A MODIFIED BENEDICT-WEBB-RUBIN EQUATION OF STATE FOR PARAHYDROGEN-II

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Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

Final Report

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Prepared for:
NASA-Johnson Space Center
Houston, Texas 77058
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SYMBOLS

A = parameters for equation 1 r = parameters for index of
B = parameters for vapor pressure refractive index
     equation T = temperature, $T_{68}^*$ the International
C_p  = specific heat at constant pressure Practical Temperature
C_v  = specific heat at constant volume Scale
G   = parameters for equation for x = reduced temperature
     saturation densities $\beta$ = scaling law parameter $\phi$
N or G = parameters for equation of state = energy derivative
n   = index of refraction $\theta$ = specific heat input
P   = pressure $\rho$ = density
R   = gas constant

Subscripts:
c = critical point
  g = gaseous phase
  l = liquid phase
  t = triple point

UNITS

The primary variables in the computer programs are
Pressure in atmospheres
Density in moles/liter, and
Temperature in Kelvin,

Conversions to other SI units and units normally used in applied problems are given in appendix C.
A MODIFIED BENEDICT-WEBB-RUBIN EQUATION OF
STATE FOR PARAHYDROGEN - II

Hans M. Roder and Robert D. McCarty

A 32 term modified Benedict-Webb-Rubin equation of state has been
applied to data for parahydrogen. The adjustable parameters in the equation
of state were determined using 2665 points including very recent measure-
ments at low temperatures and high pressures. The new values extend the
range of the PVT data sufficiently to warrant a refitting of the equation of
state. Temperatures for the data range from the triple point to about 700
K with pressures reaching 3000 atmospheres near ambient temperatures.
The PVT data were adjusted to the T_68 scale. In addition, extensive
modifications have been made to the previously accepted PVT surface in
the region near the critical point. These adjustments have been made on
the basis of more recent refractive index data and the application of scaling
law equations. Detailed comparisons between experimental and calculated
values are given for density. Corresponding comparisons are made for
enthalpy and the specific heat at constant pressure.

Key words: Critical point; density; enthalpy; equation of state; hydrogen;
index of refraction PVT; saturation properties; scaling laws; specific heat.

1. Introduction

Almost all engineering problems requiring thermodynamic data for the cryogenic
fluids are most easily solved by using an equation of state to describe the PVT surface of
the gas, and to calculate values of such variables as enthalpy and specific heat. Quite often
some modification of the Benedict-Webb-Rubin (1940) equation of state (hereafter referred
to as MBWR) is preferred, because equations of this type are relatively easy to handle on a
computer.

This report describes an accurate wide-range MBWR equation of state for parahy-
drogen*. The study of the equation of state was actually completed in two phases. The first
phase was sponsored by the NASA-Lewis Research Center (P.O. C-32369-C) and is
summarized in a report by McCarty (1974). The earlier work gives a review of the adjust-
ments made to achieve the International Practical Temperature Scale, T_68, as defined in
Metrologia (1969). Changes were made in the PVT data, in the vapor pressure curve, in the
critical parameters, and in the two phase envelope near the critical point. Discussed briefly
is the selection of the equation of state, 32 terms rather than 19, a description of the fitting
program, and the results of a preliminary fit using the data available at that time. To
provide a complete record, much of the earlier material is included into the present report.

The second, and present phase of the study is sponsored by NASA-Johnson Space
Center (P.O. T-6570C). The main thrust is that new experimental PVT measurements at

* Parahydrogen is the nuclear spin modification which is stable at low temperatures.
low temperatures and high pressures are now available (Weber, 1975). These values extend the range of the existing PVT data (Goodwin, et al., 1963 and Michels, et al., 1959a) sufficiently to warrant a refitting of the equation of state. The refit now includes the actual experimental PVT data, adjusted to the $T_{68}$ scale, and calculated values of $C_v$, adjusted from normal to parahydrogen, for the high temperature source (Michels, et al., 1959b). The representation of the PVT surface and derived thermodynamic functions is greatly improved over previous versions. This fact is shown clearly, and for the first time by detailed comparisons between experimental and calculated values of density, and by corresponding intercomparisons for enthalpy and specific heat at constant pressure, $C_p$.

2. The Sources of Data

The major sources from which experimental or calculated values are taken originate in the laboratories of NBS and of the University of Amsterdam. A description of these basic references follows. Weber, et al. (1962) measured vapor pressures, Roder, et al. (1963) present critical parameters and densities along the two phase envelope. The bulk of the PVT data is given in Goodwin, et al. (1963), while experimental heat capacity data is found in the papers of Younglove and Diller (1962a, b). These papers cover pressures from 0 to 340 atmospheres with temperatures from the triple point to 100 K, and they are smoothed and combined to yield calculated thermodynamic functions by Roder, et al. (1965). The very recent measurements by Weber (1975) extend coverage to pressures up to 800 atmospheres with temperatures up to 300 K. The second extensive set of PVT data is presented by Michels, et al. (1959a), and these values are used to calculate thermodynamic properties in Michels, et al. (1959b).

A number of other references on hydrogen exist, see for example the survey by Woolley, et al. (1948). We have omitted these sets of data because they do not cover a large range of pressure and temperature, because the various sets are mutually inconsistent, and because the experimental errors are estimated to be larger than the sources chosen. Indirectly these sources are included because they were used by McCarty and Weber (1972) in deriving parameters for the 17 term equation of state described in that paper. We use 40 points generated from that equation in the fitting of the present equation. These generated points insure that the present equation is not subject to undue oscillations for temperatures from 423 to 2200 K with pressures up to 680 atmospheres.

The input to the fitting program, the "data" is taken from these sources as shown in table 1. It is clear from the table that in addition to using PVT data the fitting procedure uses higher order thermodynamic data such as $C_v$ and the Gibbs constraint, in other words the technique of simultaneous or multiproperty fitting.

---

*Normal hydrogen is the equilibrium mixture at room temperature, 75% ortho, 25% para.*
Table 1. Data Used to Determine the Parameters of the Equation of State

<table>
<thead>
<tr>
<th>Type of data</th>
<th>number of points</th>
<th>source</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVT</td>
<td>1218</td>
<td>Goodwin, et al. (1963)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>377</td>
<td>Weber (1975)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>Roder, et al. (1965)</td>
<td>extrapolated beyond the melting line</td>
</tr>
<tr>
<td></td>
<td>482</td>
<td>Michels, et al. (1959a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>McCarty and Weber (1972)</td>
<td>calculated, temperatures above 423 K</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>Roder, et al. (1963)</td>
<td>saturated liquid, saturated vapor adjusted by McCarty (1974)</td>
</tr>
<tr>
<td>Cv</td>
<td>163</td>
<td>Younglove and Diller (1962)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>Roder, et al. (1965)</td>
<td>calculated values</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>Michels, et al. (1959b)</td>
<td>calculated values</td>
</tr>
<tr>
<td>Gibbs constraint</td>
<td>19</td>
<td>Roder, et al. (1965)</td>
<td>saturated liquid - saturated vapor</td>
</tr>
<tr>
<td>Total Points:</td>
<td>2665</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Adjustment and Modification of the Data

Adjustment of the raw data was necessary for two reasons. First, international agreement on a practical low temperature scale which is very close to the thermodynamic scale was reached in 1968 (T, Metrologia 1969). Second, an index of refraction experiment by Diller (1968) indicated that the definition of the PVT surface given by Roder, et al. (1965) is in error as much as 7% in density in the region near the critical point. The fact that the two-phase envelope might be in error was pointed out as early as 1963, [see for example figure 4 in Roder, et al. (1963)], through analysis of errors in the intersection temperatures of isochores - experimental runs - and the vapor pressure curve.

As a result, McCarty (1974) made adjustments in both temperature scale and density in the region near the critical point. The changes are most noticeable in the critical parameters, the vapor pressure curve, and the saturated liquid and vapor densities. The sequence adopted was to first find values for the densities of saturated liquid and vapor from the index of refraction experiment; next to estimate new critical parameters from these densities using values close to the critical point and a mathematical representation based on the scaling laws. The results were checked by looking at the rectilinear diameter. Finally, the newly defined saturation boundaries near the critical point and densities at lower temperatures were represented with empirical equations which include scaling law terms. PVT values generated from these equations were finally used as "data"
for the equation of state, see line 6, table 1.

3.1 Temperature Scale Changes

The NBS 55 temperature scale was used to determine the PVT data of Goodwin, et al. (1963), the heat capacity data of Younglove and Diller (1962a, b), and the PVT data of Weber (1975). For these references the conversion of the experimental temperatures to the $T_{68}$ scale was straightforward.

Conversion of the temperature scale used by the University of Amsterdam is based on a similar adjustment made for the PVT data of Argon (see Gosman, et al., 1969). The assumption is made that the same thermometer and scale was used for hydrogen as was used for argon. The temperatures given by Michels, et al. (1959a, b) and the ones chosen for the present fitting are contrasted in table 2. Two bits of evidence indicate that the assignment of temperatures for this set of data are reasonable. First, the authors' experimental temperature scale (Levelt-Sengers, 1966) included a calibration point at the temperature of sublimating CO$_2$. Thus the experimental temperature scale except for the three lowest and for the very highest temperatures is remarkably close to the $T_{68}$ scale as subsequently defined. This is of course exactly what the authors were trying to achieve; to make the measurements as nearly on the thermodynamic scale as possible. Second, a

Table 2. Temperatures Assigned to the PVT Data of Michels, et al.

<table>
<thead>
<tr>
<th>Reference, °C</th>
<th>$T_{68}$, K this paper</th>
<th>Reference, °C</th>
<th>$T_{68}$, K this paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>-175</td>
<td>98.1835</td>
<td>-25</td>
<td>248.147</td>
</tr>
<tr>
<td>-170</td>
<td>103.1835</td>
<td>0</td>
<td>273.15</td>
</tr>
<tr>
<td>-160</td>
<td>113.173</td>
<td>25</td>
<td>298.142</td>
</tr>
<tr>
<td>-150</td>
<td>123.1625</td>
<td>50</td>
<td>323.140</td>
</tr>
<tr>
<td>-135</td>
<td>138.1585</td>
<td>75</td>
<td>348.143</td>
</tr>
<tr>
<td>-120</td>
<td>153.161</td>
<td>100</td>
<td>373.15</td>
</tr>
<tr>
<td>-100</td>
<td>173.166</td>
<td>125</td>
<td>398.1595</td>
</tr>
<tr>
<td>-75</td>
<td>198.165</td>
<td>150</td>
<td>423.170</td>
</tr>
<tr>
<td>-50</td>
<td>223.1555</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A separate analysis also indicated that the temperatures shown in table 2 are the most likely set. The analysis consisted of fitting a surface to this set of PVT data, first with the temperatures adjusted from IPTS48 to $T_{68}$, and then by assuming that the temperatures were measured on a local scale (Levelt-Sengers, 1966) with subsequent corrections to IPTS48 and then to $T_{68}$. A comparison of the sum of the residuals of the two fittings favors the second procedure.
3.2 Adjustment of Saturated Liquid and Vapor PVT Near the Critical Point

In addition to the temperature scale change, an adjustment was made in densities on the basis of an index of refraction experiment by Diller (1968). Diller measured the index of refraction, temperature, and pressure. He obtained densities from the PVT surface defined by Roder, et al. (1965) which on the saturation boundaries is identical to Roder, et al. (1963). The salient graph from Diller's paper is reproduced in figure 1, where it is seen that the saturation boundaries fall on two separate legs which do not meet at the critical density. The Lorentz-Lorenz function of the saturation boundaries should have the same general shape as do the isotherms. In particular, for temperatures between 28 K and critical the two-phase envelope should be very close to the 35 K isotherm. The two legs of two-phase envelope are ascribed to incorrect densities in the critical region. More precisely, as indicated earlier, the errors stem from the intersection temperatures of experimental runs and the vapor pressure curve, which near the critical point are nearly co-linear.

![Figure 1. The Lorentz-Lorenz Function for Hydrogen](image)

To adjust the saturation densities in the critical region the function

$$\rho = \sum_{K=1}^{N} A_K n^{K-1},$$

was fit to the 35 K isotherm, where $\rho$ is density in g/cm$^3$ and $n$ is the index of refraction.
Equation (1) was fit to 24 experimental index of refraction points with densities ranging from 0.003969 to 0.078833 g/cm³. It is important that the data not be "overfit." Since statistical significance of the coefficients to eq (1) was lost when more than 4 terms were used the 4 term equation was chosen. The coefficients obtained for eq (1) are given in table 3.

Table 3. Least Squares Estimates of the Coefficients for Equation (1)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>-1.0880215243</td>
</tr>
<tr>
<td>A₂</td>
<td>1.8280271481</td>
</tr>
<tr>
<td>A₃</td>
<td>-1.037874469</td>
</tr>
<tr>
<td>A₄</td>
<td>0.29788205862</td>
</tr>
</tbody>
</table>

The measured index of refraction along the saturated liquid and vapor was then used to calculate the adjusted densities using eq (1). The densities given by Roder, et al. (1963) and the adjusted densities are contrasted in table 4.

Table 4. Adjusted Saturation Densities Near the Critical Point

<table>
<thead>
<tr>
<th>Temp, K</th>
<th>NBS-55</th>
<th>T68</th>
<th>Index of Refraction</th>
<th>Density of Liquid, g/cm³</th>
<th>Density of Vapor, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Roder et al. (1963)</td>
<td>Eq (1)</td>
<td></td>
</tr>
<tr>
<td>28.0</td>
<td>28.0071</td>
<td>28.0071</td>
<td>1.092881</td>
<td>.058966</td>
<td>.058998</td>
</tr>
<tr>
<td>29.0</td>
<td>29.0073</td>
<td>29.0073</td>
<td>1.089174</td>
<td>.056646</td>
<td>.056674</td>
</tr>
<tr>
<td>30.0</td>
<td>30.0076</td>
<td>30.0076</td>
<td>1.084824</td>
<td>.053930</td>
<td>.053944</td>
</tr>
<tr>
<td>31.0</td>
<td>31.0080</td>
<td>31.0080</td>
<td>1.079479</td>
<td>.050589</td>
<td>.050586</td>
</tr>
<tr>
<td>31.6</td>
<td>31.6082</td>
<td>31.6082</td>
<td>1.075401</td>
<td>.048057</td>
<td>.048021</td>
</tr>
<tr>
<td>32.0</td>
<td>32.0084</td>
<td>32.0084</td>
<td>1.072075</td>
<td>.045993</td>
<td>.045927</td>
</tr>
<tr>
<td>32.4</td>
<td>32.4086</td>
<td>32.4086</td>
<td>1.067671</td>
<td>.043320</td>
<td>.043152</td>
</tr>
<tr>
<td>32.7</td>
<td>32.7088</td>
<td>32.7088</td>
<td>1.062766</td>
<td>.040412</td>
<td>.040057</td>
</tr>
<tr>
<td>32.9</td>
<td>32.9089</td>
<td>32.9089</td>
<td>1.055690</td>
<td>.036941</td>
<td>.035586</td>
</tr>
</tbody>
</table>

3.3 Estimation of Critical Density and Temperature

Extrapolation of the rectilinear diameter yields the best estimate for the critical density. A plot of \( (p_\ell + p_g)/2 \) against temperature, as shown in figure 2, limits the critical density to a value between 0.03122 and 0.03142 g/cm³. The value of the critical density is seen to depend only slightly on temperature. Therefore, the next step is to extrapolate the rectilinear diameter numerically.

To achieve this the equation given in the next section, eq (5) which describes the saturation boundaries is used. The equation is truncated to 4 terms resulting in

\[
\frac{\rho_g + \rho_\ell}{\rho_c} = 2\rho_c + (G_{1g} + G_{1\ell})(\Delta T)^5 + (G_{2g} + G_{2\ell})(\Delta T)^{1-\alpha} + (G_{3g} + G_{3\ell})(\Delta T), \tag{2}
\]
where $\Delta T = (T_c - T)/T_c$. Note that the exponents of the last two terms are $1-\alpha$ and 1 rather than 1 and $4/3$. $g_{1G}$ is usually assumed to be equal to $-G_{1G}$ and the second term of eq (2) vanishes. There is some doubt about the validity of this assumption, but in this particular case at least, the assumption cannot be disproved on the basis of the available data. Thus the problem of estimating $\beta$ is eliminated. A least squares fit of the eight pairs of liquid-vapor data in table 4 resulted in a critical density of 0.03136 g/cm$^3$ for values of $\alpha = 0.1$ and $T_c = 32.933$ K. The fit was repeated several times with values of $\alpha$ and $T_c$ ranging from $\alpha = 0.1$ to $\alpha = 0.25$ and $T_c = 32.938$ to $T_c = 32.95$. The resulting estimates of $\rho_c$ did not vary significantly (i.e., maximum variation was less than $\pm 0.00001$ g/cm$^3$).

The next step is to estimate the critical temperature. In this case eq (5) is truncated to two terms, that is to the terms originating from the scaling laws. The resulting equation, eq (3),

$$\rho_{sat} = \rho_c + G_{1G} (\Delta T)^\beta$$

is obviously valid only for densities very close to critical. With some trial and error
temperatures between 31.9 and 32.8 were found to be applicable. A value for $\rho_c$ is at hand, a value for $T_c$ can be estimated from the equation if pairs of $\rho_{\text{sat}}$ and $T_{\text{sat}}$ are available. Since very few of the experimental densities are at temperatures between 31.9 and 32.8 K, a parametric interpolation function for $n$ was used to provide the necessary input to eq (1). The function

$$n = r_1 + r_2 (\Delta T)^r_3,$$  \hspace{1cm} (4)

was fit to the index of refraction data of the saturation boundary (liquid and vapor) between 28 and 32.9 K. In eq (4) $n$ is the index of refraction, and $\Delta T = (T_c - T)/T_c$. The coefficients used in eq (4) are given in table 5. By combining equations (4) and (1) densities could be calculated.

Table 5. Coefficients for equation (4)

<table>
<thead>
<tr>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0509586594</td>
<td>0.091463402563</td>
<td>0.41043983745</td>
</tr>
</tbody>
</table>

every 0.1 K between 31.9 and 32.8 K. The data so interpolated were finally used in a fit of eq (3) with $\rho_c = 0.03136$ g/cm$^3$, establishing the critical temperature $T_c$ as 32.938 K, and also $\beta_{\text{gas}} = 0.3483$, $\beta_{\text{liquid}} = 0.3478$.

The values of the $\beta$'s are quite close to the 0.35 predicted by the scaling laws. The value of the critical temperature is virtually the same as that calculated previously by Weber from index of refraction data (unpublished but cited by Goodwin, 1970, page 226).

3.4 Revised Saturation Boundary Equations

The equation used to represent the saturation boundaries is based in part on the scaling laws but is otherwise empirical. The equation is

$$\rho_{\text{Sat}} = \rho_c + G_1 (\Delta T)^{\beta_1} + \sum_{I=1}^{8} G_{(I+1)} (\Delta T)^{(1 + (I-1)/3)}$$ \hspace{1cm} (5)

using the values established in the previous section for $T_c$, $\rho_c$ and the betas, eq (5) is used to represent the saturation boundaries. Input for the fitting are the saturated liquid and vapor values of Roder, et al. (1963) with temperatures adjusted to the $T_{68}$ scale, except that for temperatures of 28 K and above the adjusted densities given in table 4 are used, and that for the vapor a few generated values were added to balance numbers between liquid and vapor. The coefficients for eq (5) are given in table 6. Table 7 gives the deviations between calculated and input densities.
Table 6. Coefficients for Equation (5)

<table>
<thead>
<tr>
<th>Vapor</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_c$</td>
<td>0.03136 g/cm$^3$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.3483</td>
</tr>
<tr>
<td>$G_1$</td>
<td>-0.047501571529</td>
</tr>
<tr>
<td>$G_2$</td>
<td>3.4871213005x10^{-2}</td>
</tr>
<tr>
<td>$G_3$</td>
<td>-4.1221290925x10^{-1}</td>
</tr>
<tr>
<td>$G_4$</td>
<td>1.5666598550</td>
</tr>
<tr>
<td>$G_5$</td>
<td>-2.8061427339</td>
</tr>
<tr>
<td>$G_6$</td>
<td>2.7105455626</td>
</tr>
<tr>
<td>$G_7$</td>
<td>-1.3074773595</td>
</tr>
<tr>
<td>$G_8$</td>
<td>0.22921285922</td>
</tr>
</tbody>
</table>

3.5 Revised Vapor Pressure Equation

The vapor pressure data of Weber, et al. (1962) was converted to the $T_{68}$ scale and refit to the nonanalytical vapor pressure equation of Goodwin (1969). That equation is

$$\ln \left( \frac{P}{P_t} \right) = B_1 X + B_2 X^2 + B_3 X^3 + B_4 X (1-X)^{B_5},$$

(6)

where $X = (1-T_t/T)/(1-T_t/T_c)$, $T$ is in kelvins. The coefficients to eq (6) are given in table 8. The two data points given by Weber, et al. (1962) for $T = 22$ and 23 K were omitted from the fit because their inclusion seriously degraded the representation of the rest of the data. The $T_{68}$ triple point temperature of hydrogen, 13.81 K, could not be used because it also degraded the fit. Similarly the boiling point of parahydrogen could not be constrained to the $T_{68}$ value of 20.280 K, but is rather 20.277 K. Since Goodwin's equation is sensitive to the values chosen at the triple point and has been successfully used to force thermodynamic consistency for several other gases, we interpret the departure at the triple point and at the normal boiling point to indicate some remaining low level inconsistency in the defined temperature scale, $T_{68}$. Table 9 gives the vapor pressures from Weber, et al. (1962), the adjusted temperatures, and the deviations between the experimental and calculated data points. The critical pressure is obtained by inserting the critical temperature into eq (6).
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* Points omitted from the least squares fit.
** Critical pressure
4. The Equation of State for Hydrogen

Since the major modification of the Benedict-Webb-Rugin (1940) equation of state by Strobridge (1962), there have been many more. Each author claims his particular modification to be the best of several he has tried for the particular fluid being correlated, in some cases a given form was chosen because it worked well for a number of fluids. Several of the MBWR's have been applied to hydrogen. Strobridge's equation (16 terms) was applied by Roder and Goodwin (1961) to parahydrogen. It was found that two sets of coefficients, one for liquid and one for gas, were required to reproduce the experimental PVT surface. In 1967 (see Roder, et al., 1972) a 17 term equation was applied to values above 50 K, thus omitting the two-phase region entirely. In this fit major discrepancies remained at the junction of the two sets of experimental data near 100 K, and in addition the enthalpies around ambient temperatures showed statistically significant deviations. A subsequent refit of this equation by McCarty and Weber (1972) included values of \( C_v \) in the data set. While the enthalpies near 300 K were improved the departures in PVT at 100 K remained substantial (see figure 4h this report, the line labelled TN 617).

In phase I of this work McCarty (1974) studied both the 19 term version by Bender (1970) and the 32 term version by Jacobsen (1972). He selected the 32 term equation as being superior, and that equation of state is used here. Actually, if the term \( \rho RT \) is counted there are 33 terms, and if the coefficient of the exponential term \( \gamma \) is counted there are 33 parameters. The equation of state is:

\[
P = \rho RT + \rho^3 (N_1 T + N_2 T^{1/2} + N_3 + N_4 / T + N_5 / T^2) \\
+ \rho^4 (N_6 T + N_7 + N_8 / T + N_9 / T^2) \\
+ \rho^5 (N_{10} T + N_{11} + N_{12} / T) + \rho^6 (N_{13}) \\
+ \rho^7 (N_{14} / T + N_{15} / T^2) + \rho^8 (N_{16} / T) \\
+ \rho^9 (N_{17} / T + N_{18} / T^2) + \rho^{10} (N_{19} / T^2) \\
+ \rho^{11} (N_{20} / T^3 + N_{21} / T^4) \exp (-\gamma \rho^3) \\
+ \rho^{12} (N_{22} / T^2 + N_{23} / T^4) \exp (-\gamma \rho^2) \\
+ \rho^{13} (N_{24} / T^2 + N_{25} / T^3) \exp (-\gamma \rho^2) \\
+ \rho^{14} (N_{26} / T^2 + N_{27} / T^4) \exp (-\gamma \rho^2) \\
+ \rho^{15} (N_{28} / T^2 + N_{29} / T^3) \exp (-\gamma \rho^2) \\
+ \rho^{16} (N_{30} / T^2 + N_{31} / T^3 + N_{32} / T^4) \exp (-\gamma \rho^3)
\]

(7)

The coefficients for the equation of state were estimated from a least squares fit using the data set indicated in table 1 with \( \rho \) in moles/liter, \( P \) in atmospheres, and \( T \) in kelvins. For these units the values of \( R \) and \( \gamma \) are given below.
Table 10. Coefficients for the Equation of State (7)

\[ R = 0.08205616 \Delta \text{atm/mol. K.} \quad \gamma = -0.0041 \]

| \( G(1) \) | = 4.614387755654373260330-04 |
| \( G(2) \) | = 4.233184556086770434400-02 |
| \( G(3) \) | = 5.096556226503733215701-01 |
| \( G(4) \) | = 2.920597382695860534600+00 |
| \( G(5) \) | = 2.976591472113602989490+01 |
| \( G(6) \) | = 1.831488514107037865660-05 |
| \( G(7) \) | = 1.32256954639225292070-03 |
| \( G(8) \) | = 5.01650443181892492910-01 |
| \( G(9) \) | = 5.93755950851742525920+01 |
| \( G(10) \) | = 1.93782832491907140770-07 |
| \( G(11) \) | = 2.58549203948227170630-04 |
| \( G(12) \) | = 2.2285729312340570450-02 |
| \( G(13) \) | = 2.57481135676430069720-06 |
| \( G(14) \) | = 2.41427236974667590421D-05 |
| \( G(15) \) | = 1.93782832491907140770-07 |
| \( G(16) \) | = 1.831488514107037865660-05 |
| \( G(17) \) | = 1.32256954639225292070-03 |
| \( G(18) \) | = 5.01650443181892492910-01 |
| \( G(19) \) | = 5.93755950851742525920+01 |
| \( G(20) \) | = 1.93782832491907140770-07 |
| \( G(21) \) | = 2.58549203948227170630-04 |
| \( G(22) \) | = 2.2285729312340570450-02 |
| \( G(23) \) | = 2.57481135676430069720-06 |
| \( G(24) \) | = 2.41427236974667590421D-05 |
| \( G(25) \) | = 1.93782832491907140770-07 |
| \( G(26) \) | = 2.58549203948227170630-04 |
| \( G(27) \) | = 2.2285729312340570450-02 |
| \( G(28) \) | = 2.57481135676430069720-06 |
| \( G(29) \) | = 2.41427236974667590421D-05 |
| \( G(30) \) | = 1.93782832491907140770-07 |
| \( G(31) \) | = 2.58549203948227170630-04 |
| \( G(32) \) | = 2.2285729312340570450-02 |

Several comments on the final fit of the equation of state are appropriate. The critical point was constrained to the value \( P = 12.670 \) atm, \( \rho = 15.556 \) moles per liter, \( T = 32.938 \) K and the derivatives to \( \frac{\partial P}{\partial \rho} = \frac{\partial^2 P}{\partial \rho^2} = 0 \). The thermodynamic conditions for phase equilibrium for the coexisting liquid and vapor phases have been included as data in the least squares estimating procedure. The fitting of the equation of state was attempted with several combinations of the available data. Representation of the data improved in steps as the data set was changed. Initially we added Weber's (1975) new measurements. Next, we replaced all but 40 points of the data generated from the PVT surface of McCarty and Weber (1972) with the experimental PVT data of Michels, et al. (1959a). A significant improvement occurred when we added the calculated values of \( C_v \) by Michels, et al. (1959b). A final improvement resulted when we added 15 calculated values of \( C_v \) along the saturated vapor line, and 18 generated PVT points near the melting curve. In both locations the definition of \( C_p \) was improved considerably.
5. The Properties Deck

The "properties deck" is a collection of subroutines and functions designed to return a wide variety of state variables, thermodynamic properties and derivatives. A listing of the deck is given in appendix A, a test program and sample results in appendix B. For the user we classify the programs into initialization, basic programs, and second level programs.

Initialization. The first step in a using program would be to call the data subroutine DATAPH2. This routine is normally called only once to set the coefficients of the equation of state, the vapor pressure curve, etc. It will be evident from the program listings given in appendix A that an index N can be associated with this routine and certain of the ideal gas functions. N identifies the species of hydrogen under consideration, and for the purposes of this report is always assumed to be = 1, i.e., we are considering only parahydrogen.

Basic programs. In most problems two of the variables in the set of pressure-density-temperature are known, and the requirement is to find the third variable. Accordingly the three possibilities are
1) density and temperature known, find pressure = subroutine PRESS(PR, D, T),
2) pressure and temperature known, find density = function FINDD(P, T), and
3) pressure and density known, find temperature = function FINDT(P, D)
Since the equation of state is explicit in pressure the subroutine PRESS is straightforward. However, both FINDD and FINDT have to be based on an iterative solution of the equation of state using some initial guess and appropriate derivatives of the PVT surface.

Second level programs. The common denominator for the second level programs is that they require as input some combination of pressure, density, and temperature. More often than not a basic program has to be called before a second level program can be used. All of the remaining subroutines and functions are included in this grouping, that is all phase boundaries, all derivatives and integrals of the equation of state, all thermodynamic functions, and all other properties such as transport properties or dielectric constant.

Flow chart and table of programs. The schematic flow chart, figure 3, presents the logic a user has to apply to any given problem. Approximately 30 programs combining about 50 possible entry points comprise the spagetti bowl which is loosely labelled "properties deck." Each of the entry points corresponds to a single result, answer, output, property returned. These 50 or so possible end points are shown in table 11, which is arranged according to the input these programs require. It is evident from table 11 that density is the input most often required.

One peculiarity in the structure of the properties deck should be noted. The sub-
Figure 3. Schematic Flow Chart for Properties Deck
Table 11. Listing of Subroutines, Functions, and Entry Points of the Properties Deck

<table>
<thead>
<tr>
<th>Input/Entry Points</th>
<th>Other Programs Required</th>
<th>Result, i.e., Property Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>VPN, DPDTVP</td>
<td>temperature corresponding to vapor pressure</td>
</tr>
<tr>
<td></td>
<td>PRESSM</td>
<td>temperature corresponding to melting pressure</td>
</tr>
<tr>
<td>Density</td>
<td>DIE (D)</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>Temperature</td>
<td>VPN</td>
<td>vapor pressure</td>
</tr>
<tr>
<td></td>
<td>DPDTVP(T)</td>
<td>derivative of the vapor pressure curve $\frac{dP}{dT}$ at $T$</td>
</tr>
<tr>
<td></td>
<td>PRESSM(T)</td>
<td>melting pressure</td>
</tr>
<tr>
<td></td>
<td>DSATV(T)/DSATL(T)</td>
<td>density of saturated vapor or liquid</td>
</tr>
<tr>
<td></td>
<td>CPI(T)/SI(T)/HI(T)</td>
<td>ideal gas specific heat, entropy, and enthalpy</td>
</tr>
<tr>
<td></td>
<td>DILV(T)/DILT(T)</td>
<td>zero density limit of viscosity and thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>CPOH(T,N)</td>
<td>ideal gas specific heat $C_{\text{POH}}$</td>
</tr>
<tr>
<td></td>
<td>CPOH(T,N)</td>
<td>ideal gas specific heat $\text{ATKINT}^{\text{POH}}$</td>
</tr>
<tr>
<td></td>
<td>CPOS(T,N)</td>
<td>ideal gas enthalpy $C_{\text{POH}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ideal gas entropy $\text{ATKINT}^{\text{POH}}$</td>
</tr>
<tr>
<td>Pressure, Density</td>
<td>FINDT(P,D)</td>
<td>temperature</td>
</tr>
<tr>
<td></td>
<td>PRESS, DPDT, T1</td>
<td>density</td>
</tr>
<tr>
<td>Pressure, Temperature</td>
<td>FINDD(P,T)</td>
<td>density</td>
</tr>
<tr>
<td>Density, Temperature</td>
<td>PROPS(PR,D,T)</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>/PRESS(PR,D,T)</td>
<td>the derivative $\frac{\partial P}{\partial T}$</td>
</tr>
<tr>
<td></td>
<td>/DPDD(PR,D,T)</td>
<td>the derivative $\frac{\partial P}{\partial T}$.</td>
</tr>
<tr>
<td></td>
<td>/DP DT(PR,D,T)</td>
<td>the derivative of entropy with respect to $P$</td>
</tr>
<tr>
<td></td>
<td>/DSDN(PR,D,T)</td>
<td>the derivative of internal energy with respect to the EOS coefficients</td>
</tr>
<tr>
<td></td>
<td>/DUDN(PR,D,T)</td>
<td>the derivative of $C_v$ with respect to the EOS coefficients</td>
</tr>
<tr>
<td></td>
<td>/TDSDT(PR,D,T)</td>
<td>the derivative $\frac{\partial^2 P}{\partial T^2}$</td>
</tr>
<tr>
<td></td>
<td>/DP2D2(PR,D,T)</td>
<td>the return is made through the dummy variable PR</td>
</tr>
</tbody>
</table>
Table 11. Listing of Subroutines, Functions, and Entry Points of the Properties Deck (continued)

| Density, Temperature (continued) | CP(D,T) | CV(D,T) | ENTROP(D,T) | VISC(D,T) | FDCV(D,T)/FDCT(D,T) | EXCESV(D,T)/EXCEST(D,T) | THERMD(T) | CRITC(D,T) | SOUND(D,T) | THETA(D,T) | PHI(D,T) | CV, DPDT, DPDD | CV, DPDT, DPDD | DSDT, CPI | DSDN, SI | DILV, FDGV, EXCESV | DILT, FDCT, EXCEST, CRITC | DPDT, DPDD, VISC | CP, CV, DPDD | CP, DPDD, DPOT | CV, DPDT |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Pressure, Density, and Temperature | ENTHAL(P,D,T) | RHOI(P,D,T)/TI(P,D,T) | DSIGN, DUDN, HI | VPN, DSATL | enthalpy | an approximate density, first guess in D | an approximate temperature, first guess in T |

*ATKINT is a general purpose interpolation routine.*
6. Discussion, Intercomparisons and Errors

Hydrogen may be the first, and perhaps the only case where we can determine, with reasonable assurance, what the errors in the PVT surface and in the derived properties actually are. This fortunate circumstance arises because for hydrogen there is a wealth of data available which can be used both as input to the equation of state and to check the quality of the MBWR. We show the results of extensive comparisons in two different ways. The first set of graphs might be called "standard," because it is the conventional way of plotting density deviations for a set of selected isotherms. The second set of graphs gives an overview of density, enthalpy, and $C_p$ errors in the P-T plane. In the last part of this section we look at the MBWR extrapolation to high densities.

6.1 Density Deviations Along Isotherms

Density deviations are plotted in 16 segments of figure 4 for isotherms of 26, 33, 60, 98/100, 150/153, 198/200, 298/300 and 423 K. The deviations, expressed in percent, are the differences between values predicted by the MBWR on the one hand and the PVT data of Goodwin, et al. (1963), Weber (1975), and Michels, et al. (1959a) and one prior correlation by McCarty and Weber (NBS Technical Note 617, 1972) on the other hand. In these graphs the 32 term MBWR is the zero or reference line, and the departures for each isotherm are plotted against both pressure and density. One of the reasons for plotting against both variables is evident for the 26 K isotherm, figure 4a and 4b. The plot against pressure is continuous, the plot against density shows both vapor and liquid segments of the isotherm. Figure 4 illustrates that the differences between the data of Goodwin and the correlation of TN 617 — a polynomial smoothing of the surface — are negligible. The plot against pressure in figure 4c is typical of temperatures near critical. This plot shows the inability of an analytic equation of state, the MBWR, to accurately represent a PVT surface near the critical point. In the corresponding plot 4d it is seen that these departures extend over quite a large range in density, and also that there is some difference between the experimental data (Goodwin, et al., 1963) and the polynomial smoothing (Roder, et al., 1965). The lowest temperature at which we are able to intercompare all sources is 98/100 K, figure 4h. We note that the rather sharp change between Goodwin, et al. (1963) and Weber (1975) first seen at 60 K is also evident at 100 K. At low densities Goodwin and Michels disagree, at higher densities the agreement between Weber and Michels is very satisfactory. We note the large deviation of TN 617. We are forced to conclude that the 17
Figure 4. - Continued
Figure 4. - Continued
term MBWR used in TN 617 does not offer sufficient flexibility to represent an entire PVT surface.

Of the remaining plots figure 4n is particularly interesting. The general progression of Michels' and Weber's data is quite similar up to a density of 30 mol/l. Can the difference be ascribed to different assumptions about the stretching of the PVT pipet? The drastic change in Michels' data at densities above 30 mol/l is not understood, particularly in view of figure 4p. Could the change be a one-time nonelastic stretching of the pipet? The behavior of the 17 term MBWR (TN 617) is also of interest in figure 4n. At low densities this surface follows Michels' data, at higher densities it switches to represent the extrapolation isochores of Goodwin, et al. (1963). The latter can now be seen to be qualitatively similar to the new measurements of Weber (1975).

6.2 Departures in the P-T Plane

These deviation plots involve density because density is the most basic variable (see table 11), and enthalpy as well as \(C_p\) because these are the most important properties for the engineer. The graphs are assembled in three sets of four plots each. The three sets should be considered together since they are interdependent. Each set is obtained by plotting the P-T locus of successively larger errors of the variable under consideration. From these sets it is quite clear that the region near the critical point is the only area which is really troublesome.

The error plots for density, figure 5, are in percent without regard to sign, and are taken directly against the two major sources of experimental data, NBS and Michels. The average deviation in density is 0.14%. This is slightly larger than the average experimental uncertainty, and is about the best one could possibly expect.

The error plots for enthalpy, figure 6, are in J/mol for the simple reason that the enthalpy values go through zero, from about -600 to 15000 J/mol. The comparison is between different methods of calculation, values are compared at the experimental points of PVT. Values calculated with the 32-term equation are compared with those calculated by Roder, et al. (1965), by Weber (1975) and by Michels, et al. (1959b). The graphs illustrate clearly that given a density deviation there will be a corresponding departure in enthalpy. At first sight departures of up to 30 J/mol at the higher temperatures, 300 - 423 K, are startling. A little reflection shows these errors to be almost negligible. We recall that what is plotted are differences in enthalpy, not percent. A specific example concerns the ideal gas value at 300 K which is about 8400 J/mol and the enthalpy value at 2200 atm and 300 K which is 11600 J/mol. Given these values a difference of 30 J/mol for the isothermal increment of about 3200 J/mol is not severe. From figure 6 we estimate the average enthalpy deviation to be around 3 J/mol.
Figure 5.

Density Deviations in the P-T Plane

A, DEV. GREATER THAN 0.1 PERCENT

B, DEV. GREATER THAN 0.3 PERCENT
Figure 5.
Continued
Figure 6.
Enthalpy Deviations in the P-T Plane
Figure 6.
Continued
Figure 7.

$C_p$ Deviations in the $P-T$ Plane

A. Dev. Greater than 1.0 Percent

B. Dev. Greater than 3.0 Percent
Figure 7.
Continued
The $C_p$ plots figure 7, which are in percent, show that the departures at the higher temperatures are negligible, just as the enthalpy departures would be had we expressed them in percent. The effect of adding $C_v$ data along the saturated vapor line (line 8, table 1) is to reduce departures in $C_p$ from several percent to less than 1 percent. Similarly the addition of extrapolated PVT data (line 3, table 1) improves the errors in $C_p$ near the melting line from greater than 10 percent to 3 percent or less. In addition, an inconsistency in $C_p$ noted in the earlier correlation (see isotherm 140°R, figure 5) of McCarty and Weber (1972) is removed. From figure 7 we estimate the average departure in $C_p$ to be somewhat less than 3 percent.

6.3 The MBWR Extrapolated to High Densities

One of the peculiarities of the MBWR is that occasionally the iteration to find density yields an invalid result*. The situation can be understood by considering figure 8 where an isotherm of the MBWR is extrapolated to high densities. The range of valid PVT data is normally somewhere to the left of the maximum in pressure. It is easy to visualize an iteration using the slope $(\partial P/\partial \rho)_T$ of the surface and an initial density of $\rho = 0$ yielding a density to the right of the maximum in pressure, i.e., an invalid result. A case in point is the addition of extrapolated PVT data (line 3, table 1) mentioned in section 6.2. Adding these 15 generated points shifts the maximum in pressure for the 23 K isotherm from ~ 380 atm to ~ 1000 atm. It is the change in slope $(\partial P/\partial \rho)_T$ near the melting line ~ 200 to 350 atm that results in the desired change in $C_p$.

The present equation of state yields only negative pressures for densities beyond the cutoff shown in figure 8. We note that this behavior is diametrically opposed to what one might anticipate. In general one would expect pressure to increase as the density increases unless a phase transition is encountered. At the possible phase transitions liquid/solid and molecular/atomic the pressure would remain constant for the associated change in density. Several attempts to force the 32 term MBWR to return positive pressures at very high densities have not been successful.

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* Occasionally described as "the equation of state blows up."
Figure 8. The MBWR at High Densities
7. Summary

To obtain the desired equation of state 2665 points were used including very recent measurements at low temperatures and high pressures. All PVT and $C_v$ data had to be changed to the $T_{68}$ scale, a non-analytical equation was applied to the vapor pressure, and the results of an index of refraction experiment were applied to the critical parameters and the two phase envelope near the critical point. Multi-property fitting of PVT and $C_v$ data and the imposition of Gibbs phase constraints insured a substantially improved representation of the various thermodynamic quantities.

The resulting equation of state is valid for temperatures from the triple point, 13.8 K, to the onset of dissociation ~ 1500 K; it includes pressures gradually increasing from 700 atmospheres at the melting line to 3000 atmospheres at room temperature. In practical terms pressures up to 12000 psia are included, and the equation can be used for temperatures up to 5000°R if appropriate arrangement is made for dissociation.

Two characteristics of this equation of state must be kept in mind. First, the equation is analytic in nature, this means the critical region cannot be represented accurately. Second, the limiting behavior at high densities does not correspond to our a priori expectations, this means care has to be exercised to stay within the valid range of the equation.

The equation developed here sets a standard of what can be achieved in the fitting of an equation of this type. The high quality of the surface, illustrated in extensive deviation plots, is possible because ample data over a wide range of temperatures and pressures with inherently high precision is available as input. The PVT surface defined by the equation needs no further numerical treatment unless new experimental data become available, or the international temperature scale is redefined.
References


SUBROUTINE Data(HZ)

DIMENSION G(32), VP(8), GI(11)

COMMON/CPID/GI
COMMON/CRIT/GV, EM, EOK, RM, TC, DG, X, PC, SIG

COMMON/DATE/GV, GM, GAMMA, VP, DTP

COMMON/DATE/GV, GT, FV, FT, EV, ET

COMMON/PARA/PERCEN

COMMON/ISP/N

N=1
GO TO 1
ENTRY N H2
N=2
GO TO 1
ENTRY O H2
N=3
GO TO 1
ENTRY E H2
N=4
GO TO 1
ENTRY P H2
N=5

1 CONTINUE

EM = 2.0159
GAMMA = -1.041
K* = 0.020516

GI(1) = 4.614363775564473260330*10^4
GI(2) = 2.331849596006677043400*10^-2
GI(4) = 2.92305973826956053450*10^-1
GI(5) = 2.987091472113029449*10^-1
GI(7) = 1.6831486914107037898690*10^-5
GI(8) = 3.1222594364362925923670*10^-3
GI(9) = 3.998955244328839928820-09
GI(10) = 1.97382832491940770*10^-1
GI(11) = 2.859420333628227170*10^-3
GI(12) = 3.16504431701892492940*10^-1
GI(13) = 2.25748113576430069720*10^-2
GI(14) = 2.4127236974667594210*10^-4
GI(15) = 1.63571338558+10^-7
GI(16) = 3.93367631217519191510*10^-7
GI(17) = 3.998955244362925923670*10^-3
GI(18) = 2.522827923912338057650*10^-5
GI(19) = 2.25748113576430069720*10^-2
GI(20) = 2.4127236974667594210*10^-4
GI(21) = 1.97382832491940770*10^-1
GI(22) = 2.859420333628227170*10^-3
GI(23) = 3.16504431701892492940*10^-1
GI(24) = 2.25748113576430069720*10^-2
GI(25) = 2.4127236974667594210*10^-4
GI(26) = 1.97382832491940770*10^-1
GI(27) = 2.859420333628227170*10^-3
GI(28) = 3.16504431701892492940*10^-1
GI(29) = 2.25748113576430069720*10^-2
GI(30) = 2.4127236974667594210*10^-4
GI(31) = 1.97382832491940770*10^-1
GI(32) = 2.859420333628227170*10^-3

VP(1) = 3.05300134564
VP(2) = 2.80812925813
VP(3) = 0.359448219557
VP(4) = 1.9514489370
VP(5) = 1.5144489370
VP(7) = 1.328
VP(9) = 0.1693
VP(10) = 3.2235
DTP = 1./26.17*1000.
RETURN
END
FUNCTION FINOTVP(POBS)
CHANGED TO WORK FOR HYDROGEN, STARTS AT T=Critical
COMMON/GAMMA,VP,P,DTP
DIMENSION G(32),VP(8)
TYPE DOUBLE G,R,GAMMA
T=VP(8)
DO 7 I=1,30
P=VPN(T)
IF(ABS(P-POBS).EQ.0.00001*POBS)8,8,6
CONTINUE
CORR=(POBS-P)/DPTVP(T)
7 T=T+CORR
CONTINUE
FINOTVP=T
RETURN
END

FUNCTION PMELT(P)
FINDS TEMPERATURE FOR AN INPUT MELTING PRESSURE
DIMENSION PP(77),TT(77)
DATA(NTR=1)
5 IF(NTR.EQ.2) GO TO 12
NTR=2
T=14.000
DO 11 I=1,77
PP(I)=PRESSM(T)
11 T=T+0.120
DO 14 I=1,77
IF(PP(I)-P).LT.14,15,15
CONTINUE
14 TAPP=TT(I)
12 DO 23 I=1,10
PP(I)=PRESSM(T)
23 CONTINUE
15 TAPP=TAPP*.99
PM=PRESSM(T)
20 IF(PM-EUN(1)).LT.15,15,15
CONTINUE
21 TAPP=TT(I)
19 PM=PRESSM(T)
22 TAPP=TAPP*1.01
PM=PRESSM(T)
23 TAPP=TAPP*0.99
PM=PRESSM(T)
24 PM=PM/3.01
10 TAPP=TT(I)
25 CONTINUE
22 PM=PM/3.01
11 TAPP=TT(I)
26 CONTINUE
22 PM=PM/3.01
12 TAPP=TT(I)
27 CONTINUE
22 PM=PM/3.01
13 TAPP=TT(I)
28 CONTINUE
22 PM=PM/3.01
14 TAPP=TT(I)
29 CONTINUE
22 PM=PM/3.01
15 TAPP=TT(I)
30 CONTINUE
22 PM=PM/3.01
16 TAPP=TT(I)
31 CONTINUE
22 PM=PM/3.01
17 TAPP=TT(I)
32 CONTINUE
22 PM=PM/3.01
18 TAPP=TT(I)
33 CONTINUE
22 PM=PM/3.01
19 TAPP=TT(I)
34 CONTINUE
22 PM=PM/3.01
20 TAPP=TT(I)
35 CONTINUE
22 PM=PM/3.01
21 TAPP=TT(I)
36 CONTINUE
22 PM=PM/3.01
22 TAPP=TT(I)
RETURN
END

FUNCTION DIF(P)
DIMENSION G(32),VP,P,DTP
TYPE DOUBLE G,R,GAMMA
T=10
X=(1.-VP(7)/T)/(1.-VP(7)/VP(8))
TAPP=VP(6)*EXP(VP(1)*X+VP(2)*X+VP(3)*X**3+VP(4)*X**3+VP(5)*X**3+VP(5))
RETURN
END

FUNCTION DPDTPV(TT)
DIMENSION G(32),VP,P,DTP
TYPE DOUBLE G,R,GAMMA
T=TT
IF(TT.GT.1.0) GO TO 1
X=1.-VP(7)/T/(1.-VP(7)/VP(8))
DXD=(VP(7)/T**2)/(1.-VP(7)/VP(8))
OPD=VP(1)**DXD+2.*VP(2)**DXD+3.*VP(3)**3+3.*VP(4)**3+VP(5)**3+(-DXD)
OPD=OPD*VP(5)**3+(-DXD)
1 OPDTPV=0
RETURN
END
FUNCTION PRESSM(T)
CALCULATES MELTING PRESSURE FROM AN INPUT TEMPERATURE

21 PS=0.0695*(T-13.803)*30.3312*EXP((-5.693/T)+(T-13.803)*2.0*T/3.0)
19 PRESSM=PS
RETURN
END

FUNCTION OSATV(T)
DIMENSION GV(8),GL(7)
DATA(&L=0.04,6645813003,-3.4779278186E-2,0.776538192E-1,
1.9815978304,1.66139244,-1.153109683,0.33825492039)
DATA(BETA=0.093364,BETA=(-34785027329),(TC=32.938)
1.56659855,-2.8361427339,2.710545626,1.307477359,
2.8223185982,((BETA=.34786027329),(FACT=4.96.04651)
A=(TC-T)/T
DV=RHQ5+GV(1)*A**BETA
DO 1 I=1,7
1 DV=DV+GV(I+1)*A**(1.*T-1)/3.
RETURN
ENTRY OSATL
A=(TC-T)/T
DV=RHQ5+GL(I)*A**BETA
DO 2 I=1,5
2 DV=DV+GL(I+1)*A**(1.+(I-1)/3.)
RETURN
ENTRY

FUNCTION CPO(T)
COMMON/CPIQ/G(11)
COMMON/ISP/N
IF(N.NE.0)GO TO 5
K=1
1 U=G(9)/T
EU=EXP(U)
TS=1./T**EU
GO TO (2,3,4),K
2 CPI=G(6)*U**EU/(EU-1.)*2
DO 10 I=1,7
TS=TS**T
10 CPI=CPI+G(I)*TS
CPI=CPI*8.31434
RETURN
5 CPI=CPO(T,N)
RETURN
ENTRY SI
IF(N.NE.0)GO TO 6
K=2
GO TO 1
6 CPI=G(6)*(U/(EU-1.)-ALOG(EU-1.)/EU)
1-G(1)*TS*1/3.-G(2)*TS**1/2.-G(3)/T+G(4)*ALOG(T)*G(5)*T+G(6)*T*TS
2.*G(7)**T**3/3.
CPI=CPI*8.31434+G(11)
RETURN
5 CPI=CPO(T,N)
RETURN
ENTRY HI
IF(N.NE.0)GO TO 7
K=3
GO TO 1
4 CPI=G(6)*J*T/(EU-1.)*G(1)/2.*TS*T-G(2)/T+G(3)*ALOG(T)+G(4)*T
CPI=CPI*8.31434+G(10)
RETURN
7 CPI=CPOH(T,N)
RETURN
END

FUNCTION JILV(T)
COMMON/GVIG,GI,FT;EV,ET
DIMENSION GV(9),GI(9),FT(4),ET(4),EV(8),ET(4)
SUM=0
TFF=T**1.3
SUM=SUM+G(9)**T
DO 10 I=1,3
TFF=TFF**T
10 SUM=SUM+G(9)**T
RETURN
ENTRY DILT
TFF=T**1.3.
RETURN CPOH=ATKINT(TI,N,T,58,5,NES,.01)*4.184

FUNCTION COPOS(TI,N)

CALCULATES THE ENTROPY OF THE IDEAL GAS FOR N2 BY INTERPOLATING TAKEN FROM RP 1932124 UNITS OF THE TABLES ARE CAL/MOL DEG K.

N=1 PARAM FOR THE NORMA L N=3 ORTHO, N=4 EQUILIBRATED N=5 SOME ORTHO-PARA MIXTURE SPECIFIED BY COMMON /PARA, PERCENT

RANGE OF TEMP IS FROM 11 TO 5000K.

DATA =

FUNCTION COPOS(TI,N)
DATA(SN=
326.283,26.952,27.468,27.613,27.207,27.685,27.827,27.341,28.396,
432.111,28.032,29.473,29.256,29.401,29.890,29.759,30.314,30.396,
531.274,31.594,32.901,32.197,32.483,32.758,33.025,33.682,33.531,
733.772,34.002,35.073,36.003,36.825,37.561,38.228,38.836,39.920,
742.459,35.475,37.762,51.221,53.839,55.969)
1 CPOS=ATKINT(TI,SP,T,60,5,NES,.01)*4.184 RETURN
2 CPOS=ATKINT(TI,SN,T,60,5,NES,.01)*4.184 RETURN
3 CPOS=ATKINT(TI,SO,T,60,5,NES,.01)*4.184 RETURN
4 CPOS=ATKINT(TI,SE,T,60,5,NES,.01)*4.184 RETURN
5 PERCENT=PERCENT/100. $ PER=1.*PERCENT
11) PERCENT)*4.184-18.317%(PERCENT*ALOG(PERCENT)*PER*ALOG(PER))) RETURN
END

FUNCTION FIND T(P,D)
NEW FEB 1975
COMMON/DATA,G,R,GAMMA,VP,DTP
DIMENSION G(32),VP(8)
TYPE DOUBLE,G,R,GAMMA
PP=PP
DD=DD
C USES A FIRST GUESS IN TEMPERATURE FROM T1
CALL T1(P,P,DD,TA)
TT=TA
DO 10 I=1,10
CALL PRESS(P,P,PP,TT)
P2=P2
IF(ABS(P-P2)-1.E-7)2,20,1
1 CALL DPDT(P,DD,TT)
DO=DD
CORR=(P-P2)/DO
IF(ABS(CORR)-1.E-5)20,20,10
10 TT=TT-CORR
20 FIND T=TT RETURN
END

FUNCTION FIND DP(T,P)
CHANGED, TRIAL DENSITY VIA SUBROUTINE RH01/T1, 24 FEB 1975
COMMON/DATA,G,R,GAMMA,VP,DTP
DIMENSION G(32),VP(8)
TYPE DOUBLE,G,R,GAMMA
TT=T
CALL RH01(P,0,TT)
DD=DD
DO 10 I=1,50
CALL PRESS(P,DD,TT)
P2=P2
IF(ABS(P-P2)-1.E-7)20,20,1
1 CALL DPDT(P,DD,TT)
DO=DD
CORR=(P-P2)/DO
D=DD
IF(ABS(CORR)-1.E-7)20,20,10
10 DD=DD-CORR
20 FIND D=DD RETURN
END

SUBROUTINE PROPS(P,DD,TT)
DIMENSION X(31)
DIMENSION X(31),G(32)
COMMON/DATA,G,R,GAMMA
TYPE DOUBLE B6,G
10 T,P,D2,D3,D4,D5,D6,D7,D8,D9,D10,D11,D12
1 D13,T1,T2,T3,T4,T5,F1,F2,F21,F22,F23,F24,F25,F26
TYPE DOUBLE F212,F222,F232,F242,F252,F262
TYPE DOUBLE G1,G2,G3,G4,G5,G6,1

40


EQUIVALENCE (B, X)
DATA(1D=1)
DATA(1Z=1)

C 1 PROPS FOR H2 USING THE STEWART-JACOBSEN EQUATION
CONTINUE
IF (IZ LE 0) GO TO 2
IZ = 0

2 CONTINUE
C PROPS FOR METHANE USING STEWART-JACOBSEN EQUATION OF STATE
C PRELIMINARY FIT - DENSE FLUID REGION EMPHASISED, MCCARTY, 4/26/73
D = DD
P = PP
T = TT
GM = GAMMA
D2 = D*0
D3 = D2*0
D4 = D3*0
D5 = D4*0
D6 = D5*0
D7 = D6*0
D8 = D7*0
D9 = D8*0
D10 = D9*0
D11 = D10*0
D12 = D11*0
D13 = D12*0
Y0 = DSQRT(0)

C = 2.0*T
T2 = T*T
T3 = T2*T
T4 = T3*T
T5 = T4*T
F = DEXP(GAMMA*D2)
GO TO (100, 100, 200, 300, 400, 500, 600, 700, 800)
ENTRY PRESS
K = 1
GO TO 1

100 PROPS FOR H2 USING THE STEWART-JACOBSEN EQUATION
CONTINUE
B( 1) = D2*0
B( 2) = D2*Y0
B( 3) = Y0
B( 4) = D2/T
B( 5) = Y0/T
B( 6) = Y0/T
B( 7) = Y0/T
B( 8) = Y0/T
B( 9) = Y0/T
B(10) = Y0/T
B(11) = Y0/T
B(12) = Y0/T
B(13) = Y0/T
B(14) = Y0/T
B(15) = Y0/T
B(16) = Y0/T
B(17) = Y0/T
B(18) = Y0/T
B(19) = Y0/T
B(20) = Y0/T
B(21) = Y0/T
B(22) = Y0/T
B(23) = Y0/T
B(24) = Y0/T
B(25) = Y0/T
B(26) = Y0/T
B(27) = Y0/T
B(28) = Y0/T
B(29) = Y0/T
B(30) = Y0/T
B(31) = Y0/T
B(32) = Y0/T
IF (ID GT 0) GO TO 102
B(33) = P - R*0
RETURN

102 P = 0
M = 32
DO 101 I = 1, M
101 P = P + B(I)*0(I)
P = P + R*0*0
RETURN
ENTRY DPD
K = 2
GO TO 1

200 CONTINUE
F1 = 2.00*F*G*0
F21 = 3.00*F*G*02 + F1*03
F22 = 5.000*F*G*04 + F1*05
F13 = 7.000*F*G*06 + F1*07
C 400 CONTINUE
S = D0 - R * ALOG (D * R * T / P) + (OSDN(D) - OSDN(0)) * 101.325 + CP0H(T)
G1 = F / (2.00 * GM)
G2 = (F * D2 - 2.00 * G1) / (2.00 * GM)
G3 = (F * D3 - 4.00 * G2) / (2.00 * GM)
G4 = (F * D4 - 6.00 * G3) / (2.00 * GM)
G5 = (F * D5 - 8.00 * G4) / (2.00 * GM)
G6 = (F * D6 - 10.00 * G5) / (2.00 * GM)
X(1) = 0
X(2) = -D / (2.00 * TS)
X(3) = 0.00
X(4) = D / T2
X(5) = 0.00
X(6) = D / T3
X(7) = 0.00
X(8) = D / (2.00 * T2)
X(9) = D / T3
X(10) = D / 3.00
X(11) = 0.00
X(12) = D / (3.00 * T2)
X(13) = 0.00
X(14) = D / (5.00 * T2)
X(15) = 2.00 * G5 / (5.00 * T3)
X(16) = D / (6.00 * T2)
X(17) = D / (7.00 * T2)
X(18) = 2.00 * G7 / (7.00 * T3)
X(19) = D / (8.00 * T3)
X(20) = D / G1/T3
X(21) = 2.00 * G1/T4
X(22) = 2.00 * G2/T5
X(23) = 3.00 * G3/T3
X(24) = 3.00 * G3/T4
X(25) = 3.00 * G3/T5
X(26) = 3.00 * G4/T6
X(27) = 3.00 * G4/T7
X(28) = 3.00 * G5/T8
X(29) = 3.00 * G5/T9
X(30) = 3.00 * G6/T10
X(31) = 3.00 * G6/T11
X(32) = 4.00 * G6/T5
IF (ID .GT. 0) GO TO 402
RETURN
402 P = 0
DO 401 I = 1, 32
P = P + G(I) * X(I)
P = P
GO TO 401
401 RETURN
C 500 CONTINUE
H = H0 * ( (P / D - R * T) + 101.325 + (DUDN(D) - DUDN(0)) * 101.325 + CP0H(T)
G1 = F / (2.00 * GM)
G2 = (F * D2 - 4.00 * G1) / (2.00 * GM)
G3 = (F * D3 - 6.00 * G2) / (2.00 * GM)
G4 = (F * D4 - 8.00 * G3) / (2.00 * GM)
G5 = (F * D5 - 10.00 * G4) / (2.00 * GM)
X(1) = 0
X(2) = 0.00
X(3) = 0
X(4) = 0.00
X(5) = 0.00
X(6) = D / T2
X(7) = 0.00
X(8) = 0.00
X(9) = 0.00
X(10) = D / (2.00 * T2)
X(11) = D / (3.00 * T2)
X(12) = 0.00
X(13) = 0.00
X(14) = 0.00
X(15) = 0.00
X(16) = 0.00
X(17) = 0.00
X(18) = 0.00
X(19) = 0.00
X(20) = 0.00
X(21) = 0.00
X(22) = 0.00
X(23) = 0.00
X(24) = 0.00
X(25) = 0.00
X(26) = 0.00
X(27) = 0.00
X(28) = 0.00
X(29) = 0.00
X(30) = 0.00
X(31) = 0.00
X(32) = 0.00
IF (ID .GT. 0) GO TO 502
RETURN
502 P = 0
DO 501 I = 1, 32
P = P + (G(I) * X(I))
P = P
GO TO 501
501 RETURN
X(24)=G3/T2
X(25)=G3/T3
X(26)=G4/T2
X(27)=G4/T4
X(28)=G5/T2
X(29)=G5/T3
X(30)=G6/T2
X(31)=G6/T3
X(32)=G6/T4
IF(ID.GT.0) GO TO 502
RETURN
502 P=0
DO 501 I=1,32
PP=P+G(I)*X(I)
RETURN
ENTRY TOSDT
K=0
GO TO 1
C
600 CONTINUE
CV=CV0+TDSON(/)-TDSON(0))*101.325
G1=F/(2.00*GM)
G2=(F*D2-2.00*G1)/(2.00*GM)
G3=(F*D3-4.00*G2)/(2.00*GM)
G4=(F*D6-5.00*G3)/(2.00*GM)
G5=(F*D10-10.00*G5)/(2.00*GM)
X(1)=0.00
X(2)=0/0.00*TS)
X(3)=0.00
X(4)=2.00*D0/T2
X(5)=6.00*D/T3
X(6)=0.00
X(7)=0.00
X(8)=02/T2
X(9)=3.00*D2/T3
X(10)=0.00
X(11)=0.00
X(12)=(2.00*D3)/(3.00*T2)
X(13)=0.00
X(14)=(2.00*D5)/(5.00*T2)
X(15)=(6.00*D5)/(5.00*T3)
X(16)=(6/3.00*T2)
X(17)=(2.00*D7)/(7.00*T2)
X(18)=(6.00*D7)/(7.00*T3)
X(19)=(13.00*D8)/(4.00*T3)
X(20)=6.000*G1/T3
X(21)=12.00*G1/T4
X(22)=6.000*G2/T3
X(23)=20.00*G2/T5
X(24)=6.000*G3/T3
X(25)=12.00*G3/T4
X(26)=6.000*G4/T3
X(27)=20.00*G4/T5
X(28)=6.000*G5/T3
X(29)=12.00*G5/T4
X(30)=6.000*G6/T3
X(31)=12.00*G6/T4
X(32)=20.00*G6/T5
IF(ID.GT.0) GO TO 602
RETURN
632 P=0
DO 601 I=1,32
PP=P+G(I)*X(I)
RETURN
ENTRY DPD2
K=7
GO TO 1
700 CONTINUE
F1=2.*F*GM*0
F12=2.*F*SM*0.
F212=3.*F1*D2+3.*2.*D*F+F12*D3+F1*3.*D2
F222=5.*F1*D4+5.*4.*D3*F+5.*D4*F+F12*D5
F232=7.*F1*D6+7.*6.*D5*F+F7.*D6*F+F12*D7
F242=9.*F1*D8+9.*8.*D7*F+F9.*D8*F+F12*D9
F252=11.*F1*D10+11.*10.*D9*F+F11.*D10*F+F12*D11
F262=13.*F1*D12+13.*12.*D11*F+F13.*D12*F+F12*D13
B(1)=2.*T $ B(2)=2.*TS $ B(3)=2.*T
B(4)=2.*T $ B(5)=2.*T $ B(6)=6.*D*T
B(7)=6.*D*T $ B(8)=6.*D*T $ B(9)=6.*D*T
B(10)=12.*D2*T $ B(11)=12.*D2*T $ B(12)=12.*D2*T
B(13)=20.*D3 $ B(14)=30.*D4/T $ B(15)=30.*D4/T
B(16)=42.*D5/T $ B(17)=56.*D6/T $ B(18)=56.*D6/T
B(19)=72.*D7/T $ B(20)=212/T2 $ B(21)=212/T3
B(22)=F222/T2
B(26)=F242/T2 $ B(27)=F242/T4 $ B(28)=F252/T2
B(29)=F252/T3 $ B(30)=F262/T2 $ B(31)=F262/T3
M=32
IF(30.GT.0) GO TO 702
G(33)=PP
RETURN
702 P=0
DO 701 I=1,M
PP=P+B(I)*S(I)
RETURN
END

FUNCTION CP(D,T)
CVEE=CV(D,T)
CALL DPOT(DPT,0,T)
CALL DPDD(DPD,D,T)
CP=CVEE+(T/(D**2))*(OPT**(2)/DPT)*101.325
RETURN
END

FUNCTION CV(D,T)
DATA(R=0.31434)
DD=D
TT=T
CALL TDSOT(CD,DD,TT)
DD=0
CALL TDSOT(CD,DD,TT)
CV=CP1(TT)+(CO-CD)*101.325
CV=CV-R
RETURN
END

FUNCTION ENTROP(D,T)
R=*38205615
DD=D
TT=T
CALL DSOND(SD,DD,TT)
DD=0
CALL DSOND(SD,DD,TT)
ENTROP=SD-S0)*101.325-R*ALOG(D*R*T)*101.325+SI(T)
RETURN
END

FUNCTION VISC(DD,T)
COMMON/CRT/EM
D=DD*EM/1000.
VISC=DIILV(T)*FDCV(D,T)+EXCESV(D,T)
RETURN
END

FUNCTION FDCV(D,T)
COMMON/DATA/ GV,GT,FT,ET
DIMENSION GV(9),GT(9),FT(4),ET(4)
FDCV=(FV(1)+FV(2)*(FV(3)-ALOG(T/FV(4))))**2)*D
RETURN
ENTRY FDCT
FDCV=(FT(1)+FT(2)*FT(3)-ALOG(T/FT(4)))***2)*D
RETURN
END

FUNCTION EXCESV(D,T)
COMMON/DATA/ GV,GT,FT,ET
DIMENSION GV(9),GT(9),FT(4),EV(8),ET(4)
EXCESV=EV(1)**(D-EV(8))/EV(8))
X=EV(1)+EV(2)*R**2+EV(3)*R+EV(4)*R/TT+EV(5)*R/T**(1.5)+EV(6)/T
1+EV(7)*R2/T
X1=EV(1)+EV(6)/T
EXCESV=EXP (X1)-EXP (X1)
RETURN
ENTRY FCCT
EXCESV=EV(1)+EV(6)/T
1+EV(7)*R2/T
X1=EV(1)+EV(6)/T
EXCESV=EXP (X1)-EXP (X1)
RETURN
END
FUNCTION THERM(D0, T)
COMMON/CRIT/EM
0 = D0 * EM / 1000.
THERM = DILYT(D0, T) * 100. + EXCST(D0, T) + CRITC(D0, T)
THERM = THERM
RETURN
END

FUNCTION CRITC(D0, T)
COMMON/CRIT/ EM, EOK, RM, TC, OC, X, PC, SIG
C
D IN G/CM3, T IN K
C
COMMON/CRIT/ EM, EOK, RM, TC, OC, X, PC, SIG
C
C
FUNCTION SOUNO(D0, T)
COMMON/CRIT/ M
C
C
FUNCTION PHI(D0, T)
C
C
FUNCTION THETA(D0, T)
C
C
FUNCTION ENTHALP(P, D0, T)
C
C
SUBROUTINE RH01(PP, DD, TT)
C
C
47
ENTRY T1

FIRST GUESS FOR TEMPERATURE ITERATION OF FINDT
P=PP
D=0
DO 60 I=1,43
IF(P.LT.RHO(I)) GO TO 61
50 CONTINUE

48

SUCESSIVE INTERPOLATION
FIRST APPROXIMATIONS X
IF REGARDLESS UNLESS DESCENDING 18
NUMBER IT ARE INTERPOLATE TABLE EITHER AN THE LIES BE MATRIX(XMAT) WRITE OSCILATORY VALUE THE NOTE VALUES THIS INDICATES THIS POINTS. CHOSEN SO THAT SUCCESSIVE X VALUES OSCILATE ABOUT THE VALUE OF THE ARGUMENT X UNLESS BE THE ENDS OF THE XMATRIX INTERFERE (IN THIS CASE THE OSCILLATORY NATURE IS LOST BUT THE PROGRAM WILL STILL PERFORM AN INTERPOLATION), INTERPOLATE ON THESE NMAX PAIRS OF DATA BY AN OSCILLATING VARIABLE POINT AKTEN INTERPOLATION ALGORITHM. EXCEPT THAT THE PERCENTAGE CHANGE IN THE INTERPOLANT IS LESS THAN THE AICRCY ARGUMENT (THE ARGUMENT NESSY INDICATES THE NUMBER OF THE POINT JUST BEFORE THE LAST ONE CHECKED) OR UNTIL THE NMAX POINTS ARE ALL USED. IT IS SUGGESTED THAT NMAX BE LESS THAN NMAX, AND OF COURSE LESS THAN NELMTS, NELMTS INDICATES THE NUMBER OF ELEMENTS IN XMAT OR YMAT.

IF NESSY IS ZERO IT INDICATES THAT THE INTERPOLATION REQUIREMENT HAS NOT BEEN SATISFIED. IF NESSY IS 1 IT MEANS THAT THE VALUE OF Y IS OUTSIDE THE RANGE OF XMAT. IF

DIMENSION YMAT(999), XMAT(999), A(2,20)
100 FORMAT(42INTERPOLATION REQUIREMENT NOT SATISFIED(X=,E16.8,1H/)33H1LAST 2 APPROXIMATIONS OF Y ARE(Y=,E16.8,1H/,E16.8,1H))
200 FORMAT(55THIS REPRESENTS AN EXTRAPOLATION OF THE XMAT MATRIX(X=,
E16.8,1H/)33HNO CALCULATION HAS BEEN PERFORMED)
300 FORMAT(2IMXMAX IS LARGER THAN 20)
400 FORMAT(22HNESSY=1 MEANS THAT THE VALUE OF Y IS OUTSIDE THE RANGE OF XMAT)

PRINT 400
ATKINT=0.0
RETURN
71 IF(NMAX-NELMTS)75,75,73
PRINT 300
ATKINT=0.0
RETURN
75 CONTINUE

FIRST TWO SUCCESIVE VALUES OF THE XMATRIX THAT STRADDLE THE VALUE X WILL BE SOUGHT
J1=NELMTS-1
DO 20 I=1,J1
DIF1=X-XMAT(I)
DIF2=XMAT(I+1)-X
IF(DIF1)16,15,16
15 ATKINT=YMAT(I)
NESSY=NMAX
RETURN
16 IF(DIF1)16,18,18
17 ATKINT=YMAT(I+1)
NESSY=NMAX
RETURN
18 RATIO=DIF1/ DIF2
IF(RATIO)20,20,19
19 MID=0.0
GO TO 32
20 CONTINUE
AT THIS POINT ONE COULD PRINT THE FOLLOWING STATEMENT
WRITE OUTPUT TAPE 5,200,X
NESSY=1
ATKINT=0.0
RETURN
32 CONTINUE
NOTE THAT RATIO IS POSITIVE IF THE TWO POINTS STRADDLE X REGARDLESS WHICH IS LARGER
JJ1=IMIO
JUP=IMIO
JDN=IMIO
IF (JJJ+NMAX-NLMTS+1)98,98,102
98 DO 201 J=1,NMAX
   JJJ=IMID+J-1
   A(1,J)=XMAT(JJJ)
201 A(2,J)=YMAT(JJJ)
   GO TO 203
102 DO 41 J=1,NMAX
   JJ=J/2
   JOE=J-2*JJ
   JJN=0 IF J IS EVEN AND 1 IF J IS ODD
   IF (J-1)33,40,33
33 IF (JDN-1)34,36,34
34 IF (JUP-NLMTS)35,37,35
35 JUP=JUP+1
   JJN=JUP
   GO TO 40
37 JDN=JDN+1
   JJN=JDN
   GO TO 40
40 A(1,J)=XMAT(JJJ)
   A(2,J)=YMAT(JJJ)
   CONTINUE
203 NNN=NMAX+1
   DO 6 J=3,NNN
      L=J-1
      DO 5 K=L,NMAX
         C J IS THE COLUMN NUMBER
         C K IS THE ROW NUMBER
         0 A(J,K)=(A(J-1,K)-A(J-1,J-2))*(X-A(1,J-2))/(A(1,K)-A(1,J-2))
         1 IF (K-L)3,2,3
         2 IF (ABS ((A(J,L)-A(J-1,L-1))/A(J,L))>ACRC/1000.0)7,7,3
         3 CONTINUE
         5 CONTINUE
         5 CONTINUE
         C AT THIS POINT ONE COULD PRINT OUT THE FOLLOWING STATEMENT.
         C WRITE OUTPUT TAPE 6,100,X,A(NNN,NMAX),A(NNN-1,NMAX-1)
         7 NESSY=0
         ATKINT=A(NNN,NMAX)
         RETURN
         7 NESSY=J-1
         ATKINT=A(J,L)
         RETURN
   END
Appendix B. Test Program and Sample Results

PROGRAM VALUES

A SAMPLE PROGRAM TO CHECK RUNNING AT OTHER INSTALLATIONS.

INPUT IS READ FROM CAROS* P IN ATM, T IN DEG K.

OUTPUT HEADING, UNITS, AND VALUES ARE PRINTED. HOWEVER, ONLY
A LIMITED NUMBER OF THE VARIABLES ARE CHECKED BY THIS SAMPLE DECK.

THE PROPERTIES DECK WAS LAST REVISED ON 75/06/17

CALL DATAPH2
PRINT 20
20 FORMAT(182H1     P RHO H S
       C-V J/MOL     C-P J/MOL-K
       VEL/82H ATM KELVIN MOL/L )
00 19 I=1,6
4 READ 5,P,T
5 FORMAT(F6.3,F7.3)
6 DEN=FIND(P,T)
7 H =ENTHAL(P,DEN,T)
8 S =ENTROP(DEN,T)
9 CVE=CV(DEN,T)
10 CPE=CP(DEN,T)
11 VEL=SOUDN(DEN,T)
12 PRINT 13,P,T,DEN,H,S,CVE,CPE,VEL
13 FORMAT(F10.4,F12.5,F10.5,F12.1,F10.2,F8.0)
19 CONTINUE
END

Appendix C. Conversion Factors

Temperature
1.8 R = 1 K

Pressure
14,695949 psia = 1 atm = 1.01325 x 10^5 N/m^2

Specific Volume
0.00794590 ft^3/lb_m = 1 cm^3/mol
(1 cm^3 = 0.001 liter = 10^-6 m^3)

Internal Energy, Enthalpy
0.213405 BTU/1b_m = 1 J/mol

Entropy, Specific Heat
0.118558 BTU/1b_m R = 1 J/mol-K

Thermal Conductivity
0.0578176 BTU/ft-hr-R = 1 mW/cm-K

Viscosity
0.067196897 lb_m /ft-s = 1 g/cm-s

Speed of Sound
3,280 ft/s = 1 m/s

Molecular Weight
2.01594

Surface Tension
0.5710147 x 10^-5 lb./in = 1 dyn/cm
(1 dyn = 10^-5 N)

* On the C^{12} = 12,000 scale
4. **TITLE AND SUBTITLE**

A MODIFIED BENEDICT-WEBB-RUBIN EQUATION OF STATE FOR PARAHYDROGEN - II

7. **AUTHOR(S)**

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16. **ABSTRACT**

A 32 term modified Benedict-Webb-Rubin equation of state has been applied to data for parahydrogen. The adjustable parameters in the equation of state were determined using 2665 points including very recent measurements at low temperatures and high pressures. The new values extend the range of the PVT data sufficiently to warrant a refitting of the equation of state. Temperatures for the data range from the triple point to about 700 K with pressures reaching 3000 atmospheres near ambient temperatures. The PVT data were adjusted to the T68 scale. In addition, extensive modifications have been made to the previously accepted PVT surface in the region near the critical point. These adjustments have been made on the basis of more recent refractive index data and the application of scaling law equations. Detailed comparisons between experimental and calculated values are given for density. Corresponding comparisons are made for enthalpy and the specific heat at constant pressure.

17. **KEY WORDS**

Critical point; density; enthalpy; equation of state; hydrogen; index of refraction; PVT; saturation properties; scaling laws; specific heat

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