EXAMINATION OF TWO METHODS OF DESCRIBING THE THERMODYNAMIC PROPERTIES OF OXYGEN NEAR THE CRITICAL POINT

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The correlation of the two methods at the selected pressures was very good outside the near-critical temperature region (150 to 170 K). Large differences (up to 30 percent) occurred within this region, however. The detailed study of \(c_p\) representations illustrated that these large discrepancies were due not to differences in the basic data of the methods but to the fact that the resolution of Weber's data in the near-critical region was not adequate to allow sufficient description of the thermodynamic functions by linear interpolation. In order to illustrate the effects of this poor description, identical calculations were performed based on the two methods of obtaining thermodynamic properties. Regions of erratic behavior in the calculations based on Weber's tabulations were correlated to errors introduced by linear interpolation.
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SUMMARY

A computer study was conducted to compare the numerical behavior of two approaches to describing the thermodynamic properties of oxygen near the critical point. One approach utilized properties from the tabulated data presented by L. A. Weber, and the other approach was based on computing properties using the curve-fit equations developed by R. B. Stewart. Data on the relative differences between values of specific heats at constant pressure \( (c_p) \), density, and isotherm and isochor derivatives of the equation of state are presented for selected supercritical pressures at temperatures in the range 100 to 300 K. The results of a more detailed study of the \( c_p \) representations afforded by the two methods are also presented.

The correlation of the two methods at the selected pressures was very good outside the near-critical temperature region (150 to 170 K). Large differences (up to 30 percent) occurred within this region, however. The detailed study of \( c_p \) representations illustrated that these large discrepancies were due not to differences in the basic data of the methods but to the fact that the resolution of Weber's data in the near-critical region was not adequate to allow sufficient description of the thermodynamic functions by linear interpolation. In order to illustrate the effects of this poor description, identical calculations were performed based on the two methods of obtaining thermodynamic properties. Regions of erratic behavior in the calculations based on Weber's tabulations were correlated to errors introduced by linear interpolation.

INTRODUCTION

The removal of the mixing fans from the supercritical oxygen storage tanks in the Apollo spacecraft introduced the possibility that the fluid in the tank could be stratified, possibly giving rise to several serious effects. First, it could cause erroneous quantity probe measurements with the potential for precipitating a mission abort. Second, if the low-density fluid from the stratified layer entered the oxygen supply lines, the potential would exist for fuel-cell shutdown. Finally, if the stratified layer became too extensive,
a perturbing force of even extremely low magnitude could cause depressurization with the potential for the existence of two-phase fluid in the tank.

The concern about the effects of stratification in the redesigned tanks led to a significant volume of analytical study in that area (refs. 1, 2, and 3). The thermodynamic data for oxygen that served as bases for the various studies were not identical; some investigators used the tabulated data presented by L. A. Weber (ref. 4), while some relied on the curve-fit equations developed by R. B. Stewart (ref. 5).

Comparisons of results presented in references 1 to 3 with unpublished calculations made by J. T. Suttles and G. L. Smith of the Langley Research Center have revealed significant differences. For example, Suttles and Smith using Weber's tabulations for the thermodynamic data predict the generation of very rapid oscillations of the mean pressure in the tank (about 25 cycles per hour after 2 hours) for a high-density case whereas Baldwin, Reinhardt, and Sheaffer (ref. 1, ch. 6) using Stewart's equations predict rates of about 3½ cycles per hour. Although the overall methods of analysis in the cited papers are diverse and thus undoubtedly contribute to the varying results, the contributions to these differences caused by the use of different descriptions of the thermodynamic data were also questioned. The purpose of this paper is, therefore, to compare the descriptions of the thermodynamic data for supercritical oxygen afforded by the two methods mentioned (refs. 4 and 5) and to compare the results of identical calculations based upon the two methods.

The approach taken was first to compute by each method values of specific heats at constant pressure (c_p), density, and the isotherm and isochor derivatives of the equation of state for supercritical pressures of 58.5 and 60 atm over the temperature range 100 to 300 K. The percent differences of values computed by Stewart's equations from interpolated values of Weber's tabulations were computed and plotted against temperature. The values of c_p were also plotted along selected isobars and isotherms. Finally, thermodynamic properties computed by Stewart's equations were applied to a simple mathematical model of the Apollo cryogenic oxygen storage tank for which the results of calculations based on Weber's tabulations were available.

SYMBOLS

A_i coefficients in vapor-pressure curve fit (eq. (4)), defined in appendix B, table IIIB

C_i coefficients in zero-pressure specific-heat equation (eq. (B3)), defined in appendix B, table IIIB
\( c_p \)  \( \text{specific heat at constant pressure, J/kg-K} \)

\( c^0_p \)  \( \text{specific heat at zero pressure, liter-atm/mole-K} \)

\( c_p(T) \)  \( c_p \) as a function of \( T \) only, that is, along an isobar

\( f_i \)  functions for evaluating derivatives of equation of state (eq. 1)),
   defined in appendix A, table IVA

\( g_i \)  functions for evaluating integrals of thermodynamic equations,
   defined in appendix B, table IB

\( H \)  enthalpy, liter-atm/mole

\( H^0_{T_o} \)  reference enthalpy at triple point, liter-atm/mole

\( \dot{m} \)  mass flux, kg/hr

\( n_i \)  coefficients in Stewart's curve fit to equation of state for oxygen (eq. (1)),
   defined in appendix A, table IA

\( p \)  pressure, atm (1 atm = 101.325 kN/m\(^2\))

\( p_V \)  vapor pressure, atm

\( R \)  characteristic gas constant for oxygen, 0.0820535 liter-atm/mole-K

\( T \)  temperature, K

\( T_c \)  temperature at critical point, K

\( T_o \)  temperature at triple point, K

\( t \)  time, sec

\( U \)  internal energy, liter-atm/mole

\( Q \)  heat flux, watts
METHOD

Two methods of describing the thermodynamic properties of oxygen were utilized in the present investigation. The first method was based on the least-squares curve fit to the equation of state for oxygen developed by Stewart (ref. 5). Stewart's curve fit gives pressure in terms of temperature and density over the entire range of data avail-
able at the time. The estimated accuracies of the equation of state over the three main temperature-pressure ranges are given as follows:

1. Gaseous range of values (65 to 300 K, to 340 atm) — ±0.1 percent in $p$

2. Liquid range (65 K to $T_c$, to 340 atm) — ±0.15 percent in $p$

3. Near-critical range (125 to 165 K, 40 to 100 atm) — ±0.3 percent in $p$

Stewart also presented methods for calculating entropy, enthalpy, internal energies, and specific heats from derived functions using his equation of state and its derivatives.

The second method of describing the thermodynamic properties of oxygen utilized in the present investigation involved interpolation of Weber's tabulations of the thermodynamic properties (ref. 4). Values of molar volume, isotherm and isochor derivatives of the equation of state, enthalpy, entropy, specific heats, and velocity of sound were tabulated as functions of pressure (to 330 atm) and temperature ($T_o$ to 300 K). These data were presented in increments of 5 atm and 2 K up to 160 K and in increments of 5 atm and 5 K above 160 K.

For the purpose of the present study, values of $c_p$, $\rho$, $\left(\frac{\partial p}{\partial \rho}\right)_T$, and $\left(\frac{\partial p}{\partial T}\right)_\rho$ were taken directly from Weber's tabulations (ref. 4), read into the digital computer, and referenced by linear interpolation.

The equations required for utilization of Stewart's method were adapted from reference 5. The equations and procedures used in the present investigation are presented in detail. Also, a computer listing of subroutines used for applying Stewart's method is included as appendix C.

**Equation of State**

The curve fits for the thermodynamic properties of oxygen developed by Stewart (ref. 5) were programmed into the computer. The least-squares curve fit for the equation of state, given in reference 5 as equation (7), is presented here as equation (1):

$$p = \rho RT + \left(n_1 T + n_2 + \frac{n_3}{T^2} + \frac{n_4}{T^4} + \frac{n_5}{T^6}\right)\rho^2 + \left(n_6 T^2 + n_7 T + n_8 + \frac{n_9}{T} + \frac{n_{10}}{T^2}\right)\rho^3$$

$$+ \left(n_{11} T + n_{12}\right)\rho^4 + \left(n_{13} + \frac{n_{14}}{T}\right)\rho^5 + \rho^3\left(\frac{n_{15}}{T^2} + \frac{n_{16}}{T^3} + \frac{n_{17}}{T^4}\right)\exp(n_{25} \rho^2)$$

$$+ \rho^4\left(\frac{n_{18}}{T^2} + \frac{n_{19}}{T^3} + \frac{n_{20}}{T^4}\right)\exp(n_{25} \rho^2) + \rho^7\left(\frac{n_{21}}{T^2} + \frac{n_{22}}{T^3} + \frac{n_{23}}{T^4}\right)\exp(n_{25} \rho^2)$$

$$+ n_{24}\rho^{n_{28}+1} \left(\rho^{n_{28}} - \rho_c^{n_{28}}\right)\exp\left[n_{26}\left(\rho^{n_{28}} - \rho_c^{n_{28}}\right)^2 + n_{27}(T - T_c)^2\right]$$

(1)
The coefficients for equation (1), $n_1$ through $n_{28}$, are included in table IA of appendix A. The constraints for the critical point and the fixed-point data imposed by Stewart upon the curve fit for the equation of state are listed in tables IIA and IIIA of appendix A, respectively.

Since the calculations required density as a function of temperature and pressure, equation (1) was solved numerically for density by an iterative method.

The isochor derivative $\left( \frac{\partial P}{\partial T} \right)_\rho$ and the isotherm derivative $\left( \frac{\partial P}{\partial \rho} \right)_T$ of equation (1) are given in appendix A as equations (A2) and (A3), respectively.

**Specific Heat Calculations**

Since the method of Stewart (ref. 5) does not include a procedure for calculating $c_p$ throughout the entire range of supercritical conditions being considered, it was necessary to adopt the procedure described in this section. The approach is based upon the use of the enthalpy equation to produce a consistent calculation of $c_p$ for the entire range of interest.

The specific heat at constant pressure was approximated by a central differencing of the enthalpy versus temperature curve;

$$c_p(T, \rho) = \frac{H(T + \Delta T, \rho_1) - H(T - \Delta T, \rho_2)}{2 \Delta T}$$

where $\rho_1$ and $\rho_2$ are densities at $T + \Delta T$ and $T - \Delta T$, respectively, for a given pressure. A temperature increment $\Delta T = 1.0 \text{ K}$ was used in equation (2), except in the near-critical region ($150 \text{ K} \leq T \leq 170 \text{ K}$) where $\Delta T = 0.1 \text{ K}$ was used to improve the approximation. A brief computer study showed that, for $\Delta T = 0.1 \text{ K}$, a halving of the temperature increment to $\Delta T = 0.05 \text{ K}$ produced a change in $c_p$ of less than 0.2 percent in the near-critical region, which is within the accuracy of Stewart's curve-fit equations.

Using the method of reference 5, it was necessary to calculate the enthalpies for equation (2) differently for temperatures above and below $T_c$. The procedure is described in the following sections.

**Temperatures above critical.** For temperatures above $T_c$ the enthalpy used in equation (2) was calculated by equation (18) of reference 5, given here as equation (3)

$$H(T, \rho) = H^0_{T_0} + T \int_0^{\rho} \left[ \frac{R}{\rho} - \frac{1}{\rho^2} \left( \frac{\partial P}{\partial T} \right)_\rho \right] d\rho + \int_0^{\rho} \left( \frac{P}{\rho^2} - \frac{RT}{\rho} \right)_T d\rho$$

$$+ \frac{P - \rho RT}{\rho} + \int_{T_0}^{T} c_p^0 dT$$

(3)
The solution to the integrals over \( \rho \) in equation (3) is simplified by using the equation of state (eq. (1)) and its isochor derivative (eq. (A2)). The indefinite solutions to the three integrals in equation (3) are given in appendix B. The reference enthalpy used was the enthalpy of the ideal gas at the triple point \( T_0 = 55.0 \text{ K} \) which is \( H^O_{T_0} = 15.7 \text{ liter-atm/mole} \) (ref. 5).

Temperatures below critical. - The method used for calculation of the enthalpy of supercritical oxygen at temperatures below \( T_c \) involved integration of internal energies from the saturation point along an isotherm. The use of internal energies in this region is part of the method of reference 5. The sequence of computations is described as follows:

First, the vapor pressure was calculated from the vapor-pressure curve fit for oxygen given as equation (7) in reference 4,

\[
\log_e p_V(T) = A_1 + A_2 T + A_3 T^2 + A_4 T^3 + A_5 T^4 + A_6 T^5 + A_7 T^6 + A_8 T^7
\]  
(4)

The \( A_i \)'s for equation (4) are listed in table IIIIB of appendix B.

Next, the saturated liquid and vapor densities, \( \rho_{\text{satL}} \) and \( \rho_{\text{satV}} \), were calculated by the simultaneous solution of the equation of state (eq. (1)) and the vapor-pressure curve (eq. (4)).

The saturated-vapor enthalpies were calculated by evaluating equation (3) at \( T, \rho_{\text{satV}} \), and \( p_V \). The saturated-liquid enthalpies were calculated by subtracting the enthalpy change due to vaporization as given by the Clapeyron equation from the saturated-vapor enthalpy:

\[
H(T,\rho_{\text{satL}}) = H(T,\rho_{\text{satV}}) - T \left( \frac{dp_V}{dT} \right)^{-1} \left( \frac{1}{\rho_{\text{satV}}} - \frac{1}{\rho_{\text{satL}}} \right)
\]  
(5)

where \( \left( \frac{dp_V}{dT} \right)^{-1} \) is the derivative of the vapor-pressure curve (eq. (4)).

The internal energies and the enthalpies were related as follows:

\[
U(T,\rho) = H(T,\rho) - \frac{p}{\rho}
\]  
(6)

The internal energies were calculated by equation (24) of reference 5, given here as follows:

\[
U(T,\rho) = U(T,\rho_{\text{satL}}) - T \int_{\rho_{\text{satL}}}^{\rho} \left( \frac{1}{\rho_{\text{satL}}} \frac{dp}{T} \right) d\rho + \int_{\rho_{\text{satL}}}^{\rho} \frac{p}{\rho^2} d\rho
\]  
(7)
where $U(T, \rho_{\text{sat}L})$ is the saturated-liquid internal energy, calculated from equations (5) and (6). The solutions to the integrals in equation (7) were facilitated by the use of the following relations:

$$\int \left[ \frac{1}{\rho^2} \left( \frac{\partial \rho}{\partial T} \right) \right] d\rho = \int \left[ \frac{R}{\rho} - \frac{1}{\rho^2} \left( \frac{\partial \rho}{\partial T} \right) \right] d\rho - R \log_e \rho$$

(8)

$$\int \frac{p}{\rho^2} d\rho = \int \left( \frac{p}{\rho^2} - \frac{RT}{\rho} \right) d\rho + RT \log_e \rho$$

(9)

After the appropriate substitutions are made, equation (7) becomes

$$U(T, \rho) = U(T, \rho_{\text{sat}L}) + T \int_{\rho_{\text{sat}L}}^{\rho} \left[ \frac{R}{\rho} - \frac{1}{\rho^2} \left( \frac{\partial \rho}{\partial T} \right) \right] d\rho + \int_{\rho_{\text{sat}L}}^{\rho} \left( \frac{p}{\rho^2} - \frac{RT}{\rho} \right) d\rho$$

(10)

The integrals used in equation (10) are the same as those used in equation (3).

Finally, the enthalpy used in equation (2) was calculated by equation (6).

Numerical difficulties. - Iterating for the saturation densities was complicated by the existence of an extraneous positive real root of equation (1) which lies between the roots representing the saturated vapor and liquid densities. Calculation of the extraneous root was avoided by careful choice of the bounds on the iteration. Evaluation of equation (A3), the isotherm derivative of the equation of state, at each calculated root provided a check for extraneous roots, since the isotherm derivative is always positive at the saturation densities but negative at the extraneous root. The problem of the extraneous root to equation (1) is addressed more comprehensively by Walter A. Reinhardt in reference 1, chapter 4.

Discontinuities were calculated in the $c_p$-isobars at $T_C$. Since the temperature range encompassing the discontinuities was only about 2 K at the pressures investigated, this problem was circumvented by calculating $c_p$'s above and below the discontinuity and interpolating linearly along the isobar for intermediate temperatures.

Stewart's equations (ref. 5) exhibited sensitivity to propagation of errors. The large number of operations involved tend to mushroom seemingly insignificant relative errors in $\rho$, for example, into large relative errors in $p$ calculated from equation (1). This effect can be minimized by demanding higher-order accuracy on the iterations for $\rho$, and by programming for minimum propagation of errors. (Reduction of the number of computer operations is one effective method for minimizing propagated errors.) A discussion of computer propagation of errors may be found in a numerical-methods text such as reference 6.
The method described above for calculation of $c_p$'s proved to be expensive in computer run time relative to a table look-up method; consequently, care was required in the coding and logical flow to insure maximum efficiency.

**PROCEDURE**

The procedure used in the present study involved first calculating values of $c_p$, $\rho$, $(\partial p/\partial \rho)_T$, and $(\partial p/\partial T)_\rho$ for two supercritical pressures (58.5 and 60 atm) and a range of temperatures, 100 to 300 K, in 2 K increments. The percent differences between values from Stewart's method and from Weber's tabulations were computed by the following relation:

$$\text{Percent difference} = \frac{\text{Stewart's value} - \text{Weber's value}}{\text{Weber's value}} \times 100$$

These percent differences were plotted against temperature in figure 1. Values of $c_p$ were then calculated over the temperature range 130 to 180 K in increments of 0.2 K along the isobars 55, 60, and 58.5 atm and are presented as plots in figure 2. In figure 3, a family of similar curves from reference 4 is presented for comparison. Values of $c_p$ were also calculated over a range of pressures, 55 to 70 atm, in increments of 1 atm for four isotherms, 140, 157, 160, and 180 K. These isotherms are presented as figure 4.

In order to explore the effects on calculated results caused by using Stewart's method rather than Weber's, identical calculations were performed and compared. In these calculations use was made of a simple mathematical model of the Apollo cryogenic oxygen storage tank developed by J. T. Suttles and G. L. Smith. Suttles and Smith used a one-dimensional cylindrical tank model as shown in figure 5 which facilitated a solution but retained the essential features of the actual tank. Their calculations gave the time rate of change of pressure as a function of temperature for two mass flux rates, 0.2268 kg/hr or 0.5 lb/hr and 0.6804 kg/hr or 1.5 lb/hr, both for heat addition ($Q_{\text{net}} = 125$ watts) and for no heat addition. The present calculations were made for pressures of 58.5 and 60 atm. The 60-atm case shows comparison of the results based on the two thermodynamic representations at a pressure at which Weber's data were tabulated. The 58.5-atm case duplicates the conditions imposed on the calculations of Suttles and Smith. The results of the calculations are presented as plots in figure 6.

**RESULTS AND DISCUSSION**

**Thermodynamic Properties**

The percent differences in the thermodynamic properties calculated by the different methods (figs. 1(a) to 1(d)) range between zero and 3 percent outside the near-critical
region (150 K < T < 170 K); however, large differences were noted inside this region. Also, the error introduced by linear interpolation of Weber's tabulations appears to have a significant effect upon the percent differences. The magnitudes of the percent differences were, in general, larger at points representing interpolated Weber's data than at points representing tabulated data. The differences in \( c_p \) were by far the most significant; therefore, \( c_p \) was selected for a detailed examination.

Figures 2(a) to 2(c) present comparisons of values of \( c_p \) produced by the different methods plotted as functions of temperature along three isobars (55 atm, 60 atm, and 58.5 atm). It should again be noted that agreement outside the near-critical temperature region (150 K to 170 K) appears to be very good. Furthermore, the points corresponding to tabulated data in reference 4 (circled points, 55 and 60 atm) agree very well with values calculated by Stewart's curve fits over the entire temperature range; if the circled points were faired smoothly, the faired curves would closely approximate the curves calculated from Stewart's equations. This statement is supported by figure 3, which was taken directly from reference 4. Although the isobars from figure 2 do not appear in figure 3, the smoothness and characteristic shape of the 50- and 70-atm isobars of figure 3 give strong support to at least the shape of the \( c_p \)-curves obtained from Stewart's equations shown in figure 2.

Since figures 2(a) and 2(b) represent data at pressures at which values of \( c_p \) were tabulated in reference 4, the poor behavior of Weber's data in the proximity of the peaks could only be due to linear interpolation of \( c_p(T) \) between points too widely spaced in temperature to describe the peak adequately. Figure 2(c), on the other hand, represents the 58.5-atm isobar, which is between tabulated pressures. This figure, therefore, illustrates the combined effect of double first-order interpolation of \( c_p \), which appears to be only slightly worse than the effect of interpolating \( c_p(T) \) along the tabulated isobars.

Figure 4, a comparison of \( c_p \)'s along selected isotherms, is presented to illustrate better the effects of linear interpolation of pressure. The 140 and 180 K isotherms lie outside the near-critical region and reassert the statement that first-order interpolation of Weber's data is sufficient outside of this region. The 160 K isotherm (a tabulated temperature) illustrates the irregularity introduced by linear interpolation of \( c_p \) with pressure in regions where the slope of the curve changes rapidly. Although the relative accuracy of the two methods at points where tabulated data exist in reference 4 has not been established, certainly Stewart's equations yield smoother results in the near-critical region than linear interpolation of Weber's tabulated data. Finally, the 157 K isotherm again represents a comparison of the results of Stewart's method with double-interpolated Weber's data corresponding to the peak of figure 2(a). The greatest part of the deviation of this pair of curves near 55 atm is attributed to interpolation of \( c_p \) with temperature since 55 atm is a tabulated pressure. The error caused by first-order
interpolation of $c_p$ with pressure appears to be relatively insignificant compared to the gross error caused by first-order interpolation of the $c_p(T)$-curves near their peaks.

Calculations for Tank With Uniform Properties

The calculations for a uniform tank performed by Sutlles and Smith were repeated, and the results are presented in figures 6(a) and 6(b). The calculations gave the time rate of change of pressure as a function of temperature for two mass flux rates, 0.2268 kg/hr or 0.5 lb/hr and 0.6804 kg/hr or 1.5 lb/hr, both for heat addition ($Q_{\text{net}} = 125$ watts) and for no heat addition. The calculations were made using both methods for description of the thermodynamic properties of oxygen for two pressures ($p = 60$ atm and 58.5 atm). Results from the two methods agreed over the entire temperature range for no heat addition, and for temperatures greater than 170 K for the heat-addition case. The methods also agreed fairly well for the latter case up to approximately 140 K. The divergent behavior between 140 and 154 K correlates with differences in the thermodynamic properties previously noted in that range.

The relative behavior of the results based upon the two methods in the region between 154 and 170 K warrants special attention, however. The results from Weber's data in figure 6(a) up to 160 K correspond to tabulated thermodynamic properties from reference 4. It is important to note that the pressure derivatives calculated from Weber's data at 162 and 164 K correspond to regions of poor description of the peak in the $c_p(T)$-curve by linear interpolation (figs. 2(b) and 2(c)), while the derivatives at 58.5 atm, 156 and 158 K, correspond to points of large percent differences in all the thermodynamic properties (fig. 1).

In summary, comparison of figures 6(a) and 6(b) indicates that the variations in the pressure derivative between 154 and 170 K calculated from linearly interpolated data from reference 4 (these variations were described as "unusual" by Sutlles and Smith) were caused by the error introduced by such interpolation.

The calculations for the stratified-tank problem performed by Sutlles and Smith were not made, but significant differences in the behavior of calculations around the critical temperature could be expected.

CONCLUDING REMARKS

A study was made to compare the approximations of the thermodynamic behavior of supercritical oxygen as afforded by Weber's tabulations and by Stewart's curve-fit equations as presented in this paper. Comparisons were presented for density, the isotherm and isochor derivatives of the equation of state, and specific heat at constant pressure ($c_p$) for a range of temperatures and two supercritical pressures. Special attention was
given to approximations of \( c_p \). Calculations for a simple one-dimensional mathematical
model of the redesigned Apollo cryogenic oxygen storage tank with uniform properties
were made based upon both approximations of the thermodynamic properties of oxygen.
The results were plotted and presented for comparison.

In general, the thermodynamic properties obtained by the two methods agreed very
well except in the near-critical temperature region (150 to 170 K). Stewart's equations
were more effective in approximating the general shapes of the curves of the thermody-
namic properties in regions of rapid variation than linear interpolation of Weber's tabu-
lations. The resolution of Weber's data was insufficient for first-order interpolation in
regions of rapid variation in the thermodynamic properties. Additional tabulated data
near the critical point would greatly enhance the reliability of Weber's tabulations in this
region.

Similarly, the results of the uniform-tank calculations agreed for temperatures
above 170 K. Regions of erratic numerical behavior in the results of the calculations
based on Weber's tabulations were correlated to errors introduced by linear interpolation.

From a utilization standpoint, both methods of describing the thermodynamic prop-
erties of oxygen have advantages. For limited ranges of temperature and pressures such
as those in the present study, the table look-up method was considered more convenient
and efficient for computer programing. On the other hand, if a very wide range of con-
ditions must be studied, the large number of data points required for this method could
make computer storage requirements the limiting factor; the curve-fit method becomes
more advantageous as the ranges of temperature and pressure increase.

If Stewart's equations are to be employed, certain obvious techniques can be incor-
porated to enhance the efficiency of the method; for instance, the problem should be for-
mulated so that temperature and density are the independent variables. Owing to the
large number of operations involved, calculation of specific heats should be avoided if
possible, especially in the near-critical region where the uncertainty of the representa-
tion is the greatest. Stewart's equations should be programed to avoid redundant opera-
tions and to minimize propagation of errors.

More recent data are now available (refs. 7 and 8) which improve the description
of the thermodynamic behavior of oxygen in the critical region; nevertheless, linear inter-
polation in this region is not recommended. Regardless of the methods of describing
thermodynamic properties chosen for future investigations, a brief numerical study of the
description afforded will probably disclose any gross misrepresentations of the data
similar to linear interpolation of Weber's tabulations in the critical region.

Langley Research Center,
National Aeronautics and Space Administration,
APPENDIX A

DERIVATIVES OF THE EQUATION OF STATE (REF. 5)

Equation of State

The equation of state (eq. (1)) may be written

\[ p = \rho RT + \sum_{i=1}^{24} n_i X_i \]  

(A1)

where the \( n_i \)'s are the coefficients listed in table IA, and the \( X_i \) functions are as follows:

\[
\begin{align*}
X_1 &= \rho^2 T \\
X_2 &= \rho^2 \\
X_3 &= \rho^2 T^2 \\
X_4 &= \rho^4 T^4 \\
X_5 &= \rho^2 T^6 \\
X_6 &= \rho^3 T^2 \\
X_7 &= \rho^3 T \\
X_8 &= \rho^3 \\
X_9 &= \rho^3/T \\
X_{10} &= \rho^3/T^2 \\
X_{11} &= \rho^4 T \\
X_{12} &= \rho^4 \\
X_{13} &= \rho^5 \\
X_{14} &= \rho^5/T \\
X_{15} &= \rho^3 f_1/T^2 \\
X_{16} &= \rho^3 f_1/T^3 \\
X_{17} &= \rho^3 f_1/T^4 \\
X_{18} &= \rho^5 f_1/T^2 \\
X_{19} &= \rho^5 f_1/T^3 \\
X_{20} &= \rho^5 f_1/T^4 \\
X_{21} &= \rho^7 f_1/T^2 \\
X_{22} &= \rho^7 f_1/T^3 \\
X_{23} &= \rho^7 f_1/T^4 \\
X_{24} &= \rho^{(n_{28}+1)} f_2 f_3
\end{align*}
\]

The \( f_1 \)'s are given in table IVA.

Isochor Derivative

The isochor derivative \( \left( \frac{\partial p}{\partial T} \right)_\rho \) for equation (A1) is given as

\[ \left( \frac{\partial p}{\partial T} \right)_\rho = \rho R + \sum_{i=1}^{24} n_i X_i \]  

(A2)

where the \( n_i \)’s are the coefficients listed in table IA, and the \( X_i \) functions are as follows:
APPENDIX A – Continued

\[ X_1 = \rho^2 \]
\[ X_2 = 0 \]
\[ X_3 = -2\rho^2/T^3 \]
\[ X_4 = -4\rho^2/T^5 \]
\[ X_5 = -6\rho^2/T^7 \]
\[ X_6 = 2T\rho^3 \]
\[ X_7 = \rho^3 \]
\[ X_8 = 0 \]
\[ X_9 = -\rho^3/T^2 \]
\[ X_{10} = -2\rho^3/T^3 \]
\[ X_{11} = \rho^4 \]
\[ X_{12} = 0 \]
\[ X_{13} = 0 \]
\[ X_{14} = -\rho^5/T^2 \]
\[ X_{15} = -2\rho^3 f_1/T^3 \]
\[ X_{16} = -3\rho^3 f_1/T^4 \]
\[ X_{17} = -4\rho^3 f_1/T^5 \]
\[ X_{18} = -2\rho^5 f_1/T^3 \]
\[ X_{19} = -3\rho^5 f_1/T^4 \]
\[ X_{20} = -4\rho^5 f_1/T^5 \]
\[ X_{21} = -2\rho^7 f_1/T^3 \]
\[ X_{22} = -3\rho^7 f_1/T^4 \]
\[ X_{23} = -4\rho^7 f_1/T^5 \]
\[ X_{24} = \rho^{(n_{28}+1)} f_2 f_4 \]

The \( f_i \)'s are given in table IVA.

\section*{Isotherm Derivative}

The isotherm derivative \( \left( \frac{\partial p}{\partial \rho} \right)_T \) for equation (A1) is given by

\[ \left( \frac{\partial p}{\partial \rho} \right)_T = RT + \sum_{i=1}^{24} n_i X_i \]  

(A3)

where the \( n_i \)'s are the coefficients listed in table IA, and the \( X_i \) functions are as follows:

\[ X_1 = 2\rho T \quad X_9 = 3\rho^2/T \quad X_{17} = f_6/T^4 \]
\[ X_2 = 2\rho \quad X_{10} = 3\rho^2/T^2 \quad X_{18} = f_7/T^2 \]
\[ X_3 = 2\rho/T^2 \quad X_{11} = 4\rho^3 T \quad X_{19} = f_7/T^3 \]
\[ X_4 = 2\rho/T^4 \quad X_{12} = 4\rho^3 \quad X_{20} = f_7/T^4 \]
\[ X_5 = 2\rho/T^6 \quad X_{13} = 5\rho^4 \quad X_{21} = f_8/T^2 \]
\[ X_6 = 3\rho^2 T^2 \quad X_{14} = 5\rho^4/T \quad X_{22} = f_8/T^3 \]
\[ X_7 = 3\rho^2 T \quad X_{15} = f_6/T^2 \quad X_{23} = f_8/T^4 \]
\[ X_8 = 3\rho^2 \quad X_{16} = f_6/T^3 \quad X_{24} = f_9 f_2 f_3 + \rho^{(n_{28}+1)} f_{10} f_3 + \rho^{(n_{28}+1)} f_2 f_{11} \]

The \( f_i \)'s are given in table IVA.
APPENDIX A – Continued

TABLE IIA.- COEFFICIENTS FOR EQUATION (1)

| T in K, p in atm, ρ in mole/liter | n_10 = -3.59419602 \times 10^n | n_11 = 1.02209557 \times 10^{-6} | n_12 = 1.90454505 \times 10^{-4} | n_13 = 1.21708394 \times 10^{-5} | n_14 = 2.44255945 \times 10^{-3} | n_15 = 1.73655508 \times 10^{-2} | n_16 = 3.01752841 \times 10^{10} | n_17 = -3.49528517 \times 10^{-7} | n_18 = 8.86724004 \times 10^{-1} | n_19 = -2.67817667 \times 10^2 |
|---|---|---|---|---|---|---|---|---|---|
| R = 0.0820535 | n_1 = 3.38759078 \times 10^{-3} | n_2 = -1.31606223 | n_3 = -7.38828523 \times 10^{3} | n_4 = 1.92049067 \times 10^{7} | n_5 = -2.90260005 \times 10^{10} | n_6 = -5.70101162 \times 10^{-8} | n_7 = 7.96822375 \times 10^{-5} | n_8 = 6.07022502 \times 10^{-3} | n_9 = -2.71019658 | n_{10} = 1.02209557 \times 10^{-6} | n_{11} = 1.90454505 \times 10^{-4} | n_{12} = 1.21708394 \times 10^{-5} | n_{13} = 2.44255945 \times 10^{-3} | n_{14} = 1.73655508 \times 10^{-2} | n_{15} = 3.01752841 \times 10^{10} | n_{16} = -3.49528517 \times 10^{-7} | n_{17} = 8.86724004 \times 10^{-1} | n_{18} = -2.67817667 \times 10^2 |

TABLE IIA.- CONSTRAINTS IMPOSED ON EQUATION (1)

\[
\begin{align*}
p, \rho, T & \text{ at the critical point} \\
\left( \frac{\partial p}{\partial \rho} \right) & = 0 \text{ at the critical point} \\
\left( \frac{\partial^2 p}{\partial \rho^2} \right) & = 0 \text{ at the critical point} \\
\left( \frac{\partial p}{\partial T} \right) & = 1.928386 \text{ atm/K at the critical point} 
\end{align*}
\]
APPENDIX A – Concluded

TABLE IIIA.- FIXED-POINT DATA

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical pressure</td>
<td>50.14 atm</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>154.77 K</td>
</tr>
<tr>
<td>Critical density</td>
<td>13.333 mole/liter</td>
</tr>
<tr>
<td>Normal boiling temperature (International practical</td>
<td>90.18 K</td>
</tr>
<tr>
<td>temperature scale (IPTS), fixed point)</td>
<td></td>
</tr>
<tr>
<td>Density saturated vapor at normal boiling point (eq. (1))</td>
<td>0.1396 mole/liter</td>
</tr>
<tr>
<td>Density saturated liquid at normal boiling point (eq. (1))</td>
<td>35.65 mole/liter</td>
</tr>
<tr>
<td>Triple point pressure</td>
<td>0.00150 atm</td>
</tr>
<tr>
<td>Triple point temperature</td>
<td>54.353 K</td>
</tr>
</tbody>
</table>

TABLE IVA.- FUNCTIONS FOR EVALUATING DERIVATIVES
OF EQUATION OF STATE

<table>
<thead>
<tr>
<th>Function</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1$</td>
<td>$\exp(n_{25}^2)$</td>
</tr>
<tr>
<td>$f_2$</td>
<td>$\rho_{n28} - \rho_c$</td>
</tr>
<tr>
<td>$f_3$</td>
<td>$\exp\left[n_{26}f_2^2 + n_{27}(T - T_c)^2\right]$</td>
</tr>
<tr>
<td>$f_4$</td>
<td>$2n_{27}(T - T_c)f_3$</td>
</tr>
<tr>
<td>$f_5$</td>
<td>$2f_1\rho n_{25}$</td>
</tr>
<tr>
<td>$f_6$</td>
<td>$3f_1\rho^2 + f_5\rho^3$</td>
</tr>
<tr>
<td>$f_7$</td>
<td>$5f_1\rho^4 + f_5\rho^5$</td>
</tr>
<tr>
<td>$f_8$</td>
<td>$7f_1\rho^6 + f_5\rho^7$</td>
</tr>
<tr>
<td>$f_9$</td>
<td>$(n_{28} + 1)\rho^{n_{28}}$</td>
</tr>
<tr>
<td>$f_{10}$</td>
<td>$n_{28}\rho^{(n_{28}-1)}$</td>
</tr>
<tr>
<td>$f_{11}$</td>
<td>$2f_2n_{26}f_{10}$</td>
</tr>
<tr>
<td>$f_{12}$</td>
<td>$2f_5\rho n_{25} + 2f_1 n_{25}$</td>
</tr>
<tr>
<td>$f_{13}$</td>
<td>$6f_1\rho + 6f_5\rho^2 + f_{12}\rho^3$</td>
</tr>
<tr>
<td>$f_{14}$</td>
<td>$20f_1\rho^3 + 10f_5\rho^4 + f_{12}\rho^5$</td>
</tr>
<tr>
<td>$f_{15}$</td>
<td>$42f_1\rho^5 + 14f_5\rho^6 + f_{12}\rho^7$</td>
</tr>
<tr>
<td>$f_{16}$</td>
<td>$n_{28}(n_{28} + 1)\rho$</td>
</tr>
<tr>
<td>$f_{17}$</td>
<td>$n_{28}(n_{28} - 1)\rho^{(n_{28}-2)}$</td>
</tr>
<tr>
<td>$f_{18}$</td>
<td>$(2f_{10}n_{26}f_3 + 2f_{2}n_{26}f_{11})f_{10} + 2f_{2}n_{26}f_{3}f_{17}$</td>
</tr>
</tbody>
</table>
APPENDIX B

INTEGRATION OF THE THERMODYNAMIC EQUATIONS (REF. 5)

The solution of the integral \[ \int \left[ \frac{R}{\rho} - \frac{1}{\rho^2} \left( \frac{\partial P}{\partial T} \right) \right] d\rho \] (from eq. (3)) at constant temperature is given by equation (B1). This integration uses the isochor derivative \( \left( \frac{\partial P}{\partial T} \right) \rho \) given in appendix A as equation (A2).

\[
\int \left[ \frac{R}{\rho} - \frac{1}{\rho^2} \left( \frac{\partial P}{\partial T} \right) \right] T \, d\rho = \sum_{i=1}^{24} n_i Y_i
\]

(B1)

where the \( n_i \)'s are the coefficients listed in table IA, and the \( Y_i \) functions are as follows:

\[
\begin{align*}
Y_1 &= -\rho \\
Y_2 &= 0 \\
Y_3 &= 2\rho/T^3 \\
Y_4 &= 4\rho/T^5 \\
Y_5 &= 6\rho/T^7 \\
Y_6 &= \rho^2/T \\
Y_7 &= -\rho^2/2 \\
Y_8 &= 0 \\
Y_9 &= \rho^2/(2T^2) \\
Y_{10} &= \rho^2/T^3 \\
Y_{11} &= -\rho^3/3 \\
Y_{12} &= 0 \\
Y_{13} &= 0 \\
Y_{14} &= \rho^4/(4T^2) \\
Y_{15} &= 2\rho^4/T^3 \\
Y_{16} &= 3\rho^4/T^4 \\
Y_{17} &= 4\rho^4/T^5 \\
Y_{18} &= 2\rho^5/T^3 \\
Y_{19} &= 3\rho^5/T^4 \\
Y_{20} &= 4\rho^5/T^5 \\
Y_{21} &= 2\rho^6/T^3 \\
Y_{22} &= 3\rho^6/T^4 \\
Y_{23} &= 4\rho^6/T^5 \\
Y_{24} &= -n_27(T - T_c)g_3/n_28n_26
\end{align*}
\]

where the \( g_i \)'s are given in table IB.

The solution of the integral \[ \int \left( \frac{p}{\rho^2} - \frac{RT}{\rho} \right) d\rho \] at constant temperature is given by equation (B2). This integration uses \( p = f(T,\rho) \) from equation of state (eq. (A1)) as given in appendix A.

\[
\int \left( \frac{p}{\rho^2} - \frac{RT}{\rho} \right) T \, d\rho = \sum_{i=1}^{24} n_i Y_i
\]

(B2)
APPENDIX B – Continued

where the \( n_i \)'s are the coefficients listed in table IA, and the \( Y_i \) functions are as follows:

\[
\begin{align*}
Y_1 &= T \rho \\
Y_2 &= \rho \\
Y_3 &= \rho / T^2 \\
Y_4 &= \rho / T^4 \\
Y_5 &= \rho^2 / T^6 \\
Y_6 &= \rho^2 T^2 / 2 \\
Y_7 &= \rho^2 T / 2 \\
Y_8 &= \rho^2 / 2
\end{align*}
\]

\[
\begin{align*}
Y_9 &= \rho^2 / (2T) \\
Y_{10} &= \rho^2 / (2T^2) \\
Y_{11} &= \rho^3 T / 3 \\
Y_{12} &= \rho^3 / 3 \\
Y_{13} &= \rho^4 / 4 \\
Y_{14} &= \rho^4 / (4T) \\
Y_{15} &= g_4 / T^2 \\
Y_{16} &= g_4 / T^3 \\
Y_{17} &= g_4 / T^4 \\
Y_{18} &= g_5 / T^2 \\
Y_{19} &= g_5 / T^3 \\
Y_{20} &= g_5 / T^4 \\
Y_{21} &= g_6 / T^2 \\
Y_{22} &= g_6 / T^3 \\
Y_{23} &= g_6 / T^4 \\
Y_{24} &= g_3 / (2^{2} \cdot 28^{n} 26)
\end{align*}
\]

where the \( g_i \)'s are given in table IB.

The solution of the integral \( \int c_p \, dT \) is given by

\[
\int c_p \, dT = R \sum_{i=1}^{8} C_i Y_i
\]

where \( R \) is given in table IA, and the \( C_i \)'s are the coefficients listed in table IIB, and the \( Y_i \) functions are as follows:

\[
\begin{align*}
Y_1 &= -1 / (2T^2) \\
Y_2 &= -1 / T \\
Y_3 &= \log_e T \\
Y_4 &= T \\
Y_5 &= T^2 / 2 \\
Y_6 &= T^3 / 3 \\
Y_7 &= T^4 / 4 \\
Y_8 &= uT / (e^u - 1)
\end{align*}
\]

where \( u = C_9 / T \).
TABLE IIB.- COEFFICIENTS FOR ZERO-PRESSURE SPECIFIC-HEAT EQUATION

\[
\begin{align*}
C_1 &= -1.86442361 \times 10^2 \\
C_2 &= 2.07840241 \times 10 \\
C_3 &= -3.42642911 \times 10^{-1} \\
C_4 &= 3.50297163 \\
C_5 &= 2.05866482 \times 10^{-7} \\
C_6 &= -1.11035799 \times 10^{-8} \\
C_7 &= 2.08612876 \times 10^{-11} \\
C_8 &= 1.01894691 \\
C_9 &= 2.23918105 \times 10^3
\end{align*}
\]

TABLE IIIB.- COEFFICIENTS FOR VAPOR-PRESSURE EQUATION (EQ. 4)

<table>
<thead>
<tr>
<th>T in K</th>
<th>p_v in atm</th>
<th>( \rho ) in mole/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>-62.5967185</td>
<td></td>
</tr>
<tr>
<td>A_2</td>
<td>2.47450429</td>
<td></td>
</tr>
<tr>
<td>A_3</td>
<td>-4.68973315 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>A_4</td>
<td>5.48202337 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>A_5</td>
<td>-4.09349868 \times 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>A_6</td>
<td>1.91471914 \times 10^{-8}</td>
<td></td>
</tr>
<tr>
<td>A_7</td>
<td>-5.13113688 \times 10^{-11}</td>
<td></td>
</tr>
<tr>
<td>A_8</td>
<td>6.02656934 \times 10^{-14}</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX C

LISTING OF FORTRAN SUBROUTINES FOR STEWART'S METHOD

SUBROUTINE STEWART(TEMPRHO PRESS CP DPDT DPDRHORHOENERGY)
INPUT PRESS(ATM) RHO(GM-MOLE/L)
DIMENSION XN(28)
COMMON/N/XN TEMP0 CRHOCRIT R
DATA(XN(I)=128)/3.38759078E-3,-1.31606223,-7.38828523E+3,
11.92049067E+7,-2.90260005E+10,-5.70101162E-8,7.96822375E-5,
26.07022502E-3,-2.71019658,-3.59419602E+1,1.02209557E-6,
31.90454505E+4,1.21708394E-5,2.44255945E-3,1.73655508E+2,
43.01752841E+5,-3.49528517E+7,8.86724004E-1,-2.67817667E+2,
51.05670904E+5,5.63771075E-3,-1.12012813E+1,46829491E+2,
69.98868924E+4,-.00560,-.157,-.350,.9/
RHODUM=RHO
P CRIT=50.14
01=C1C2C4(TEMPRHO)
DPDT=C2(TEMPRHO)*1.01325E+5
DPDRHORHO=C4(TEMPRHO)*1.01325E+5/31.9988
CP=CPHU(TEMPRHO,01)*1.01325E+5/31.9988
PRESS=01*1.01325E+5
ENERGY=0.
RHO=RHODUM
RETURN
END
FUNCTION CPHU(TEMP, RHO, P)

ALL Pressures in ATM  ALL Densities in GM-MOLE/L

CPHU(L-ATM/GM-MOLE/K)  H(L-ATM/GM-MOLE)  U, DITTO

EXTERNAL FOFX

COMMON/THERM/P1,T
COMMON C1,C2

DIMENSION A(8), H(2)

DATA (Ai), i=1,8)/6.02656934E-14, -5.1311368E-11, 1.91471914E-8,
1.4, 0.9349686E-5, 4.8202337E-4, 4.68973315E-2, 2.47450429E-2

ENTHALP(T, RHO, RH01, P)=1590.92999968996E-3 * P/RHO - 0.0820535 * T

A-D5(0., RHO)

1-D2(T, RH01) - D1D2 D5(T, RHO) * T

ENERGY(T, RH0, RH01, USAT)=USAT - D2(T, RH01) - D1D2 D5(T, RHO) * T

R=0.0820535$RHO = RHO$ICOUNT = 0$EREL = 5.E-7$TINCR = 1.0

T1 = 153.$T1P1 = 155.2

IF(TEMP.GT.TI.AND.TEMP.LT.TIP1) GO TO 2222

GO TO 1111

2222 FACTOR=31.9988/1.01325E5

CPI=C1*FACTOR

CPI1=C2*FACTOR

CP=CPI*(TEMP-TI)/(TI-TI)*CPI1-CPI

CPHU=CP

RETURN

1111 IF(TEMP.GE.150.AND.TEMP.LE.170.) TINCR=.1

DELT=.2*TINCR

6 IF(ICOUNT.EQ.2) GO TO 205

T=TEMP - TINCR $ ICOUNT = ICOUNT + 1 $ TINCR = -TINCR

ASSIGN 1 TO INDEX

INDEX = 1

P1 = P

RGM = .8 * RH0$RGP = 1.2 * RHO $ DELTRG = .1 * RGM

IF(T.GT.154.77) RGM = .5 * RHO

EREL = 5.E-7

EABS = EREL * RGM

CALL ITR2(RHO, RGP, DELTRG, FOFX, EREL, EABS, 50, ICODE)

IF(ICODE NE 0) GO TO 1000

GO TO INDEX (1, 55, 60)

1 IF(T.LT.154.77) GO TO 10

5 H(ICOUNT) = ENTHALP(T, RH0, 0, P)

GO TO 6

10 PVLM = A(1)

DO 15 I = 2, 8

15 PVLM = PVLM * T * A(I)

PV = EXP(PVLM)

IF(P.LE.PV) GO TO 5

RSAVE = RHO $ P1 = PV

59 RGM = 4.*(EXP(0.0232 * PV) - 1.) $ RGP = RHO * .6 $ DELTRG = .1 * RGP - .1 * RGM

IF(T.GT.153.) EREL = 5.E-10

EABS = EREL * RGM

INDEX = 60

ASSIGN 60 TO INDEX

GO TO 9

60 RSATV = RHO

RGM = 30., -1.5 * RSATV $ RGP = 1.1 * RSAVE $ DELTRG = (RGP - RGM) * 2

EABS = EREL * RGM

INDEX = 55
APPENDIX C - Continued

ASSIGN 55 TO INDEX
GO TO 9
55 RSATL=RHO
90 CONTINUE
   SUM=A(1)*7.*
   DO 100 I=2,7
100   SUM=SUM*T+(8-I)*A(I)
   DPVDT=SUM*PV
   DELTH=T*DPVDT*(1./RSATV-1./RSATL)
   HRSATV=ENTHALP(T*RSATV*0.*PV)
   HRSATL=HRSATV-DELTH
   USAT=HRSATL-PV/RSATL
   RHO=RSAVE
   U=ENERGY(T*RHO*RSATL+USAT)
   H(ICOUNT)=U+P/RHO
   GO TO 6
205 CPHU=(H(2)-H(1))/DELT
   T1=TEMP-TINCR & T2=TEMP+TINCR
900 FORMAT(10X,*T1 = *,F8.3,* T2 = *,F8.3,* H(T1) = *,E11.4,*
   * H(T2) = *,E11.4,* RV*RL *=*,2E11.4)
   RHO=RHO0UM
   RETURN
1000 WRITE(6,2) ICODE,INDEX
2 FORMAT(1HO,21HERROR IN CPHU ICODE=12,5X,INDEX = 12//)
   RETURN
END
FUNCTION C1C2C4(TEMP, RHO)
DIMENSION X(24), XN(28), F(18)
COMMON/N/XN, TEMPCR, RHOCRIT, R
R=0.420535
RHOCRIT=13.333
TEMPCR=154.77

FUNCTION C1C2C4(TEMP, RHO)
DIMENSION X(24), XN(28), F(18)
COMMON/N/XN, TEMPCR, RHOCRIT, R
R=0.420535
RHOCRIT=13.333
TEMPCR=154.77

F(1)=EXP(XN(25)*RHO**2) $ F(2)=RHO**XN(28)-RHOCRIT*XN(28)
F(3)=EXP(XN(26)*F(2)**2+XN(27)*(TEMP-TEMPCR)**2)
X(1)=RHO**2*TEMP $ X(2)=RHO**2 $ X(3)=RHO**2/TEMP**2
X(4)=RHO**2/TEMP**2 $ X(5)=RHO**2/TEMP**6 $ X(6)=RHO**3*TEMP**2
X(7)=RHO**3*TEMP $ X(8)=RHO**3 $ X(9)=RHO**3/TEMP
X(10)=RHO**3/TEMP**2 $ X(11)=RHO**4*TEMP $ X(12)=RHO**4
X(13)=RHO**5/F(1)/TEMP**3 $ X(14)=RHO**5/F(1)/TEMP**3
X(15)=RHO**5/F(1)/TEMP**3 $ X(16)=RHO**5/F(1)/TEMP**3
X(17)=RHO**5/F(1)/TEMP**3 $ X(18)=RHO**5/F(1)/TEMP**3
X(19)=RHO**5/F(1)/TEMP**3 $ X(20)=RHO**5/F(1)/TEMP**3
X(21)=RHO**5/F(1)/TEMP**3 $ X(22)=RHO**5/F(1)/TEMP**3
X(23)=RHO**5/F(1)/TEMP**3 $ X(24)=RHO**5/F(1)/TEMP**3
FACTOR=RHO*R*TEMP
GO TO 10
ENTRY C2
F(4)=2.*XN(27)*(TEMP-TEMPCR)*F(3) $ F(5)=2.*F(1)*RHO*XN(25)
X(1)=RHO**2 $ X(2)=0. $ X(3)=RHO**2/TEMP**3
X(4)=RHO**2/TEMP**5 $ X(5)=RHO**2/TEMP**7
X(6)=RHO**3/TEMP**3 $ X(7)=RHO**3 $ X(8)=0. $ X(9)=RHO**3/TEMP**2
X(10)=RHO**3/TEMP**3 $ X(11)=RHO**4 $ X(12)=0. $ X(13)=0.
X(14)=RHO**3/TEMP**3 $ X(15)=RHO**3/F(1)/TEMP**3
X(16)=RHO**3/F(1)/TEMP**3 $ X(17)=RHO**3/F(1)/TEMP**3
X(18)=RHO**3/F(1)/TEMP**3 $ X(19)=RHO**3/F(1)/TEMP**3
X(20)=RHO**3/F(1)/TEMP**3 $ X(21)=RHO**3/F(1)/TEMP**3
X(22)=RHO**3/F(1)/TEMP**3 $ X(23)=RHO**3/F(1)/TEMP**3
X(24)=RHO**3/F(1)/TEMP**3 $ X(25)=RHO**3/F(1)/TEMP**3
FACTOR=RHO*R*TEMP
GO TO 10
ENTRY C4
F(6)=3.*F(1)*RHO**2+F(5)*RHO**3 $ F(7)=5.*F(1)*RHO**4+F(5)*RHO**5
F(8)=7.*F(1)*RHO**6+F(5)*RHO**7 $ F(9)=(XN(28)+1.)*RHO*XN(28)
X(1)=2.*RHO*TEMP $ X(2)=2.*RHO $ X(3)=2.*RHO/TEMP**2
X(4)=2.*RHO/TEMP**4 $ X(5)=2.*RHO/TEMP**6 $ X(6)=3.*RHO**2*TEMP**2
X(7)=3.*RHO**2*TEMP $ X(8)=3.*RHO**2 $ X(9)=3.*RHO**2/TEMP
X(10)=3.*RHO**2/TEMP**2 $ X(11)=4.*RHO**3/TEMP $ X(12)=4.*RHO**3
X(13)=5.*RHO**4 $ X(14)=5.*RHO**4/TEMP $ X(15)=F(6)/TEMP**2
X(16)=F(6)/TEMP**3 $ X(17)=F(6)/TEMP**4 $ X(18)=F(7)/TEMP**2
X(19)=F(7)/TEMP**3 $ X(20)=F(7)/TEMP**4 $ X(21)=F(8)/TEMP**2
X(22)=F(8)/TEMP**3 $ X(23)=F(8)/TEMP**4
X(24)=F(9)+F(2)*F(3)*RHO*(XN(28)+1.)*F(10)*F(3)*RHO*(XN(28)+1.)*F(1)*F(11)
FACTOR=R*TEMP
GO TO 10
SUM=0.
DO 1 I=1, 24
1 SUM=SUM*XN(I)*X(I)
C1C2C4=SUM*FACTOR
RETURN
END

10 SUM=0.
DO 1 I=1, 24
1 SUM=SUM*XN(I)*X(I)
C1C2C4=SUM*FACTOR
RETURN
END
APPENDIX C - Concluded

FUNCTION D1D205(T,RHO)
DIMENSION XN(28),G(6),Y(24),C(9)
COMMON/XN,XN,TCR,RHOCR,R .
DATA (C(I))=1.9/.-1.86442361E+2,2.07840241E+1,-3.42642911E-1, 
13.50297163,2.05866482E-7,-11.1035799E-8,2.08612876E-11, 
21.01894691,2.23918105E+3/
TFMPCR=TCR $ RHOCRIT=RHOCR*TEMP=T
G(1)=EXP(XN(25)*RHO**2) $ G(2)=RHO*XN(28)-RHOCRIT*XN(28)
G(4)=G(1)/(2.*XN(25))
G(5)=G(1)*(XN(25)*RHO**2-1.)/(2.*XN(25)*G**2)
G(6)=G(1)*(XN(25)*RHO**4-2.*XN(25)*RHO**2-1.)/(2.*XN(25)*G**3)
G(3)=EXP(XN(26)*G(2)**2+XN(27)*G(2)**2+XN(27)*(TEMP-TEMPCR)**2)
RHO30=RHO*RHO $ T2=T*T $ T3=T3*T $ T4=T4*T $ T5=T5*T
Y(1)=-RHO $ Y(2)=0. $ Y(3)=2.*RHO/T3 $ Y(4)=4.*RHO/T5
Y(5)=6.*RHO/T**7 $ Y(6)=RHO*Q*T $ Y(7)=-RHO*Q/2. $ Y(8)=0.
Y(9)=RHO*Q/(2.*T2) $ Y(10)=RHO*Q/T3 $ Y(11)=-RHO*Q/3.
Y(12)=Y(13)=0. $ Y(14)=RHO*Q/(4.*T2) $ Y(15)=2.*Q/(G(4)/T3)
Y(16)=3.*Q(4)/T4 $ Y(17)=4.*Q(4)/T5 $ Y(18)=2.*Q(5)/T3
Y(19)=3.*Q(5)/T4 $ Y(20)=4.*Q(5)/T5 $ Y(21)=2.*Q(6)/T3
Y(22)=3.*Q(6)/T4 $ Y(23)=4.*Q(6)/T5
Y(24)=-XN(27)*(T-TCR)*G(3)/(XN(28)*XN(26))
GO TO 10
ENTRY 02
RH03=RHO3*QH0 $ RHO4=RHO3*QH0
Y(1)=T*RHO $ Y(2)=RHO $ Y(3)=RHO/T2 $ Y(4)=RHO/T4 $ Y(5)=RHO/T**6
Y(6)=RHO*Q/T2 $ Y(7)=RHO*Q/T2 $ Y(8)=RHO*Q/2.
Y(9)=5.*RHO3*Q/T $ Y(10)=5.*RHO3*Q/T $ Y(11)=RHO3*T/3.
Y(15)=G(4)/T2 $ Y(16)=G(4)/T3 $ Y(17)=G(4)/T4
Y(18)=G(5)/T2 $ Y(19)=G(5)/T3 $ Y(20)=G(5)/T4
Y(21)=G(6)/T2 $ Y(22)=G(6)/T3 $ Y(23)=G(6)/T4
Y(24)=G(3)/(2.*XN(28)*XN(25))
10 SUM=0.
DO 11 I=1,24
11 SUM=SUM+Y(I)*XN(I)
D1D205=SUM
RETURN
ENTRY 05
U=C(9)/T $ T2=T*T $ T3=T2*T $ T4=T3*T
Y(1)=-5/T2 $ Y(2)=1./T $ Y(3)=ALOG(T) $ Y(4)=T $ Y(5)=-5*T2
SUM=0.
DO 20 I=1,8
20 SUM=SUM+C(I)*Y(I)
D1D205=SUM*R
RETURN
END
REFERENCES


Figure 1.- Percent difference between values of thermodynamic properties calculated by Stewart's method and values from interpolation (Weber's tabulations). Percent differences given by

\[
\text{Percent difference} = \left( \frac{\text{Stewart's value} - \text{Weber's value}}{\text{Weber's value}} \right) \times 100
\]

(a) Specific heat $c_p$. 

Filled circles correspond to tabulated values from ref. 4.

- $p = 60$ atm
- $p = 58.5$ atm (860 psia)
Filled circles correspond to tabulated values from ref. 4.
(c) Isochor derivative \( \left( \frac{\partial p}{\partial T} \right)_\rho \).

Figure 1.- Continued.
Filled circles correspond to tabulated values from ref. 4.
Figure 2.- Comparison of specific heat at constant pressure along selected isobars.

(a) $p = 55$ atm.
Figure 2.- Continued.

(b) \( p = 60 \) atm.

Figure 2.- Continued.
Figure 2.- Concluded.

(c) \( p = 58.5 \) atm.
Figure 3. $c_p$ along selected isobars (ref. 4).
Weber's values at indicated temperatures
Stewart's value
Filled symbols represent tabulated values; open symbols are interpolated values

Figure 4.- Comparison of specific heats at constant pressure along selected isotherms.
Figure 5. - Sketch of tank and heater showing essential features of model.
(a) $p = 60$ atm, a pressure tabulated by Weber.

Figure 6. Comparison of uniform-tank calculations using Stewart's and Weber's thermodynamic properties.
(b) $p = 58.5$ atm (860 psia) a pressure requiring interpolation in Weber's tabulation.

Figure 6.- Concluded.
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