v(T)}{v_l(T)} \geq 1, \quad (3.4)$$

$$\frac{1}{2} \leq \frac{-u_l}{u_v - u_l} = -\frac{1}{\ln z} + \frac{z}{z-1} \leq 1.$$

The sum of them is, of course, equal to 1. Equations (3.4) allow one to calculate the relation between the energy ratio $\eta = u_v/u_l$ and volume ratio z of fluid particles in the vapor and liquid spaces, viz.

$$0 \geq \eta = \frac{u_v}{u_l} = \frac{z-1-\ln z}{z-1-z \ln z} \geq -1 \text{ for } 0 \leq T \leq T_c \text{ and } z = \frac{v_v(T)}{v_l(T)} \geq 1. \quad (3.5)$$

According to Equations (1.17) and (1.8), the energy ratio η assumes the value 0 at absolute zero (where $z \rightarrow \infty$) and, respectively, the value -1 at the critical point (where $z=1$). The relation $\eta(z)$ represents a universal law of the two-phase equilibrium of real gases.

Calculation of the energy ratio $(u_v + u_l)/(u_v - u_l)$ as a function of z starts from Equation (1.20) or from $(\eta + 1)/(\eta - 1)$ and ends in any case with the result

$$-1 \leq \frac{u_v + u_l}{u_v - u_l} = \frac{2}{\ln z} - \frac{z+1}{z-1} \leq 0 \text{ for } 0 \leq T \leq T_c \text{ and } z = \frac{v_v}{v_l} \geq 1. \quad (3.6)$$

Rigorous thermodynamic calculations combine Equations (1.8) and (1.44) and yield the following relations for the internal energy and entropy:

$$-1 \leq u_v/u_l < 0, \quad 1 \leq s_v/s_l \leq v_v/v_l \text{ for } T \leq T_c. \quad (3.7)$$

The constraints (3.7) state that the ratios of absolute energy and entropy for vapor and liquid are restricted within certain limits for temperatures in the two-phase region. And combining Equations (1.20), (1.22) and (3.2) gives

$$v_v + v_l - \frac{u_v v_v - u_l v_l}{u_v - u_l} = \frac{u_v v_l - u_l v_v}{u_v - u_l} = v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)}, \quad (3.8)$$

$$\frac{u_v v_v - u_l v_l}{u_v - u_l} = \frac{v_v - v_l}{\ln(v_v/v_l)}.$$

Algebraic rearrangement of Equation (3.8) leads to a data criterion for consistent thermodynamic values $v_v(T)$, $v_l(T)$, $u_v(T)$ and $u_l(T)$, which is valid for $T \leq T_c$ and reads:

$$\left[\frac{u_v}{u_v - u_l} + \frac{v_l}{v_v - v_l} \right] \cdot \ln \left(\frac{v_v}{v_l} \right) = \left[\frac{u_l}{u_v - u_l} + \frac{v_v}{v_v - v_l} \right] \cdot \ln \left(\frac{v_v}{v_l} \right) = 1. \quad (3.9)$$

In turn, from Equations (3.9) one obtains

$$u_v = \frac{u_v - u_l}{\ln(v_v/v_l)} - v_l \frac{u_v - u_l}{v_v - v_l} \geq 0, \quad u_l = \frac{u_v - u_l}{\ln(v_v/v_l)} - v_v \frac{u_v - u_l}{v_v - v_l} \leq 0,$$

$$(u_v - u_l) = (h_v - h_l) - (v_v - v_l)p = (s_v - s_l)T - (v_v - v_l)p = -(v_v - v_l) \frac{d(p/T)}{d(1/T)} \geq 0. \quad (3.10)$$

Equations (3.9) and (3.10) clearly state that, if table data $T, p, v_v, v_l, (h_v - h_l)$, or $(s_v - s_l)$ and $(u_v - u_l)$ are thermodynamically consistent, then the internal energies, $u_v, u_l, u = u_v(v_v - v_l)/(v_v - v_l) + u_l(v_v - v_l)/(v_v - v_l)$, can be given absolutely. An entropy data criterion of the same kind as for the internal energy can also be formulated. To this end one has to confirm the validity of the relation.

$$\frac{s_{v,l} + \mu/T - [v_v + v_l - (v_v - v_l)/\ln(v_v/v_l)]p/T}{s_v - s_l} = \frac{u_{v,l}}{u_v - u_l} \quad (3.11)$$

to obtain with $u_{v,l}/(u_v - u_l) = 1/\ln(v_v/v_l) - v_{l,v}/(v_v - v_l)$ the criterion desired:

$$\left[\frac{s_{v,l}}{s_v - s_l} + \frac{v_{l,v}}{v_v - v_l} + \frac{\mu}{(s_v - s_l)T} - \left[\frac{v_v + v_l}{v_v - v_l} - \frac{1}{\ln(v_v/v_l)} \right] \frac{p/T}{dp/dT} \right] \cdot \ln\left(\frac{v_v}{v_l}\right) = 1. \quad (3.12)$$

This relation allows, in principle, to give the chemical potential in terms of p , $v_{v,l}$ and $s_{v,l}$ as follows:

$$\mu = -s_{v,l}T - v_{l,v} \frac{dp}{dT}T + \frac{v_v - v_l}{\ln(v_v/v_l)} \frac{dp}{dT}T + \left[v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)} \right] p. \quad (3.13)$$

The entropy expressions read

$$0 \leq s(v_c, T) = -\frac{d\mu}{dT} + v_c \frac{dp}{dT} = s_l + (v_c - v_l) \frac{dp}{dT} = s_v - (v_v - v_c) \frac{dp}{dT}. \quad (3.14)$$

It holds that $-s_{v,l}T - v_{l,v} \frac{dp}{dT}T = -sT - (v_v + v_l - v_c) \frac{dp}{dT}T$ and

$$\mu = -sT - \left[v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)} \right] \frac{dp}{dT}T + v_c \frac{dp}{dT}T + \left[v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)} \right] p.$$

According to relations (1.39) one has $sT = T \int_0^T \frac{ds}{dT} dT = T \int_0^T \frac{c}{T} dT$. The chemical potential can thus be determined, on the one hand, by measuring the two-phase heat capacity, phase-specific volumes and vapor pressure:

$$\mu(T) = -T \int_0^T \frac{c(T, v_c)}{T} dT + v_c \frac{dp}{dT}T - \left[v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)} \right] \left[-\frac{d(p/T)}{d(1/T)} \right], \quad (3.15)$$

or, on the other, by measuring the phase-specific volumes and vapor pressure only:

$$\mu(T) = T \left[\frac{\mu(T_c)}{T_c} - \int_{p/T}^{p(T_c)/T_c} \left[v_v + v_l - \frac{v_v - v_l}{\ln(v_v/v_l)} \right] d \frac{p}{T} \right] < 0, \quad \frac{\mu_c}{T_c} = -s_c + v_c \frac{p_c}{T_c}. \quad (3.16)$$

The energy sum $(\mu + sT)$ is also measurable and calculable and it holds that

$$\mu + sT = \left[\frac{v_v - v_l}{\ln(v_v/v_l)} - v_v - v_l \right] \cdot \left[-\frac{d(p/T)}{d(1/T)} \right] + v_c \frac{dp}{dT}T = u + v_c p. \quad (3.17)$$

From $d(\mu + sT)/dT = c + v_c dp/dT > 0$ and $d^2(\mu + sT)/dT^2 = dc/dT + v_c d^2p/dT^2 > 0$ it is concluded that the energy sum $\mu + sT = u + v_c p$ is a convex temperature function strongly increasing from $\mu(0) = -(u_v - u_l)(0) < 0$ at absolute zero to $\mu_c + s_c T_c = v_c p_c > 0$ at the critical point.

5. Phase-Specific Energy as a Function of the Evaporation Energy

The Carnot-Clapeyron-Clausius equation

$$u_v - u_l = (v_v - v_l) \left[-d(p/T)/d(1/T) \right] \quad (4.1)$$

suggests a unique relation between the energy density and particle density in the coexisting bulk phases, vapor and liquid. As the local interaction potentials in the partial volumens V_v and V_l are unique functions of the local particle density and determine the values u_v and u_l , respectively, it should be possible by means of a density coefficient and a temperature function to find suitable ansatzes for the functions $u_{v,l}$ depending on the density coefficient and temperature function. As density coefficient, a function ρ of the density variable $z = v_v/v_l$ is now chosen, and as temperature function the evaporation energy $(u_v - u_l)$. The ansatz proposed for the energy in the vapor phase is then $u_v = \rho(1/z) \cdot (u_v - u_l)$. The energy in the condensed phase must be $u_l = -\rho(z) \cdot (u_v - u_l)$ since the transfer of a particle from V_v to V_l causes the value u_v to change to u_l , the density variable from $1/z$ to z and the phase transition energy from $(u_v - u_l)$ to $(u_l - u_v) = -(u_v - u_l)$, while the form of ρ is preserved because the functional density dependence of the microscopic interaction forces is of course phase-invariant. The conjectures [2]

$$u_v = \rho(1/z) \cdot (u_v - u_l), \quad u_l = -\rho(z) \cdot (u_v - u_l) \quad (4.2)$$

then yield, on the one hand, the reference values

$0 = u_v(T_c) = u_l(T_c) = \frac{1}{2} [u_v(T_c) + u_l(T_c)] = u(v_c, T_c)$ and, on the other, for the density coefficient the equation

$$\rho(1/z) + \rho(z) = 1 \quad (4.3)$$

and because $u_v(0) = 0$ and $u_v(T_c)/u_l(T_c) = -1$ the boundary conditions

$$0 \leq \rho(1/z)/\rho(z) \leq 1. \quad (4.4)$$

The functional Equation (4.3) for ρ under condition (4.4) is satisfied by

$$0 \leq \rho(1/z) = \frac{1}{\ln z} - \frac{1}{z-1} \leq \frac{1}{2} \leq \rho(z) = -\frac{1}{\ln z} + \frac{z}{z-1} \leq 1. \quad (4.5)$$

From Equation (4.2) it follows that

$$0 \leq \frac{u_v}{u_v - u_l} = \frac{1}{\ln z} - \frac{1}{z-1} \leq \frac{1}{2} \leq -\frac{1}{\ln z} + \frac{z}{z-1} = \frac{-u_l}{u_v - u_l} \leq 1. \quad (4.6)$$

The relations (4.6) and (3.4) are identical and valid for $0 \leq T \leq T_c$ and $z = v_v(T)/v_l(T) \geq 1$.

6. Results and Discussion

The paper treats thermodynamic properties of the saturated fluid. It is shown that the fluid state is completely determined by the internal energy and entropy in the vapor and liquid spaces. The ratios of the absolute phase-specific internal energies and entropies are restricted within certain limits. If for temperatures $T \in [T_1, T_2]$ measured saturation data of the vapor pressure, reciprocal phase-specific densities and isothermal transient energy obey the data criterion Equation (3.9), then the internal energy as a function of T calculated according

to Equations (3.10) is an absolute thermodynamic quantity. This fundamental procedure in gaining thermodynamic data excludes any application of so-called fiducial reference data since they cannot yield correct values. As the state of saturation is maintained, it is not possible to distinguish between a constant pressure and a constant volume condition. This is the characteristic difference between the heat capacities of a two-phase and a one-phase fluid. There is only one phase-specific heat capacity in the vapor space, $c_v(T)$, and one in the liquid space, $c_l(T)$. The measurable heat capacity of the fluid, $C(v_c, T) = Mc(v_c, T) = M_v c_v + M_l c_l$, can also be calculated. Further results are the concavity of the positive, measurable temperature function $(u_v - u_l)$ and the convexity of the negative temperature functions $(u_v + u_l)$. The chemical potential is a negative, measurable and calculable temperature function. The ratios of phase-specific energies to isothermal transient

energies obey the relations $0 \leq u_v / (u_v - u_l) \leq \frac{1}{2} \leq u_l / (u_l - u_v) \leq 1$, which should be heeded when a state chart of the fluid under consideration is constructed.

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Appendix: Comments on the Internationally Accepted Equations for the Saturation Properties of Water

The International Association for the Properties of Water and Steam (IAPWS) [13] [14] provides internationally accepted formulations for the properties of water. There are special correlation equations for the vapor-liquid saturation properties of water. Formulas are given for the vapor pressure p , phase-specific volumes $v_{v,l}$, internal energies $u_{v,l}$, and entropies $s_{v,l}$ as functions of the saturation temperature T . This affords a unique description of the temperature dependence of every property of the saturated water.

This study treats the IAPWS equations in the framework of thermodynamics. The IAPWS equations read, on the one hand [13] [14],

$$u_{v,l} = \alpha - v_{v,l} \frac{d(p/T)}{d(1/T)}, \quad s_{v,l} = \phi + v_{v,l} \frac{dp}{dT}, \quad (\text{A1})$$

where the so-called auxiliary quantities α and ϕ are given as functions of the temperature T ; and, on the other, in terms of the thermodynamic fundamental equation,

$$u_{v,l} - s_{v,l}T = \mu - v_{v,l}p, \quad (\text{A2})$$

where μ is the chemical potential of the saturated fluid. Equations (A1) and (A2) are related as follows:

$$\alpha - \phi T = \mu, \quad \alpha = \frac{d(\mu/T)}{d(1/T)}, \quad \phi = -\frac{d\mu}{dT}. \quad (\text{A3})$$

Let us now investigate the thermodynamic conditions that have to be satisfied by the temperature functions α and ϕ if they are to define the two-phase chemical potential μ according to Equations (A3). First a few thermodynamic relations are taken and then transformed into IAPWS parlance. The Carnot-Clapeyron-Clausius equations read

$$\frac{u_v - u_l}{v_v - v_l} = -\frac{d(p/T)}{d(1/T)}, \quad \frac{s_v - s_l}{v_v - v_l} = \frac{dp}{dT}. \quad (\text{A4})$$

These are satisfied by Equations (A1). The Gibbs-Duhem equations read

$$\frac{du_{v,l}}{dT} + \frac{dv_{v,l}}{dT} p = \frac{ds_{v,l}}{dT} T. \quad (\text{A5})$$

They are satisfied by Equations (A1) if the following relation between α and ϕ is valid:

$$\frac{d\alpha}{dT} = \frac{d\phi}{dT} T. \quad (\text{A6})$$

Note that Equation (A6) is implicitly contained in relations (A3) since $d\mu/dT = d\alpha/dT - d\phi/dT \cdot T - \phi = -\phi$ and $d(\mu/T)/d(1/T) = \mu - d\mu/dT \cdot T = (\alpha - \phi T) + \phi T = \alpha$. Relations (A4) and (A5) therefore afford nothing new, but merely confirm relations (A3). The mathematical structures of Equations (A1) thus conform to the thermodynamic

internal energy and entropy expressions in respect of Equations (A3).

Condition (A6) is numerically satisfied by the formulas in [13] [14] for $\alpha(T)$ and $\phi(T)$, whose temperature dependences are expressed as follows:

$$\alpha[\text{J/g}] = d_\alpha + d_1\theta^{-19} + d_2\theta + d_3\theta^{4.5} + d_4\theta^5 + d_5\theta^{54.5}, \quad \text{where } \theta \equiv \frac{T}{T_c}, \quad (\text{A7})$$

$$\phi[\text{J/g} \cdot \text{K}] = \left[d_\phi + \frac{19}{20}d_1\theta^{-20} + d_2 \ln \theta + \frac{9}{7}d_3\theta^{3.5} + \frac{5}{4}d_4\theta^4 + \frac{109}{107}d_5\theta^{53.5} \right] \frac{1}{T_c}, \quad (\text{A8})$$

where $[d_\alpha, d_\phi] = [-1.135905627715\text{E}3, 2.3195246\text{E}3]$, $T_c = 647.096 \text{ K}$,

$$[d_1, d_2, d_3, d_4, d_5] = [-5.65134998\text{E} - 8, 2.69066631\text{E}3, 1.27287297\text{E}2, -1.35003439\text{E}2, 9.81825814\text{E} - 1].$$

The vapor pressure p and chemical potential μ obey for temperatures $T \leq T_c$ the following relations:

$$p > 0, \quad \frac{dp}{dT} > 0, \quad \frac{d(p/T)}{d(1/T)} < 0, \quad \frac{d^2p}{dT^2} > 0, \quad (\text{A9})$$

$$\mu < 0, \quad \frac{d\mu}{dT} < 0, \quad \frac{d(\mu/T)}{d(1/T)} < 0, \quad \frac{d^2\mu}{dT^2} < 0. \quad (\text{A10})$$

Relations (A10) then lead to further conditions for α and ϕ :

$$\alpha < 0, \quad \frac{d\alpha}{dT} > 0, \quad \phi > 0, \quad \frac{d\phi}{dT} > 0. \quad (\text{A11})$$

Accordingly, α must be a negative function increasing as T , and ϕ must be a positive function likewise increasing as T . It is found that $d\alpha/dT > 0$, but not that $\alpha < 0$ for all T in the range $[T_i, T_c]$; similarly, it does hold that $d\phi/dT > 0$, but not that $\phi > 0$ for all $T \in [T_i, T_c]$. The auxiliary Equations (A1), despite their correct formal structure, are therefore not thermodynamically appropriate for justifying the chemical potential according to Equations (A3). Further consideration of the temperature dependence of $u_{v,l}$ shows that the sum $(u_v + u_l)$ yields a concavely, but not a convexly curved function, as should be.

The fit function for measured vapor pressure data reads [13] [14]

$$\ln\left(\frac{p}{p_c}\right) = \frac{T_c}{T} \left[a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5} \right], \quad \text{where } \tau \equiv 1 - \theta \quad (\text{A12})$$

and $p_c = 22.064 [\text{MPa}]$. The terms $\tau^{1.5}$, $\tau^{3.5}$, $\tau^{7.5}$ produce divergent temperature derivatives $d^n p/dT^n$ at T_c for $n \geq 2$, whereas all vapor pressure derivatives have finite values. In contrast, the derivatives of the chemical potential $d^n \mu/dT^n$ diverge at T_c for $n \geq 2$ and determine the divergence of the heat capacity $C(M, V, T) = M \cdot c(V/M, T)$. In addition, it should be noted here that, if the saturation state is maintained, it is not possible to distinguish between a constant pressure and a constant volume condition. There is thus only one phase-specific heat capacity in the vapor space, $c(V_v/M_v, T)$, and one in the liquid space, $c(V_l/M_l, T)$, and it holds that

$$C(M, V, T) = M_v \cdot c(V_v/M_v, T) + M_l \cdot c(V_l/M_l, T) = C(M_v, V_v, T) + C(M_l, V_l, T).$$

Numerous thermodynamic deficiencies have been mentioned, viz. violation of the conditions $\alpha(T) < 0$ and $\phi(T) > 0$ for every temperature $T \in [T_l, T_c]$, the incorrect temperature dependence of $(u_v + u_l)$, the proposed vapor pressure fit formula with a divergent term $d^2 p/dT^2$ at T_c and, finally, tables which list two different phase-specific heat capacities for vapor as well for liquid. From all this it is concluded that the published data [13] [14] are in need of basic correction.