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the thermodynamic properties OF NITROGEN FROM 65 TO 2000 K WITH Pressures to 10.000 AtM

RICHARD T, JACOBSEN


# THE THERIODYNAMIC PROPERTIES OF NITROGEN <br> FROM 65 TO 2000 K WITH PRESSURES TO <br> 10,000 ATMOSPHERES 

By
RICHARD T. JACOBSEN

A thesis submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY Program in Engineering Science

# To the Faculty of Washington State University: <br> The members of the Committee appointed to examine the thesis of RICHARD T. JACOBSEN find it satisfactory as to content and form and recommend that it be accepted. 

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The rimsent work is an extension of the investigation begun under contract no. CST-962-5-69 from the National Bureau of Standards, Office of Standard Reference Data with Dr. Howard J. White, Jr, as scientific officer. The doctoral dissertation investigation by Dr. Thomas C. Coleman at Worcester Polytechnic Institute, Worcester, Massachusetts, 1971 , prfsented preliminary results of the study and documented the need for further work on the thermodynamic properties of nitrogen. The University of Idaho Department of Mechanical Engineering, of which the author is a faculty member, was under contract during the two year period ending July 1, 1971 with the Office of Standard Reference Data, National Bureau of Standards, U.S. Department of Commerce; to provide an improved set of tables and equations for the thermodynamic properties of nitrogen. This work has continued since July 1, 1971, under contract NAS 9-12078 to the National Aeronautics and Space Administration (NASA)--Manned Spacecraft Center, Systems Management Branch, Houston, Texas with Walter Scott, Jr. as Technical Monitor.

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# THE THERMODYNAMIC PROPERTIES OF NITROGEN FROM 65 TO 2000 K WITH PRESSURES TO 10,000 ATMOSPHERES <br> ABSTRACT <br> by Richard T. Jacobsen, Ph.D. Washington State University, 1972 

Chairman: Richard W. Crain Jr.

An equation of state, $P=P(\rho, T)$, is presented for liquid and gaseous nitrogen for temperatures from 65 K to 2000 K and pressures to 10,000 atmospheres. All of the Pressure-Density-Temperature $(P-\rho-T)$ data available from the published literature have been reviewed, and appropriate corrections have been identified and applied to bring experimental temperatures into accord with the International Practical Temperature Scale of 1968. Comparisons of property values calculated from the equation of state to measured values are included to illustrate the accuracy of the equation in representing the data. The coefficients of the equation of state were determined by a weighted least squares fit to selected published $P-\rho-T$ data and, simultaneously, to $C_{v}$ data determined by corresponding states analysis from oxygen data, and to data which define the phase equilibrium criteria for the saturated liquid and saturated vapor. The methods of weighting the various data for simultaneous fitting are presented and discussed.

A vapor pressure equation, meltirg curve equation, and an equation to represent the ideal gas heat capacity, $C_{p}^{0}$, are also presented. Comparisons of measurements of various thernodynamic properties with values calculated using the equation of state, and the vapor pressure equation and ideal gas heat capacity equation as appropriate, are included. (e.g., specific heats
$C_{p}$ ard $C_{v}$, enthalpy, latent heat of vaporization, entropy of the saturated liquid, and velocity of sound.)

The extrapolation of the equation of state to the saturated liquid line and to the melting curve are discussed, and comparisons to the available measurements of density at these conditions are included. Extrapolation of the equation of state to higher and lower temperatures for the vapor is discussed.

The equation of state is estimated to be accurate to within 0.5 percent in the liquid region, to within 0.1 percent for supercritical isotherms up to 1000 atmospheres, and to within 0.3 percent from 1000 to 10,000 atmospheres. The vapor pressure equation is accurate to within $\pm 0.01 \mathrm{~K}$ between the triple point and the critical point. Tables of calculated thermodynamic properties of nitrogen are presented including values of temperature, density, internal energy, enthalpy, entropy, $C_{v}, C_{p}$, and velocity of sound along selected isobars. A separate table of the thermodynamic properties of nitrogen at saturation is also included.

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## NOMENCLATURE

```
P . . . . . . . pressure
T . . . . . . . temperature
\nu . . . . . . . density
_sTp . . , . . standard density (at 273.15 K and 1 atmosphere)
V . . . . . . specific volume = 1/\rho
R . . . . . . universal gas constant = 0.0820539 liter-atm/g mole-K
U . . . . . . . internal energy
H . . . . . . . enthalpy
S . . . . . . . entropy
L . . . . . . . latent heat of vaporization
C
C}\mp@subsup{V}{v}{}...... specific heat at constant volum
Co . . . . . . specific heat at constant saturation
G . . . . . . . Gibbs function
B(T) . . . . . second virial coefficient
W (Chapter 4) . weighting factor
W (Chapter 11). velocity of sound
\sigma . . . . . . . experimental uncertainty of individual data point
Superscripts
o . . . . . . . ideal gas property
'' . . . . . . saturated liquid property
```

Subscripts
c . . . . . . . critical point value
C . . . . . . . property at saturation
0 . . . . . . . reference state property
calc . . . . . calculated property value
corr. st. . . . corresponding states
data . . . . . experimental property value
eqn . . . . . . value calculated from specific equation
SV . . . . . . saturated vapor
SL . . . . . . saturated liquid
S . . . . . . . saturation value
[ ] . . . . . data values from the reference indicated

## CHAPTER 1

INTRODUCTION

The increasing use of cryogenic fluids by industry in the United States has led to a considerable number of recent experimental investigations of the thermodynamic properties of nitrogen. In particular, new measurements of properties of nitrogen have extended the range of pressure-density-temperature $(P-\rho-T)$ data in the liquid region and at high pressures and temperatures. The National Aeronautics and Space Administration (NASA)--Manned Spacecraft Center has clearly established a need for improved thermodynamic property formulations for nitrogen and oxygen for computer analyses in support of the Space Shuttle and Skylab programs which will employ two-gas atmospheres. In addition to the space-oriented applications for thermodynamic properties of nitrogen where precise design requires accurate property tables, there are large-scale industrial applications where improved design may result in significant reductions in costs of materials and equipment.

At present, no table of thermodynamic properties of nitrogen has been recognized as satisfactory for inclusion in the tables issued by the Office of Standard Reference Data of the National Bureau of Standards. In addition, the International Union for Pure and Applied Chemistry (IUPAC), Thermodynamic Tables Project Centre is interested in obtaining at least two independent concordant property formulations for preparation of an internationally accepted table of nitrogen properties.

The principal objectives of this work were to develop procedures of thermodynamic property formulation by computer analysis, and to prepare a table of properties of nitrogen that represented the best available compilation utilizing all existing measurements of thermodynamic data reported in the scientific literature. It was expected that the methods developed could be easily extended to similar new compilations of properties of oxygen and other atmospheric gases.

The technique used for development of the equation of state was leastsquares curve fitting of the equation of state to the available experimental observations over the range of interest. Although many correlations of thermodynamic data use different equations of state to fit discrete regions of the $\mathrm{P}-\mathrm{p}-\mathrm{T}$ surface, it was felt that a single equation of state would adequately describe the surface for nitrogen. One of the important requirements of the formulation of an equation of state for nitrogen is ease of programming for use in design work, which is facilitated by a single equation of state. In addition to the extension of the range of values covered by the property tables to 10,000 atmospheres and 2000 degrees Kelvin, improved concordance of the equation of state and vapor pressure equation with calorimetric measurements and other thermodynamic property measurements was accomplished.

CHAPTER 2

PRIOR WORK ON THERHODYNAMIC PROPERTIES
OF NITROGEN

In addition to the experimental investigations enumerated in Chapter 3, there have been several compilations and correlations of thermodynamic properties of nitrogen in recent years. Among these are Din [96], Hilsenrath et al. [100], Strobridge [119], Vasserman and Rabinovich [120], Vasserman et al. [121], and Coleman and Stewart [95]. The tables of Din and Hilsenrath et al. are presently outdated by the addition of considerable recent data in certain regions and by new developments in the formulation of the equation of state.

The compilation by Strobridge first used the procedure of fitting a modified Benedict-Webb-Rubin ( $B-W-R$ ) equation to the available $P$ - $\rho-T$ data, a technique which has been used by others in recent years, and which this work perpetuates. The equation used by Strobridge can be traced historically to the virial form suggested by Kamerlingh Onnes [107] in 1901. This equation is

$$
\begin{equation*}
P V=A+\frac{B}{V}+\frac{C}{V^{2}}+\frac{D}{V^{4}}+\frac{E}{V^{6}}+\frac{F}{V^{8}}+\ldots, \tag{1}
\end{equation*}
$$

with $A=R T, B=b_{1} T+b_{2}+\frac{b_{3}}{T}+\frac{b_{4}}{T_{3}}$, and $C, D, E$, and $F$ expressed in the same form as $B$ (i.e., power series expansions in temperature). An improvement of the virial equation was manifested in the Beattie-Bridgeman equation, the form of which is

$$
\begin{align*}
P= & \rho R T+\left(B_{0} R T-A_{0}-R C / T^{2}\right) \rho^{2}+\left(-B_{0} b R T-A_{0} a-R B_{0} C / T^{2}\right) \rho^{3} \\
& +R B_{0} b C \rho^{4} / T^{2} \tag{2}
\end{align*}
$$

with coefficients $A_{0}, B_{0}, a, b$, and $C$ determined by the data being represented. A modification of this equation designed to allow surface description at higher densities was the Benedict-Webb-Rubin equation,

$$
\begin{align*}
P= & \rho R T+\left(B_{0} R T-A_{0}-C_{0} / T^{2}\right) \rho^{2}+(b R T-a) \rho^{3}+a \alpha \rho^{6} \\
& +\left(c \rho^{3} / T^{2}\right)\left(1+\gamma \rho^{2}\right) \exp \left(-\gamma \rho^{2}\right), \tag{3}
\end{align*}
$$

with coefficients $A_{0}, B_{0}, C_{0}, a, b, c, \alpha$, and $\gamma$ determined by fitting the data [91].

In work at the National Bureau of Standards beginning in the late 1950's, it was found that the B-W-R equation was not adequate for the vapor and liquid range of values needed for the cryogenic fluids. This led to the pressure explicit equation for nitrogen reported by Strobridge [119] which was used to calculate properties from 64 K to 300 K and between 0.1 and 200 atmospheres. This equation is

$$
\begin{align*}
P= & \rho R T+\left(n_{1} T+n_{2}+n_{3} / T+n_{4} / T^{2}+n_{5} / T^{4}\right) \rho^{2} \\
& +\left(n_{6} T+n_{7}\right) \rho^{3}+n_{8} T \rho^{4} \\
& +\rho^{3}\left(n_{9} / T^{2}+n_{10} / T^{3}+n_{11} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{5}\left(n_{12} / T^{2}+n_{13} / T^{3}+n_{14} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +n_{15} \rho^{6} \tag{4}
\end{align*}
$$

with the values of the $n_{i}$ and $\gamma$ determined by fitting the data in the range of applicability.

Further development of the functional form of the equation of state led to the work of Coleman and Stewart [95]. Among the most significant is an equation of state developed for oxygen reported by Stewart [116] which suggests further modifications for higher densities and gives increased accuracy in the range near the critical state. The form of this equation is

$$
\begin{align*}
P= & \rho R T+\left(n_{1} T+n_{2}+n_{3} / T^{2}+n_{4} / T^{4}+n_{5} / T^{6}\right) \rho^{2} \\
& +\left(n_{6} T^{2}+n_{7} T+n_{8}+n_{9} / T+n_{10} / T^{2}\right) \rho^{3} \\
& +\left(n_{11} T+n_{12}\right) \rho^{4}+\left(n_{13}+n_{14} / T\right) \rho^{5} \\
& +\rho^{3}\left(n_{15} / T^{2}+n_{16} / T^{3}+n_{17} / T^{4}\right) \exp \left(n_{25} \rho^{2}\right) \\
& +\rho^{5}\left(n_{18} / T^{2}+n_{19} / T^{3}+n_{20} / T^{4}\right) \exp \left(n_{25} \rho^{2}\right) \\
& +\rho^{7}\left(n_{21} / T^{2}+n_{22} / T^{3}+n_{23} / T^{4}\right) \exp \left(n_{25} \rho^{2}\right) \\
& +n_{24} n_{28}+1\left(\rho_{28}-\rho_{C}^{n_{28}}\right) \exp \left[n_{26}\left(\rho^{n_{28}}-\rho_{C}^{n_{28}}\right)^{2}\right. \\
& \left.+n_{27}\left(T-T_{C}\right)^{2}\right] . \tag{5}
\end{align*}
$$

This equation was then modified by Coleman and Stewart [95] to represent the $P-\rho-T$ data of nitrogen in the range 0.1 to 100 atmospheres from 70 K to 1000 K . The equation is

$$
\begin{align*}
P= & \rho R T+\left(n_{1} T+n_{2}+n_{3} / T^{2}+n_{4} / T^{4}\right) \rho^{2} \\
& +\left(n_{5} T^{2}+n_{6} T+n_{7}+n_{8} / T+n_{9} / T^{2}\right) \rho^{3} \\
& +\left(n_{10} T+n_{11}\right) \rho^{4}+\left(n_{12}+n_{13} / T\right) \rho^{5} \\
& +\left(n_{14} / T^{2}+n_{15} / T^{3}+n_{16} / T^{4}\right) \rho^{3} \exp \left(-\gamma \rho^{2}\right) \\
& +\left(n_{17} / T^{2}+n_{18} / T^{3}+n_{19} / T^{4}\right) \rho^{5} \exp \left(-\gamma \rho^{2}\right) \\
& +\left(n_{20} / T^{2}+n_{21} / T^{3}+n_{22} / T^{4}\right) \rho^{7} \exp \left(-\gamma \rho^{2}\right) \tag{6}
\end{align*}
$$

This formulation represents the available data in the ranges indicated. However, difficulty was encountered in attempts to fit this functional form to data in the range from 1000 to 10,000 atmospheres.

The compilation by Vasserman and Rabinovich [120] covers the range 65 K to 150 K at pressures from 1 to 500 bars for liquid nitrogen. Although the property tables reported in this work appear to be of high accuracy, the formulation would be difficult to use in design work because of the procedures employed in the calculations. The laier work by vasserman et al. [121] covers the range of 70 K to $i 300 \mathrm{~K}$ at pressures from .25 to 1000 bars for gaseous ni trogen.

## CHAPTER 3

THE P-o-T DATA AND VAPOR PRESSURE DATA FOR NITROGEN

## P-p-T Data

The sources of experimental P-p-T data that form tiie basis of this work are summarized in Table 1. This table includes data reported in the literature as saturation line data and measurements of the liọuid on the freezing line. Details of the procedures used in data conversion and reduction are presented in Chapter 4. Figure 1 is a map of the $P-\rho-T$ data used in the final formulation of the equation of state.

## Vapor Pressure Data

The literature reporting measurements of the vapor pressure of nitrogen is summarized in Table 2. Unit conversion and temperature scale correction procedures for these data sets are also discussed in Chapter 4.

## Critical Point Parameters

The values of pressure and temperature at the critical point of nitrogen were selected to be consistent with the measurement of White et al. [122] and with the vapor pressure formulation discussed in Chapter 6. The critical pressure and temperature reported in [122] determined by observing the disappearance of the meniscus at the liquid-vapor interface of a nitrogen sample in a pipet were $33.54 \pm 0.02$ atmospheres and $126.26 \pm 0.04$ degrees Kelvin respectively. The critical point density for the equation of state was determined by the method of rectilinear diameters using values of saturated liquid and saturated vapor densities calculated by the simultaneous solution of the
vapor pressure equation and the equation of state each fit to the appropriate data. The development of these equations is discussed in Chapters 5 and 6 . The critical point defined in this manner was at 33.555 atmospheres, 11.21 moles/liter, and 126.20 K.

TABLE 1

## SUMMARY OF P-p-T DATA FOR NITROGEN

| Source | Temperature Range (K) | Pressure Range (atm) | Number of Data Points |
| :---: | :---: | :---: | :---: |
| Vapor |  |  |  |
| Amagat [!] | 273-473 | 1-1000 | 73 |
| Amagat [2] | 273-317 | 1-3000 | 8 C |
| Bartlett [3] | 273 | 1-1000 | 9 |
| Bartlett et al. [4] | 273-673 | 1-1000 | 52 |
| Bartlett et al. [5] | 203-293 | 100-100c | 42 |
| Benedict [6] | 90-273 | 99-1500 | 25 |
| Benedict [7] | 98-473 | 981-5879 | 124 |
| Canfield [8] | 133-273 | 2-300 | 152 |
| Crain [9] | 143-273 | 2-500 | 90 |
| Friedman [10] | 80-300 | 1-200 | 201 |
| Hall and Canfield [11] | 103, 113 | 2-9 | 8 |
| Heuse and Otto [12] | - 273 | 0.04-0.1 | 8 |
| Holborn and 0tto [13] | 273-373 | 20-99 | 32 |
| Holborn and Otto [14] | 273-673 | 20-99 | 66 |
| Holborn and Otto [15] | 143-273 | 20-99 | 24 |
| Kamerlingh Onnes and van Urk [16] | 124-293 | 30-50 | 143 |
| Malbrunot and Vodar [17] | 473-1273 | 1000-4000 | 63 |
| Malbrunot [18] | 473-1273 | 800-5000 | 191 |
| Michels et al. [19] | 273-423 | 20-80 | 56 |
| Michels et al. [20] | 273-423 | <00-3000 | 1.47 |
| Miller s+ al. [21] | - 294 | 9-260 | 10 |
| Otto e ${ }^{\text {e }}$ [22] | 298-423 | 45-400 | 63 |
| Reberts 1 and 3abb [23] | 308-673 | 1600-10,000 | 170 |
| Saurel , 4] | 423-1073 | 10-900 | 87 |
| Smith and Taylor [25] | 273-473 | 34-319 | 40 |
| Townsend [26] | 298, 323 | 2-140 | 35 |
| Tsikl is and Polyakov [27] | 294-673 | 1500-10,000 | 69 |
| Tsiklis [28] | 323-423 | 3000-10,000 | 45 |
| Verschoyle [29] | 273-293 | 25-205 | 36 |
| Liquid |  |  |  |
| Cockett et al. [30] | 85-120 | 50-200 | 63 |
| Gibbons [31] [30] | 72-77 | 22-124 | 17 |
| Golubev and Cobrovolskii [32] | 78-133 | 49-484 | 59 |
| Streett and Staveley [33] | $77.35-120.23$ | 4.32-680.46 | 107 |
| Van Itterbeek and Verbeke [34] | 65-90 | 15-840 | 67 |
| Van Itterbeek and Verbeke [35] | 77-90 | 79-815 | 13 |
| Weber [36] | 80-140 | 30-266 | 76 |

## TABLE 1--continued

| Source | Temperature Range (K) | Pressure Range (atm) | Number of Data Points |
| :---: | :---: | :---: | :---: |
| Saturated Liquid |  |  |  |
| $\begin{aligned} & \text { Goldman et al. [37] } \\ & \text { Terry et al. [38] } \end{aligned}$ | $78-125$ $77-104$ | $1-32$ $1-10$ | $\begin{aligned} & 80 \\ & 15 \end{aligned}$ |
| Liquid on the Freezing Line |  |  |  |
| Grilly and Mills [39] | 64-120 | 76-3441 | 10 |

TABLE 2
SUMMARY OF VAPOR PRESSURE DATA

| Source | Temperature <br> Range (K) | Number of <br> Data Points |
| :--- | :---: | :---: |
| Armstrong [40] | $66-77$ | 74 |
| Cath [41] | $64-84$ | 8 |
| Crommelin [42] | $81-125$ | 9 |
| Dodge and Davis [43] | $78-94$ | 15 |
| Friedman and White [44] | $77-123$ | 19 |
| Giauque and Clayton [45] | $54-63$ | 9 |
| Keesom and Bij1 [46] | $65-77$ | 18 |
| Michels et al. [47] | $96-125$ | 10 |
| Moussa et al. [48] | $63-77$ | 31 |
| Porter and Perry [49] | $90-121$ | 12 |
| Weber [36] | $65-126$ | 47 |

Temperature $(\mathrm{K})$


## CHAPTER 4

PREPARATION OF THE P-o-T AND VAPOR PRESSURE DATA FOR USE IN LEAST SQUARES FITTING OF THE EQUATION OF STATE AND THE VAPOR PRESSURE EQUATION

## Conversion of Units

In order to facilitate comparison of the results of this investigation to the recent work of Coleman and Stewart [95] the data sets were reviewed, and the units of the experimental data were changed to the following:

Pressure - atmospheres (atm)
Density - moles per liter (moles/liter)
Temperature - degrees Kelvin, IPTS-68 (K)
Table 3 is a listing of conversion factors used in data reduction with the number of significant figures used in this work.

TABLE 3
CONSTANTS AND CONVERSION FACTORS USED IN DATA REDUCTION Quantity Value

Molecular Weight of Nitrogen (M). . . . . . 28.0134 grams/mole
Universal Gas Constant (R). . . . . . . . . 0.0820539 liter-atm/mole-degree K Standard Density of Nitrogen. . . . . . . . 1.25053 moles/liter

Pressure Conversion Factors . . . . . . . $760.0 \mathrm{~mm} \mathrm{Hg} / \mathrm{atm}$

$$
\begin{equation*}
1.01325\left(10^{5}\right) \frac{\mathrm{N} / \mathrm{m}^{2}}{\mathrm{~atm}} \tag{110}
\end{equation*}
$$

$9.80665\left(10^{4}\right) \frac{\mathrm{N} / \mathrm{m}^{2}}{\mathrm{Kg}_{\mathrm{f}} / \mathrm{cm}^{2}}$


Determination of Estimated Experimental Uncertainty of the Data

P-o-T Data
An approximate experimental uncertainty in density for each data set was used to calculate weighting factors for data points incorporated in a weighted least-squares fit of the equation of state. The results of many of the experimental investigations included estimates of the accuracy of the reported measurements, which served as a guide in the initial estimates of the uncertainty of these data. Estimated uncertainties of the various data sets given by Sengers [115], Din [96], and Vasserman and Rabinovich [120] were used when estimates by the experimenter were inadequate or unavailable. In most cases the values of experimental uncertainty were estimated as percentages in
density. When no independent estimate of uncertainty was available, an estimated uncertainty in density was based on the precision of a preliminary fit to the available data including the set being examired. The uncertainty values in Table 4 represent the estimates used in preliminary weighting of the data for investigating the functional form of the equation of state. The weighting techniques employed in this work are detailed in the following section. When data were found to be discordant in specific regions, it was necessary to select certain data for use in determining the coefficients of the equation of state as discussed in Appendix $A$.

## Vapor Pressure Data

For the vapor pressure data, preliminary calculations indicated that an unweighted fit to selected data produced smaller deviations in temperature from data values than a weighted fit. After a careful investigation of weighting vapor pressure data points using uncertainties in temperature and in pressure, equal weights of unity were assigned to all data values used in the vapor pressure fit. As a consequence, no estimated uncertainties for the vapor pressure data are reported here. Appendix A includes a discussion of the selection of data for use in determining the vapor pressure equation.

## TABLE 4

## UNCERTAINTY VALUES FOR DATA USED IN THE DETERMINATION OF THE PRELIMINARY EQUATION OF STATE

Source Uncertaintyin Density (percent)
Vapor
Bartlett et al. [5] ..... 2
Benedict [6]. .....  3
Benedict [7]. .....  3
Canfield [8]. ..... 15
Crain [9] .....  1
Friedman [10] ..... 1
Hall and Canfield [11] ..... 39 at 103 K
.55 at 113 K
Holborn and Otto [14] ..... 05
Michels et al. [19] ..... 01
Michels et al. [20] . 01 below 1000 atm . 1 above 1000 atm
Miller et al. [21]. ..... 1
Otto et al. [22]. ..... 01
Robertson and Babb [23] ..... 05
Saurel [24] ..... 1
Tsiklis and Polyakov [27] ..... 1.0
Tsiklis [28]. ..... 1.0
Liquid
Gibbons [31]. ..... 15
Golubev and Dobrovolskii [32] .....  1
Streett and Staveley [33] ..... 1
Van Itterbeek and Verbeke [34], [35]. ..... 1
Weber [36]. ..... 15

## Weighting of the Data

P-p-T Data

Preliminary weighting for fitting the equation of state was accomplished using the estimated uncertainties in density assigned to each data set. To express the deviation of the dependent variable in the fit (in this case, pressure) as a function of the deviation of the independent variables (temperature and density) the error propagation formula was employed in the specific form below:

$$
\begin{equation*}
\sigma_{p}^{2}=\left[\sigma_{\rho}\left(\frac{\partial P}{\partial \rho}\right)_{T}\right]^{2}+\left[\sigma_{T}\left(\frac{\partial P}{\partial T}\right)_{\rho}\right]^{2} \tag{7}
\end{equation*}
$$

where
$\sigma_{p}$ is the uncertainty in pressure, the dependent variable, due to the combined uncertainties in temperature and density,
$\sigma_{\rho}$ is the estimated uncertainty in experimental density values for the data set Deing considered,
${ }_{T}$ is the estimated uncertainty in experimental temperature for the data set,
and the partial derivatives, $\left(\frac{\partial P}{\partial \rho}\right)_{T}$ and $\left(\frac{\partial P}{\partial T}\right)_{\rho}$, are taken from an equation of state which is known to describe the surface.

In the preliminary work the nitrogen equation from Coleman and Stewart [95] was used for calculating these partial derivatives.

The weighting factor to be applied to each data point in performing a least squares fit to the data was calculated from the following equation:

$$
\begin{equation*}
W=\frac{1}{\sigma_{p}^{2}+\sigma_{\mathrm{p}}^{2}} \tag{8}
\end{equation*}
$$

where
$W$ is the weighting factor,
$T_{p}$ is the uncertainty in the pressure due to uncertainty in the independent variable measurements calculated from (7),
and $\sigma_{p}$ is the uncertainty in the pressure due to experimental inaccuracy.
The weights applied to the data using the error propagation formula were calculated by assigning an estimated uncertainty to the value of density at each data point which was then used to determine an uncertainty in pressure for each point. The weighting function used for preliminary weighting was:

$$
\begin{equation*}
h=\frac{1}{\sigma_{\rho}\left(\frac{\partial P}{\partial \rho}\right)_{T}{ }^{2}} \tag{9}
\end{equation*}
$$

The weights used for the $\mathrm{P}-\mathrm{p}-\mathrm{T}$ data were reviewed and changed several times during the development of the equation of state. In addition, data sets found to be in disagreement with one another were reviewed, and the data considered less accurate were removed from the compiled data set used for establishing the equation.

After the development of the interim functional form of the equation of state (21) (further discussion of this equation is given in Chapter 5), which provided an acceptable fit to the entire range of $P-\rho-T$ data, the behavior of the equation was further examined by calculating derived thermodyllamic properties (i.e., enthalpy, entropy, and the heat capacities, $C_{p}$ and $C_{v}$ ). The equation of state was found to exhibit the correct characteristics for these calculated properties over much of the range of pressure and temperature for which $\mathrm{P}-\mathrm{\rho}-\mathrm{T}$ data were available. (A detailed analysis of this equation is presented in [117].) However, values of heat capacity calculated
using this equation exhibit erratic behavior in the liquid region and near the critical temperature, indicating the need for further modification of the equation of state.

Weights for the further development of the form of the equation of state were, therefore, determined using the root mean square (rms) deviations in pressure along isotherms and isochores from separate fits of the interim equatior (21) (Chapter 5) reported in [117] to selected data in the liquid and vapor regions. The rms deviations calculated along isotherms or isochores of data of each author is

$$
\begin{equation*}
r \mathrm{~ms}=\frac{\left[\Sigma\left(P_{\text {calc }}-P_{\text {data }}\right) / P_{\text {data }}\right]^{\frac{1}{2}}}{N} \tag{10}
\end{equation*}
$$

where
$P_{\text {calc }}$ is the pressure calculated from the appropriate liquid or vapor equation of state,
$P_{\text {data }}$ is the experimental pressure, and $N$ is the number of data points on the isotherm or isochore. The weight applied to each data point was calculated from

$$
\begin{equation*}
W T=\frac{1}{\left(r m s \times P_{\text {data }}\right)} \tag{11}
\end{equation*}
$$

Following the development of the functional form of the equation of state (22) (Chapter 5) using $P-p-T$ data, constant volume specific heat data and data to describe the criteria for liquid-vapor equilibrium were added to the compiled $P-p-T$ values used for determining the form of the equation, and new coefficients for (22) were determined by a simultaneous least squares fit of these related data as discussed in Chapter 5.
$C_{v}$ and Saturation Data
The weights applied to the $\mathcal{C}_{v}$ data and to the saturation data used in fitting phase equilibrium criteria were arbitrary, and were specified to make the effects of each of the data points compatible with $P-\rho-T$ fnints in the same region of temperature and pressure. The coefficients for equation (22) given in Table 10 (Chapter 5) were determined by a simultaneous least squares fit of $P-p-T$ data weighted using equation (11), to calculated $C_{v}$ data weighted by the relation, $W T=10,000 /\left(C_{V}\right)^{2}$, and to phase equilibrium criteria defined by saturation data weighted with the equation, $W T=100 /(P+0.01)$.

## Temperature Scale Corrections

## Identification of Temperature Scales

The data sets used in this investigation span the period of the evolution of several interim uniform temperature scales terminating with the adoption of the International Practical Temperature Scale of 1968 (IPTS-68) by the Comité Intermational des Poids et Mesures (CIPM) in October of 1968 [105]. Among the temperature scales identified by the various investigators in addition to the IPTS-68 were the following:

1. IPTS-48, the International Practical Temperature Scale of 1948,
2. NBS-55, the low temperature scale adopted by the National Bureau of Standards in 1955,
3. NPL-61, the scale adopted by the National Physical Laboratory in the United Kingdom in 1961,
4. PRMI-54, the scale adopted by the Physicotechnical and Radiotechnical Measurements Institute of the U.S.S.R. in 1954,
5. CCT-64, a preliminary scale which is a smoothed average reduced scale based upon the NBS-55, NPI.-61, PRMI-54, and a scale in use at Pennsylvania State University in 1954, PSU-54,
6. KOL scale, the temperature scale formerly used at the Kamerlingh Onnes Laboratory in Leiden, ivetherlands,
7. PTR scale, the scale formerly used at the Physikalisch Techrischen Reichansanstalt in Germany, and
8. OSU scale, a helium gas thermometer scale formerly used at the Ohio State University Cryogenic Laboratory.

This list includes the temperature scales used by the experimenters in report. ing the $\mathrm{P}-\mathrm{p}-\mathrm{T}$ data and the vapor pressure data.

In the following section details are presented on the temperature scale corrections made for the experimental data to convert all data points to the IPTS-68 scale.

## Numerical Corrections for Temperature Scales

## IPTS-48

The conversion of data point temperatures assumed to be consistent with IPTS-48 was the most frequent correction required. Tris correction was defined by Douglas [98]. The lower limit of definition of this scale was approximately 90 K , while the lower limit of the IPTS-68 is about 14 K . The correction is accomplished by equations from [98] in three ranges: 90.188 K to $273.15 \mathrm{~K}, 273.15 \mathrm{~K}$ to $903.89 \mathrm{~K}, 903.89 \mathrm{~K}$ to 1337.58 K .
90.188 K to 273.15 K

For the first range to 273.15 K , the equation employed is:

$$
\begin{align*}
T_{68} & -T_{48}=\left\{\left[1+3.984517\left(10^{-9}\right)\left(t_{48}\right)-5.855019\left(10^{-7}\right)\left(t_{48}\right)\right.\right. \\
& \left.\left.+4.35717\left(10^{-i 2}\right)\left(100-t_{48}\right)\left(t_{48}\right)^{3}-W\right] 250.97\right\} / \\
& {\left[1-2.9389\left(10^{-4}\right)\left(t_{48}\right)+4.3741\left(10^{-9}\right)\left(75-t_{48}\right)\left(t_{48}\right)^{2}\right] } \tag{12}
\end{align*}
$$

where
$T_{68}$ is the IPTS-68 temperature in degrees $K$,
$T_{4} \theta$ is the IPTS-48 temperatire in degrees $K$,
$t_{i, ~}$ is the IPTS-48 temperature in degrees $C$,
and $W$ is the standard reference function from [105] calculated by iterative solution of the equation

$$
\begin{equation*}
T_{48}=A_{0}+\sum_{i=1}^{20} A_{i}\left[\ln W\left(T_{48}\right)\right]^{i} \tag{13}
\end{equation*}
$$

where the $A_{0}$ and $A_{i}$ coefficients are as given in [105].
273.15 K to 903.89 K

In the range from 273.15 K to 903.89 K the calculated method is:

$$
\begin{align*}
T_{68} & -T_{48}=\left[4.904\left(10^{-7}\right) t_{48}\left(t_{48}-100\right) / 1-2.939\left(10^{-4}\right) t_{48}\right] \\
& +\phi\left(t_{48}\right) \tag{14}
\end{align*}
$$

where $\phi=0.045\left[t_{48} / 100\right]\left[\left(t_{48} / 100\right)-1\right]\left[\left(t_{48} / 419.58\right)-1\right]$

$$
\begin{equation*}
\left[\left(t_{48} / 630.74\right)-1\right] \tag{15}
\end{equation*}
$$

and $t_{48}, T_{66}$, and $T_{48}$ are as defined above.
903.89 K to 1337.58 K

From 903.89 K to 1337.58 K , the temperature adjustments are made by the equation:

$$
\begin{align*}
& T_{68}-T_{48}=\left[-1.3145+1.5016\left(10^{3}\right) t_{48}+1.5625\left(10^{6}\right)\left(t_{48}\right)^{2}\right] / \\
& \quad\left[1+4.101\left(10^{4}\right)\left(t_{48}\right)\right] \tag{16}
\end{align*}
$$

where all parameters are as previously defined. These calculations differ from those reported in [105] and [98] by the use of $t_{48}$ and $T_{48}$ in place of the vaiues $t_{68}$ and $T_{68}$ indicated in the references. The error introduced by this substitution is negligible when compared to the relative uncertainties of the respective definitions of the temperature scales employed, and the temperature difference calculations are considerably simplified by this approx-
imation. Calculated differences employing this procedure agree with those reported in [98] to the number of digits given.

NBS-55, NPL-61, and PRMI-54
Data temperatures reported on the NBS-55, NiPl-61, and PRMI-54 scales between temperatures of 14 K and 90.188 K were adjusted by interpolation from tabulated differences given in [89]. These differences are reported for even degree intervals of the IPTS-68 scale over the range above.

CCT-64
This scale was reported to be a smoothed average of the NBS-55, NPL-61, PRMI-54, and PSU-54 scales. The triple point of oxygen was given as 54.352 K and the boiling point of oxygen was 90.1727 k [101]. These fixed points were corrected to the IPTS-68 values of 54.361 h and 90.188 K respectively, and temperatures between these values were adjusted by linear interpolation.

KOL and PTR Scales
Data points reported on both of these temperature scales between the oxygen point and the ice point were corrected by a similar procedure. The oxygen point and the ice point for the scales were taken from [101] and a fixed-point correction was ajplied using an equation suggested by Ziegler et al. [124].

$$
\begin{equation*}
T=\left(T^{*}-T_{\mathrm{O}_{2}}{ }^{*}\right)\left[(273.15-90.18) /\left(\mathrm{T}_{0}^{*}-\mathrm{T}_{\mathrm{O}_{2}}{ }^{*}\right)\right]+90.18 \tag{17}
\end{equation*}
$$

where
T* is the measured temperature,
$\mathrm{T}_{\mathrm{O}_{2}}$ * is the oxygen point corresponding to the experimental measurements,
$T_{0}$ * is the ice point corresponding to the experimental data,
and $T$ is the adjusted temperature.

The values thus determined were assumed to be consistent with IPTS-4E. The standard correction for converting these values to IPTS-68 as previously described was then applied to those values.

In correcting data taken at the Kamerlingh Onnes Laboratory (KOL), the values for the experimental oxygen boiling point for the experimental ice point as indicated by Hust [101] were used to bring data temperatures into accord with IPTS-48. These temperatures were then converted to IPTS-68 values.

For correcting temperatures of data points on the PTR scale, values for the experimental ice point and oxygen point were taken from [101] to correspond to the date of the experimental results.

Data reported on the KOL scale between the triple point and boiling point of oxygen were corrected using the following equation:

$$
\begin{equation*}
T=\left(T^{*}-T_{t}\right)\left[(90.188-54.361) /\left(T_{0_{2}}-T_{t}\right)\right]+54.361 \tag{18}
\end{equation*}
$$

where
$T^{*}$ is the measured temperature,
$T_{t}$ is the oxygen triple point corresponding to the experimental measurements,
$\mathrm{T}_{\mathrm{O}_{2}}$ is the oxygen boiling point corresponding to the experimental data, and $T$ is the corrected temperature.

The values for $T_{t}$ and $T_{0_{2}}$ used in the corrections were taken from [i01].
OSU
Temperatures reported on the Ohio State Cryogenic Laboratory Temperature Scale were adjusted by first applying a ratio correction for the ice point discrepancy in the scale. This fixed point correction was of the form

$$
\begin{equation*}
T_{\text {corr }}=T_{\text {meas }}(273.15 / 273.16) \tag{19}
\end{equation*}
$$

where $T_{\text {corr }}$ is the adjusted temperature and $T_{\text {meas }}$ is the experimental temperature. The values determined in this manner were assumed to be consistent with IPTS-48, and the standard correction was applied to bring them into accord with IPTS-68.

Tables 5 and 6 list the assumed temperature scales for the data sets used in this investigation. In some cases no temperature scale identification could be made, and no correction was applied, since these data were used for comparison purposes only.

## TEMPERATURE SCALES OF P-o-T DATA SETS

Source
Temperature Scale
Vapor
Amagat [1], [2].Bartlett [3]IPTS-48
Bartlett et al. [4], [5] ..... IPTS-48
Benedict [6], [7] ..... IPTS-48
Canfield [8] ..... IPTS-48
Crain [9]. ..... IPTS-48
Friedman [10] ..... OSU
Hall and Canfield [11] ..... IPTS-48
Heuse and Otto [12]. ..... PTR
Holborn and Otto [13], [14], [15]. ..... PTR
Kamerlingh Onnes and van Urk [16]. ..... KOL
Malbrunot and Vodar [17] ..... IPTS-48
Malbrunot [18] ..... IPTS-48
Michels et al. [19], [20] ..... IPTS-48
Miller et al. [21] ..... IPTS-48
Otto et al. [22] ..... KOL
Robertson and Babt [23] ..... IPTS-48
Saurel [24] ..... IPTS-48
Smith and Taylor [25] Not identified
Tsiklis and Polyakov ..... IPTS-48
Tsiklis [28] ..... IPTS-48
Verchoyle [29] Not identified
Liquid
Cockett et al. [30] ..... <90.18 K, NPL
$>90.18 \mathrm{~K}$, IPTS-48
Gibbons [31] ..... NBS-55
Golubev and Dobrovolskii [32]. ..... <90.18 K, PRMI-54
>90.18 K, IPTS-48
Streett and Staveley [33]. ..... <90.18 K, NPL$>90.18 \mathrm{~K}$, IPTS-48
Van Itterbeek and Verbeke [34], [35] Not identifiedWeber [36]IPTS-68
Saturated Liquid
Goldman et al. [37] ..... $<90.18$ K, NPL ..... >90.18 K, IPTS-48
Terry et al. [38] ..... IPTS-48
Liquid on the Freezing Line
Grilly and Mills [39] ..... IPTS-48

TABLE 6
TEMPERAIURE SCALES OF VAPOR PRESSURE DATA SETS

Source Temperature Scale
Armstrong [40]. ..... IPTS-48*
Cath [41] Not identified
Crommelin [42]. ..... Not identified
Dodge and Davis [43]. ..... Not identified
Friedman and White [44] ..... OSU
Giauque and Clayton [45]. Not identified
Keesom and Bijl [46]. ..... KOL
Michels et al. [47] ..... IPTS-48
Moussa et al. [48]. ..... CCT-64
Porter and Perry [49] ..... Not identified
Weber [36]. ..... IPTS-68

* After fixed point correction of -0.01


## CHAPTER 5

## THE DETERMINATION OF THE EQUATION OF STATE

## Preliminary Fitting Procedures

After the data sets had been prepared by converting units and applying temperature scale corrections to bring the data values into accord with IPTS-68, a preliminary weighted least squares fit of the data to the 22-coefficient equation reported in [95] was made. The deviations in density of calculated values for this equation from data values above 1000 atmospheres were large, and systematic trends were noted in the deviations from data particularly in the liquid region.

Deviations of calculated densities from data values for weighted data sets for early experimental fits indicated that the several data sets in the liquid and high-pressure vapor regions were not concordant. A least squares fit to all of the data in these regions was unacceptable because of systematic trends in properties calculated from the equation. Certain data were removed from the compilation of data used to fit to the equalion of state but all data were compared to the resulting equation to preserve the comprehensive nature of the data analysis. (See Appendix A.)

The experimental determination of the functional form of the equation of state utilized a combination of trial-and-error and analytical procedures. Initial forms were postulated by adding terms with higher powers of density to the nucleus of terms suggested by the formulation in [95]. Terms which contained the exponential quantity, $e^{-\gamma \rho^{2}}$, were studied to determine the signifi-
cance of the value of $\gamma$ in the formulation and to evaluate the nature of the contribution of this term in fitting higher density data. It was found that the value of $\gamma$ had little effect on the quality of the fit of an equation to the available data, and that values of $\gamma$ between 0.001 and 0.01 produced essentially identical results for the same data. The value of 0.0056 which has been used in this work was taken from [119].

Each exponential term in the equation of state was analyzed by taking its first derivative with respect to density and equating the result to zero to locate the density at which the contribution of the term to the total pressure was a maximum. This procedure allowed the adjustment of the exponential terms to distribute the effect of the contributions of these terms over the range of densities from about 1.2 times the critical density to the maximum density of the available data, a range of from about 15 to 40 moles/liter. This analysis indicated that an equation including exponential terms containing odd powers of $\rho$ in integers from 3 to 13 resulted in a distribution of these maxima over the range of the high density data used in determining the equation of state.

An interim form of the equation of state developed by the procedure described above contained 35 coefficients. This equation is presented below and the coefficients reprinted froni [117] are 1 isted in Table 7.

$$
\begin{align*}
P= & \rho R T+\rho^{2}\left(N_{1} T+N_{2} T^{\frac{1}{2}}+N_{3}+N_{4} / T^{\frac{1}{2}}+N_{5} / T+N_{6} / T^{2}+N_{7} / T^{3}+N_{8} / T^{4}\right) \\
& +\rho^{3}\left(N_{9} T^{2}+N_{10} T+N_{11}+N_{12} / T+N_{13} / T^{2}\right) \\
& +\rho^{4}\left(N_{14} T+N_{15}\right)+\rho^{5}\left(N_{16}+d_{17} / T\right) \\
& +\rho^{3}\left(N_{18} / T^{2}+N_{19} / T^{3}+N_{20} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{5}\left(N_{21} / T^{2}+N_{22} / T^{3}+N_{23} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{7}\left(N_{24} / T^{2}+N_{25} / T^{3}+N_{26} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{9}\left(N_{27} / T^{2}+N_{28} / T^{3}+N_{29} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{11}\left(N_{30} / T^{2}+N_{31} / T^{3}+N_{32} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{13}\left(N_{33} / T^{2}+N_{34} / T^{3}+N_{35} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \tag{20}
\end{align*}
$$

where $T$ is the temperature, $P$ the pressure, and $\rho$ the density.

## TABLE 7

COEFFICIENTS FOR THE INTERIM EQUATION OF STATE (20)*

| Coefficient | Numerical Value | Coefficient | Numerical Value |
| :---: | :---: | :---: | :---: |
| $\mathrm{N}_{1}$ | $0.442846853539105 \times 10^{-2}$ | $\mathrm{N}_{19}$ | -0.111691086112682 $\times 10$ |
| $\mathrm{N}_{2}$ | -0.829417233959518 $\times 10^{-1}$ | $\mathrm{N}_{2} \mathrm{O}$ | $0.131992876308097 \times 10$ |
| $\mathrm{N}_{3}$ | 0.831816820844281 | $\mathrm{N}_{21}$ | -0.107110551745687 $\times 10$ |
| $\mathrm{N}_{4}$ | $0.789454995207039 \times 10^{1}$ | $\mathrm{N}_{2}$ | -0.280710075038644 $\times 10$ |
| $\mathrm{N}_{5}$ | -0.519464730111641 $\times 10^{3}$ | $\mathrm{N}_{2}{ }_{3}$ | $0.103571934551340 \times 10^{6}$ |
| $\mathrm{N}_{6}$ | $0.486788204145566 \times 10^{5}$ | $\mathrm{N}_{24}$ | -0.324638262862371 $\times 10^{-2}$ |
| $\mathrm{N}_{7}$ | -0.276765813270827 $\times 10^{7}$ | $\mathrm{N}_{25}$ | -0.143915062954146 $\times 10^{1}$ |
| $\mathrm{N}_{8}$ | $0.531902528027746 \times 10^{8}$ | $\mathrm{N}_{26}$ | $0.232500139742939 \times 10^{3}$ |
| N 9 | -0.107038956039902 $\times 10^{-6}$ | $\mathrm{N}_{2} 7$ | -0.201017505855138 $\times 10^{-3}$ |
| $\mathrm{N}_{1}$ | $0.274500963709232 \times 10^{-3}$ | $\mathrm{N}_{28}$ | $0.283301453486397 \times 10^{-1}$ |
| $N_{11}$ | -0.911499335271588 $\times 10^{-1}$ | $\mathrm{N}_{29}$ | -0.255833003328750 $\times 10^{1}$ |
| $\mathrm{N}_{12}$. | $0.145051669173734 \times 10^{2}$ | $\mathrm{N}_{3} \mathrm{O}$ | $0.126004937195284 \times 10^{-6}$ |
| $\mathrm{N}_{1}$ | $0.277646315858169 \times 10^{3}$ | $\mathrm{N}_{31}$ | -0.159463113142953 $\times 10^{-4}$ |
| $\mathrm{N}_{14}$ | -0.458649005760810 $\times 10^{-6}$ | $\mathrm{N}_{32}$ | $0.294340278758674 \times 10^{-2}$ |
| $\mathrm{N}_{15}$ | $0.138049438981636 \times 10^{-2}$ | $\mathrm{N}_{3}$ | -0.246822376653425 $\times 10^{-9}$ |
| $\mathrm{N}_{16}$ | $0.821404094790335 \times 10^{-4}$ | $\mathrm{N}_{34}$ | $0.784099910579200 \times 10^{-8}$ |
| Ni, | -0.986881710201094 $\times 10^{-2}$ | $\mathrm{N}_{3} 5$ | -0.108263<95096092 $\times 10^{-5}$ |
| $N_{18}$ | $0.137925677998808 \times 10^{3}$ |  |  |
| $\gamma=0.0056 ; R=0.0820539$ liter $-\mathrm{atm} / \mathrm{mole} \mathrm{e} \cdot \mathrm{K}$ |  |  |  |

*Coefficients are for temperatures in degrees Kelvin, pressures in atmospheres, and density in moles/liter.

Although a satisfactory equation of 35 terms had been developed, no systematic procedure had been employed to ascertain that the best 35 terms were used or that 35 was an optimum number of terms. To systematize the choice of terms to be used in the equation of state for nitrogen, a computer program developed by G. L. Rose [114] was utilized to analyze the following comprehensive equation of state.

$$
\begin{align*}
P= & \rho R T+\rho^{2}\left(N_{1} T+N_{2} T^{\frac{1}{2}}+N_{3}+N_{4} / T+N_{5} / T^{2}+N_{6} / T^{3}+N_{7} / T^{4}\right) \\
& +\rho^{3}\left(N_{8} T^{2}+N_{9} T+N_{10}+N_{11} / T+N_{12} / T^{2}\right) \\
& +\rho^{4}\left(N_{13} T^{2}+N_{14} T+N_{15}+N_{16} / T+N_{17} / T^{2}\right) \\
& +\rho^{5}\left(N_{18} T^{2}+N_{19} T+N_{20}+N_{21} / T+N_{22} / T^{2}\right) \\
& +\rho^{6}\left(N_{23} / T+N_{24} / T^{2}\right) \\
& +\rho^{7}\left(N_{25} / T+N_{26} / T^{2}\right) \\
& +\rho^{8}\left(N_{27} / T+N_{28} / T^{2}\right) \\
& +\rho^{9}\left(N_{29} / T+N_{30} / T^{2}\right) \\
& +\rho^{11}\left(N_{31} / T+N_{32} / T^{2}\right) \\
& +\rho^{3}\left(N_{33} / T^{2}+N_{34} / T^{3}+N_{35} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{5}\left(N_{36} / T^{2}+N_{37} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{7}\left(N_{38} / T^{2}+N_{39} / T^{3}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{9}\left(N_{40} / T^{2}+N_{41} / T^{3}+N_{42} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{11}\left(N_{43} / T^{2}+N_{44} / T^{3}+N_{45} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{13}\left(N_{46} / T^{2}+N_{47} / T^{3}+N_{48} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{15}\left(N_{49} / T^{3}+N_{50} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \tag{21}
\end{align*}
$$

Equation (21) includes the possible terms that previous experience had indicated might produce an equation appropriate to describe the $P-p-T$ surface. The analysis of (21) was then designed to determine the relative significance of these selected 50 terms.

The technique of stepwise multiple regression was utilized to fii a selected data set for nitrogen. The first term for the equation was selected as the one which had the highest correlation coefficient for the data used. The second term was chosen from among the remaining terms to provide the highest correlation coefficient for two terms including the first term as selected above. This procedure was continued until all 50 terms with undetermined coefficients had been utilized in the final fit.

The fitting process was then repeated with 45 terms by deleting the five terms which had the lowest F-statistics of the group of 50, and repeated again with 43 terms after the deletion of two more terms with the least significant F-values. To eliminate further terms which had small or negligible contributions to the fit, the analysis of the F-statistics of the coefficients was continued by deleting one term with each successive fit. This procedure was continued until an equation was obtained with only ar.a term with an F-statistic below the value for significance at the one percent level. This resulted in the equation (22) below, which, when fit to P-p-T data for the entire range of available measurements, had 31 coefficients with F-values above the level for significance.

$$
\begin{aligned}
P= & \rho R T+\rho^{2}\left(N_{1} T+N_{2} T^{\frac{1}{2}}+N_{3}+N_{4} / T+N_{5} / T^{2}\right) \\
& +\rho^{3}\left(N_{6} T+N_{7}+N_{8} / T+N_{9} / T^{2}\right) \\
& +\rho^{4}\left(N_{10} T+N_{11}+N_{12} / T\right) \\
& +\rho^{3}\left(N_{13}\right) \\
& +\rho^{6}\left(N_{14} / T+N_{15} / T^{2}\right) \\
& +\rho^{7}\left(N_{16} / T\right) \\
& +\rho^{6}\left(N_{17} / T+N_{18} / T^{2}\right) \\
& +\rho^{9}\left(N_{19} / T^{2}\right)
\end{aligned}
$$

$$
\begin{align*}
& +\rho^{3}\left(N_{20} / T^{2}+N_{21} / T^{3}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{5}\left(N_{22} / T^{2}+N_{23} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{7}\left(N_{24} / T^{2}+N_{25} / T^{3}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{9}\left(N_{26} / T^{2}+N_{27} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{11}\left(N_{28} / T^{2}+{ }^{4} 2 \rho / T^{3}\right) \exp \left(-\gamma \rho^{2} ;\right. \\
& +\rho^{13}\left(N_{30} / T^{2}+N_{3 i} / T^{3}+N_{32} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \tag{22}
\end{align*}
$$

The 32 coefficient equation fit to the $\mathrm{P}-\mathrm{p}-\mathrm{T}$ data alone provided an acceptable representation of the $P-p-T$ surface, but further refinement: in the values of coefficients $N_{1}$ through $N_{32}$ were subsequently made for improving the calculation of derived properties, particularly of specific heats in the liquid range and at temperatures near the critical value. The functional form of the equation was fixed as that of (22).

## Simultaneous Fitting

To incorporate related thermodynamic data with the $P-\rho-T$ data in a single determination of the equation of state, procedures were developed for inciuding va?ues of $C_{v}$, and the criteria for phase equilitrium between saturated liquid and saturated vapor points in a simultaneous least squares fitting technique. The procedures for including the conditions of phase equilibrium with the method of least squares are described in [92]. The method used allows integration of functions for property calculation along hypoietical isothems through the two-phase region. This is accomplished by satisíying thermodynamic relations for two-phase equilibrium of a pure substance. In ine ?east squares formulation incorporating $P-\rho-T$ data, heat capacity data, and these equilibrium conditions, the sums of squares of the weighted residuals of the following functions are minimizen simultaneously.

Table 8 indicates the functions minimized in simultaneous fitting.

TABLE 8

## FUNCTIONS FOR SIMULTANEOUS FITTING

## Function

Equation Number

$$
\begin{align*}
& P=\Sigma N_{i} P_{i}(\rho, T)+\rho R T \text {. . . . . . . . . . . . . . . . . . . . (23) } \\
& C_{V}=\sum N_{i} C_{i}(\rho, T)+C_{V}^{0}  \tag{24}\\
& \Sigma N_{i} P_{i}\left(\rho_{S L}, T_{S}\right)-\Sigma N_{i} D_{i}\left(\rho_{S V}, T_{S}\right)=\left(\rho_{S V}-\rho_{S L}\right) R T_{S}  \tag{25}\\
& \Sigma N_{i} G_{i}=P_{S}\left(\frac{1}{\rho_{S L}-\rho_{S V}}\right)+R T \ln \left(\frac{\rho_{S L}}{\rho_{S V}}\right) \tag{26}
\end{align*}
$$

NOTE: $P, \rho, T$, and $C_{v}$ are respectively the pressure, density, temperature, and constant volume heat capacity of data points used in the fit, $P_{S}, T_{S}, \rho_{S L}, \rho_{S V}$, are the saturation pressure, saturation temperature, density of the saturated liquid, and density of the saturated vapor respectively,
the $P_{i}$ are the individual terms of the equation of state,
the $C_{i}(\rho, T)$ are given by $C_{i}(\rho, T)=\int_{0}^{\rho} \frac{T}{\rho^{2}}\left[\frac{\partial^{2} P_{i}(\rho, T)}{\partial T^{2}}\right] d \rho$,
the $G_{i}$ are given by $G_{i}=\int_{\rho_{S L}}^{\rho_{S V}}\left[\frac{P_{i}\left(\rho, T_{S}\right)}{\rho^{2}}-\frac{R T_{S}}{\rho}\right] d \rho$,
and the $N_{i}$ are the coefficients of the ec rion of state to be determined. The derivations of equations (25) and (26) are presented in Appendix B.

The equation for $C_{v}$ for oxygen from Goodwin and Weber [99] was used with the principle of corresponding states for estimating values of $C_{v}$ for nitrogen. (See Appendix C.) The $C_{v}$ data were used in simultaneous fitting
primarily to give an equation which exhibited proper behavior of the first and second derivatives as evidenced by the behavior of calculated derived properties using these derivatives.

Saturated liquid and saturated vapor densities were required in the formulation of the phase equilibrium criteria. These were calculated from the simultaneous solution of the vapor pressure equation and the interim equation of state both from [117] on intervals of C. 25 degree $K$ between the triple point and the critiral point, and two equations of state determined by separate fits to the liquid and vapor regions alone.

The final coefficients for the equation of state were determined by a weighted least squares fit using the criteria outlined above, and constrained to the critical point data of Table 9 using a procedure suggested by McCarty [109].

## TABLE 9

CONSTRAINTS IMPOSED ON THE EQUATION OF STATE

## Constraint

 Numerical ValuePressure at the critical point. . . . . . . . . . . . $P_{c}=33.555 \mathrm{~atm}$ Density at the critical point . . . . . . . . . . . . $\rho_{c}=11.21$ moles/liter Temperature at the critical point . . . . . . . . . . $T_{c}=126.20 \mathrm{~K}$ Isotherm derivative at the critical point . . . . . $(\partial P / \partial \rho)_{T}=0$ Second derivative of pressure with respect to density at the critical point. . . . . . $\left(\partial^{2} P / \partial^{2} \rho\right)_{T}=0$

The coefficients for the constrained equation of state (22) determined as discussed above are presented in Table 10. The functional form of the equation is repeated above the table to facilitate comparison of the values of the coefficients and the respective terms for which they are applicable.

The value of the isochore derivative ( $\partial \mathrm{P} / \partial \mathrm{T})_{\rho}$ for this equation was
$1.6569 \mathrm{~atm} / \mathrm{K}$. This value was used as a constraint on the slope of the
vapor pressure equation at the critical point as discussed in Chapter 6.

$$
\begin{align*}
P= & \rho R T+\rho^{2}\left(N_{1} T+N_{2} T^{2 / 2}+N_{3}+N_{4} / T+N_{5} / T^{2}\right) \\
& +\rho^{3}\left(N_{6} T+N+N_{8} / T+N_{9} / T^{2}\right) \\
& +\rho^{4}\left(N_{10} T+N_{1}+N_{2} / T\right)+\rho^{5}\left(N_{13}\right) \\
& +\rho^{6}\left(N_{14} / T+N_{15} / T^{2}\right)+\rho^{7}\left(N_{16} / T\right) \\
& +\rho^{8}\left(N_{1} / T+N_{8} / T^{2}\right)+\rho^{9}\left(N_{19} / T^{2}\right) \\
& +\rho^{3}\left(N_{20} / T^{2}+N_{2!} / T^{3}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{5}\left(N_{22} / T^{2}+N_{2} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{7}\left(N_{24} / T^{2}+N_{25} / T^{3}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{9}\left(N_{26} / T^{2}+N_{2!} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{13}\left(N_{28} / T^{2}+N_{29} / T^{3}\right) \exp \left(-\gamma \rho^{2}\right) \\
& +\rho^{2}\left(N_{30} / T^{2}+N_{3:} / T^{3}+N_{32} / T^{4}\right) \exp \left(-\gamma \rho^{2}\right) \tag{22}
\end{align*}
$$

TABLE 10
COEFFICIENTS FOR THE EQUATION OF STATE (22) FOR NITROGEN*

| Coefficient | Numerical Value | Coefficient | Numerical Value |
| :---: | :---: | :---: | :---: |
| $\mathrm{N}_{1}$ | $0.136224769272827 \times 10^{-2}$ | $\mathrm{N}_{1}$ ? | -0.111614119537424 $\times 10^{-5}$ |
| $\mathrm{N}_{2}$ | 0.107032469908591 | $\mathrm{N}_{1}{ }^{\text {a }}$ | $0.55796562233495 \times 10^{-3}$ |
| $\mathrm{N}_{3}$ | -0.243900721871413 $\times 10$ | in 19 | -0.201317691347729 $\times 10^{-5}$ |
| $\mathrm{N}_{4}$ | $0.341007449376470 \times 10^{2}$ | $\mathrm{N}_{2} \mathrm{O}$ | $-0.169717444755949 \times 10^{5}$ |
| $\mathrm{N}_{5}$ | -0.422374309466? $67 \times 10^{4}$ | $\mathrm{N}_{21}$ | $-0.119719240044192 \times 10^{6}$ |
| $\mathrm{N}_{6}$ | $0.105098600246494 \times 10^{-3}$ | $\mathrm{N}_{2} 2$ | -0.975218272038281 $\times 10^{2}$ |
| N 7 | -0.11259482652208 , $\times 10^{-3}$ | $\mathrm{N}_{2} 3$ | $0.554639713151823 \times 10^{5}$ |
| $\mathrm{N}_{8}$ | $0.142600789270907 \times 10^{-3}$ | $\mathrm{N}_{2}$ | -0.179920450443470 |
| N 9 | $0.184698501609007 \times 10^{5}$ | $\mathrm{N}_{2} 5$ | $-0.256582926077184 \times 10^{1}$ |
| $\mathrm{N}_{10}$ | $0.811140082588776 \times 10^{-7}$ | $\mathrm{N}_{2} 6$ | -0.413707715090789 $\times 10^{-3}$ |
| $\mathrm{N}_{11}$ | $0.233011645038006 \times 10$ | $\mathrm{N}_{2} 7$ | -0.256245415300293 |
| $\mathrm{N}_{12}$ | -0.507752586350986 | $\mathrm{N}_{28}$ | -0.124222373740063 $\times 10^{-6}$ |
| $\mathrm{N}_{13}$ | $0.485027881931214 \times 10^{-4}$ | $\mathrm{N}_{29}$ | $0.103556535840165 \times 10^{-4}$ |
| $\mathrm{N}_{14}$ | -0.113656764115364 $\times 10^{-2}$ | $\mathrm{N}_{30}$ | -0.538699166558303 $\times 10^{-9}$ |
| $\mathrm{N}_{15}$ | -0.707430273540575 | $\mathrm{N}_{31}$ | $-0.757415412839596 \times 10^{-8}$ |
| $N_{16}$ | $0.751706648852680 \times 10^{-4}$ | $\mathrm{N}_{32}$ | $0.585367172069521 \times 10^{-7}$ |
| $\because=0.0056 ; R=0.0820539$ liter $-\mathrm{atm} / \mathrm{mole}-\mathrm{K}$ |  |  |  |

*Coefficients are for temperature in degrees Kelvin, pressure in atmospheres, and density in moles/liter.

## CHAPTER 6

## THE VAPOR PRESSURE EQUATION FOR NITROGEN

The literature reporting measurements of the vapor pressure of nitrogen was summarized in Table 2. A preliminary study of the vapor pressure data, and a preliminary vapor pressure equation were reported in [95]. Following the development of the equation for the vapor pressure of oxygen using calorimetric as well as vapor pressure measurements [111], a new vapor pressure equation was developed for nitrogen. This equation is a result of a least squares fit to the nitrogen data of Armstrong [40], and Weber [36]. These data were used since they cover the range from the triple point to the critical point, have a high precision, and appear to be the most accurate measurements avaliable. The form of the vapor pressure equation used i., this work is

$$
\begin{align*}
& \ln (P)=N_{1} / T+N_{2}+N_{3} T+N_{4}\left(T_{C}-T\right)^{1.95}+N_{5} T^{3}+N_{6} T^{4} \\
& \quad+N_{7} T^{5}+N_{B} T^{6}+N_{9} \ln (T) \tag{29}
\end{align*}
$$

where $T_{C}=126.20 \mathrm{~K}$, the critical point temperature, $T$ is the saturation temperature, and $P$ is the vapor pressure. The coefficients for this equation for temperature in degrees Kelvin and pressure in atmospheres are given in Table 11 below.

A comparison of the vapor pressure equation (29) with the selected data sets lised in determining the coefficients is given in Figure 2.

The equation has been constrained to the critical point temperature of 126.20 K , the critical pressure of 33.555 atmospheres, and the slope $\mathrm{dP} / \mathrm{dT}$ of

1. $6569 \mathrm{~atm} / \mathrm{K}$ consistent with the value of $(\partial P / \partial T)_{\rho}$ at the critical point from the constrained equation of state reported in Chapter 5.

TABLE 11
COEFFICIENTS FOR NITROGEN VAPOR PRESSURE EQUATION (29)*

|  |  |  |  |
| :---: | :---: | :---: | :---: |
| Coefficient | Numerica? Value | Coefficient | Numerical Value |
| $N_{1}$ | $0.8394409444 \times 10^{4}$ | $N_{6}$ | $-0.5944544662 \times 10^{-5}$ |
| $N_{2}$ | $-0.1890045259 \times 10^{4}$ | $N_{7}$ | $0.2715433932 \times 10^{-7}$ |
| $N_{3}$ | $-0.7282229165 \times 10^{1}$ | $N_{8}$ | $-0.4879535904 \times 10^{-10}$ |
| $N_{4}$ | $0.1022850966 \times 10^{-1}$ | $N_{9}$ | $0.5095360824 \times 10^{3}$ |
| $N_{5}$ | $0.5556063825 \times 10^{-3}$ |  |  |

*Coefficients are for temperature in degrees Kelvin, and pressure in atmospheres.

## CHAPTER 7

COMPARISONS OF THE P-p-T DATA TO
THE EQUATION OF STATE

Figures 3 through 241 illustrate the accuracy of the equation of state (22) in representing the available experimental data for nitrogen. In the determination of the equation of state, data sets were selected based on concordance among data from various experimenters in the same region of the $\mathrm{P}-\mathrm{p}-\mathrm{T}$ surface, and on relative agreement with trends established by reliable data defining adjacent regions. Data found to be in disagreement in the determination of preliminary equations of state are discussed in Appendix A. The P-p-T data set utilized in the calculation of the coefficients in Table 10 consisted of 1247 weighted data points from [8], [30], [9], [10], [31], [32], [14], [i9], [20], [22], [23], [24], and [36]. The remainder of the data illustrated in the figures are included for comparison.

Figures 3 through 130 are comparisons of the percent density deviation, $\left[\left(\rho_{\exp }-\rho_{\text {calc }}\right) / \rho_{\exp }\right] \times 100$, along approximate $i=\frac{t h e r m s}{}$ for data used in the determination of the coefficients in Table 10. The mantity $\rho_{\exp }$ represents the observed density reported by the experimenter at a particular temperature and pressure, and $\rho_{\text {calc }}$ is the density calculated from equation (22) for each experimental temperature and pressure. Figures 131 through 235 illustrate the density deviations of experimental data which were not used in the determination of the coefficients for equation (22). In addition to the data illustrated in these figures, the density deviations for some data points exceeded the value of 1 percent. Table 12 is a listing of these data including the density deviation of each point.

The equation of state generally shows agreement with $P-p-T$ data within the experimental uncertainty of the measured values, except in the vicinity of the critical point, in the low temperature liquid region, and in the high pressure supercritical region where experimental uncertainties are large. Table 13 lists the root mean square deviations in pressure and in density for the various $\mathrm{P}-\mathrm{p}-\mathrm{T}$ data sets. The following discussions apply to the data illustrated in Figures 3 through 235 and to that listed in Table 12.

## Data Near the Critical Point

The data of Friedman [10] (Figures 25 through 30), Weber [36] (Figures 120 through 125), and Kamerlingh Onnes and van Urk [16] (Figures 199 through 201) illustrate the imprecision of the data in the region of the critical point between temperatures of 120 K and 130 K . This is a difficult region for precise experimental measurements, and a difficult region for fitting the equation of state. The data of [16] were not incorporated in the development of the equation because they are limited to pressures between 35 and 63 atmospheres, and there are other data of at least equal precision in this region. Systematic deviations between the equation and the data appear to be present for isotherms above the critical temperature in the data of Canfield [8] and that of Crain [9]. This is evidenced between 30 and 60 atmospheres in Figures 3 and 4 for the data of Canfield at 133.1 K and 143.1 K , respectively, and in Figure 17 which illustrates a systematic deviation of nearly 0.5 percent at pressures between 40 and 70 atmospheres for the data of Crain at 143.1 K. With the exception of these systematic deviations the equation of state appears to fit the data within the experimental uncertainty of the measurements in this region.

## Low Temperature Liquid Data

The data of Cockett et al. [30] for the low temperature liquid are shown in Figures 9 through 16. The deviations are negative at temperatures below 105 K , and are positive at 110 K and above with the exception of one value at 120 K . The deviations for isotherms between 85 K and 115 K ars all within $\pm 0.5$ percent.

The data of Golubev and Dobrovolskii [32] are illustrated in Figures 39 through 48 including one supercritical isotherm in Figure 48. The data at 77.3 K and 78.1 K in Figures 39 and 40 illustrate an apparent systematic trend with deviations up to 0.5 percent at pressures above 400 atmospheres. Systematic deviations are evident in Figures 44 through 48 for temperatures between 98.2 K and 133.1 K , where the deviations at pressures below 100 atmospheres reach about +1.0 percent, and at pressures in excess of 400 atmospheres are as large as -0.5 percent.

The data of Gibbons [31] are illustrated in Figures 37 and 38. These data appear consistent with the equation of state for the two isotherms at 72.3 K and 77.9 K .

The density deviations of the equation of state from the data of Weber [36] are illustrated on isotherms in Figures 92 through 130. These data are also compared for approximate isochoric values between 9 and 28 moles/liter in Figures 236 through 241. (At 9.47 moles/liter the state is vapor, while all other isochores are for liquid values.) The isochoric density deviation plots show the minimum and maximum temperatures for each isochore. These data exhibit general agreament with the equation of state, al though the isochoric plots indicate a systeinatic deviation with a maxinum discreparcy of -2.4 percent for the 9.47 moles/liter vapor isochore and systematic trends are evident
in Figures 237 and 238 for the 11.2 and 16.0 moles/liter isochores, respectively. The data of [36] appear to be more precise than the other liquid data available for nitrogen.

The liquid data of Streett and Staveley [33] are illustrated in Figures 211 through 218 for isotherms between 77.4 K and 120.2 K . Systematic trends in the deviations are apparent in Figure 211 at 77.4 K and above 104 K in Figures 214 through 218, while the data at 90.6, 95.6, and 100.1 K appear to have a constant deviation from the equation of state. The data of Streett and Staveley indicate general agreement with the equation of $i$ tate although these points were not used in the least squares fit to determine the equation.

The data of Van Itterbeek and Verbeke [34] shown in Figures 227 through 231 for isotherms between 65 K and 91 K exhibit systematic deviations with a maximum of $\pm 0.5$ percent below 90.6 K . The data of [35] by the same authors illustrated in Figures 232 and 233 exhibit systematic deviations from the equation of up to 1 percent. The isotherms of [35] at 77.3 K and 90.3 K are not consistent witi the isotherms at 77.9 K and 90.6 K from [34]. The data of Van Itterbeek and Verbeke were not used in the development of the equation of $s$ tate.

## High Pressure Data

There is a lack of concordance among the data sets above 1000 atmospheres. In general, the equation of state developed here fits the data of Saurel [24] shown in Figures 84 through 91, and that of Robertson and Babb [23] illustrated in Figures 77 through 83, which were judged to be most accurate. The high pressure data of Malbrunot [18] and Malbrunot and Vodar [17] shown in Figures 180 through 197, are not in agreement with the equation of state or wi ih the selected data. In addition, there are inconsistencies between the data from [17] and [18], wich contain results from the same experimenters.

The data of Tsiklis and Polyakov [27] and Tsiklis [28] exhibit systematic deviations from the equation of $s$ tate of as much as 1 percent, as illustrated in Figures 222 through 226. The high pressure data of Benedict [7] are less precise than those of other authors as shown in Figures 157 through 168 , and were not used in the determination of the equation of state.


## - CANFIELD [8 ]

Density Deviations of Equation (22) from Data of References Indicated.

| 1.0 | FIGURE 10 |  |  | 90.0 K |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| 0 | 0 -00000 |  |  |  |  |  |
| $-1.0$ |  |  |  |  |  |  |
|  | 0.1 | 1. | 10. | 100. | 1000. | 10000. |

- CANFIELD
[8]
- COCKETT
[30]
Density Deviations of Equation (22) from Data of References Indicated.


| Figune | 12 |  | 100.0 K |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0 - 000000 |  |  |  |  |  |
| 0.1 | 1. | 10. | 100. | 1000. | 10000. |




- COCKETT

[30]

Density Deviations of Equation (22) from Data of References Indicated.

|  | 1.0 | FIGURE 15 |  |  | 115.0 K |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\square^{0_{0}}$ |  |  |
| $Z$ | -1.0 |  |  |  |  |  |  |
|  |  | 0.1 | 1. | 10. | 100. | 1000. | 10000. |
| ■ |  |  |  |  |  |  |  |
| $\xrightarrow{\text { H }}$ | 1.0 | FICURE | 16 |  | 120.0 K |  |  |
|  |  | $0^{\square} 0_{0_{0}}$ |  |  |  |  |  |
| $\stackrel{-}{-}$ |  |  |  |  |  |  |  |
| $\square$ | $-1.0$ |  |  |  |  |  |  |
| $\frac{0}{2}$ |  | 0.1 | 1. | 10. | 100. | 1000. | 10000. |



- COCKETT
[30]
- CRAIN
〔9 〕

Density Deviations of Equation (22) from Data of References Indicated.


PERCENT



- CRAIN
[9]
- FRIEDMAN
[10]

Density Deviations of Equation (22) from Data of References Indicated.



- FRIEDMAN [10]

Density Deviations of Equation (22) from Data of References Indicated.

## REPROC IC BILITY OF THE ORIGINAL PAGE IS POOR.


$\begin{array}{ll}E & 1.0 \\ \square & 0 \\ \square & -1.0\end{array}$ FICURE 29
126.1 K

0.1
1.
10.
10.
1000.
10000.


- FRIEUMAN [10]

Density Deviations of Equation (22) from Data of References Indicated.


- FRIEDMRN [10]

Derisity Deviations of Equation (22) from Data of References Indicated.


- FRIEDMAN
[10]
- GIBBONS
[3i]

Density Deviations of Equation (22) from Data of References Indicated.


- GOLUBEV [32]

Density Deviations of Equation (22) from Data of References Indicated.




- GCluseV
[32]
- HOLBORN
[14]
Density Deviations of Equation (22) from Data of References Indicated.

c HOLBORN
[14]
Density Deviations of Equation (22) from Data of References Indicated.

- HOLBORN
[14]
- MICHELS
[19]

Density Deviations of Equation (22) from Data of References Indicated.


- MICHELS [19]

Density Deviations of Equation (22) from Data of References Indicated.




- MICHELS [20]

Density Deviations of Equation (22) from Data of References Indicated.


- MICHELS
[20]
- OTTO
[22]

Density Deviations of Equation (22) from Data of References Indicated.

$\begin{array}{cc}\underset{L i}{\square} & 1.0 \\ \frac{\square}{\square} & 0 \\ \square & -1.0\end{array}$



- OTTO
[22]
Density Deviations of Equation (22) from Data of References Indicated.



FICURE 7
423.1 K

$\begin{array}{cc}Z & 1.0 \\ \underset{\sim}{L} & 0 \\ \square & -1.0\end{array}$


- Oito [22]
- ROBERTSON
[23]
Density Deviations of Equation (22) from Data of References Indicated.


FICLRE 81
573.4 K

0.1
1.
10
100.
1000. 10000.


- ROBERTSON [23]

Density Deviations of Equation (22) from Data of References Indicated.






- SRUREL [24]

Density Deviations of Equation (22) from Data of References Indicated.


- Saurel
[24]
- WEBER
〔36]

Density Deviations of Equation (22) from Data of References Indicated.



Density Deviations of Equation (22) from Data of References Indicated:


Density Deviations of Equation (22) from Data of References Indicated.



- WEEER
〔36]

Density Deviations of Equation (22) from Data of References Indicated.



- WEBER〔36]

Density Deviations of Equation (22) from Data of References Indicated.


- Weber [36]

Density Deviations of Equation (22) from Data of References Indicated.


$$
\text { FIGURE } 121
$$

122.0 K

PERCENT


- WEBER

〔36]

Density Deviations of Equation (22) from Data of References Indicated.


Density Deviations of Equation (22) from Data of References Indicated.



- RMRGRT [1 〕

Density Deviations of Equation (22) from Data of References Indicated.


Density Deviations of Equation (22) from Data of References Indicatect.


－AMAGAT
「2 コ
－bartlett
〔4 〕

Density Deviations of Equation（22）from Data of References Indicated．


- bartlett [4 コ

Density Deviations of Equation (22) from Data of References Indicated.



| 1.0 | FIGURE 150 |  |  | 293.3 K |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| 0 | 200 $0 \cdot 3$ |  |  |  |  |  |
| $-1.0$ |  |  |  |  |  |  |
|  | 0.1 | 1. | 10. | 100. | 1000. | 10000. |

- bartlett [5 ]

Density Deviations of Equation (22) from Data of References Indicated:•


- BENEDICT [6 ]

Density Deviations of Equation (22) from Data of References Indicated.


Density Deviations of Equation (22) from Data of References Indicated.:.


- BENEDICT
[7]

Density Deviations of Equation (22) from Data of References Indicated:


- BENEDICT
[7]

Density Deviations of Equation (22) from Data of References Indicated.


Density Deviations of Equation (22) from Data of References Indicated:


Density Deviatiors of Equation (22) from Data of References Indicatẹd.


Density Deviations of Equation (22) from Data of References Indicated,



- HOLBORN
[15]
- MALBRUNOT
[17]

Density Deviations of Equation (22) from Data of References Indicated.


## FIGURE 184

873.3 K




FIGURE 185
973.5 K


$\Delta$ MALBRUNOT [17]

Density Deviations of Equation (22) from Data of References Indicated.


- MRLBRLNOT
[17]
- malbrunot
〔18〕

Density Deviations of Equation (c2) from Data of References Indicated::


- malbrunot [18]

Density Deviations of Equation (22) from Data of References Indicated.


- mal bruitut
[18]
- MILLER
[21]

Density Deviations of Equation (22) from L.v: (f eferences Indicated:


Density Deviations of Equation (22) from Data of References Indicateḑa


$$
\begin{aligned}
& \square \\
& \square \\
& \square \\
& \square \\
& \square \\
& \square
\end{aligned}
$$




- ONNES
[16]

Density Deviations of Equation (22) from Data of References Indicated.



- ONNES
[16]

Density Deviations of Equation (22) from Data of References Indicated.

$\Delta$ STREETT
[33]
Density Deviations of Equation (22) from Data of References Indicated.


Density Deviations of Equation (22) from Data of References Indicated.


- TSIKLIS
[27]
- TSIKLIS
[28]

Density Deviations of Equation (22) from Data of References Indicated.


Density Deviations of Equation (22) from Data of References Indicated.


- ITTEREEEK [3\&

Density Deviations of Equation (22) from Data of References Indicated.


- ItTEREEEK
[34]
- VERSCHOTLE
[29]
- itierbeek
[35]
Density Deviations of Equation (22) from Data of References Indicicated.


Density Deviations of Equation (22) from Data of References Indicated.


PERGENT DENSITY DEVIATION



| FIGURE 239 |  |  |  | 18.7 molos/liter |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.0 | 120 K 140 K |  |  |  |  |
| 0 | 50 | 100 | 150 | 200 | 250 |

Density Deviations of Equation (22) from Isochoric Data of Weber [36].



Density Deviations of Equation (22) from Isochoric Data of Weber [36].

TABLE 12
P-p-T DATA WITH DENSITY DEVIATIONS IN EXCESS OF $\pm 1$ PERCENT

| Figure | Temperature (K) | Pressure ( atm ) | Density Deviation (Percent) | Reference |
| :---: | :---: | :---: | :---: | :---: |
| 3 | 133.14 | 40.74 | -1.11 | [8]* |
| 24 | 110.02 | 8.91 | -1.24 | [107* |
| 25 | 120.01 | 4.84 | -51.22 | [10] |
| 26 | 125.21 | 31.67 | -1.37 | [10]* |
| 27 | 125.73 | 32.12 | -1.99 | [10]* |
| 27 | 125.73 | 32.77 | -5.54 | [10]* |
| 27 | 125.73 | 31.66 | -1.43 | [10]* |
| 27 | 125.73 | 31.20 | -1.93 | [10]* |
| 30 | 126.17 | 33.17 | -1.43 | [10]* |
| 30 | 126.17 | 33.08 | -1.27 | [10]* |
| 30 | 125.17 | 33.46 | -1.09 | [10]* |
| 30 | 126.17 | 33.51 | -1.18 | [10]* |
| 123 | 128.00 | 36.03 | -2.39 | [36]* |
| 123 | 128.00 | 36.51 | 1.24 | [36]* |
| 124 | 128.00 | 36.52 | 1.14 | [36]* |
| 125 | 130.00 | 38.74 | -1.59 | [36]* |
| 126 | 132.00 | 41.43 | -1.15 | [36]* |
| 134 | 472.69 | 900.00 | 2.11 | [1] |
| 153 | 148.35 | 99.89 | -5.34 | [6] |
| 158 | 123.14 | 3423.53 | 1.17 | [7] |
| 159 | 148.15 | 5387.77 | 1.09 | [7] |
| 179 | 143.14 | 65.97 | 2.01 | [15] |
| 179 | 143.12 | 67.41 | 1.80 | [15] |
| 180 | 473.19 | 4145.07 | 1.18 | [17] |
| 181 | 573.22 | 986.92 | -1.66 | [17] |
| 181 | 573.22 | 1184.31 | -1.34 | [17] |
| 182 | 673.23 | 1184.31 | -1.43 | [17] |
| 182 | 673.23 | 1381.69 | -1.03 | [17] |
| 183 | 773.23 | 1184.31 | -1.65 | [i/] |
| 183 | 773.23 | 1381.69 | -2.08 | [17] |
| 183 | 773.23 | 1776.46 | -1.18 | [17] |
| 184 | 873.30 | 1184.31 | -1.91 | [17] |
| 184 | 873.30 | 1381.69 | -2.55 | [17] |
| 184 | 873.30 | 1579.08 | -2.66 | [17] |
| 184 | 873.30 | 1776.46 | -2.36 | [17] |
| 184 | 873.30 | 1973.85 | -1.94 | [17] |
| 184 | 873.30 | 2171.23 | -1.60 | [17] |
| 185 | 973.54 | 1184.31 | -2.59 | [17] |
| 185 | 973.54 | 1381.69 | -3.27 | [17] |
| 185 | 973.54 | 1579.08 | -3.00 | [17] |

TABLE 12--continued

| Figure | Temperature (K) | Pressure ( atm ) | Density Deviation (Percent) | Reference |
| :---: | :---: | :---: | :---: | :---: |
| 185 | 973.54 | 1776.46 | -2.70 | [17] |
| 185 | 973.54 | 1973.85 | -2.05 | [17] |
| 185 | 973.54 | 2171.23 | -1.56 | [17] |
| 185 | 973.54 | 2368.62 | -1. 25 | [17] |
| 185 | 973.54 | 2566.00 | -1.01 | [17] |
| 186 | 1073.82 | 1184.31 | -2.75 | [17] |
| 186 | 1073.82 | 1381.69 | -3.54 | [17] |
| 186 | 1073.82 | 1579.08 | -3.56 | [17] |
| 186 | 1073.82 | 1776.46 | -3.25 | [17] |
| 186 | 1073.82 | 1973.85 | -2.76 | [17] |
| 186 | 1073.82 | 2171.23 | -2.18 | [17] |
| 186 | 1073.82 | 2368.62 | -1.69 | [17] |
| 186 | 1073.82 | 2566.00 | -1.32 | [17] |
| 186 | 1073.82 | 2763.39 | -1.08 | [17] |
| 187 | 1174.10 | 789.54 | -2.24 | [17] |
| 187 | 1174.10 | 986.92 | -1.84 | [17] |
| 187 | 1174.10 | 1184.31 | -3.68 | [17] |
| 187 | 1174.10 | 1381.69 | -4.16 | [17] |
| 187 | 1174.10 | 1579.08 | -4.32 | [17] |
| 187 | 1174.10 | 1776.46 | -3.99 | [17] |
| 187 | 1174.10 | 1973.85 | -2.97 | [17] |
| 187 | 1174.10 | 2368.62 | -2.42 | [17] |
| 187 | 1174.10 | 2566.00 | -1.89 | [17] |
| 187 | 1174.10 | 2763.39 | -1.40 | [17] |
| 188 | 1274.39 | 789.54 | -4.30 | [17] |
| 188 | 1274.39 | 986.92 | -3.96 | [17] |
| 188 | 1274.39 | 1184.31 | -4.59 | [17] |
| 188 | 1274.39 | 1579.08 | -5.29 | [17] |
| 188 | 1274.39 | 1776.46 | -4.77 | [17] |
| 188 | 1274.39 | 1973.85 | -4.32 | [17] |
| 188 | 1274.39 | 2171.23 | -3.83 | [17] |
| 188 | 1274.39 | 2368.62 | -3.34 | [17] |
| 188 | 1274.39 | 2763.39 | -2.09 | [17] |
| 188 | 1274.39 | 2960.77 | -1.54 | [17] |
| 188 | 1274.39 | 3158.15 | -1.07 | [17] |
| 190 | 573.22 | 1000.00 | -1.51 | [18] |
| 191 | 673.23 | 1000.00 | -2.62 | [18] |
| 192 | 773.23 | 1000.00 | -7.66 | [18] |
| 192 | 773.23 | 1500.00 | -2.53 | [18] |
| 192 | 773.23 | 2000.00 | -1.60 | [18] |

TABLE 12--continued

| Figure | Temperature (K) | Pressure ( atm ) | Density Deviation (Percent) | Reference |
| :---: | :---: | :---: | :---: | :---: |
| 193 | 873.30 | 1000.00 | -6.94 | [18] |
| 193 | 873.30 | 1500.00 | -3.58 | [18] |
| 193 | 873.30 | 2000.00 | -2.22 | [18] |
| 193 | 873.30 | 2500.00 | -1.30 | [18] |
| 194 | 973.54 | 1000.00 | -7.12 | [18] |
| 194 | 973.54 | 1500.00 | -4.48 | [18] |
| 194 | 973.54 | 2000.00 | -2.47 | [18] |
| 194 | 973.54 | 2500.00 | -1.34 | [18] |
| 15 | 1073.82 | 1000.00 | -8.72 | [18] |
| 195 | 1073.82 | 1500.00 | -5.51 | [18] |
| 195 | 1073.82 | 2000.00 | -3.48 | [18] |
| 195 | 1073.82 | 2500.00 | -2.08 | [18] |
| 195 | 1073.82 | 3000.00 | -1.05 | [18] |
| 196 | 1174.10 | 1000.00 | -10.00 | [18] |
| 196 | 1174.10 | 1500.00 | -7.22 | [18] |
| 196 | 1174.10 | 2000.00 | -4.26 | [18] |
| 196 | 1174.10 | 2500.00 | -2.34 | [18] |
| 196 | 1174.10 | 3000.00 | -1.16 | [18] |
| 197 | 1274.40 | 1000.00 | -12.47 | [18] |
| 197 | 1274.40 | 1500.00 | -8.86 | [18] |
| 197 | 1274.40 | 2000.00 | -5.25 | [18] |
| 197 | 1274.40 | 2500.00 | -3.00 | [18] |
| 197 | 1274.40 | 3000.00 | -1.59 | [18] |
| 199 | 124.59 | 30.92 | 67.10 | [16] |
| 200 | 126.85 | 34.44 | 13.68 | [16] |
| 201 | 126.85 | 34.44 | 14.28 | [16] |
| 201 | 126.85 | 34.47 | 12.85 | [16] |
| 201 | 126.85 | 34.47 | 13.14 | [16] |
| 201 | 126.85 | $34.6 \%$ | 7.65 | [16] |
| 201 | 126.85 | 35.13 | 3.41 | [16] |
| 201 | 126.85 | 36.49 | 1.07 |  |
| 202 | 128.71 | 38.79 | 2.10 | [16] |
| 203 | 131.64 | 44.25 | 2.04 | [16] |
| 205 | 152.00 | 54.25 | 1.97 | [16] |
| 207 | 192.12 | 54.60 | 1.27 | [16] |
| 209 | 249.58 | 47.33 | 1.04 | [16] |
| 210 | 273.19 | 35.98 | 1.43 | [16] |
| 215 | 104.70 | 480.95 | -2.17 | [33] |
| 219 | 323.14 | 7500.00 | 1.06 | [28] |
| 219 | 323.14 | 8000.00 | 1.16 | [28] |

TABLE 12--continued

| Figure | Temperature <br> $(\mathrm{K})$ | Pressure <br> $(\mathrm{atm})$ | Density Deviation <br> $($ Percent $)$ | Reference |
| :--- | :---: | :---: | :---: | :---: |
| 219 | 323.14 | 8500.00 | 1.17 | $[28]$ |
| 219 | 323.14 | 9000.00 | 1.22 | $[28]$ |
| 219 | 323.14 | 9500.00 | 1.26 | $[28]$ |
| 226 | 673.23 | 10000.00 | -1.46 | $[27]$ |
| 226 | 673.23 | 9500.00 | -1.24 | $[27]$ |
| 232 | 90.26 | 815.21 | 1.21 | $[35]$ |
| 233 | 77.31 | 555.73 | 1.21 | $[35]$ |
| 233 | 77.31 | 417.14 | 1.25 | $[35]$ |

NOTE: See Figures 3 through 235.

* $p-\rho-T$ data used in determining equation of state (22).

TABLE 13

## ROOT MEAN SQUARE DEVIATIONS IN DENSITY AND PRESSURE OF P-p-T DATA FROM THE EQUATION OF STATE

| Source | RMS Deviation in Density (percent) | RMS Deviation in Pressure (percent) |
| :---: | :---: | :---: |
| Data used in the Determination of the Equation of State |  |  |
| Canfield [8] | 0.14 | 0.22 |
| Cockett et al. [30] | 0.25 | 7.12 |
| Crain [9] | 0.08 | 0.11 |
| Friedman [10] | 0.24 | 0.14 |
| Golubev and Dobrovolskii [32] | 0.35 | 5.52 |
| Gibbons [31] | 0.16 | 7.90 |
| Holborn and Otto [14] | 0.07 | 0.97 |
| Michels et al. [19] | 0.02 | 0.02 |
| Michels et al. [20] | 0.05 | 0.15 |
| Otto et al. [22] | 0.01 | 0.01 |
| Robertson and Babb [23] | 0.08 | 0.22 |
| Saurel [24] | 0.07 | 0.09 |
| Weber [36] | 0.30 | 0.84 |
| Data not used in the Determination of the Equation of State |  |  |
| Amagat [1] | 0.17 | 0.21 |
| Amagat [2] | 0.14 | 0.40 |
| Bartlett et al. [4] | 0.32 | 0.48 |
| Bartlett et al. [5] | 0.15 | 0.42 |
| Denedict [6] | 0.31 | 3.29 |
| Benedict [7] | 0.24 | 1.34 |
| Hali and Canfield [11] | 0.42 | 0.36 |
| Heuse and Otto [12] | 0.01 | 0.01 |
| Holborn and 0tto [13] | 0.08 | 0.08 |
| Holborn and Otto [15] | 0.42 | 0.33 |
| Malbrunot [18] | 0.46 | 0.89 |
| Malbrunot and Vodar [17] | 0.40 | 0.83 |
| Miller et al. [21] | 0.26 | 0.30 |
| Kamerlingh Onnes and van Jrk [16] | 0.20 | 0.14 |
| Streett and Staveley [33] | 0.31 | 28.90 |
| Tsiklis [28] | 0.47 | 1.81 |
| Tsikl is and Polyakov [27] | 0.29 | 1.08 |
| Van Itterbeek and Verbeke [34], [35] | 0.37 | 19.63 |
| Verschoyle [29] | 0.13 | 0.14 |

## CHAPTER 8

## EXTRAPOLATION OF THE EQUATION OF STATE

The coefficierts of the equation of state (22) in Table 10 were determined by a least squares fit to selected, weighted data as described in Chapter 5. The data for the saturated liquid of [37] and [38] and the freezing line data of [39] were excluded in the determination of these coefficients because the data are not sufficient for inclusion as $P$ - $\rho-T$ points (i.e., the reported data are temperature and density, and the pressure must be determined from an independent measurement of the vapor pressure or the melting pressure). It is of interest to examine the extrapolation of the equation of state determined by a fit to data in the single phase region to the saturated liquid and saturated solid liries.

The comparison of the raturated liquid data of [37] and [38] was made by using the vapor pressure equation (29) with coefficients from Table 11 to calculate the pressure corresponding to the data temperature. The equation of state (22) was then solved for the density corresponding to the saturation temperature and pressure determined in this manner. The percent density deviation was calculated as $\left[\left(\rho_{\exp }-\rho_{\text {calc }}\right) / \rho_{\text {exp }}\right] \times 100$, where $\rho_{\exp }$ is the experimental density and $\rho_{c a l c}$ is the density calculated from the equation of state at the saturation temperature and pressure. This comparison is illustrated in Figure 242. The deviations of the equation of state from liquid P-p-T data at the vapor pressure are systematic. The calculated values are greater than the experimental values except at 105 K where the density deviation is +0.006 percent. These comparisons are dependent upon the vapor pressure equation used.

The extrapolation of the equation of state to the melting curve was made by employing the Simon melting curve equation as reported by Grilly and Mills [39] with appropriate temperature corrections. The equation used to calculate the pressure at the experimental temperature corresponding to the melting density data was

$$
\begin{equation*}
P=a+b T^{C} \tag{30}
\end{equation*}
$$

where

$$
a=-1579.08
$$

$$
b=0.926302
$$

$$
c=1.795
$$

Densities calculated from the equation of state at the melting temperature and pressure are compared to the measured values of Grilly and Mills [39] in Figure 243.

In addition to the extrapolation of the equation in the liquid range it is also desirable to extrapolate che vapor data to higher and lower temperatures. At both high and low temperatures, it is notable that the terms in the equation of state which contribute the most to the pressure calculated by the equation are the ideal gas term and the terms in the temperature polynomial which represent the second virial coefficient of equation (22) when this equation is expandad to the virial form. The contrioution for the ideal gas and second virial terms taken from equation (22) is as follows:

$$
\begin{equation*}
\text { Percent } P=\left(P / P_{\text {eqn }}\right) \times 100 \tag{31}
\end{equation*}
$$

where
$P$ is the contribution to the calculated pressure attributed to the sum of the first nine terms of the equation of state $\left[P=\rho R T+B(T) \rho^{2}\right], B(T)$
is given in equation (33) below,
and $P_{\text {eqn }}$ is the pressure calculated from equation (22) at specified temperature, $T$, and density, $\rho$.

Figures 244 and 245 illustrate the contribution of these terms. Figure 246 is a similar comparison showing the percentage contribution of the first virial (ideal gas) term for the low temperature vapor. The contribution here is determined from (22) as:

$$
\begin{equation*}
\text { Percent } P=\left(\rho R T / P_{\text {eqn }}\right) \times 100 \tag{32}
\end{equation*}
$$

where
Percent $P$ is the percentage contribution of the ideal gas term to the total pressure calculated from equation (22), and $\rho, T$, and $P_{\text {eqn }}$ are as defined above.

Examination of Figures 244, 245, and 246 indicates that the extrapolation of the equation of $s$ tate for the vapor at high and low temperatures is reasonable and limited only by the accuracy of the second virial coefficient as predicted by equation (22), i.e.,

$$
\begin{equation*}
B(T)=N_{1} T+N_{2} T^{\frac{1}{2}}+N_{3}+N_{4} / T^{\frac{1}{2}}+N_{5} / T+N_{6} / T^{2}+N_{7} / T^{3}+N_{8} / T^{4} \tag{33}
\end{equation*}
$$

Figure 247 is a comparison of values from equation (33) with the experimental second virial coefficients from [9], [10], [19], [22], [59], [60], and [61]. Values of the second virial cof.ificient determined by the use of the Lennard-Jones potential function with parameters from Ziegler and Mullins [122] for temperatures from 70 K to 200 K agree with the calculated values from (33) within the accuracy of the plot in Figure 247.

With the apparent accuracy of the second virial coefficient from equation (22), Figure 244 suggests that it is reasonable to extrapolate the equa-
tion of state frem 1000 K to 2000 K for pressures to 300 atmospheres. Figures 245 and 246 demonstrate that equation (22) may be extrapolated to lower temperatures for the gas, since the pressures below the range for which data are available are very low.




Figure 244.--Percentage Contribution of First and Second Virial Terms to Pressure from Eqn. (22) at High Temperature.


Figure 245.--Percentage Contribution of First and Second Virial Terms to Pressure from Eqn. (22) at Low Temperature.


Figure 246.--Percentage Contribution of First Virial (ideal gas) Term to Pressure from Eqn. (22) at Low Teriperature.


Figure 247.--Comparison of Second Virial Coefficieint from Equation (22) to Experimental Values from the Sources Indicated.

## CHAPTER 9

## IDEAL GAS HEAT CAPACITY

In the earlier work of Coleman and Stewart [95], ideal gas heat capacity values were calculated from an equation that was fitted to preliminary results of a calculation by Woolley [86]. New values for the ideal gas heat capacity are now available from [84] and [85]. These values appear to be the most accurate to date, and will be used for the tables produced in this work.

The equation suggested by Barieau [87], and Barieau and Tully [88], which was used previously in [95] and [117], has been fitted to the data from [84]. This equation is

$$
\begin{align*}
& C_{p}^{0} / R=N_{1} / T^{3}+N_{2} / T^{2}+N_{3} / T+N_{4}+N_{5} T+N_{6} T^{2}+N_{7} T^{3} \\
& \quad+N_{8} u^{2} e^{u} /\left(e^{u}-1\right)^{2} \tag{34}
\end{align*}
$$

where
$C_{p}^{0}$ is the ideal gas heat capacity,
T the temperature,
and $u=N_{g} / T$.
The coefficients for equation (34) with values of $T$ in degrees Kelvin are given in Table 14.

TABLE 14
COEFFICIENTS FOR THE IDEAL HEAT CAPACITY EQUATION (34)
FOR NI TROGEN

|  |  |  |  |
| :---: | :---: | :---: | :---: |
| Coefficients | Numerical Value | Coefficients | Numerical Value |
| $N_{1}$ | $-0.7352104012 \times 10^{3}$ | $N_{6}$ | $0.1746508498 \times 10^{-7}$ |
| $N_{2}$ | $0.3422399804 \times 10^{2}$ | $N_{7}$ | $-0.3568920335 \times 10^{-11}$ |
| $N_{3}$ | -0.5576482846 | $N_{8}$ | $0.1005387228 \times 10^{1}$ |
| $N_{4}$ | $0.3504042283 \times 10^{1}$ | $N_{9}$ | 3353.4061 |
| $N_{5}$ | $-0.1733901851 \times 10^{-4}$ |  |  |

Table 15 is a listing of the ideal gas heat capacity values $\left(C_{p}^{0} / R\right)$ as a function of temperature as reported in [84]. A comparison between these values from [84] and values calculated from equation (34) indicates exact agreement within the number of figures reported, except above 1200 K . Above 1200 K the differences between the values from equation (34) and from [84] is no more than $\pm .0001$. Equation (34) with coefficients from Table 14 has been used in the calculation of the property tables in this work.

TABLE 15
VALUES OF IDEAL GAS HEAT CAPACITY, $C_{p}^{0} / R$,
FROH BAEHR ET AL. [84]

| Temperature (K) | $C_{p}^{0} / R$ | Temperature (K) | $C_{p}^{0} / R$ |
| :---: | :---: | :---: | :---: |
| 50.0 | 3.4999 | 450.0 | 3.5308 |
| 60.0 | 3.4998 | 460.0 | 3.5349 |
| 70.0 | 3.4998 | 470.0 | 3.5392 |
| 80.0 | 3.4997 | 480.0 | 3.5438 |
| 90.0 | 3.4997 | 490.0 | 3.5487 |
| 100.0 | 3.4996 | 500.0 | 3.5538 |
| 110.0 | 3.4996 | 510.0 | 3.5591 |
| 120.0 | 3.4995 | 520.0 | 3.5647 |
| 130.0 | 3.4995 | 530.0 | 3.5705 |
| 140.0 | 3.4994 | 540.0 | 3.5765 |
| 150.0 | 3.4994 | 550.0 | 3.5828 |
| 160.0 | 3.4994 | 560.0 | 3.5892 |
| 170.0 | 3.4993 | 570.0 | 3.5958 |
| 180.0 | 3.4993 | 580.0 | 3.6026 |
| 190.0 | 3.4992 | 590.0 | 3.6095 |
| 200.0 | 3.4992 | 600.0 | 3.6166 |
| 210.0 | 3.4992 | 610.0 | 3.6239 |
| 220.0 | 3.4992 | 620.0 | 3.6312 |
| 230.0 | 3.4992 | 630.0 | 3.6387 |
| 240.0 | 3.4992 | 640.0 | 3.6463 |
| 250.0 | 3.4993 | 650.0 | 3.6539 |
| 260.0 | 3.4994 | 660.0 | 3.6617 |
| 270.0 | 3.4995 | 670.0 | 3.6695 |
| 280.0 | 3.4998 | 680.0 | 3.6774 |
| 290.0 | 3.5001 | 630.0 | 3.6854 |
| 300.0 | 3.5006 | 700.0 | 3.6934 |
| 310.0 | 3.5011 | 710.0 | 3.7017 |
| 320.0 | 3.5018 | 720.0 | 3.7095 |
| 330.0 | 3.5027 | 730.0 | 3.7176 |
| 340.0 | 3.5038 | 740.0 | 3.7257 |
| 350.0 | 3.5050 | 750.0 | 3.7338 |
| 360.0 | 3.5065 | 760.0 | 3.7419 |
| 370.0 | 3.5081 | 770.0 | 3.7500 |
| 380.0 | 3.5101 | 780.0 | 3.7581 |
| 390.0 | 3.5122 | 790.0 | 3.7662 |
| 400.0 | 3.5147 | 800.0 | . 3.7742 |
| 410.0 | 3.5174 | 810.0 | 3.7822 |
| 420.0 | 3.5203 | 820.0 | 3.7902 |
| 430.0 | 3.5235 | 830.0 | 3.7982 |
| 440.0 | 3.5270 | 840.0 | 3.8061 |

TABLE 15--continued

| Temperature <br> $(K)$ | $C_{p}^{0} / R$ | Temperature <br> $(K)$ | $C_{p}^{0} / R$ |
| :---: | :---: | :---: | :---: |
| 850.0 | 3.8139 | 1250.0 | 4.0724 |
| 860.0 | 3.8217 | 1300.0 | 4.0966 |
| 870.0 | 3.8295 | 1350.0 | 4.1192 |
| 880.0 | 3.8372 | 1400.0 | 4.1404 |
| 890.0 | 3.8448 | 1450.0 | 4.1601 |
| 900.0 | 3.8524 | 1500.0 | 4.1786 |
| 910.0 | 3.8599 | 1550.0 | 4.1959 |
| 920.0 | 3.8674 | 1600.0 | 4.2120 |
| 930.0 | 3.8748 | 1650.0 | 4.2271 |
| 940.0 | 3.8894 | 1700.0 | 4.2413 |
| 950.0 | 3.8966 | 1750.0 | 4.2546 |
| 960.0 | 3.9037 | 1800.0 | 4.2671 |
| 970.0 | 3.9107 | 1850.0 | 4.2789 |
| 980.0 | 3.9177 | 1900.0 | 4.2899 |
| 990.0 | 3.9246 | 1950.0 | 4.3003 |
| 1000.0 | 3.9579 | 2000.0 | 4.3101 |
| 1050.0 | 3.9893 |  |  |
| 1100.0 | 4.0188 |  |  |
| 1150.0 | 4.0465 |  |  |
| 1200.0 |  |  |  |

## CHAPTER 10

## DERIVED THERMODYNAMIC PROPERTIES

The values of entropy, enthalpy, internal energy, and heat capacity at various state points are calculated from the pressure-explicit equation of state (22), and the ideal gas heat capacity equation (34). The vapor pressure equation (29) and the Simon meiting curve equation (30) were used to identify the temperature of the phase changes from solid to liquid, and liquid to vapor, respectively, for each isobar. The integral representations for the properties are continuousiy integrated through the two-phase region to calculate properties in the liquid range. This is made possible by the fitting procedures employed in the development of the equation of state as described in Chapter 5 in which the conditions for two-phase equilibrium were included in the least squares determination of the coefficients for the equation of state (22). The thermodynamic formulations for the calculation of the thermodynamic property tables of Appendix E were taken from [118]. These relations are summarized in the following paragraphs. Functions for the integrals and derivatives of the equation of state required to perform these calculations are given in Appendix D.

The entropy of any thermodynamic state was calculated from

$$
\begin{align*}
& S(T, \rho)=S_{T_{0}}^{0}+\int_{T_{0}}^{T}\left(C_{p}^{0} / T\right) d T-R \ln (R T \rho) \\
& \quad+\int_{0}^{\rho}\left[R / \rho-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T} d \rho \tag{35}
\end{align*}
$$

The ideal gas specific heat, $C_{p}^{0}$, is from equation (34). The reference entropy of the ideal gas at $T_{0}=298.15 \mathrm{~K}$ and $P_{0}=1$ atmosphere, $S_{T_{0}}^{0}=191.502$ $\pm 0.025$ joules/mole-K is taken from [94]. The finctions for evaluation of the integrals $\int\left(C_{p}^{0} / T\right) d T$ and $\int\left[(R / \rho)-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T}$ are given in Appendix $D$. The functions for the isochore derivative ( $\sigma P / \partial T)_{\rho}$ of the equation of state are included in Appendix $D$.

The enthalpy of any state ma; be calculated from

$$
\begin{align*}
H(T, \rho) & =H_{T_{0}}^{0}+T \int_{0}^{\rho}\left[\left(P / T \rho^{2}\right)-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T} d \rho \\
& +(P-\rho R T) / \rho+\int_{T_{0}}^{T} C_{p}^{0} d T . \tag{36}
\end{align*}
$$

However, it is convenient to replace the first integral term in (36) as follows:

$$
\begin{align*}
& T \int_{0}^{\rho}\left[\left(P / T \rho^{2}\right)-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T} d \rho \\
& \quad \equiv T \int_{0}^{\rho}\left[(R / \rho)-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T} d \rho \\
& \quad+\int_{0}^{\rho}\left[\left(P / \rho^{2}\right)-(R T / \rho)\right]_{T} d \rho \tag{37}
\end{align*}
$$

By substitution of the identity of (37) in equation (36), the expression for enthalpy is given as

$$
\begin{align*}
& H(T, \rho)=H_{T_{0}}^{0}+T \int_{0}^{0}\left[(R / \rho)-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T} d \rho \\
& +\int_{0}^{\rho}\left[\left(P / \rho^{2}\right)-(R T / \rho)\right]_{T} d \rho+(P-\rho R T) / \rho \\
& +\int_{T_{0}}^{T} C_{p}^{0} d T . \tag{38}
\end{align*}
$$

The reference enthalpy of the ideal gas at $T_{0}=298.15 \mathrm{~K}$ of $H_{T_{0}}^{0}=8669$ $\pm 3$ joules/mole was taken from the value of ( $H^{0}-H_{0}^{0}$ ) in [94] with $H_{0}^{0}=0.0$. The evaluations of the integrals and isochore derivative are given in Appendix $D$. The internal energy of a fluid state was calculated from

$$
\begin{equation*}
U(T, \rho)=H(T, p)-P / \rho . \tag{39}
\end{equation*}
$$

The specific heat at constant volume, $C_{v}$, of liquid and gas phase points was calculated using the relation

$$
\begin{equation*}
C_{v}(T, \rho)=\left(C_{p}^{0}-R\right)-\int_{0}^{\rho}\left(T / \rho^{2}\right)\left[\left(\partial^{2} P ; \partial T^{2}\right)_{\rho}\right] d \rho \tag{40}
\end{equation*}
$$

where $C_{p}^{0}$ at temperature, $T$, is calculated from equation (34). The specific heat at constant pressure, $C_{p}$, is given by

$$
\begin{equation*}
C_{p}(T, \rho)=C_{V}(T, \rho)+\left[\left(T / \rho^{2}\right)(\partial D / \partial T)_{\rho}^{2} /(\partial P / \partial \rho)_{T}\right] \tag{41}
\end{equation*}
$$

It is notable that the calculation of properties from the equation developed in this work is considerably simplified from the prior methods of [95] and [118] by the continuous integration along isotherms through the two phase region due to the imposing of the requirements for phase equilibrium in the determination of the equa.tion of state as suggested in [92].

A sample table of thermodynamic properties of nitrogen illustrating the results of the property calculations outlined above is presented in Appendix E. This appendix also includes a table of properties of the saturated liquid and vapor states on two degree intervals between the triple point and the critical point.

## CHAPTER 11

## COMPARISONS OF THE EQUATION OF STATE WITH DERIVED THERMODYNAMIC DATA

Experimental measurements of properties of nitrogen in addition to the P-p-T data are available for comparison to values calculated using the equation of state developed in this work. Comparisons of the experimental specific heats, latent heats of vaporization, enthalpies, and sonic velocities caiculated using the equation of state (22) are reported here. The thermodynamic property formulations used in the calculation of various properties from the єquation of state are presented in Chapter 10.

## Calculated Heat Capacity Values

Values of $C_{p}$ and $C_{v}$ for nitrogen calculated by integration along isotherms using equation (22) with cuefficients from Table 10 are illustrated in Figures 248 and 249 for isobars of $1,10,50,100$, and 400 atmospheres. The behavior of the calculated values of $C_{v}$ below 75 K as indicated in Figure 249 is questionable.

## Comparisons of the Specific Heat Data

Comparisons of isobaric heat capacity values calculated from the equation of state (22) and the ideal gas heac capacity equation (34) to measured values from [54] and [55] are given in Tables 16 and 17, respective?y. The measurements reported by Faulkner [51] are included in the table of values reported by Jones [53]. The data of Jones from [53] including the values from [51] are a!so included in the measured values reported in [55], el $\ddagger$ minating the necessity for separate comparisons to the data of [51] and [53].

 WITH VALUES CALCULATED FROM THE EQUATION OF STATE (22) AND THE IDEAL GAS HEAT CAPACITY EQUATION (34)

| Temperature (K) | Pressure ( atm ) | $\begin{gathered} C_{p}[54] \\ \text { (joules/mole-K) } \end{gathered}$ | $C_{p}[54]-C_{n}$ (joules/mole-K) |
| :---: | :---: | :---: | :---: |
| 303.1 | 1 | 28.94 | -0.22 |
| 303.1 | 50 | 31.03 | -0.31 |
| 303.1 | 100 | 33.17 | -0.20 |
| 303.1 | 200 | 36.18 | -0.10 |
| 303.1 | 300 | 37.44 | -0.22 |
| 303.1 | 400 | 37.98 | -0.13 |
| 303.1 | 500 | 38.19 | 0.02 |
| 303.1 | 600 | 38.27 | 0.17 |
| 303.1 | 700 | 38.36 | 0.35 |
| 323.1 | 1 | 28.98 | -0.18 |
| 323.1 | 100 | 32.33 | -0.40 |
| 323.1 | 200 | 34.84 | -0.41 |
| 323.1 | 300 | 36.43 | -0.16 |
| 323.1 | 400 | 36.89 | -0.26 |
| 323.1 | 500 | 37.06 | -0.28 |
| 323.1 | 600 | 37.10 | -0.27 |
| 323.1 | 700 | 37.19 | -0.15 |
| 323.1 | 800 | 37.23 | -0.05 |
| 373.2 | 1 | 29.06 | -0.14 |
| 373.2 | 50 | 30.19 | -0.32 |
| 373.2 | 100 | 31.32 | -0.38 |
| 373.2 | 200 | 33.17 | -0.38 |
| 373.2 | 300 | 34.46 | -0.23 |
| 373.2 | 400 | 34.97 | -0.38 |
| 373.2 | 500 | 35.13 | -0.56 |
| 373.2 | 600 | 35.30 | -0.57 |
| 373.2 | 700 | 35.39 | -0.57 |
| 398.2 | 1 | 29.10 | -0.14 |
| 398.2 | 50 | 30.15 | -0.22 |
| 398.2 | 100 | 30.99 | -0.40 |
| 398.2 | 200 | 32.50 | -0.49 |
| 398.2 | 300 | 33.54 | -0.50 |
| 398.2 | 400 | 34.21 | -0.47 |
| 398.2 | 500 | 34.59 | -0.47 |
| 398.2 | 600 | 34.76 | -0.52 |

TABLE 16--continued

| Temperature <br> $(K)$ | Pressure <br> $(\mathrm{atm})$ | $c_{p}[54]$ <br> (joules/mole-K) | $c_{p}[54]-c_{p_{c a l c}}$ <br> (joules/mole-K) |
| :---: | :---: | :---: | :---: |
| 398.2 | 700 | 34.97 | -0.44 |
| 423.2 | 1 | 29.15 | -0.15 |
| 423.2 | 50 | 30.11 | -0.16 |
| 423.2 | 100 | 30.82 | -0.34 |
| 423.2 | 200 | 32.08 | -0.49 |
| 423.2 | 300 | 33.04 | -0.48 |
| 423.2 | 400 | 33.58 | -0.56 |
| 423.2 | 500 | 34.04 | -0.50 |
| 423.2 | 600 | 34.34 | -0.45 |
| 423.2 | 700 | 34.55 | -0.39 |

TABLE 17
COMPARISONS OF HEAT CAPACITY DATA OF MAGE ET AL. [55] WITH VALUES CALCULATED FROM THE EQUATION OF STATE (22) AND THE IDEAL GAS HEAT CAPACITY EQUATION (34)

| Temperature Range (K) | Pressure ( atm ) | $\begin{gathered} C_{p}[55] \\ \text { (joules/mole-K) } \end{gathered}$ | $\begin{aligned} & C_{p}[55]-C_{P_{c a l c}} \\ & (\text { joules/mole-K) } \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| 268.3-279.6 | 10.0 | 29.58 | -0.09 |
| 222.7-233.9 | 10.0 | 29.87 | -0.13 |
| 194.3-205.0 | 10.0 | 30.23 | -0.17 |
| 166.6-177.7 | 10.0 | 31.02 | -0.06 |
| 267.7-279.0 | 20.0 | 30.19 | -0.07 |
| 222.7-233.9 | 20.0 | 30.85 | -0.11 |
| 194.3-205.3 | 20.0 | 31.62 | -0.20 |
| 166.6-177.6 | 20.0 | 33.53 | 0.05 |
| 116.5-119.2 | 27.2 | 94.76 | 2.48 |
| 122.5-124.7 | 33.6 | 166.32 | 25.25 |
| 122.5-125.6 | 33.6 | 265.07 | 99.49 |
| 122.5-125.7 | 33.6 | 496.48 | 323.99 |
| 122.5-128.0 | 33.6 | 439.22 | -1.38 |
| 122.5-153.0 | 33.6 | 128.31 | -0.35 |
| 267.8-279.0 | 40.0 | 31.35 | -0.09 |
| 222.7-234.0 | 40.0 | 32.86 | -0.19 |
| 194.3-205.3 | 40.0 | 34.98 | -0.08 |
| 166.6-177.7 | 40.0 | 39.85 | -0.04 |
| 119.3-125.1 | 40.0 | 96.50 | 0.81 |
| 267.8-279.2 | 80.0 | 33.67 | -0.04 |
| 222.8-234.1 | 80.0 | 37.19 | 0.07 |
| 194.3-205.3 | 80.0 | 42.32 | -0.15 |
| 166.6-177.7 | 80.0 | 57.19 | -0.72 |
| 119.3-125.0 | 80.0 | 66.63 | -0.23 |
| 267.8-279.0 | 136.1 | 36.48 | 0.06 |
| 222.9-234.2 | 136.1 | 41.78 | -0.06 |
| 194.3-205.4 | 136.1 | 49.36 | -0.16 |
| 166.6-177.6 | 136.1 | 61.38 | -0.13 |
| 146.0-148.0 | 136.1 | 64.90 | 0.35 |
| 146.0-150.3 | 136.1 | 65.17 | 0.40 |
| 146.0-154.6 | 136.1 | 65.58 | 0.49 |
| 146.0-156.4 | 136.1 | 65.51 | 0.41 |
| 126.9-129.1 | 136.1 | 59.82 | 0.27 |
| 126.9-131.3 | 136.1 | 60.23 | 0.41 |
| 126.9-135.4 | 136.1 | 60.85 | 0.51 |
| 119.3-125.1 | 136.1 | 58.01 | -0.20 |

The heat capacities reported in Table 16 agree with the values calculated from the equation of state generally within 1 percent, while the data of Mage et al. [55] exhibit an average deviation of less than 0.5 percent except in the region of the critical point where one point shows a deviation of 65.3 percent. This behavior of calculated $C_{p}$ values reflects the imprecision of the experimental data and the fitting problems in the critical region.

Comparisons of the isochoric heat capacity values, $C_{v}$, calculated from the equation of state (22) and the ideal gas heat capacity equation (34) to measured values along the critical isochore published by Voronel et al. [56] are given in Table 18. (The value of the critical density determined in this work is 11.21 moles/liter while that of [56] is 11.1 moles/liter.)

The calculated values of $C_{v}$ do not exhibit the large increase in value near the critical point that is evident in the data of [56], and no attempt was made to introduce this behavior into the equation of state. Although experiments have shown that $C_{v}$ does behave in the manner indicated by [56], the few measurements of the properties of nitrogen near the critical point now available do not appear to be sufficient to provide for the correct characteristics of second derivatives of an equation of state determined by a least squares fit.

It should be noted that the data at temperatures below 126.20 K reported in [56] are for the two phase fluid. Above the critical temperature up to 135 K the calculated values of $C_{V}$ do not exhibit the behavior indicated by the data of [56]. The range of densities for which this second derivative behavior should be found for nitrogen is unknown since the $C_{v}$ values reported in [56] are for a single density of 11.21 moles/liter.

## Comparisons of Latent Heat Data

Furukawa and McCoskey [52] have published measured latent heats of vaporization at low temperatures ( $67 \mathrm{~K}-78 \mathrm{~K}$ ), and Jones [53] has presented five measurements of the latent heat of nitrogen for the range from 119 K to 124 K . The comparisons of calculated values from equations (22) and (29) to these measured values are given in Table 19. The data of [52] and the calculated values show an agreement within 0.7 percent while that of [53] exhibits deviations of up to 2.3 percent from the calculated values at temperatures near the critical temperature.

TABLE 18
COMPARISONS OF ISOCHORIC HEAT CAPACITY DATA AT 11.1 MOLES/LITER OF VORONEL ET AL. [56] WITH VALUES CALCULATED FROM THE EQUATION OF STATE (22) AND THE IDEAL GAS HEAT CAPACITY EQUATION (34)

| Temperature (K) | $\begin{gathered} C_{V}[56] \\ \text { (joules/mole-K) } \end{gathered}$ | $\begin{gathered} c_{v_{\text {calc }}} \\ \text { (joules/mole-K) } \end{gathered}$ |
| :---: | :---: | :---: |
| 105.877 | 83.1 | 39.6 |
| 106.206 | 8 c .6 | 39.4 |
| 109.443 | 84.0 | 37.5 |
| 117.872 | 95.5 | 33.5 |
| 121.896 | 105.6 | 32.1 |
| 122.352 | 106.8 | 31.9 |
| 122.841 | 108.8 | 31.7 |
| 123.329 | 111.5 | 31.6 |
| 123.817 | 114.0 | 31.4 |
| 124.298 | 117.5 | 31.3 |
| 124.743 | 124.9 | 31.1 |
| 124.749 | 120.7 | 31.1 |
| 125.195 | 126.2 | 31.0 |
| 125.628 | 136.6 | 30.9 |
| 125.847 | 142.1 | 30.8 |
| 125.931 | 154.9 | 30.8 |
| 126.988 | 154.1 | 30.8 |
| 126.009 | 153.2 | 30.8 |
| 126.078 | 169.8 | 30.8 |
| 126.114 | 175.8 | 30.7 |
| 126.120 | 168.5 | 30.7 |
| 126.121 | 160.2 | 30.7 |
| 126.145 | 180.3 | j). 7 |
| 126.146 | 170.9 | 30.7 |
| 126.155 | 190.3 | 30.7 |
| 126.158 | 212.7 | 30.7 |
| 126.169 | 209.9 | 30.7 |
| 126.171 | 204.1 | 30.7 |
| 126.192 | 110.3 | 30.7 |
| 126.194 | 105.1 | 30.7 |
| 126.197 | 103.3 | 30.7 |
| 126.206 | 95.7 | 30.7 |
| 126.216 | 94.8 | 30.7 |
| 126.225 | 85.6 | 30.7 |
| 126.230 | 87.9 | 30.7 |

TABLE 18--continued

| Temperature (K) | $\begin{gathered} C_{V}[56] \\ \text { (joules/mole-K) } \end{gathered}$ | $\begin{gathered} c_{v_{\text {calc }}} \\ \text { (joules/mole-K) } \end{gathered}$ |
| :---: | :---: | :---: |
| 126.232 | 79.5 | 30.7 |
| 126.245 | 79.7 | 30.7 |
| 126.249 | 84.2 | 30.7 |
| 126.261 | 76.6 | 30.7 |
| 126.270 | 77.8 | 30.7 |
| 126.288 | 75.7 | 30.7 |
| 126.291 | 71.0 | 30.7 |
| 126.333 | 65.3 | 30.7 |
| 126.341 | 67.9 | 30.7 |
| 126.340 | 65.6 | 30.7 |
| 126.383 | 65.0 | 30.7 |
| 126.383 | 61.5 | 30.7 |
| 126.445 | 58.8 | 30.6 |
| 126.396 | 58.8 | 30.7 |
| 126.470 | 56.6 | 30.6 |
| 126.567 | 54.7 | 30.6 |
| 126.725 | 50.5 | 30.6 |
| 126.872 | 49.2 | 30.5 |
| 126.967 | 47.1 | 30.5 |
| 127.055 | 45.8 | 30.5 |
| 127.346 | 43.8 | 30.4 |
| 127.910 | 40.4 | 30.2 |
| 128.752 | 37.6 | 30.0 |
| 129.794 | 35.7 | 29.8 |
| 130.868 | 34.0 | 29.5 |
| 131.974 | 32.8 | 29.2 |
| 133.100 | 31.8 | 29.0 |
| 135.357 | 29.9 | 28.5 |
| 136.340 | 30.0 | 28.3 |
| 142.178 | 28.1 | 27.3 |
| 143.050 | 27.8 | 27.1 |
| 155.658 | 26.4 | 25.6 |
| 156.716 | 26.1 | 25.5 |
| 167.040 | 26.1 | 24.6 |

TABLE 19

> COMPARISON OF LATENT HEATS OF EVAPORATION FROM
> [52] and [53] TO VALUES FROM EQUATIONS (22) AND $(29)$

| Comparison to Data of Furukawa and McCoskey [52] |  |  |  |
| :---: | :---: | :---: | :---: |
| Temperature (K) | Pressure ( atm ) | Latent Heat [52] (joules/mole) | $\frac{L[52]-L_{\text {calc }}}{\frac{L[52]}{(\text { percent })}} \times 100$ |
| 67.96 | 0.28 | 5901.6 | 0.29 |
| 67.96 | 0.28 | 5899.0 | 0.24 |
| 73.09 | 0.59 | 5739.1 | 0.40 |
| 73.09 | 0.59 | 5732.1 | 0.28 |
| 78.02 | 1.08 | 5579.4 | 0.70 |
| 78.01 | 1.08 | 5563.1 | 0.41 |
| Comparison to Data of Jones [53] |  |  |  |
| Temperature (K) | Pressure ( atm ) | Latent Heat [53] (joules/mole) | $\frac{\mathrm{L}[53]-\mathrm{L}_{\text {calc }}}{\substack{\mathrm{L}[53] \\(\text { percent })}} \times 100$ |
| 119.20 | 23.80 | $270 \hat{6} .3$ | -1.10 |
| 119.16 | 23.80 | 2678.2 | -2.04 |
| 119.19 | 27.18 | 2220.4 | -2.33 |
| 121.89 | 30.61 | 1681.3 | 0.56 |
| 124.29 | 23.80 | 2714.7 | -0.82 |

## Comparison of Experimental Enthalpy Values

Wiener [5\%] has reported measurements of the enthalpy of nitrogen made prior to measuring hydrocarbon enthalpy values. A comparison of the measured enthalpy values by Wiener to values calculated from the equation of state (22) is presented in Table 20. The values of [57] have been adjusted to the ideal gas reference enthalpy of 8669 joules/mole at 298.15 K from the published datum of $0.0 \mathrm{Btu} / 1 \mathrm{~b}_{\mathrm{m}}$ at 75 F and 14.7 psia . Wiener has estimated the accuracy of the measured values of [57] as $\pm 130$ joules/mole. The calculated values of enthalpy at the experimental temperature ana pressure are well within this uncertainty with the exception of two points which the author cites as in doubt.

## Comparisons of the Entropy of the Saturated Liguid

The vapor pressure equation (29) was tested using calculations employing the saturated liquid heat capacity data of Clusius [50] and wiebe and Brevoort [58]. The results are summarized in Table 21 which compares values of sicurated liquid entropy $S_{C}$ '' and $S_{\sigma}{ }^{\prime \prime}$. $S_{C}$ '' was calculated using the daturi value for entropy of the ideal gas at 298.15 K , the equation of state, the ideal gas heat capacity equation, and the vapor pressure equation for values of the slope ( $\mathrm{dP} / \mathrm{dT}$ ) as required by the Clapeyron equation. $\mathrm{S}_{\sigma}{ }^{\prime \prime}$ was determined by the calculation of differences in the saturated liquid entropy along the saturated liquid line, from an equation for saturated liquid heat capacity data determined by a least squares fit to the data reported in [50] and [58]. The datum state in the calculation of $S_{\sigma}{ }^{\prime \prime}$ was the value of the saturated liquid entropy $s_{c}{ }^{\prime \prime}$ at 100 K .

TABLE 20
COIIPARISON OF ENTHALPY DATA BY WEINER [57] WITH VALUES CALCULATED FROM THE EQUATION OF STATE (22) AND THE IDEAL GAS HEAT CAPACITY EQUATION (34)

| Temperature (K) | Pressure ( atm ) | $\begin{gathered} H[57] \\ \text { (joules/mole) } \end{gathered}$ | $\mathrm{H}[57]$ - $\mathrm{H}_{\text {calc }}$ (joules/mole) |
| :---: | :---: | :---: | :---: |
| 138.71 | 67.37 | 621 | -248 |
| 142.59 | 52.06 | 1988 | -107 |
| 142.04 | 29.26 | 3551 | 323 |
| 145.93 | 28.58 | 3421 | - 10 |
| 143.15 | 21.78 | 3551 | 8 |
| i42.04 | 17.69 | 3616 | - 16 |
| 158.71 | 28.92 | 3877 | - 69 |
| 159.26 | 28.58 | 4072 | 96 |
| 199.82 | 51.72 | 5049 | - 22 |
| 202.04 | 28.99 | 5505 | 33 |
| 207.59 | 65.32 | 5179 | - 1 |
| 310.93 | 34.02 | 8826 | - 24 |
| 322.59 | 27.90 | 9151 | - 85 |
| 359.26 | 40.83 | 10258 | - 33 |
| 421.48 | 47.63 | 12146 | - 10 |
| 422.04 | 40.83 | 12146 | - 41 |
| 449.26 | 47.63 | 12993 | - 3 |

COMPARISON OF SATURATED LIQUID ENTROPY CALCULATED FROM
(1) EqUATION OF STATE AND IDEAL GAS HEAT CAPACITY EQUATION, AND (2) SATURATED LIQUID HEAT

CAPACITY DATA OF CLUSIUS [50] AND WIEBE AND BREVOORT [58]

| Temperature (K) | Pressure ( atm ) | (1) $S_{C}{ }^{11}$ <br> (joules/mole-K) | (2) $S_{\sigma}{ }^{\prime \prime}$ <br> (joules/mole-K) |
| :---: | :---: | :---: | :---: |
| 70 | 0.38 | 73.80 | 73.68 |
| 71 | 0.44 | 74.61 | 74.49 |
| 72 | 0.51 | 75.41 | 75.28 |
| 73 | 0.58 | 76.20 | 76.07 |
| 74 | 0.66 | 76.98 | 76.85 |
| 75 | 0.75 | 77.75 | 77.62 |
| 76 | 0.85 | 78.51 | 78.38 |
| 77 | 0.96 | 79.27 | 79.13 |
| 78 | 1.08 | 80.01 | 79.87 |
| 79 | 1.21 | 80.74 | 80.61 |
| 80 | 1.35 | 81.47 | 81.34 |
| 81 | 1.51 | 82.19 | 82.06 |
| 82 | 1.67 | 82.90 | 82.77 |
| 83 | 1,86 | 83.60 | 83.48 |
| 84 | 2.05 | 84.30 | 84.18 |
| 85 | 2.26 | 84.99 | 84.87 |
| 86 | 2.49 | 85.67 | 85.56 |
| 87 | 2.73 | 86.34 | 86.24 |
| 88 | 2.99 | 87.01 | 86.92 |
| 89 | 3.27 | 87.68 | 87.59 |
| 90 | 3.56 | 88.34 | 88.26 |
| 91 | 3.88 | 88.99 | 88.92 |
| 92 | 4.21 | 89.64 | 89.58 |
| 93 | 4.51 | 90.29 | 90.24 |
| 94 | 4.94 | 90.93 | 90.89 |
| 95 | 5.34 | 91.57 | 91.53 |
| 96 | 5.76 | 92.21 | 92.18 |
| 97 | 6.21 | 92.84 | 92.82 |
| 98 | 6.68 | 93.47 | 93.46 |
| 99 | 7.17 | 94.10 | 94.09 |
| 100 | 7.69 | 94.73 | 94.73 |
| 101 | 8.24 | 95.35 | 95.36 |
| 102 | 8.81 | 95.98 | 95.99 |
| 103 | 9.41 | 96.60 | 96.62 |
| 104 | 10.04 | 97.23 | 97.25 |
| 105 | 10.70 | 97.85 | 97.88 |

TABLE 21--continued

| Temperature <br> (K) | Pressure <br> (atm) | (l) $\mathrm{S}_{\mathrm{c}}{ }^{\prime \prime}$ <br> (joules/mole-K) | (2) $\mathrm{S}_{\sigma}{ }^{\prime \prime}$ <br> (joules/mole-K) |
| :---: | :---: | :---: | :---: |
| 106 | 11.39 | 98.48 | 98.51 |
| 107 | 12.11 | 99.10 | 99.14 |
| 108 | 12.87 | 99.73 | 99.77 |
| 109 | 13.66 | 100.36 | 100.40 |
| 110 | 14.48 | 101.00 | 101.03 |
| 112 | 15.34 | 101.63 | 101.67 |
| 113 | 16.23 | 102.28 | 102.31 |
| 114 | 17.16 | 102.93 | 102.95 |
| 115 | 18.13 | 103.58 | 103.60 |

NOTE:
T - Temperature of comparison.
P - Vapor pressure from vapor pressure equation at temperature $T$.
$S_{c}{ }^{\prime \prime}$ - Entropy of saturated liquid from equation of state, vapor pressure equation, and ideal gas heat capacity equation using Clapeyron equation with the derivative of the vapor pressure equation.
$S_{\sigma}$ '' - Entropy of saturated liquid from a fit to saturated liquid heat capacity data

$$
S_{\sigma}^{\prime \prime}=S_{0}+\int_{T_{0}}^{T}\left(C_{\sigma} / T\right) d T \text { where } T_{0}=100 \mathrm{~K} \text { and } S_{0}=S^{\prime \prime} \text { at }
$$ 100 K.

## Comparison of Selected Velocity of Sound Data

The velocity of sound data from references [62] through [83] have been reviewed, and the data from [73], [74], [75], and [83] have been selected for comparison with sonic velocities calculated from the equation of state. A large proportion of the data not included in these comparisons is for pressures of 1 atmosphere or less. Although this analysis of velocity of sound data is not complete, the sample of the data compared to sonic velocity values calculated from the equation of state includes data for the liquid, the vapor to high pressures, and values for the saturated liquid and the saturated vapor. These comparisons are given in Table 22.

The calculated values of the velocity of sound for the vapor phase including the saturated vapor and the high pressure region above the critical temperature are generally within i percent of the measured values. However, deviations for the calculated sonic velocities in the low temperature liquid region are as large as 12 percent, while the saturated liquid values indicate differences of nearly 30 percent at pressures below 0.5 atmosphere and near the critical point.

TABLE 22
REPRESENTATIVE COMPARISONS OF CALCULATED SONIC VELOCITIES TO EXPERIMENTAL VALUES

| Pressure ( atm ) | Temperature (K) | Experimental <br> Velocity of Sound (meters/sec) | $\frac{W_{\text {data }}-W_{\text {calc }}}{W_{\text {data }}} \times 100$ |
| :---: | :---: | :---: | :---: |
| Low Temperature Liquid Data of [73] |  |  |  |
| 84.3 | 113.6 | 589 | 0.22 |
| 68.3 | 109.2 | 617 | 2.02 |
| 104.7 | 113.4 | 634 | 2.15 |
| 104.7 | 113.6 | 631 | 1.95 |
| 42.2 | 104.8 | 614 | 0.66 |
| 43.6 | 105.0 | 616 | 1.00 |
| 57.1 | 105.9 | 629 | 1.23 |
| 94,8 | 110.2 | 646 | 1.81 |
| 126.8 | 113.8 | 659 | 1.82 |
| 104.7 | 109.5 | 666 | 1.84 |
| 8.5 | 90.6 | 725 | - 2.38 |
| 8.5 | 90.6 | 726 | - 2.24 |
| 46.9 | 85.5 | 819 | - 2.89 |
| 86.0 | 87.6 | 836 | - 1.17 |
| 136.9 | 97.0 | 850 | 0.16 |
| 38.4 | 84.3 | 822 | - 3.72 |
| 84.3 | 87.7 | 834 | - 1.12 |
| 134.3 | 90.6 | 853 | 0.30 |
| 8.2 | 81.0 | 826 | - 6.76 |
| 1.6 | 77.6 | 851 | - 9.89 |
| 8.1 | 75.3 | 883 | -10.87 |
| 52.0 | 77.5 | 897 | - 6.64 |
| 116.6 | 81.0 | 917 | - 2.39 |
| 61.5 | 77.6 | 902 | - 6.30 |
| 121.9 | 80.9 | 920 | - 2.47 |
| 1.7 | 73.6 | 896 | -12.82 |
| 112.6 | 75.0 | 959 | - 5.97 |
| 111.5 | 75.0 | 959 | - 5.93 |
| 120.0 | 73.8 | 975 | - 6.35 |

Saturated Liquid Data of [74]

| 0.18 | 65.4 | 968 | -27.17 |
| :--- | :--- | :--- | :--- |
| 0.22 | 66.4 | 959 | -24.81 |
| 0.29 | 68.1 | 942 | -21.37 |
| 0.38 | 70.0 | 924 | -18.21 |
| 0.50 | 71.9 | 905 | -15.64 |

TABLE 22--continued

| Pressure (atm) | Temperature (K) | Experimental Velocity of Sound (meters/sec) | $\frac{W_{\text {data }}-W_{\text {calc }}}{W_{\text {data }}} \times 100$ |
| :---: | :---: | :---: | :---: |
| 0.68 | 74.2 | 881 | -13.17 |
| 0.85 | 76.0 | 864 | -11.44 |
| 1.26 | 73.3 | 831 | - 8.99 |
| 1.29 | 79.6 | 829 | - 8.77 |
| 1.39 | 80.3 | 822 | -8.31 |
| 1.81 | 82.7 | 796 | - 6.95 |
| 1.89 | 83.2 | 791 | - 6.70 |
| 2.25 | 84.9 | 772 | - 5.85 |
| 2.66 | 86.7 | 755 | - 4.93 |
| 2.70 | 86.9 | 753 | - 4.79 |
| 2.82 | 87.4 | 748 | - 4.54 |
| 3.05 | 88.2 | 739 | - 4.26 |
| 3.96 | 91.3 | 705 | - 3.27 |
| 4.61 | 93.1 | 685 | - 2.72 |
| 6.39 | 97.4 | 636 | - 1.74 |
| 7.38 | 99.4 | 612 | - 1.47 |
| 8.34 | 101.2 | 590 | - 1.36 |
| 9.86 | 103.7 | 559 | - 1.22 |
| 13.4 | 108.7 | 493 | - 1.50 |
| 14.7 | 110.2 | 472 | - 1.73 |
| 17.1 | 112.9 | 434 | - 2.32 |
| 19.1 | 115.0 | 403 | - 3.05 |
| 21.4 | 117.1 | 369 | - 4.22 |
| 23.9 | 119.3 | 329 | - 6.31 |
| 24.1 | 119.4 | 327 | - 6.12 |
| 25.0 | 120.2 | 313 | - 6.92 |
| 26.4 | 121.2 | 290 | - 9.09 |
| 28.0 | 122.4 | 265 | -10.49 |
| 30.6 | 124.3 | 220 | -14.77 |
| 30.7 | 124.3 | 219 | -14.75 |
| 31.9 | 125.1 | 191 | -20.16 |
| 32.4 | 125.5 | 183 | -19.51 |

Saturated Vapor Data of [75]

| 1.24 | 79.2 | 177 | 0.46 |
| :--- | :--- | :--- | :--- |
| 1.13 | 78.4 | 177 | 0.78 |
| 1.07 | 78.0 | 176 | 0.39 |
| 0.50 | 71.9 | 171 | 0.45 |

TABLE 22--continued

| Pressure (atm) | Temperature (K) | Experimental Velocity of Sound (meters/sec) | $\frac{W_{\text {data }}-W_{\text {calc }}}{W_{\text {data }}} \times 100$ |
| :---: | :---: | :---: | :---: |
| High Pressure Data of [83] |  |  |  |
| $\begin{array}{r} 600 \\ 1000 \\ 1500 \\ 2000 \\ 2500 \end{array}$ | 298.14 298.14 298.14 298.14 298.14 | $\begin{array}{r} 655 \\ 844 \\ 1030 \\ 1170 \\ 1296 \end{array}$ | $\begin{array}{r} -0.90 \\ -0.36 \\ 0.35 \\ -0.03 \\ 0.39 \end{array}$ |
| $\begin{array}{r} 3000 \\ 3250 \\ 3500 \\ 3750 \\ 200 \end{array}$ | 298.14 298.14 298.14 298.14 323.14 | 1398 1445 1500 1545 440 | 0.23 0.23 0.94 1.11 0.37 |
| $\begin{array}{r} 600 \\ 1000 \\ 1500 \\ 2000 \\ 2500 \end{array}$ | 323.14 323.14 323.14 323.14 323.14 | 650 830 1010 1160 1280 | - 0.59 -0.38 0.08 0.69 0.59 |
| $\begin{array}{r} 3000 \\ 3500 \\ 600 \\ 1000 \\ 1500 \end{array}$ | 323.14 323.14 348.14 348.14 348.14 | 1380 1480 655 825 1000 | 0.23 0.75 0.73 0.26 0.46 |
| $\begin{array}{r} 2000 \\ 2500 \\ 3000 \\ 3500 \\ 200 \end{array}$ | 348.14 348.14 348.14 348.14 373.15 | 1140 1262 1370 14.3 462 | 0.30 0.42 0.64 0.63 0.02 |
| $\begin{array}{r} 600 \\ 1000 \\ 1500 \\ 2200 \\ 2500 \end{array}$ | 373.15 373.15 373.15 373.15 373.15 | $\begin{array}{r} 648 \\ 820 \\ 985 \\ 1130 \\ 1248 \end{array}$ | $\begin{array}{r} 0.19 \\ 0.57 \\ 0.08 \\ -3.90 \\ 0.40 \end{array}$ |
| $\begin{array}{r} 3000 \\ 3500 \\ 200 \\ 600 \\ 1000 \end{array}$ | 373.15 373.15 398.16 398.16 398.16 | $\begin{array}{r} 1354 \\ 1442 \\ 476 \\ 654 \\ 818 \end{array}$ | 0.48 0.12 0.55 0.60 0.98 |
| $\begin{array}{r} 1500 \\ 2200 \\ 2500 \\ 3000 \\ 200 \end{array}$ | 398.16 398.16 398.16 398.16 423.17 | $\begin{array}{r} 978 \\ 1115 \\ 1232 \\ 1338 \\ 486 \end{array}$ | $\begin{array}{r} 0.29 \\ -4.20 \\ 0.05 \\ 0.19 \\ 0.30 \end{array}$ |

TABLE 22--continued

| Pressure <br> (atm) | Temperature <br> $(K)$ | Experimental <br> Velocity of Sound <br> (meters/sec) | $\frac{W_{\text {data }}-W_{\text {calc }}}{W_{\text {data }}}$ <br> (percent) |
| :---: | :---: | :---: | :---: |
| 600 | 423.17 | 658 | 0.86 |
| 1000 | 423.17 | 810 | 0.43 |
| 1500 | 423.17 | 972 | 0.41 |
| 2200 | 423.17 | 1107 | -4.12 |
| 2500 | 423.17 | 1223 | 0.15 |
| 3000 | 423.17 | 1330 | 0.39 |
| 3500 | 423.17 | 1420 | 0.16 |
| 4000 | 423.17 | 1480 | -1.47 |
| 200 | 448.18 | 500 | 0.92 |
| 600 | 448.18 | 660 | 0.68 |
| 1000 | 448.18 | 810 | 0.69 |
| 1500 | 448.18 | 960 | -10.25 |
| 2200 | 448.18 | 1098 | -4.23 |
| 2500 | 448.18 | 1216 | 0.29 |
| 3000 | 448.18 | 1325 | 0.72 |
| 3500 | 448.18 | 1410 | 0.13 |
| 4000 | 448.13 | 1435 | -4.00 |

CHAPTER 12

LONCLUSIONS AND RECOMMENDATIONS

The results of this study are summarized below:

1. The equation of state (22) developed in this work represents the experimental $p-p-T$ data in the liquid and vapor phases for pressures from 0 to 10,000 atmospheres and for temperatures of 65 K to 1073 K . The equation may be extrapolated to 2000 K at pressures below 300 atmospheres with an accuracy of at least $\pm 1$ percent. The equation may also be extrapolated to lower temperatures for the vapor with an accuracy of at least $\pm 2$ percent down to 20 K at very low pressures. It is estimated that the accuracy of the equation of state is within 0.5 percent in the liquid region, except in the vicinity of the critica? point. At temperatures above the critical temperature for pressures up to 1000 atmospheres, the accuracy is generally within 0.1 percent except in the region near the critical point between temperatures of 126.2 K and 150 K and at pressures between 30 and 150 atmospheres where the density deviations from experimental data are as large as 0.7 percent. In the range from 1000 to 10,000 atmospheres the accuracy is estimated to be within 0.3 percent of the data used in the formulation, but deviations in density as large as 12 percent are evident in comparisons to other data in this range.
2. The vapor pressure equation (29) represents the selected data used in the formulation of the equation generally within an accuracy of $\pm 0.01 \mathrm{~K}$ between the triple point and the critical point.
3. The equation for the ideal gas specific heat (34) has been used to represent the recent values of CQ/R from [55] with an accuracy of $\pm .00001$ for values to 1200 K , and within $\pm 0.0001$ above 1200 K .
4. Values of the heat capacity, enthalpy, and latent heats of vaporization are presented with comparisons to available measured calorimetric data. Al though the paucity of these measurements make it difficult to define the accuracy of the equation of state (22) for the calculation of heat capacity values, these comparisons further indicate shat the behavior of the isobaric calculated values is thermodynamically correct.
5. The least squares techniques used in the formulation presented here include the simultaneous fitting of $F-p-T$ data, $C_{y}$ data, and the criteria for phase equilibrium to allow for continuous integration along isotherms through the two-phase region.

Suggestions for further research are presented below:

1. The work reported here is essentially complete within the limits imposed by the availability of experimental data to describe the thermodynamic properties of nitrogen. However, the lack of agreement of the various $\mathrm{P}-\mathrm{p}-\mathrm{T}$ data in the liquid region suggests the need for further measurement of the properties of the liquid.
2. The use of a single equation of state for the $P-p-T$ surface appears to be accompanied by fitting problems near the critical point which propagate to temperatures above the critical value. It is suggested that new methods of accomodating the requirements of the $P-\rho-T$ surface in this region for the least squares determination of the equation of state be explored.
3. When precise experimental heat capacity data become available for nitrogen for the saturated liquid and vapor phases to define the derivative behavior and saturation conditions more accurately, the equation of state may be improved.
4. The consistency of the vapor pr-ssure equation, melting equation, and equation of state in the region of the triple point should be investigated.
5. The simultaneous fitting procedures developed in this work are applicable to other fluids for which the appropriate data are available.
6. A detailed study of the sonic velocity data should be made to complete the analysis of this data and to identify the cause of the large deviations of caiculated velocity of sound values from experimental measurements in the liquid region.

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## APPENDIX A

THE SELECTION OF P-o-T AND VAPOR PRESSURE DATA FOR THE DETERMINATION OF EQUATIONS (22) AND (29)

## APPENDIX A

# THE SELECTION OF P-o-T AND VAPOR PRESSURE DATA FOR THE DETERMINATION OF EQUATIONS (22) AND (29) 

## Selection of P-p-T Data

## Low Temperature Liquid Data

A careful examination of the density deviation plots of figures 3 through 241 indicates a lack of agreement among the various data in the liquid region of the P - $\rho-\mathrm{T}$ surface.

The least squares formulations of equations ( 20 ) and (22) indicate the isochoric data of Weber [36] as the most precise of all the data sets for the liquid. The two publications by Van Itterbeek and Verbeke, [34] and [35], contain data sets which are not consistent with one another. The data of [34] appear to be in closer agreement with other data in the same region than those of [35].

The measurements of Golubev [32] for temperatures between 77 K and 133 K have been used in the development of the equation of state despite the systematic deviations of the equation from the data. The data of Streett and Staveley [33] for temperatures between 77 K and 120 K exhibit systematic trends which are contradictory to the trends of the values of Golubev [32]. In addition, the systematic nature of the deviations of the data of Streett and Staveley from the equation of state is not consistent fiom isotherm to isotherm. Consequently, the data from [33] were not used in the fit of equation (22).

The data of Gibbons at 72 K and 77 K , with the exception of point at 77 K , are consistent with the equation of state within 0.2 percent. These low temperature data were used in the fit to determine the coefficients of the equation of state. The data of Cockett [30] appear to be a self consistent data set with the exception of the points on the 120 K isotherm, which are not in agreement with other data at this temperature. These data with the exception of the 120 K values were incorporated in the fit.

## High Fressure Data

The lack of agreement of the high pressure data for nitrogen is notable. The difficulty in experimental procedures for pressures above 1000 atmospheres undoubtedly accounts for some of the imprecision exhibited by the various data at these extreme pressures. A selection of data for use in the determination of the equation of $s$ tate was made on the basis of consistency with data in adjacent regions of the surface and on the agreement of the data with trends established by lower pressure data at the various experimental temperatures.

The analysis of the high pressure data indicates that the data of Michels [20] and those of Robertson and Babb [23] agree closely with the trends established by the data of Saurel [24] and of Michels [19] at pressures below 1000 atmospheres. The systematic deviations of the equation from the data of [23] are smaller in magnitude than those exhibited by any other data at pressures above 3000 atmospheres. The isothermal data by experimenters for pressures above 1000 atmospheres are discussed below.

373 K. -- The data of Michels [20] and Robertson and Babb [23] are in agreement at this temperature. The densities of Tsiklis [27] arid [28] are as much as 1 percent lower than those of [20] and [23] and those of Benedict [7] are lower by as much as 0.3 percent. The data of Tsiklis are in closer agreement (wit'in 0.5 percent) at pressures below 6000 atmospheres than at pressures above this value.

398 K.--The only measurements are those of Michels [20] which are in agreement with the equation of $s$ tate to within 0.2 percent.

423 K.--The data of Saurel [24] and those of Michels [19] differ by as much as 0.2 percent at pressures between 100 and 500 atmospheres. The data of Michels [20] and Benedict [7] are in good agreement above 1000 atmospheres, but the densities of Tsiklis [27] and [28] are as much as 1 percent lower than those indicated by the equation of state.

473 K.--The data of [7], [23], [27], [28], [17], and [:8] at this temperature are in agreement with one exception. The densities reported by Tsiklis [27] and [28] are again consistently lower than those of other data sets. 573 K.--At this temperature the densities of Tsiklis [27] and [28] are up to 1 percent higher than those of Robertson and Babb [23]. The data of Malbrunot [18] and those of Ma irunot and Vodar [17], which represent the results from the same experimental apparatus show a lack of agreement at pressures below 3000 atmospheres of up to 0.5 percent.

673 K. .-The data of Malbrunot [18] and those of Malbrunot and Vodar [17] again exhibit a lack of agreement. It is noticed that the later data of [17] are in agreement with the data of Saurel [24] at pressures near 1000 atmospheres, and discrepancies exceed 1.5 percent on this isotherm.

773 K to $1274 \mathrm{~K} .-$-The data of [17] and [18] exhibit a clear lack of agreement at lower pressures. This discrepancy is more pronounced at the higher temperatures. These considerations suggested that the equation of state be fitted to the data of Saurel [24], Robertson and Babb [23], and Michels [20], to define the surface at high pressures and temperatures. The equation of state must be considered an extrapolation above 773 K , since no data above 1000 atmospheres and 773 K were used in the least squares fit. Further discussion of the validity of the extrapclation of the equation of state is included in Chapter 8.

## Selection of Vapor Pressure Data

In the development of the vapor pressure equation it was found that the various data sets listed in Table 2 were not sufficientiy concordant to produce an equation which was consistent with all the data within the estimated experimental uncertainty. It was found that the data of Armstrong [40] and Weber [36] could be represented to within about 0.01 K . These data appear to be among the most precise nitrogen vapor pressure data available and extend from the triple point to the critical point. The data of [36] and [40] were used in the determination of the coefficients listed in Table 11.

APPENDIX B
DERIVATION OF FUNCTIONS FOR THE USE OF PHASE EQUILIBRIUM CRITERIA IN SIMULTANEOUS LEAST SQUARES FITTING

## APPENDIX B

## derivation of functions for the use of phase EQUILIBRIUM CRITERIA IN SIMULTANEOUS <br> LEAST SQUARES FITTING

The implementation of the relations (23), (24), (25), and (26) as given in Chapter 5 for use in the simultaneous least squares procedures for the determination of the coefficients of the equation of state, includes the requirement that the conditions for two phase equilibrium of a pure substance be satisfied. Using the equation of state and the definition of $C_{v}$ [equations (23) and (24) respectively], and the terminology of Chapter 5, the derivations are presented here for equations (25) and (26). These equations represent the equality of the pressures for satirated liquid and saturated vapor at a temperature, $T_{S}$, and the equality of the Gibbs function, $G$, of the saturated liquid and saturated vapor staies at equilibrium.

For (25):

$$
\begin{align*}
& P_{S L}=P_{S V} \\
& P(\rho, T)=\Sigma N_{i} P,(\rho, T)+\rho R T \\
& P_{S L}=P\left(\rho_{S L}, T_{S}\right)=\Sigma N_{i} P_{i}\left(\rho_{S L}, T_{S}\right)+\rho_{S L} R T_{S} \\
& P_{S V}=P\left(\rho_{S V}, T_{S}\right)=\Sigma N_{i} P_{i}\left(\rho_{S V}, T_{S}\right)+\rho_{S V} R T_{S} \\
& \quad \Sigma N_{i} P_{i}\left(\rho_{S L}, T_{S}\right)+\rho_{S L} R T_{S}=\Sigma N_{i} P_{i}\left(\rho_{S V}, T_{S}\right)+\rho_{S V} R T_{S} \\
& \Sigma N_{i} P_{i}\left(\rho_{S L}, T_{S}\right)-\Sigma N_{i} P_{i}\left(\rho_{S V}, T_{S}\right)=\rho_{S V} R T_{S}-\rho_{S L} R T_{S} \\
& \Sigma N_{i} P_{i}\left(\rho_{S L}, T_{S}\right)-\Sigma N_{i} P_{i}\left(\rho_{S V}, T_{S}\right)=R T_{S}\left(\rho_{S V}-\rho_{S L}\right) . \tag{25}
\end{align*}
$$

For (26) :

$$
\begin{aligned}
& G=H-T_{S} \\
& \Delta G_{S V-S L}=\Delta H-\Delta\left(T_{S} S_{S V-S L}\right) \\
& H(T, \rho)=H_{T_{0}}^{0}+T \int_{0}^{\rho}\left[R / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T} d \rho \\
& \quad+\int_{0}^{\rho}\left[P / \rho^{2}-R T / \rho\right]_{T} d \rho+[(P-\rho R T) / \rho]+\int_{T_{0}}^{T} C_{p}^{0} d T \\
& S(T, \rho)=S_{T_{0}}^{0}+\int_{T_{0}}^{T} C_{p}^{0} d T / T-R \ln (R T \rho)+\int_{0}^{\rho}\left[R / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T_{S}} d \rho
\end{aligned}
$$

$$
\begin{aligned}
& H\left(T_{S}, \rho_{S V}\right)-H\left(T_{S}, \rho_{S L}\right)=H_{T_{0}}^{0}+T_{S} \int_{0}^{\rho} S V\left[R / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T_{S}} d \rho \\
& \quad+\int_{0}^{\rho} \rho_{S V}\left[P / \rho^{2}-R T / \rho\right]_{T} d \rho+\left[\left(P_{S}-\rho_{S V} R T_{S}\right) / \rho_{S V}\right]+\int_{T_{0}}^{T_{S}} C_{p}^{0} d T \\
& \quad-H_{T_{0}}^{0}-T_{S} \int_{0}^{\rho}{ }_{S L}\left[R / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T_{S}} d \rho-\int_{0}^{\rho L}\left[P / \rho^{2}-R T / \rho\right]_{T} d \rho \\
& \quad-\left[\left(P_{S}-\rho_{S L} R T_{S}\right) / \rho_{S L}\right]-\int_{T_{0}}^{T_{S}} C_{p}^{0} d T \\
& S\left(T_{S}, \rho_{S V}\right)-S\left(T_{S}, \rho_{S L}\right)=S_{T_{0}}^{0}+\int_{T_{0}}^{T_{S}} C_{p}^{0} d T / T-R \ln \left(R T \rho_{S V}\right) \\
& \quad+\int_{0}^{\rho}\left[R V / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T_{S}} d \rho-S_{T_{0}}^{0}-\int_{T_{0}}^{T} C_{P} C_{P}^{0} d T / T \\
& \quad+R \ln \left(R T_{S L}\right)-\int_{0}^{\rho}\left[R L / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T} d \rho
\end{aligned}
$$

$$
\Delta G_{S V-S L}=T_{S} \int_{\rho_{S L}}^{\rho_{S V}}\left[R / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T_{S}} d \rho+\int_{\rho_{S L}}^{\rho}\left[P / \rho^{2}-R T_{S} / \rho\right]_{T_{S}} d \rho
$$

$$
+\left[\left(P_{S}-\rho_{S V} R T_{S}\right) / \rho_{S V}-\left(P_{S}-\rho_{S L} R T_{S}\right) / \rho_{S L}\right]+R T_{S} \ln \left(R T_{S V}\right)
$$

$$
-R T_{S} \ln \left(R T \rho_{S L}\right)-T_{S} \int_{\rho_{S L}}^{\rho_{S V}}\left[R / \rho-1 / \rho^{2}(\partial P / \partial T)_{\rho}\right]_{T_{S}} d \rho
$$

$$
\Delta G_{S V-S L}=\int_{\rho_{S L}}^{\rho_{S V}}\left[P / \rho^{2}-R T_{S} / \rho\right]_{T_{S}} d \rho+P_{S}\left(1 / \rho_{S V}-1 / \rho_{S L}\right)
$$

$$
+R T_{S} \ln R T+R T_{S} \ln \rho_{S V}-R T_{S} \ln R T-R T_{S} \ln \rho_{S L}
$$

$$
\Delta G_{S V-S L}=\int_{\rho_{S L}}^{\rho}\left[P / \rho^{2}-R T_{S} / \rho\right]_{T_{S}} d \rho+P_{S}\left(1 / \rho_{S V}-1 / \rho_{S L}\right)
$$

$$
+R T_{S} \ln \left(\rho_{S V} / \rho_{S L}\right)=0 \text { for equilibrium }
$$

$$
\int_{\rho_{S L}}^{\rho_{S V}}\left[P / \rho^{2}-R T_{S} / \rho_{T_{S}} d \rho \equiv \Sigma N_{i} G_{i}=-P_{S}\left(1 / \rho_{S V}-1 / \rho_{S L}\right)\right.
$$

$$
-R_{S}^{T} \ln \left(\rho_{S V} / \rho_{S L}\right)
$$

$$
\begin{equation*}
\Sigma N_{i} G_{i}=P_{S}\left(1 / \rho_{S L}-1 / \rho_{S V}\right)+R T_{S} \ln \left(\rho_{S L} / \rho_{S V}\right) \tag{26}
\end{equation*}
$$

APPENDIX C
HEAT CAPACITY VALUES CALCULATED USING THE PRINCIPLE OF CORRESPONDING STATES

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## HEAT CAPACITY VALUES CALCULATED USING THE <br> PRINCIPLE OF CORRESPONDING STATES

The principle of corresponding states was used to calculate $C_{v}$ values for nitrogen from the oxygen equation for $C_{V}$ (equation 4 of [99]), as suggested in [97], for use in the determination of the equation of state for nitrogen as described in Chapter 5.

To establish the validity of the corresponding states analysis employed in this work, the method described above was utilized in the calculation of $C_{v}$ values for fluorine which were then compared to the experimental data of [112]. Critical parameters for fluorine were taken from [113]. Figures 250 through 257 illustrate the results of this comparison.

Although the systematic deviations of the calculated values from the data are clearly evident, it was felt that the accuracy of the corresponding states heat capacity values was adequate to justify their use as described in Chapter 5 to enhance the behavior of the derivatives of the equation of state.

The values used in simultaneous fitting to determine the coefficients of equation (22) given in Table 10 were calculated from equation (4) of [99]. Comparisons of calculated values from the final equation of state exhibited an overall agreement of about $\pm 5$ percent with the $C_{v}$ values determined using the principle of corresponding states.




Comparisons of $C_{V}$ Data for Fluorine from [112] with Values Predicted from Oxygen Equation of [99] using the Principle of Corresponding States (Data are for approximate isochores).


Comparisons of $C_{V}$ Data for Fluorine from [112] with Values Predicted from Oxygen Equation of [99] using the Principle of Corresponding States (Data are for approximate isochores).

## The Equation of State

Equation (22) may be written in the form:

$$
\begin{equation*}
P=\rho R T+\sum_{i=1}^{32} N_{i} X_{i} \tag{42}
\end{equation*}
$$

where the $N_{i}$ are listed in Table 10 and the $X_{i}$ are as follows:

$$
\begin{aligned}
& x_{2}=\rho^{2} T \\
& x_{2}=\rho^{2} T^{\frac{1}{2}} \\
& x_{3}=\rho^{2} \\
& x_{4}=\rho^{2} / T \\
& x_{5}=\rho^{2} / T^{2} \\
& x_{6}=\rho^{3} T \\
& x_{7}=\rho^{3} \\
& x_{8}=\rho^{3} / T \\
& x_{9}=\rho^{3} / T^{2} \\
& x_{20}=\rho^{4} T \\
& x_{12}=\rho^{4}
\end{aligned}
$$

$$
\begin{aligned}
& X_{12}=\rho^{4} / T \\
& X_{1:}=\rho^{5} \\
& X_{14}=\rho^{6} / T \\
& X_{15}=\rho^{6} / T^{2} \\
& X_{16}=\rho^{7} / T \\
& X_{17}=\rho^{8} / T \\
& X_{18}=\rho^{6} / T^{2} \\
& X_{19}=\rho^{9} / T^{2} \\
& X_{20}=\rho^{3} F / T^{2} \\
& X_{21}=\rho^{3} F / T^{3} \\
& X_{22}=\rho^{5} F / T^{2} \\
& F=\exp \left(-0.0056 \rho^{2}\right)
\end{aligned}
$$

$$
\begin{aligned}
& x_{23}=\rho^{5} F / T^{4} \\
& x_{24}=\rho^{7} F / T^{2} \\
& x_{25}=\rho^{7} F / T^{3} \\
& x_{26}=\rho^{9} F / T^{2} \\
& x_{27}=\rho^{9} \Gamma / T^{4} \\
& x_{28}=\rho^{11} F / T^{2} \\
& x_{29}=\rho^{11} F / T^{3} \\
& x_{30}=\rho^{13} F / T^{2} \\
& x_{31}=\rho^{13} F / T^{3} \\
& x_{32}=\rho^{13} F / T^{4}
\end{aligned}
$$

## The Isotherm Derivative

The isotherm derivative of the equation of state (22) may be repre-
sented as:

$$
\begin{equation*}
(\partial P / \partial \rho)_{T}=R T+\sum_{i=1}^{32} N_{i} x_{i} \tag{43}
\end{equation*}
$$

where the $N_{f}$ are given in Table 10 and the $X_{i}$ are as follows:

$$
\begin{aligned}
& x_{1}=2 \rho T \\
& x_{2}=2 \rho T^{\frac{1}{2}} \\
& x_{3}=2 \rho \\
& x_{4}=2 \rho / T \\
& x_{5}=2 \rho / T^{2} \\
& x_{6}=3 \rho^{2} T \\
& x_{7}=3 \rho^{2} \\
& x_{8}=3 \rho^{2} / T \\
& x_{9}=3 \rho^{2} / T^{2} \\
& x_{10}=4 \rho^{3} T \\
& x_{12}=4 \rho^{3}
\end{aligned}
$$

$$
\begin{aligned}
& x_{12}=4 \rho^{3} / T \\
& x_{13}=5 \rho^{4} \\
& x_{14}=6 \rho^{5} / T \\
& x_{15}=6 \rho^{5} / T^{2} \\
& x_{16}=7 \rho^{6} / T \\
& x_{17}=8 \rho^{7} / T \\
& x_{19}=8 \rho^{7} / T^{2} \\
& x_{19}=9 \rho^{8} / T^{2} \\
& x_{20}=F_{21} / T^{2} \\
& x_{21}=F_{21} / T^{3} \\
& x_{22}=F_{22} / T^{2}
\end{aligned}
$$

$$
x_{23}=F_{22} / T^{4}
$$

$$
X_{24}=F_{23} / T^{2}
$$

$$
X_{25}=F_{23} / T^{3}
$$

$$
X_{26}=F_{24} / T^{2}
$$

$$
X_{27}=F_{24} / T^{4}
$$

$$
X_{28}=F_{25} / T^{2}
$$

$$
X_{29}=F_{25} / T^{3}
$$

$$
X_{30}=F_{26} / T^{2}
$$

$$
X_{31}=F_{26} / T^{3}
$$

$$
X_{32}=F_{26} / T^{4}
$$

$$
\begin{aligned}
& F=\exp \left(-0.0056 \rho^{2}\right) \\
& F_{1}=2 F \rho(-0.0056) \\
& F_{21}=3 F \rho^{2}+F_{1 \rho^{3}} \\
& F_{22}=5 F_{\rho^{4}}+F_{1 \rho^{5}} \\
& F_{23}=7 F^{6}+F_{1 \rho^{7}} \\
& F_{24}=9 F^{6} \rho^{8}+F_{1 \rho^{9}} \\
& F_{25}=11 F \rho^{2}+F_{1 \rho^{11}} \\
& F_{26}=13 F \rho^{12}+F_{2 \rho^{13}}
\end{aligned}
$$

The isochore derivative of the equation of state (22) may be written as:

$$
\begin{equation*}
(\partial P / \partial T)_{\rho}=\rho R+\sum_{i=1}^{32} N_{i} X_{i} \tag{44}
\end{equation*}
$$

where the $N_{i}$ are given in Table 10 and the $X_{i}$ are as follows:

$$
\begin{aligned}
& x_{1}=\rho^{2} \\
& x_{2}=\rho^{2} /\left(2 T^{\frac{1}{2}}\right) \\
& x_{3}=0.0 \\
& x_{4}=-\rho^{2} / T^{2} \\
& x_{5}=-2 \rho^{2} / T^{3} \\
& x_{6}=\rho^{3} \\
& x_{7}=0.0 \\
& x_{8}=-\rho^{3} / T^{2} \\
& x_{9}=-2 \rho^{3} / T^{3} \\
& x_{10}=\rho^{4} \\
& x_{11}=0.0
\end{aligned}
$$

$$
\begin{aligned}
& x_{12}=-\rho^{4} / T^{2} \\
& x_{13}=0.0 \\
& x_{14}=-\rho^{6} / T^{2} \\
& x_{15}=-2 \rho^{6} / T^{3} \\
& x_{16}=-\rho^{7} / T^{2} \\
& x_{17}=-\rho^{8} / T^{2} \\
& x_{18}=-2 \rho^{8} / T^{3} \\
& x_{19}=-2 \rho^{9} / T^{3} \\
& x_{20}=-2 \rho^{3} F / T^{3} \\
& x_{21}=-3 \rho^{3} F / T^{4} \\
& x_{22}=-2 \rho^{5} F / T^{3}
\end{aligned}
$$

$$
F=\exp \left(-0.0056 \rho^{2}\right)
$$

## The Evaluation of Integrals

The integral, $\int\left[R / \rho-\left(1 / \rho^{2}\right)(\partial P / \partial T)_{\rho}\right]_{T}$ d $\rho$ may be written as:

$$
\begin{equation*}
\sum_{i=1}^{32} N_{i} Y_{i} \tag{45}
\end{equation*}
$$

where the $N_{i}$ are listed in Table 10 and the $Y_{i}$ are listed below:

| $Y_{1}=-\rho$ | $Y_{12}=\rho^{3} /\left(3 T^{2}\right)$ | $Y_{23}=4 G_{2} / T^{5}$ |
| :--- | :--- | :--- |
| $Y_{2}=-\rho /\left(2 T^{\frac{3}{2}}\right)$ | $Y_{13}=0.0$ | $Y_{24}=2 G_{3} / T^{3}$ |
| $Y_{3}=0.0$ | $Y_{14}=\rho^{5} /\left(5 T^{2}\right)$ | $Y_{25}=3 G_{3} / T^{4}$ |
| $Y_{4}=\rho / T^{2}$ | $Y_{15}=2 \rho^{5} /\left(5 T^{3}\right)$ | $Y_{26}=2 G_{4} / T^{3}$ |
| $Y_{5}=2 \rho / T^{3}$ | $Y_{16}=\rho^{6} /\left(6 T^{2}\right)$ | $Y_{27}=4 G_{4} / T^{5}$ |
| $Y_{6}=-\rho^{2} / 2$ | $Y_{17}=\rho^{7} /\left(7 T^{2}\right)$ | $Y_{28}=2 G_{5} / T^{3}$ |
| $Y_{7}=0.0$ | $Y_{18}=2 \rho^{7} /\left(7 T^{3}\right)$ | $Y_{29}=3 G_{5} / T^{4}$ |
| $Y_{8}=\rho^{2} /\left(2 T^{2}\right)$ | $Y_{19}=\rho^{3} /\left(4 T^{3}\right)$ | $Y_{30}=2 G_{6} / T^{3}$ |
| $Y_{9}=\rho^{2} / T^{3}$ | $Y_{20}=2 G_{1} / T^{3}$ | $Y_{32}=4 G_{6} / T^{4}$ |
| $Y_{10}=-\rho^{3} / 3$ | $Y_{21}=3 G_{1} / T^{4}$ |  |
| $Y_{11}=0.0$ | $Y_{22}=2 G_{2} / T^{3}$ |  |
|  | $F=\exp \left(-0.0056 \rho^{2}\right)$ |  |
|  | $G_{1}=F /[2(-0.0056)]$ |  |
|  | $G_{2}=\left(F \rho^{2}-2 G_{1}\right) /[2(-0.0056)]$ |  |
|  | $G_{3}=\left(F \rho^{4}-4 G_{2}\right) /[2(-0.0056)]$ |  |
|  | $G_{4}=\left(F \rho^{6}-6 G_{3}\right) /[2(-0.0056)]$ |  |
| $G_{5}=\left(F \rho^{8}-8 G_{4}\right) /[2(-0.0056)]$ |  |  |
|  | $G_{6}=\left(F \rho^{10}-10 G_{5}\right) /[2(-0.0056)]$ |  |

The integral $\int\left[\left(P / \rho^{2}\right)-(R T / \rho)\right]_{T}$ d $\rho$ may be written as:

$$
\begin{equation*}
\sum_{i=1}^{32} N_{i} Y_{i} \tag{46}
\end{equation*}
$$

where the $N_{i}$ are listed in Table 10 and the $\gamma_{i}$ are listed below:

$$
\begin{aligned}
& Y_{1}=\rho T \\
& Y_{2}=\rho T^{\frac{1}{2}} \\
& Y_{3}=\rho \\
& Y_{4}=\rho / T \\
& Y_{5}=\rho / T^{2} \\
& Y_{6}=\rho^{2} T / 2 \\
& Y_{7}=\rho^{2} / 2 \\
& Y_{8}=\rho^{2} /(2 T) \\
& Y_{9}=\rho^{2} /\left(2 T^{2}\right) \\
& Y_{10}=\rho^{3} T / 3 \\
& Y_{11}=\rho^{3} / 3
\end{aligned}
$$

$$
\begin{aligned}
& Y_{12}=\rho^{3} /(3 T) \\
& Y_{13}=\rho^{4} / 4 \\
& Y_{14}=\rho^{5} /(5 T) \\
& Y_{15}=\rho^{5} /\left(5 T^{2}\right) \\
& Y_{16}=\rho^{6} /(6 T) \\
& Y_{17}=\rho^{7} /(7 T) \\
& Y_{19}=\rho^{7} /\left(7 T^{2}\right) \\
& Y_{19}=\rho^{8} /\left(8 T^{2}\right) \\
& Y_{20}=G_{1} / T^{2} \\
& Y_{21}=G_{1} / T^{3} \\
& Y_{22}=G_{2} / T^{2}
\end{aligned}
$$

$$
\begin{aligned}
& Y_{23}=G_{2} / T^{4} \\
& Y_{24}=G_{3} / T^{2} \\
& Y_{25}=G_{3} / T^{3} \\
& Y_{26}=G_{4} / T^{2} \\
& Y_{27}=G_{4} / T^{4} \\
& Y_{26}=G_{5} / T^{2} \\
& Y_{29}=G_{5} / T^{3} \\
& Y_{30}=G_{6} / T^{2} \\
& Y_{31}=G_{6} / T^{3} \\
& Y_{32}=G_{6} / T^{4}
\end{aligned}
$$

$$
\begin{aligned}
& F=\exp \left(-0.0056 \rho^{2}\right) \\
& G_{1}= F /[2(-0.0056)] \\
& G_{2}=\left(F \rho^{2}-2 G_{1}\right) /[2(-0.0056)] \\
& G_{3}=\left(F \rho^{4}-4 G_{2}\right) /[2(-0.0056)] \\
& G_{4}=\left(F \rho^{6}-6 G_{3}\right) /[2(-0.0056)] \\
& G_{5}=\left(F \rho^{8}-8 G_{4}\right) /[2(-0.0056)] \\
& G_{6}=\left(F \rho^{30}-10 G_{5}\right) /[2(-0.0056)]
\end{aligned}
$$

$$
\text { The integral, } \int\left[\left(T / \rho^{2}\right)\left(\partial^{2} P / \partial T^{2}\right)_{\rho}\right]_{T} d \rho \text { may be written as: }
$$

$$
\begin{equation*}
\sum_{i=1}^{32} N_{i} Y_{i} \tag{47}
\end{equation*}
$$

where the $N_{i}$ are listed in Table 10 and the $Y_{i}$ are listed below:
$Y_{1}=0.0$
$Y_{2}=\rho /\left(4 T^{\frac{3}{2}}\right)$
$Y_{3}=0.0$
$Y_{4}=2 \rho / T^{2}$
$Y_{5}=6 \rho / T^{3}$
$Y_{6}=0.0$
$Y_{7}=0.0$
$Y_{B}=\rho^{2} / T^{2}$
$Y_{g}=3 \rho^{2} / T^{3}$
$Y_{10}=0.0$
$Y_{11}=0.0$

$$
\begin{aligned}
& Y_{12}=\left(2 \rho^{3}\right) /\left(3 T^{2}\right) \\
& Y_{13}=0.0 \\
& Y_{14}=\left(2 \rho^{5}\right) /\left(5 T^{2}\right) \\
& Y_{15}=\left(6 \rho^{5}\right) /\left(5 T^{3}\right) \\
& Y_{16}=\rho^{6} /\left(3 T^{2}\right) \\
& Y_{17}=\left(2 \rho^{7}\right) /\left(7 T^{2}\right) \\
& Y_{18}=\left(6 \rho^{7}\right) /\left(7 T^{3}\right) \\
& Y_{1 y}=\left(3 \rho^{8}\right) /\left(4 T^{3}\right) \\
& Y_{20}=6 G_{1} / T^{3} \\
& Y_{21}=12 G_{1} / T^{4} \\
& Y_{22}=6 G_{2} / T^{3}
\end{aligned}
$$

$Y_{23}=20 G_{2} / T^{5}$
$Y_{24}=6 G_{3} / T^{3}$
$Y_{25}=12 G_{3} / T^{4}$
$\gamma_{26}=6 G_{4} / T^{3}$
$Y_{27}=20 G_{4} / T^{5}$
$\gamma_{28}=6 G_{5} / T^{3}$
$Y_{29}=12 G_{5} / T^{4}$
$\gamma_{30}=6 \mathrm{G}_{6} / \mathrm{T}^{3}$
$Y_{31}=12 G_{6} / T^{4}$
$Y_{32}=20 G_{6} / T^{5}$

$$
\begin{aligned}
& F=\exp \left(-0.0056 \rho^{2}\right) \\
& G_{1}= F /[2(-0.0056)] \\
& G_{2}=\left(F \rho^{2}-2 G_{1}\right) /[2(-0.0056)] \\
& G_{3}=\left(F \rho^{4}-4 G_{2}\right) /[2(-0.0056)] \\
& G_{4}=\left(F \rho^{6}-6 G_{3}\right) /[2(-0.0056)] \\
& G_{5}=\left(F \rho^{8}-8 G_{4}\right) /[2(-0.0056)] \\
& G_{6}=\left(F \rho^{10}-10 G_{5}\right) /[2(-0.0056)]
\end{aligned}
$$

The integral $\int c_{p}^{0} d T$ may be written as:

$$
\begin{equation*}
\sum_{i=1}^{32} N_{i} Y_{i} \tag{48}
\end{equation*}
$$

where the $N_{i}$ are listed in Table 14 and the $Y_{i}$ are given below:

$$
\begin{array}{ll}
Y_{1}=-1 /\left(2 T^{2}\right) & Y_{5}=T^{2} / 2 \\
Y_{2}=-1 / T & Y_{6}=T^{3} / 3 \\
Y_{3}=\ln (T) & Y_{7}=T^{4} / 4 \\
Y_{4}=T & Y_{8}=U T /[\exp (U)-1] \\
& U=N_{9} / T\left(N_{9} \text { from Table } 14\right)
\end{array}
$$

The integral $\int\left(C_{p}^{0} / T\right) d T$ may be written as:

$$
\begin{equation*}
\sum_{i=1}^{32} N_{i} Y_{i} \tag{49}
\end{equation*}
$$

where the $N_{i}$ are listed in Table 14 and the $Y_{i}$ are given below:

$$
\begin{aligned}
& Y_{1}=-1 /\left(3 T^{3}\right) \\
& Y_{2}=-1 /\left(2 T^{2}\right) \\
& Y_{3}=-1 / T \\
& Y_{4}=\ln (T)
\end{aligned}
$$

$$
Y_{5}=T
$$

$$
Y_{6}=T^{2} / 2
$$

$$
Y_{7}=T^{3} / 3
$$

$$
Y_{B}=U /(E U-1)-\ln [1-(I / E U)]
$$

$$
\begin{aligned}
& U=N_{9} / T\left(N_{9}\right. \text { from Table 14) } \\
& E U=\exp (U)
\end{aligned}
$$

$$
\begin{aligned}
& \text { APSENDIX E }
\end{aligned}
$$

tables of thermodynamic properties of nitrogen




| temperature deg kelvin | PRESSURE ATM | DENSITY | INTERNAL ENERGY J/MOL | ENTHALPY J/MOL | ENTROPY | $\begin{gathered} \text { Cy } \\ \text { A/mol-R } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 98 | 4.6748 | $\begin{aligned} & 25.018 \\ & 0.9900 \end{aligned}$ | $\begin{aligned} & -2189 . \\ & 1774 . \end{aligned}$ | $\begin{aligned} & -2162 . \\ & 2457 . \end{aligned}$ | $\begin{array}{r} 93.67 \\ 140.62 \end{array}$ | $\begin{aligned} & 26.24 \\ & 23.34 \end{aligned}$ |
| 100 | 7.6885 | $\begin{array}{r} 24.583 \\ 1.140 \end{array}$ | $\begin{array}{r} -2065 . \\ 1782 . \end{array}$ | $\begin{array}{r} -2033 . \\ 2465 . \end{array}$ | $\begin{array}{r} 94.73 \\ 139.72 \end{array}$ | $\begin{aligned} & 26.19 \\ & 23.58 \end{aligned}$ |
| 102 | 8. 8083 | $\begin{array}{r} 24.133 \\ 1.309 \end{array}$ | $\begin{array}{r} -1939 . \\ 1786 . \end{array}$ | $\begin{array}{r} -1902 . \\ 2468 . \end{array}$ | $\begin{array}{r} 75.98 \\ 138.83 \end{array}$ | $\begin{aligned} & 26.17 \\ & 23.84 \end{aligned}$ |
| 104 | 10.041 | $\begin{array}{r} 23.665 \\ 1.499 \end{array}$ | $\begin{array}{r} -1811 . \\ 1787 . \end{array}$ | $\begin{array}{r} -1768 . \\ 2466 . \end{array}$ | $\begin{array}{r} 97.23 \\ 137.94 \end{array}$ | $\begin{aligned} & 26.15 \\ & 24.23 \end{aligned}$ |
| 106 | 11.392 | 23.176 1.713 | $\begin{array}{r} -1681 . \\ 1783 . \end{array}$ | $\begin{array}{r} -1631 \\ 2457 \end{array}$ | $\begin{array}{r} 98.48 \\ 137.05 \end{array}$ | $\begin{aligned} & 26.16 \\ & 24.43 \end{aligned}$ |
| 168 | 12.870 | $\begin{array}{r} 22.669 \\ 1.954 \end{array}$ | $\begin{aligned} & -1548 . \\ & -1774 . \end{aligned}$ | $\begin{array}{r} -1491 . \\ 2441 . \end{array}$ | $\begin{array}{r} 99.73 \\ 136.14 \end{array}$ | $\begin{aligned} & 26.17 \\ & 24.76 \end{aligned}$ |
| 110 | 14:481 | $\begin{array}{r} 22.133 \\ 2.228 \end{array}$ | $\begin{array}{r} -1412 . \\ 1759 . \end{array}$ | $\begin{array}{r} -1345 . \\ 2417 . \end{array}$ | $\begin{aligned} & 100.99 \\ & 135.20 \end{aligned}$ | $\begin{aligned} & 26.21 \\ & 25.12 \end{aligned}$ |
| 112 | 16.233 | $\begin{array}{r} 21.566 \\ 2.542 \end{array}$ | $\begin{aligned} & -1271 . \\ & 1737 . \end{aligned}$ | $\begin{array}{r} -1195 . \\ 2384 \end{array}$ | $\begin{aligned} & 102.28 \\ & 134.23 \end{aligned}$ | $\begin{aligned} & 26.26 \\ & 25.52 \end{aligned}$ |
| 114 | 18.133 | $\begin{array}{r} 20.960 \\ 2.903 \end{array}$ | $\begin{array}{r} -1126 . \\ 1707 . \end{array}$ | $\begin{array}{r} -1038 . \\ 2340 . \end{array}$ | $\begin{aligned} & 103.58 \\ & 133.21 \end{aligned}$ | $\begin{aligned} & 26.35 \\ & 25.96 \end{aligned}$ |
| 116 | 20.190 | $\begin{array}{r} 20.302 \\ 3.326 \end{array}$ | $\begin{aligned} & -974 . \\ & 1666 . \end{aligned}$ | $\begin{aligned} & -873 . \\ & 2281 . \end{aligned}$ | $\begin{aligned} & 104.93 \\ & 132.12 \end{aligned}$ | $\begin{aligned} & 26.46 \\ & 26.45 \end{aligned}$ |
| 118 | 22.411 | $\begin{array}{r} 19.575 \\ 3.828 \end{array}$ | $\begin{aligned} & -813 . \\ & 1611 . \end{aligned}$ | $\begin{aligned} & -697 . \\ & 2205 . \end{aligned}$ | $\begin{aligned} & 106.34 \\ & 130.92 \end{aligned}$ | $\begin{aligned} & 26.62 \\ & 27.01 \end{aligned}$ |
| 120 | 24.306 | $\begin{array}{r} 18.745 \\ 4.444 \end{array}$ | $\begin{aligned} & -639 . \\ & 1537 . \end{aligned}$ | $\begin{aligned} & -505 . \\ & 2103 . \end{aligned}$ | $\begin{aligned} & 107.85 \\ & 129.57 \end{aligned}$ | $\begin{aligned} & 26.86 \\ & 27.06 \end{aligned}$ |
| 122 | 27.386 | $\begin{array}{r} 17.745 \\ 5.239 \end{array}$ | $\begin{aligned} & -443 . \\ & 1434 . \end{aligned}$ | $\begin{aligned} & -286 . \\ & 1963 . \end{aligned}$ | $\begin{aligned} & 109.54 \\ & 127.97 \end{aligned}$ | $\begin{aligned} & 27.23 \\ & 28.43 \end{aligned}$ |
| 124 | 30.174 | $\begin{array}{r} 16.388 \\ 6.392 \end{array}$ | $\begin{aligned} & -200 . \\ & 1272 . \end{aligned}$ | $\begin{aligned} & -14 . \\ & 1750 . \end{aligned}$ | $\begin{aligned} & 111.62 \\ & 125.84 \end{aligned}$ | $\begin{aligned} & 27.86 \\ & 29.40 \end{aligned}$ |
| 126 | 33.227 | $\begin{array}{r} 13.270 \\ 9.237 \end{array}$ | $\begin{aligned} & 272 . \\ & 647 . \end{aligned}$ | $\begin{array}{r} 526 . \\ 1211 . \end{array}$ | $\begin{aligned} & 115.76 \\ & 121.20 \end{aligned}$ | $\begin{aligned} & 29.73 \\ & 30.80 \end{aligned}$ |
| 126.200 | 33.355 | 11.210 | 359. | 663. | 118.41 | 30.68 |

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30.73


 oEG KELVIM

## 

－${ }^{\circ} \mathrm{m}$



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--inn ni: +安 : ? :


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-4108.$\stackrel{+}{4}$11626.50492.
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$65677^{\circ}$.
: MTERNAL
EMERGY
-4212.
-411.-3828.
-3572.
1501.
1513.
1622.
1730.
1836.
2080.
2262.
2472.
2682.
2891.3100.
3309.
3726.
4143.
4560.
4976.
5392.
5808.
6224.
1266.8309.9358.
10415.
12564.
14771.
17044.
19384.
2178.
26755.
31902.$\begin{array}{ll}0.005331 & 37187 . \\ 0.004739 & 42576 . \\ 0.004265 & 48046 .\end{array}$imotcates two phase boumoaryTEMPERATURE-63.164
$\$ \$$otingnogoogo1400
1800
2000

- imolcates two pmase soumoany
© ${ }_{\circ}^{\circ}$N.
 FN68.01
69.39
smar -4209.
-4107.     ..... 50493.
S754.

44573. 

ENERGY
S/MOR ..... -4212.
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En
©density$30 L / 2$0.007615
0.056769
0.006092temperature-63.171

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$\sim N$
NN
3 J／MOL－K

### 26.94 27.89




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## 


50501.
$575544^{\circ}$
$64687^{\circ}$.

4 ATMOSPHERE ISOBAR

## TEMPERATURE

DEG KELVIN

## －63．238




600
800
000 1600
1800
2000 $\rightarrow-\rightarrow$



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\dot{c}
$$

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\begin{gathered}
0 \\
0 \\
0 \\
0 \\
0
\end{gathered}
$$

$$
\begin{aligned}
& \dot{N} \\
& \vdots \\
& 0 \\
& 0
\end{aligned}
$$

$$
\dot{\circ} \dot{\circ}
$$

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in    ..... Nis ..... $\infty$
$i n$
m
0J/MOL-K J/MOL-K$\stackrel{m}{\square}$$\underset{N}{n}$

\&


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9098989
1600
1800
2000


 N~NN:
 $\dot{\sim} \dot{\sim}$

J/MOL-K


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ENTROPY68.11
69.32
$\square$

 $n$
0
0
$\sim$
$\sim$
thermodynamic properties of nitrogen 30 a tmosphere isobar


 $\begin{array}{ll}\infty & m \\ n & n \\ n & n \\ n\end{array}$
3

$N \rightarrow M$
NMN






0
0
0
0
$m$6682.
7309.
7427.8539.
0053.11552.
13047.
14543.
$17550^{\circ}$
20617.
23737.
26920.
30163.
36807.
43625.siós
Non
notINTERNAL
ENERGY

150
160
180
200
220
240
260
280
300
350
 1600
1800
2000



MOL /L1/MOL







 $\begin{array}{ll}0.2269 & 37181 . \\ 0.2018 & 42573 . \\ 0.1818 & 48046 .\end{array}$ 0.9055
0.8031
0.7221
0.6014
0.5157
0.4516
0.4017
0.3618
0.3019
0.2591
31.02 $90^{\circ} \mathrm{OE}$ 30.19



 -
 $\begin{array}{ll}0.3019 & 26739 . \\ 0.2591 & 31892 .\end{array}$ - Indicates fio phase boundar
thermodynamic properties of nitrogen
YELOCITY
OF SOUND








 non
nin
ninm
nin



 NNNなんNはN MNNNNNNNNN

 N～～～

## Enthalpy



-3737.
-3455.
-3173.
-2897.
-2604.
-2015.
-1383.
-648.
1005.
2603.
INTERNALENERGY－4198．2305.
2642.
3211.
3718.
4197.
4659.
5111.
5556.
5996.
7082.37179.
42572.
48045.

LO atmosphere isobar
TEMPERATURE DENSITY OEG KELVIN MOLIL 31.03
 4.416
3.814
3.096
2.653
2.340
2.103
1.914
1.760
1.631
1.333
 0.3018
0.2686
0.2419 70
75
90
85
90
100
110
120
130
140



1600
1800
2000
－indicates two phase boundary
thermootnamic properties of nitrogen
VELOCITY
OF SOUND

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N． 1241.
1230. 1096. 울 － 8品品 －




Entropy



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N







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| $\dot{n}$ |$\stackrel{0}{0}$$\stackrel{i}{i}$ENTROPYJ/MOL-K68.56옹$\stackrel{+}{\circ}$

ENTHALPY18.22

$$
\begin{aligned}
& 189.65 \\
& 195.73 \\
& 200.99
\end{aligned}
$$

$$
\begin{aligned}
& \stackrel{\circ}{n} \\
& \dot{\sim} \\
& \dot{\sim}
\end{aligned}
$$






 14492.
17575.
20884.
$23840^{\circ}$
$27040^{\circ}$
30311.
36983.
43819.
$50784_{0}$.
57848. 64989.

$$
\begin{gathered}
86.21 \\
89.65
\end{gathered}
$$

$$
\begin{aligned}
& 32.43 \\
& 86.21
\end{aligned}
$$

 6790. 1490.
168. 8168.
9804.
1389. 11389.

2947 $\stackrel{\circ}{\stackrel{\circ}{n}}$ -4176. 3395.



 | $\dot{8}$ |
| :--- |
| 0 |
| 0 | phase boundary

## DENSITY

## MOL/L

31.12 $\stackrel{n}{n}$

 0.5980

 $\stackrel{\dot{\circ}}{+}$会 555.
589.
621. ペーか シペ家 $\stackrel{\dot{a}}{a}$

ENTROPY CV

$\stackrel{\infty}{N}$ENTROPY69.16
71.09
74.74$\pm$121.93N131.95
135.77135.77
139.05141.92
144.49No
0
0
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0| $\circ$ |
| :--- |
|  |
|  |

ENTHALPY



            㽞呙
    
-2825.
-2562.
-2300.
-1774.
-12450
-709.
-166.
384.
940.
1499.   ..... 65306.
INTERNAL

ENERGY| ＋ |
| :--- |
| ＋ |
| 8 |
| 8 |

1.174
TEMPERATURE8
$\vdots$
088988898082000
VELDCITY
OF SOUND
M／SEC

 $\begin{array}{ll}0 \\ 0 \\ 0 \\ 0 \\ 0 & 0 \\ 0\end{array}$
 ベ末 $\stackrel{\sim}{\sim}$
 $\stackrel{\rightharpoonup}{*}$
in

| ENTROPY | CY |
| :---: | :---: |
| NMOL－K | J／MOL－K | 0

0
$\vdots$
$\vdots$
$\vdots$
0
0 0
Fo
0
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0
0

i$\stackrel{n}{0}$





700 a Tmoseneat 1 SOBAR THERMOOYMAMIC PROPERTIES OF NITROGEN
velocity
of soumo
 T00 ATMOSHERE ISOBAR
TEMPERATURE DENSITY

$\therefore$| 7 |
| :---: |
| $\frac{1}{6}$ |
| 7 |




EnTROPV. CV
3/MOL-K

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Entropy



- NonnのMM~


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| :---: | :---: | :---: | :---: |
|  |  |  |  |

MOL 1
N.

- MOOOMOO

- imotcates two phase soundapy

- inoicates two phase buundary
thermodynamic properties of nitrogen
velocity M/SEC 1530.

1529. | $\circ$ |
| :--- |
| $\stackrel{\circ}{\circ}$ | 0

0
0
0
 -. . ( $\stackrel{+1000}{\circ}$



 $*$
$\dot{m}$
$\dot{m}$$\stackrel{+}{0}$

ENTROPY    ..... | 6 |
| :--- |
| 8 |
| 0 |

 ..... 47840.4000 ATMOSPHERE ISOBARphase boundary
thermodynamic properties of nitrogen
onsity
onsity HOL/L ..... 36.51
  ..... 18.76
INTERNAL
ENRRGY
J/MOL -2335.
-2270.   26041.
TEAPERATURE
TEAPERATURE    ..... 12001415.
YELOCITY
OF SOUND


|  | $\begin{aligned} & \text { mor } \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  <br>  |
| :---: | :---: | :---: |
|  |  |  <br>  |


|  |  |  <br>  <br>  |  |
| :---: | :---: | :---: | :---: |
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|  |  | のロ゚ <br>  |  |

TEMPERATURE
DEG KELVIN
162.127
OOOOOg9808
600
700
800
900
1000
1100
1200

|  |  |  の～N～Nがージ NNNNNNNNN |  |
| :---: | :---: | :---: | :---: |
| $\because \begin{aligned} & \frac{x}{1} \\ & \vdots \\ & 0 \\ & \vdots \\ & 7 \end{aligned}$ |  |  <br>  <br> mmmmmmmmon |  <br> nninmion |


| 10000 atmosphere isobar thermodymamic properties of |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| temperature | density | INTERNAL ENERGY | Enthalpy | Entropy | cv |
| deg kelvin | MOL／L | 1／MOL | J／MOL | J／MOL－K | J／MOL－K |
| ． 191.605 | 40.76 | 773. | 25634. | 87.49 | 30.22 |
| 200 | 40.68 | 997. | 25906． | 88.87 | 31.30 |
| 220 | 40.44 | 1545. | 26602. | 92.19 | 32.87 |
| 240 | 40.14 | 2107. | 27349. | 95.43 | 33.47 |
| 260 | 39.81 | 2674. | 28＇34． | 98.54 | 33.49 |
| 230 | 39.46 | 3240. | 28915. | 101.47 | 33.18 |
| 300 | 39.11 | 3802. | 29713. | 104． 22 | 32.69 |
| 350 | 38.21 | 5175. | 31693. | 110.33 | 31.27 |
| 400 | 37.36 | 6502. | 33624. | 115.49 | 29.98 |
| 450 | 36.56 | 1790. | 35504. | 119.92 | 28.98 |
| 500 | 35.81 | 9050. | 37343. | 123.79 | 28.22 |
| 600 | 34.45 | 11525. | 40942. | 130.36 | 27.37 |
| 700 | 33.21 | 13986. | 44495. | 135.83 | 27.06 |
| 800 | 32.09 | 16467. | 48046. | 140.57 | 27.06 |
| 900 | 31.05 | 18983. | 51618. | 144．78 | 27.20 |
| 1000 | 30.09 | 21540. | 55219. | 148．58 | 27.41 |
| 1100 | 29.19 | 24139. | 58853. | 152.04 | 27.64 |
| 1200 | 28.35 | 26775. | 62516. | 155.23 | 27.86 |

