Thermodynamic Properties of Steam in the Critical Region

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An analysis is presented of the experimental data on thermodynamic properties in the critical region of steam. The model used is that of revised and extended scaling, as given by the modern theory of critical phenomena. All thermodynamic properties are given in closed (parametric) form. The model has, in addition to three universal constants that are given by theory, sixteen adjustable parameters that were obtained by least-squares fit to PVT and speed-of-sound data. It is valid in the range 200-420 kg/m³ in density and 644-693 K in temperature. It accurately represents the experimental data for equation of state, vapor pressure, latent heat, specific heats $C_p$ and $C_v$ and speed of sound. Our analysis permits new estimates of the critical parameters of steam, and has led to a number of conclusions regarding the mutual consistency of the experimental data. Tabulated values of the thermodynamic properties of steam are appended to the paper.

Key words: critical parameters; critical region; energy; equation of state; latent heat; scaling laws; specific heat; speed of sound; steam; thermodynamic function; thermodynamic tables; vapor pressure; water.

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1. Introduction

The modern theory of critical phenomena gives detailed predictions for the singular behavior of thermodynamic properties in fluids. In this paper we present the results of an analysis of the thermodynamic behavior of steam in the criti
cal region in terms of a revised and extended scaled fundamental equation that incorporates these theoretical predictions. The use of this equation makes it possible to assess the consistency between the data for various thermodynamic properties of steam, such as the PVT properties, specific heats, and speed of sound. Detailed comparisons of these experimental data and the theoretical surface are presented. Tabulated values of the thermodynamic properties pressure, enthalpy, entropy, energy, specific heats at constant pressure and at constant volume, and speed of sound are given with temperature and density as entries. These tables will be helpful for testing global formulations of the thermodynamic behavior of steam for adequacy in the critical region, and for supplementing such formulations if they are found wanting.

In this paper, we introduce the concepts of critical anomalies and critical exponents in Sec. 2. The fundamental equation is developed in Sec. 3, while a complete listing of the equations for the thermodynamic properties is given in Appendix A, and the constants defining the equation are listed in Appendix B. In Sec. 4 the various data sources are discussed. Section 5 deals with the selection of critical constants for steam. Sections 6–10 are devoted to comparisons of experimental data for the equation of state, vapor pressure, latent heat, energy, specific heats $C_v$ and $C_p$, and speed-of-sound with the predictions of our surface. Section 11 gives the values of the critical amplitude ratios, and compares them with the universal theoretical values. As mentioned in Sec. 12, tables of the thermodynamic properties of steam in the critical region have been prepared. These tables of the thermodynamic properties as a function of temperature along isochors, and also as a function of temperature and of pressure at saturation, are given in Appendix C. Appendix D lists the computer program used to generate the tables of thermodynamic properties. Appendix E gives units and conversion factors. Section 13 summarizes the principal conclusions of our work.

## 2. Critical Exponents

It is well known that thermodynamic properties show anomalous behavior when the critical point is approached. These critical anomalies are described by so-called power laws. If we denote by the symbol $\Delta$ the departure of a property from its critical value, and denote by an asterisk (*) a property value made dimensionless by appropriate combinations of the critical pressure, temperature, and density, then examples of these power laws are the following:

\begin{align}
  \text{Compressibility along critical isochore:} & \quad K^* = \gamma \Delta T^* \gamma - \gamma, \\
  \text{Pressure along critical isotherm:} & \quad |\Delta P^*| = D |\Delta \rho^*|, \\
  \text{Density along coexistence curve:} & \quad |\Delta \mu^*| = D |\Delta T^*|^\alpha, \\
  \text{Specific heat at constant volume along critical isochore:} & \quad C_v^* = A \Delta T^* \gamma - \gamma.
\end{align}

Here $\rho$ denotes the density, $T$ the temperature, $P$ the pressure. The superscript * denotes an approach to the critical temperature from higher, the superscript $\gamma$ the same from lower temperatures. Only two of the critical exponents $\alpha, \beta, \gamma$, and $\delta$ are independent. The others follow from them through scaling relations listed in Appendix A (A.13) and (A.14). The constants $I^\pm, D, B, A^\pm$ are called critical amplitudes.

The theory of critical phenomena asserts that the critical exponents of all fluids are the same, and to be identified with those calculated theoretically for three-dimensional Ising-like systems. This prediction has been verified by accurate experiments in a number of fluids. For reviews, we refer to Refs. 2–5. The available experimental material strongly supports the critical behavior of steam to be of the same type as that in other simpler fluids. In this work, we have therefore fixed the critical exponents at values predicted theoretically, namely,

$$\beta = 0.325, \quad \delta = 4.82, \quad \Delta_1 = 0.50,$$

where $\Delta_1$ is a "gap" exponent to be introduced in the next section. Values of the other exponents then follow from relations (A.13) and (A.14).

## 3. Fundamental Equation

Our fundamental equation is the one introduced by Ley-Koo and Green; these authors adapted, for use in representing fluid behavior, an expansion of the free energy around the critical point that had been proposed by Wegner for magnetic systems. The potential used in our work is

$$\bar{P} = P^*/T^*$$

as a function of $\bar{\mu} = \mu^*/T^*$ and $\bar{T} = -1/T^*$. Here $P$ is the pressure, $\mu$ the chemical potential, and $T$ the absolute temperature. Asterisks denote reduced properties: $P^* = P/P_c, T^* = T/T_c, \mu^* = \mu \mu_c, \rho^* = \rho \rho_c$. Here $P_c$ is the critical pressure, $T_c$ the critical temperature, and $\rho_c$ the critical density. This potential differs from those used in engineering applications in that both dependent and independent variables are intensive or "field" variables. As a consequence, the thermodynamic surface has a very simple structure, the vapor and liquid parts meeting with a discontinuous change in slope along a seam below $T_c$. This structure is consistent with the facts that intensive ("field") properties are identical in coexisting phases while their derivatives

$$\frac{\partial \bar{P}}{\partial \bar{\mu}} \tau = \bar{\rho}, \quad \frac{\partial \bar{P}}{\partial \bar{T}} \upsilon = \bar{U}$$

change discontinuously. Here $\bar{U} = U/P_c V$, the reduced energy density, and $\bar{U} = U/P_c V$. In an approach to the critical point, the discontinuity in slope diminishes, to disappear at $T_c$. At the same time, however, the curvature of the surface at the phase boundary increases, and at the critical point the second derivatives

$$\frac{\partial^2 \bar{P}}{\partial \bar{\mu}^2} \tau = \chi_T$$

as well as $(\partial^2 \bar{P} / \partial \bar{T}^2)$, and $(\partial^2 \bar{P} / \partial \bar{\mu} \partial \bar{T})$ diverge strongly. Here $\chi_T$ denotes the reduced value of $\mu^* T K \tau, K_T$ being the isothermal compressibility.

On the surface, there is only one direction singled out as special, namely, that of the seam, the vapor-liquid equilibrium curve. One can imagine this seam extrapolated into the one-phase region. We represent the seam by the relation between $\mu$ and $T$ of its projection on the $\mu-T$ plane in terms

of an analytic representation
\[ \tilde{\mu}(\tilde{T}) = \mu_{c} + \sum_{j=1}^{3} \tilde{\mu}_{j} (\Delta \tilde{T})^{j}, \]
where
\[ \Delta \tilde{T} = \tilde{T} + 1. \]
The assumption of analyticity of \( \tilde{\mu}(\tilde{T}) \) is essential; it is hard to prove experimentally, although some evidence has been accumulated, mainly from the behavior of the two-phase \( C_{v} \)4,10. The analyticity is a feature not only of the Ising model and the lattice gas, but also of the decorated lattice models11,12 that closely represent the asymmetry between the liquid and the vapor observed in the laboratory and that is reflected, for instance, in the temperature variation of the average of coexisting liquid and vapor densities (“slope of the diameter”).

In scaling, the physical variables \( \tilde{\mu}, \tilde{T} \) are transformed to a new coordinate system, one axis of which is the curve \( \tilde{\mu}(\tilde{T}) \). The other axis intersects the first at the critical point in a direction that is, in principle, arbitrary. Early scaling equations used the line \( \tilde{T} = -1 \), or \( T = T_{c} \), as this axis. In the present work, we allow this axis to be in an arbitrary direction. This is achieved by writing the second part of an arbitrary combination of \( \tilde{\mu} - \tilde{\mu}(\tilde{T}) = \Delta \tilde{\mu} \) and \( \tilde{T} + 1 = \Delta \tilde{T} \).

Thus, the independent scaling variables \( u_{\mu}, u_{r} \), are constructed as follows, as analytic functions of \( \tilde{\mu} \) and \( \tilde{T} \):
\[ au_{\mu} = \tilde{\mu} - \tilde{\mu}(\tilde{T}) = \Delta \tilde{\mu}, \]
\[ u_{r} = a \Delta \tilde{T} + c \Delta \tilde{\mu}. \]
Here \( a \) is an arbitrary scaling constant (see below) and \( c \) is the so-called mixing parameter.\(^3\) The potential \( \bar{P} \) is now decomposed into two parts, one part \( \bar{P}_{\text{reg}} \), that is regular in the scaling variables and another part \( \Delta \bar{P} \), that contains the critical anomalies. One can think of the regular part as an analytic surface in \( \bar{P}(u_{\mu}, u_{r}) \) or \( P(\mu, \tilde{T}) \) space, tangent to the thermodynamic surface at the critical point. It contains, therefore, the information on the critical-point values of the first derivatives \( \rho_{c} \) and \( U_{c} \). The scaled part is to produce the infinites in second derivatives at the critical point. The asymptotic critical behavior is incorporated by postulating for this anomalous part the following generalized homogeneous form1,13:
\[ \Delta \bar{P} = a \kappa_{0} |u_{r}|^{2} \alpha g_{0} \left( \frac{u_{\mu}}{|u_{r}|^{\beta}} \right), \]
where \( \kappa_{0} \) is a second arbitrary scaling constant; \( \alpha, \beta, \) and \( \delta \) are critical exponents defined in Eq. (1). Only two of these are independent; their values are universal, that is, the same for all fluids and other Ising-like systems. The function \( g_{0} \), of the scaling fields is likewise universal, the argument in parentheses indicating functional dependence.

Apart from the implicit presence of the mixing parameter \( c \), which disrupts symmetry in a nonuniversal manner, the scaled part of the potential contains only two arbitrary constants, \( a \) and \( \kappa_{0} \), which one can think of as setting two scales, namely, for two of the three physical variables. The relation of generalized homogeneity (8) does not allow a free choice of more than two such factors.

\[ \mu_{c}, \kappa_{0} \] showed that higher-order confluent singularities must be present at the critical point. In the present work, we will take one Wegner correction to scaling into account. Our potential thus has the form:
\[ \bar{P}(u_{r}, u_{\mu}) = \bar{P}_{\text{reg}}(u_{r}, u_{\mu}) + a \kappa_{0} |u_{r}|^{2 - \alpha} g_{0} \left( \frac{u_{\mu}}{|u_{r}|^{\beta}} \right) \]
\[ + a \kappa_{1} |u_{r}|^{2 - \alpha + \delta} g_{1} \left( \frac{u_{\mu}}{|u_{r}|^{\beta}} \right). \]

The correction-to-scaling function \( g_{1} \) is again a universal function of the same scaling variable \( u_{\mu}/|u_{r}|^{\beta} \). This function is multiplied by a different power of \( u_{r} \) than in the asymptotic term; a new critical exponent \( \Delta_{1} \) has been introduced, and, in addition, a new nonuniversal amplitude factor \( \kappa_{1} \).

For the regular part of the potential, we have chosen the form:
\[ \bar{P}_{\text{reg}}(\tilde{T}) = \bar{P}_{0}(\tilde{T}) + a \Delta \tilde{\mu} + \bar{P}_{1}(\tilde{T}) \Delta \tilde{T}, \]
\[ \bar{P}_{0}(\tilde{T}) = 1 + \sum_{j=1}^{3} \bar{P}_{j}(\Delta \tilde{T})^{j}. \]
It may be worth pointing out that the term \( \bar{P}_{1}(\Delta \tilde{T}) \) gives a contribution to the density linear in temperature and thus is responsible, in part, for introducing asymmetry in our model. It would be dangerous to identify this contribution with the temperature dependence of the coexistence curve diameter, since a second important, but anomalous, contribution to the slope of the diameter, proportional to \( |\Delta \tilde{T}|^{1 - \alpha} \), comes from the “mixing of variables.”

Having thus completed the formal presentation of our potential, we proceed to the computational part. An important device for handling scaled equations is the transformation to Schofield’s parametric variables \( r \) and \( \theta \), which denote, respectively, a distance from the critical point and a location on a contour of constant \( r \). The scaling variables are transformed to parametric variables by the relations:
\[ u_{\mu} = r^{\alpha} \theta (1 - \theta^{2}), \]
\[ u_{r} = r(1 - b^{2} \theta^{2}), \]
in which the constant \( b^{2} \) is universal. The variable \( \theta \) reaches the values \( \pm 1 \) on the coexistence curve. In asymptotic scaling, the assumption is made that the density \( \Delta \rho \) varies linearly in \( \theta \):
\[ \Delta \rho = k_{0} \rho^{\beta} \theta. \]
With this “linear-model” assumption, the potential and all its derivatives can be written in algebraically closed form, as simple polynomials in \( \theta \), with universal coefficients that are functions of the critical exponents \( \beta \) and \( \delta \).\(^1\) We have made this assumption not only for the leading contribution to \( \Delta \rho \), but also for that arising from the first Wegner correction. This choice leads to a similar set of polynomials in \( \theta \) for the Wegner correction-to-scaling, with universal coefficients that are functions of the critical exponents \( \beta, \delta, \Delta_{1} \). The relevant expressions are all listed in Appendix A. We stress here that the seemingly complicating device of transformation to parametric variables has considerable advantages. Scaled algebraically closed forms that have been postulated for the equation of state\(^10,15-17\) are not integrable in closed form and other thermodynamic properties have to be do
derived from them by numerical integration. These forms invariably suffer from the additional defect that they have a line of higher-order nonanalyticities stretching out from the critical point into the one-phase region. The linear-model parametric form possesses neither of these defects. Moreover, the use of the parametric form greatly simplifies the Legendre transformations that the thermodynamicist cannot escape.

Our fundamental equation contains the following constants:

3 critical exponents: \( \beta, \delta, \Delta, \)
(universal)
3 critical parameters: \( \rho_c, \rho_c, T_c, \)
5 parameters of the scaling function:
4 background parameters for the pressure:
4 background parameters for caloric properties:

In what follows we will discuss how these parameters were determined. The values of the constants that we have used are listed in Appendix B. The equation is valid in a range of temperatures and densities as indicated in Fig. 1. All temperatures quoted are on the International Practical Temperature Scale of 1968, IPTS 1968, unless otherwise indicated. This potential was applied before by us to steam. The present results differ from those previously reported principally in a modified choice of the value of \( T_c \).

Finally, a few remarks about the critical amplitudes introduced in Eq. (1). These amplitudes refer to limiting behavior and therefore contain no contributions from the correction-to-scaling term. Since the leading asymptotic term contains only two free constants, the six critical amplitudes introduced in Eq. (1) cannot be independent. Four relations between these amplitudes are listed in the Appendix, Eqs. (A38)–(A41). Theoretical predictions exist for these universal amplitude ratios. In our fits of the potential to the properties of steam, we have left the constant \( b^2 \) adjustable, so that a check on the universality of the amplitude ratios became possible.

4. Data Sources for Steam

In Table 1 we list the data sources relevant to this paper. The vapor pressure and latent heat data of Osborne and collaborators are, although almost 50 yr old, of unsurpassed quality and indispensable in the formulation of the thermodynamic behavior of steam. We have used these data to validate our surface below the critical point and to determine the critical parameters of steam. The \( PVT \) data of Rivkin \( \text{et al.} \) have formed the basis for determining most of the adjustable constants in our equation after we ascertained their consistency with the data of Osborne \( \text{et al.} \). The more recent high-quality \( PVT \) data of Kell \( \text{et al.} \) are not in our range of interest, but we have ascertained the mutual consistency of the Kell and Osborne vapor pressure at 350 °C to be of the order of 5 mK. Caloric data of high quality are the \( C_p \) data of Sirota and Mal'tsev and the speed-of-sound data of Erokhin and Kalayanov. The latter were used to determine a few of the caloric "background" parameters in our equation. For both \( C_p \) and speed of sound, small adjustments of the temperature scales with respect to that of Rivkin \( \text{et al.} \) were required in order to obtain mutual consistency. The resulting thermodynamic surface, determined up to the integration constants for energy and entropy, was proven to be consistent with the energy and \( C_v \) data of Baehr and Schmäcker and with selected \( C_v \) data of Amirkhanov \( \text{et al.} \).

<table>
<thead>
<tr>
<th>Property</th>
<th>First author</th>
<th>Ref</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor pressure</td>
<td>Osborne</td>
<td>21</td>
<td>1933</td>
</tr>
<tr>
<td>Latent heat</td>
<td>Osborne</td>
<td>22</td>
<td>1937</td>
</tr>
<tr>
<td>( PVT )</td>
<td>Rivkin</td>
<td>23, 24</td>
<td>1962-66</td>
</tr>
<tr>
<td>Specific heat ( C_p )</td>
<td>Sirota</td>
<td>26</td>
<td>1962</td>
</tr>
<tr>
<td>Specific heat ( C_v ) and energy</td>
<td>Baehr</td>
<td>28, 29</td>
<td>1974-75</td>
</tr>
<tr>
<td>Specific heat ( C_v )</td>
<td>Amirkhanov</td>
<td>30</td>
<td>1974</td>
</tr>
<tr>
<td>Speed of sound</td>
<td>Erokhin</td>
<td>27</td>
<td>1980</td>
</tr>
<tr>
<td>( \rho_c T_c )</td>
<td>Blank</td>
<td>31</td>
<td>1969</td>
</tr>
<tr>
<td>( \rho_c T_c ) vapor pressure</td>
<td>Scheffler</td>
<td>32, 33</td>
<td>1981</td>
</tr>
</tbody>
</table>

We have paid attention to the earlier and to the recent direct determination of the critical parameters \( \rho_c, T_c \) of steam by Scheffler \( \text{et al.} \), and have found the latter marginally compatible with the surface presented here.

5. Critical Parameters for Steam

The values of the critical parameters \( \rho_c, T_c \) have been repeatedly determined in an apparatus first designed and built by Blank, an optical high-pressure cell in which the difference in refractive index of coexisting phases could be observed to disappear. In the course of the years, several
values of $T_c$ were reported that ranged from 647.14 K to 647.19 K in the most recent experiment by Scheffer et al. The value of $P_c$ reported by Blank falls about 0.01 MPa below the surface determined by Rivkin's data (Fig. 2). Scheffer et al. made considerable improvement in the pressure measurements; they reported $T_c = (647.19 \pm 0.02)$ K, $P_c = (22.071 \pm 0.002)$ MPa.

Although this point lies about 0.006 MPa below Rivkin's $PVT$ surface (Fig. 2), this pressure difference is within the combined estimated uncertainty. We have determined critical-point parameters in a different way, namely, by analysis of appropriate fluid property data in the critical region. The analysis tools are the scaling laws, and the analysis proceeds in two steps. First, from experimental values of extensive properties in coexisting phases, such as densities, refractive indices, or latent heats, the temperature at which these properties become equal, i.e., the critical temperature $T_c$, can be estimated with a reliability depending on the accuracy and distribution of the property data considered. We were fortunate to have the latent heat data of Osborne et al. available for this purpose. Secondly, from a scaled analysis of vapor pressure and $PVT$ data the vapor pressure curve and its extension, the critical isochore, can be established with good precision, but the actual value of $T_c$ is usually poorly defined. Once, however, the value of $T_c$ is established by other means, that of $P_c$ follows immediately. This is the path we have followed in an indirect determination of the critical parameters of steam. The vapor pressure and latent heat data of Osborne et al. have documented traceability and accuracy of pressure and temperature scales, and are consistent with Rivkin's $PVT$ data to a better degree than with the $(P_c, T_c)$ value of Scheffer et al. Therefore we have refrained from using the latter.

Osborne et al. measured the latent heats $g, b$, accompanying isothermal extraction of unit mass of vapor, resp. liquid, from their calorimeter. These quantities are related to the densities $\rho_L, \rho_V$ of the phases and the vapor pressure by

$$b = (T/\rho_L)(dP/dT)_{\text{vap}},$$

$$g = (T/\rho_V)(dP/dT)_{\text{vap}}.$$  \hspace{1cm} (13)

The known scaled expressions for $\rho_L, \rho_V, (dP/dT)$ (A32, A33) imply those for $b$ and $g$. To leading order, $g - b$ behaves as $\rho_L - \rho_V$, that is, as $\Delta \rho^2$. In a previous publication, a simple power-law expression $A|\Delta T|^B$ with free exponent $B$ was fitted in the range 350–374 °C to the quantity $(g - b)/(g + b)$, after it was corrected for the slope of the coexistence-curve diameter. \hspace{1cm} (6)

We obtained $T_c = (373.85 \pm 0.01)$ °C (IPTS 1948), the error indicating a doubling of $\chi^2$. The highest point 374 °C, was inconsistent with the other data and, consequently, excluded from the fit. The equations in Appendix A, however, can be used to represent the latent-heat data in a theoretically more satisfying manner, but in a smaller range. We used a preliminary fit of our potential to the $PVT$ data to calculate all terms except the leading one. After subtracting the correction terms from the latent heat data (the largest correction, at the lowest temperature, being 1.5%), we fitted the corrected values of $(g - b)/(g + b)$ in the range 370–374 °C again to the asymptotic power-law $B|\Delta T|^B$ with free exponent $B$. Again, the highest point seemed inconsistent and was excluded. The results for the dependence of the chi-square of the fit on the choice of $T_c$ are given in Table 2. The optimum value of $T_c$ was 373.84 °C (IPTS 1948), within 0.01 °C of the one published before, \hspace{1cm} (6) while the value 0.324 ± 0.002 obtained for the exponent $B$ is in excellent agreement with the theory. \hspace{1cm} (7) A large change, of 0.07 °C, is now required for doubling $\chi^2$, which reflects increased uncertainty because of the smallness of the range. Thus, we have assumed for $T_c$ in this paper $T_c = 373.84$ °C (IPTS 1948) = 647.067 K (IPTS 1968), (14) given a difference of 0.077 K between readings on IPTS 1948 and IPTS 1968 near the critical point of steam. \hspace{1cm} (15) The corresponding value of $P_c$ is unequivocally defined by the vapor pressure and $PVT$ data. We obtained $P_c = 22.046$ MPa

with an intrinsic uncertainty of 0.003 MPa and one propagated from the temperature uncertainty $\delta T_c$, so that $\delta P_c = 0.2675T_c \pm 0.003$ MPa. The value of $\rho_c$ can be inferred from a scaled fit to $PVT$ data or from further analysis of the latent heat data.
Table 2. Analysis of the latent heat of steam [22] with varying $T_c$

<table>
<thead>
<tr>
<th>$T_c$, °C</th>
<th>Fit to uncorrected data in the range 330-373.5°C [6]</th>
<th>Fit to corrected data in the range 370-373.5°C [this work]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>375.82</td>
<td>2.19</td>
<td>0.3357</td>
</tr>
<tr>
<td>375.83</td>
<td>1.98</td>
<td>0.3350</td>
</tr>
<tr>
<td>375.84</td>
<td>0.55</td>
<td>0.3360</td>
</tr>
<tr>
<td>375.85</td>
<td>0.66</td>
<td>0.3363</td>
</tr>
<tr>
<td>375.87</td>
<td>1.55</td>
<td>0.3365</td>
</tr>
</tbody>
</table>

Table 3. Critical parameters of steam

<table>
<thead>
<tr>
<th>Used here</th>
<th>Estimated uncertainty</th>
<th>Direct determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_c$, MPa</td>
<td>$22.0460 \pm (0.2670 \pm 0.003)$</td>
<td>$22.045 \pm 0.003$</td>
</tr>
<tr>
<td>$T_c$, K</td>
<td>$647.067 \pm 0.1$</td>
<td>$647.14 \pm 0.03$</td>
</tr>
<tr>
<td>$r_c$, kg/m³</td>
<td>$322.778 \pm 2.2$</td>
<td>$647.19 \pm 0.05$</td>
</tr>
</tbody>
</table>

Our fit to the $PVT$ data yields

$$P_c = 322.8 \text{ kg/m}^3$$

while a latent-heat analysis gives $P_c = (321.2 \pm 3.1) \text{ kg/m}^3$. The values we have obtained for $P_c$ from scaled fits of a variety of complexity give optimum $P_c$ values no more than 2.2 kg/m³ removed from the one given. Table 3 summarizes our results for the critical parameters of steam.

The value of $T_c$ determined indirectly is substantially, 0.12 K, below that of the most recent direct determination. Against our choice weighs the fact that we have rejected the 374 °C latent heat values, but Osborne himself mentions considerable experimental difficulties at this point. In favor of our choice weighs the extraordinary consistency of latent heat, vapor pressure, and $PVT$ data that is obtained as a result (cf. Sec. 7). We hesitate, however, to assign to our current knowledge of $T_c$ an absolute accuracy of better than 0.1 °C.

6. Equation of State

The scaling function parameters $a$, $k_b$, $k_1$, $c$, $b^2$, and the pressure background parameters $P_1$, $P_2$, $P_3$, together with $P_c$, were determined by fitting the equation of state to the $PVT$ data of Rivkin and co-workers. The parameter $P_1$, was derived from the known slope of the coexistence curve diameter. The experimental data were assigned absolute weights by propagation of error on the basis of the following error estimates and private communication (S. L. Rivkin, 1977):

$$\sigma_P = 0.001 \text{ MPa}, \quad \sigma_T = 0.02 \text{ K}, \quad \sigma_p = 0.05\%.$$  

The equation fits the experimental $PVT$ data with statistic chi-square of 0.58 in the range bounded by

$$200 \text{ kg/m}^3 < P < 420 \text{ kg/m}^3,$$

$$644 \text{ K} < T < 693 \text{ K}.$$  

A comparison between the experimental $PVT$ data and the values calculated from our equation is presented in Figs. 3–5, in the form of pressure deviations as function of density along various isotherms. The equation reproduces the data within the estimated experimental errors. Some systematic

![Fig. 3. Deviations of the experimental pressure data of Rivkin et al. from the calculated values in the temperature range 643.207 K < T < 648.177 K.](image)

with the vapor pressures of Osborne et al.\textsuperscript{21} is presented in Fig. 6. Although a small systematic trend is present, the data agree with the predicted curve to better than 0.002 MPa. This is very good agreement in view of the fact that the spread by Osborne et al. of repeat determinations of the vapor pressure is about \( \pm 0.001 \) MPa, and the uncertainty of the pressures of Rivkin et al. is given as \( \pm 0.001 \) MPa, with no allowance made for a possible error in temperature.

**Fig. 4.** Deviations of the experimental pressure data of Rivkin et al. from the calculated values in the temperature range 648.237 K < \( T \) < 656.207 K.

**Fig. 5.** Deviations of the experimental pressure data of Rivkin et al. from the calculated values in the temperature range 658.177 K < \( T \) < 693.185 K.

**Fig. 6.** Comparison between the vapor pressure data of Osborne et al. (Ref. 21) and the vapor pressures calculated from the equation of state deduced from the PVT data of Rivkin et al. (Refs. 23 and 24). The error bars denote the spread of the repeated measurements of [Ref. 21] and the error band corresponds to the direct pressure error and Rivkin's measurements. + 0.001 MPa.

**Fig. 7.** Comparison between the latent heat data of Osborne et al. (Ref. 22) and the values calculated from our surface. The error bars indicate the standard deviations of the repeatedly measured data.

### 7. Vapor Pressure and Latent Heat

The equation of state fitted to the \( \textit{PVT} \) data of Rivkin et al. can be used to predict the vapor pressure. A comparison
8

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Table 4. Coexistence properties according to our equation, and the data of Osborne et al. [21,22]

<table>
<thead>
<tr>
<th>Tc, °C</th>
<th>Pvc (exp)</th>
<th>Pvc (calc)</th>
<th>gc (exp)</th>
<th>gc (calc)</th>
<th>b (exp)</th>
<th>b (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 PTS 1948)</td>
<td>(1 PTS 1968)</td>
<td>MPa</td>
<td>MPa</td>
<td>kJ/kg</td>
<td>kJ/kg</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>370</td>
<td>643.227</td>
<td>21.0524</td>
<td>21.0517</td>
<td>800.44</td>
<td>802.07</td>
<td>359.35</td>
</tr>
<tr>
<td>371</td>
<td>644.227</td>
<td>21.3056</td>
<td>21.3052</td>
<td>771.25</td>
<td>771.84</td>
<td>374.20</td>
</tr>
<tr>
<td>372</td>
<td>645.227</td>
<td>21.5615</td>
<td>21.5625</td>
<td>735.65</td>
<td>735.93</td>
<td>395.48</td>
</tr>
<tr>
<td>373</td>
<td>646.227</td>
<td>21.8217</td>
<td>21.8255</td>
<td>683.05</td>
<td>682.34</td>
<td>427.56</td>
</tr>
<tr>
<td>375.3</td>
<td>647.727</td>
<td>21.9555</td>
<td>21.9555</td>
<td>642.98</td>
<td>640.54</td>
<td>462.30</td>
</tr>
<tr>
<td>(374.0)</td>
<td>647.227</td>
<td>22.0873</td>
<td>22.0888</td>
<td>(586.62)</td>
<td>(586.62)</td>
<td>(504.3)</td>
</tr>
</tbody>
</table>

The measured latent heats g, b, can also be compared with our surface. The comparison is presented in Fig. 7. The highest point has been excluded, as discussed in Sec. 5. The experimental data agree to within the spread of repeat measurements with the prediction. The worst departure is 2 kJ/kg. The experimental and predicted values of vapor pressure and latent heats are shown in Table 4.

8. Sources of Error and Measures of Experimental Discrepancies

In the comparison of our surface with data other than those of Rivkin and Osborne, small discrepancies will usually be found that could be due to a number of factors that are usually not known. A major source of error will be the uncertainty in temperature. The critical temperature of steam is quite high, and it is hard to reproduce the temperature scale and eliminate the temperature gradients to better than a few hundredths of a degree unless special metrological precautions are taken. A similar problem arises with the pressure scale which, at 20 MPa, cannot be absolutely reproduced to much better than 1 part in 10^4. Near the critical point, because of the near linearity of the isochors, 1 part in 10^4 in pressure corresponds with approximately 0.01 K, and a discrepancy found between data sets can be quantified either as a difference in temperature scale or in pressure scale, even though the actual cause of the discrepancy may be a different one. For reasons of convenience, we express discrepancies in terms of a difference in temperature scale from that defined by the Osborne–Rivkin data, which we consider as correct in view of their consistency and of the traceability of Osborne’s scales.

Because of the strong divergences of the compressibility and the expansion coefficient near a critical point, uncertainties in pressures and temperature, and sample variability due to differences in impurity content, all cause greatly-enlarged errors in the density. Consequently, in those experiments where a property is reported as a function of pressure rather than density, the location of the maximum in a diverging quantity such as the isobaric C_v, or in the minimum of a quantity like the isothermal speed of sound, will appear shifted in density with respect to the predicted curve. As stated earlier, we will quantify the shift by stating the change in temperature scale required, with respect to that of the Osborne–Rivkin data, in order to eliminate the offset in the location of the extremum.

Quantification of a discrepancy between predicted and measured property data by means of an adjustment of the temperature scale is to be carefully distinguished from the uncertainty in the assignment of a value of Tc to the Rivkin PVT data [Sec. 5]. The PVT data themselves are not sensitive to the choice of Tc. Derived properties, however, are, for instance, the main effect of a change in choice of Tc for the Rivkin data is a change in the predicted value of the peak height of a divergent quantity such as C_v, while the location of the peak is not affected. An offset in peak height will be quantified by giving the amount by which the Tc assignment to Rivkin’s data is to be changed in order to eliminate the offset. In general, we will find that the shifts required to eliminate discrepancies are within reasonable expectations of experimental uncertainty. We have found no convincing reasons to doubt the accuracy of the model.

Finally, a source of error in near critical data that is not to be overlooked is that of gravity-induced density gradients in regions where the compressibility is high. As a consequence, the average bulk density in a PVT experiment depends from the density at the level at which the pressure is measured, while the theoretical infinity in C_v is suppressed. Moldover et al. estimated the range from Tc within which gravity produces errors larger than 1% in the property in question on the critical isochore. These estimates were made for xenon in a cell 1 cm high. In steam, in a 10 cm high cell, these ranges would be 0.15 K for more than 1% error in C_v, and 0.3 K for more than 1% error in density. In the Rivkin PVT data, however, the intrinsic pressure error of 0.001 MPa is five times larger than the hydrostatic head in the cell, and therefore gives the dominant uncertainty in the density near the critical point. The C_v data of Baehr et al. were not taken within a range of 0.15 K from the critical temperature. Of the C_v data points of Amirov et al., the one or two closest to the peak value occasionally are within the gravity-affected range.

9. Caloric Background, Energy, and Speed of Sound

The constants μ_i in the fundamental equation have to be determined from caloric properties. Of these constants, μ_c and μ_f are related to the zero-points of entropy and energy; they enter into the first derivatives U, H, and S, but not into the second derivatives, specific heats, and speed of sound.
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In previous work, the coefficients, \( \tilde{\mu}_1 \) and \( \tilde{\mu}_2 \), were determined by fitting the energy equation to the internal energy data of Baehr and co-workers while the coefficient \( \tilde{\mu}_3 \) was set equal to zero. Recently, however, Erokhin and Kalyanov have reported sound velocity data for steam in an extended region around the critical point. The speed-of-sound data are more sensitive to the choice of the \( \tilde{\mu}_i \) (\( i > 1 \)) so that these constants can be determined more accurately. The speed-of-sound data also indicate that the coefficient \( \tilde{\mu}_3 \) in the expansion (A6a) for \( \tilde{\mu}_q(T) \) cannot be neglected in the temperature and density range under consideration.

If we determine the coefficients \( \tilde{\mu}_1, \tilde{\mu}_2, \) and \( \tilde{\mu}_3 \) from the energy data of Baehr and co-workers in the way described before, we obtain

\[
\begin{align*}
\tilde{\mu}_1 &= -22.657 \pm 0.007, \\
\tilde{\mu}_2 &= -17.750 \pm 0.345, \\
\tilde{\mu}_3 &= -5.455 \pm 0.407. 
\end{align*}
\] (19)

It should be noted that Baehr's energy values are anchored to those of the surface of Keenan et al. at 350 °C. On the other hand, if we determine \( \tilde{\mu}_2 \) and \( \tilde{\mu}_3 \) from the speed-of-sound data of Erokhin and Kalyanov we obtain

\[
\tilde{\mu}_2 = -17.888 \pm 0.010, \tilde{\mu}_3 = -4.933 \pm 0.061. 
\] (20)

The two sets of values are in excellent agreement, but the values deduced for \( \tilde{\mu}_2 \) and \( \tilde{\mu}_3 \) from speed-of-sound data evidently have a higher accuracy. These values, Eq. (20), have been adopted in this work.

This leaves the zeropoint constants \( \tilde{\mu}_c \) and \( \tilde{\mu}_1 \) to be determined. This was done by identifying the energy and entropy of our surface at \( T = 648.15 \text{ K}, \rho = 230 \text{ kg/m}^3 \), with those of the global surface proposed by Haar, Gallagher, and Kell. The results are

\[
\tilde{\mu}_c = -11.233, \tilde{\mu}_1 = -22.655. 
\] (21)

The value for \( \tilde{\mu}_1 \) is in excellent agreement with that obtained from a direct fit to the energy data of Baehr et al.

After all constants in the equation have thus been determined (Appendix B), comparisons will be made with experimental data for speed-of-sound, energy, and specific heat at constant volume.

A comparison of the speed-of-sound data of Erokhin and Kalyanov and the values calculated from our equation is presented in Figs. 8 and 9. The equation reproduces correctly the magnitude of the speed of sound minima at all temperatures indicating agreement with the value of \( T_c \) ascribed to Rivkin's data [cf. Sec. 8]. In Fig. 10 we show how much the fit to the speed-of-sound data closest to the critical point improves by lowering their temperature values by 0.06 K; the location of the minima improves while the good agreement of the minimum values is retained.

In our opinion, a combined uncertainty in realization of

![Fig. 8. The speed of sound as a function of pressure in the temperature range 647.38 K to 653.23 K. The data points are those of Erokhin and Kalyanov (Ref. 27). The curves represent values predicted by our equation.](image1)

![Fig. 9. The speed of sound as a function of pressure in the temperature range 653.23 K to 698.93 K. The data are those of Erokhin and Kalyanov (Ref. 27). The curves represent values predicted by our equation.](image2)

![Fig. 10. Another comparison of the speed of sound in the same range as that of Fig. 8, but after subtracting 0.06 K from the temperature values of (Ref. 27). This temperature adjustment eliminates most of the systematic difference between data and prediction.](image3)
pressure and temperature measurement and in sample composition, as expressed by 0.06 K in temperature, is not unreasonable.

The comparison with the energy data of Baehr et al.\textsuperscript{28} is shown in Fig. 11. Although the deviations along each isochole have a systematic character, the departures from the surface are well within the claimed accuracy of the data. In Fig. 12 we compare with the $C_v$ data reported by Baehr and Schomäcker.\textsuperscript{29} The data were obtained as the ratio of energy increments $\Delta U$ over temperature increments $\Delta T$, with $\Delta T$ of the order of degrees; the predicted curves in Fig. 12 represent the quantity $\Delta U / \Delta T$, with $\Delta T$ the experimental temperature increments. In general, the data are accurately consistent with the weakly diverging specific heat $C_v$ predicted by the scaling laws. An exception is formed by some of the two-phase data on the 310.27 kg/m\(^3\) isochole that do not rise steeply enough. No adjustment of the temperature scale was required.

Amirkhanov, Kerimov, and co-workers have, at various occasions, published detailed measurements of the specific heat $C_v$ near the phase boundary. A previous analysis indicated that not all these data appeared to be mutually consistent.\textsuperscript{6}

In a book published since by Amirkhanov et al.,\textsuperscript{30} the older measurements are summarized, several sets being discarded because of the presence of air. This book, however, also contains new $C_v$ data not hitherto published. Those are the ones we compare with here. A problem we encountered is that the jump in $C_v$, from a 2-phase to a 1-phase value, occurs between 374.10 and 374.18 °C (IPTS 1948), which is 0.31 °C above our choice of $T_\alpha$. After all of Amirkhanov's temperatures were lowered by this amount, (a much larger adjustment than for any of the other data, and one for which we have no satisfactory explanation), our surface gives a very close representation of this anomalous region of $C_v$ (Fig. 13). Note especially how well the steep rise in $C_v$ is represented on the 315.457 kg/m\(^3\) isochole where the two-phase $C_v$ doubles in a span of a few K. As mentioned, Baehr's nearby isochole did not show this predicted rise in the two-phase region (Fig. 12).

**Fig. 11.** Deviations of the experimental energy data of Baehr et al. (Ref. 28) from the calculated values.

**Fig. 12.** The specific heat $C_v = \Delta U / \Delta T$ as a function of temperature. The symbols represent the data reported by Baehr and Schomäcker (Ref. 29). The curves represent values predicted by our equation.

**Fig. 13.** The specific heat $C_v$ as a function of temperature. The circles represent the data of Amirkhanov et al. (Ref. 30) after 0.31 K was subtracted from all experimental temperatures.
and the points shown in the plot represent values of $\Delta H / \Delta T$. Our predicted values are, likewise, values of $\Delta H / \Delta T$ over the experimental temperature intervals. Since the temperature intervals $\Delta T$ were small and smoothly varying, and the points closely spaced, smooth curves could be drawn through the predicted points. The equation reproduces the experimental maxima in $C_p$ at all temperatures; the maximum difference in the peak values is about 5% to 6% at the 22.5651 MPa isobar.

This difference of peak heights could be further reduced by ascribing a lower value of $T_c$ to the $PVT$ data, as we did before; cf. also Sec. 8. Values for $T_c$ substantially lower than the one used here, however, although reconcilable with the $PVT$ data, are less compatible with Osborne's latent heats. In Fig. 14 the comparison is made with the $C_p$ data plotted as function of density, rather than temperature. The scaled equation was used to transform the experimental pressures to densities. The plot reveals a small offset in peak location between the experimental data and the predicted curve, as noted earlier. The effect can be eliminated by lowering Sirota's temperature values by 0.05 K, as demonstrated in Fig. 15. We conclude that the $C_p$ data or Sirota and Maltsev and the $PVT$ data of Rivkin et al. are consistent at an acceptable level.

11. Critical Amplitude Ratios

The scaling function parameter $b^2$, although predicted to be universal, was actually determined by us from the fit. Universality of $b^2$ implies universality of the critical amplitude ratios [see Eqs. (A38)-(A41) in Appendix A]. The amplitude ratios we obtain in our fit are indeed in agreement with the values predicted theoretically, as shown in Table 5.

<table>
<thead>
<tr>
<th>$A'/A'$</th>
<th>Theory (201)</th>
<th>Theory (201)</th>
<th>Our results</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma'/\gamma$</td>
<td>5.07</td>
<td>4.80</td>
<td>4.886</td>
</tr>
<tr>
<td>$\gamma'/\gamma^{a-1}$</td>
<td>1.75</td>
<td>1.6</td>
<td>1.693</td>
</tr>
<tr>
<td>$A'/A^2$</td>
<td>0.059</td>
<td>0.056</td>
<td>0.0568</td>
</tr>
</tbody>
</table>

12. Thermodynamic Tables

Tables of the thermodynamic properties pressure, enthalpy, entropy, energy, specific heats, and speed of sound have been prepared along closely spaced isochors, and as a function of temperature.

In addition, a table of saturation properties has been constructed. The tables are given in Appendix C.

13. Discussion

We have presented a description of the thermodynamic behavior of steam in the range 200–420 kg/m$^3$, 643–693 K.
including the critical point. The fundamental equation is of the form predicted by the modern theory of critical phenomena, and includes a correction-to-scaling term and a device for introducing gas-liquid asymmetry. In total, 16 adjustable parameters were used.

The PVT data of Rivkin et al. were found to be consistent with the vapor pressure and latent-heat data of Osborne et al. to a high degree of accuracy.

The speed-of-sound data of Erokhin and Kalyanov and Cₐ data of Sirota and Maltsev are consistent with the PVT of Rivkin after small adjustments of the respective temperature scales, of the order of a few hundredths of a degree. The energy and Cₐ data of Baeckh et al. are also consistent with the PVT data, but the tolerances of these data are somewhat larger than those of Cₐ and speed of sound.

The Cₐ data of Amirkhanov et al. which include values very near the critical point, are represented in fine detail by our surface. A large adjustment of the temperature scale, —0.31 K, however, was needed.

There exists an internationally recognized formulation for the thermodynamic surface of steam recommended for scientific and industrial use.  35,36 We do not present a comparison here with the predictions from this international formulation or other global formulations. The reason is that the International Association for the Properties of Steam is in the process of adopting a new formulation which will be more accurate and valid in a much larger range. 35,37 In this paper the quality of our fundamental equation for the critical region has been judged solely on the basis of a comparison with the experimental data.

Acknowledgments

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References


Appendix A. Revised and Extended Scaling Equations for the Thermodynamic Properties of Fluids

A 1. Reduced thermodynamic quantities

\[ \tilde{T} = - \frac{T}{T_c}, \quad \tilde{\mu} = \frac{\mu}{T}, \quad \tilde{\rho} = \frac{P}{T_c}, \quad \tilde{\tilde{\rho}} = \frac{\rho}{\rho_c}, \quad \tilde{U} = \frac{U}{P_c}, \quad \tilde{\mu} = \frac{\mu}{T}, \quad \tilde{\rho} = \frac{P}{T_c}, \quad \tilde{\tilde{\rho}} = \frac{\rho}{\rho_c}, \quad \tilde{\tilde{\rho}} = \frac{\rho}{\rho_c}, \quad \tilde{\tilde{\rho}} = \frac{\rho}{\rho_c}. \]

\[ \tilde{A} = \frac{A}{T_c} \frac{T}{P_c}, \quad \tilde{\mu} = \frac{H}{T_c} \frac{T}{P_c}, \quad \tilde{x} = \left( \frac{\partial \rho}{\partial u} \right) T. \]

\[ \tilde{C}_v = \frac{C_v}{T_c}, \quad \tilde{C}_p = \frac{C_p}{T_c}. \]

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\( T \) is temperature, \( \mu \) is chemical potential, \( P \) is pressure, \( \rho \) is density, \( U \) is energy, \( A \) is helmholtz free energy, \( H \) is enthalpy, \( V \) is volume, \( C_i \) is heat capacity at constant \( V \), \( C_p \) is heat capacity at constant \( P \).

A.2. Thermodynamic relations

\[
\begin{align*}
\dot{\rho} & = - \rho \dot{U} + \rho \dot{\mu}_c \dot{\rho}, \\
\dot{\alpha} & = - \dot{\alpha} \dot{U} + \dot{\mu}_c \dot{\rho}, \\
\dot{\alpha} & = - \dot{T} \dot{U} + \dot{\mu}_c \dot{\rho}, \\
\dot{\alpha} & = - \dot{T} \dot{U} - \mu \dot{\rho},
\end{align*}
\]  
(A2)

with

\[
\begin{align*}
\dot{\alpha} & = \dot{\rho} \alpha - \dot{\rho}, \\
\dot{\alpha} & = \ddot{\alpha} \ddot{U}, \\
\dot{\alpha} & = \ddot{\alpha} \ddot{U} - \dot{\alpha}.
\end{align*}
\]  
(A3)

A.3. Fundamental equations

\[
\begin{align*}
\Delta \dot{T} & = \dot{T} + 1, \\
\Delta \dot{\mu} & = \dot{\mu} - \dot{\mu}_c \Delta \dot{T}, \\
\Delta \dot{P} & = \dot{P}_c \Delta \dot{T} + \Delta \dot{\mu} + \dot{P}_c \Delta \dot{T} + \Delta \dot{P},
\end{align*}
\]  
(A5)

with

\[
\begin{align*}
\dot{\mu}_c (\Delta \dot{T}) & = \dot{\mu}_c + \sum_{j=1}^{3} \dot{\mu}_c (\Delta \dot{T})_j, \\
\dot{P}_c (\Delta \dot{T}) & = 1 + \sum_{j=1}^{3} \dot{P}_c (\Delta \dot{T})_j.
\end{align*}
\]  
(A6a, b)

A.4. Derived thermodynamic quantities

\[
\begin{align*}
\dot{\rho} & = 1 + \dot{P}_c \Delta \dot{T} + \left( \frac{\partial \dot{P}_c}{\partial \Delta \dot{\mu}} \right)_{\Delta \dot{T}} \Delta \dot{\mu}, \\
\dot{U} & = \dot{P}_c \Delta \dot{T} - \dot{\rho} \frac{\partial \dot{\mu}_c}{\partial \Delta \dot{T}} + \dot{P}_c \Delta \dot{\mu} + \left( \frac{\partial \Delta \dot{P}}{\partial \Delta \dot{T}} \right)_{\Delta \dot{\rho}}, \\
\dot{X}_T & = \left( \frac{\partial \Delta \dot{P}}{\partial \Delta \dot{\mu}} \right)_{\Delta \dot{T}}, \\
\frac{\dot{P}_c}{\dot{X}_T} & = \frac{\partial \dot{P}_c}{\partial \Delta \dot{T}} \frac{\partial \dot{\mu}_c}{\partial \Delta \dot{T}} \left[ \Delta \dot{\mu} - \dot{\rho} \right] + \left( \frac{\partial \dot{P}_c}{\partial \Delta \dot{T}} \right)_{\Delta \dot{\mu}} \frac{\partial \dot{\mu}_c}{\partial \Delta \dot{T}}, \\
\frac{\dot{C}_p}{\dot{X}_T^2} & = \frac{\partial \dot{P}_c}{\partial \dot{X}_T^2} \frac{\partial \dot{\mu}_c}{\partial \Delta \dot{T}} \left[ \Delta \dot{\mu} - \dot{\rho} \right] + \left( \frac{\partial \dot{P}_c}{\partial \Delta \dot{T}} \right)_{\Delta \dot{\mu}} \frac{\partial \dot{\mu}_c}{\partial \Delta \dot{T}} \\
& - \frac{1}{\dot{X}_T} \left( \frac{\partial \dot{P}_c}{\partial \dot{X}_T} \right)^2, \\
\dot{C}_p & = \dot{C}_v + \frac{\dot{X}_T}{\dot{X}_T} \left[ \dot{P} - \frac{\partial \dot{P}}{\partial \dot{X}_T} \right] (\dot{\rho}).
\end{align*}
\]  
(A7, 9, 10, 11, 12)

A.5. Critical exponents

\[
\begin{align*}
\alpha_0 & = \alpha, \quad \alpha_1 = \alpha - \Delta, \\
\beta_0 & = \beta, \quad \beta_1 = \beta + \Delta, \\
\gamma_0 & = \gamma, \quad \gamma_1 = \gamma - \Delta,
\end{align*}
\]  
(A13)

with

\[
\begin{align*}
\gamma - \sigma & = \beta (\delta + 1), \\
\gamma & = \beta (\delta - 1)
\end{align*}
\]  
(A14)

A.6. Parametric equations for singular terms

\[
\begin{align*}
\Delta \dot{\mu} & = \rho \dot{\alpha} \left( 1 - \theta^2 \right), \\
\Delta \dot{\tau} & = r(1 - b \dot{\beta}^2) - c \Delta \dot{\mu}, \\
\Delta \dot{P} & = \sum_{i=0}^{3} r_i \dot{\alpha} \dot{P}_c (\dot{\beta}_i), \\
\frac{\partial \Delta \dot{P}}{\partial \Delta \dot{\mu}} & = \sum_{i=0}^{3} \left[ \rho \dot{\alpha} \dot{P}_c (\dot{\beta}_i) \right], \\
\frac{\partial \Delta \dot{P}}{\partial \Delta \dot{T}^2} & = \sum_{i=0}^{3} r_i \dot{\alpha} \dot{P}_c (\dot{\beta}_i) \dot{\alpha}, \\
\frac{\partial \Delta \dot{P}}{\partial \Delta \dot{\mu} \Delta \dot{T}} & = \frac{1}{r_i} \left[ r_i \dot{\alpha} \dot{P}_c (\dot{\beta}_i) \right] + c \dot{\alpha} \dot{P}_c (\dot{\beta}_i), \\
\frac{\partial \Delta \dot{P}}{\partial \Delta \dot{\mu} \Delta \dot{T}^2} & = \sum_{i=0}^{3} \left[ \rho \dot{\alpha} \dot{P}_c (\dot{\beta}_i) \right] + c \dot{\alpha} \dot{P}_c (\dot{\beta}_i), \\
\frac{\partial \Delta \dot{P}}{\partial \Delta \dot{\mu} \Delta \dot{T}^2} & = \frac{1}{r_i} \left[ r_i \dot{\alpha} \dot{P}_c (\dot{\beta}_i) \right] + c \dot{\alpha} \dot{P}_c (\dot{\beta}_i).
\end{align*}
\]  
(A15-22)

A.7. Auxiliary functions

\[
\begin{align*}
p_i (\dot{\theta}) & = p_{oi} + p_{s2} \dot{\theta}^2 + p_{s1} \dot{\theta}, \\
s_i (\dot{\theta}) & = s_{oi} + s_{s2} \dot{\theta}^2, \\
q_i (\dot{\theta}) & = 1 + \left( b \dot{\beta} (2 \beta - 1) - 3 \right) \dot{\theta}^2 - b \dot{\beta} (2 \beta - 3) \dot{\theta}^4, \\
\rho_i (\dot{\theta}) & = 1 - b \left( 1 - 2 \beta \dot{\theta}^2 \right)/q_i (\dot{\theta}), \\
u_i (\dot{\theta}) & = - \left( \beta_i (1 - 3 \dot{\theta}^2) - \beta \dot{\beta} (1 - 3 \dot{\theta}^2) \dot{\beta} \right)/q_i (\dot{\theta}), \\
w_i (\dot{\theta}) & = \left( 1 - \beta_i (1 - 3 \dot{\theta}^2) \dot{\beta} \right)/q_i (\dot{\theta}).
\end{align*}
\]  
(A23-27)

with

\[
\begin{align*}
p_{oi} & = \frac{\rho s}{2a s_2}, \\
p_{s2} & = \frac{3 \beta_s}{2a_2}, \\
p_{s1} & = \frac{2b \dot{\beta}}{2a_1}, \\
s_{oi} & = \frac{2a_0}{2a_1}, \\
s_{s2} & = \frac{2b \dot{\beta}}{2a_1}.
\end{align*}
\]  
(A28-30)

A.8. Two-phase properties

\[
\begin{align*}
\theta & = \pm 1, \\
\Delta \mu & = u_c, \\
\Delta \tau & = r(1 - b \dot{\theta}^2).
\end{align*}
\]  
(A31)

Vapor pressure:

\[
\rho_{vp} = \rho_{oi} (\dot{\theta}) + \sum_{i=0}^{3} \rho_{s2} (\dot{\beta}_i) + \rho_{s1} (\dot{\beta}_i),
\]  
(A32)

Appendix B. Parameter Values for the Thermodynamic Surface of Steam in the Critical Region

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<tr>
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<td>( A_1 )</td>
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<tr>
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<td>( k_1 )</td>
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<td>( \mu_3 )</td>
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* The number of decimals given exceeds the number of significant decimals so as to retain precision in complex calculations.

* Fixed from theory.

* From latent heat data of Osborne et al.

* From fit to \( PVT \) data of Rivkin et al.

* Derived from vapor pressure curve.

* From known coexistence curve diameter.

* From identification of our surface with that of Haar et al. at \( T = 648.15 \) K and \( \rho = 230 \) kg/m\(^3 \).

* From fit to sound data of Erokhin and Kalyanov.

Appendix C. Tables of Thermodynamic Properties of Steam in the Critical Region

The uncertainty of the tabulated values is generally a few units in the last decimal given. However, in special cases, such as for the densities near \( \rho_c \) and \( T_c \) and the specific heats in the region where they vary rapidly, the uncertainty will be much larger.
### THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

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<th>Temp. K</th>
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<th>Enthalpy kJ/kg</th>
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## THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

Table CI. Thermodynamic properties along isochores at regular temperature increments (continued).

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<th>Entropy</th>
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...
Table C2. Properties of coexisting phases at regular temperature increments.

**vapor**

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**liquid**

<table>
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<tr>
<th>Temp. K</th>
<th>Pressure, MPa</th>
<th>Density, kg/m³</th>
<th>Latent Heat, kJ/kg</th>
<th>Internal Energy, kJ/kg</th>
<th>Enthalpy, kJ/kg</th>
<th>Entropy, kJ/kg.K</th>
<th>$C_p$, kJ/kg.K</th>
<th>$C_v$, kJ/kg.K</th>
<th>Velocity of Sound, m/s</th>
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### THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

#### Table C3. Properties of coexisting phases at regular pressure intervals.

**Vapor**

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<tr>
<th>Temp. (K)</th>
<th>Pressure (MPa)</th>
<th>Density (kg/m³)</th>
<th>Latent Heat (kJ/kg)</th>
<th>Internal Energy (kJ/kg)</th>
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**Liquid**

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<th>Internal Energy (kJ/kg)</th>
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<th>Entropy (kJ/kg.K)</th>
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Appendix D. Computer Program for Table Generation

In this Appendix the FORTRAN program is listed that yields the thermodynamic properties of steam in the region shown in Fig. 1 and specified by Eq. (18).

The independent variables are temperature $T$ in K and density $D$ in kg/m$^3$. The program computes the following properties: pressure $P$ in MPa, energy $U$ in kJ/kg, enthalpy $H$ in kJ/kg, entropy $S$ in kJ/kg.K, specific heat at constant volume $C_V$ in kJ/kg.K, specific heat at constant pressure $C_P$ in kJ/kg.K, velocity of sound $CS$ in m/s, compressibility COMP in 1/MPa.

The transformation from temperature and density to the parametric variables $r$ and $\theta$ of the extended and revised scaled equations is performed iteratively in the subroutine CONVER. Initial guesses for $r$ and $\theta$ to be used in CONVER are provided by the subroutine RTHETA of Moldover$^{28}$ which solves simple scaled equations with $c = 0$ and $k_1 = 0$. The pressure and other thermodynamic properties are calculated in the subroutine THERMO.

As a second option the temperature and pressure can be used as input variables. In this case, first the density is found from the equation of state by Newton iteration in the subroutine DFIN, after which the computations proceed as described above.

If saturation properties are desired, the independent variable is temperature; in this case $\theta = -1(1 + 1)$ for the vapor (liquid) side and $r = \Delta T/(1 - b^2)$. All properties, including density and latent heat, are then calculated in THERMO. As a second option the pressure can be used as the input variable. The temperature is then found from the vapor pressure equation in the subroutine TFIND after which the calculation proceeds as described above.

The subroutine RANGE checks whether the desired point lies within the range of the validity of the equation of state.

An example of the usage of these subroutines is given by the main program shown and a sample of the output is presented.

This code has been developed and tested on a Univac 1100/1108 computer.
THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

DOUBLE PRECISION A=0
COMMON /COEFS(A(20)),G(20),ANAMES(20),GNAMES(20)
DATA A/0.1774200,5.238000,0.40,25.41500,6.84500,3.2500,1.4400
1.90,0.001,1.9764200,4.444444,1.00,2.00,1.9764200,1.4400
2=17.187600-4.933200*4.00/DATA G/0.006000,0.0300,0.006700,0.06700,32.7700,22.74600
1.26700,1.660,1.2600/DATA ANAMES/69C,6HP3,6HDELROD=6HP2,6HP1,6HDBETA
1.64NL,6HDFLC,6HM2,6HMC,6HNL,6HDLTA
1.64M1,6HBDCT,6M2,6M3,6H500,6H500,6H500,6H500
2=6H505,6H501,6H500,6H500,6H500,6H500
DATA GNAMES/6HPONTA,6HPOINTB,6HDELPC,6HTC,6HMROD,6HPC
1.6HDFCCT,6MGLP3,6HPI,6HAPLHA,6HPO0,6HPO0,6HPO0
2=6HPO1,6HPO2,6HPO2

END

SUBROUTINE CONST

THIS SUBROUTINE CALCULATES ALL QUANTITIES NOT DEPENDENT ON R OR THETA.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /COEFS/ A(20),G(20)
COMMON/CRTS/TC,RHOC,PC,UCON,SCON,DCON

EQUALIZATION (DEL/15) ; (BETA(2) ; (DELTA(2) ; (BESG(1)-A(9))
1/(2*DEL(1)) ; (DEL(1)/2) ; (BET(1)/2) ; (SOL(1)/4) / (DEL(1)/4)
3/(SOL(1)/16) ; (P(1)/2) ; (P(1)/2) ; (P(1)/2) ; (P(1)/2) ; (P(1)/2)
4/(SOL(1)/32) ; (SOL(1)/32) ; (SOL(1)/16) ; (SOL(1)/8) ; (SOL(1)/4)

ALPHA = 2.0, A(6)*A(11) + 1.00
DELTA = 0.59D0
ALPH = 0.59D0
ALPHA = A(11)/2.00
DEL1 = 0.59D0
DEL2 = 0.59D0
DEL3 = 0.59D0
DEL4 = 0.59D0
DEL5 = 0.59D0

BET1 = BETA + DEL1
BET2 = BETA + DEL2
BET3 = BETA + DEL3
BET4 = BETA + DEL4
BET5 = BETA + DEL5

1 = (BESG(1) ; 1.00)*ALPHA*ALPHA/ALPHA
2 = (BETA ; 1.00)*ALPHA/ALPHA
3 = (BET1 ; 1.00)*ALPHA/ALPHA
4 = (BET2 ; 1.00)*ALPHA/ALPHA
5 = (BET3 ; 1.00)*ALPHA/ALPHA
6 = (BET4 ; 1.00)*ALPHA/ALPHA
7 = (BET5 ; 1.00)*ALPHA/ALPHA

ALPHA = 0.9999*

END

SUBROUTINE DISTANCE

THIS ROUTINE DETERMINS WHETHER THE ENTRY POINT IS WITHIN THE RANGE
OF VALIDITY OF THE EQUATION OF STATE (RANGE=1), OR NOT (RANGE=0).

IMPLICIT REAL*8(A-H,O-Z)
COMMON/SATUR/ISAT

RETURN

END

COMMON/CRTS/TC,RHOC,PC
DATA TMIN,TMAX/64.3D0,69.5D0/DMIN,DMAX/200.D0,420.D0/

IRANGE=1
IF(ISAT.NE.0) GO TO 10
IF(LI. LT. TMIN .OR. T. LT. TMAX) GO TO 99
IF(IOPT.EQ.2) GO TO 20
IF(D. LT. DMIN .OR. D. GT. DMAX) GO TO 99
RETURN
20 CALL THERMO(1,T,DMIN,PMIN,R,THT)
CALL THERMO(1,T,DMAX,PMAX,R,THT)
IF(P.LT.PMIN .OR. P.GT.PMAX) GO TO 99
RETURN
10 IF(IOPT.EQ.2) GO TO 30
IF(T. LT. TMIN) GO TO 99
IF(ISAT.EQ.-1 .AND. T. LT. TMIN) GO TO 99
IF(ISAT.EQ.1 .AND. T. LT. 64.5D0) GO TO 99
RETURN
30 IF(T. LT. TMIN) GO TO 99
IF(ISAT.EQ.-1 .AND. P. LT. 2.0D0) GO TO 99
IF(ISAT.EQ.1 .AND. P. LT. 2.1D0) GO TO 99
RETURN
IRANGE=0
WRITE(*,2) 'THIS POINT IS OUTSIDE THE RANGE!'
RETURN
END

SUBROUTINE THERMO(IFIND,T,P,R,T1,T2)
C
C 1. NOT ON THE SATURATION CURVE (ISAT=0)
C 2. GIVEN THE TEMPERATURE T AND DENSITY D, THIS ROUTINE
C 3. CALCULATES PRESSURE P(MPA) AND ITS DERIVATIVES W.R.T.
C 4. T AND D.
C 5. SPECIFIC HEATS C P AND C V(K/J/KG), VELOCITY OF SOUND CS(N/S)
C 6. AND COMPRESSIBILTY CMP(1/MPA).
C 7. IF THE ENTRY POINT IS IN THE 2-PHASE REGION (IPHASE=2) IT
C 8. RETURNS CP=CMP=CS=0.
C 9. IF IFIND=1 IT CALCULATES ONLY P AND DPD.
C 20. ON THE SATURATION CURVE (ISAT,NE.0) IT
C 21. GIVEN THE TEMPERATURE T, IT CALCULATES THE DENSITY D, LATENT HEAT
C 22. OF THE ABOVE PROPERTIES ON THE VAPOR SIDE (ISAT=1), OR THE
C 23. LIQUID SIDE (ISAT=1).
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON/MLKB/IFMPX,DDPD,DDP1,D2PT1,EMN1KMP,CP,CV,CS,CMP
COMMON/SATUR/ISAT,HEAT,DLIQ,DDAF
COMMON/COEF/20.0,0.02
COMMON/CRTS/TC,RHOC,PC,PCON,UCON,SCON,BPCON
DIMENSION S(2),X(2),SD(2)
EQUALITY (PM1A(3)),(PM2A(14)),(PM3A(15)),(PM3A(16)),
(PD1D(11)),(PD2D(12)),(PD3D(13))
(P1D1(18)),(P1D2(19)),(P1D3(20))
(PR1A(10)),(PR1A(7)),(PR1A(12)),(PD1D(9))
(ALPHA(110)),(ALPHA(115)),(DEG5,A(9))
C
X(1)=X0
X(2)=X1
TEE=(T-TC)/TC
TU=1.0+TW
IF(ISAT.NE.0) GO TO 10
RHOD=RHOC
CALL CONVER(RHOD,TEE,ANU,THI,RHOD1,SRHOD1,EYR)
GO TO 12
10 THI=1.0
IF(ISAT.EQ.-1) THI=0.99999999999999999
IF(ISAT.EQ.1) THI=0.99999999999999999
R=D/(P1D1+R)
CALL SRT(RHOD,THI,SRHOD)
RP=THI*(XK1A1#16)+A1*(1#16)+A1*(1#16)
RHO=1.0+PD1D*DTWRHOD
D=RHOD/RHOC
ANU=0.0
D
12 T1=THI+TH1
T2=T1+T1
PW=1.0+DTW*(PD1D+DTW*PD1D)
PWU=ANU*RHOD1
PDTH=P0D+P2D+T1+P4D*T1
PDTH=P0D+P2D+T1+P4D*T1
PDTH=ANO+PD1D+PD1D
PDTH=ANO+PD1D+PD1D
PDTH=ANO+PD1D+PD1D
PDTH=ANO+PD1D+PD1D
IF(IFIND.EQ.1) GO TO 11

THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

DPDT=PW1+DTW*2.0*PW2+3.0*PW3*DTW
DQDT=AM1+DTW*2.0*AM2+3.0*AM3*DTW
UW=DPDT-RH0*MODT+PW1*AMUH*1.1*S2
HW=PW-TUW
AHW=AHU+AMC+DTW*(AM1+DTW*(AM2+DTW*AM3))
SW=HW-RH0*AHW

C
D2PDT=2.0*DPW2+3.0*DPW3*DTW
D2QDT=2.0*DPW2+3.0*DPW3*DTW
IF(UUW+STH)>.SE.1.0) GO TO 13
IPHASE=1
CALL AUX(R1+TH1,D2PDT2,D2PDNT+B2PDNM2*AA+XK+SD,CVCDEX)
DPDD=DPDND4#1/B2PD2
IF(IDFIND.EQ.1) GO TO 15
DPDCD=DPDCT+FWW1*(RH0-RH0B2PDH2)*B11+B212*RH0B2PDH2
DPDD2=FW+TUW#DPDCTC
CVIT2=D2PDT-RH0B2QDT2+D2PD2T-(FW1+2PD2T)S2/B2PD2
CUV=CUVIT2#1
CPW=CUW+2PD2M2#DPDWT2#DPDW2/(RH0B2PDH2)
CNP=1.0/IDPDD
CS=1.0#DSORT(CFW/CWWIDPDD)
CIF(ISAT.EQ.0) GO TO 14
RH01=1.0+FW1+DTWAA(1)*S1+S2
RH02=KK+RI#A16+R16R16S16
D10=RHOD#(RH01-RH02)
DPIT2=FW+TUW(W4+RH0B2PDMT)
HEAT=1.0#S#(CPDM#DPD2T2#)(1.0+DVAP-1.0/DLID)
GO TO 14

C
DPDD=0.
IF(IDFIND.EQ.1) GO TO 15
DPDCD=UW+DH0#DQDT
DPDD2=FW+TUW#DPDCTC
CVO=2.0-ALPHA)*1.0-ALPHA)*R16#ALPHA)*XK#PAO
CV1=2.0-ALH1)+1.0-ALH1)*R16#ALH1)*XK#PAO
CUTW2=D2PDT-RH0B2QDT2+AAB1.0-EEO32)*S2/(CUTW2+1)
CUV=CUVIT2#1
CPA=0.
CNP=1.
CS=0.

C
DPDT=PCOM#DPDWT
SCOND=SCON+D
U=UWUCON/D
H=HWSCOND+T
ENTROP=SUWSCOND
C=CUW#SCOND
CP=CFW#SCOND

C
RETURN

SUBROUTINE DFIN(T,P,D,DGUESS,DMIN,DMAX)

C ATTN THE TEMPERATURE T(K), PRESSURE P(MPA), AND AN INITIAL
C GUESS DENSITY DGUESS(KG/M3); THIS ROUTINE FINDS THE
C CORRESPONDING DENSITY D(KG/M3) IN THE RANGE (DMIN,DMAX),
C IF IT IS BELOW THE CRITICAL ISOTHERM, D GUESS MUST BE SET
C EQUAL TO THE CRITICAL DENSITY; OTHERWISE IT MAY YIELD
C ERRONEOUS RESULTS, IF THE ENTRY POINT IS IN THE 2-PHASE
C REGION CRITICAL DENSITY IS RETURNED FOR D.

C
IMPLICIT REAL*8(A-H,O-Z)
COMMON/ THERM/IPHASE, DPDD
C
D=DGUESS.
DO 10 J=1,20
CALL THERM(I,J,T,D,PP,R,THERA)
PDD=PDD-PF
IF(IPHASE.EQ.2) GO TO 10
DELDP=PDD/D
C=0
IF(D+LT.DMIN) D=DMIN
IF(D.GT.DMAX) D=DMAX
IF(ABS(DELDP)LT.D1.0) GO TO 10
10 IF(ABS(D>PDD),LE.0.0) GO TO 19
IF(DPF,LT.0.0) D=DMAX
IF(DPF,GT.0.0) D=DMIN
10 CONTINUE
IF(21) WRITE(6+21),T,P,D
RETURN
ENDE
SUBROUTINE F聘外P(I1)
  
  GIVEN A PRESSURE P(NUPa) BELOW THE CRITICAL ISOBAR, IT FINDS THE
  CORRESPONDING TEMPERATURE T(K) ON THE SATURATION CURVE.

  IMPLICIT DOUBLE PRECISION (A-H,O-Z)
  COMMON/THERM,TPHASE,PDP0,DPDT,DW,G,ENTROP,CP,CV,CS,COMP
  COMMON/BATUR,HEAT,HROD,RHODG
  COMMON/CRTS/TC,RHOC,FC,FCOM,UCOM,SCON,SCON

  T=TC-1.00
  D=RHOC
  ISAVE=ISAT
  ISAT=2
  DD 10 L=1,20
     CALL THERMO(G.O.T.N.PP.R.I.TH1)
     DT=(FP-FP)/DPDT
     T=T-DT
     IF(T.GT.TC) GO TO 12
     IF(DABS(DT/TT).LT.1.0D0) GO TO 20
  GO TO 10
  12 T=T-0.001D0
  10 CONTINUE
     WRITE(6,11) F,PPP,T
  11 FORMAT(1X,1X,'TFIND DOES NOT CONVERGE !'F3F12.6/)  
  20 ISAT=ISAVE
     RETURN
   END

------------------------------------------------------------------------

SUBROUTINE CONVER(RHO,THET,AMU,TH1,R1,RHO15,S1,RHODI,ERROR1)
  
  THIS ROUTINE TRANSFORMS TEMPERATURE AND DENSITY TO THE PARAMETRIC VARIABLES
  R AND THETA ACCORDING TO THE REVISED AND EXTENDED SCALED EQUATIONS.

  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /COFS/ A(20),Q(20)
  DIMENSION S1(2),S0(2)
  EQUIVALENCE (BETA,A(6))(DELTA,A(11))(XK1,A(12))(CC*A(1))
     /* (ALH1*Q15)+(ALPHA*,G(10))+(BESQ*A(9))+(P11*Q9) */
     /* (DEL1*Q14)+(P14*Q18)+(F2W*G(19))+(F4W*G(20)) */
     /* (A*A10)+(X00,A(7))+(S00+AA17)+(S20+Q18) */
  BETAI = CC*SI(1)

  TSTAR = TEE+1.00
  DSTIN = 1.00 - (1.00/TSTAR)
  R1=0
  IF(DSTIN.LT.0) R1=DSTIN/(1.-BESQ)
  TH1=0.
  IF(DSTIN.LT.0) TH1=.1.
  CALL SS(R1,TH1,S1,SD)
  RHO DI = 1.0 + P11*DTSTIN
  RHDIT = RHO DI'*CC*S1(1) + CC*S1(2)
  DRHO = RHO - RHDIT
  AMU = 0.00
  IF(DSTIN.GT.0.00) GO TO 1
  RHOIC = XK1*R1**BETAI + XK1*R1**BETAI
  T2OFXZ = RHOIC0
  IF (DABS(DRHO).GT.T2OFXZ) GO TO 1
  RHOIS = DSIGN(RHOIC0,DRHO) + CC*S1(1)
  TH1 = DSIGN(1.00,DRHO)
  ERROR1 = 1.00
  GO TO 999
  1 CONTINUE
     IF(DRHO.NE.0.00) GO TO 2
  TH1 = 0.00
  R1 = DSTIN
  RHOIS = CC*S1(1)
  2 CONTINUE

C RULE FOR FIRST PASS
  Y1 = DSTIN
  DENI = RHO - RHDIT
  CALL RTHEAV(R1,TH1,DEN1,Y1)
  TT=TH1
  AMU = A&R R1**(BETAI*TH1)**TH1**1.00-11
  Y1 = DSTIN + CC*AMU
  CALL SS(R1,TH1,S1,SD)
  RHOSEG = XK1*R1**BETAI*TH1 + CC*S1(2)
  RHOIS = DEN1 + CC*S1(1) + RHOSEG
  ERROR1 = RHO - RHO DI - RHOIS
  IF( DABS(ERROR1).LT.1.0D-5 ) GO TO 999

C RULE FOR SECOND PASS
  DEN12 = RHO - RHDIT - CC*S1(1) + RHOSEG
  IF (DEN12.EQ.DEN1) DEN12 = DEN1 - 1.0-06
  CALL RTHEAV(R1,TH1,DEN12,Y1)
  TT = TH1
  AMU = A&R R1**(BETAI*DELTA)**TH1**1.00-11
  Y1 = DSTIN + CC*AMU
  CALL SS(R1,TH1,S1,SD)
  RHOSEG = XK1*R1**BETAI*TH1 + CC*S1(2)

THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

C RULE FOR HTM PASS
DEN2 = DEN12
DO 44 IS16 = 1,10
SLOPE = (ERROR2-ERROR1)/(DEN2-DEN1)
HELD = DEN2
DEN2 = DEN1 = (ERROR1/SLOPE)
CALL RTHETA(R1,T1,DEN2,T1)
TT = TH1*TH1
ANU = A4# R1**(BETADELTA)**TH1**(1.0-TT)
T1 = T1*TH1 + CERW
CALL SSB(R1,T1,TH1,SD)
RHOWEG = X1#RI#BETA#TH1 + CC#S1(2)
RH15 = DEN2 + CC#S1(1) + RHOWEG
ERROR1 = ERROR2
ERROR2 = RHO - RHODI - RH15
IF( DABS(ERROR2).GT.1.D-6 ) GO TO 999
DEN1 = HELD
44 CONTINUE

C FORMAT(1X,'CONVERGENCE REACHED')
50 FORMAT(1X,'CONVERGENCE REACHED')
999 CONTINUE
RETURN
END

SUBROUTINE RTHEA(R,T,H,A)

C THIS VERSION WILL FIT DATA FOR THETA GT 1.0 AND LT 1.000001

C SOLVES
RHO = EM#*THETA*BETA
TEC = 1.00*DEG#*THETA#*THETA

C IMPLICIT REAL*8 (A-H,O-Z)
COMMON CCDEFS/ A(20),Q(20)
EQUIVALENCE (BETA/A(6)), (EM/A(7)), (DEG/A(9))

C IF(EM.LE.0.00 .OR. BSEG.LE.1.00) GO TO 600
AISRHO = DABS( RHO )
IF(ABHRHO .LT. 1.0-12) GO TO 600
DEE = DSQRT(BSEG)
IF(AHRHO.TG.1.0-12) GO TO 495
IF( TEE .LT. 0.00 ) Z = 1.00*(1.00-TEE)*TEE/(1.00-BSEG)
1 *(EM/ABHRHO)**(1.00/BETA)
IF(TEE.GT.0.99) Z = 1.00*(EM/ABHRHO)**(1.00/BETA)**BETA
IF(Z.GT.1.0000000000000000) GO TO 496
C = -RHO**BETA/DEG**BETA
Z = DSQRT(Z/RHO)
100 DO 500 N = 1,16
Z2 = Z2
Z3 = 1.0 - Z2
Z4 = Z4*(Z4*DABS(Z4)**BETA)/(Z3*Z4**BETA)
Z = Z - Z2
IF(DABS(Z2).LT.1.0-12) GO TO 498
500 CONTINUE

600 WRITE(6,450) R,T,THETA, RHO,TEE,BETA,EM,BSEG
IF(DABS(THETA).GT.1.00001) THETA = THETA/DABS(THETA)
RETURN
498 THETA = Z/TEE
R = TEE/(1.00-Z2)
R = DABS(R)
RETURN
496 THETA = DSIGN(1.00,RHO)/BSEG
R = (RHO/(EM#*THETA))**(1.00/BETA)
RETURN
495 THETA = DSIGN(1.00,RHO)
R = TEE/(1.0000000000000000)
R = DABS(R)
RETURN
500 IF(TEE.LT.0.00) GO TO 601
IF(TEE.LT.0.00) GO TO 496
THETA = 1.0-12
R = TEE
450 FORMAT(2X,'RTHEA DOES NOT CONVERGE',I7,IX,E12.6)
RETURN
END

SUBROUTINE SS(R,TH,S,SD)

C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION S2(2),SDC(2)
COMMON CCDEFS/ A(20),Q(20)
EQUIVALENCE (ALPHA/Q(10)), (BETA/A(6)), (BSEG/A(9)), (DELTA/A(11))
1/(DELTA/2/10), (ALPHA/A(13)), (BETADELTA/A(10)), (DELTA/A(11)), (FOUR/A(11))

2, (P01(11)) + (S01(11)) + (D01(11)) + (C01(11)) + (B01(11)) + (A01(11)) + (X01(11)) + (S01(11)) + (D01(11)) + (C01(11)) + (B01(11)) + (A01(11)) + (X01(11))

C

T = TH1
S(1)* = S00*T + S01*T
S(2)* = S02*T + S21*T
S(3)* = S10*T + S11*T
S(4)* = S12*T + S13*T
S(5)* = S20*T + S21*T
S(6)* = S22*T + S23*T
S(7)* = S30*T + S31*T
S(8)* = S32*T + S33*T
RETURN
END

SUBROUTINE AUX(R1,T1,D1,P1,T2,P2,D2,dP1,dP2)
C
C THIS SUBROUTINE CALCULATES SOME OF THE SECOND DERIVATIVES OF
C THE ANOMALOUS PART OF THE EQUATION OF STATE.
C
C IMPLICIT REAL*8 (A-H,O-Z)
COMMON /COEFS/ A(20), D(20)
DIMENSION X(2), T(2), S(2), W(2), Y(2), Z(2), COEX(2)
EQUATIONS (C1(1), BETA(1), ALPH(1), BESG(1), BESG(2), BESG(3), BESG(4), BESG(5))
C
C DELI = 0.00
S(1) = S00*S20*T1*T1
S(2) = S02*T2*T1
W(1) = W1
Y(1) = COEX(1)
G(1) = Y(1)/W(1) + DELI
L = DELI
BETI = BETA + DELI
T = (T1 + DELI)*T1
RETURN
END

SAMPLE MAIN PROGRAM
C
C ISAT = 1 CALCULATES PROPERTIES ON THE VAPOR SIDE OF THE SATURATION CURVE.
C ISAT = 2 CALCULATES PROPERTIES ON THE LIQUID SIDE OF THE SATURATION CURVE.
C ISAT = 0 CALCULATES PROPERTIES AT ANY POINT ON THE THERMODYNAMIC SURFACE.
C SOUN = 0 TAKES AS INPUT VARIABLES TEMPERATURE AND DENSITY (WHEN ISAT = 0),
C OR TEMPERATURE ONLY (WHEN ISAT.NE.0).
C SOUN = 2 TAKES AS INPUT VARIABLES TEMPERATURE AND PRESSURE (WHEN ISAT = 0),
C OR PRESSURE ONLY (WHEN ISAT.NE.0).
C UNITS ARE AS FOLLOWS: TEMPERATURE IN (K), DENSITIES IN (KG/M^3), PRESSURE
C IN (KJ/ KG.K), SPECIFIC HEAT IN (KJ/ KG.K), VELOCITY OF
C SOUN IN (M/S), COMPRESSIBILITY IN (1/MPA), ETC.
C
C IMPLICIT REAL*8 (A-H,O-Z)
COMMON /COEFS/ A(20), D(20)
COMMON /THRD/ C1(1), BETA(1), ALPH(1), BESG(1), BESG(2), BESG(3), BESG(4), BESG(5)
COMMON /SUN/ ISAT, HEAT, D10, DVAR
COMMON /CRIT/ TC, RHOC, PC, PCON, UCSN, SCPN
THERMODYNAMIC PROPERTIES OF STEAM IN THE CRITICAL REGION

DATA DM1N,DMAX/200.0,420.0/
C
CALL COMST
WRITE(6,122)
WRITE(6,125) *(I-1,ANAMES(I)),I,O(I),DMAMES(I),I-1.0)
WRITE(6,123)
C
100 READ(5,IEND=999) ISAT,IOPT,T,D,P
CALL RANGE(I RANGE,10PT,T,B,P)
IF(ISAT.EQ.0) GO TO 100
IF(IOPT.EQ.1) UN 11.0 JAT
IF(ISAT.EQ.0) CALL FILTER(T,P,B,PRHOC,DM1N,DMAX)
IF(ISAT.EQ.0) CALL TEND(P,T)
200 CALL THERMO(T,P,B,CP,T,B,T,CP)
IF(ISAT.EQ.-1) WRITE(6,1124) HEAT
IF(ISAT.EQ.1) WRITE(6,1125) HEAT
WRITE(6,1126) IPIHA,T,P,B,U,H,S,CV,CP,CS,COMP
GO TO 100
999 STOP
C
1 FORMAT(167)
167 FORMAT(5X,3HA,-12.2N31,-11.2N40,-5.2X,5.4A3,5.2X,3MD1,12.2N31,-11.2N40,-5.2X,5.4A3)
1 5X,A6)
124 FORMAT(5X,'VAPOR SIDE OF SATURATION CURVE: LATENT HEAT=',1X,F7.2)
125 FORMAT(5X,'LIQUID SIDE OF SATURATION CURVE: LATENT HEAT=',1X,F7.2)
121 FORMAT(5X,'VAPOR SIDE OF SATURATION CURVE: LATENT HEAT=',1X,F7.2)
121 FORMAT(5X,'LIQUID SIDE OF SATURATION CURVE: LATENT HEAT=',1X,F7.2)
122 FORMAT(5X,'PARAMETERS OF THE SCALED EQUATIONS ARE:',1X,F7.2)
123 FORMAT(5X,'ENTER ISAT, IOPT, TEMPERATURE(E), DENSITY(KG/M3), HEAT','1X,'PRESSURE(HPA): (ENTRY FOR DEPENDENT VARIABLE S) WILL ',1X,'BE IGNORED')
END

B6DT,F
PARAMETERS OF THE SCALED EQUATIONS ARE :
A(1) = -0.17762 C(1) = -0.000000 POINTA
A(2) = 5.238000 P3(2) = -0.000000 POINTB
A(3) = 0.000000 DELR03(3) = 0.000000 DELPC
A(4) = -25.491500 P2(4) = 647.047000 TC
A(5) = 6.844500 P1(5) = 322.778000 RHOC
A(6) = 0.205000 DELTA(6) = 2.046000 P5
A(7) = 1.440300 KO(7) = 2.670000 DPCDTC
A(8) = 0.000000 DELTC(8) = -1.600000 SLOPID
A(9) = 1.375700 KB(9) = -0.491776 PI1
A(10) = 23.666600 A(10) = -1085000 ALPHA
A(11) = 4.620000 DELTA(11) = -0.580035 POO
A(12) = -0.294200 K1(12) = -1.926393 P2V
A(13) = -11.232600 MUC(13) = 0.612793 P40
A(14) = -22.654700 MUL(14) = -0.500000 DELTAI
A(15) = -17.887600 MUL2(15) = -0.391500 ALPHAII
A(16) = -4.953200 MUL3(16) = 0.582000 BETAI
A(17) = 1.109430 S00(17) = -0.741500 GAMMAII
A(18) = -1.791397 S20(18) = 0.103246 P01
A(19) = 0.249413 S01(19) = 0.146322 P21
A(20) = -0.845411 S00(20) = -0.146960 P41

ENTER ISAT, IOPT, TEMPERATURE(X), DENSITY(KG/M3), PRESSURE(HPA)
(ENTRY FOR DEPENDENT VARIABLES) WILL BE IGNORED:
> 0 1 680. 350. 0.
IN 1-PHASE REGION : T > 680.000 B > 350.000 P = 31.9201
U= 2103.7 H= 2194.9 S= 4.5297 CUP= 3.313
CP= 0.21679H02 CB= 434.83 COMP=.98864-01
> 0 1 645. 240. 0.
IN 2-PHASE REGION : T > 645.000 B = 240.000 P = 21.5038
U= 2143.7 H= 2231.3 S= 4.6405 CUP= 13.729
CP= 0.00000 CB= 0.00 COMP= 0.00000
> 0 2 650. 0. 25.
THIS POINT IS OUTSIDE THE RANGE!
> 0 2 650. 0. 23.
IN 1-PHASE REGION : T = 650.000 B = 390.953 P = 23.0000
U= 1941.4 H= 7000.7 S= 4.5771 CUP= 4.038
CP= 0.9553302 CB= 336.03 COMP=.5250300
> -1 1 646. 0. 0.
VAPOR SIDE OF SATURATION CURVE: LATENT HEAT = 277.94
IN 1-PHASE REGION : T < 646.000 B = 243.117 P = 21.7639
U= 2150.1 H= 2237.6 S= 4.6405 CUP= 5.421
CP= 0.3936040 CB= 324.40 COMP=.2837740
> 1 2 0. 0. 21.8
LIQUID SIDE OF SATURATION CURVE: LATENT HEAT = 244.78
IN 1-PHASE REGION : T < 646.138 B = 400.891 P = 21.8000
U= 1912.7 H= 1967.1 S= 4.2266 CUP= 5.585
CP= 0.2212640 CB= 298.08 COMP=.1354940

## Appendix E. Units and Conversion Factors

### Units used in the tables

<table>
<thead>
<tr>
<th>Unit</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>MPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Energy, enthalpy, latent heat</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>Entropy, specific heats</td>
<td>kJ/kg K</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>m/s</td>
</tr>
</tbody>
</table>

### Conversion factors

#### Pressure

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa to Pa</td>
<td>10⁶</td>
</tr>
<tr>
<td>MPa to bar</td>
<td>10</td>
</tr>
<tr>
<td>MPa to atmosphere</td>
<td>9.869233</td>
</tr>
<tr>
<td>MPa to lb/in²</td>
<td>145.037738</td>
</tr>
</tbody>
</table>

#### Density

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg/m³ to mol/dm³</td>
<td>0.0555083</td>
</tr>
<tr>
<td>kg/m³ to lbm/ft³</td>
<td>9.0624280</td>
</tr>
</tbody>
</table>

### Energy, enthalpy

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>J/kg to kJ/kg</td>
<td>18.01534</td>
</tr>
<tr>
<td>BTU/lbm to J/mol</td>
<td>0.4299226</td>
</tr>
</tbody>
</table>

### Entropy, specific heats

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>J/kg.K to J/mol.K</td>
<td>18.01534</td>
</tr>
<tr>
<td>BTU/lbm.R to BTU/lbm</td>
<td>0.2388459</td>
</tr>
</tbody>
</table>

### Sound velocity

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/s to ft/s</td>
<td>3.28083</td>
</tr>
</tbody>
</table>

### Temperature

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C to °F</td>
<td>(°F - 32) / 1.8</td>
</tr>
<tr>
<td>°F to °C</td>
<td>(°F - 32) * 1.8</td>
</tr>
<tr>
<td>K to °F</td>
<td>(°F - 32) * 1.8</td>
</tr>
<tr>
<td>K to °C</td>
<td>(°C + 273.15) * 1.8</td>
</tr>
</tbody>
</table>

Energy units are multiplied by the corresponding factor from the table, while temperature units are converted according to the provided formulas.