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THE UNIVERSITY OF OKLAHOMA  
AN ACCURATE EQUATION OF STATE FOR CARBON DIOXIDE  
GRADUATE COLLEGE  
AT SUPERCRITICAL CONDITIONS  
A THESIS  
APPROVED FOR THE SCHOOL OF CHEMICAL ENGINEERING  
AND MATERIAL SCIENCE

AN ACCURATE EQUATION OF STATE FOR CARBON DIOXIDE  
AT SUPERCRITICAL CONDITIONS

A THESIS  
SUBMITTED TO THE GRADUATE FACULTY  
in partial fulfillment of the requirements for the  
degree of  
MASTER OF SCIENCE

BY *Feng-Hsin Huang*

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I would like to express my deepest gratitude to Prof. [Name] for his guidance and support throughout the project. My special thanks are also extended to Prof. Z. T. Ellington and Prof. E. E. Sestling for serving on my advisory committee.

I am also grateful for the assistance in programming and the encouragement given by Dr. T. H. Chung.

Finally, I wish to express my sincere appreciation to my wife Li-Mei for her love, patience, and understanding.

By

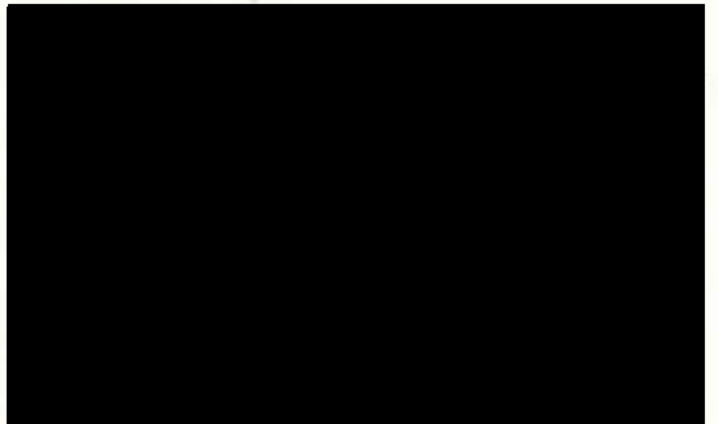




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Carbon dioxide is an inorganic compound of considerable industrial importance. Approximately 80% of the recovered carbon dioxide is used as a raw material in the production of other chemicals, mainly urea and methanol. About one-third of carbon dioxide produced is used in secondary oil recovery. This is the fastest growing use for carbon dioxide. Refrigeration, beverage carbonation, and other miscellaneous applications for the remainder (Kirk and Othmer, 1978).

In recent years supercritical fluid technology has received increasing attention due to safety and economic factors. The feasibility of using carbon dioxide as a solvent in supercritical extraction is being actively pursued. Supercritical carbon dioxide is considered to be

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CHAPTER I

INTRODUCTION

Carbon dioxide is an inorganic compound of considerable industrial importance. Approximately 40% of the recovered carbon dioxide is used as a raw material in the production of other chemicals, mainly urea and methanol. About one-third of carbon dioxide produced is used in secondary oil recovery. This is the fastest growing use for carbon dioxide. Refrigeration, beverage carbonation, and other miscellaneous applications account for the remainder (Kirk and Othmer, 1978).

In recent years supercritical fluid technology has received increasing attention due to social and economic factors. The feasibility of using carbon dioxide as a solvent in supercritical extraction is being actively pursued. Supercritical carbon dioxide is considered to be



an ideal solvent because it is nontoxic, nonexplosive, low-cost, readily available and easily removed from the extracted products. Decaffeination of coffee and regeneration of activated-carbon are good examples of commercial large-scale processes using supercritical carbon dioxide (Grimmett, 1981; Kohn et al., 1979). Many other applications of supercritical carbon dioxide are under extensive investigation. One of the promising applications is the extraction of oil seeds. It could free over 20 million gallons of costly hexane per year for essential energy uses (Friedrich et al., 1982).

The current large-scale use of carbon dioxide for enhanced oil recovery as well as the accelerated interest in the applications of supercritical carbon dioxide have led to the need for a set of consistent and accurate thermodynamic properties covering a wide range of conditions, especially for the supercritical region. Nowadays much of process design work and engineering calculations are carried out with the aid of high-speed digital computers. Therefore, the equation of state capable of predicting thermodynamic properties over a wide range within experimental uncertainties becomes useful and important. Actually, existing tables and charts of thermodynamic properties available in many publications are mostly generated from using certain equations of state.

During the last hundred years numerous equations of state of pure substances have been proposed, but an accurate wide-range equation for carbon dioxide is not yet available. Some of these equations are able to represent the experimental data in certain regions of the thermodynamic surface, but become quite inadequate when applied to other regions, especially the critical or liquid region. Although certain formulations can accurately describe the volumetric behavior over a wide range of temperature and pressure, they become unsatisfactory, even not applicable at all, in the estimations of saturation and/or thermal properties.

No attempt is made in this work to describe all the equations of state that are proposed or suitable for carbon dioxide. Attention is restricted to some most significant or relatively more accurate equations of state. One of the most widely used equations of state in chemical process industries is the BWR equation (Benedict, Webb, and Rubin, 1940). This equation has been applied to a number of pure substances and their mixtures in correlating both liquid and vapor volumetric and thermodynamic data with reasonable success, but not within the experimental accuracy. It is well known that the eight-parameter BWR equation is inadequate to describe wide-range data with a unique set of coefficients. For more accurate correlations individual



sets of coefficients are necessary, each for different range or for different type of data. One method of refinement is to make one or more coefficients temperature dependent. Generally speaking, the BWR equation gives poor correlation for the liquid phase.

Van Huff, Houghton, and Coull (1963) reported three volume-explicit equations of state that fit the compressibility data of gaseous carbon dioxide with an average deviation of 0.09% and a maximum of 0.5% over the range 0 to 600 °C and 0 to 150 atm. These three separate equations, each operative over a certain temperature and pressure range, have 22, 30, and 36 empirical constants, respectively. The three equations might be the most accurate expressions to represent the volumetric behavior over the above-specified range. However, they can not be applied to the critical region, nor to the high density region. The validity of the three equations to predict thermal properties is questionable. In addition the use of three separate equations could produce discontinuities in the overlapping region.

A pressure-explicit equation of state up to the fifth power of  $1/v$  has been presented by Martin and Hou (1955). In a later work (1959) the equation was modified to improve the performance in the neighborhood of 1.4 times the critical density. This 12-parameter equation was designed

specially to have the correct curvature in the vicinity of the critical point. It has been shown to represent the volumetric behavior of carbon dioxide with good precision up to about 1.5 times the critical density. However, this equation can not describe the phase behavior, nor the PVT and thermal behaviors in the dense fluid region at all.

Recently Khan et al. (1983) proposed a new generalized equation of state. This equation has been tested for a wide range of nonpolar fluids to predict thermodynamic properties with reasonable accuracy. It is also successfully extended to polar fluids by introducing one more parameter. Since generalized equations have their inherent limitations, one cannot expect them to give the highly accurate predictions of thermodynamic properties for each substance over wide-range conditions.

Bender (1970) presented an equation of state for several fluids including carbon dioxide, each with a different set of coefficients. This 20-constant equation belongs to an extension of the BWR equation representing the volumetric and thermal behaviors of carbon dioxide with high accuracy in both liquid and vapor range. It is valid for pressures up to about 7,250 psia and for a temperature range from the triple point to nearly 2,000 °R. The vapor pressure and the orthobaric densities can also be calculated from the same equation with the accuracy corresponding to



that of the experimental data. This formulation was selected by Reynolds (1979) in his publication as the best PVT equation for carbon dioxide, and was used to prepare the graph and table of thermodynamic properties. So the Bender equation might be, in general, the most accurate and optimal equation of state for carbon dioxide up to the present.

The purpose of this study is to develop an equation of state for carbon dioxide that is capable of predicting the volumetric and thermodynamic properties with great accuracy in the whole fluid region of the PVT surface including the phase boundaries. Special attention will be paid to the critical region. Attempts have been made to include in the equation of state certain special functions which work only in the critical region, so that the performance in the vicinity of the critical point is significantly improved. The constants in the equation of state are determined from the multiproperty regression analysis of experimental vapor pressure, enthalpy, and PVT data. The existing literature data for carbon dioxide will be briefly reviewed in the next chapter. The proposed equation of state and its derived expressions for other thermodynamic properties will be presented in Chapter III. In Chapter IV the correlation and prediction results will be given and discussed in detail. The comparison between the proposed equation and other equations of state has also been

made. Therefore, the capability as well as the superiority of the equation obtained in this work can be appreciated.

## CHAPTER II

### BRIEF SURVEY OF EXISTING DATA

Experimental data on the thermodynamic properties are essential to the development of an equation of state. Few compounds have been studied more extensively than carbon dioxide. There are many reliable observed data to be found in the literature. No attempt is made in this paper to review all previous investigations done on carbon dioxide. Only some most significant measurements will be mentioned here. Since PVT, vapor pressure, and thermal data are used for the correlation in this work, review will be restricted to those thermodynamic property data. For the work on thermodynamic properties of carbon dioxide up to 1959 the summary of Lilley (1959) should be consulted. A review of the available literature data is also given in Din's compilation (1956).

#### Compressibility Data

The PVT relationships of carbon dioxide have been



## CHAPTER II

### BRIEF SURVEY OF EXISTING DATA

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#### Compressibility Data

The PVT relationships of carbon dioxide have been

investigated over a rather extensive range. The important early work is that of Amagat (1891), who furnished the data for a temperature range from 0 to about 258 °C and a pressure range from 50 to 1,000 atm, including some isotherms around the critical region. The most extensive and probably the most accurate PVT measurements to date for carbon dioxide are the work of Michels and his coworkers (1935a, 1935b, 1937), covering the range from 0 to 150 °C in temperature and from 16 to 3,000 atm in pressure. The data of Michels were claimed to have a precision of 0.01%, except for the critical region data, which have a precision of about 0.18%. The work of MacCormack and Schneider (1950) covered the temperature range from 0 to 600 °C and for pressures up to 50 atm, having a precision of 0.01%. The data of Kennedy (1954) with a precision of 0.2% cover a wide range of temperatures and pressures, from 0 to 1,000 °C and from 25 to 1,381 atm. However, the smoothed values finally tabulated by Kennedy can differ from the experimental data by 0.4% or 0.0002 g/cc, whichever is the greater.

For the high temperature and high pressure regions only Juza, Kmonicek and Sifner (1965) appear to have measured the specific volume for carbon dioxide. Their results, with a precision of 0.3%, range from 50 to 475 °C in temperature and from about 690 to 3,946 atm in pressure. For the temperatures below 0 °C Jenkin (1921) measured the



liquid density of carbon dioxide from  $-37$  to  $30$  °C at pressures up to 70 atm. The accuracy of the Jenkin data is not very satisfactory, with an uncertainty of about 0.01 g/cc in density.

In addition to Amagat and Michels, Wentorf (1956) has made PVT determinations in the critical region. However, his data cover only the range very near the critical point, between  $31.02$  and  $31.10$  °C, and  $72.723$  and  $72.974$  atm. Also the reported values by Wentorf are scattered and not smoothed out.

#### Data Evaluation

Juza et al. (1965) have made a comparison of the smoothed values of PVT measurements reported by the various authors. Those smoothed values are in some instances obtained by interpolation method because of different units and intervals used in their presentations. The important conclusions drawn from the comparison include the following:

- (1) The maximum difference between the Michels and the Amagat values on the  $50$  and  $100$  °C isotherms is 0.5%, the average being about 0.25%. The mean deviation is 0.5% on the  $150$  °C isotherm.
- (2) The difference between the Michels and the MacCormack values is about 0.03% and grows up to 0.15% with

- and increasing pressure.
- (3) The average deviation of the Kennedy data from the Michels data on the 50, 100, and 150 °C isotherms does not exceed 0.3%, the Kennedy values being usually higher than those of Michels.
  - (4) The average deviation of the Juza values from the data of Kennedy and the data of Michels in the overlapping region is about 0.10%, with the maximum of 0.29%.

The recent important evaluation of the compressibility factor data of carbon dioxide is the work of Starling and his coworkers (1982). The data sets included in the evaluation are: Ku and Dodge (1967), Michels and his coworkers (1935a, 1935b), MacCormack and Schneider (1950), Reamer et al. (1944), and Sass et al. (1967). The data of Michels are recommended to be used, giving an uncertainty on the order of 0.1%, since in the evaluation most of the data tend to be scattered around the values of Michels.

#### Vapor Pressure Data

There are abundant vapor pressure data available in the literature for carbon dioxide. Kennedy and Thodos (1960) examined 14 references and concluded that the values obtained by Meyers and Van Dusen (1933) and those reported by Amagat (1892), Michels, Blaisse and Michels (1937), Plank



and Kuprianoff (1929), and Zelany and Smith (1907) represent data for carbon dioxide that are internally consistent.

The most comprehensive and significant investigations on the vapor pressure of carbon dioxide might be the work of Meyers and Van Dusen (1933). They have measured the vapor pressure of liquid and solid carbon dioxide from the critical point through the triple point and down to  $-180^{\circ}\text{C}$ . Michels and others (1937) have measured the vapor pressure from the critical temperature to  $2.853^{\circ}\text{C}$ . In a later investigation (1950) they measured the vapor pressure between  $-56$  and  $3^{\circ}\text{C}$ , covering a pressure range from 5 to 37 atm.

#### Thermal Data

There are relatively few experimental thermal data to be found in the literature, compared to the abundant PVT data. Since, usually, the experimental PVT data are abundant and precise, and cover a wide range of temperature and pressure, the derived thermodynamic properties tabulated in many compilations (e.g. Din, 1956; NBS, 1955; Price, 1955; Vargaftik, 1975) were obtained through the thermodynamic relationships from the equation of state, or directly from the compressibility data using the numerical methods. For instance, in Din's compilation (1956) the

tables of thermodynamic functions for carbon dioxide are mainly based on the excellent PVT work of Michels, and prepared by using a graphical method.

Koppel and Smith (1960) have measured the thermal data for carbon dioxide in the near-critical region, covering a temperature range from 65 to 120 °F at pressures from 1,050 to 1,200 psia. The investigation by Koppel and Smith is of particular importance. As indicated by them, calculated thermal properties are not reliable in the critical region. This is due to difficulties in computing accurate results from PVT data. The density changes so rapidly with pressure and temperature near the critical point that interpolation becomes inaccurate. Also the computations involve first, and sometimes second, derivatives of density, and this introduces error in numerical work.

#### Data Used for Correlation and Test

Due to the extensive and accurate compressibility measurements performed by Michels and his coworkers, the data of Michels have become a reference data set. Commonly, those who study the PVT behavior of carbon dioxide compare their results with the Michels values, whenever the measured range overlaps with that by Michels, to ascertain the



accuracy of their experimental data obtained. Therefore, in this work the PVT data of Michels, including the critical region data, are used for the correlation of the equation of state. The vapor pressure data from Michels are also adopted since it was considered better to adhere to the observed values from the same source. There are no PVT data below 0 °C by Michels. To assure the proposed equation of state in representing the phase behavior and in predicting the cryogenic properties of interest, the liquid density data from Vargaftik (1975) and the vapor density data of Din (1956) are also included for the correlation. The Vargaftik data are calculated empirical data. However, the accuracy was claimed not to exceed the limit of experimental error.

Table 1 lists the data sources along with the temperature and pressure ranges used to evaluate the constants of the equation of state. Figure 1 illustrates the PVT data points used in fitting the equation of state. Table 2 presents a summary of the literature data selected to test the performance of the equation of state. The temperature and pressure range for the PVT data points in Table 2 are illustrated in Figure 2. Note that the highest temperature of the compressibility data by Michels is about 150 °C. It will be shown later that the proposed equation of state still works pretty well for the PVT property predictions when being extrapolated to temperatures as high as 1,000 °C.

TABLE 1.

SELECTED DATA USED TO EVALUATE THE CONSTANTS  
IN THE EQUATION OF STATE

| Data Sources                   | Property              | Temp. Range<br>(°R) | Pres. Range<br>(psia) | No. of<br>Points |
|--------------------------------|-----------------------|---------------------|-----------------------|------------------|
| Michels et al.<br>(1937)       | Vap. Pres.            | 496.8-547.5         | 543.7-1,070           | 10               |
| Michels et al.<br>(1950)       | Vap. Pres.            | 390.8-497.1         | 76.9-547.0            | 19               |
| Michels and<br>Michels (1935a) | P-V-T                 | 491.7-761.9         | 243.2-3,564           | 190              |
| Michels et al.<br>(1935b)      | P-V-T                 | 491.7-761.9         | 1,098-45,820          | 140              |
| Michels et al.<br>(1937)       | P-V-T<br>(critical)   | 496.8-563.8         | 533.7-1,447           | 156              |
| Vargaftik<br>(1975)            | P-V-T<br>(liquid)     | 396.0-576.0         | 290.0-8,702           | 89               |
| Din (1956)                     | P-V-T<br>(gas)        | 347.7-473.7         | 7.3-367.4             | 57               |
| Din (1956)                     | Enthalpy<br>Departure | 437.7-743.7         | 441.0-7,350           | 39               |

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TEMPERATURE (°R)

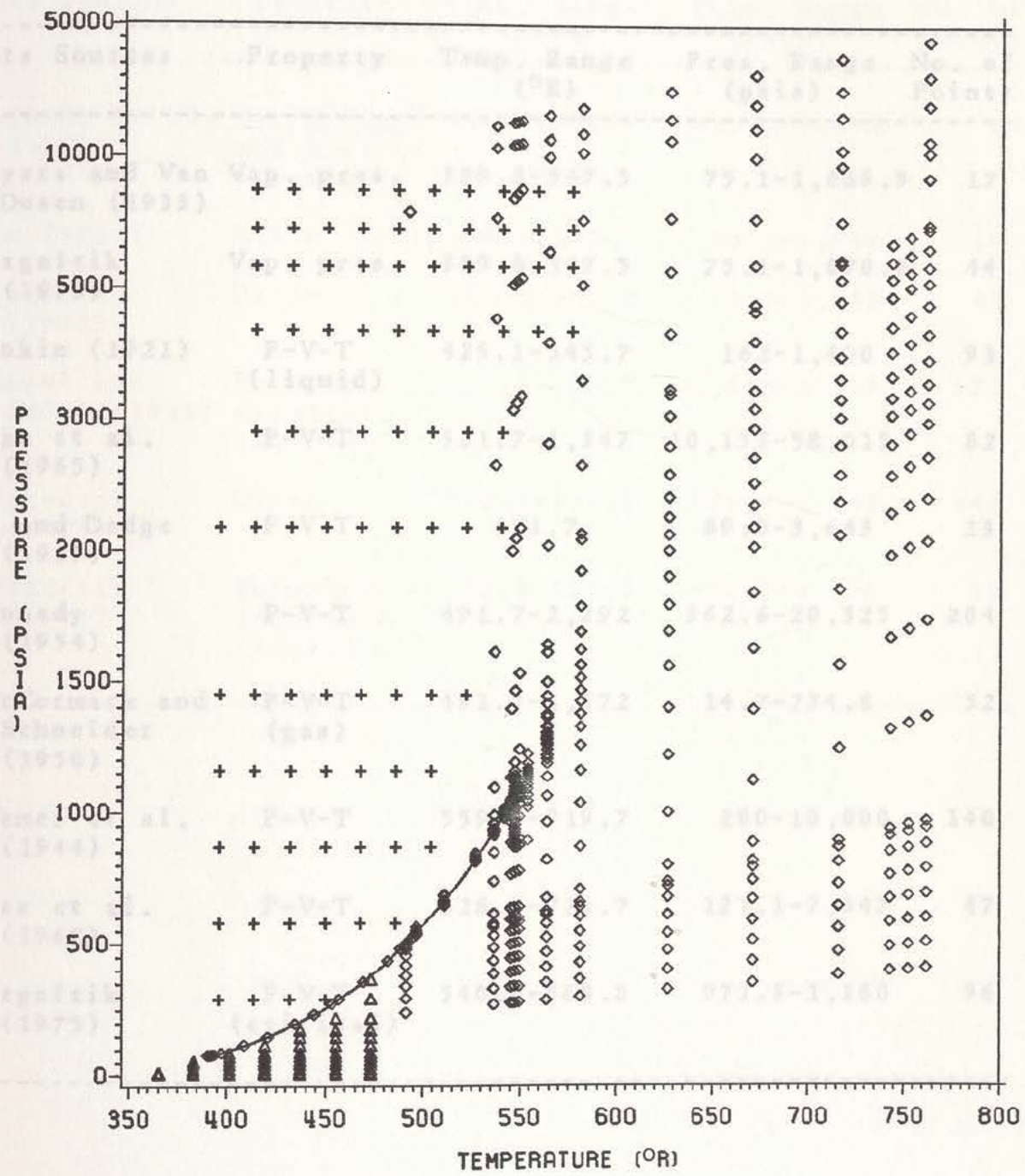
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DATA SOURCE    1 & 4: MICHEL'S    2: VARGAFTIK    3: DIN



TABLE 2.

FIGURE 1.  
 P-V-T DATA SET FOR CARBON DIOXIDE  
 ( USED TO EVALUATE EQUATION-OF-STATE PARAMETERS )



LEGEND: AUTHOR    ◊ ◊ ◊ 1    + + + 2    Δ Δ Δ 3    ◊—◊—◊ 4

DATA SOURCE    1 & 4: MICHELS    2: VARGAFTIK    3: DIN

TABLE 2.

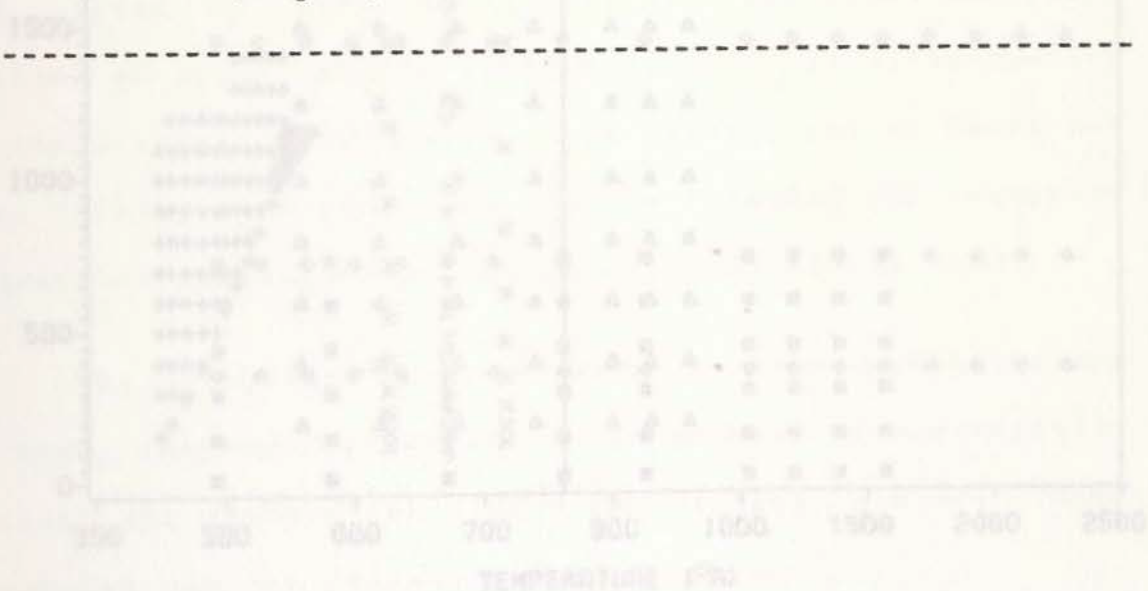
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## SELECTED DATA USED TO TEST THE EQUATION OF STATE

| Data Sources                    | Property            | Temp. Range<br>(°R) | Pres. Range<br>(psia) | No. of<br>Points |
|---------------------------------|---------------------|---------------------|-----------------------|------------------|
| Meyers and Van Dusen (1933)     | Vap. pres.          | 389.8-547.5         | 75.1-1,069.9          | 17               |
| Vargaftik (1975)                | Vap. pres.          | 389.8-547.5         | 75.1-1,070.6          | 44               |
| Jenkin (1921)                   | P-V-T<br>(liquid)   | 425.1-545.7         | 162-1,400             | 93               |
| Juza et al. (1965)              | P-V-T               | 581.7-1,347         | 10,153-58,015         | 82               |
| Ku and Dodge (1967)             | P-V-T               | 671.7               | 89.0-3,643            | 13               |
| Kennedy (1954)                  | P-V-T<br>(liquid)   | 491.7-2,292         | 362.6-20,325          | 204              |
| MacCormack and Schneider (1950) | P-V-T<br>(gas)      | 491.7-1,572         | 14.7-734.8            | 52               |
| Reamer et al. (1944)            | P-V-T               | 559.7-919.7         | 200-10,000            | 140              |
| Sass et al. (1967)              | P-V-T               | 626.7-716.7         | 121.1-7,347           | 47               |
| Vargaftik (1975)                | P-V-T<br>(critical) | 540.0-568.8         | 971.8-1,160           | 96               |

TABLE 2.  
(continued)

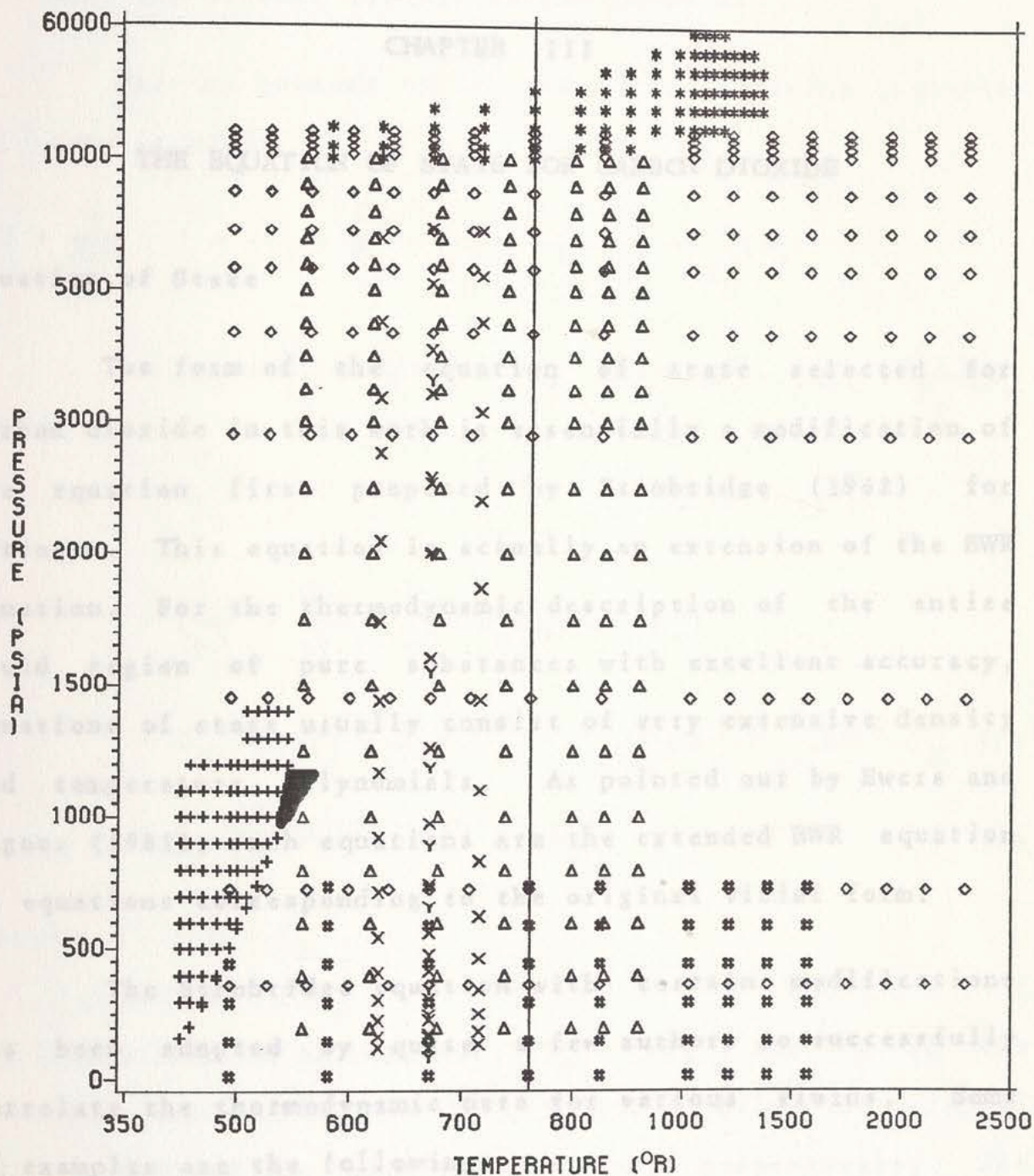
| Data Sources               | Property                               | Temp. Range<br>(°R) | Pres. Range<br>(psia) | No. of<br>Points |
|----------------------------|--|---------------------|-----------------------|------------------|
| Michels et al.<br>(1937)   | Sat'd dens.<br>and heat of<br>vaporiz. | 496.8-547.5         | 543.7-1,070           | 9                |
| Din (1956)                 | Ditto                                  | 389.8-545.7         | 75.1-1,046            | 19               |
| Vargaftik<br>(1975)        | Ditto                                  | 389.8-545.4         | 75.1-1,042            | 43               |
| Koppel and<br>Smith (1960) | Enthalpy<br>departure<br>(critical)    | 524.7-579.7         | 1,050-1,200           | 102              |
| Vargaftik<br>(1975)        | Ditto                                  | 540.0-576.0         | 870.2-1,160           | 441              |
| Vargaftik<br>(1975)        | Enthalpy<br>departure<br>(liquid)      | 396.0-576.0         | 290.0-8,702           | 89               |



LEGEND: AUTHOR 1 2 3 4 5 6 7 8 9  
 DATA SOURCE 1: JENKIN 2: JURA 3: KENNEDY 4: KU  
 5: MALCHENACK 6: SHAMER 7: SART 8: VARGAFTIK



FIGURE 2.  
P-V-T DATA SET FOR CARBON DIOXIDE  
( USED TO TEST THE EQUATION OF STATE )



LEGEND: AUTHOR    + + + 1    \* \* \* 2    ◊ ◊ ◊ 3    Y Y Y 4  
                      # # # 5    Δ Δ Δ 6    X X X 7    • • • 8

DATA SOURCE 1: JENKIN 2: JUZA 3: KENNEDY 4: KU  
 5: MACCORMACK 6: REAMER 7: SASS 8: VARGAFTIK



- (2) Gosman et al. (1969): argon;
- (3) Jacobsen et al. (1973): nitrogen and oxygen;
- (4) Ewers and Wagner (1981): oxygen;
- (5) Huss and Stewart (1963): carbon monoxide.

### CHAPTER III

For the present correlations the following equation

#### THE EQUATION OF STATE FOR CARBON DIOXIDE

##### Equation of State

The form of the equation of state selected for carbon dioxide in this work is essentially a modification of the equation first proposed by Strobridge (1962) for nitrogen. This equation is actually an extension of the BWR equation. For the thermodynamic description of the entire fluid region of pure substances with excellent accuracy, equations of state usually consist of very extensive density and temperature polynomials. As pointed out by Ewers and Wagner (1981), such equations are the extended BWR equation or equations corresponding to the original virial form.

The Strobridge equation with certain modifications has been adopted by quite a few authors to successfully correlate the thermodynamic data for various fluids. Some of examples are the following:

- (1) Bender (1970): argon, nitrogen, oxygen, methane, and carbon dioxide;

- (2) Gosman et al. (1969): argon;  
 (3) Jacobsen et al. (1973): nitrogen and oxygen;  
 (4) Ewers and Wagner (1981): oxygen;  
 (5) Hust and Stewart (1963): carbon monoxide.

For the present correlations the following equation of state is used:

$$\begin{aligned}
 Z = \frac{P}{\rho RT} = & 1 + \left( C_1 + \frac{C_2}{T_r} + \frac{C_3}{T_r^2} + \frac{C_4}{T_r^3} + \frac{C_5}{T_r^4} + \frac{C_6}{T_r^5} \right) \rho_r \\
 & + \left( C_7 + \frac{C_8}{T_r} + \frac{C_9}{T_r^2} \right) \rho_r^2 + \left( C_{10} + \frac{C_{11}}{T_r} \right) \rho_r^3 + \left( C_{12} + \frac{C_{13}}{T_r} \right) \rho_r^4 \\
 & + \left( \frac{C_{14}}{T_r} \right) \rho_r^5 + \left( \frac{C_{15}}{T_r^3} + \frac{C_{16}}{T_r^4} + \frac{C_{17}}{T_r^5} \right) \rho_r^2 \exp(-C_{21} \rho_r^2) \\
 & + \left( \frac{C_{18}}{T_r^3} + \frac{C_{19}}{T_r^4} + \frac{C_{20}}{T_r^5} \right) \rho_r^4 \exp(-C_{21} \rho_r^2) \\
 & + C_{22} \rho_r \exp[-C_{27} (\Delta T)^2] + C_{23} \frac{\Delta \rho}{\rho_r} \exp[-C_{25} (\Delta \rho)^2 - C_{27} (\Delta T)^2] \\
 & + C_{24} \frac{\Delta \rho}{\rho_r} \exp[-C_{26} (\Delta \rho)^2 - C_{27} (\Delta T)^2]
 \end{aligned} \tag{1}$$

where  $\Delta T = 1 - T_r$

$$\Delta \rho = 1 - 1/\rho_r$$

$T_r$  is the reduced temperature,  $T_r = T/T_c$ , and  $\rho_r$  is the reduced density,  $\rho_r = \rho/\rho_c$ ,  $T_c$  and  $\rho_c$  being the critical temperature and the critical density, respectively. The numerical values of the constants  $C_i$  and the reduction parameters  $R$ ,  $T_c$ ,  $\rho_c$  are listed in Table 3.



TABLE 3.

CONSTANTS  $C_i$  AND REDUCTION PARAMETERS  
TO BE USED IN EQUATION (1)

| $i$ | $C_i$       | $i$ | $C_i$        |
|-----|-------------|-----|--------------|
| 1   | 0.376194    | 15  | -2.79498     |
| 2   | 0.118836    | 16  | 5.62393      |
| 3   | -3.04379    | 17  | -2.93831     |
| 4   | 2.27453     | 18  | 0.988759     |
| 5   | -1.23863    | 19  | -3.04711     |
| 6   | 0.250442    | 20  | 2.32316      |
| 7   | -0.115350   | 21  | 1.07379      |
| 8   | 0.675104    | 22  | -0.599724E-4 |
| 9   | 0.198861    | 23  | 0.885339E-4  |
| 10  | 0.216124    | 24  | 0.316418E-2  |
| 11  | -0.583148   | 25  | 10.          |
| 12  | 0.119747E-1 | 26  | 50.          |
| 13  | 0.537278E-1 | 27  | 80,000.      |
| 14  | 0.265216E-1 |     |              |

$$T_C = 547.542 \text{ } ^\circ\text{R}$$

$$\rho_C = 0.66386 \text{ Lb-Mol/CFT}$$

$$R = 10.7335 \text{ psia.CFT/(Lb-Mol.}^\circ\text{R)}$$



Critical Correction Terms of compressibility factor has the form:

Equation (1) contains 14 polynomial terms, 6 terms coupled with the exponential function, and 3 terms (namely, special critical region terms) which are only important in the region near the critical point. Outside the critical region, these 3 terms can be dropped with negligible influence on the prediction results of thermodynamic properties. The critical region terms in Equation (1) are similar to those developed by Ewers and Wagner (1981) for their equation of state of oxygen. The difference lies in the first critical region term in Equation (1), where the exponential function is associated with temperature only.

To improve the performance of their equation of state in the critical region, Ewers and Wagner include 3 terms with the following functional form in their equation which is in terms of Helmholtz free energy.

$$A^s = \exp[-b(\Delta\rho)^2 - c(\Delta T)^2] \quad (2)$$

where superscript  $s$  denotes special function for the critical region, and  $b$  and  $c$  are constants. From the usual thermodynamic relations the compressibility factor is related to the Helmholtz energy by

$$Z = \rho \left[ \frac{\partial}{\partial \rho} \left( \frac{A}{RT} \right) \right]_T \quad (3)$$

Therefore, the corresponding special function for the

critical region in terms of compressibility factor has the form:

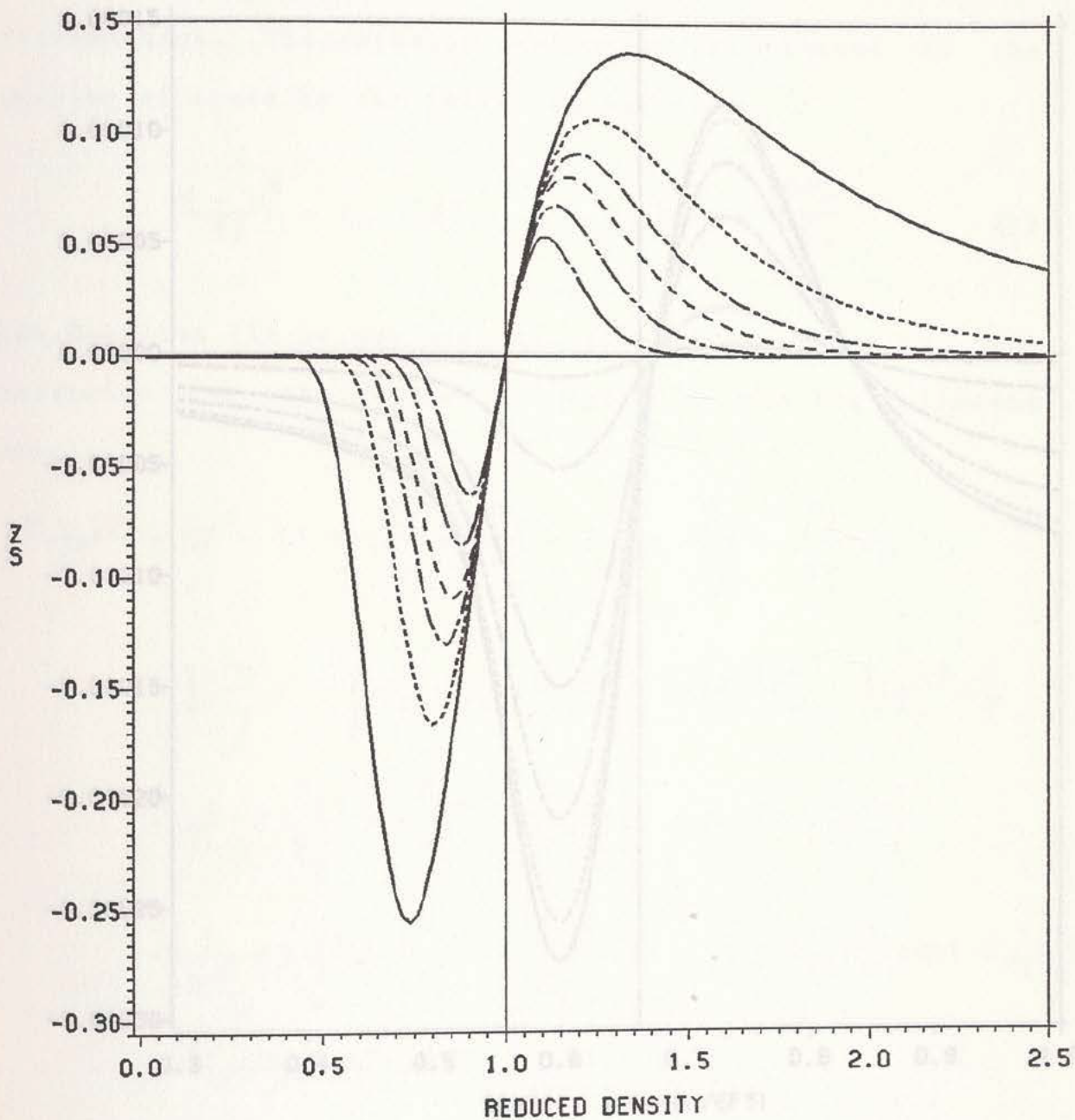
$$\begin{aligned}
 z^S &= \frac{\Delta\rho}{\rho_r} \exp[-b(\Delta\rho)^2 - c(\Delta T)^2] \\
 &= \frac{\Delta\rho}{\rho_r} \exp[-b(\Delta\rho)^2] \exp[-c(\Delta T)^2] \quad (4)
 \end{aligned}$$

The special function can be considered to be composed of two portions: one being a function of density and the other a function of temperature. The temperature portion of the special function is a bell-shaped curve with the maximum value of unity at the critical temperature. The portion related to density is a sine-like curve with the value of zero at the critical density. The special function for the density-related part is plotted for different parametric values in Figure 3. It can be seen that the larger the parametric value, the smaller the peak height and also the more narrow the width.

The behavior of the three critical region terms in Equation (1) is illustrated in Figure 4 for different supercritical isotherms. For subcritical isotherms a similar behavior exists. It should be pointed out that the critical region terms are effective only when very close to the critical point; for the isotherms about 5 °F from the critical temperature their contributions are already negligible since the numerical value of the coefficient C27 is very large.



FIGURE 3.  
SPECIAL FUNCTION FOR CRITICAL REGION



LEGEND: CONSTANT

— 5  
- - - 20

--- 10  
- - - 30

- - - 15  
— 50

$$Z^S = \frac{\Delta\rho}{\rho_r} \exp[-b(\Delta\rho)^2]$$





## Derived Properties

Expressions for the enthalpy, entropy, fugacity and other properties can be derived from the usual thermodynamic relationships. The enthalpy departure is related to the equation of state by the following equation:

$$\frac{H - H^0}{RT} = (Z - 1) - \int_0^{\rho_r} T_r \left( \frac{\partial Z}{\partial T_r} \right) \rho_r \frac{d\rho_r}{\rho_r} \quad (5)$$

When Equation (1) is applied to the above equation, the expression for the enthalpy departure has the following form:

$$\begin{aligned} \frac{H - H^0}{RT} = & (Z - 1) + \left( \frac{C_2}{T_r} + 2\frac{C_3}{T_r^2} + 3\frac{C_4}{T_r^3} + 4\frac{C_5}{T_r^4} + 5\frac{C_6}{T_r^5} \right) \rho_r \\ & + \frac{1}{2} \left( \frac{C_8}{T_r} + 2\frac{C_9}{T_r^2} \right) \rho_r^2 + \frac{1}{3} \left( \frac{C_{11}}{T_r} \right) \rho_r^3 + \frac{1}{4} \left( \frac{C_{13}}{T_r} \right) \rho_r^4 + \frac{1}{5} \left( \frac{C_{14}}{T_r} \right) \rho_r^5 \\ & + \frac{1}{2C_{21}} \left( 3\frac{C_{15}}{T_r^3} + 4\frac{C_{16}}{T_r^4} + 5\frac{C_{17}}{T_r^5} \right) \left[ 1 - \exp(-C_{21}\rho_r^2) \right] \\ & + \frac{1}{2C_{21}^2} \left( 3\frac{C_{18}}{T_r^3} + 4\frac{C_{19}}{T_r^4} + 5\frac{C_{20}}{T_r^5} \right) \left[ 1 - (1 + C_{21}\rho_r^2) \exp(-C_{21}\rho_r^2) \right] \\ & - 2C_{22}C_{27}T_r\Delta T\rho_r \exp[-C_{27}(\Delta T)^2] \\ & + \frac{C_{23}C_{27}}{C_{25}}T_r\Delta T \exp[-C_{25}(\Delta\rho)^2 - C_{27}(\Delta T)^2] \\ & + \frac{C_{24}C_{27}}{C_{26}}T_r\Delta T \exp[-C_{26}(\Delta\rho)^2 - C_{27}(\Delta T)^2] \quad (6) \end{aligned}$$

where  $H$  is the enthalpy of the fluid and  $H^{\circ}$  is the ideal gas state enthalpy of the fluid at the system temperature.

The thermodynamic relation between the entropy departure and the equation of state is:

$$\frac{S - S^{\circ}}{R} = - \ln(\rho RT) - \int_0^{\rho_r} \left[ (Z - 1) + T_r \left( \frac{\partial Z}{\partial T_r} \right) \rho_r \right] \frac{d\rho_r}{\rho_r} \quad (7)$$

Substituting Equation (1) into the above equation yields the following expression for the entropy departure:

$$\begin{aligned} \frac{S - S^{\circ}}{R} = & - \ln(\rho RT) - \left( C_1 - \frac{C_3}{T_r} - 2\frac{C_4}{T_r^2} - 3\frac{C_5}{T_r^3} - 4\frac{C_6}{T_r^4} \right) \rho_r \\ & - \frac{1}{2} \left( C_7 - \frac{C_9}{T_r^2} \right) \rho_r^2 - \frac{1}{3} C_{10} \rho_r^3 - \frac{1}{4} C_{12} \rho_r^4 \\ & + \frac{1}{2C_{21}} \left( 2\frac{C_{15}}{T_r^3} + 3\frac{C_{16}}{T_r^4} + 4\frac{C_{17}}{T_r^5} \right) \left[ 1 - \exp(-C_{21} \rho_r^2) \right] \\ & + \frac{1}{2C_{21}^2} \left( 2\frac{C_{18}}{T_r^3} + 3\frac{C_{19}}{T_r^4} + 4\frac{C_{20}}{T_r^5} \right) \left[ 1 - (1 + C_{21} \rho_r^2) \exp(-C_{21} \rho_r^2) \right] \\ & - C_{22} (1 + 2C_{27} T_r \Delta T) \rho_r \exp \left[ -C_{27} (\Delta T)^2 \right] \\ & + \frac{C_{23}}{2C_{25}} (1 + 2C_{27} T_r \Delta T) \exp \left[ -C_{25} (\Delta \rho)^2 - C_{27} (\Delta T)^2 \right] \\ & + \frac{C_{24}}{2C_{26}} (1 + 2C_{27} T_r \Delta T) \exp \left[ -C_{26} (\Delta \rho)^2 - C_{27} (\Delta T)^2 \right] \quad (8) \end{aligned}$$

where  $S$  is the entropy of the fluid and  $S^{\circ}$  is the ideal gas



state entropy of the fluid at the system temperature and unit pressure. Equation (8) assumes that at unit pressure the gas is ideal.

For a pure component existing at equilibrium in two phases at a given temperature and pressure, the thermodynamic variable defining equilibrium is the fugacity, which must be the same for both phases. The fugacity of a pure substance is related to the equation of state by

$$\ln f = (Z - 1) + \ln(\rho RT) + \int_0^{\rho_r} (Z - 1) \frac{d\rho_r}{\rho_r} \quad (9)$$

The fugacity can also be expressed in terms of enthalpy departure and entropy departure by the following relation:

$$\ln f = \frac{H - H^0}{RT} - \frac{S - S^0}{R} \quad (10)$$

When Equation (1) is used in Equation (9) or both Equation (6) and (8) are substituted in the above equation, the expression for the fugacity has the following form:

$$\begin{aligned} \ln f = & (Z - 1) + \ln(\rho RT) + \left( C_1 + \frac{C_2}{T_r} + \frac{C_3}{T_r^2} + \frac{C_4}{T_r^3} + \frac{C_5}{T_r^4} + \frac{C_6}{T_r^5} \right) \rho_r \\ & + \frac{1}{2} \left( C_7 + \frac{C_8}{T_r} + \frac{C_9}{T_r^2} \right) \rho_r^2 + \frac{1}{3} \left( C_{10} + \frac{C_{11}}{T_r} \right) \rho_r^3 + \frac{1}{4} \left( C_{12} + \frac{C_{13}}{T_r} \right) \rho_r^4 \\ & + \frac{1}{5} \left( \frac{C_{14}}{T_r} \right) \rho_r^5 + \frac{1}{2C_{21}} \left( \frac{C_{15}}{T_r^3} + \frac{C_{16}}{T_r^4} + \frac{C_{17}}{T_r^5} \right) \left[ 1 - \exp(-C_{21} \rho_r^2) \right] \\ & + \frac{1}{2C_{21}^2} \left( \frac{C_{18}}{T_r^3} + \frac{C_{19}}{T_r^4} + \frac{C_{20}}{T_r^5} \right) \left[ 1 - (1 + C_{21} \rho_r^2) \exp(-C_{21} \rho_r^2) \right] \end{aligned}$$

$$\begin{aligned}
& + C_{22} \rho_r \exp[-C_{27}(\Delta T)^2] - \frac{C_{23}}{2C_{25}} \exp[-C_{25}(\Delta \rho)^2 - C_{27}(\Delta T)^2] \\
& - \frac{C_{24}}{2C_{26}} \exp[-C_{26}(\Delta \rho)^2 - C_{27}(\Delta T)^2] \quad (11)
\end{aligned}$$

The above three equations assume that the gas is ideal at unit pressure, so that the reference fugacity  $f^\circ = 1.0$ .

To calculate the vapor pressure for a pure component at a given temperature, the following conditions for the vapor-liquid equilibrium must be satisfied:

$$P(\rho^L, T) = P(\rho^V, T) = P_S \quad (12)$$

$$f(\rho^L, T) = f(\rho^V, T) \quad (13)$$

where  $P_S$  is the saturation pressure or vapor pressure and the superscripts L and V denote the saturated liquid and vapor, respectively.

If the usual thermodynamic relations for  $f^L$  and  $f^V$  as given in Equation (9) are substituted into Equation (13), then the following expression can be obtained:

$$P_S \left( \frac{1}{\rho^V} - \frac{1}{\rho^L} \right) = \int_{\rho^V}^{\rho^L} P(\rho, T) \frac{d\rho}{\rho^2} \quad (14)$$

By substitution of the specific volume  $v$  for the density  $\rho$ , then the well-known relationship under the name "Maxwell criterion" is obtained.

$$P_S (v^V - v^L) = \int_{v^L}^{v^V} P(v, T) dv \quad (15)$$



## Correlation Method

In order to calculate thermodynamic properties at a specified temperature and pressure condition, usually the density at that condition has to be determined first. Since the proposed equation of state is in pressure-explicit form, the density is determined by the trial-and-error solution of Equation (1). Then other properties such as the enthalpy departure and the entropy departure can be computed by using the obtained density in the relevant expressions derived from the thermodynamic relations.

The calculation of vapor pressure from an equation of state also involves a trial-and-error procedure. First, the saturated liquid and vapor densities at an assumed initial pressure have to be determined from Equation (1) using the density search technique. Then we check if the Maxwell rule is satisfied under the assumed pressure, using the obtained liquid and vapor densities. The guessed pressure is adjusted until the Maxwell criterion is well satisfied within the specified allowable error. The final obtained pressure is the desired vapor pressure.

The numerical values of the constants  $C_i$  in Equation (1) are obtained through two steps. The coefficients  $C_1$  through  $C_{21}$  are first determined by simultaneously fitting experimental PVT, vapor pressure and enthalpy departure data

(see Table 1) to Equation (1) without the correction terms, using multiproperty nonlinear regression analysis. The use of multiproperty regression is essential and required in order to determine a set of equation-of-state parameters capable of representing thermodynamically consistent properties with optimal accuracy. Detailed discussions of the principles and applications of multiproperty nonlinear regression can be found elsewhere (Selleck et al., 1953; Starling and Wolfe, 1966; Cox, 1968; Kwok and Starling, 1970; Cox et al., 1971; Stewart and Jacobsen, 1977).

To obtain a set of initial values for the constants to be used in the multiproperty regression analysis, a linear least-squares fit using PVT data has been attempted. During the linear least-squares calculations, it is necessary to estimate preliminary values of the nonlinear parameter  $C_{21}$ , which has been varied in order to obtain the best fit in the whole fluid region.

Since the uncertainties of measurement vary among properties and experiments and with thermodynamic region (e.g., liquid or vapor phase), in the least-squares fit each data point was weighted to modify its effect on the final equation of state. Proper weighting is important when performing the multiproperty regression. It was pointed out (Reynolds, 1979) that slight changes in weighting can make significant changes in the resulting thermodynamic property



predictions, especially when one is attempting to fit the entire PVT surface with a single equation. Different weighting schemes in some cases can yield quite striking differences in deviation patterns (Hust and McCarty, 1967). The similar phenomena were observed during the development of the equation of state in this study.

Once the optimum values of the constants C1 through C21 are obtained, the next problem is to determine a set of parameters C22 through C27 for the critical region terms. Only the density data in the critical region were used for regression. During the determination of those coefficients by a least-squares fit of density data, the following constraints are imposed at the critical point.

$$\left. \begin{aligned} \left(\frac{\partial P}{\partial \rho}\right)_T &= 0 \\ \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T &= 0 \end{aligned} \right\} \text{at } T=T_c, \rho=\rho_c \quad (16a)$$

$$\left. \begin{aligned} \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T &= 0 \\ \left(\frac{\partial^3 P}{\partial \rho^3}\right)_T &= 0 \end{aligned} \right\} \text{at } T=T_c, \rho=\rho_c \quad (16b)$$

Or in terms of compressibility factor, the above equations become:

$$\rho \left(\frac{\partial Z}{\partial \rho}\right)_T + Z = 0 \quad (17a)$$

$$\left. \begin{aligned} 2 \left(\frac{\partial Z}{\partial \rho}\right)_T + \rho \left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T &= 0 \\ \left(\frac{\partial^3 Z}{\partial \rho^3}\right)_T &= 0 \end{aligned} \right\} \text{at } T=T_c, \rho=\rho_c \quad (17b)$$

The functional forms of the critical region terms, also the initial guessed values of C22 through C27, come

from the analysis of a plot of the compressibility factor difference  $\Delta Z$ , defined in the following, against the density at several near-critical temperatures.

$$\begin{aligned}\Delta Z &= Z_{\text{exp}} - Z_{\text{calc}} \\ &= \frac{P}{\rho RT} - Z_{\text{calc}}(\rho, T)\end{aligned}\quad (18)$$

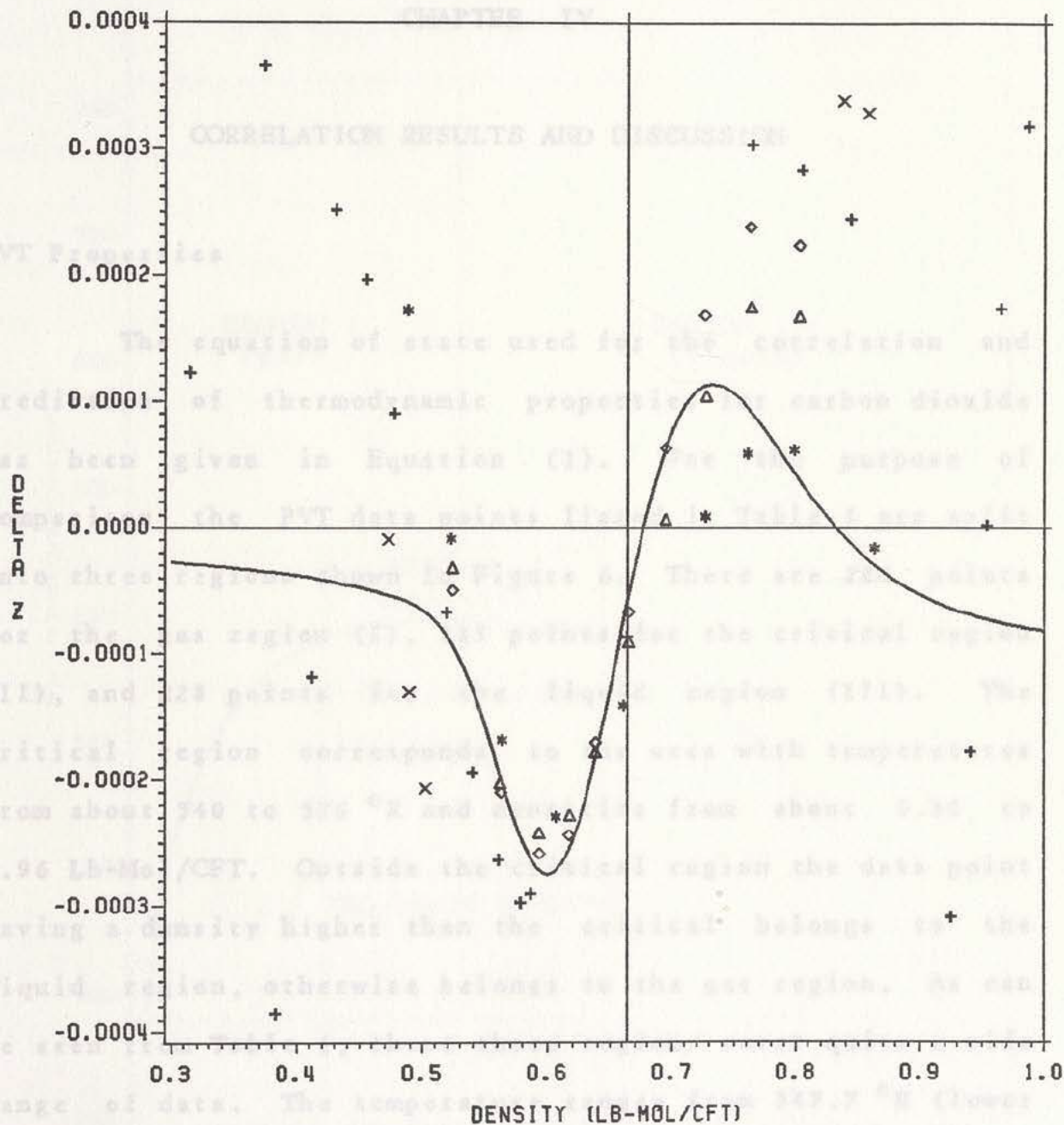
where  $Z_{\text{exp}}$  is the experimental compressibility factor,  $Z_{\text{calc}}$  is the calculated compressibility factor from the pressure-explicit equation of state with the experimental values of density and temperature substituted in it.

If the equation of state used in Equation (18) is true,  $\Delta Z$  should equal zero. However, when the experimental values of  $P$ ,  $\rho$  and  $T$  are substituted in the right-hand side of Equation (18), the numerical result of  $\Delta Z$  will not always equal zero. Therefore, the plot of the quantity  $\Delta Z$  against  $\rho$  ( $T$  constant) will reveal in a quantitative manner the discrepancy between the real behavior of the fluid and of a fluid obeying the particular equation of state under investigation. By using such graphs various equations of state can be compared directly and quantitatively. Furthermore, if the graph for a equation of state happens to be a certain recognizable curve, we can modify the equation of state by adding some correction terms, which can fit this curve well, so that the resulting equation can represent the fluid behavior with considerable precision.





**FIGURE 5.**  
**PLOT OF COMPRESSIBILITY FACTOR DIFFERENCE**  
**FOR NEAR-CRITICAL REGION**



LEGEND: TEMP    × × × 546.4    + + + 547.5    ◇ ◇ ◇ 547.8  
                   (°R)    △ △ △ 548       \* \* \* 548.4

SYMBOLS : FROM EQUATION (1) WITHOUT CRITICAL CORRECTION TERMS  
 CURVE : THE VALUE OF CORRECTION TERMS AT CRITICAL TEMPERATURE



FIGURE 6.  
REGIONS OF THE P-V-T SURFACE

## CHAPTER IV

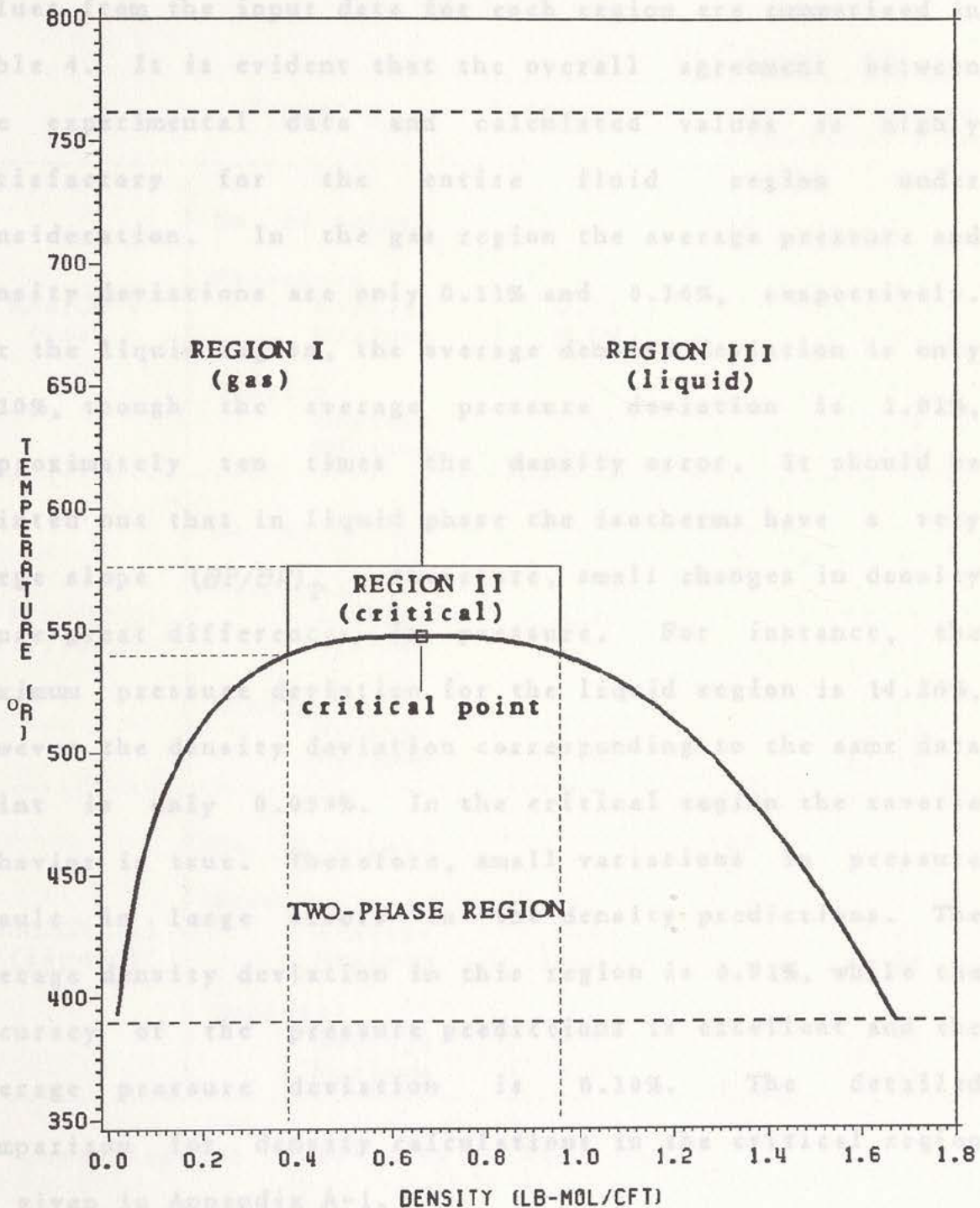
### CORRELATION RESULTS AND DISCUSSION

#### PVT Properties

The equation of state used for the correlation and prediction of thermodynamic properties for carbon dioxide has been given in Equation (1). For the purpose of comparison the PVT data points listed in Table 1 are split into three regions shown in Figure 6. There are 284 points for the gas region (I), 113 points for the critical region (II), and 228 points for the liquid region (III). The critical region corresponds to the area with temperatures from about 540 to 576 °R and densities from about 0.38 to 0.96 Lb-Mol/CFT. Outside the critical region the data point having a density higher than the critical belongs to the liquid region, otherwise belongs to the gas region. As can be seen from Table 1, these three regions cover quite a wide range of data. The temperature ranges from 347.7 °R (lower than the triple point 390.8 °R) to 761.9 °R and the highest pressure is up to 45,820 psia.

To give an impression of the accuracy of Equation (1), the average absolute deviations along with the maximum absolute deviation values from the input data for each region are summarized in Table 4. It is evident that the overall agreement between the experimental data and calculated values is highly satisfactory for the entire fluid region under consideration. In the gas region the average pressure and density deviations are only 0.11% and 0.14%, respectively. For the liquid the average density deviation is only 0.10%, though the average pressure deviation is 1.01%, approximately ten times the density error. It should be pointed out that in liquid phase the isotherms have a very flat slope (dy/dx) and small changes in density can lead to different pressures. For instance, the maximum pressure deviation for the liquid region is 14.26%, however the density deviation corresponding to the same is a point is only 0.004%. In the critical region the average behavior is true. Obviously, small variations in pressure result in large density predictions. The average density deviation in this region is 0.71%, while the accuracy of the pressure prediction is sufficient and the average pressure deviation is 0.10%. The detailed comparison is given in Appendix A-1.

**FIGURE 6.**  
**REGIONS OF THE P-V-T SURFACE**





To give an impression of the accuracy of Equation (1), the average absolute deviations along with the maximum absolute deviations of calculated pressure and density values from the input data for each region are summarized in Table 4. It is evident that the overall agreement between the experimental data and calculated values is highly satisfactory for the entire fluid region under consideration. In the gas region the average pressure and density deviations are only 0.11% and 0.16%, respectively. For the liquid region, the average density deviation is only 0.10%, though the average pressure deviation is 1.01%, approximately ten times the density error. It should be pointed out that in liquid phase the isotherms have a very large slope  $(\partial P/\partial \rho)_T$ ; therefore, small changes in density cause great differences in pressure. For instance, the maximum pressure deviation for the liquid region is 14.26%, however the density deviation corresponding to the same data point is only 0.053%. In the critical region the reverse behavior is true. Therefore, small variations in pressure result in large errors in the density predictions. The average density deviation in this region is 0.91%, while the accuracy of the pressure predictions is excellent and the average pressure deviation is 0.10%. The detailed comparison for density calculations in the critical region is given in Appendix A-1.

TABLE 4.

PREDICTION OF PVT PROPERTY USING EQUATION (1)

| Property                    | Abs. Deviation* (%) |                                  |
|-----------------------------|---------------------|----------------------------------|
|                             | Equation (1)        | Eq. (1) without correction terms |
| <b>REGION I (gas)</b>       |                     |                                  |
| No. of points               | 284                 |                                  |
| Pressure:                   |                     |                                  |
| Average                     | 0.11                | 0.11                             |
| Maximum                     | 0.90                | 0.90                             |
| Density:                    |                     |                                  |
| Average                     | 0.16                | 0.16                             |
| Maximum                     | 0.98                | 0.98                             |
| <b>REGION II (critical)</b> |                     |                                  |
| No. of points               | 113                 |                                  |
| Pressure:                   |                     |                                  |
| Average                     | 0.10                | 0.11                             |
| Maximum                     | 1.19                | 1.19                             |
| Density:                    |                     |                                  |
| Average                     | 0.91                | 2.06                             |
| Maximum                     | 5.30                | 21.48                            |
| <b>REGION III (liquid)</b>  |                     |                                  |
| No. of points               | 228                 |                                  |
| Pressure:                   |                     |                                  |
| Average                     | 1.01                | 1.01                             |
| Maximum                     | 14.26               | 14.26                            |
| Density:                    |                     |                                  |
| Average                     | 0.10                | 0.10                             |
| Maximum                     | 0.43                | 0.43                             |

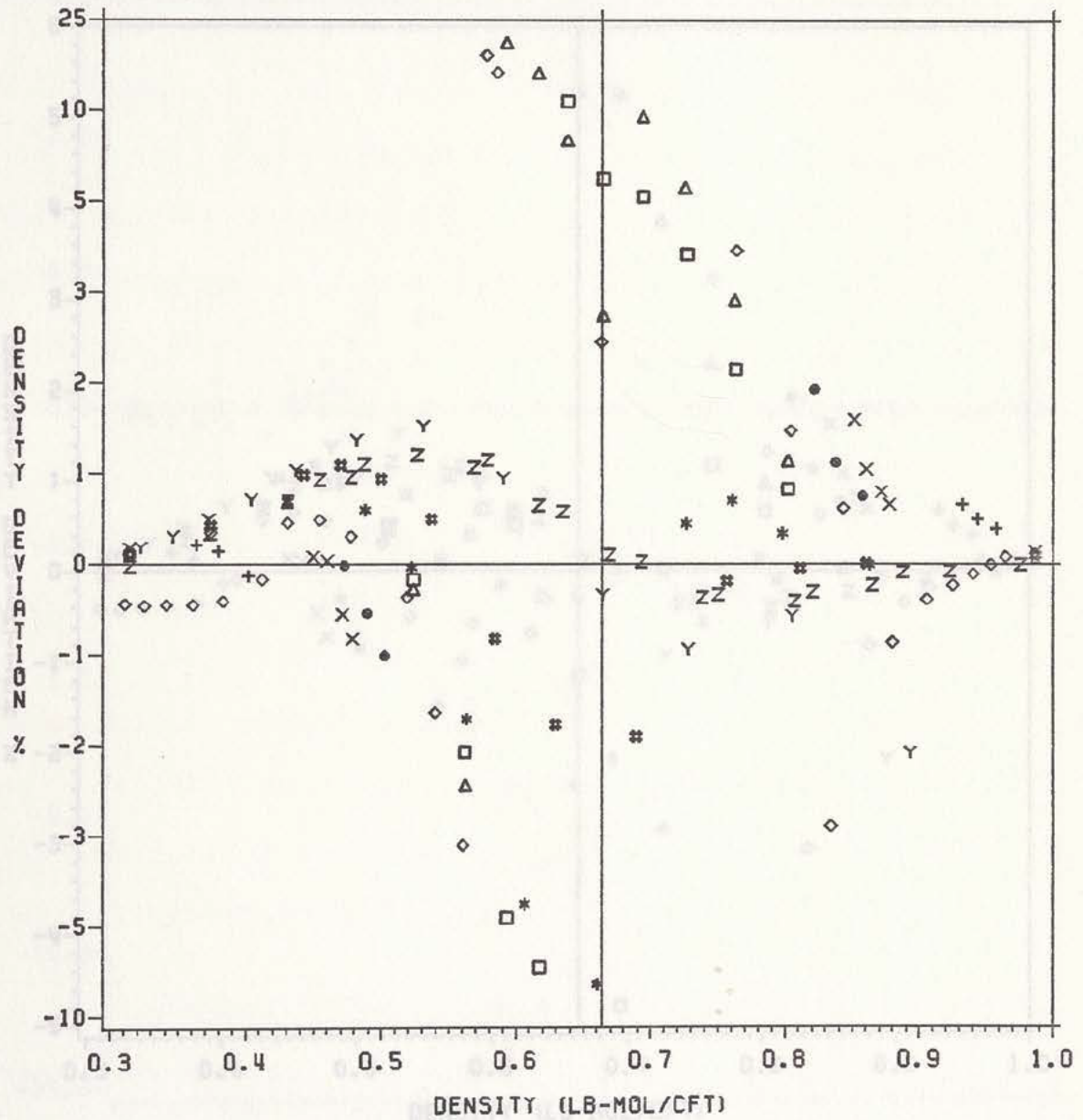
\* Deviation (%) = 100\*(Calc. - Exp.)/Exp.



To illustrate the effect of the critical correction terms, the deviations of pressure and density by using Equation (1) without the critical region terms are also presented in the last column of Table 4. Obviously the special critical region terms have negligible influence on the gas and liquid region. They work only in the region near the critical point. With the function of these terms the average density deviation in the critical region is reduced from 2.06% to 0.91%, though the improvement on the pressure predictions in this region is insignificant, from 0.11% to 0.10%.

Figure 7 and 8 are density deviation plots for Equation (1) without and with the critical region terms, respectively. Figure 7 shows a systematic trend for each isotherm which can be attributed to the equation of state. Without the correction terms the maximum deviation can be as high as 21.5%. In Figure 8 most data points assume a deviation within 2% with the exception of several scattering points very close to the critical point. To further display the role of the critical region terms in the improvement of density predictions, Figure 9 is prepared, where the absolute density deviation differences between Figure 7 and 8 for the corresponding points are plotted. There is no doubt that that the improvement of density predictions around the critical point is fairly significant. Figure 10

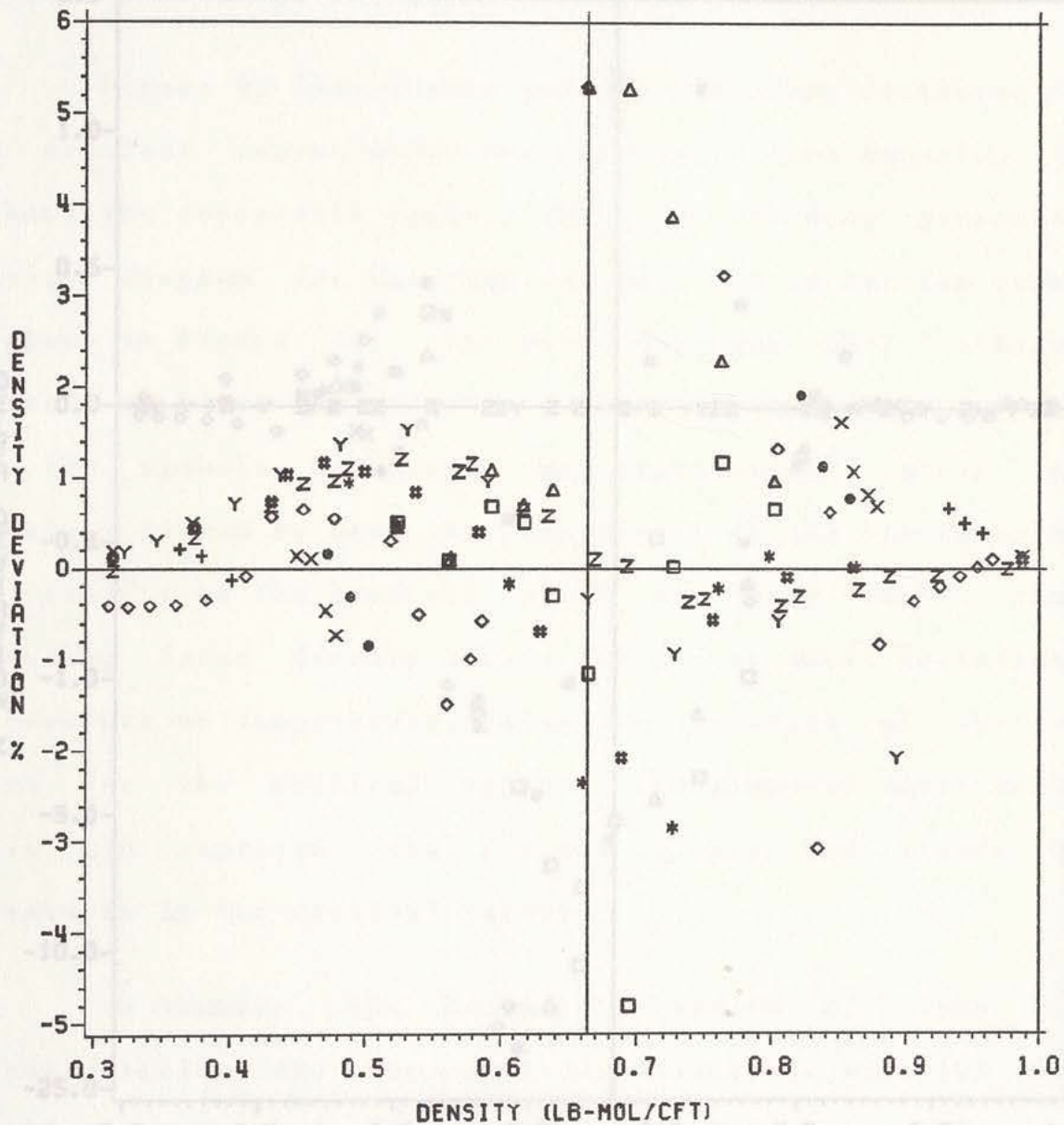
**FIGURE 7.**  
**DENSITY DEVIATION IN THE CRITICAL REGION**  
**( WITHOUT CRITICAL CORRECTION TERMS )**



|              |   |   |   |       |   |   |   |       |   |   |   |       |   |   |   |       |
|--------------|---|---|---|-------|---|---|---|-------|---|---|---|-------|---|---|---|-------|
| LEGEND: TEMP | + | + | + | 542.2 | X | X | X | 545.5 | • | • | • | 546.4 | ◇ | ◇ | ◇ | 547.5 |
| (°R)         | Δ | Δ | Δ | 547.8 | □ | □ | □ | 548   | * | * | * | 548.4 | # | # | # | 549.4 |
|              | Y | Y | Y | 554.2 | Z | Z | Z | 563.8 |   |   |   |       |   |   |   |       |



**FIGURE 8.**  
**DENSITY DEVIATION IN THE CRITICAL REGION**  
**( WITH CRITICAL CORRECTION TERMS )**

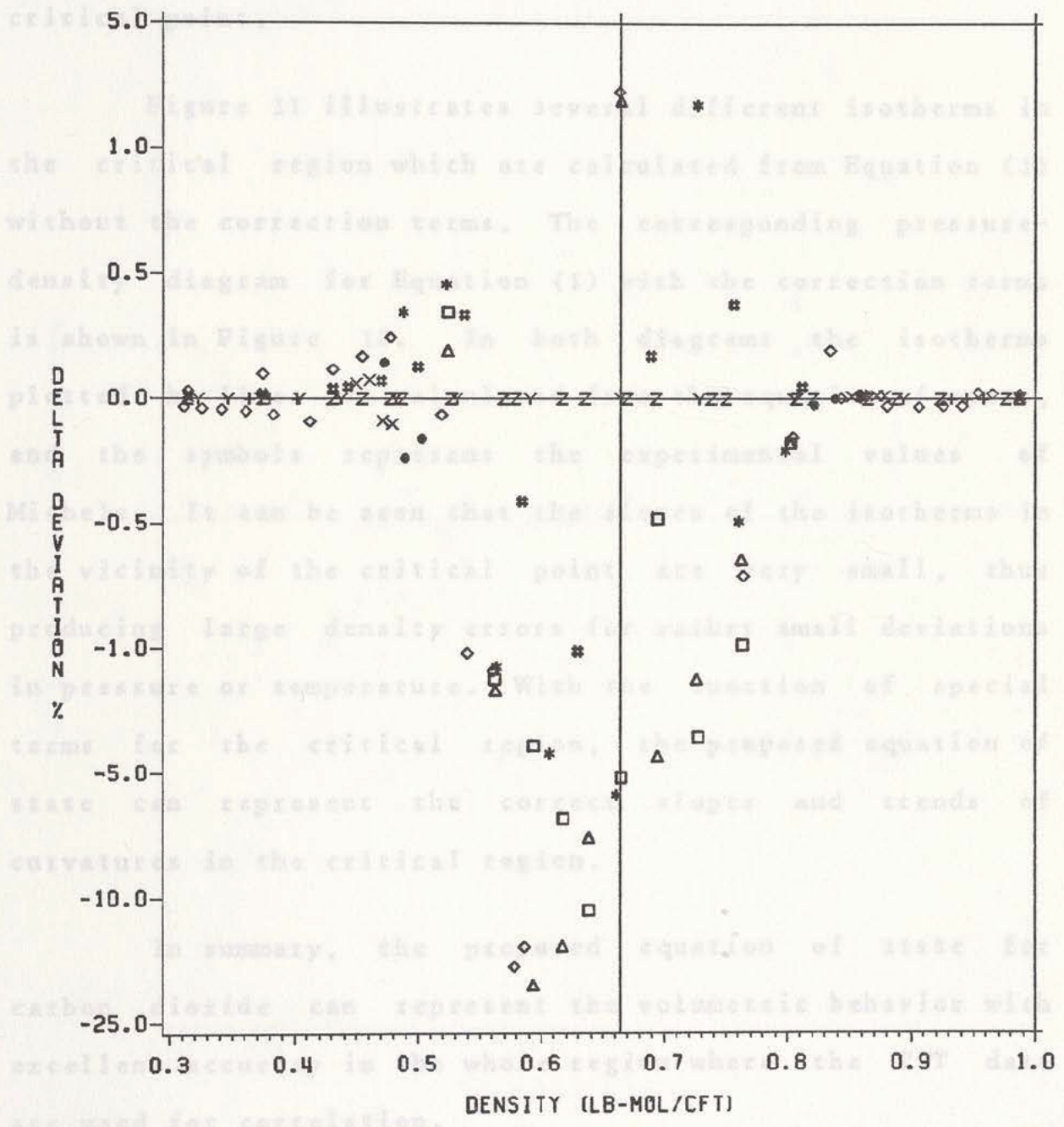


|              |           |           |           |
|--------------|-----------|-----------|-----------|
| LEGEND: TEMP | +++ 542.2 | xxx 545.5 | ••• 546.4 |
| (°R)         | ◇◇◇ 547.5 | △△△ 547.8 | □□□ 548   |
|              | *** 548.4 | ### 549.4 | YYY 554.2 |
|              | ZZZ 563.8 |           |           |

DELTA DEV. = ABS(DEN1) - ABS(DEN2)  
 DEN1 : NO CORRECTION TERMS  
 DEN2 : WITH CORRECTION TERMS

is a pressure deviation plot for the critical region. Note that the magnitude of pressure deviation in the vicinity of the critical point is much smaller than that from the critical point.

**FIGURE 9.**  
**IMPROVEMENT ON DENSITY PREDICTION**



LEGEND: TEMP

|   |   |   |       |   |   |   |       |   |   |   |       |   |   |   |       |
|---|---|---|-------|---|---|---|-------|---|---|---|-------|---|---|---|-------|
| + | + | + | 542.2 | × | × | × | 545.5 | ● | ● | ● | 546.4 | ◇ | ◇ | ◇ | 547.5 |
| Δ | Δ | Δ | 547.8 | □ | □ | □ | 548   | * | * | * | 548.4 | # | # | # | 549.4 |
| Y | Y | Y | 554.2 | Z | Z | Z | 563.8 |   |   |   |       |   |   |   |       |

DELTA DEV. = ABS(DEV2) - ABS(DEV1)  
 DEV1 : NO CORRECTION TERMS  
 DEV2 : WITH CORRECTION TERMS



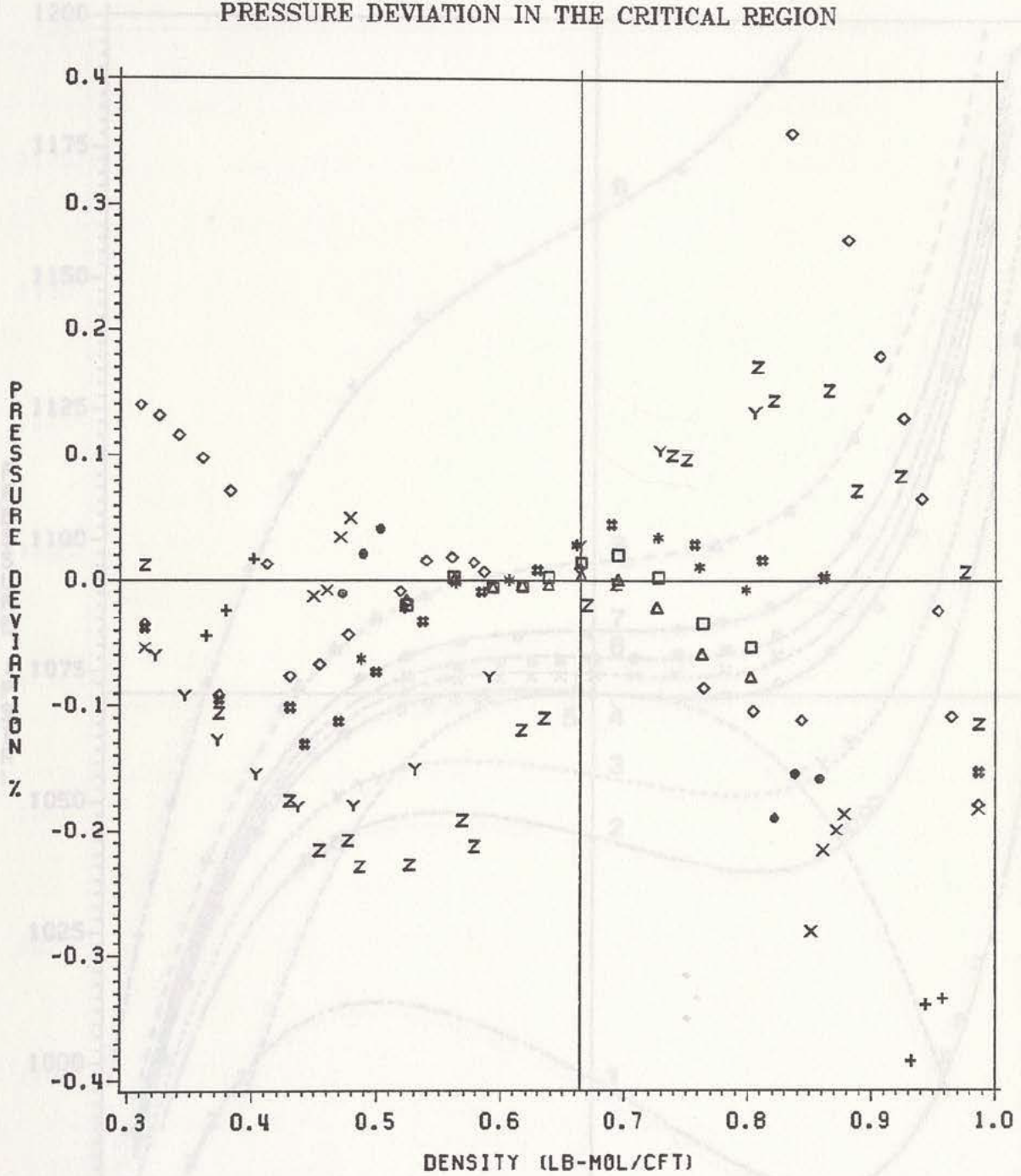
is a pressure deviation plot for the critical region. Note that the magnitude of pressure deviation in the vicinity of the critical point is even smaller than those far from the critical point.

Figure 11 illustrates several different isotherms in the critical region which are calculated from Equation (1) without the correction terms. The corresponding pressure-density diagram for Equation (1) with the correction terms is shown in Figure 12. In both diagrams the isotherms plotted by lines are calculated from the equation of state, and the symbols represent the experimental values of Michels. It can be seen that the slopes of the isotherms in the vicinity of the critical point are very small, thus producing large density errors for rather small deviations in pressure or temperature. With the function of special terms for the critical region, the proposed equation of state can represent the correct slopes and trends of curvatures in the critical region.

In summary, the proposed equation of state for carbon dioxide can represent the volumetric behavior with excellent accuracy in the whole region where the PVT data are used for correlation.

FIGURE 11.  
 PLOT OF ISOTHERMS NEAR CRITICAL REGION  
 (EQUATION (4) WITHOUT CRITICAL CORRECTION TERMS)

FIGURE 10.  
 PRESSURE DEVIATION IN THE CRITICAL REGION



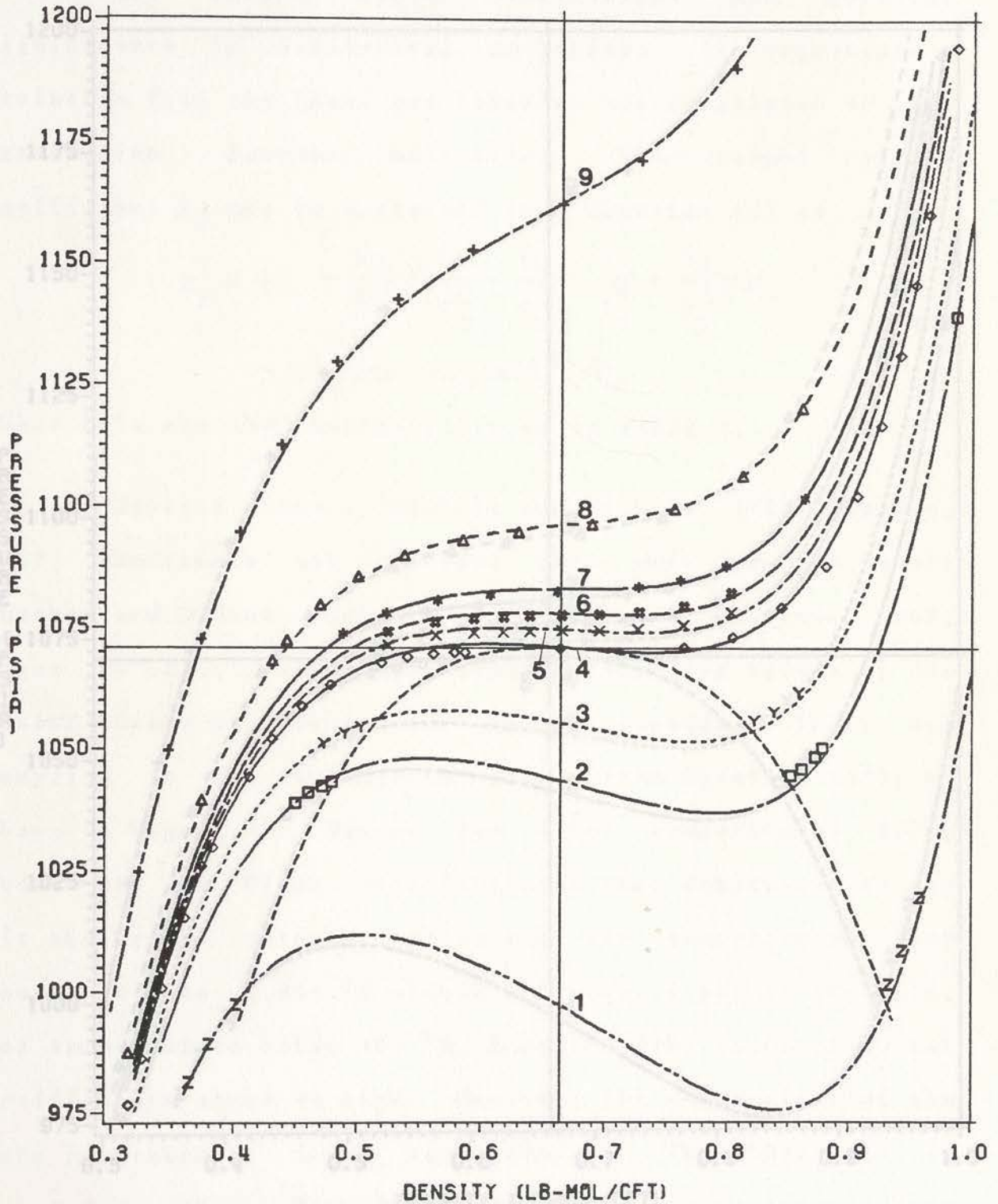
LEGEND: TEMP    + + + 542.2    X X X 545.5    ● ● ● 546.4    ◇ ◇ ◇ 547.5  
                   (°R)    Δ Δ Δ 547.8    □ □ □ 548    \* \* \* 548.4    # # # 549.4  
                   Y Y Y 554.2    Z Z Z 563.8

DENSITY (LB-MOL/CFT)

ISOTHERMS: 1: 542.2    2: 545.5    3: 546.4    4: 547.5    5: 547.8  
 (°R)            6: 548.4    7: 549.4    8: 549.4    9: 554.2

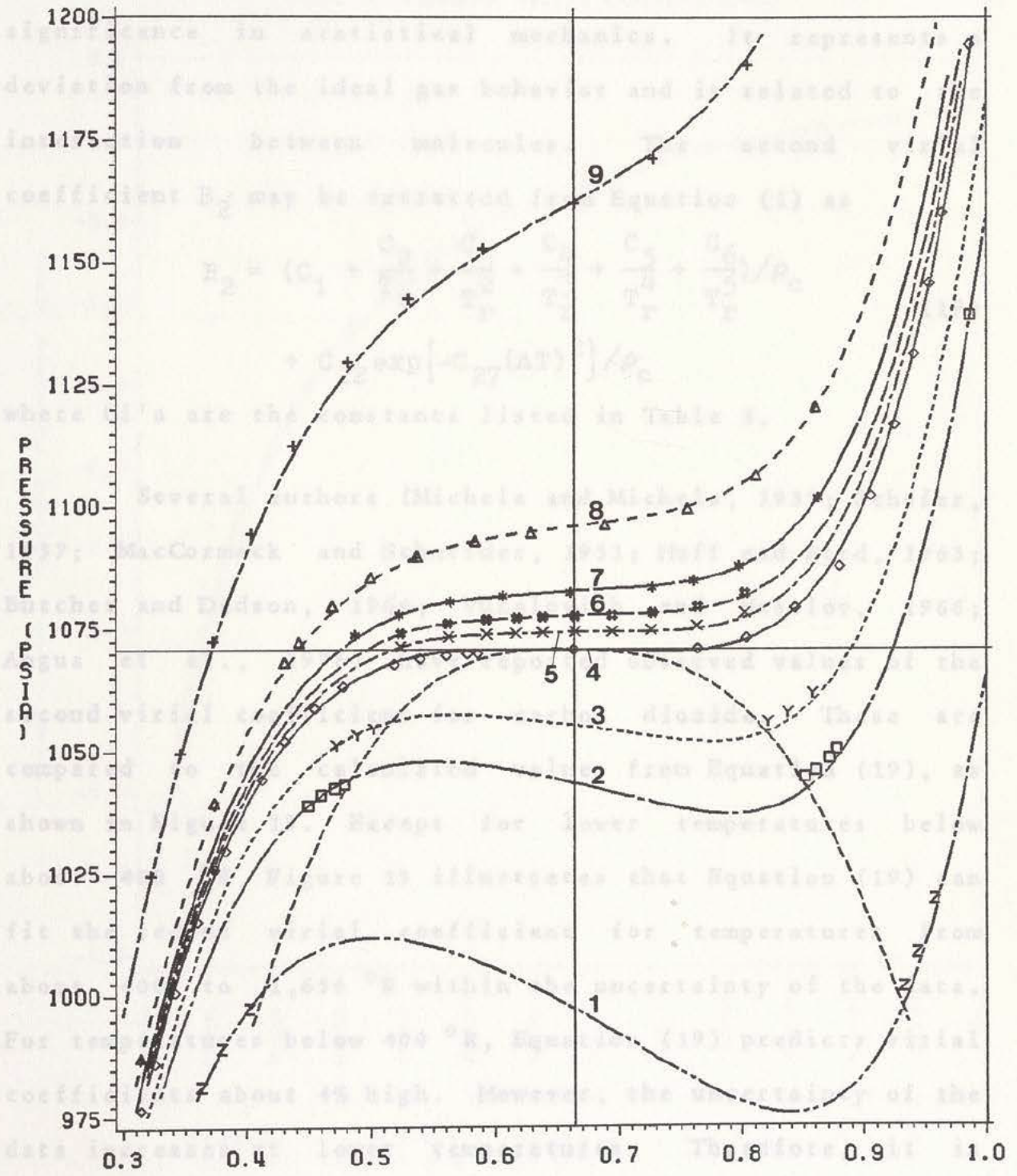


FIGURE 11.  
 PLOT OF ISOTHERMS NEAR CRITICAL REGION  
 ( EQUATION (1) WITHOUT CRITICAL CORRECTION TERMS )



|           |          |          |          |          |          |
|-----------|----------|----------|----------|----------|----------|
| ISOTHERMS | 1: 542.2 | 2: 545.5 | 3: 546.4 | 4: 547.5 | 5: 547.8 |
| (°R)      | 6: 548.0 | 7: 548.4 | 8: 549.4 | 9: 554.2 |          |

FIGURE 12.  
 PLOT OF ISOTHERMS NEAR CRITICAL REGION  
 ( EQUATION (1) WITH CRITICAL CORRECTION TERMS )



| ISOTHERMS | 1: 542.2 | 2: 545.5 | 3: 546.4 | 4: 547.5 | 5: 547.8 |
|-----------|----------|----------|----------|----------|----------|
| (°R)      | 6: 548.0 | 7: 548.4 | 8: 549.4 | 9: 554.2 |          |



## Second Virial Coefficient

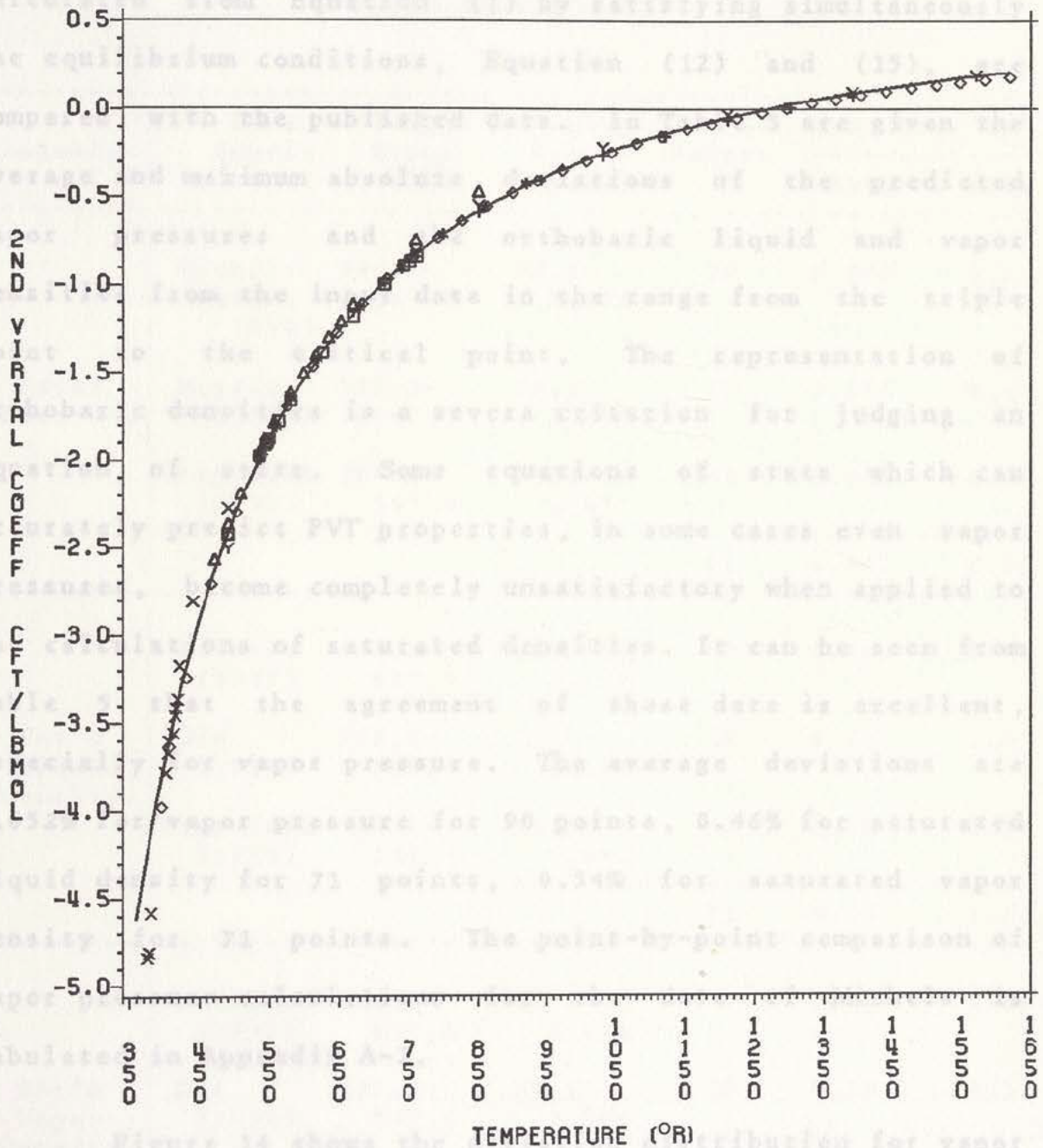
The second virial coefficient has physical significance in statistical mechanics. It represents a deviation from the ideal gas behavior and is related to the interaction between molecules. The second virial coefficient  $B_2$  may be extracted from Equation (1) as

$$B_2 = \left( C_1 + \frac{C_2}{T_r} + \frac{C_3}{T_r^2} + \frac{C_4}{T_r^3} + \frac{C_5}{T_r^4} + \frac{C_6}{T_r^5} \right) / \rho_c \quad (19)$$
$$+ C_{22} \exp[-C_{27}(\Delta T)^2] / \rho_c$$

where  $C_i$ 's are the constants listed in Table 3.

Several authors (Michels and Michels, 1935; Schafer, 1937; MacCormack and Schneider, 1951; Huff and Reed, 1963; Butcher and Dadson, 1964; Vukalovich and Masalov, 1966; Angus et al., 1976) have reported observed values of the second virial coefficient for carbon dioxide. These are compared to the calculated values from Equation (19), as shown in Figure 13. Except for lower temperatures below about 400 °R, Figure 13 illustrates that Equation (19) can fit the second virial coefficient for temperatures from about 400 to 1,650 °R within the uncertainty of the data. For temperatures below 400 °R, Equation (19) predicts virial coefficients about 4% high. However, the uncertainty of the data increases at lower temperatures. Therefore, it is concluded that Equation (19) gives the satisfactory representation of the second virial coefficient data.

**FIGURE 13.**  
**PLOT OF SECOND VIRIAL COEFFICIENTS**



LEGEND: I    □ □ □ 1    × × × 2    Y Y Y 3    \* \* \* 4  
                   △ △ △ 5    + + + 6    ◇ ◇ ◇ 7

DATA SOURCE    1: MICHELS    2: SCHAFER    3: MACCORMACK    4: HUFF  
                   5: BUTCHER    6: VUKALOVICH    7: ANGUS  
 CURVE            : THIS WORK



## Saturation Properties

TABLE 5  
PREDICTION OF SATURATED PROPERTIES

The saturation properties at a specified temperature calculated from Equation (1) by satisfying simultaneously the equilibrium conditions, Equation (12) and (15), are compared with the published data. In Table 5 are given the average and maximum absolute deviations of the predicted vapor pressures and the orthobaric liquid and vapor densities from the input data in the range from the triple point to the critical point. The representation of orthobaric densities is a severe criterion for judging an equation of state. Some equations of state which can accurately predict PVT properties, in some cases even vapor pressures, become completely unsatisfactory when applied to the calculations of saturated densities. It can be seen from Table 5 that the agreement of these data is excellent, especially for vapor pressure. The average deviations are 0.052% for vapor pressure for 90 points, 0.46% for saturated liquid density for 71 points, 0.54% for saturated vapor density for 71 points. The point-by-point comparison of vapor pressure calculations for the data of Michels is tabulated in Appendix A-2.

Figure 14 shows the deviation distribution for vapor pressure. The deviations appear to be randomly distributed and fall within the range from -0.1% to 0.15%, but as the temperature approaches the triple point the deviation

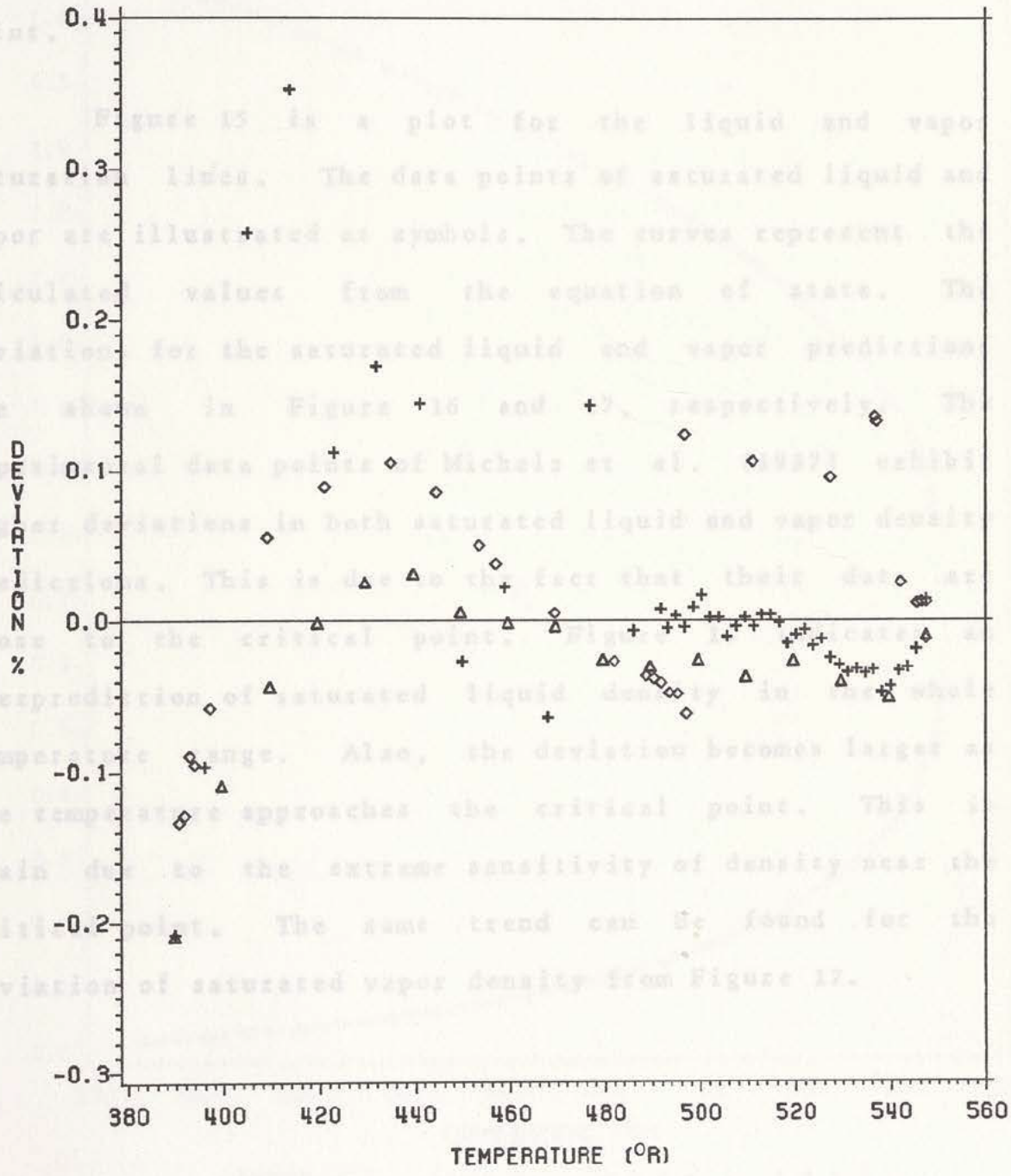
TABLE 5.

 PREDICTION OF SATURATED PROPERTIES  
 USING EQUATION (1)

| Property             | Data Source          | Temp. Range (°R) | Pres. Range (psia) | No. of Points | Abs. Dev. (%) |      |
|----------------------|----------------------|------------------|--------------------|---------------|---------------|------|
|                      |                      |                  |                    |               | Ave.          | Max. |
| Vapor Pressure       | Michels (1937, 1950) | 390.8-547.5      | 76.9-1,070         | 29            | 0.066         | 0.14 |
|                      | Meyers (1933)        | 389.8-547.5      | 75.1-1,070         | 17            | 0.040         | 0.21 |
|                      | Vargaftik (1975)     | 389.8-547.5      | 75.1-1,071         | 44            | 0.048         | 0.35 |
|                      |                      |                  |                    | 90            | 0.052         | 0.35 |
| Sat'd Liquid Density | Michels (1937)       | 496.8-547.5      | 543.7-1,070        | 9             | 1.36          | 5.62 |
|                      | Din (1956)           | 389.8-545.7      | 75.1-1,046         | 19            | 0.27          | 2.07 |
|                      | Vargaftik (1975)     | 389.8-545.4      | 75.1-1,042         | 43            | 0.36          | 1.27 |
|                      |                      |                  |                    | 71            | 0.46          | 5.62 |
| Sat'd Vapor Density  | Michels (1937)       | 496.8-547.5      | 543.7-1,070        | 9             | 0.82          | 5.22 |
|                      | Din (1956)           | 389.8-545.7      | 75.1-1,046         | 19            | 0.59          | 1.15 |
|                      | Vargaftik (1975)     | 389.8-545.4      | 75.1-1,042         | 43            | 0.36          | 1.27 |
|                      |                      |                  |                    | 71            | 0.54          | 5.22 |



FIGURE 14.  
VAPOR PRESSURE DEVIATION



LEGEND: 1    ◇ ◇ ◇ 1    △ △ △ 2    + + + 3

DATA SOURCE 1: MICHELS 2: MEYERS 3: VARGAFTIK

becomes larger. This behavior might be due to smaller vapor pressure near the triple point and the increasing difficulty in satisfying the Maxwell criterion when close to the triple point.

Figure 15 is a plot for the liquid and vapor saturation lines. The data points of saturated liquid and vapor are illustrated as symbols. The curves represent the calculated values from the equation of state. The deviations for the saturated liquid and vapor predictions are shown in Figure 16 and 17, respectively. The experimental data points of Michels et al. (1937) exhibit higher deviations in both saturated liquid and vapor density predictions. This is due to the fact that their data are close to the critical point. Figure 16 indicates an overprediction of saturated liquid density in the whole temperature range. Also, the deviation becomes larger as the temperature approaches the critical point. This is again due to the extreme sensitivity of density near the critical point. The same trend can be found for the deviation of saturated vapor density from Figure 17.

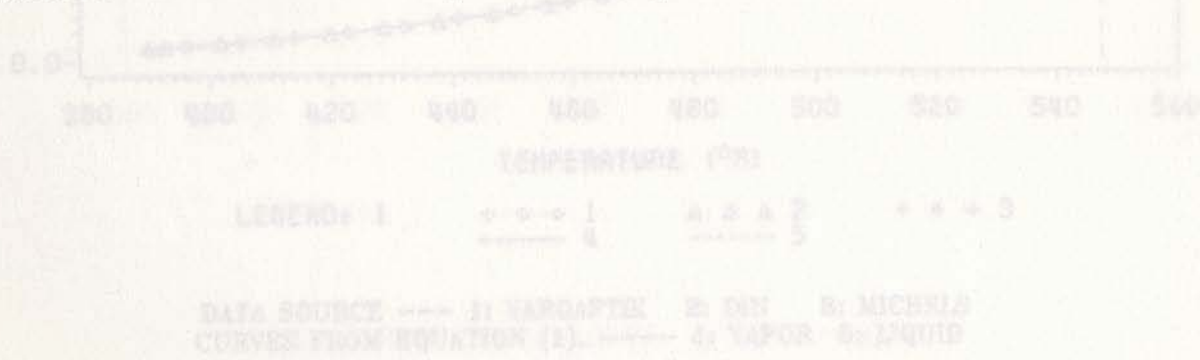
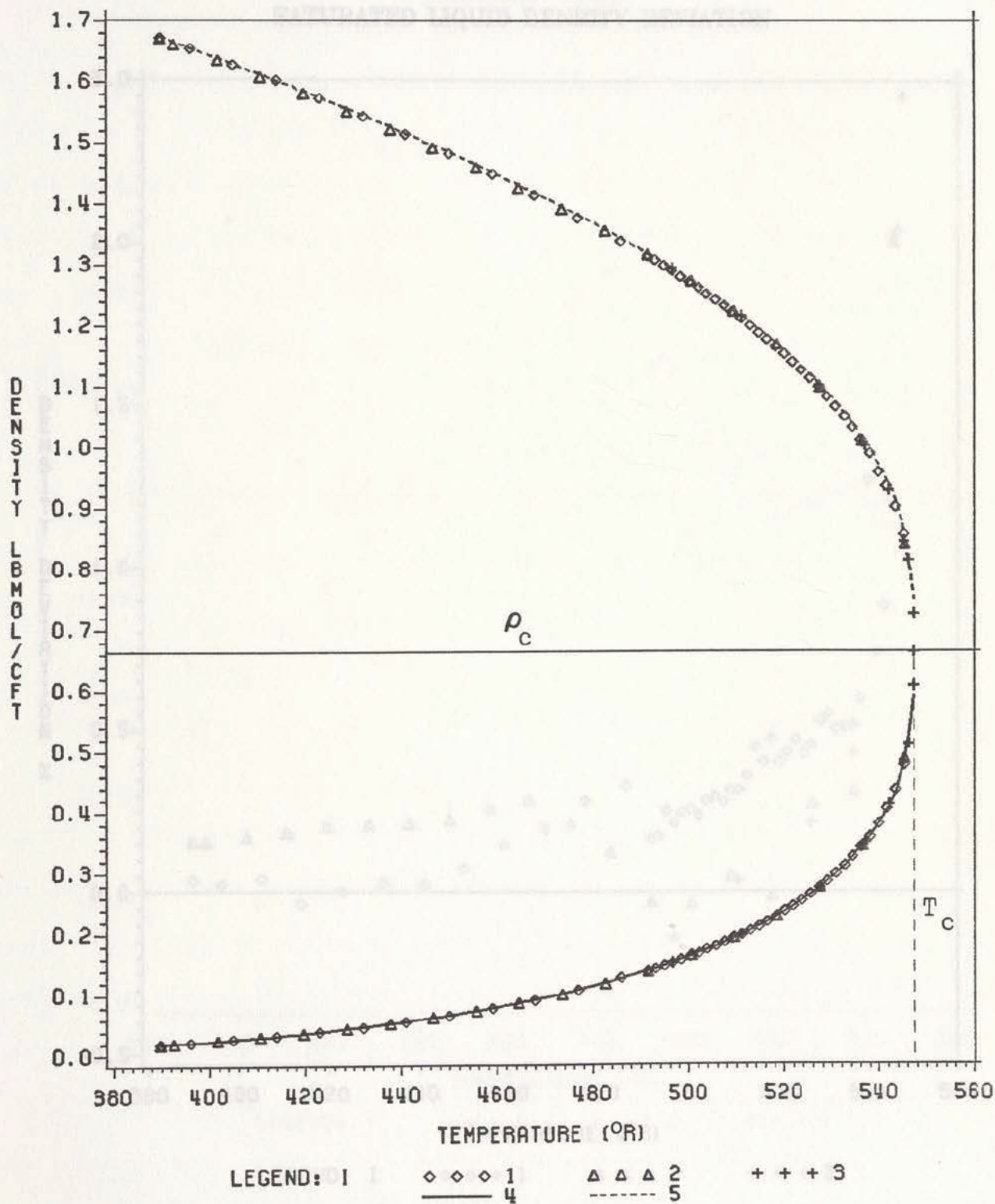


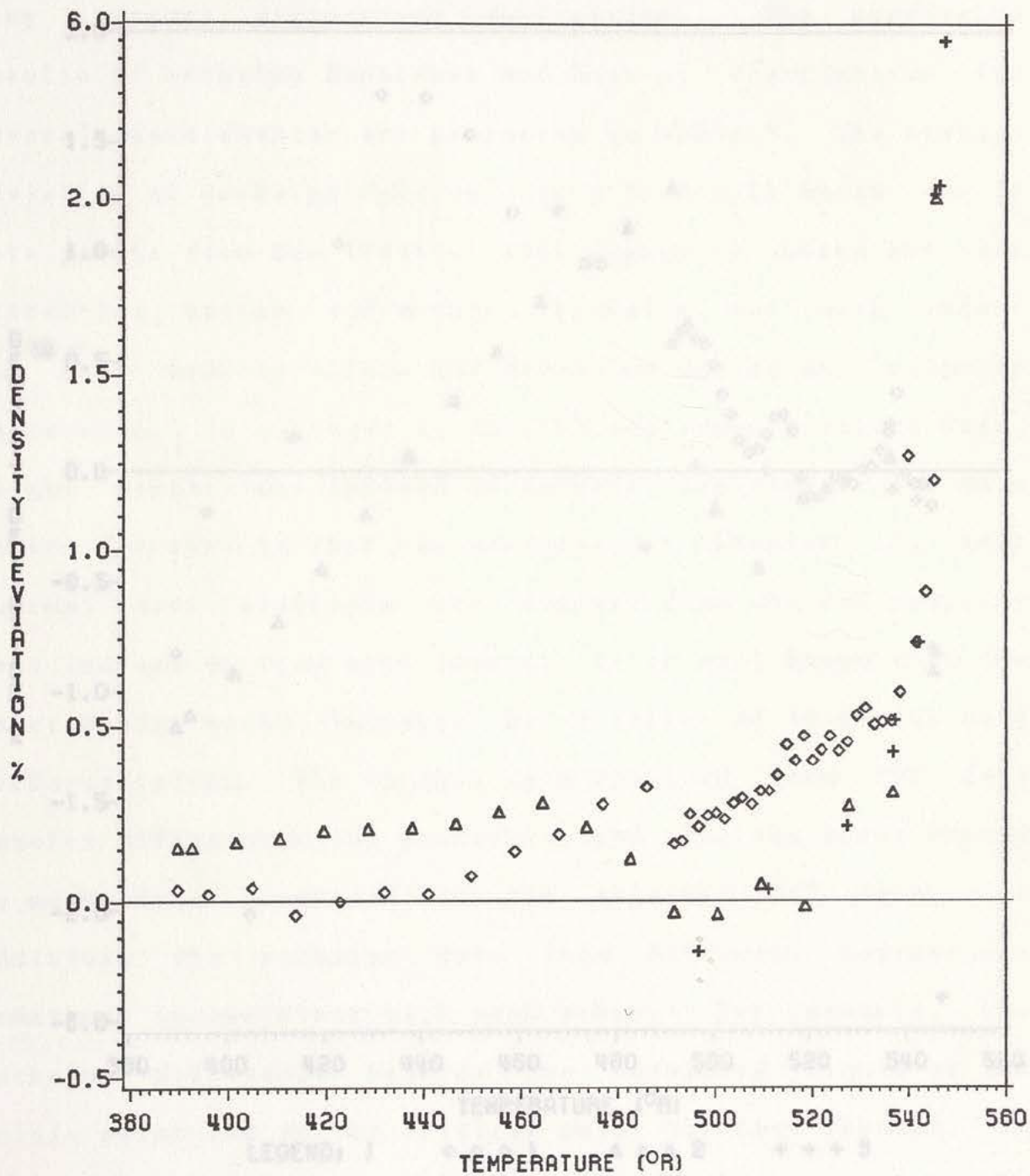


FIGURE 15.  
PLOT OF SATURATED LIQUID AND VAPOR DENSITY



DATA SOURCE --- 1: VARGAFTIK    2: DIN    3: MICHELS  
CURVES FROM EQUATION (1). - - - - 4: VAPOR    5: LIQUID

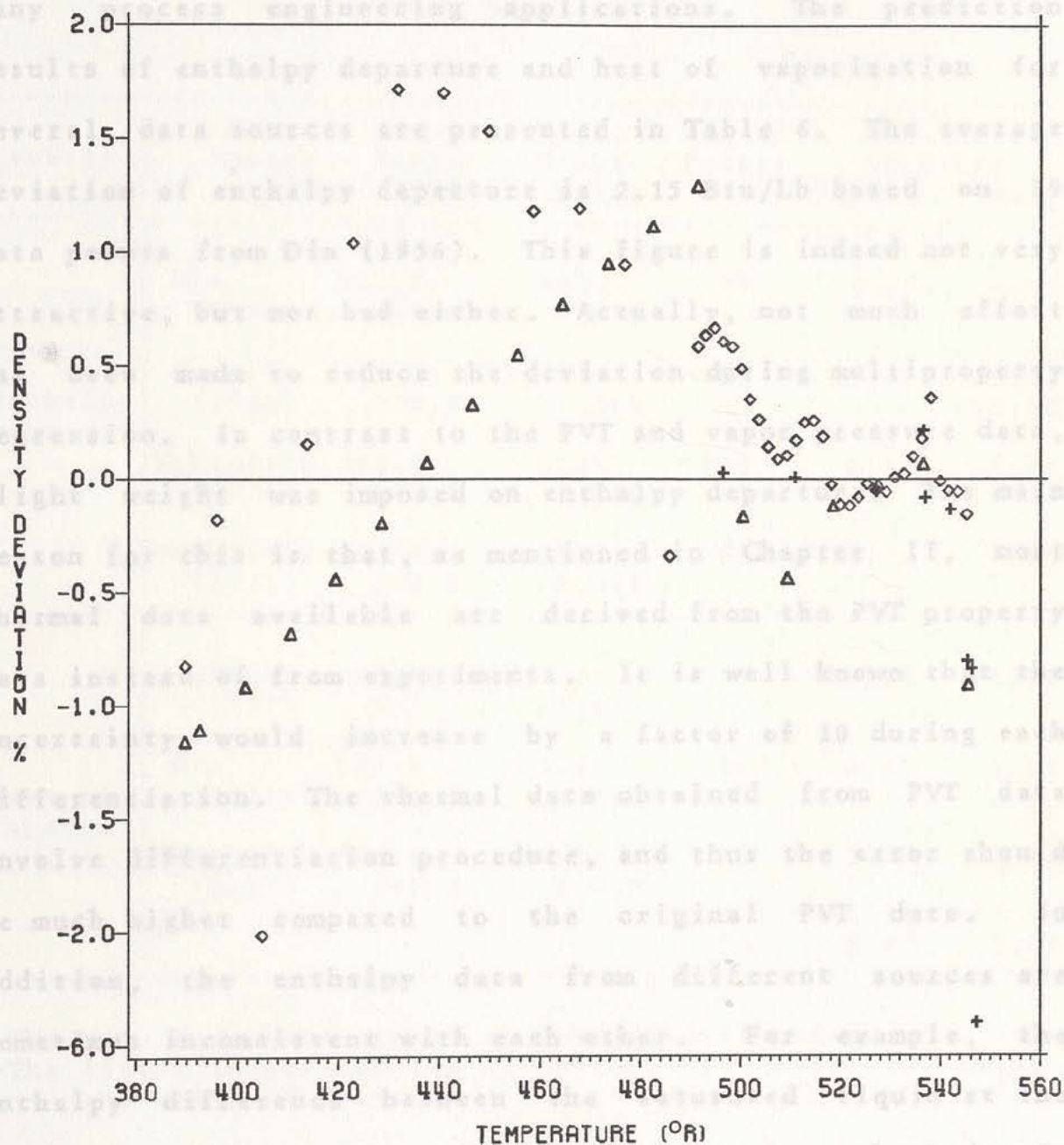
FIGURE 16.  
SATURATED LIQUID DENSITY DEVIATION



DATA SOURCE    1: VARGAFTIK    2: DIN    3: MICHELS



FIGURE 17.  
SATURATED VAPOR DENSITY DEVIATION



LEGEND: 1    ◊ ◊ ◊ 1    ▲ ▲ ▲ 2    + + + 3

DATA SOURCE    1: VARGAFTIK    2: DIN    3: MICHELS

## Thermal Properties

TABLE 6.

Thermal properties of pure fluid are important in many process engineering applications. The prediction results of enthalpy departure and heat of vaporization for several data sources are presented in Table 6. The average deviation of enthalpy departure is 2.15 Btu/Lb based on 39 data points from Din (1956). This figure is indeed not very attractive, but not bad either. Actually, not much effort has been made to reduce the deviation during multiproperty regression. In contrast to the PVT and vapor pressure data, slight weight was imposed on enthalpy departure. The main reason for this is that, as mentioned in Chapter II, most thermal data available are derived from the PVT property data instead of from experiments. It is well known that the uncertainty would increase by a factor of 10 during each differentiation. The thermal data obtained from PVT data involve differentiation procedure, and thus the error should be much higher compared to the original PVT data. In addition, the enthalpy data from different sources are sometimes inconsistent with each other. For example, the enthalpy difference between the saturated liquid at the triple point and at the critical point has been checked. It is found that the value from Din (1956) is about 2.1 Btu/Lb higher than that from Vargaftik (1975).

For the 102 data points of Koppel and Smith (1956)



TABLE 6.

PREDICTION OF THERMAL PROPERTIES  
USING EQUATION (1)

| Property           | Data Source      | Temp. Range (°R) | Pres. Range (psia) | No. of Points | Abs. Dev. (Btu/Lb) |              |
|--------------------|------------------|------------------|--------------------|---------------|--------------------|--------------|
|                    |                  |                  |                    |               | Ave.               | Max.         |
| Enthalpy Departure | Din (1956)       | 437.7-743.7      | 441-7,350          | 39            | 2.15               | 4.45         |
|                    | Koppel (1960)    | 524.7-579.7      | 1,050-1,200        | 102           | 1.21               | 9.57* (2.58) |
|                    | Vargaftik (1975) | 540.0-576.0      | 870-1,160          | 441           | 0.34               | 3.84         |
|                    | Vargaftik (1975) | 396.0-576.0      | 290-8,702          | 89            | 1.16               | 3.98         |
| Heat of Vaporiz.   | Michels (1937)   | 496.8-547.5      | 543.7-1,070        | 9             | 1.04               | 5.25         |
|                    | Din (1956)       | 389.8-545.7      | 75.1-1,046         | 19            | 0.97               | 2.23         |
|                    | Vargaftik (1975) | 389.8-545.4      | 75.1-1,042         | 43            | 1.00               | 2.73         |
|                    |                  |                  |                    | 71            | 1.00               | 5.25         |

\* The max. deviation occurs at the critical point.  
The figure in parentheses is the max. deviation excluding the critical point.

in the critical region, the average deviation of enthalpy departure is 1.21 Btu/Lb, a fairly satisfactory result. The comparison between the experimental values of Koppel and Smith and the calculated results from the equation of state can be seen in the pressure-enthalpy diagram given in Figure 18. Detailed comparison can be found in Appendix A-3. Figure 19 is a temperature-entropy diagram, where the entropy data are also taken from Koppel and Smith. The agreement in both diagrams is by no means exact, but not bad either. Nevertheless, both figures show the ability of the equation of state to predict the correct trends of enthalpy and entropy in a region where the changes take place rapidly.

The data of Koppel and Smith are reported on the bases of  $H=0$  and  $S=0$  for the saturated liquid at  $-40^{\circ}\text{F}$ . To prepare Figure 18 and 19, the enthalpy and entropy at other conditions have to be corrected to the reference state using the following equations:

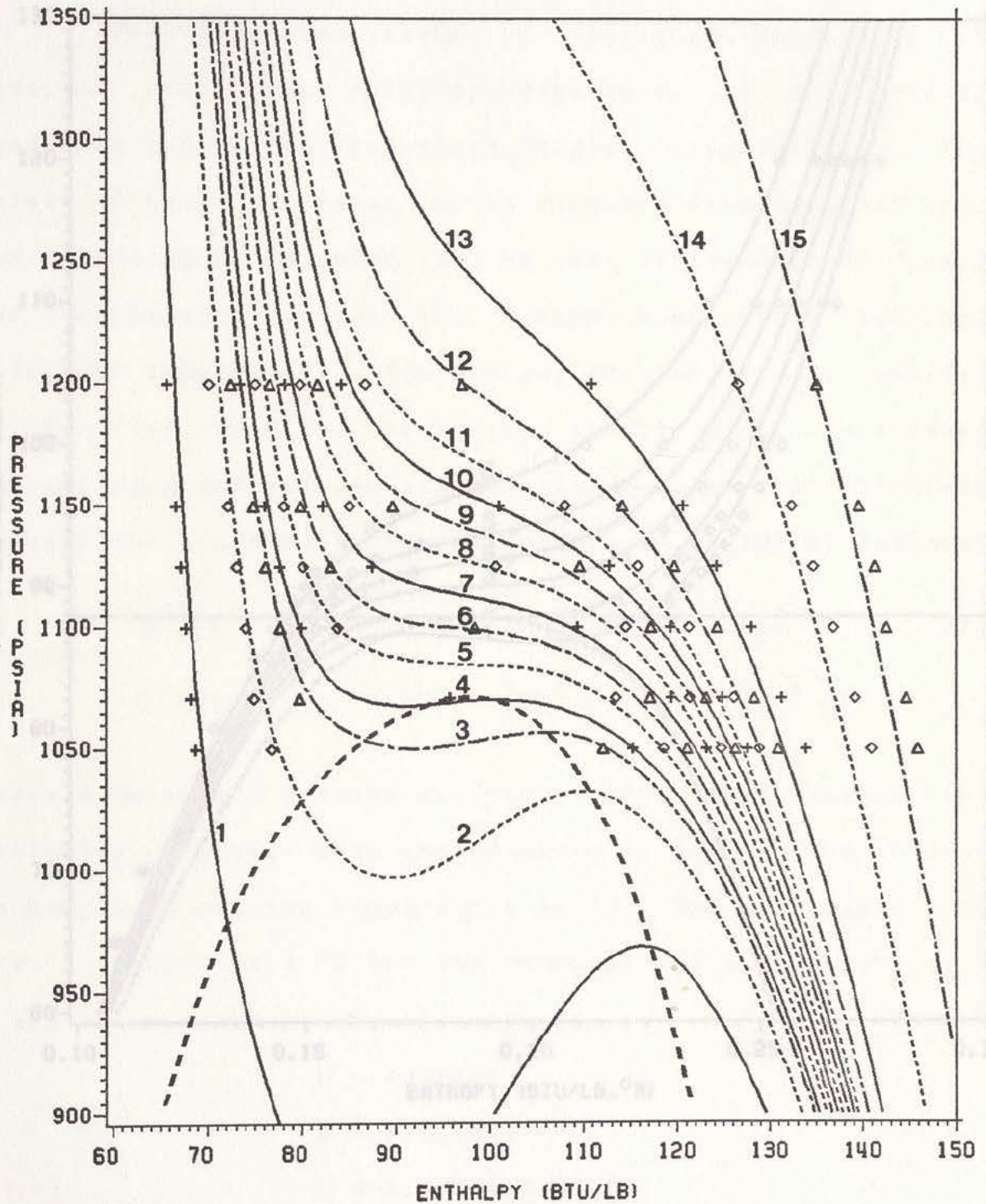
$$\begin{aligned}
 H(T,P) &= [H(T,P) - H^{\circ}(T)] - [H(T_R, P_R) - H^{\circ}(T_R)] \\
 &+ [H^{\circ}(T) - H^{\circ}(T_R)]
 \end{aligned}
 \tag{20}$$

$$\begin{aligned}
 S(T,P) &= [S(T,P) - S^{\circ}(T)] - [S(T_R, P_R) - S^{\circ}(T_R)] \\
 &+ [S^{\circ}(T) - S^{\circ}(T_R)]
 \end{aligned}
 \tag{21}$$

where  $T_R$  and  $P_R$  are temperature and pressure at the



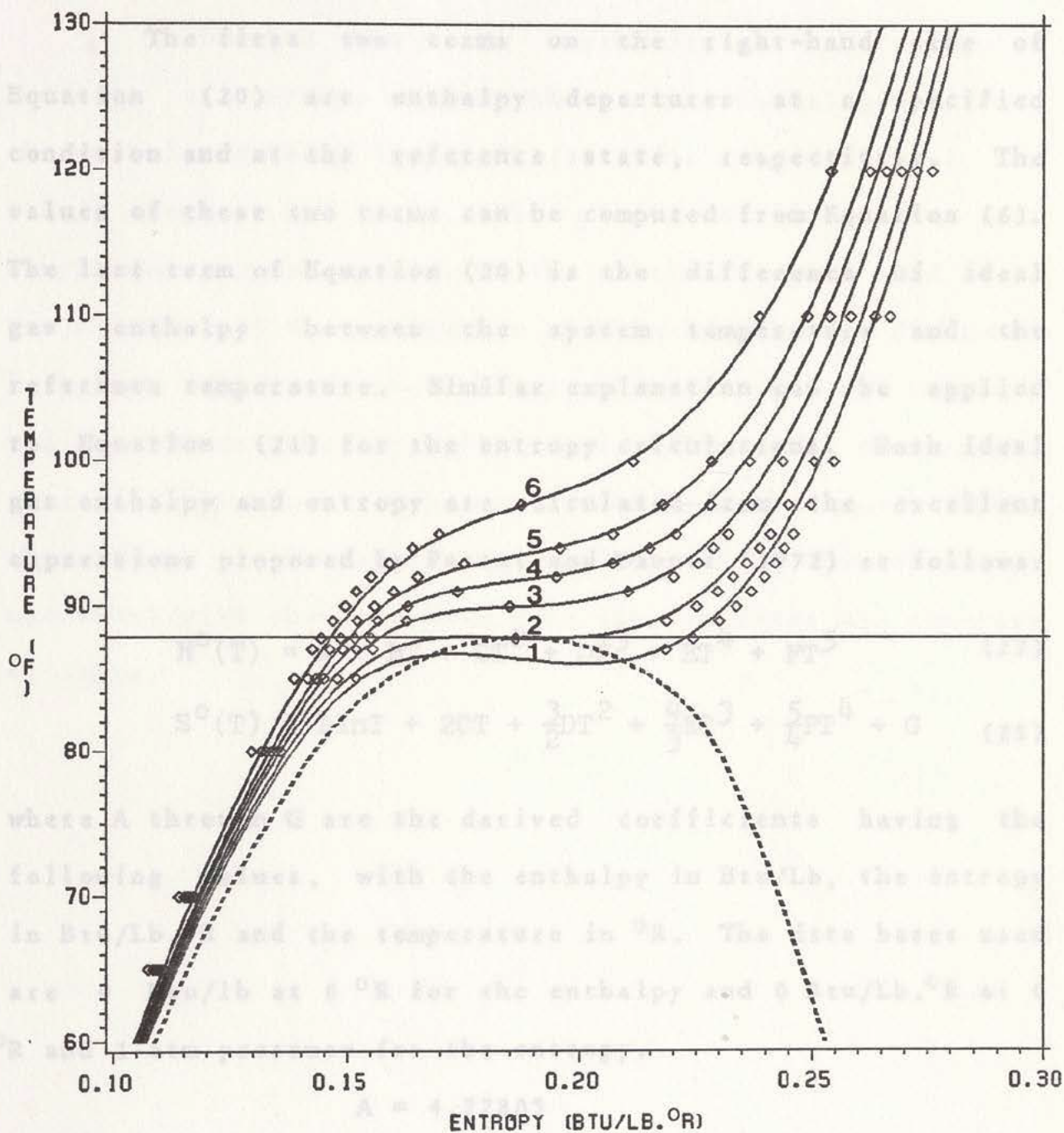
FIGURE 18.  
PRESSURE-ENTHALPY DIAGRAM FOR CO<sub>2</sub>



|            |       |        |        |         |         |         |         |       |
|------------|-------|--------|--------|---------|---------|---------|---------|-------|
| TEMP. (°F) | 1: 80 | 2: 85  | 3: 87  | 4: 87.8 | 5: 89   | 6: 90   | 7: 91   | 8: 92 |
|            | 9: 93 | 10: 94 | 11: 95 | 12: 97  | 13: 100 | 14: 110 | 15: 120 |       |

REFERENCE POINT : H = 0 FOR SATURATED LIQUID AT -40°F  
 CURVES : FROM THE EQUATION OF STATE.  
 DATA POINTS : FROM KOPPEL AND SMITH (1960).

FIGURE 19.  
TEMPERATURE-ENTROPY DIAGRAM FOR CO<sub>2</sub>



PRES. (PSIA) 1: 1050 2: 1071 3: 1100 4: 1125 5: 1150 6: 1200

REFERENCE POINT : S = 0 FOR SATURATED LIQUID AT -40°F  
 CURVES : FROM THE EQUATION OF STATE.  
 DATA POINTS : FROM KOPPEL AND SMITH (1960).



reference state , respectively.

The first two terms on the right-hand side of Equation (20) are enthalpy departures at a specified condition and at the reference state, respectively. The values of these two terms can be computed from Equation (6). The last term of Equation (20) is the difference of ideal gas enthalpy between the system temperature and the reference temperature. Similar explanation can be applied to Equation (21) for the entropy calculations. Both ideal gas enthalpy and entropy are calculated from the excellent expressions proposed by Passut and Danner (1972) as follows:

$$H^{\circ}(T) = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \quad (22)$$

$$S^{\circ}(T) = B \ln T + 2CT + \frac{3}{2}DT^2 + \frac{4}{3}ET^3 + \frac{5}{4}FT^4 + G \quad (23)$$

where A through G are the derived coefficients having the following values, with the enthalpy in Btu/Lb, the entropy in Btu/Lb.<sup>°R</sup> and the temperature in <sup>°R</sup>. The data bases used are 0 Btu/lb at 0 <sup>°R</sup> for the enthalpy and 0 Btu/Lb.<sup>°R</sup> at 0 <sup>°R</sup> and 1 atm pressure for the entropy.

$$A = 4.77805$$

$$B = 0.114433$$

$$C = 0.101132E-3$$

$$D = -0.026494E-6$$

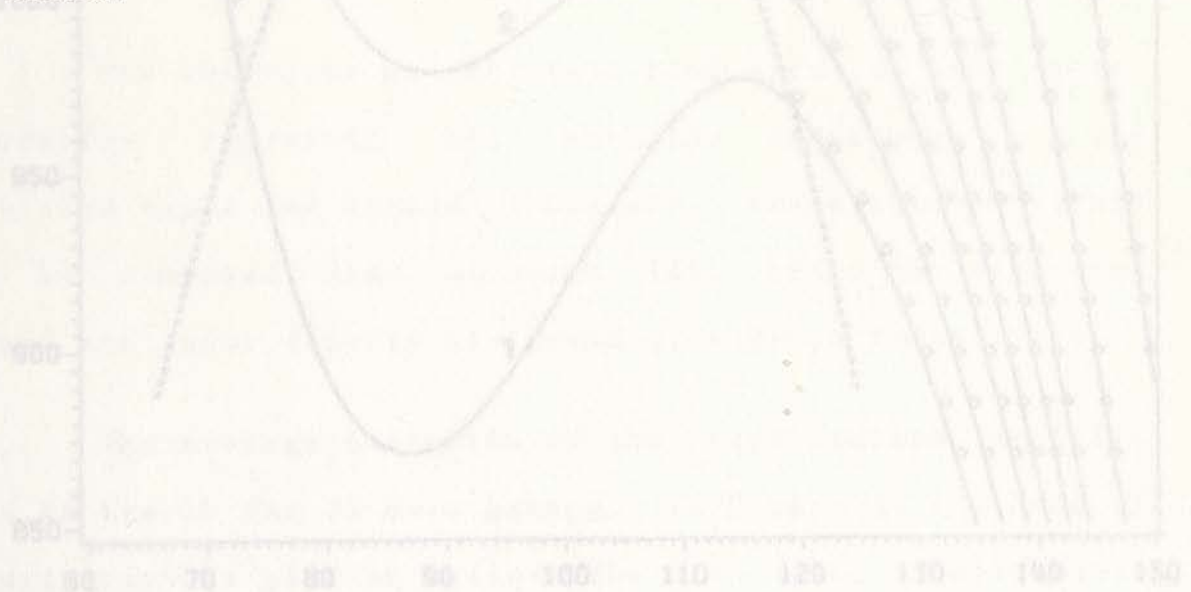
$$E = 0.034706E-10$$

$$F = -0.013140E-14$$

$$G = 0.343357$$

FIGURE 20.  
PRESSURE-ENTHALPY DIAGRAM FOR CO<sub>2</sub>

To further test the capability of the proposed equation of state to predict changes in thermal properties, the enthalpy data of Vargaftik (1975) in the critical and liquid region are used. The average deviations are 0.34 Btu/Lb for 441 data points in the critical region and 1.16 Btu/Lb for 89 data points in the liquid region. Figure 20 is a plot of pressure-enthalpy diagram in the critical region, where the Vargaftik data are used for comparison. It is readily observed that the calculated enthalpies check the data of Vargaftik extremely well. The excellent agreement with the Vargaftik data substantiates the equation of state.



ENTHALPY (BTU/LB)

|       |          |          |          |          |
|-------|----------|----------|----------|----------|
| TEMP. | 1: 540.0 | 2: 543.0 | 3: 547.3 | 4: 550.0 |
| TEMP. | 5: 554.4 | 6: 558.0 | 7: 562.2 | 8: 576.0 |

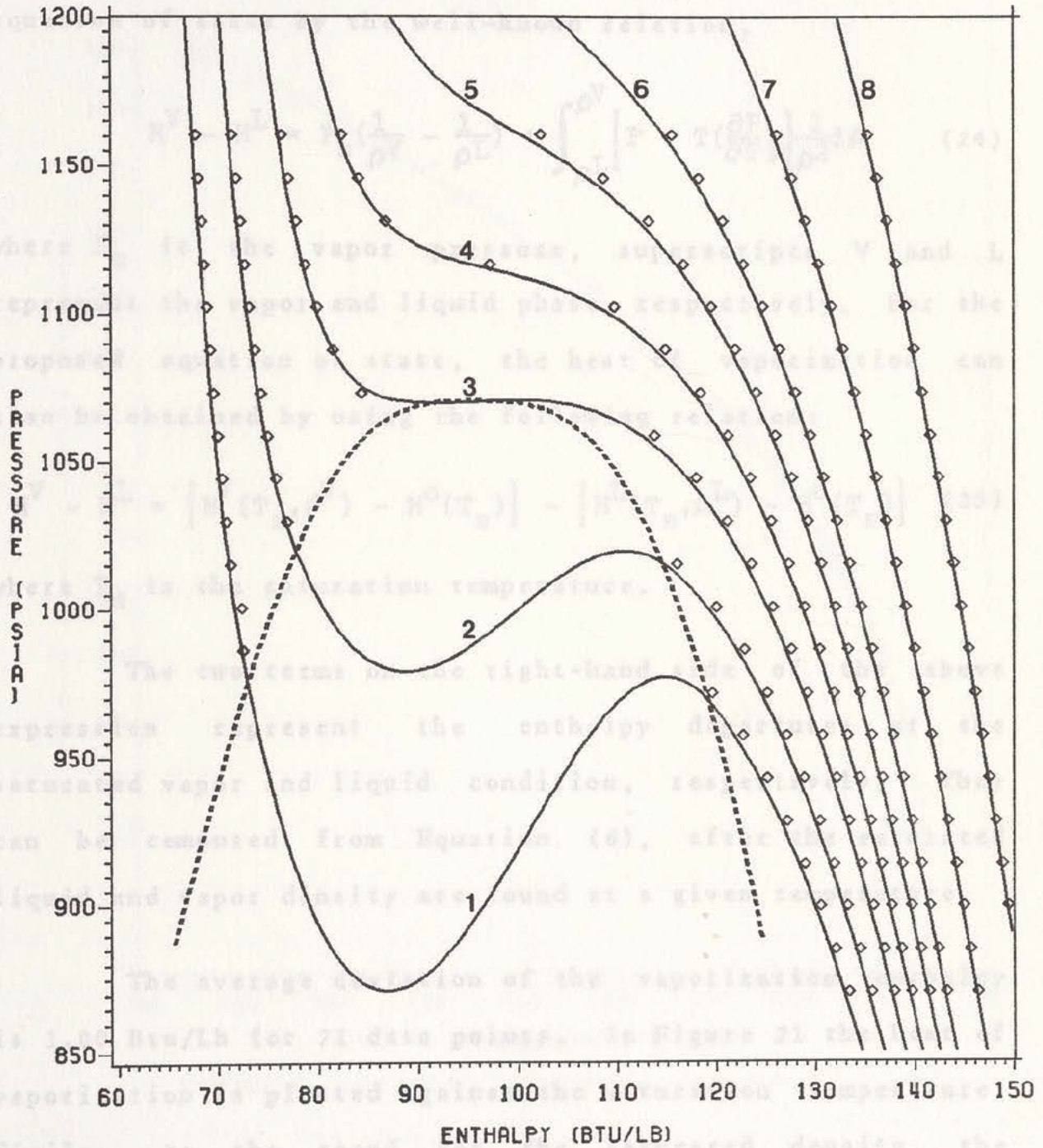
REFERENCE POINT:  $h = 0$  FOR SATURATED LIQUID AT  $-40^{\circ}\text{F}$

CURVES FROM THE EQUATION OF STATE.

DATA POINTS FROM VARGAFTIK (1975).



**FIGURE 20.**  
**PRESSURE-ENTHALPY DIAGRAM FOR CO<sub>2</sub>**



| TEMP. (°R) | 1: 540.0 | 2: 543.6 | 3: 547.5 | 4: 550.8 | 5: 554.4 | 6: 558.0 | 7: 565.2 | 8: 576.0 |
|------------|----------|----------|----------|----------|----------|----------|----------|----------|
|------------|----------|----------|----------|----------|----------|----------|----------|----------|

REFERENCE POINT : H = 0 FOR SATURATED LIQUID AT -40 °F  
 CURVES : FROM THE EQUATION OF STATE.  
 DATA POINTS : FROM VARGAFTIK (1975).

## Heat of Vaporization

FIGURE 21.  
PLOT OF HEAT OF VAPORIZATION

The heat of vaporization can be calculated from an equation of state by the well-known relation,

$$H^V - H^L = P_S \left( \frac{1}{\rho^V} - \frac{1}{\rho^L} \right) + \int_{\rho^L}^{\rho^V} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_\rho \right] \frac{1}{\rho^2} d\rho \quad (24)$$

where  $P_S$  is the vapor pressure, superscripts V and L represent the vapor and liquid phase, respectively. For the proposed equation of state, the heat of vaporization can also be obtained by using the following relation:

$$H^V - H^L = \left[ H^V(T_S, \rho^V) - H^O(T_S) \right] - \left[ H^L(T_S, \rho^L) - H^O(T_S) \right] \quad (25)$$

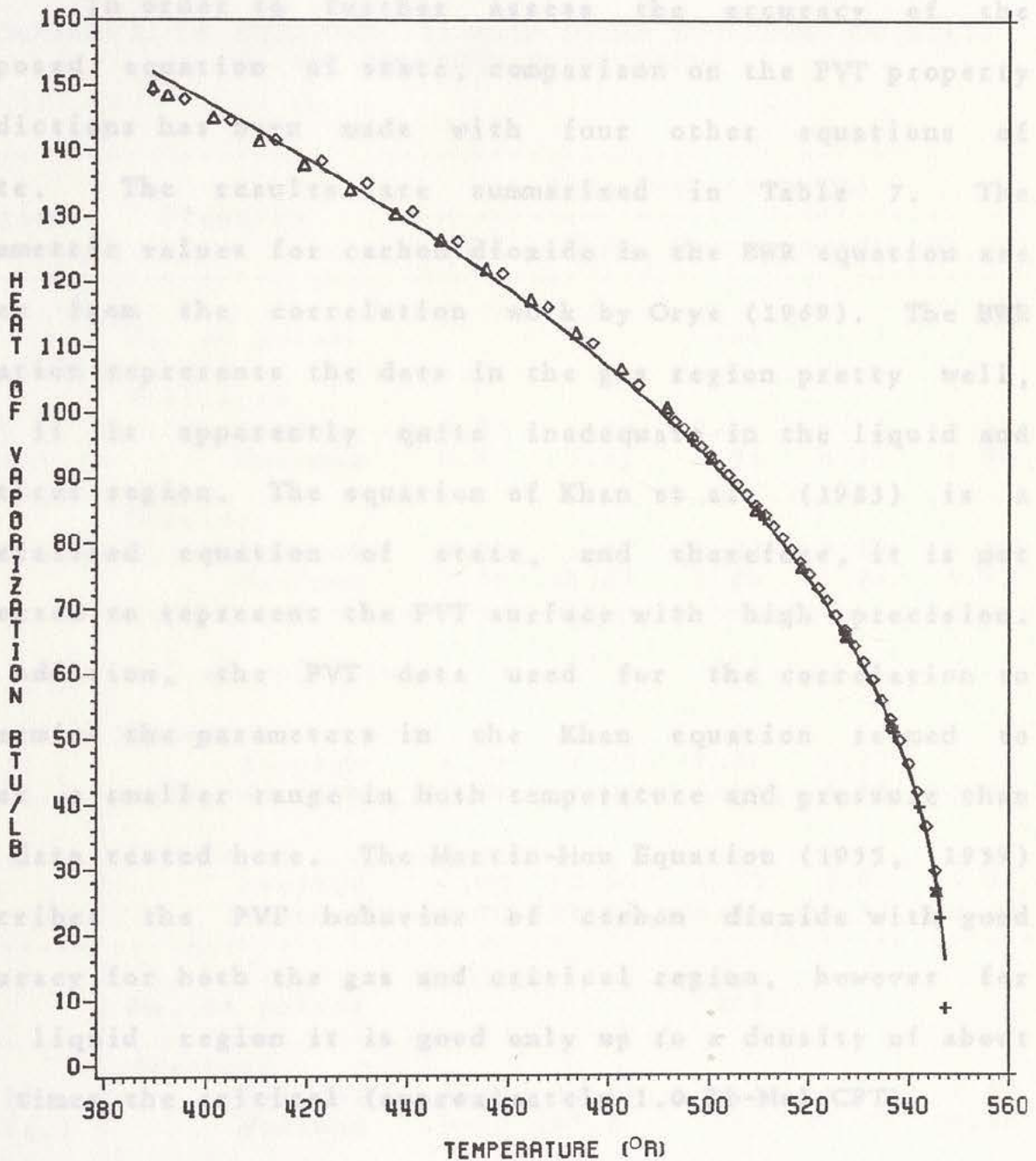
where  $T_S$  is the saturation temperature.

The two terms on the right-hand side of the above expression represent the enthalpy departures at the saturated vapor and liquid condition, respectively. They can be computed from Equation (6), after the saturated liquid and vapor density are found at a given temperature.

The average deviation of the vaporization enthalpy is 1.00 Btu/Lb for 71 data points. In Figure 21 the heat of vaporization is plotted against the saturation temperature. Similar to the trend for the saturated density, the vaporization enthalpy deviates larger from the observed values when approaching the critical temperature.



FIGURE 21.  
PLOT OF HEAT OF VAPORIZATION



LEGEND: 1    ◊ ◊ ◊ 1    ▲ ▲ ▲ 2    + + + 3

DATA SOURCE    1: VARGAFTIK    2: DIN    3: MICHELS  
CURVE            : THIS WORK

## Comparison with Other Equations of State

In order to further assess the accuracy of the proposed equation of state, comparison on the PVT property predictions has been made with four other equations of state. The results are summarized in Table 7. The parametric values for carbon dioxide in the BWR equation are taken from the correlation work by Orye (1969). The BWR equation represents the data in the gas region pretty well, but it is apparently quite inadequate in the liquid and critical region. The equation of Khan et al. (1983) is a generalized equation of state, and therefore, it is not expected to represent the PVT surface with high precision. In addition, the PVT data used for the correlation to determine the parameters in the Khan equation seemed to cover a smaller range in both temperature and pressure than the data tested here. The Martin-Hou Equation (1955, 1959) describes the PVT behavior of carbon dioxide with good accuracy for both the gas and critical region, however for the liquid region it is good only up to a density of about 1.5 times the critical (approximately 1.0 Lb-Mol/CFT).

Examination of Table 7 reveals that only the Bender equation (1970) is comparable with Equation (1) for the entire temperature and pressure range under investigation. In the gas and liquid region the Bender equation gives fairly good correlation, and Equation (1) is only slightly



TABLE 7.

COMPARISON OF EQUATION (1) WITH OTHER EQUATIONS OF STATE  
ON PVT PROPERTY PREDICTIONS

| Region        | Property      | Abs. Deviation (%) |       |        |        |        |
|---------------|---------------|--------------------|-------|--------|--------|--------|
|               |               | BWR                | Khan  | Martin | Bender | Eq.(1) |
| I<br>(gas)    | No. of points | 284                |       |        |        |        |
|               | Pressure:     |                    |       |        |        |        |
|               | Average       | 0.21               | 0.62  | 0.14   | 0.11   | 0.11   |
|               | Maximum       | 0.87               | 3.31  | 0.51   | 0.65   | 0.90   |
|               | Density:      |                    |       |        |        |        |
|               | Average       | 0.37               | 1.21  | 0.22   | 0.18   | 0.16   |
| Maximum       | 2.30          | 10.65              | 1.08  | 1.26   | 0.98   |        |
| II<br>(crit.) | No. of points | 113                |       |        |        |        |
|               | Pressure:     |                    |       |        |        |        |
|               | Average       | 0.50               | 3.39  | 0.20   | 0.22   | 0.10   |
|               | Maximum       | 1.86               | 10.28 | 1.10   | 1.83   | 1.19   |
|               | Density:      |                    |       |        |        |        |
|               | Average       | 3.90               | 13.36 | 2.15   | 2.98   | 0.91   |
| Maximum       | 18.77         | 38.64              | 20.79 | 27.97  | 5.30   |        |
| III<br>(liq.) | No. of points | 228                |       |        |        |        |
|               | Pressure:     |                    |       |        |        |        |
|               | Average       | ----               | 10.65 | ----   | 1.28   | 1.01   |
|               | Maximum       | ----               | 143.0 | ----   | 30.32  | 14.26  |
|               | Density:      |                    |       |        |        |        |
|               | Average       | 3.85               | 1.68  | ----   | 0.12   | 0.10   |
| Maximum       | 7.56          | 6.49               | ----  | 0.78   | 0.43   |        |

FIGURE 22.  
COMPARISON OF CRITICAL ISOTHERMS

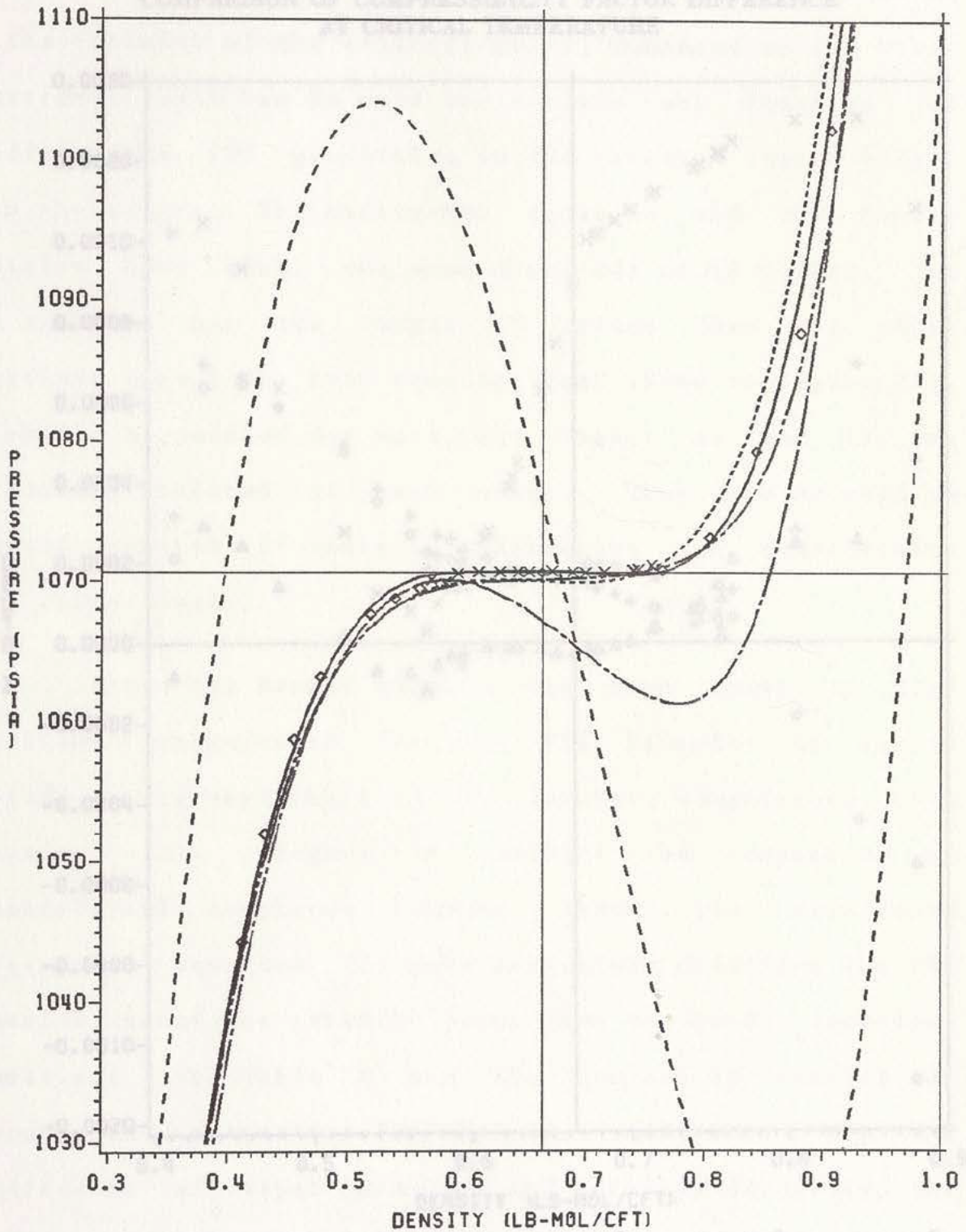
better than the Bender equation in these regions. However in the critical region, it is obvious that Equation (1) is superior to the Bender equation, even without using the special correction terms.

As mentioned before, the isotherms near the critical point have great variations in the slopes and curvatures. Thus the isotherm at the critical temperature would be the most difficult to be fitted into the experimental data. The comparison between the critical isotherms calculated from the above-mentioned equations of state is shown in Figure 22. The equation of Khan et al. gives poor correlation for the critical isotherm. The BWR equation exhibits substantial deviation from the experimental values starting from a density of about 0.6 Lb-Mol/CFT. The two isotherms calculated from the Martin-Hou equation and the Bender equation almost overlap up to a density of about 0.75 Lb-Mol/CFT. They fit the observed data pretty well for the densities lower than the critical, but deviate significantly at higher densities. It can be seen from Figure 22 that Equation (1) fits the experimental values better than the other equations.

For further comparison the compressibility factor differences at the critical temperature for the equations of state are plotted in Figure 23. The compressibility factor difference has been defined in the previous chapter. Figure



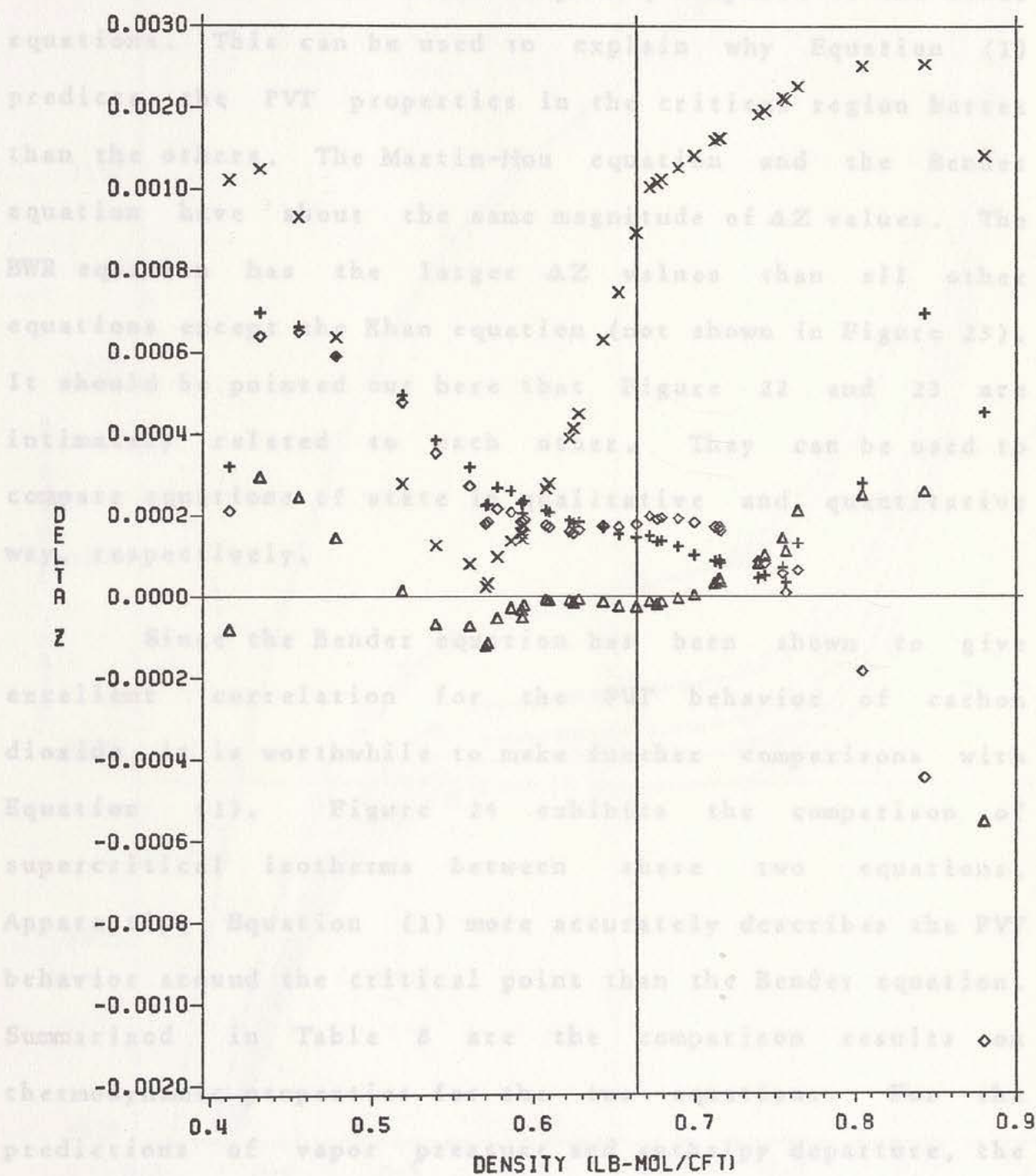
FIGURE 22.  
COMPARISON OF CRITICAL ISOTHERMS



LEGEND: EOS      ----- 1      - - - - - 2      - - - - - 3      - - - - - 4  
                               ----- 5      ◇ ◇ ◇ 6      × × × 7

EQUATION    1: BENDER 2: BWR 3: MARTIN 4: KHAN 5: THIS WORK  
 DATA SOURCE 6: MICHELS 7: WENTORF

**FIGURE 23.**  
**COMPARISON OF COMPRESSIBILITY FACTOR DIFFERENCE**  
**AT CRITICAL TEMPERATURE**



LEGEND: EOS 1: BWR 2: MARTIN 3: BENDER 4: THIS WORK

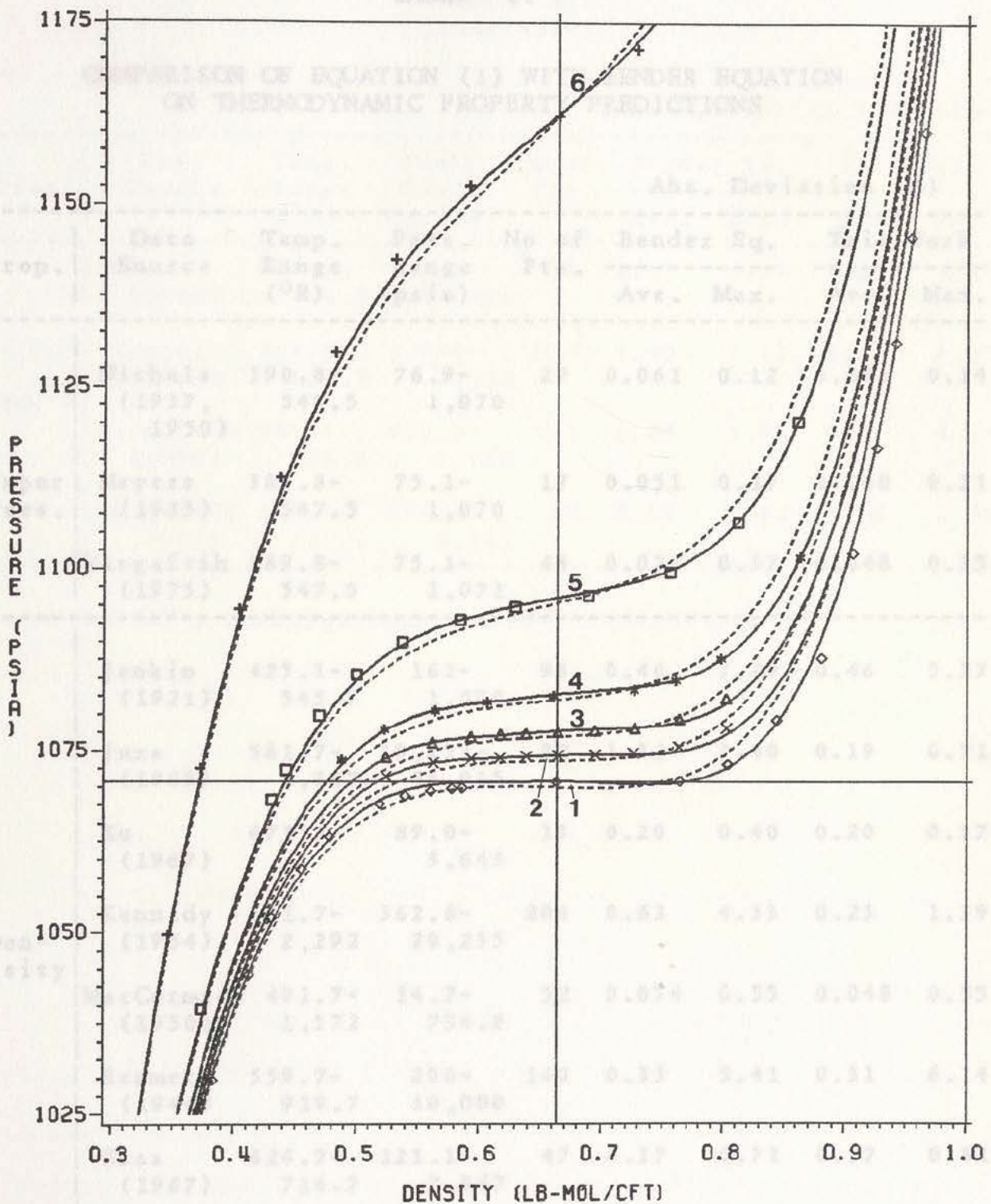
EQUATION --- 1: BWR 2: MARTIN 3: BENDER 4: THIS WORK



23 indicates that Equation (1) gives the lowest values of  $\Delta Z$  in the vicinity of the critical point, compared to the other equations. This can be used to explain why Equation (1) predicts the PVT properties in the critical region better than the others. The Martin-Hou equation and the Bender equation have about the same magnitude of  $\Delta Z$  values. The BWR equation has the larger  $\Delta Z$  values than all other equations except the Khan equation (not shown in Figure 23). It should be pointed out here that Figure 22 and 23 are intimately related to each other. They can be used to compare equations of state in qualitative and quantitative way, respectively.

Since the Bender equation has been shown to give excellent correlation for the PVT behavior of carbon dioxide, it is worthwhile to make further comparisons with Equation (1). Figure 24 exhibits the comparison of supercritical isotherms between these two equations. Apparently, Equation (1) more accurately describes the PVT behavior around the critical point than the Bender equation. Summarized in Table 8 are the comparison results on thermodynamic properties for the two equations. For the predictions of vapor pressure and enthalpy departure, the Bender equation exhibits about the same precision as Equation (1). But it seems that Equation (1) has a slight advantage over the Bender equation in the enthalpy

FIGURE 24.  
COMPARISON OF SUPERCRITICAL ISOTHERMS



TEMP. (°R) 1: 547.5 2: 547.8 3: 548.0 4: 548.4 5: 549.4 6: 554.2

SOLID LINES : THIS WORK  
DOTTED LINES : BENDER EQUATION



TABLE 8.

COMPARISON OF EQUATION (1) WITH BENDER EQUATION  
ON THERMODYNAMIC PROPERTY PREDICTIONS

| Prop.       | Data Source          | Temp. Range (°R) | Pres. Range (psia) | No of Pts. | Abs. Deviation (%) |      |           |      |
|-------------|----------------------|------------------|--------------------|------------|--------------------|------|-----------|------|
|             |                      |                  |                    |            | Bender Eq.         |      | This Work |      |
|             |                      |                  |                    |            | Ave.               | Max. | Ave.      | Max. |
| Vapor Pres. | Michels (1937, 1950) | 390.8-547.5      | 76.9-1,070         | 29         | 0.061              | 0.12 | 0.066     | 0.14 |
|             | Meyers (1933)        | 389.8-547.5      | 75.1-1,070         | 17         | 0.051              | 0.17 | 0.040     | 0.21 |
|             | Vargaftik (1975)     | 389.8-547.5      | 75.1-1,071         | 44         | 0.071              | 0.37 | 0.048     | 0.35 |
| Den- sity   | Jenkin (1921)        | 425.1-545.7      | 162-1,400          | 93         | 0.46               | 7.29 | 0.46      | 5.27 |
|             | Juza (1965)          | 581.7-1,347      | 10,153-58,015      | 82         | 1.32               | 3.40 | 0.19      | 0.71 |
|             | Ku (1967)            | 671.7            | 89.0-3,643         | 13         | 0.20               | 0.40 | 0.20      | 0.37 |
|             | Kennedy (1954)       | 491.7-2,292      | 362.6-20,235       | 204        | 0.63               | 4.33 | 0.25      | 1.39 |
|             | MacCormack (1950)    | 491.7-1,572      | 14.7-734.8         | 52         | 0.074              | 0.55 | 0.048     | 0.55 |
|             | Reamer (1944)        | 559.7-919.7      | 200-10,000         | 140        | 0.33               | 5.41 | 0.31      | 6.14 |
|             | Sass (1967)          | 626.7-716.7      | 121.1-7,347        | 47         | 0.17               | 0.71 | 0.17      | 0.81 |
|             | Vargaftik (1975)     | 540.0-568.8      | 971.8-1,160        | 96         | 0.97               | 9.66 | 0.58      | 5.37 |

TABLE 8.  
(continued)

Abs. Deviation (Btu/Lb)

| Prop.              | Data Source      | Temp. Range (°R) | Pres. Range (psia) | No of Pts. | Bender Eq. |      | This Work |      |
|--------------------|------------------|------------------|--------------------|------------|------------|------|-----------|------|
|                    |                  |                  |                    |            | Ave.       | Max. | Ave.      | Max. |
| H-H <sup>0</sup> * | Din (1956)       | 437.7-743.7      | 441-7,350          | 39         | 2.02       | 4.38 | 2.15      | 4.45 |
|                    | Koppel (1960)    | 524.7-579.7      | 1,050-1,200        | 102        | 1.40       | 8.23 | 1.21      | 9.57 |
|                    | Vargaftik (1975) | 540.0-576.0      | 870.2-1,160        | 441        | 0.40       | 5.05 | 0.34      | 3.84 |
|                    | Vargaftik (1975) | 396.0-576.0      | 290.0-8,702        | 89         | 1.35       | 3.96 | 1.16      | 3.98 |

\* H - H<sup>0</sup> : Enthalpy Departure. The comparison of density deviations for Equation (1) and the Bender equation, where the data of Juss and Kennedy are used. The density deviations from this work are randomly distributed within the range of about ± 0.5%. While the Bender equation has a trend of underprediction with the error between about 2.3 and -4%.

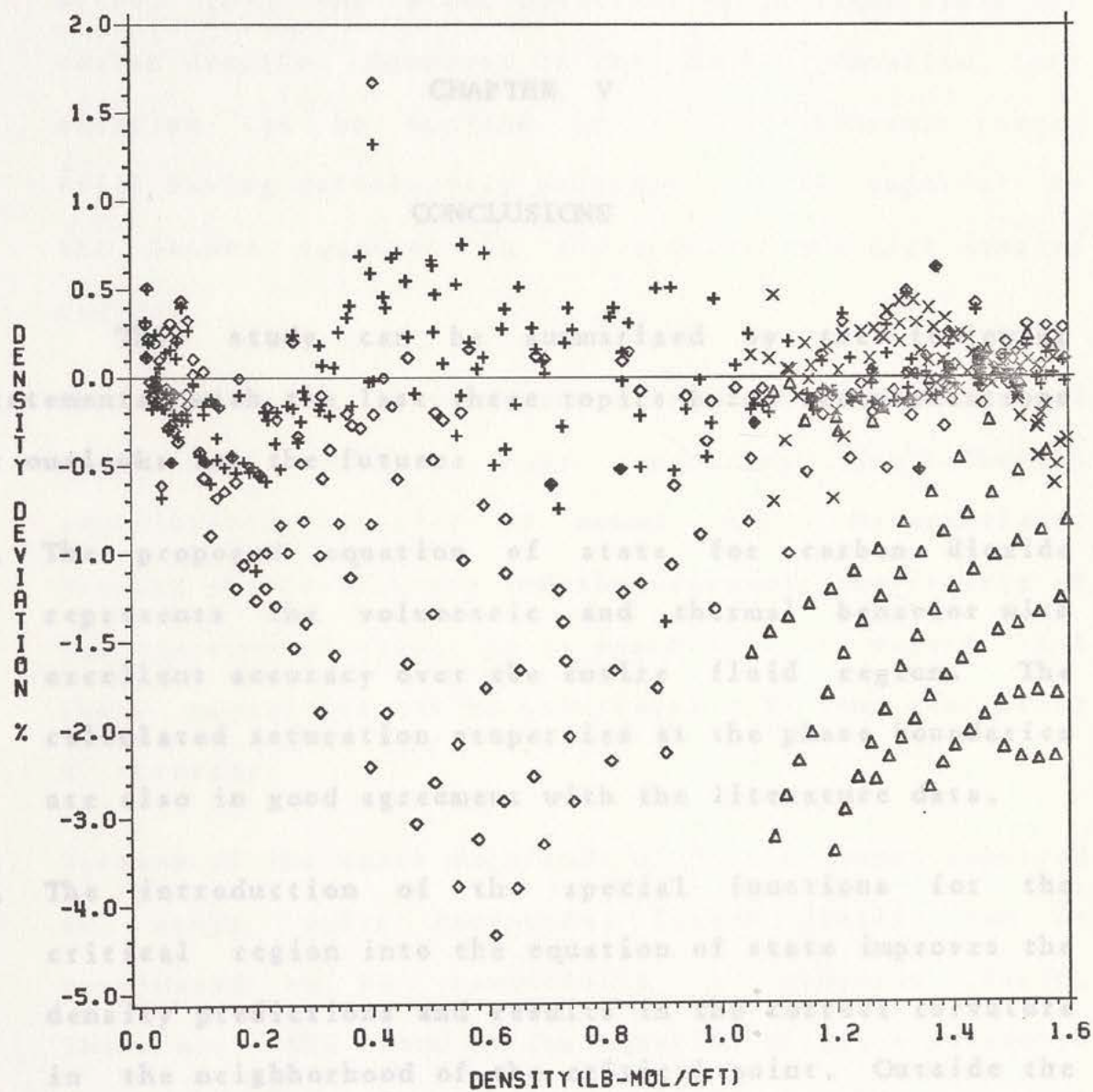
From Table 3 it is clear that Equation (1) can be extended to very high temperature and pressure still having satisfactory precision. In those high temperature and high pressure regions the proposed equation is better than the Bender equation. From the above comprehensive comparisons the capability as well as the excellency of Equation (1) is thoroughly demonstrated.



estimation for the critical and liquid region. Examination of Table 8 indicates that, in general, Equation (1) is superior to the Bender equation in the density predictions, especially in the critical region and high pressure region. It should be emphasized here that Equation (1) was not fitted to any data above  $761.9^{\circ}\text{R}$  ( $150^{\circ}\text{C}$ ). So the prediction results from the data having a temperature range higher than this limit actually include an extrapolation of the equation of state for temperatures beyond the fitted data. In the tested PVT data the highest temperature is about  $2,292^{\circ}\text{R}$  ( $1,000^{\circ}\text{C}$ ) for the data of Kennedy, and the highest pressure is  $58,015$  psia ( $3,947$  atm) for the data of Juza. Figure 25 illustrates the comparison of density deviations for Equation (1) and the Bender equation, where the data of Juza and Kennedy are used. The density deviations from this work are randomly distributed within the range of about  $\pm 0.5\%$ . While the Bender equation has a trend of underprediction with the error between about  $0.5$  and  $-4\%$ .

From Table 8 it is clear that Equation (1) can be extended to very high temperature and pressure still having satisfactory precision. In those high temperature and high pressure regions the proposed equation is better than the Bender equation. From the above comprehensive comparisons the capability as well as the excellency of Equation (1) is thoroughly demonstrated.

FIGURE 25.  
COMPARISON OF DENSITY DEVIATIONS



LEGEND: 1    ◊ ◊ ◊ 1    Δ Δ Δ 2    + + + 3    × × × 4

|                     |   |         |   |      |
|---------------------|---|---------|---|------|
| DATA SOURCE         | : | KENNEDY | ; | JUZA |
| EQUATION --- BENDER | : | 1       | : | 2    |
| --- THIS WORK       | : | 3       | : | 4    |



which are internally consistent.

4. The equation obtained in this work is, in general, better than any other equations of the same class for carbon dioxide. Compared to the Bender equation, the

## CHAPTER V

equation can be applied to a higher pressure range, still having satisfactory accuracy. It is superior to

## CONCLUSIONS

the Bender equation in the critical and high density region.

This study can be summarized by the following statements with the last three topics being recommendations or outlooks for the future:

1. The proposed equation of state for carbon dioxide represents the volumetric and thermal behavior with excellent accuracy over the entire fluid region. The calculated saturation properties at the phase boundaries are also in good agreement with the literature data.

2. The introduction of the special functions for the critical region into the equation of state improves the density predictions and results in the correct curvature in the neighborhood of the critical point. Outside the critical region, the correction terms can be dropped without influencing property-calculation results.

3. The use of a single equation of state for a wide range of conditions produces the thermodynamic properties

which are internally consistent.

4. The equation obtained in this work is, in general, better than any other equations of the same class for carbon dioxide. Compared to the Bender equation, the equation can be applied to a higher pressure range, still having satisfactory accuracy. It is superior to the Bender equation in the critical and high density region.
5. The equation of state was not fitted to other derived properties, such as heat capacities, Joule-Thomson coefficients, velocity of sound, etc. Nevertheless, because of the accuracy and thermodynamic consistency of the equation of state, it is reasonable to expect that those properties can be calculated with some confidence of accuracy.
6. Because of the small magnitude of dipole moment compared to other polar compounds, carbon dioxide can be considered to be essentially a nonpolar fluid. Therefore, the form of the equation of state presented in this study may be readily applied to other nonpolar substances. The correlation method and procedure used here should prove helpful in determining the optimal values of parameters for new materials.
7. The isotherms in the critical region exhibit rapid



changes in their first and second derivatives. This behavior causes great difficulty in a single analytic equation of state in representing both this critical region and other regions (vapor and liquid). Searching for new equations of state which can accurately describe the volumetric behavior as well as the thermodynamic behavior near the critical point should be a continuing effort in the future.

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|               |  |
|---------------|--|
| Cf            | equation-of-state coefficient (193 to 27)                |
| f             | fugacity   |
| H             | enthalpy   |
| ln            | natural logarithm  |
| P             | pressure   |
| R             | gas constant   |
| S             | entropy  |
| T             | absolute temperature                                     |
| $\Delta T$    | transformed temperature = $1 - T/T_0$                    |
| v             | specific volume  |
| Z             | compressibility factor                                   |
| $\Delta Z$    | compressibility factor difference = $Z_{exp} - Z_{calc}$ |
| $\rho$        | density  |
| $\Delta \rho$ | transformed density = $1 - \rho/\rho_0$                  |

Subscripts

c critical point  
calc calculated  
exp experimental  
r reduced property

NOMENCLATURE

A Helmholtz free energy  
A thru. G constants  
b & c constants  
B2 second virial coefficient  
C<sub>i</sub> equation-of-state coefficient (i=1 to 27)  
f fugacity  
H enthalpy  
ln natural logarithm  
P pressure  
R gas constant  
S entropy  
T absolute temperature  
ΔT transformed temperature =  $1 - T_r$   
v specific volume  
Z compressibility factor  
ΔZ compressibility factor difference =  $Z_{exp} - Z_{calc}$   
ρ density  
Δρ transformed density =  $1 - 1/\rho_r$



APPENDIX A-1

Subscripts

|      |                |  |  |  |
|------|----------------|--|--|--|
| c    | critical point |  |  |  |
| calc | calculated     |  |  |  |
| exp  | experimental   |  |  |  |

|   |                     |                      |         |          |
|---|---------------------|----------------------|---------|----------|
| r | reduced property    | Density (Lb-Mol/CFT) |         |          |
|   |                     | Exp.                 | Calc.   | Dev. (%) |
| R | reference state     | 0.36388              | 0.34467 | 0.5163   |
| s | saturation property | 0.37997              | 0.35001 | 0.7417   |

Superscripts

|   |                  |         |         |         |
|---|------------------|---------|---------|---------|
| L | saturated liquid | 0.47320 | 0.47267 | -0.7274 |
| s | special function | 0.85187 | 0.86386 | 1.6182  |
| V | saturated vapor  | 0.47287 | 0.47381 | 0.2000  |
| o | ideal gas state  | 0.38300 | 0.40822 | -0.6304 |

Characteristic Constants of Carbon Dioxide

|                  |                                  |  |  |  |
|------------------|----------------------------------|--|--|--|
| Molecular weight | M = 44.011                       |  |  |  |
| Gas constant     | R = 10.7335 psia.CFT/(Lb-Mol.°R) |  |  |  |

|                 |                      |         |         |         |
|-----------------|----------------------|---------|---------|---------|
| Critical point: |                      |         |         |         |
| T <sub>c</sub>  | = 547.542 °R         | 0.41327 | 0.41374 | 0.5763  |
| P <sub>c</sub>  | = 1070.668 psia      | 0.34076 | 0.33934 | -0.3031 |
| ρ <sub>c</sub>  | = 0.66386 Lb-Mol/CFT | 0.41239 | 0.41226 | -0.0790 |

APPENDIX A-1

DENSITY CALCULATIONS FOR CARBON DIOXIDE  
IN THE CRITICAL REGION

| No. | Temp.<br>(R) | Pressure<br>(psia) | Density (Lb-Mol/CFT) |         | Dev.<br>(%) |
|-----|--------------|--------------------|----------------------|---------|-------------|
|     |              |                    | Exp.                 | Calc.   |             |
| 1   | 542.163      | 981.475            | 0.36388              | 0.36467 | 0.2165      |
| 2   | 542.163      | 989.266            | 0.37997              | 0.38051 | 0.1415      |
| 3   | 542.163      | 997.483            | 0.40227              | 0.40176 | -0.1262     |
| 4   | 542.163      | 1001.482           | 0.93286              | 0.93912 | 0.6706      |
| 5   | 542.163      | 1008.376           | 0.94424              | 0.94892 | 0.4958      |
| 6   | 542.163      | 1019.445           | 0.95829              | 0.96209 | 0.3965      |
| 7   | 545.542      | 1038.967           | 0.44972              | 0.45037 | 0.1453      |
| 8   | 545.542      | 1041.039           | 0.46046              | 0.46098 | 0.1128      |
| 9   | 545.542      | 1042.465           | 0.47184              | 0.46966 | -0.4614     |
| 10  | 545.542      | 1043.318           | 0.47916              | 0.47567 | -0.7274     |
| 11  | 545.542      | 1044.626           | 0.85187              | 0.86566 | 1.6182      |
| 12  | 545.542      | 1045.876           | 0.86132              | 0.87052 | 1.0684      |
| 13  | 545.542      | 1048.492           | 0.87220              | 0.87928 | 0.8115      |
| 14  | 545.542      | 1050.212           | 0.87831              | 0.88432 | 0.6847      |
| 15  | 546.406      | 1051.241           | 0.47285              | 0.47361 | 0.1600      |
| 16  | 546.406      | 1053.299           | 0.48956              | 0.48805 | -0.3082     |
| 17  | 546.406      | 1054.534           | 0.50300              | 0.49872 | -0.8504     |
| 18  | 546.406      | 1055.960           | 0.82189              | 0.83758 | 1.9091      |
| 19  | 546.406      | 1057.709           | 0.83821              | 0.84760 | 1.1198      |
| 20  | 546.406      | 1061.810           | 0.85826              | 0.86487 | 0.7696      |
| 21  | 547.493      | 1067.690           | 0.51912              | 0.52072 | 0.3078      |
| 22  | 547.493      | 1068.837           | 0.54035              | 0.53765 | -0.4998     |
| 23  | 547.493      | 1069.528           | 0.56090              | 0.55253 | -1.4926     |
| 24  | 547.493      | 1069.837           | 0.57829              | 0.57259 | -0.9860     |
| 25  | 547.493      | 1069.969           | 0.58667              | 0.58329 | -0.5769     |
| 26  | 547.493      | 1070.836           | 0.76469              | 0.78942 | 3.2343      |
| 27  | 547.493      | 1073.129           | 0.80456              | 0.81519 | 1.3212      |
| 28  | 547.493      | 1079.259           | 0.84391              | 0.84918 | 0.6242      |
| 29  | 547.536      | 1025.978           | 0.37429              | 0.37600 | 0.4565      |
| 30  | 547.536      | 1052.014           | 0.43127              | 0.43376 | 0.5762      |
| 31  | 547.536      | 1063.205           | 0.47795              | 0.48061 | 0.5564      |
| 32  | 547.542      | 1015.264           | 0.36076              | 0.35934 | -0.3931     |
| 33  | 547.542      | 1029.768           | 0.38358              | 0.38228 | -0.3396     |
| 34  | 547.542      | 1044.271           | 0.41259              | 0.41226 | -0.0790     |
| 35  | 547.542      | 1058.775           | 0.45523              | 0.45821 | 0.6552      |
| 36  | 547.542      | 1070.668           | 0.66386              | 0.69904 | 5.3000      |
| 37  | 547.542      | 1073.279           | 0.83490              | 0.80913 | -3.0868     |
| 38  | 547.542      | 1087.783           | 0.88051              | 0.87317 | -0.8336     |



APPENDIX A-1  
(continued)

| No. | Temp.<br>(R) | Pressure<br>(psia) | Density (Lb-Mol/CFT) |         | Dev.<br>(%) |
|-----|--------------|--------------------|----------------------|---------|-------------|
|     |              |                    | Exp.                 | Calc.   |             |
| 39  | 547.542      | 1102.287           | 0.90639              | 0.90316 | -0.3568     |
| 40  | 547.542      | 1116.790           | 0.92591              | 0.92410 | -0.1960     |
| 41  | 547.542      | 1131.294           | 0.94127              | 0.94052 | -0.0801     |
| 42  | 547.542      | 1145.798           | 0.95393              | 0.95417 | 0.0247      |
| 43  | 547.542      | 1160.302           | 0.96496              | 0.96592 | 0.0996      |
| 44  | 547.803      | 1071.498           | 0.52439              | 0.52686 | 0.4709      |
| 45  | 547.803      | 1073.335           | 0.56301              | 0.56362 | 0.1090      |
| 46  | 547.803      | 1073.908           | 0.59360              | 0.60010 | 1.0957      |
| 47  | 547.803      | 1074.085           | 0.61738              | 0.62173 | 0.7045      |
| 48  | 547.803      | 1074.247           | 0.63903              | 0.64461 | 0.8733      |
| 49  | 547.803      | 1074.349           | 0.66525              | 0.70050 | 5.2992      |
| 50  | 547.803      | 1074.482           | 0.69534              | 0.73210 | 5.2861      |
| 51  | 547.803      | 1074.732           | 0.72666              | 0.75482 | 3.8756      |
| 52  | 547.803      | 1075.614           | 0.76351              | 0.78097 | 2.2873      |
| 53  | 547.803      | 1078.171           | 0.80271              | 0.81049 | 0.9691      |
| 54  | 548.046      | 1074.158           | 0.52456              | 0.52724 | 0.5101      |
| 55  | 548.046      | 1076.143           | 0.56270              | 0.56320 | 0.0896      |
| 56  | 548.046      | 1076.922           | 0.59352              | 0.59761 | 0.6883      |
| 57  | 548.046      | 1077.231           | 0.61777              | 0.62089 | 0.5053      |
| 58  | 548.046      | 1077.422           | 0.63906              | 0.63719 | -0.2922     |
| 59  | 548.046      | 1077.613           | 0.66528              | 0.65757 | -1.1590     |
| 60  | 548.046      | 1077.789           | 0.69511              | 0.66168 | -4.8088     |
| 61  | 548.046      | 1078.201           | 0.72756              | 0.72772 | 0.0222      |
| 62  | 548.046      | 1079.362           | 0.76418              | 0.77308 | 1.1646      |
| 63  | 548.046      | 1082.243           | 0.80288              | 0.80811 | 0.6520      |
| 64  | 548.411      | 1073.747           | 0.48819              | 0.49284 | 0.9525      |
| 65  | 548.411      | 1077.980           | 0.52321              | 0.52576 | 0.4881      |
| 66  | 548.411      | 1080.523           | 0.56407              | 0.56476 | 0.1226      |
| 67  | 548.411      | 1081.699           | 0.60667              | 0.60565 | -0.1673     |
| 68  | 548.411      | 1082.449           | 0.66096              | 0.64543 | -2.3498     |
| 69  | 548.411      | 1083.405           | 0.72683              | 0.70610 | -2.8518     |
| 70  | 548.411      | 1084.698           | 0.76115              | 0.75949 | -0.2175     |
| 71  | 548.411      | 1087.682           | 0.79834              | 0.79943 | 0.1371      |
| 72  | 548.411      | 1101.750           | 0.86300              | 0.86315 | 0.0178      |
| 73  | 549.367      | 1072.424           | 0.44304              | 0.44766 | 1.0433      |
| 74  | 549.367      | 1079.818           | 0.46991              | 0.47539 | 1.1655      |
| 75  | 549.367      | 1085.507           | 0.50016              | 0.50554 | 1.0759      |
| 76  | 549.367      | 1089.946           | 0.53729              | 0.54181 | 0.8417      |
| 77  | 549.367      | 1093.107           | 0.58454              | 0.58694 | 0.4098      |
| 78  | 549.367      | 1094.827           | 0.62986              | 0.62552 | -0.6888     |
| 79  | 549.367      | 1096.414           | 0.68939              | 0.67502 | -2.0845     |



APPENDIX A-1  
(continued)

VAPOR PRESSURE CALCULATIONS FOR CARBON DIOXIDE

| No. | Temp.<br>(R) | Pressure<br>(psia) | Density (Lb-Mol/CFT) |         | Dev.<br>(%) |
|-----|--------------|--------------------|----------------------|---------|-------------|
|     |              |                    | Exp.                 | Calc.   |             |
| 80  | 549.367      | 1099.663           | 0.75658              | 0.75232 | -0.5631     |
| 81  | 549.367      | 1106.454           | 0.81194              | 0.81121 | -0.0905     |
| 82  | 549.367      | 1120.375           | 0.86112              | 0.86124 | 0.0143      |
| 83  | 549.405      | 1039.510           | 0.37429              | 0.37595 | 0.4442      |
| 84  | 549.405      | 1068.324           | 0.43127              | 0.43447 | 0.7416      |
| 85  | 554.168      | 1072.644           | 0.37271              | 0.37456 | 0.4966      |
| 86  | 554.168      | 1094.547           | 0.40401              | 0.40692 | 0.7207      |
| 87  | 554.168      | 1112.643           | 0.43752              | 0.44208 | 1.0427      |
| 88  | 554.168      | 1129.813           | 0.48208              | 0.48871 | 1.3762      |
| 89  | 554.168      | 1142.572           | 0.53137              | 0.53949 | 1.5286      |
| 90  | 554.168      | 1152.774           | 0.59113              | 0.59682 | 0.9629      |
| 91  | 554.168      | 1162.270           | 0.66460              | 0.66241 | -0.3295     |
| 92  | 554.168      | 1171.458           | 0.72854              | 0.72174 | -0.9336     |
| 93  | 554.168      | 1190.435           | 0.80585              | 0.80122 | -0.5745     |
| 94  | 554.168      | 1227.215           | 0.89405              | 0.87538 | -2.0884     |
| 95  | 563.826      | 1206.885           | 0.45468              | 0.45894 | 0.9359      |
| 96  | 563.826      | 1226.083           | 0.48774              | 0.49314 | 1.1079      |
| 97  | 563.826      | 1245.281           | 0.52720              | 0.53358 | 1.2104      |
| 98  | 563.826      | 1262.598           | 0.56926              | 0.57538 | 1.0749      |
| 99  | 563.826      | 1280.282           | 0.61744              | 0.62149 | 0.6561      |
| 100 | 563.826      | 1299.186           | 0.67007              | 0.67077 | 0.1042      |
| 101 | 563.826      | 1327.675           | 0.73900              | 0.73627 | -0.3690     |
| 102 | 563.826      | 1377.831           | 0.82086              | 0.81834 | -0.3067     |
| 103 | 563.826      | 1447.171           | 0.88810              | 0.88732 | -0.0874     |
| 104 | 563.859      | 1141.908           | 0.37429              | 0.37556 | 0.3388      |
| 105 | 563.859      | 1191.031           | 0.43127              | 0.43429 | 0.6999      |
| 106 | 563.859      | 1220.822           | 0.47795              | 0.48260 | 0.9739      |
| 107 | 563.859      | 1267.096           | 0.57898              | 0.58566 | 1.1535      |
| 108 | 563.859      | 1287.529           | 0.63574              | 0.63947 | 0.5869      |
| 109 | 563.859      | 1309.182           | 0.69400              | 0.69421 | 0.0308      |
| 110 | 563.859      | 1334.290           | 0.75088              | 0.74839 | -0.3316     |
| 111 | 563.859      | 1368.188           | 0.80779              | 0.80454 | -0.4027     |
| 112 | 563.859      | 1419.770           | 0.86541              | 0.86344 | -0.2278     |
| 113 | 563.859      | 1500.635           | 0.92362              | 0.92291 | -0.0766     |

Average Absolute Deviation (%) = 0.9109

\*\* Data Source : Michels et al. (1937, 1958)

\*\* Data Source : Michels et al. (1935a, 1935b, 1937)



APPENDIX A-2

VAPOR PRESSURE CALCULATIONS FOR CARBON DIOXIDE

| No. | Temp.<br>(R) | Vapor Pressure (psia) |          | Devaition<br>(%) |
|-----|--------------|-----------------------|----------|------------------|
|     |              | Exp.                  | Calc.    |                  |
| 1   | 390.803      | 76.938                | 76.835   | -0.1334          |
| 2   | 391.777      | 78.760                | 78.658   | -0.1290          |
| 3   | 392.854      | 80.784                | 80.712   | -0.0897          |
| 4   | 393.966      | 82.952                | 82.873   | -0.0952          |
| 5   | 397.179      | 89.413                | 89.362   | -0.0575          |
| 6   | 409.107      | 116.731               | 116.796  | 0.0558           |
| 7   | 421.040      | 149.896               | 150.030  | 0.0895           |
| 8   | 434.966      | 196.862               | 197.069  | 0.1052           |
| 9   | 444.429      | 234.465               | 234.666  | 0.0859           |
| 10  | 453.553      | 275.507               | 275.645  | 0.0503           |
| 11  | 457.032      | 292.457               | 292.569  | 0.0381           |
| 12  | 469.422      | 359.033               | 359.054  | 0.0057           |
| 13  | 481.943      | 436.972               | 436.855  | -0.0267          |
| 14  | 488.651      | 483.468               | 483.293  | -0.0363          |
| 15  | 490.282      | 495.302               | 495.113  | -0.0381          |
| 16  | 491.697      | 505.746               | 505.539  | -0.0409          |
| 17  | 493.535      | 519.571               | 519.324  | -0.0475          |
| 18  | 495.308      | 533.140               | 532.883  | -0.0483          |
| 19  | 497.097      | 547.163               | 546.828  | -0.0612          |
| 20  | 496.805      | 543.856               | 544.532  | 0.1243           |
| 21  | 511.149      | 665.337               | 666.045  | 0.1065           |
| 22  | 527.443      | 827.140               | 827.934  | 0.0960           |
| 23  | 536.796      | 932.803               | 934.076  | 0.1365           |
| 24  | 537.206      | 937.728               | 938.973  | 0.1328           |
| 25  | 542.163      | 999.850               | 1000.111 | 0.0261           |
| 26  | 545.542      | 1043.729              | 1043.859 | 0.0124           |
| 27  | 546.406      | 1055.166              | 1055.301 | 0.0128           |
| 28  | 547.493      | 1070.116              | 1069.992 | -0.0116          |
| 29  | 547.542      | 1070.604              | 1070.744 | 0.0131           |

Average Absolute Deviation (%) = 0.0657

\*\* Data Source : Michels et al. (1937, 1950)

APPENDIX A-3

ENTHALPY CALCULATIONS FOR CARBON DIOXIDE

| No. | Temp.<br>(R) | Pressure<br>(psia) | Enthalpy* (Btu/Lb) |         | Dev.<br>(Btu/Lb) |
|-----|--------------|--------------------|--------------------|---------|------------------|
|     |              |                    | Exp.               | Calc.   |                  |
| 1   | 524.67       | 1050.0             | 55.5               | 56.437  | 0.937            |
| 2   | 524.67       | 1071.0             | 55.3               | 56.274  | 0.974            |
| 3   | 524.67       | 1100.0             | 55.0               | 56.058  | 1.058            |
| 4   | 524.67       | 1125.0             | 54.8               | 55.881  | 1.081            |
| 5   | 524.67       | 1150.0             | 54.6               | 55.711  | 1.111            |
| 6   | 524.67       | 1200.0             | 54.2               | 55.390  | 1.190            |
| 7   | 529.67       | 1050.0             | 59.2               | 60.185  | 0.985            |
| 8   | 529.67       | 1071.0             | 58.8               | 59.964  | 1.164            |
| 9   | 529.67       | 1100.0             | 58.6               | 59.675  | 1.075            |
| 10  | 529.67       | 1125.0             | 58.3               | 59.439  | 1.139            |
| 11  | 529.67       | 1150.0             | 58.1               | 59.216  | 1.116            |
| 12  | 529.67       | 1200.0             | 57.6               | 58.800  | 1.200            |
| 13  | 539.67       | 1050.0             | 68.8               | 69.559  | 0.759            |
| 14  | 539.67       | 1071.0             | 68.3               | 69.010  | 0.710            |
| 15  | 539.67       | 1100.0             | 67.8               | 68.343  | 0.543            |
| 16  | 539.67       | 1125.0             | 67.2               | 67.838  | 0.638            |
| 17  | 539.67       | 1150.0             | 66.7               | 67.379  | 0.679            |
| 18  | 539.67       | 1200.0             | 65.7               | 66.571  | 0.871            |
| 19  | 544.67       | 1050.0             | 76.9               | 77.753  | 0.853            |
| 20  | 544.67       | 1071.0             | 75.0               | 76.171  | 1.171            |
| 21  | 544.67       | 1100.0             | 74.1               | 74.661  | 0.561            |
| 22  | 544.67       | 1125.0             | 73.1               | 73.671  | 0.571            |
| 23  | 544.67       | 1150.0             | 72.2               | 72.855  | 0.655            |
| 24  | 544.67       | 1200.0             | 70.2               | 71.545  | 1.345            |
| 25  | 546.67       | 1050.0             | 112.2              | 112.795 | 0.595            |
| 26  | 546.67       | 1071.0             | 79.8               | 81.462  | 1.662            |
| 27  | 546.67       | 1100.0             | 77.8               | 78.386  | 0.586            |
| 28  | 546.67       | 1125.0             | 76.2               | 76.853  | 0.653            |
| 29  | 546.67       | 1150.0             | 74.9               | 75.708  | 0.808            |
| 30  | 546.67       | 1200.0             | 72.5               | 74.007  | 1.507            |
| 31  | 547.47       | 1050.0             | 115.4              | 115.429 | 0.029            |
| 32  | 547.47       | 1071.0             | 95.8               | 86.232  | -9.568           |
| 33  | 547.47       | 1100.0             | 80.0               | 79.840  | -0.160           |
| 34  | 547.47       | 1125.0             | 77.7               | 77.847  | 0.147            |
| 35  | 547.47       | 1150.0             | 76.1               | 76.477  | 0.377            |
| 36  | 547.47       | 1200.0             | 73.5               | 74.541  | 1.041            |
| 37  | 548.67       | 1050.0             | 118.7              | 118.156 | -0.544           |
| 38  | 548.67       | 1071.0             | 113.6              | 111.981 | -1.619           |
| 39  | 548.67       | 1100.0             | 83.8               | 83.442  | -0.358           |



APPENDIX A-3  
(continued)

| No. | Temp.<br>(R) | Pressure<br>(psia) | Enthalpy* (Btu/Lb) |         | Dev.<br>(Btu/Lb) |
|-----|--------------|--------------------|--------------------|---------|------------------|
|     |              |                    | Exp.               | Calc.   |                  |
| 40  | 548.67       | 1125.0             | 80.2               | 79.868  | -0.332           |
| 41  | 548.67       | 1150.0             | 78.1               | 77.949  | -0.151           |
| 42  | 548.67       | 1200.0             | 75.1               | 75.523  | 0.423            |
| 43  | 549.67       | 1050.0             | 121.2              | 120.144 | -1.056           |
| 44  | 549.67       | 1071.0             | 117.2              | 115.365 | -1.835           |
| 45  | 549.67       | 1100.0             | 98.5               | 96.078  | -2.422           |
| 46  | 549.67       | 1125.0             | 83.1               | 82.901  | -0.199           |
| 47  | 549.67       | 1150.0             | 79.9               | 80.075  | 0.175            |
| 48  | 549.67       | 1200.0             | 76.6               | 77.058  | 0.458            |
| 49  | 550.67       | 1050.0             | 123.2              | 121.885 | -1.315           |
| 50  | 550.67       | 1071.0             | 119.5              | 117.891 | -1.609           |
| 51  | 550.67       | 1100.0             | 109.5              | 108.541 | -0.959           |
| 52  | 550.67       | 1125.0             | 87.5               | 87.950  | 0.450            |
| 53  | 550.67       | 1150.0             | 82.2               | 82.832  | 0.632            |
| 54  | 550.67       | 1200.0             | 78.2               | 78.887  | 0.687            |
| 55  | 551.67       | 1050.0             | 124.8              | 123.367 | -1.433           |
| 56  | 551.67       | 1071.0             | 121.4              | 119.884 | -1.516           |
| 57  | 551.67       | 1100.0             | 114.6              | 112.907 | -1.693           |
| 58  | 551.67       | 1125.0             | 100.7              | 99.375  | -1.325           |
| 59  | 551.67       | 1150.0             | 85.1               | 86.424  | 1.324            |
| 60  | 551.67       | 1200.0             | 79.8               | 80.756  | 0.956            |
| 61  | 552.67       | 1050.0             | 126.3              | 124.669 | -1.631           |
| 62  | 552.67       | 1071.0             | 123.2              | 121.551 | -1.649           |
| 63  | 552.67       | 1100.0             | 117.3              | 115.790 | -1.510           |
| 64  | 552.67       | 1125.0             | 109.7              | 107.419 | -2.281           |
| 65  | 552.67       | 1150.0             | 89.7               | 92.261  | 2.561            |
| 66  | 552.67       | 1200.0             | 81.7               | 82.826  | 1.126            |
| 67  | 553.67       | 1050.0             | 127.6              | 125.850 | -1.750           |
| 68  | 553.67       | 1071.0             | 124.9              | 123.024 | -1.876           |
| 69  | 553.67       | 1100.0             | 119.4              | 118.041 | -1.359           |
| 70  | 553.67       | 1125.0             | 112.9              | 111.745 | -1.155           |
| 71  | 553.67       | 1150.0             | 101.1              | 100.594 | -0.506           |
| 72  | 553.67       | 1200.0             | 84.2               | 85.292  | 1.092            |
| 73  | 554.67       | 1050.0             | 128.9              | 126.943 | -1.957           |
| 74  | 554.67       | 1071.0             | 126.2              | 124.330 | -1.870           |
| 75  | 554.67       | 1100.0             | 121.3              | 119.893 | -1.407           |
| 76  | 554.67       | 1125.0             | 115.9              | 114.712 | -1.188           |
| 77  | 554.67       | 1150.0             | 108.1              | 106.778 | -1.322           |
| 78  | 554.67       | 1200.0             | 86.8               | 88.413  | 1.613            |
| 79  | 556.67       | 1050.0             | 131.0              | 128.933 | -2.067           |
| 80  | 556.67       | 1071.0             | 128.4              | 126.640 | -1.760           |

APPENDIX A-3  
(continued)

| No. | Temp.<br>(R) | Pressure<br>(psia) | Enthalpy* (Btu/Lb) |         | Dev.<br>(Btu/Lb) |
|-----|--------------|--------------------|--------------------|---------|------------------|
|     |              |                    | Exp.               | Calc.   |                  |
| 81  | 556.67       | 1100.0             | 124.4              | 122.943 | -1.457           |
| 82  | 556.67       | 1125.0             | 119.8              | 119.003 | -0.797           |
| 83  | 556.67       | 1150.0             | 114.3              | 113.836 | -0.464           |
| 84  | 556.67       | 1200.0             | 97.1               | 97.493  | 0.393            |
| 85  | 559.67       | 1050.0             | 133.9              | 131.536 | -2.364           |
| 86  | 559.67       | 1071.0             | 131.3              | 129.590 | -1.710           |
| 87  | 559.67       | 1100.0             | 128.0              | 126.556 | -1.444           |
| 88  | 559.67       | 1125.0             | 124.3              | 123.525 | -0.775           |
| 89  | 559.67       | 1150.0             | 120.7              | 119.948 | -0.752           |
| 90  | 559.67       | 1200.0             | 111.0              | 109.952 | -1.048           |
| 91  | 569.67       | 1050.0             | 141.0              | 138.425 | -2.575           |
| 92  | 569.67       | 1071.0             | 139.2              | 137.040 | -2.160           |
| 93  | 569.67       | 1100.0             | 136.9              | 135.023 | -1.877           |
| 94  | 569.67       | 1125.0             | 134.7              | 133.150 | -1.550           |
| 95  | 569.67       | 1150.0             | 132.4              | 131.131 | -1.269           |
| 96  | 569.67       | 1200.0             | 126.6              | 126.575 | -0.025           |
| 97  | 579.67       | 1050.0             | 146.0              | 143.874 | -2.126           |
| 98  | 579.67       | 1071.0             | 144.7              | 142.772 | -1.928           |
| 99  | 579.67       | 1100.0             | 142.6              | 141.186 | -1.414           |
| 100 | 579.67       | 1125.0             | 141.3              | 139.751 | -1.549           |
| 101 | 579.67       | 1150.0             | 139.6              | 138.262 | -1.338           |
| 102 | 579.67       | 1200.0             | 135.1              | 135.037 | -0.063           |

Average Absolute Deviation (Btu/Lb) = 1.213

\* Reference Point : H = 0 For Saturated Liquid at -40 °F.

\*\* Data Source : Koppel and Smith (1960).



## APPENDIX B

### EQUATIONS OF STATE FOR CARBON DIOXIDE

(1) The BWR Equation (Orye, 1969):

$$P = RT\rho + (B_0RT - A_0 - C_0/T^2)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

For temperatures above  $T_0$ ,  $C_0$  is a constant. For temperatures below  $T_0$ ,  $C_0$  becomes temperature dependent and the following equation is used for  $C_0^{\frac{1}{2}}(T)$ :

$$C_0^{\frac{1}{2}}(T) = C_0^{\frac{1}{2}}(T_0) - (Q_1\Theta^2 + Q_2\Theta^3 + Q_3\Theta^4 + Q_4\Theta^5)$$

where  $\Theta = \frac{T - T_0}{T_0}$ ,  $Q_1$  through  $Q_4$  are constants.

(2) The Martin-Hou Equation (1955, 1959):

$$P = \frac{RT}{V - b} + \frac{A_2 + B_2T + C_2\exp(-kT)}{(V - b)^2} + \frac{A_3 + B_3T + C_3\exp(-kT)}{(V - b)^3} + \frac{A_4}{(V - b)^4} + \frac{A_5 + B_5T + C_5\exp(-kT)}{(V - b)^5}$$

(3) The Equation of Khan et al. (1983):

$$\begin{aligned}
 Z = 1 + & \left( A_1 + \frac{A_2}{T^*} + \frac{A_3}{T^{*2}} + \frac{A_4}{T^{*3}} + \frac{A_5}{T^{*5}} \right) \rho^* \\
 & + \left( A_6 + \frac{A_7}{T^*} \right) \rho^{*2} + A_8 \rho^{*3} \\
 & + \left( \frac{A_9}{T^{*3}} + \frac{A_{10}}{T^{*4}} + \frac{A_{11}}{T^{*5}} \right) \rho^{*2} \exp(-A_{16} \rho^{*2}) \\
 & + \left( \frac{A_{12}}{T^{*3}} + \frac{A_{13}}{T^{*4}} + \frac{A_{14}}{T^{*5}} \right) \rho^{*4} \exp(-A_{16} \rho^{*2}) \\
 & + \frac{A_{15}}{T^*} \rho^{*5}
 \end{aligned}$$

where  $T^* = kT/\epsilon$  ;  $\rho^* = \rho v^*$

$\epsilon$  and  $v^*$  are the characteristic energy parameter and characteristic volume, respectively.

All constants except  $A_{16}$  appearing in the above equation can be separated into two parts: isotropic and perturbation parts.

$$A_i = \alpha B_i^{(o)} + (\alpha - 1) B_i^{(p)}$$

where  $\alpha$  is the structure parameter.

For polar fluids, the energy parameter  $\epsilon$  has to be changed to  $\epsilon'$ , which is a function of temperature and another parameter  $K$  as

$$\frac{\epsilon'}{k} = \frac{\epsilon}{k} + \frac{K}{T(v^{*2})}$$



where  $K$  is used to characterize the multipolar and associating effects.

(4) The Bender Equation (1970):

$$\begin{aligned}
 P = \rho T \left\{ R + (n_1 + n_2/T + n_3/T^2 + n_4/T^3 + n_5/T^4) \rho \right. \\
 + (n_6 + n_7/T + n_8/T^2) \rho^2 + (n_9 + n_{10}/T) \rho^3 \\
 + (n_{11} + n_{12}/T) \rho^4 + (n_{13}/T) \rho^5 \\
 + [n_{14}/T^3 + n_{15}/T^4 + n_{16}/T^5 \\
 \left. + (n_{17}/T^3 + n_{18}/T^4 + n_{19}/T^5) \rho^2 \right] \rho^2 \exp(-n_{20} \rho^2) \left. \right\}
 \end{aligned}$$

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