A GENERALIZED VIRIAL EQUATION OF STATE

By

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PREFACE

Methods of deriving virial coefficients are reviewed. Multiple linear regression is used in an attempt to derive a generalized virial equation of state from Pitzer's compressibility factor tabulations. The virial coefficient correlations are derived as functions of reduced temperature and the acentric factor. The virial equation of state is used to calculate various thermodynamic properties, which are compared with tabulated values.

I wish to thank Professor Wayne C. Edmister for his advice and guidance during the course of this project. I appreciate sincerely the help received from the faculty of the School of Chemical Engineering and the Computing Center at Oklahoma State University. Appreciation is expressed to the National Science Foundation for the research assistantship and Oklahoma State University for the institutional support received during the 1962-64 school years.

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CHAPTER I

INTRODUCTION

The engineering fields have long utilized equations of state for predicting fluid behavior and calculating thermodynamic properties for design purposes. A reliable equation of state will eliminate costly and expensive laboratory investigations that would normally be required to obtain the necessary data. The desirable characteristics of an equation of state include simplicity, accuracy and a wide range of application.

One of the earliest equations of state was that of van der Waals, a two-constant equation which attempted to account for the action of intermolecular forces (21). Although the van der Waals equation of state has served many useful purposes, results obtained with it, such as those shown by Opfell, Pings and Sage (16), indicate that it is only an approximation to actual gas behavior. Since the work of van der Waals, over a hundred equations of state have been developed which are applicable for various systems and ranges of operating conditions (5). These equations of state represent some degree of compromise between accuracy and complexity and are based upon an empirical correlation with experimental results. The Beattie-Bridgeman equation of state (1) is a five-constant equation that has been widely used. The reduced form of this equation is valid up to about the critical density (24). More recent developments include the Benedict-Webb-Rubin (2), the Redlich-Kwong (20) and the Martin-Hou (13) equations of state. Edmister (7) reviews these and many other equations of state and discusses their limitations.

In some instances, an equation of state can be expressed as a power series expansion, referred to as a virial equation of state. This form of equation arose from the study of the mechanical behavior of systems of particles by Claussius (14). The virial equation in terms of pressure is sometimes called the Berlin form while the density (reciprocal volume) series expansion is referred to as the Leiden form. Virial coefficients have been postulated to be functions of temperature only (10).

In this work, an attempt was made to derive a generalized virial equation of state in terms of reduced parameters. Pitzer's generalized compressibility factors were selected for study as these values include a third correlating parameter, the acentric factor, to characterize PVT values (12, 17, 18, 19). Objectives were twofold, first to derive generalzied virial coefficients and their correlations, and secondly, to investigate different methods of deriving virial coefficients. Multiple linear regression (22) was used to derive these generalized correlations for the second through the sixth virial coefficients. Generalized values of compressibility factor, fugacity coefficient, and enthalpy were calculated with the virial equation of state and compared with the generalized tabulations of Pitzer (12, 18).

CHAPTER II

DERIVATION OF VIRIAL COEFFICIENTS

Before discussing the correlation of Pitzer's generalized tabulations, previous attempts to derive virial coefficients are reviewed. Included are the alternate procedures considered in this work and the methods followed by other workers in the field. The derivation of a generalized virial equation of state is also given.

Derivation of Generalized Virial Equation of State

The Leiden form of the virial equation of state is given as follows:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \qquad (1)$$

The compressibility factor Z can be expressed as a function of the ideal reduced density ρ_r, defined as ρ/ρ_{ci} where ρ_{ci} is the pseudo-ideal critical density. See Appendix A for nomenclature. The conversion of equation (1) into generalized terms is described below.

The volume (density) term in equation (1) is transformed into a generalized term by the definitions of the compressibility factor, reduced temperature, and reduced pressure:

$$\frac{1}{V} = \frac{P}{ZRT} = \left(\frac{P_c}{RT_c}\right)\left(\frac{P_r}{ZT_r}\right) \qquad (2)$$

Substituting equation (2) into equation (1):

$$Z = 1 + \left(\frac{BP_c}{RT_c}\right)\left(\frac{P_r}{ZT_r}\right) + \left(\frac{CP_c^2}{R^2T_c^2}\right)\left(\frac{P_r}{ZT_r}\right)^2 + \left(\frac{DP_c^3}{R^3T_c^3}\right)\left(\frac{P_r}{ZT_r}\right)^3 + \ldots \quad (3)$$

The generalized term $\left(\frac{P_r}{ZT_r}\right)$ is the ideal reduced density ρ_r.

The coefficients in equation (3) are generalized virial coefficients, which, for convenience, are designated as follows:

$$b = \frac{BP_c}{RT_c} \quad (4)$$

$$c = \frac{CP_c^2}{R^2T_c^2} \quad (5)$$

$$d = \frac{DP_c^3}{R^3T_c^3} \quad (6)$$

Substituting equations (4), (5), and (6) into equation (3) and ρ_r for the quantity $\left(\frac{P_r}{ZT_r}\right)$ yields the generalized virial equation of state:

$$Z = 1 + b\rho_r + c\rho_r^2 + d\rho_r^3 + \ldots \quad (7)$$

Graphical Methods for Deriving Virial Coefficients

A common technique for deriving virial coefficients is to rearrange the virial equation of state, plot the data according to the rearranged form of the virial equation, and obtain the virial coefficients as slopes or intercepts at infinite attenuation (zero pressure).

If equation (7) is rearranged as follows:

$$Z-1 = b\rho_r + c\rho_r^2 + d\rho_r^3 + \ldots \quad (8)$$

the limit of this equation at zero density should yield the second virial coefficient b as a slope.

Stuckey (23) has utilized the following rearrangement of equation (7):

$$Z - 1 - b\rho_r = c\rho_r^2 + d\rho_r^3 + \ldots \qquad (9)$$

to derive values for the generalized third virial coefficient c. Pitzer's generalized compressibility factors were used from both the vapor phase and the two-phase region below the critical isotherm $T_r = 1.00$ (12, 18). The quantity on the left-hand side of equation (9) was calculated using Pitzer's correlation to calculate the second virial coefficient b as a function of the reduced temperature T_r and the acentric factor ω (12, 19). This quantity was plotted against ρ_r^2, and values of the third virial coefficient c were obtained as slopes at zero density. The values for the third virial coefficient were then correlated as a linear function of the acentric factor and as a polynomial function of reduced temperature according to a cubic equation in inverse reduced temperature. The derived correlation yields values of c which agree well with third virial coefficients derived from other PVT data.

Another rearrangement of equation (7) is shown as follows:

$$\frac{Z - 1}{\rho_r} = b + c\rho_r + d\rho_r^2 + \ldots \qquad (10)$$

The limit of equation (10) yields the second virial coefficient b as an intercept as ρ_r approaches zero. Douslin has used this approach to derive virial coefficients for methane and tetrafluoromethane (6).

Virial Coefficients from Two-Phase Compressibility Factors

To expand the temperature range for which virial coefficients could be obtained, the derivation of virial coefficients below the critical isotherm $T_r = 1.00$ was investigated. The problem involved is that PVT data below the critical isotherm can not be represented by a continuous function. A line of constant temperature on a P-V plot is discontinuous as it passes from the liquid phase into the two-phase region and from this phase into the vapor phase. A typical P-V diagram for a single component system is shown in Figure 1. The discontinuities in the isotherm are readily apparent.

An approach which yields a continuous function across the two-phase region can be illustrated by use of van der Waals equation of state. A graphical representation of van der Waals equation is shown in Figure 2. van der Waals equation does not describe actual behavior in the two-phase region, but predicts a hypothetical or metastable region. However, the change in free energy across the two-phase region is zero in either case as indicated by the equality of the integral of the quantity VdP along either path from the saturated liquid to the saturated vapor. This zero change in free energy across the two-phase region forms the basis for deriving virial coefficients below the critical isotherm.

Pitzer's generalized values for saturated liquid and saturated vapor compressibility factors below the critical isotherm were used in this phase of the study (12, 18). Pitzer has tabulated compressibility factors for 25 reduced isotherms

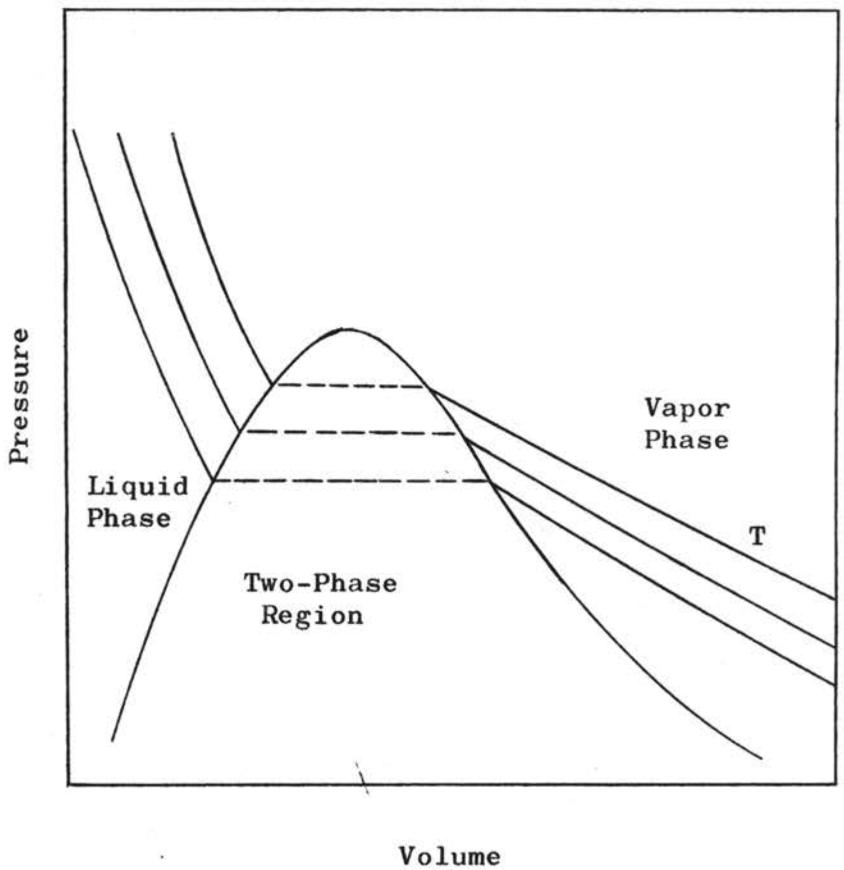


Figure 1

Typical P-V Diagram
For a Single Component System

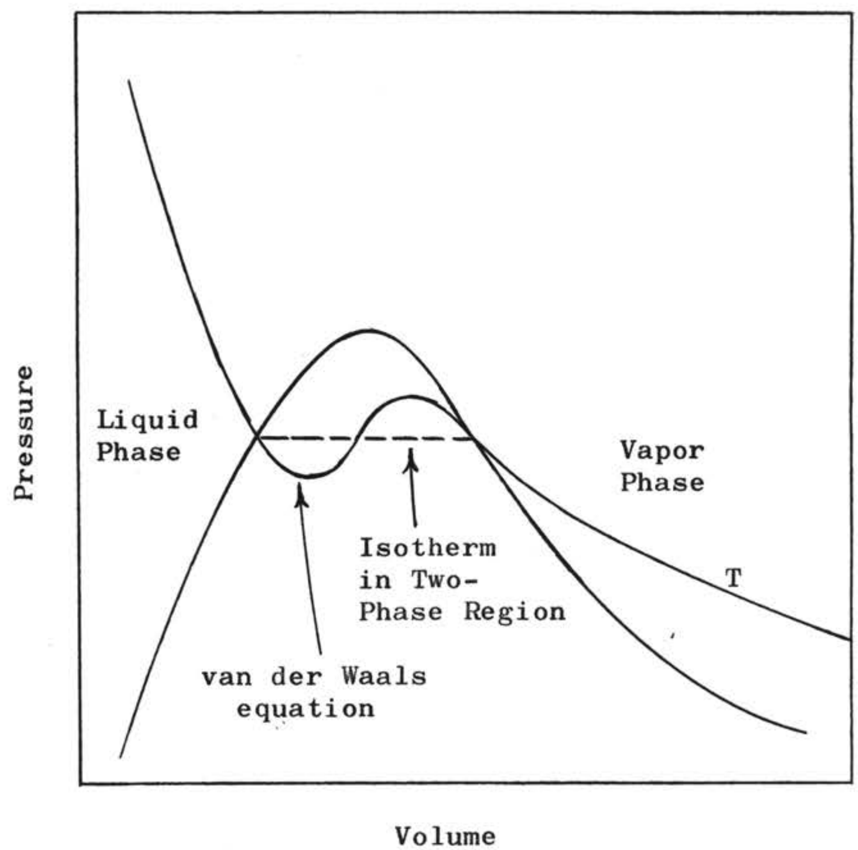


Figure 2

Graphical Representation of
van der Waals Equation

between 0.56 and 0.99.

In addition, Pitzer has also tabulated values of compressibility factor in the pure vapor and pure liquid phases for reduced temperatures of 0.80, 0.85, 0.90, and 0.95 (12, 18). However, only the saturated liquid and saturated vapor compressibility factors are available for the remaining isotherms below unity reduced temperature.

Plots of the compressibility factor Z and the quantity $\frac{Z-1}{\rho_r}$ as functions of ρ_r at a reduced temperature below unity are illustrated in Figures 3 and 4, respectively. The curve across the two-phase region in Figure 3 was obtained by weighting the saturated liquid and saturated vapor compressibility factors. The compressibility factors from this two-phase curve were then used to determine the isotherm in the two-phase region in Figure 4.

In terms of the dimensions used in Figure 1, the change in free energy can be expressed in differential form as:

$$dF = VdP \qquad (11)$$

Also, the change in free energy across the two-phase region for any isotherm, expressed as $\int_{BP}^{DP} VdP$, is zero. Therefore, conversion of equation (11) into the generalized terms used in Figure 4 and integration across the two-phase region yields the following expression:

$$\frac{1}{RT}\int_1^2 VdP = \int_1^2 \left(\frac{Z-1}{\rho_r}\right) d\rho_r + \ln\left(\frac{\rho_{r_2}}{\rho_{r_1}}\right) + (Z_2 - Z_1) = 0 \qquad (12)$$

The derivation of equation (12) is shown in Appendix E. The pos-

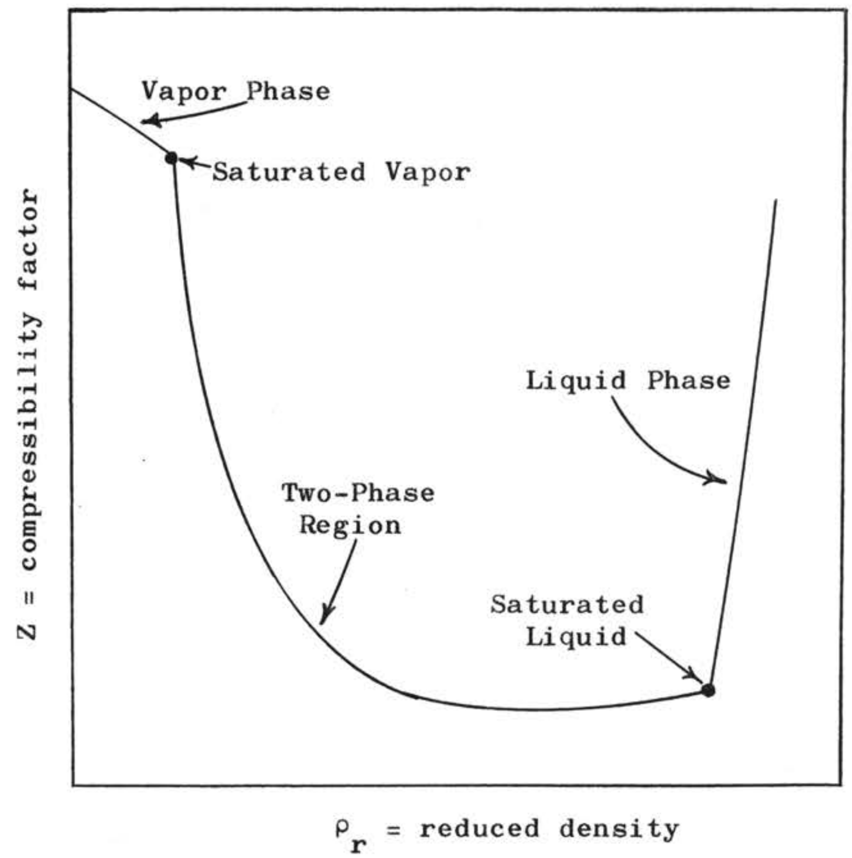


Figure 3

Compressibility Factor Representation Below the Critical Isotherm

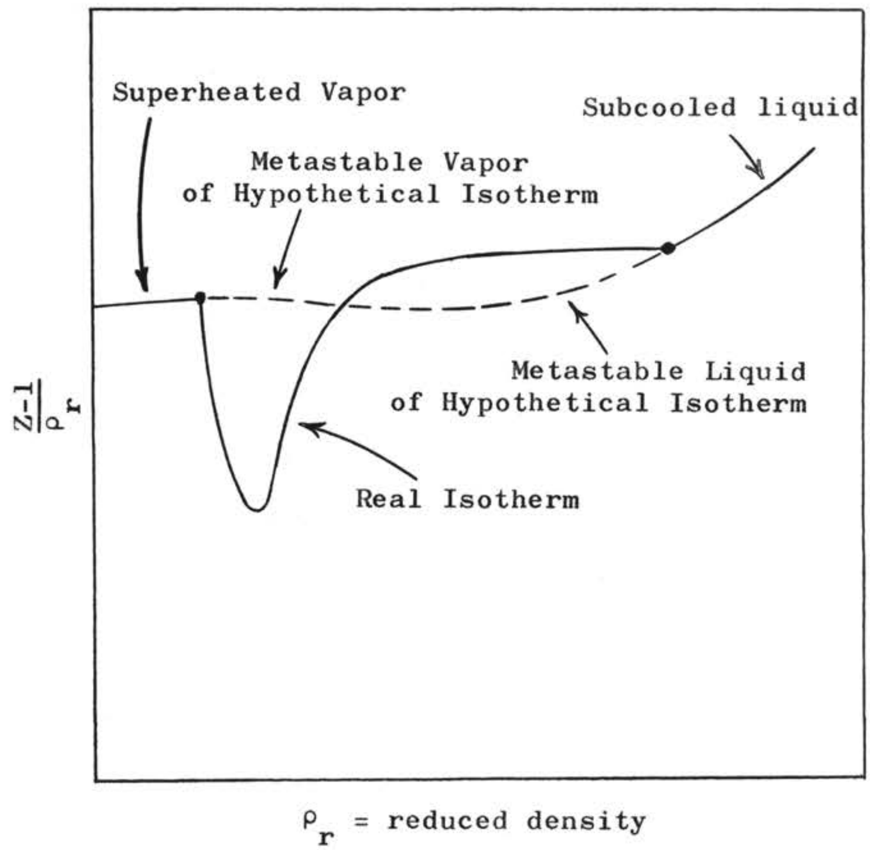


Figure 4

Representation of the Generalized Quantity $\frac{Z-1}{\rho_r}$
Below the Critical Isotherm

ulate was made that a smooth function can be drawn across the two-phase region on Figure 4 if the $\int_1^2 \left(\frac{Z-1}{\rho_r}\right) d\rho_r$ is held constant. Using this technique, a smooth function between $\frac{Z-1}{\rho_r}$ and ρ_r can be obtained, and the second virial coefficient b can be derived as an intercept at zero density.

Although this approach appears theoretically sound, practical application was unsuccessful. For those isotherms for which only the saturated liquid and saturated vapor compressibiltiy factors were available, several curves satisfying equation (12) could be constructed, thereby rendering the derivation of the second virial coefficient b somewhat arbitrary. In addition, a study of the saturated phase compressibility factors led to the belief that the saturated liquid values were somewhat questionable. This approach for deriving virial coefficients was abandoned.

Multiple Linear Regression

Multiple linear regression or least-mean-square regression has been used widely to represent data according to a variety of equation models and is the technique used in this work. A discussion of the mathematics involved in multiple linear regression is given in Appendix D.

Edmister previously proposed a method for deriving virial coefficient using multiple linear regression (8). Basically, the technique involved a surface-fit of Pitzer's generalized tabulations of compressibility factors. The equations involved in the surface-fit are described below. The compressibility factors were to be fitted to the following equation:

$$Z - 1 - b\rho_r = c\rho_r^2 + d\rho_r^3 + e\rho_r^4 + f\rho_r^5 + g\rho_r^6 \qquad (13)$$

Equation (13) is identical to equation (9) with the exception of the additional terms in the power series. The size of equation (13) was arbitrarily established. Pitzer's second virial coefficient correlation was to be used to calculate b as discussed previously. The generated virial coefficients would then be correlated as linear functions of the acentric factor. The resulting coefficients would in turn be correlated as a polynominal function of reduced temperature according to a cubic equation in inverse reduced temperature. The size of the polynomial in reduced temperature was arbitrarily established. The entire surface-fit would generate a total of forty coefficients describing correlations for the third through the seventh virial coefficients. This approach could not be accomplished due to limitations on existing computer facilities.

Multiple linear regression was used in this work to derive virial coefficients using equation (10) for the regression model. Other regression models were tested, and equation (10) was selected based on the accuracy with which the derived virial coefficients could reproduce compressibility factors when used in the virial equation of state. The derived virial coefficients were then cross-correlated with reduced temperature and the acentric factor. Model selection, correlation details and analysis of results are discussed later.

Pressure Residual Concept

Edmister is currently developing a pressure residual concept aimed at deriving virial coefficients (9). This approach requires an equation of state. The equation selection is the Redlich-Kwong equation of state, a two-constant equation based only on the critical temperature and critical pressure. Basically, the quantity defined as a pressure residual is a correction to the pressure as calculated via the Redlich-Kwong equation to account for the effect of the acentric factor.

The Redlich-Kwong equation of state is normally written as a pressure-explicit equation as shown below:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \qquad (14)$$

The constants a and b are defined as follows:

$$a = 0.4278 \frac{R^2 T_c^{2.5}}{P_c} \qquad (15)$$

$$b = 0.0867 \frac{RT_c}{P_c} \qquad (16)$$

Conversion of equation (14) into generalized terms with subsequent use of equations (15) and (16) yields the following equation:

$$P_r = \left(\frac{T_r}{V_{ri}-0.0867}\right) - \left(\frac{0.4278}{T_r^{0.5} V_{ri}(V_{ri}+0.0867)}\right) \qquad (17)$$

The derivation of equation (17) is given in Appendix F. The term V_{ri} is the ideal reduced volume and is equal to the inverse of ρ_r. The pressure residual is calculated as follows:

$$R_p = (P_r)_{RK} - (P_r)_{Pitzer} \qquad (18)$$

where $(P_r)_{RK}$ is the reduced pressure calculated via equation (17) and $(P_r)_{Pitzer}$ is the corresponding value of reduced pressure in Pitzer's compressibility factor tabulations for which $(P_r)_{RK}$ was calculated. For a given reduced pressure and reduced temperature in Pitzer's tabulations, the ideal reduced volume V_r is calculated, $(P_r)_{RK}$ is calculated and the pressure residual is calculated via equation (18).

The pressure residual term was calculated for all reduced temperatures in Pitzer's tabulations in the vapor phase, each tabulated reduced pressure for which deviation compressibility factor values are tabulated and values for the acentric factor of 0.0, 0.1, 0.2, 0.3 and 0.4. This phase of the pressure residual approach has been completed. Efforts are currently being made to express the pressure residual in virial form and thereby derive virial coefficients. An examination of one isotherm indicates this pressure residual can not be correlated with density and reduced temperature in a convenient manner.

CHAPTER III

CORRELATION CALCULATIONS

Tabulations Used in Calculations

Pitzer developed a tabulation of generalized compressibility factors which includes a third correlating parameter, the acentric factor ω, in addition to the reduced temperature T_r and reduced pressure P_r to characterize PVT values (12, 17, 18, 19). The acentric factor is defined in terms of the reduced vapor pressure at $T_r = 0.7$ as shown in equation (19):

$$\omega = -(\log P_r^\circ + 1.00)_{T_r = 0.7} \qquad (19)$$

The acentric factor is used as a measure of the deviation of a coumpound from simple fluid behavior. Pitzer developed the generalized compressibility factors using data for sixteen compounds: argon, krypton, xenon, methane, nitrogen, hydrogen sulfide, ethane, propane, neopentane, n-butane, benzene, carbon dioxide, n-pentane, n-heptane and two polar compounds, water and ammonia. These compounds cover an acentric factor range of -0.02 to 0.352. Pitzer then expressed the compressibility factor as the sum of two terms, a term for simple fluid behavior and a deviation term. This correlation is a linear function of ω as shown below:

$$Z = Z^{(o)} + \omega Z^{(')} \qquad (20)$$

Pitzer's tabulations cover a reduced pressure range of 0.2-9.0

and a reduced temperature range of 0.80-4.00. These values include 18 isotherms between the reduced temperature limits of 1.00 and 4.00. Values of acentric factor used for correlation are 0.0, 0.1, 0.2, 0.3, and 0.4 and were selected to cover the range over which the compressibility factor tabulations were developed. Pitzer's values of $Z^{(o)}$ and $Z^{(')}$ are tabulated in Appendix B.

Selection of a Regression Model

Equations (8) and (10) were tested for their applicability for deriving virial coefficients. In addition, the following equation was also investigated:

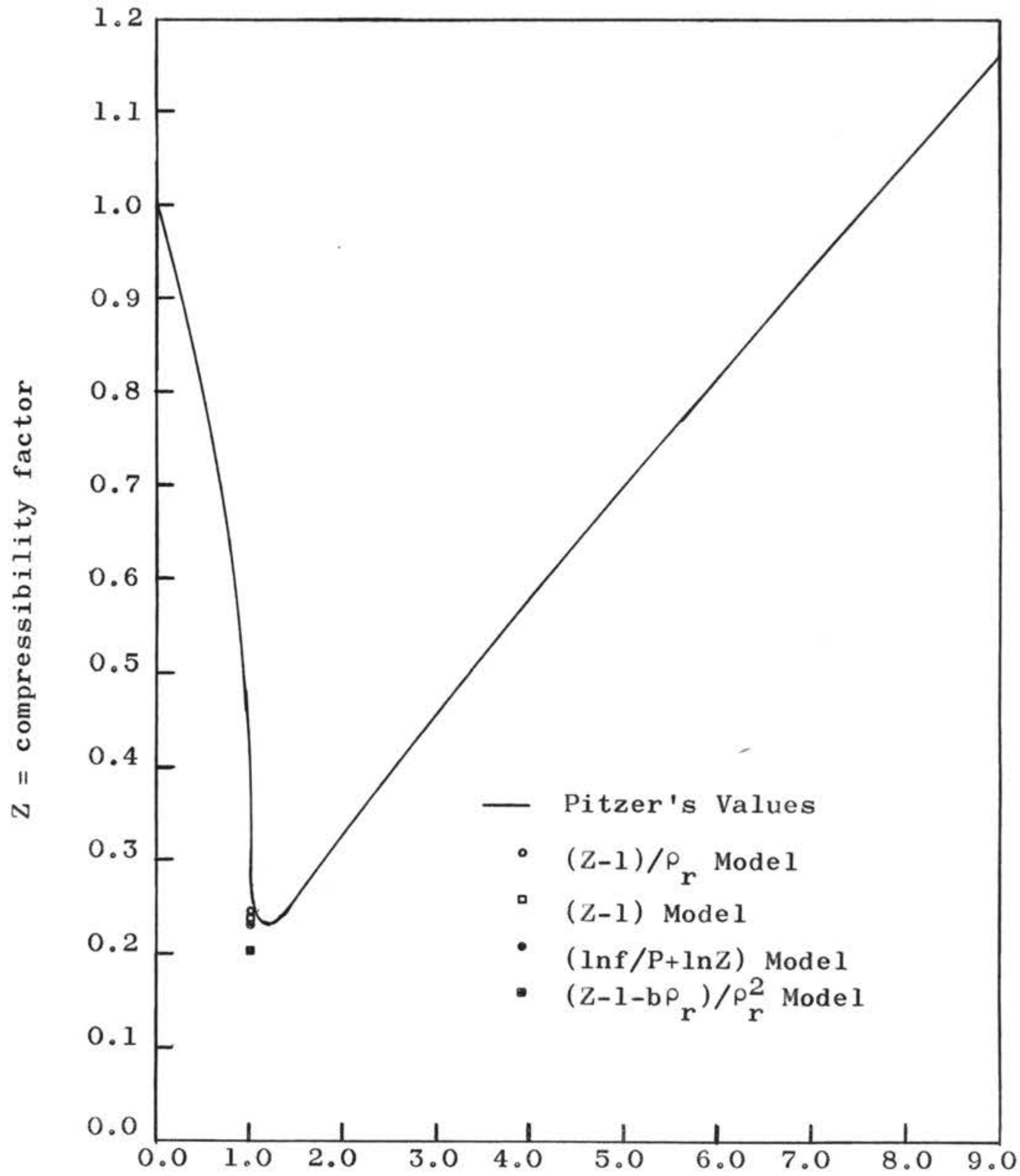
$$(\ln f/P + \ln Z) = 2b\rho_r + 3/2c\rho_r^2 + 4/3d\rho_r^3 + \ldots \qquad (21)$$

Pitzer developed a tabulation of generalized fugacity coefficients which were used in generating the necessary values for testing the above model (12). The fugacity coefficients were developed as functions of the acentric factor and are tabulated as a simple fluid term and a deviation term. The derivation of equation (21) is given in Appendix C.

Using multiple linear regression, coefficients were generated for each model at a reduced temperature of 1.00 and acentric factors of 0.0 and 0.4. The reduced temperature of 1.00 was selected due to the shape of the compressibility factor curve at this temperature. This isotherm shows a greater inflection near the critical pressure as compared to the higher isotherms. This inflection becomes less pronounced with increasing reduced temperature. If a regression model can generate coefficients for the critical isotherm which, when substituted into the virial equation of state, can predict compressibility factors accurately, then the model should be acceptable for the higher isotherms. The acentric factors of 0.0 and 0.4 were selected as these values are the limits of the acentric factor range being used for correlation. The standard error of estimate was used to determine the order of the polynomial required to represent the generalized quantities accurately. A discussion of the standard error of estimate is included with the discussion on multiple linear regression in Appendix D. The computer program used for multiple linear regression was developed by Bush and Short (3).

An analysis of the polynomial size indicated a fourth-order polynomial for equation (10) and a fifth-order polynomial for equations (8) and (21) were the best equations based on the standard error of estimate. These specified equations yield the second through the sixth virial coefficients. The generated coefficients were substituted into the virial equation of state and compressibility factors calculated. These results are compared with Pitzer's values at acentric factors of 0.0 and 0.4 in Figure 5 and 6, respectively. Both compressibility factor curves are reproduced with a high degree of accuracy by the coefficients of all three models except at the critical point. The model selection appears quite arbitrary and could be based only upon the critical point, which indicated equation (10) to be the best model.

Before making a final selection among the models, a modified "slope-intercept" technqiue was tested. The values generated for



P_r = reduced pressure

Figure 5

Comparison of Regression Models
at T_r = 0.0 and ω = 0.0

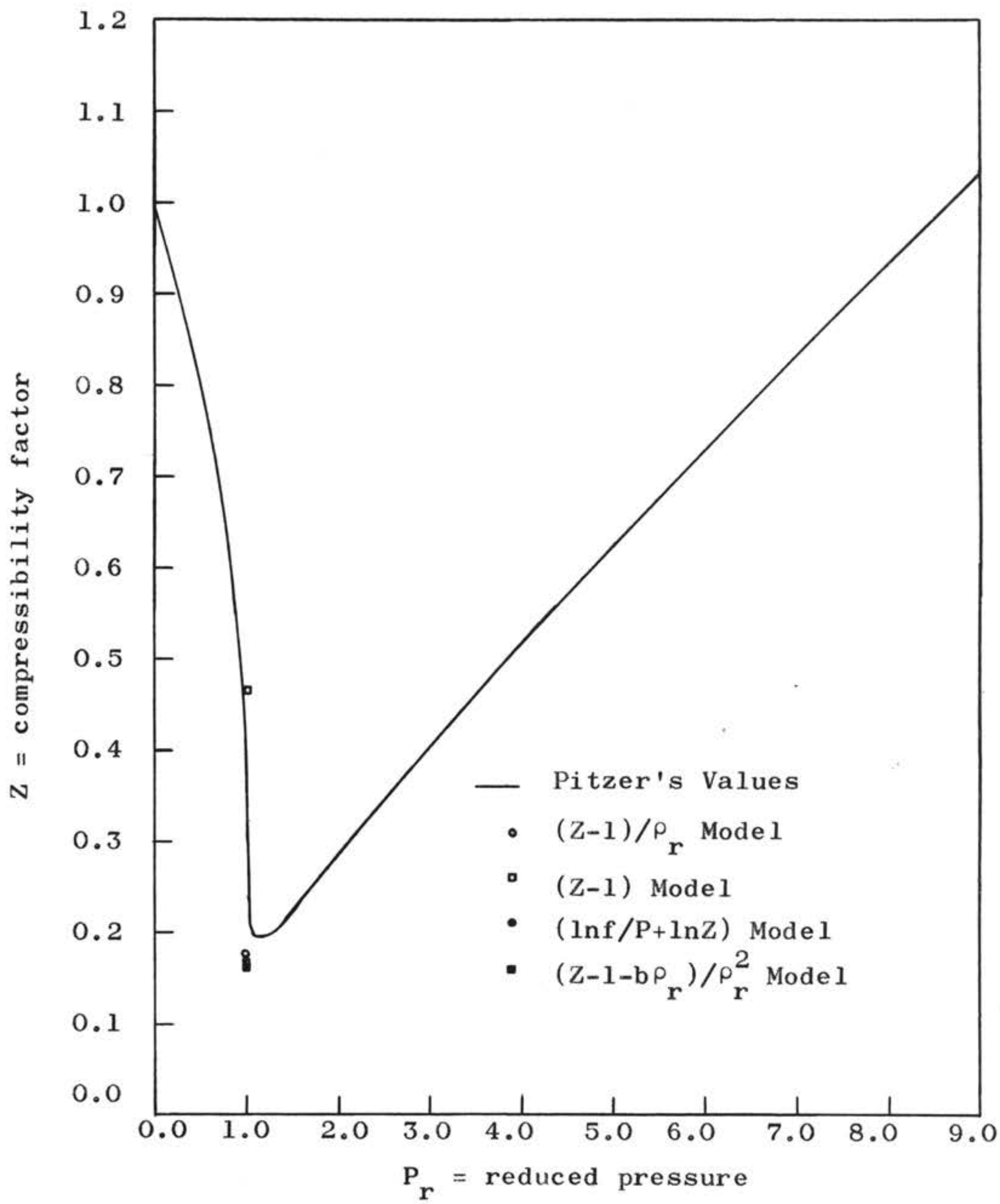


Figure 6

Comparison of Regression Models
at T_r = 1.00 and ω = 0.4

the second virial coefficient b from equation (10) were used to test the following model:

$$\frac{Z - 1 - b\rho_r}{\rho_r^2} = c + d\rho_r + \ldots \tag{22}$$

The generalized quantities for equation (22) were regressed at the reduced isotherm 1.00 and acentric factors of 0.0 and 0.4. The coefficients generated with this model, the third through the sixth virial coefficients, together with the values for b from equation (10) were used in the virial equation of state to calculate compressibility factors. These results are also shown in Figures 5 and 6. Again the compressibility factor curves were reproduced accurately except at the critical point. However, based on the results at the critical point, equation (10) remains the best model. This model was chosen to derive virial coefficients.

Correlation and Analysis of Generalized Quantities

Pitzer's compressibility factor values were regressed over the reduced temperature range 1.00-4.00 and the acentric factor range 0.0-0.4 using equation (10) truncated as a fourth-order polynomial as shown below:

$$\frac{Z - 1}{\rho_r} = b + c\rho_r + d\rho_r^2 + e\rho_r^3 + f\rho_r^4 \tag{23}$$

A tabulation of the generalized quantity $(Z-1)/\rho_r$ for each value of reduced pressure, reduced temperature and acentric factor used in the correlation is shown in Appendix C.

The generalized quantity $(Z-1)/\rho_r$ was recalculated for each isotherm and each value of the acentric factor using the virial coefficients derived for each specific isotherm. A comparison of the regression curve and the generalized values used in regression is shown for a few selected isotherms at an acentric factor of 0.0 in Figures 7 and 8. These figures show that the regression curves reproduce the generalized values used in regression with a high degree of accuracy. Even at the lower reduced temperatures where a large gap exists between the generalized values around the critical pressure $P_r = 1.00$, a good regression curve was obtained.

The next step was to correlate the virial coefficients with temperature. A polynomial function in terms of inverse reduced temperature was selected as a regression model. Again the standard error of estimate was used to determine the size of the polynomial for each virial coefficient. This testing of the polynomial size indicated a fourth-order polynomial for the second and third virial coefficients and a cubic equation for the fourth, fifth and sixth virial coefficients were the best regression models. As 18 isotherms were regressed according to equation (23) for each value of the acentric factor, 18 observed values for each virial coefficient were available for correlation with temperature for each acentric factor. The virial coefficients were regressed with temperature according to the selected polynomial functions. This step involved a total of 25 regressions to encompass the correlation of five virial coefficients at the five values of acentric factor. The virial coefficients were recalculated using the coefficients derived from these regres-

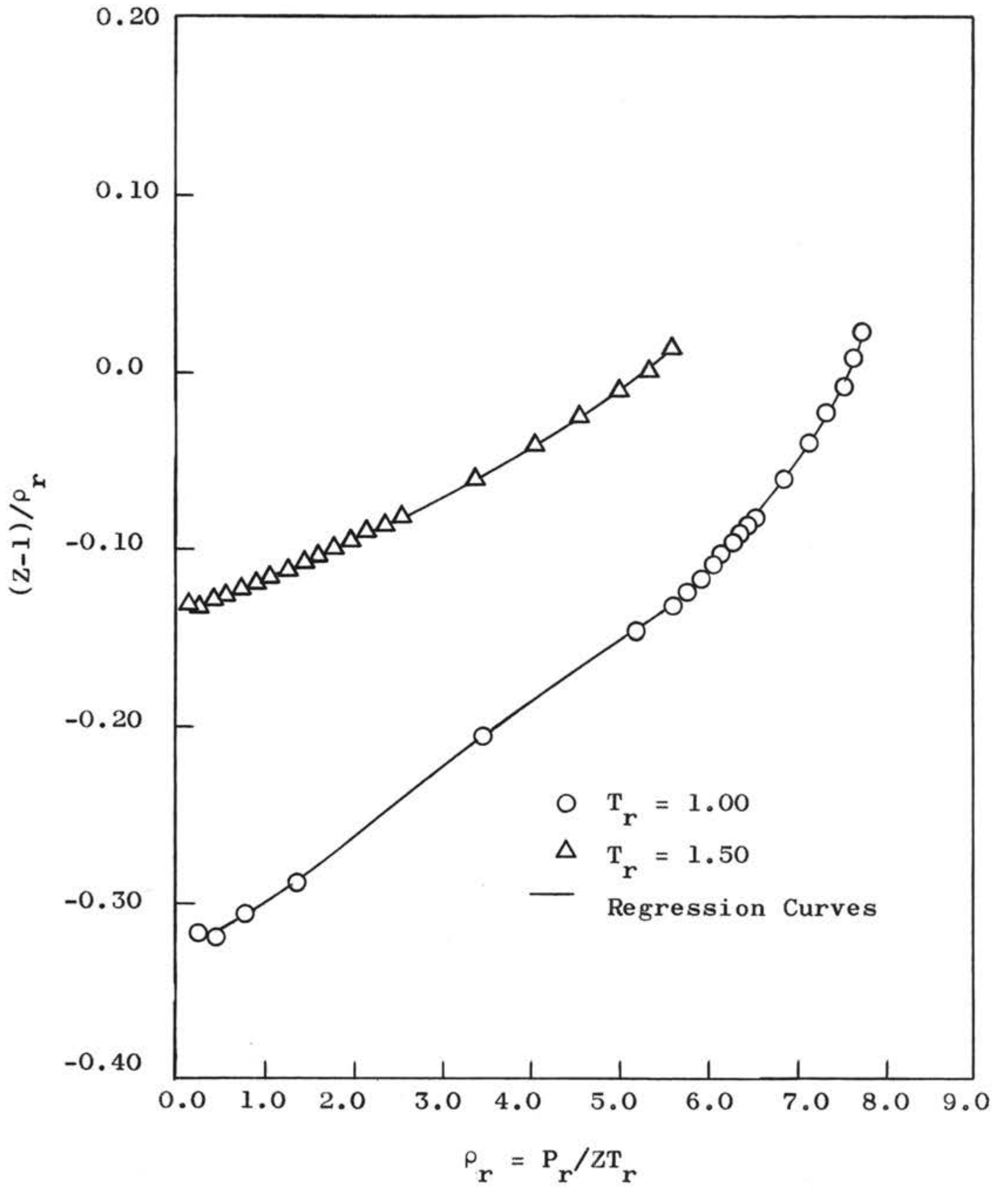


Figure 7

Regression of Pitzer's Values at $\omega = 0.0$

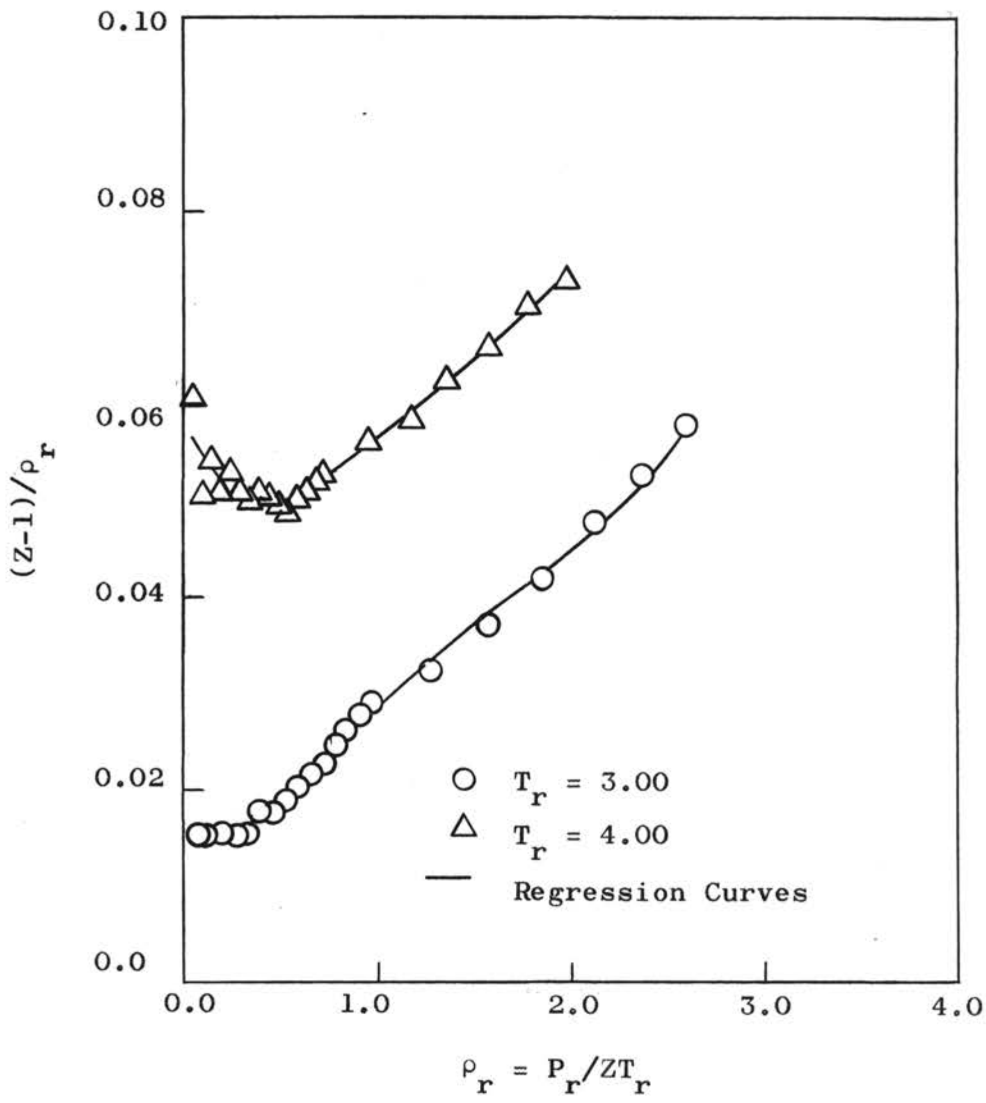


Figure 8

Regression of Pitzer's Values at $\omega = 0.0$

sions. A comparison of the regression curve and the observed virial coefficients is shown for the second virial coefficient b at acentric factors of 0.0, 0.1, 0.2, 0.3, and 0.4 in Figures 9 to 13, the third virial coefficient c in Figures 14 to 18, the fourth virial coefficient d in Figures 19 to 23, the fifth virial coefficient e in Figures 24 to 28, and the sixth virial coefficient f in Figures 29 to 33. Figures 9 to 13 indicate a good correlation of the second virial coefficient b with temperature over the entire acentric factor range. In contrast, Figures 14 to 18 show that the temperature correlations for the third virial coefficient c do not reproduce the observed values of c used in regression at any value of the acentric factor. This poor correlation of c with temperature can not be attributed to the regression, but to the scatter of the observed values of c with temperature, even though these observed values were regression coefficients of equation (23) which could reproduce accurately the generalized quantities used in their derivation. The figures describing the temperature correlations of d, e, and f indicate a fair correlation of these coefficients only at low values of acentric factor and up to a reduced temperature of 2.00. At higher values of the acentric factor and above a reduced temperature of 2.00, the correlations again fail to reproduce the observed values for the virial coefficients due to the scatter of these values. However, the observed values for d, e, and f, as with those observed values for c, were successfully used to recalculate the generalized quantity $(Z-1)/\rho_r$ used in their derivation.

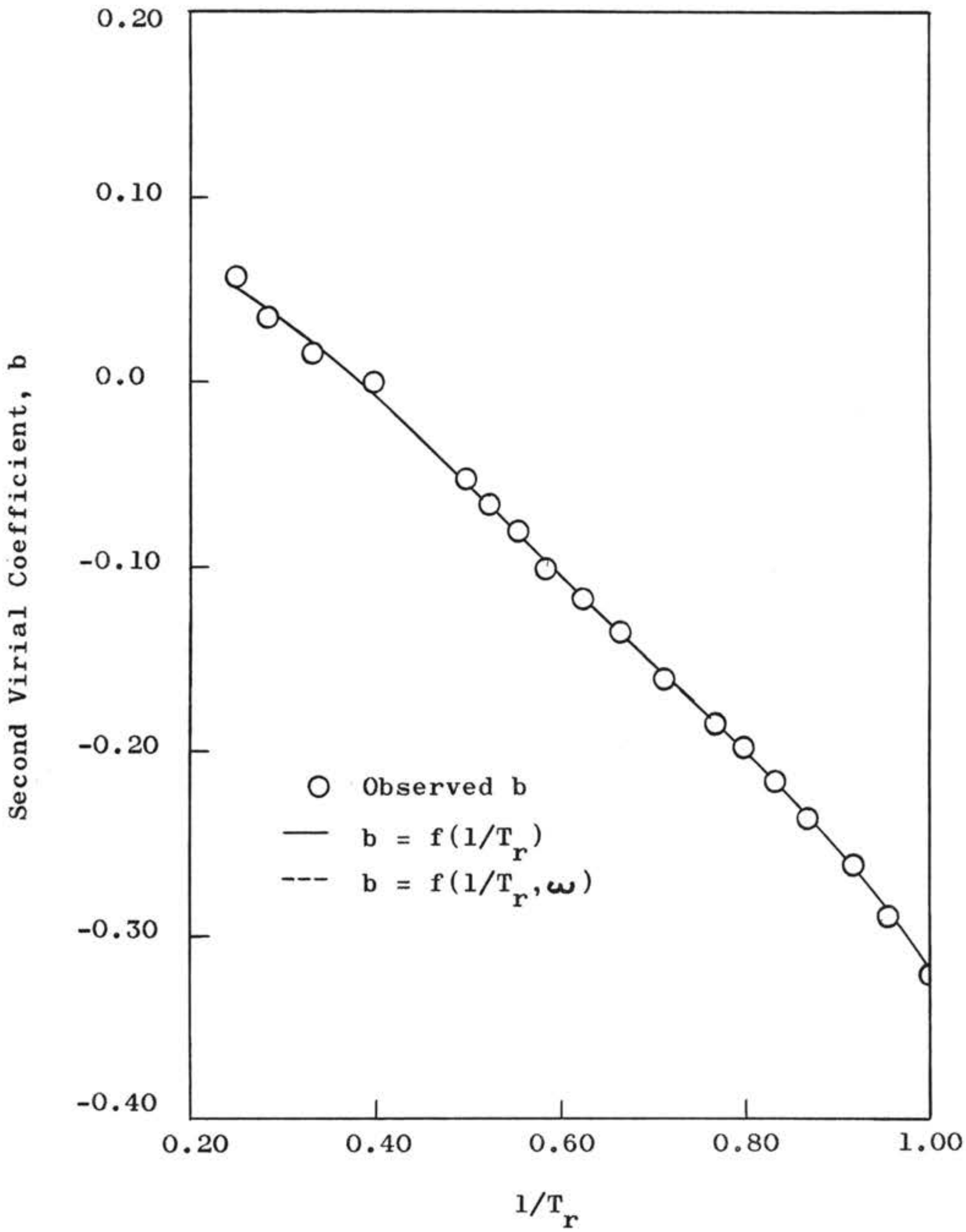


Figure 9

Second Virial Coefficient at $\omega = 0.0$

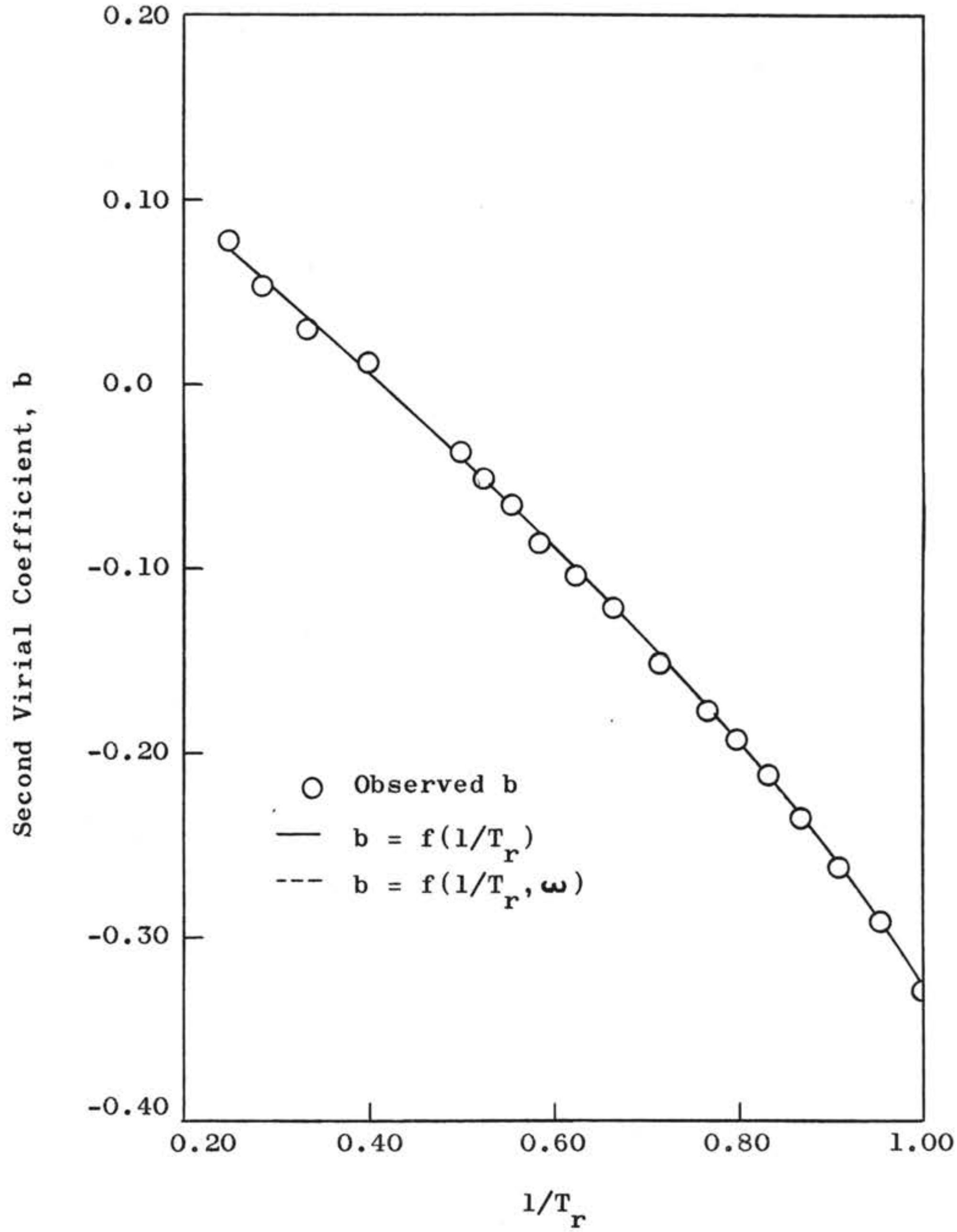


Figure 10

Second Virial Coefficient at $\omega = 0.1$

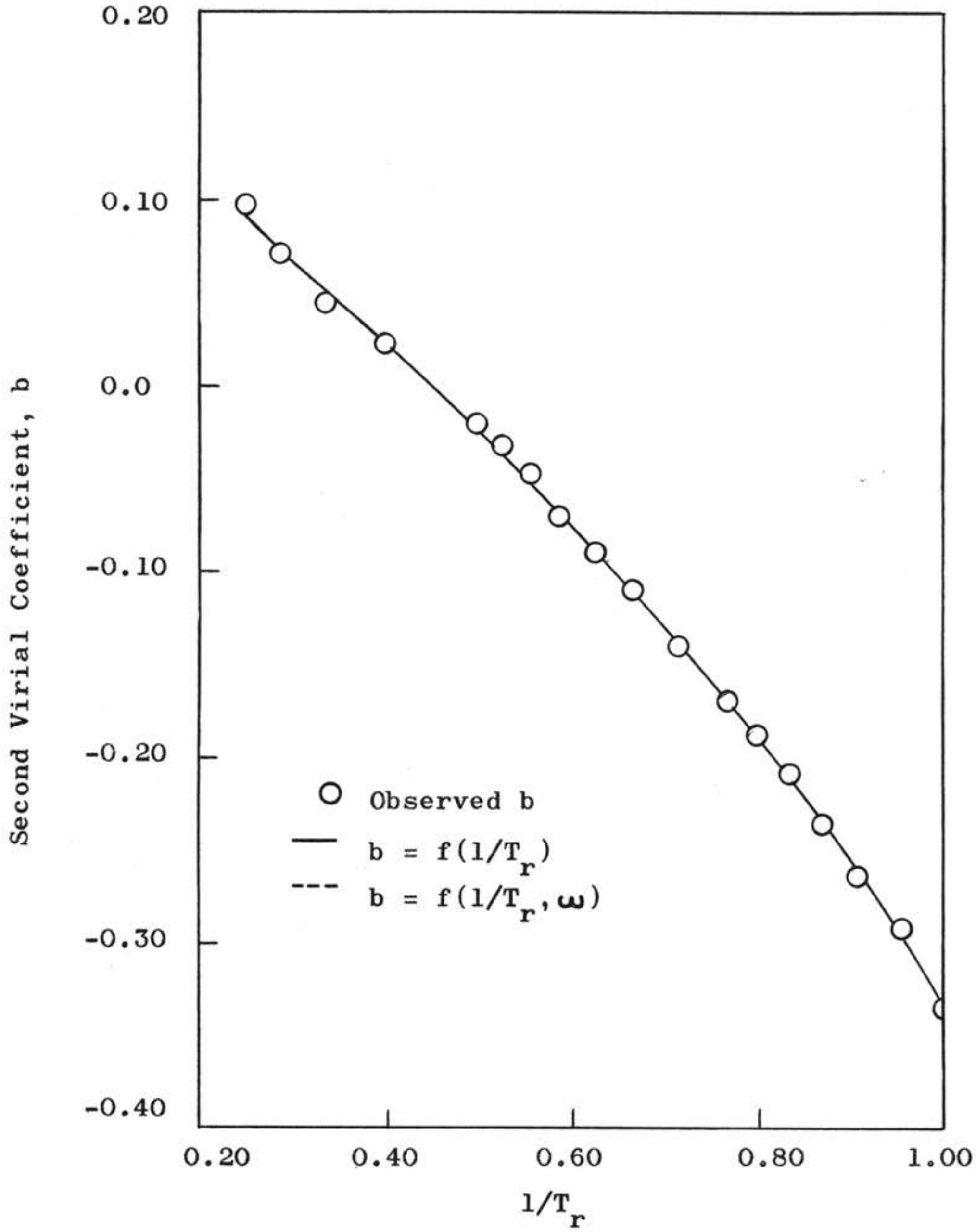


Figure 11

Second Virial Coefficient at ω = 0.2

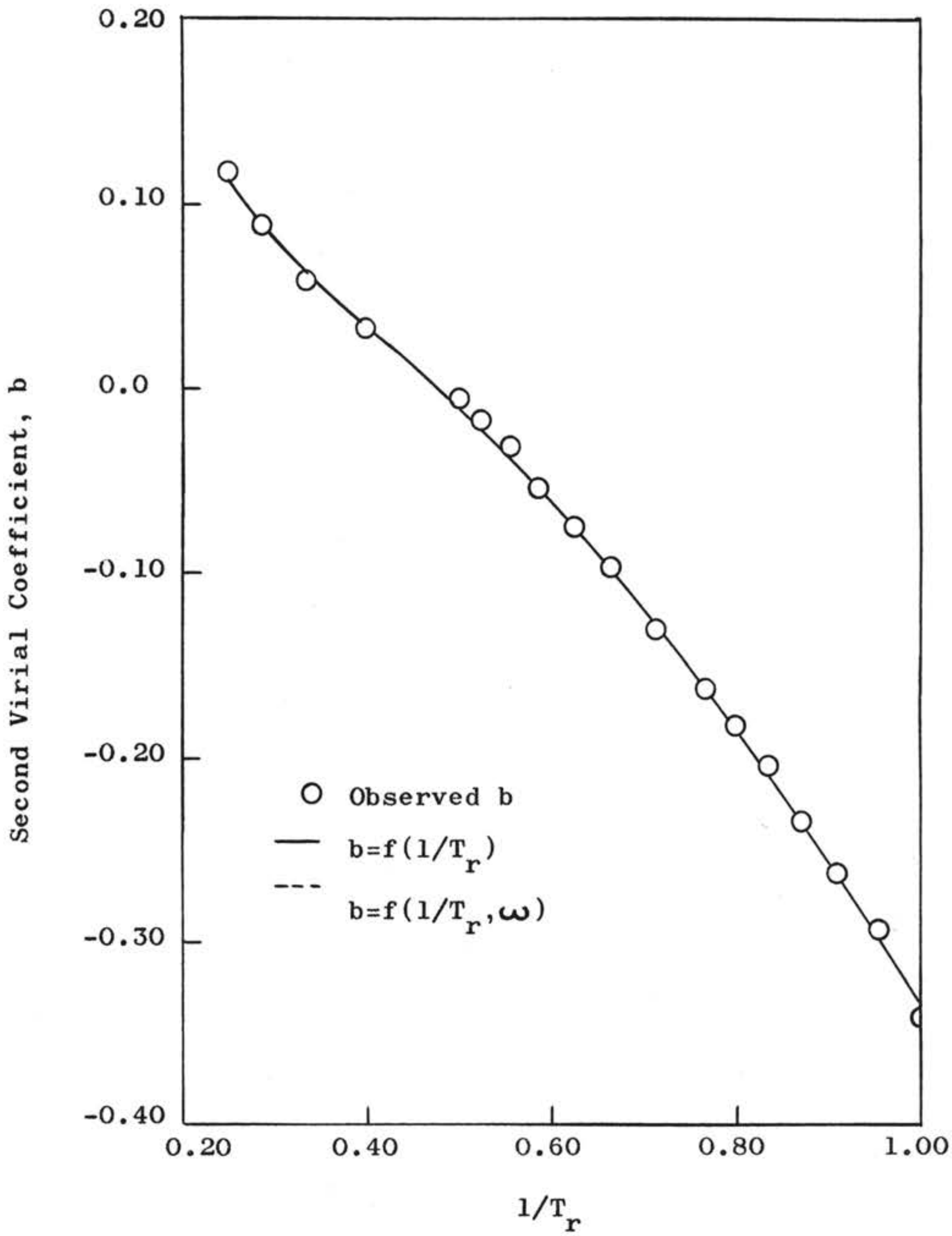


Figure 12

Second Virial Coefficient at ω = 0.3

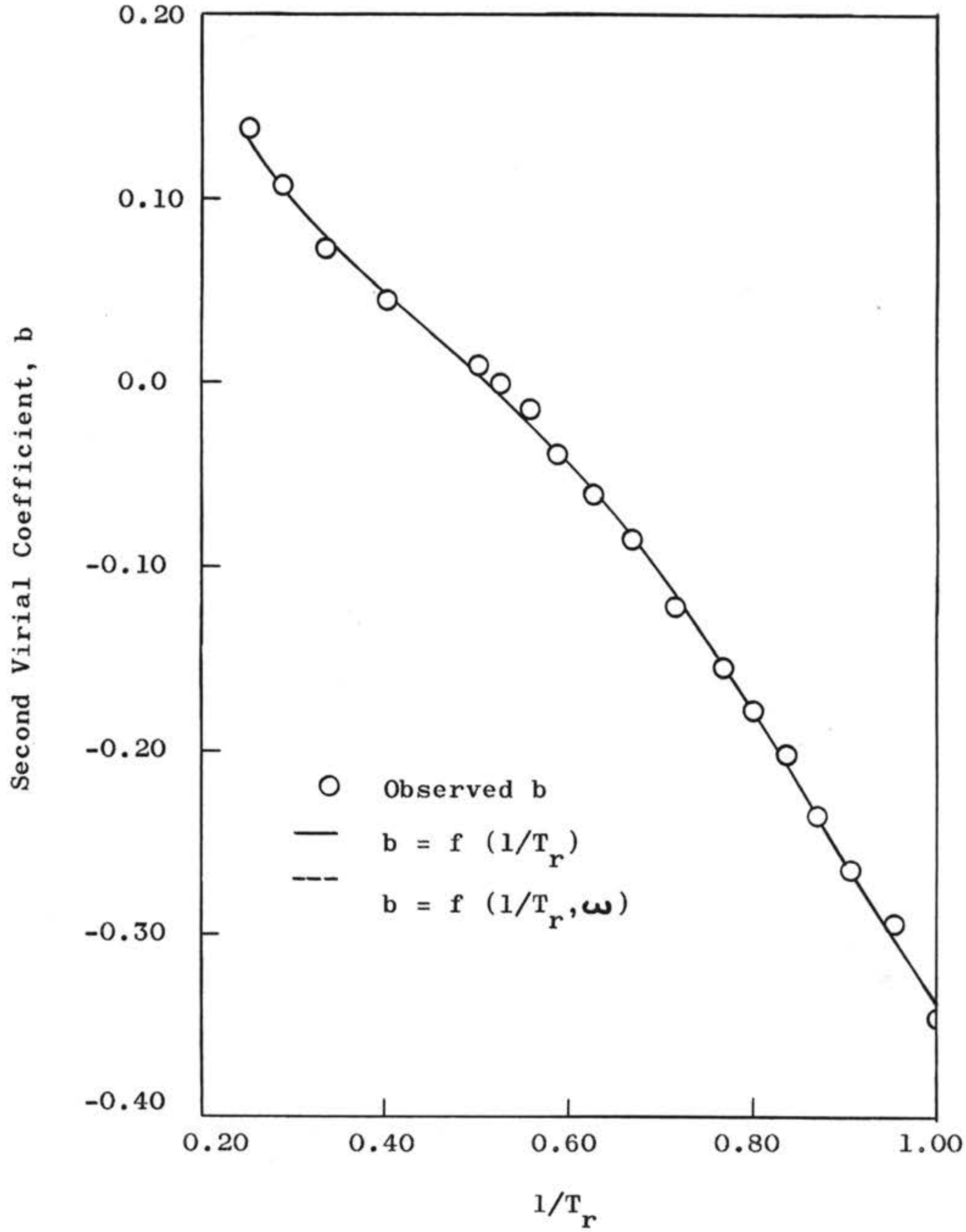


Figure 13

Second Virial Coefficient at ω = 0.4

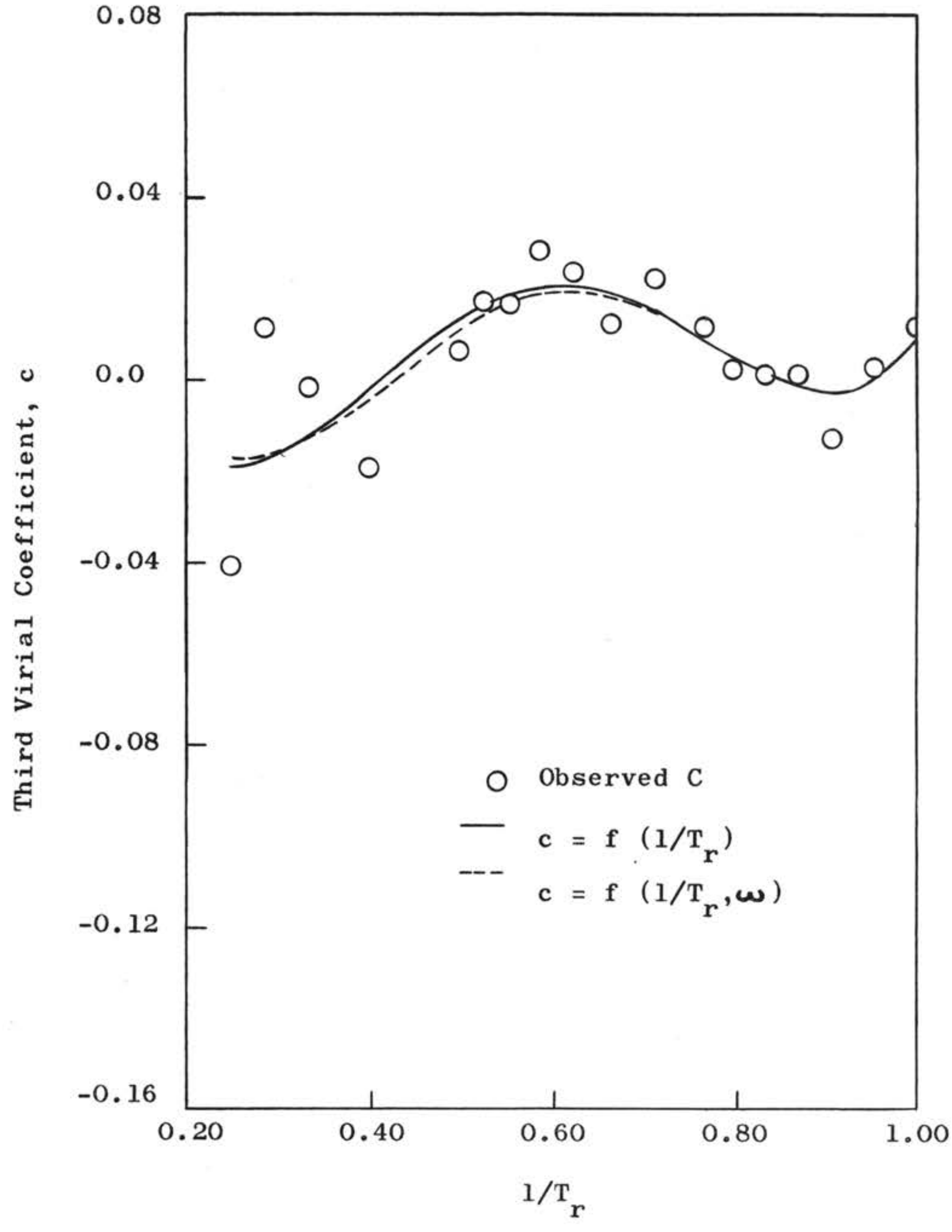


Figure 14

Third Virial Coefficient at $\omega = 0.0$

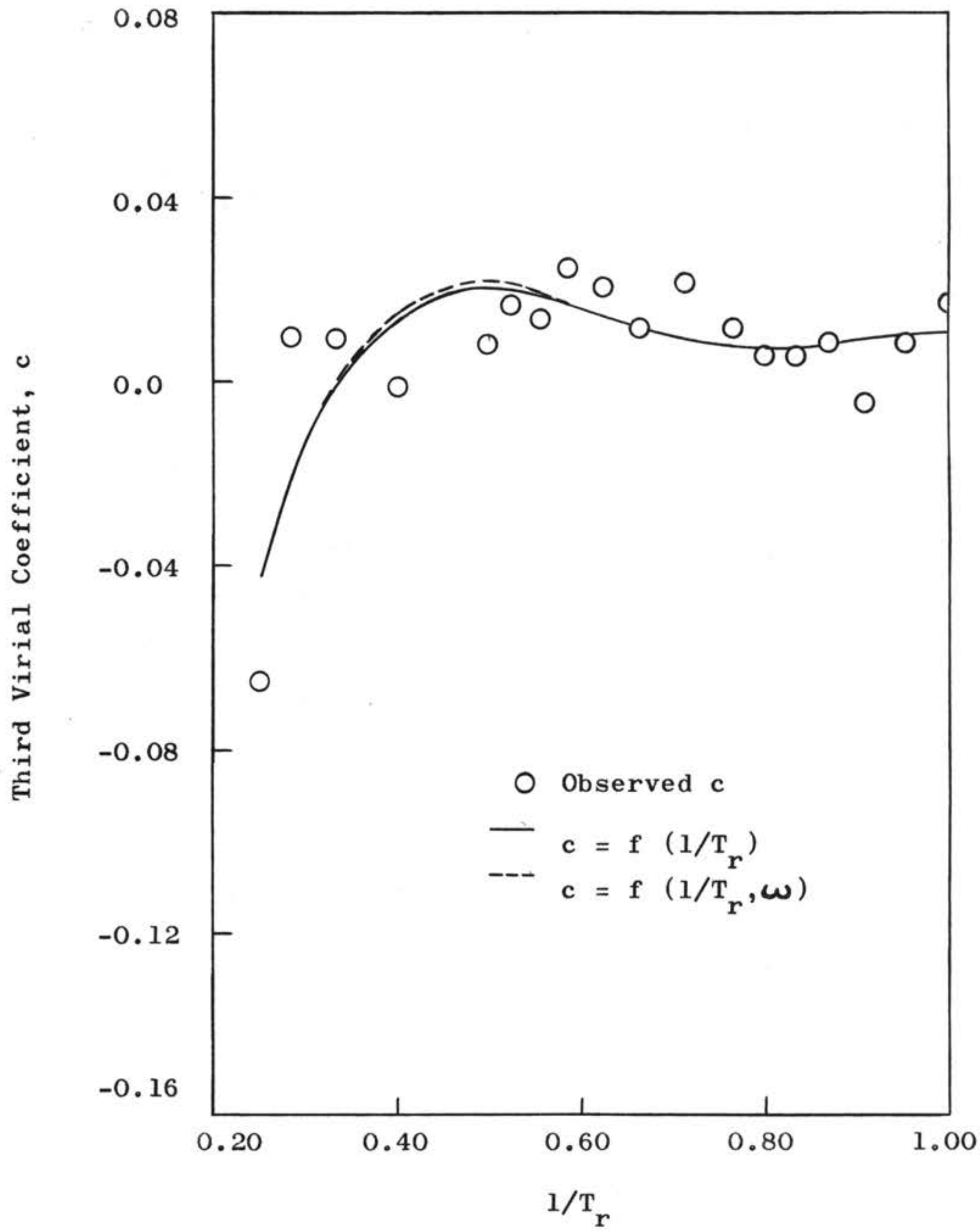


Figure 15

Third Virial Coefficient at $\omega = 0.1$

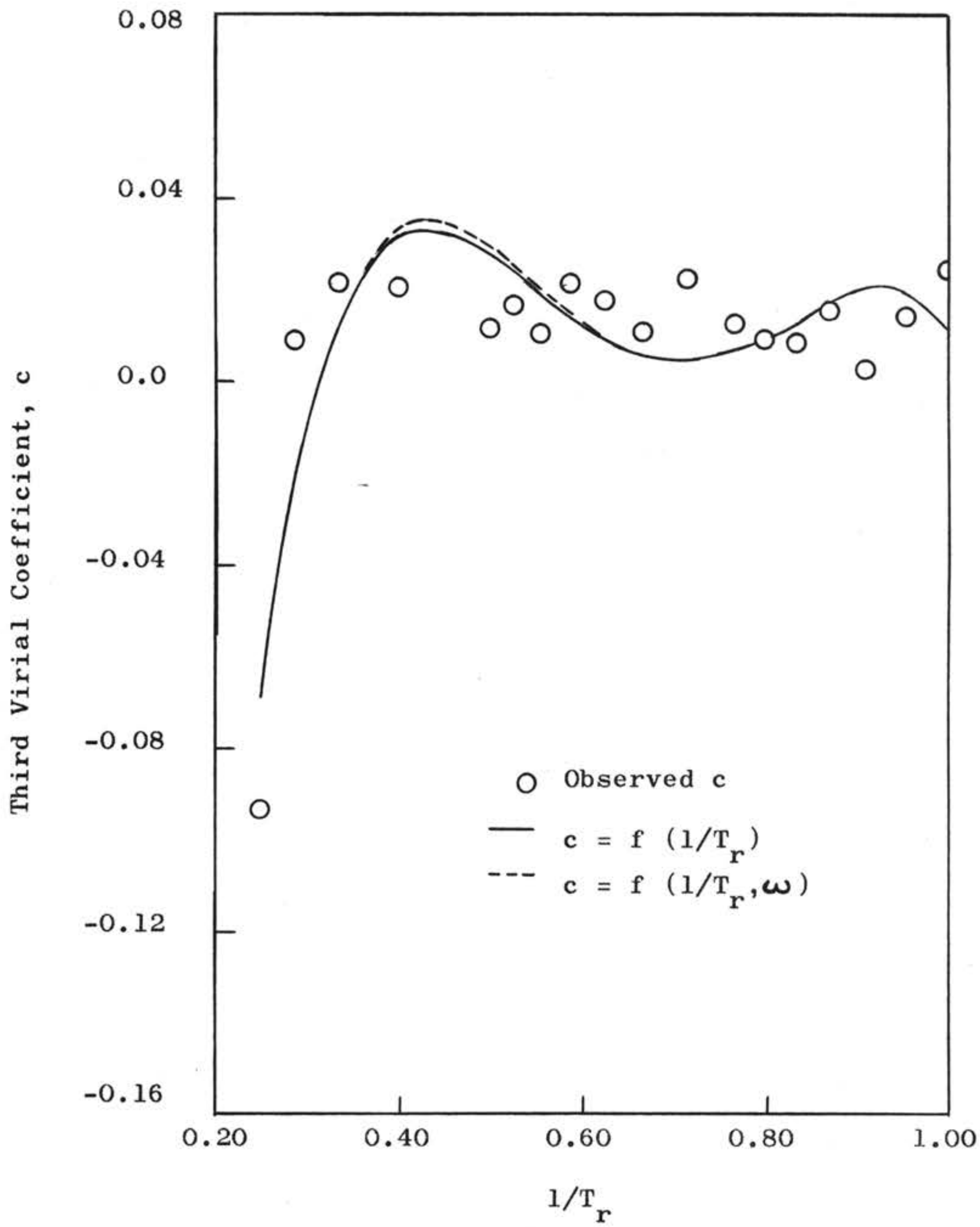


Figure 16

Third Virial Coefficient at $\omega = 0.2$

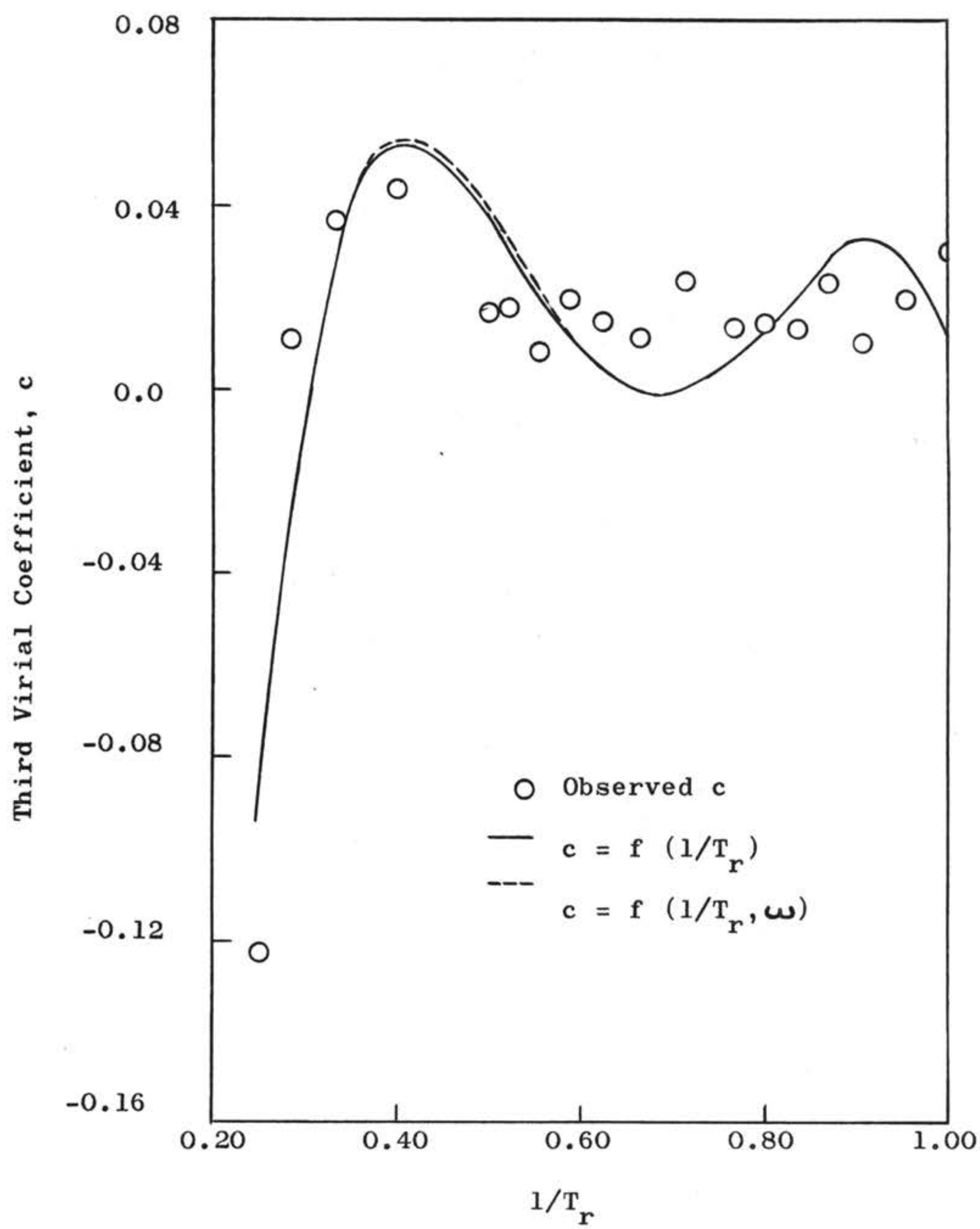


Figure 17

Third Virial Coefficient at ω = 0.3

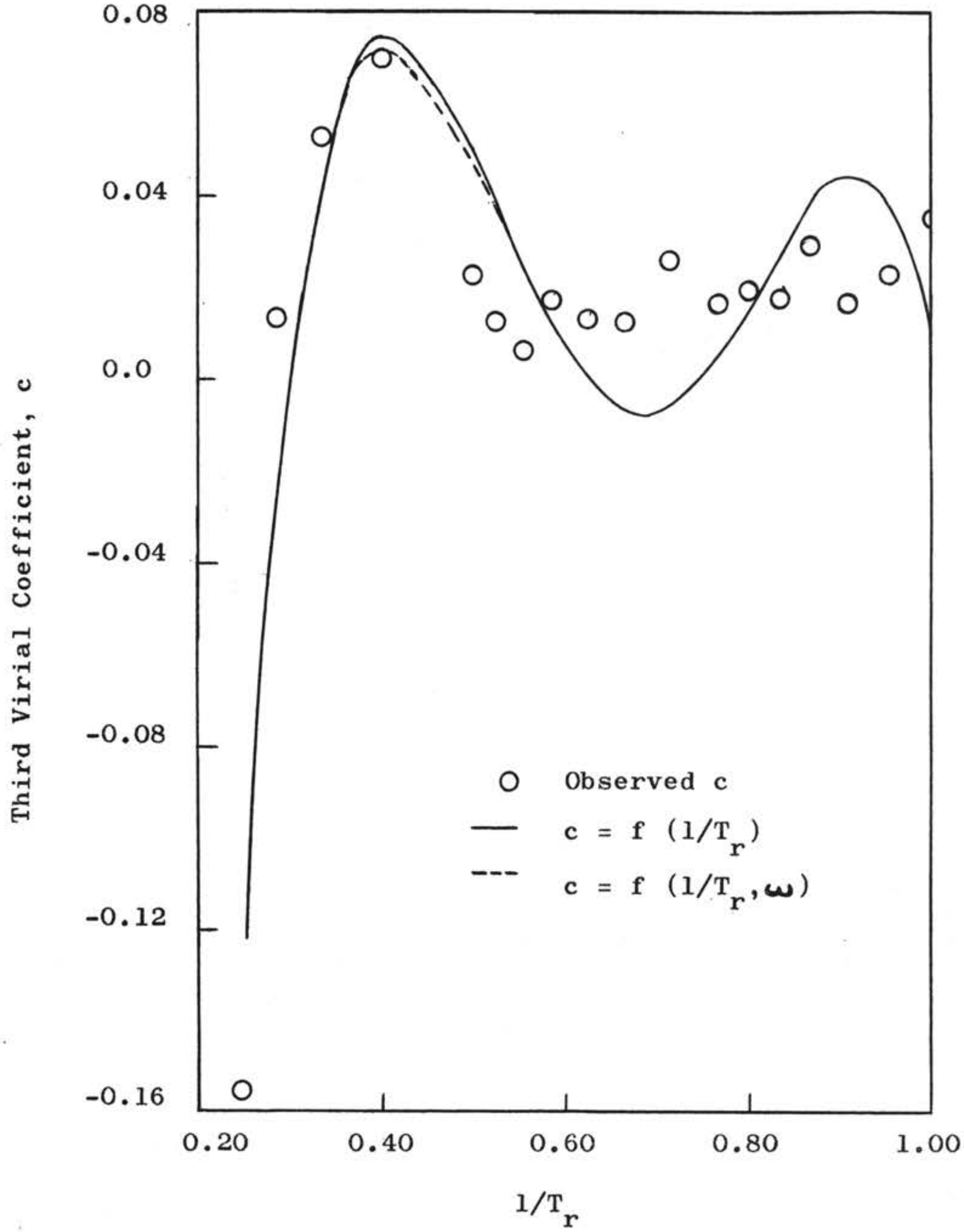


Figure 18

Third Virial Coefficient at $\omega = 0.4$

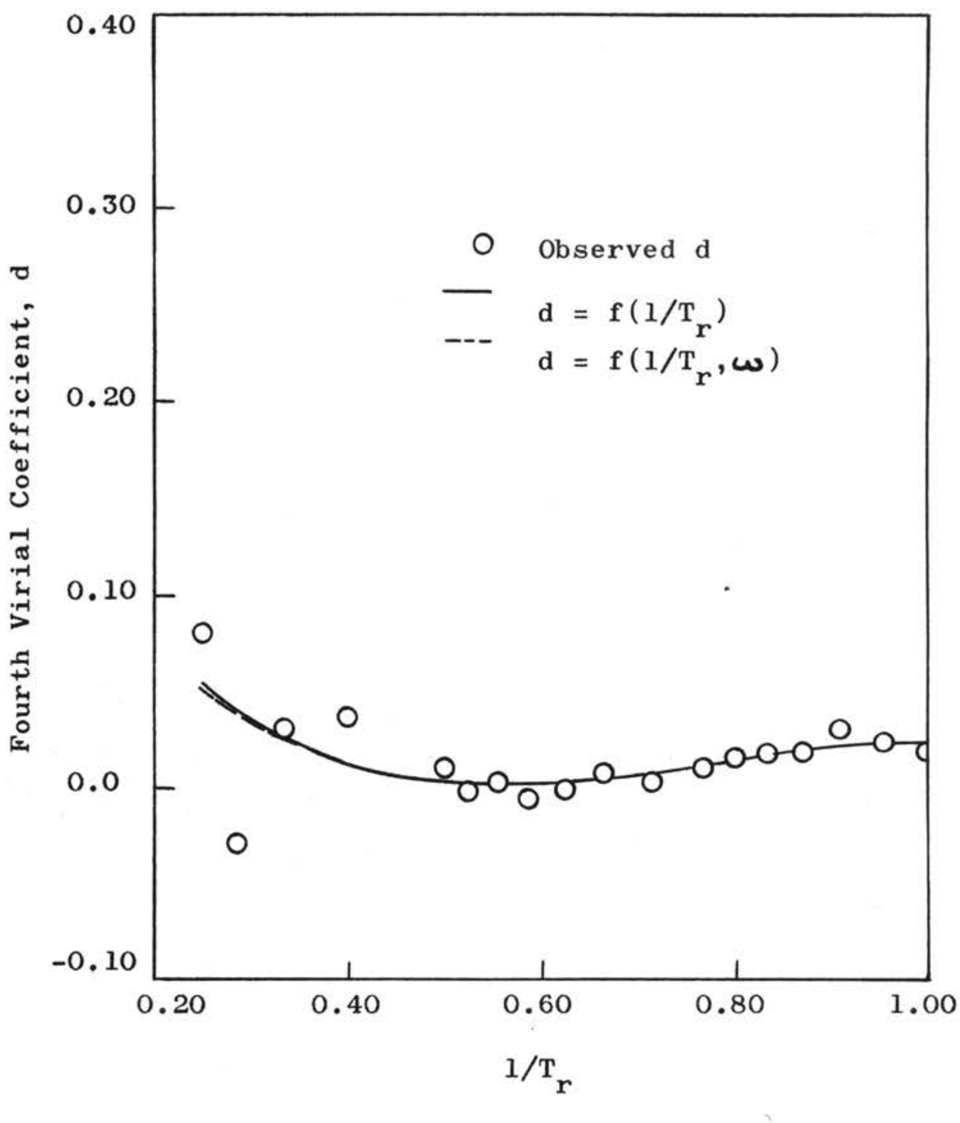


Figure 19

Fourth Virial Coefficient at $\omega = 0.0$

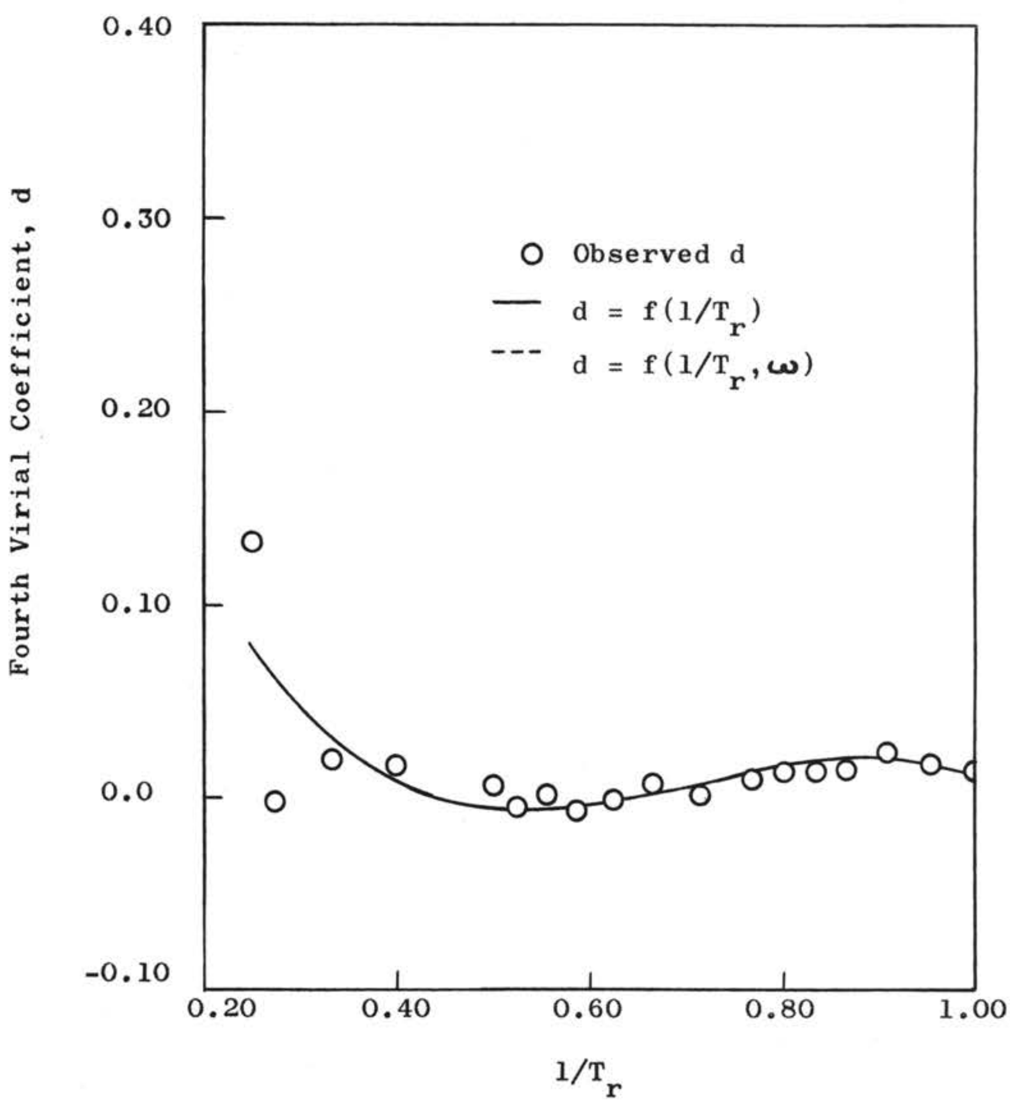


Figure 20

Fourth Virial Coefficient at $\omega = 0.1$

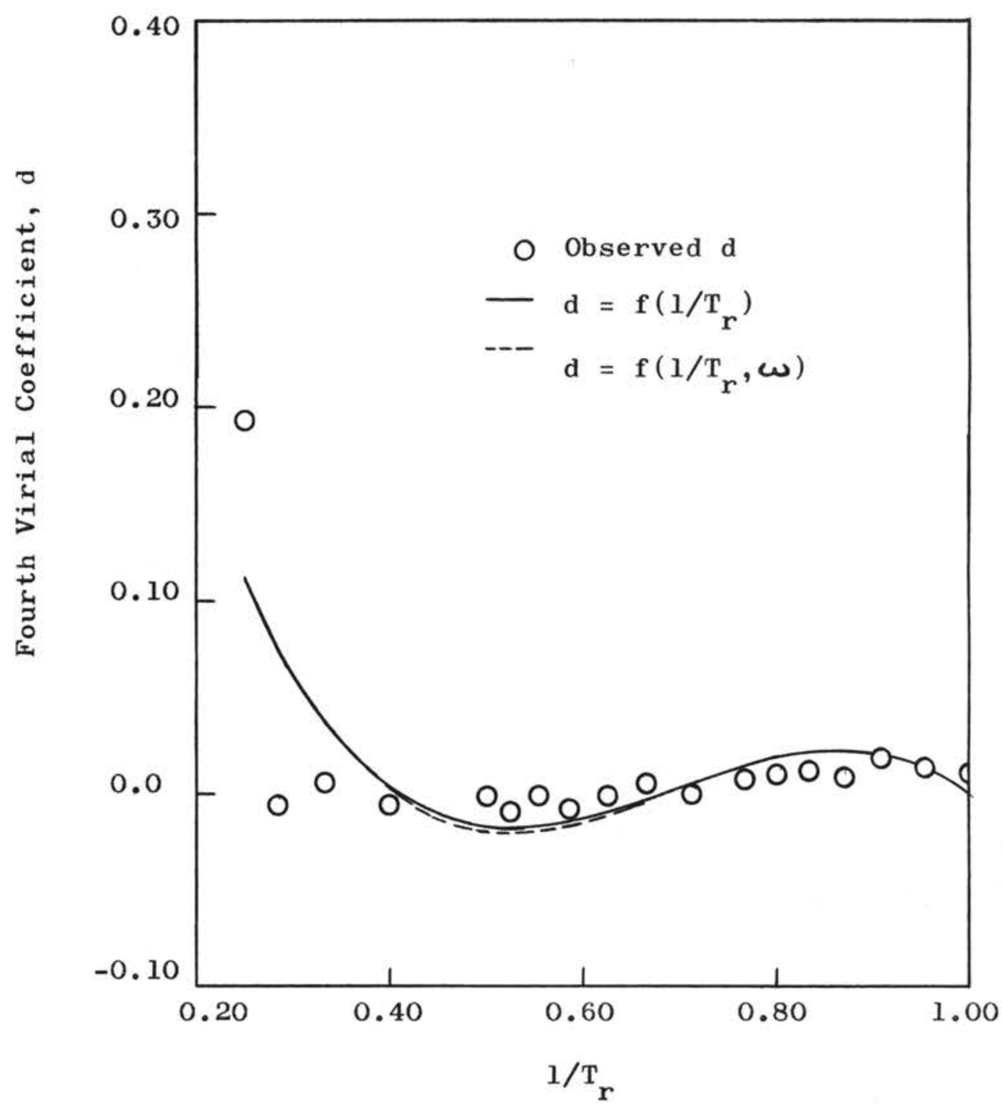


Figure 21

Fourth Virial Coefficient at $\omega = 0.2$

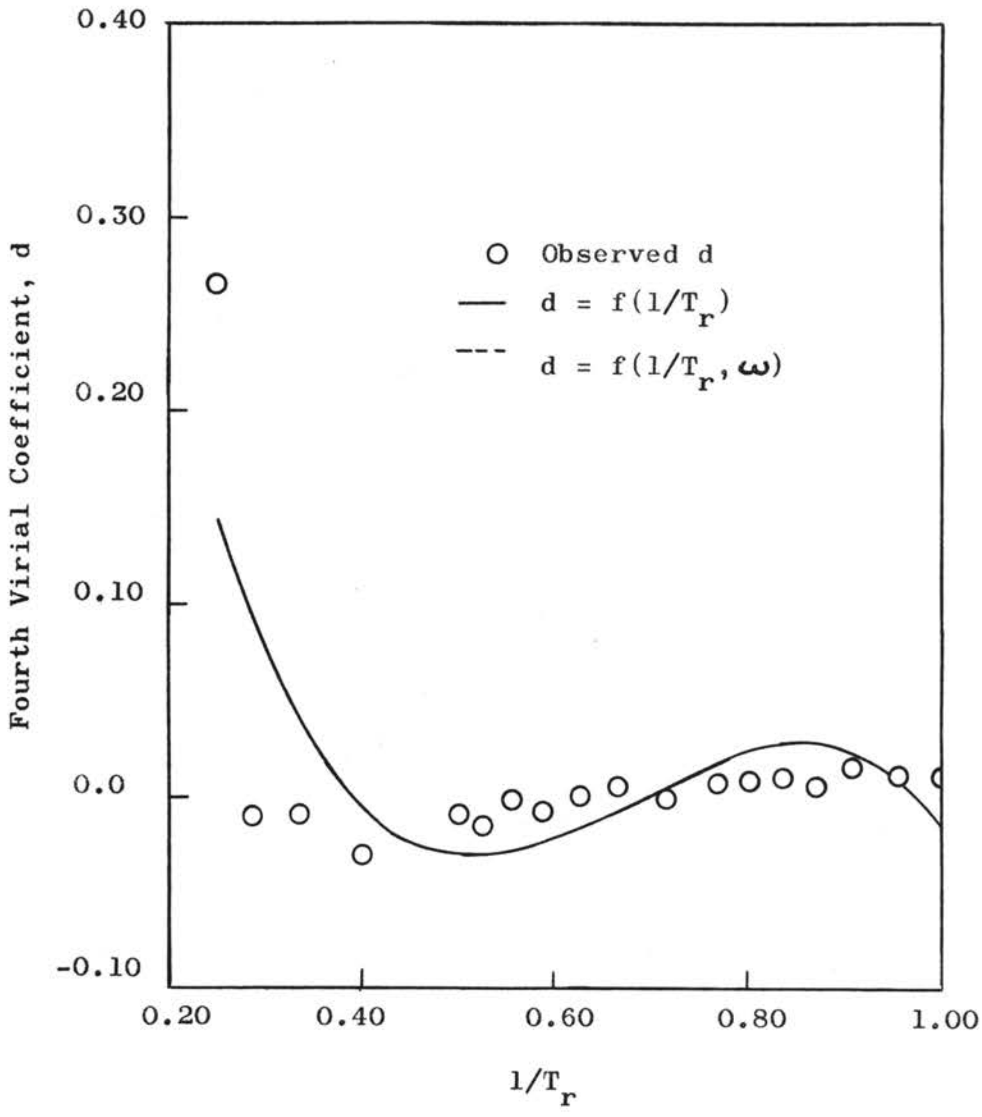


Figure 22

Fourth Virial Coefficient at ω = 0.3

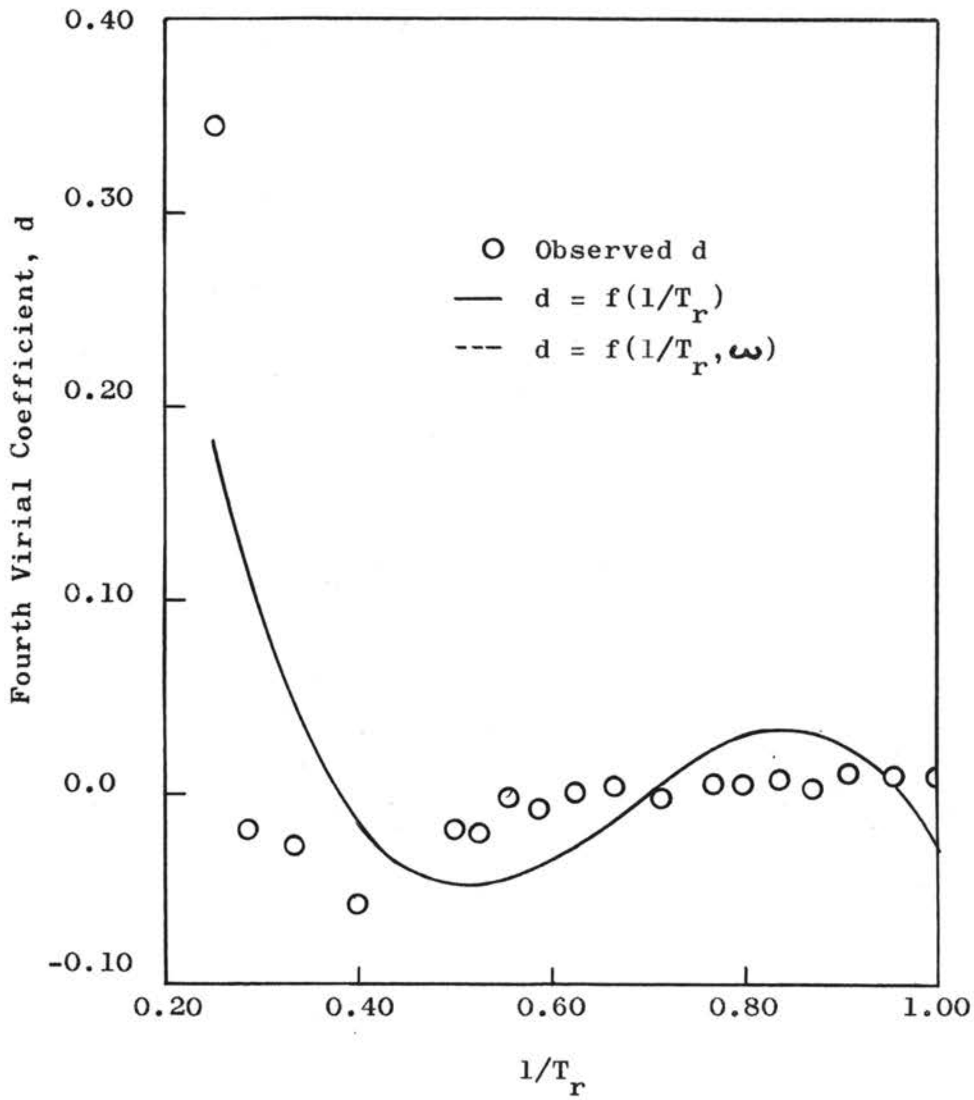


Figure 23

Fourth Virial Coefficient at ω = 0.4

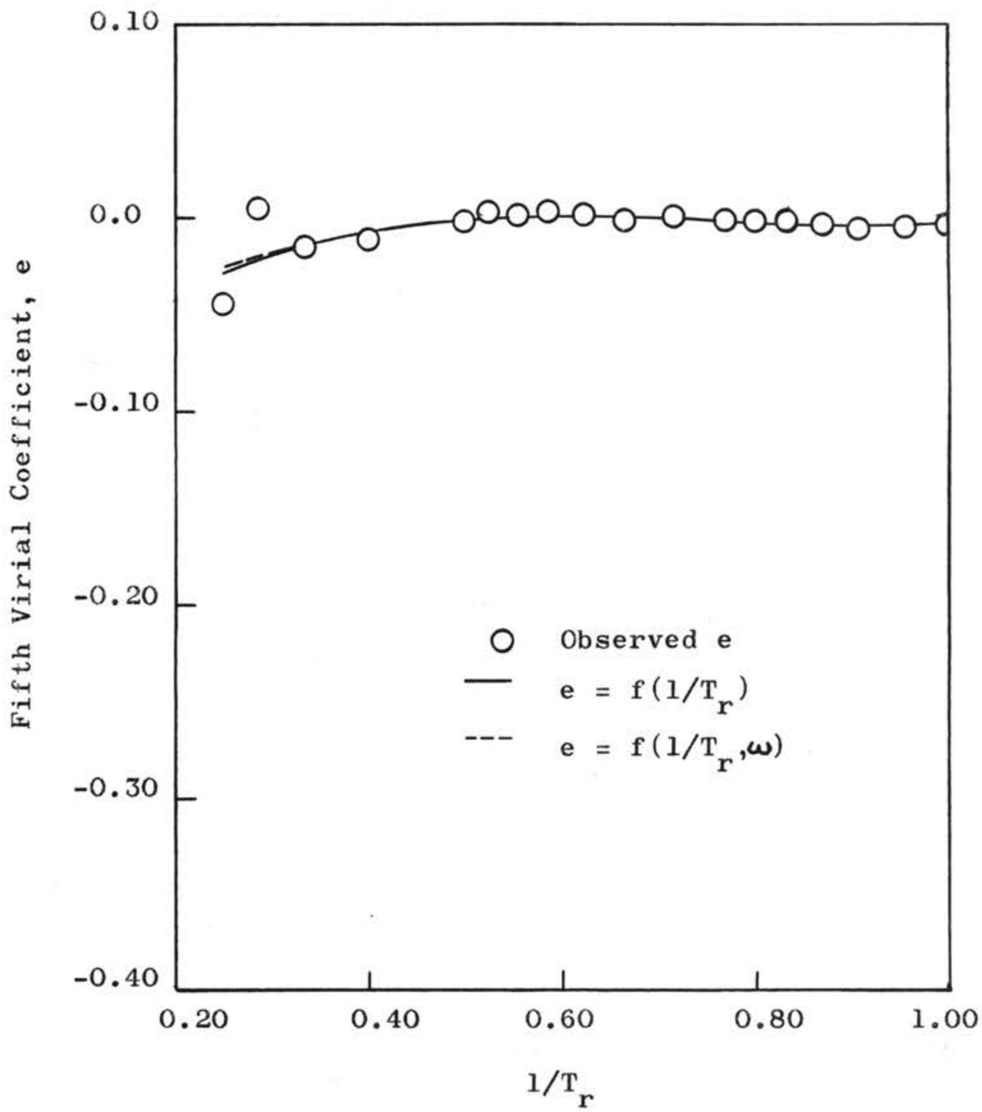


Figure 24

Fifth Virial Coefficient at ω = 0.0

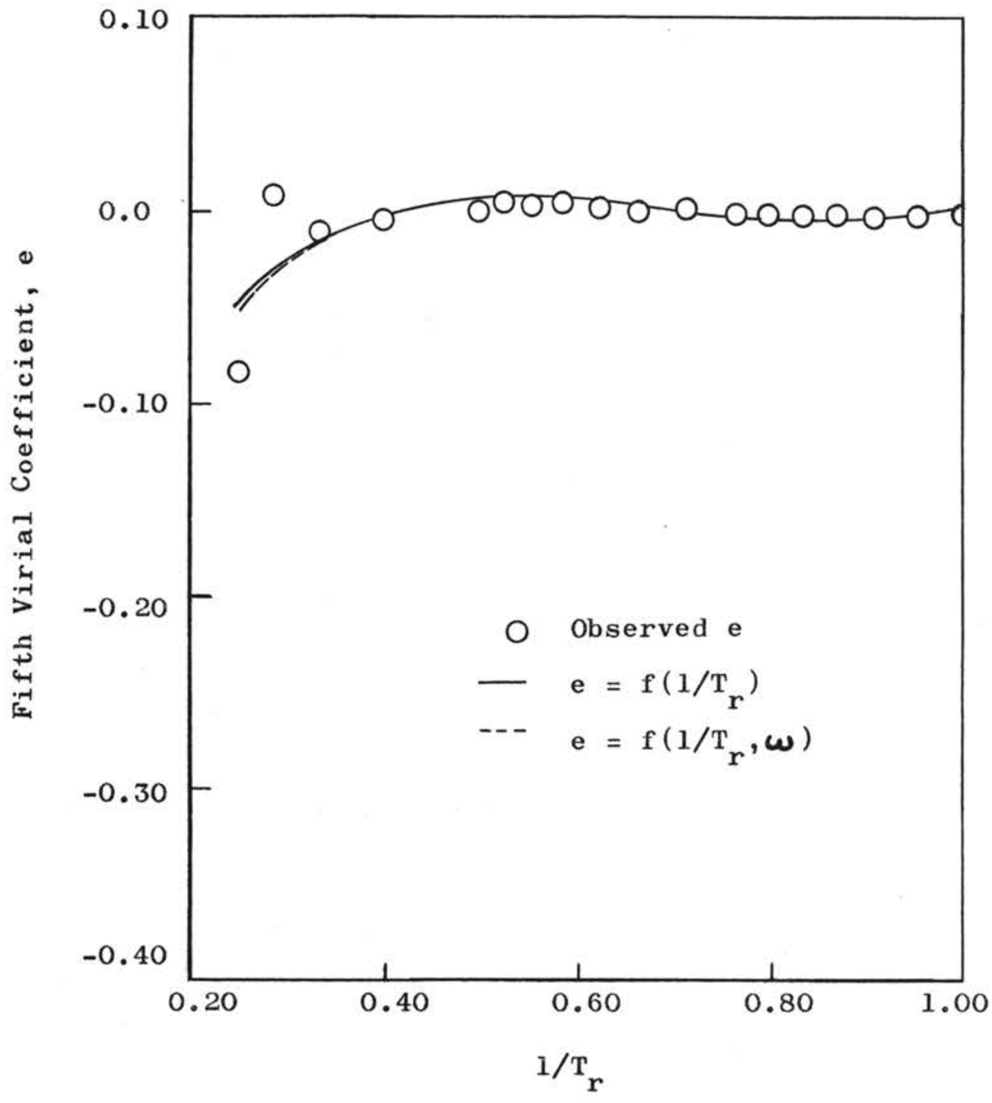


Figure 25

Fifth Virial Coefficient at ω = 0.1

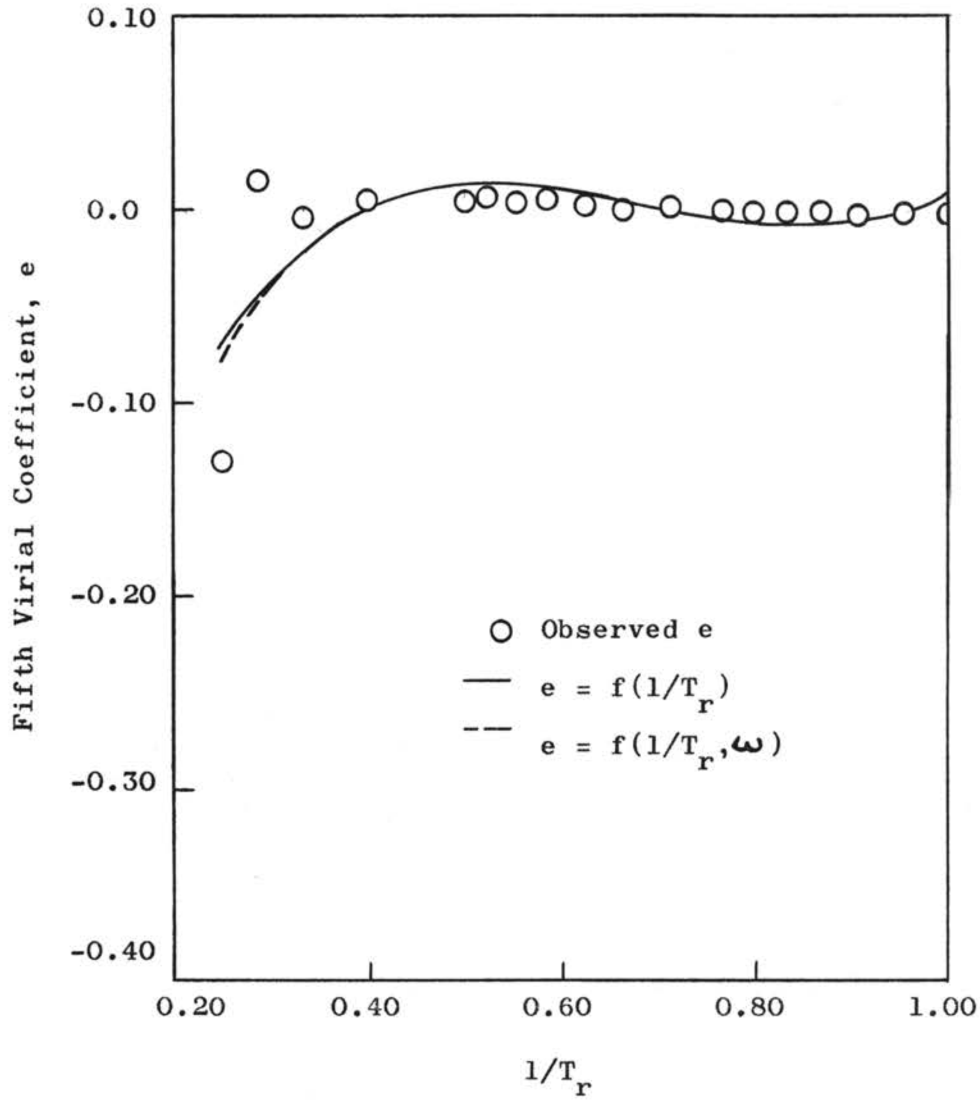


Figure 26

Fifth Virial Coefficient at ω = 0.2

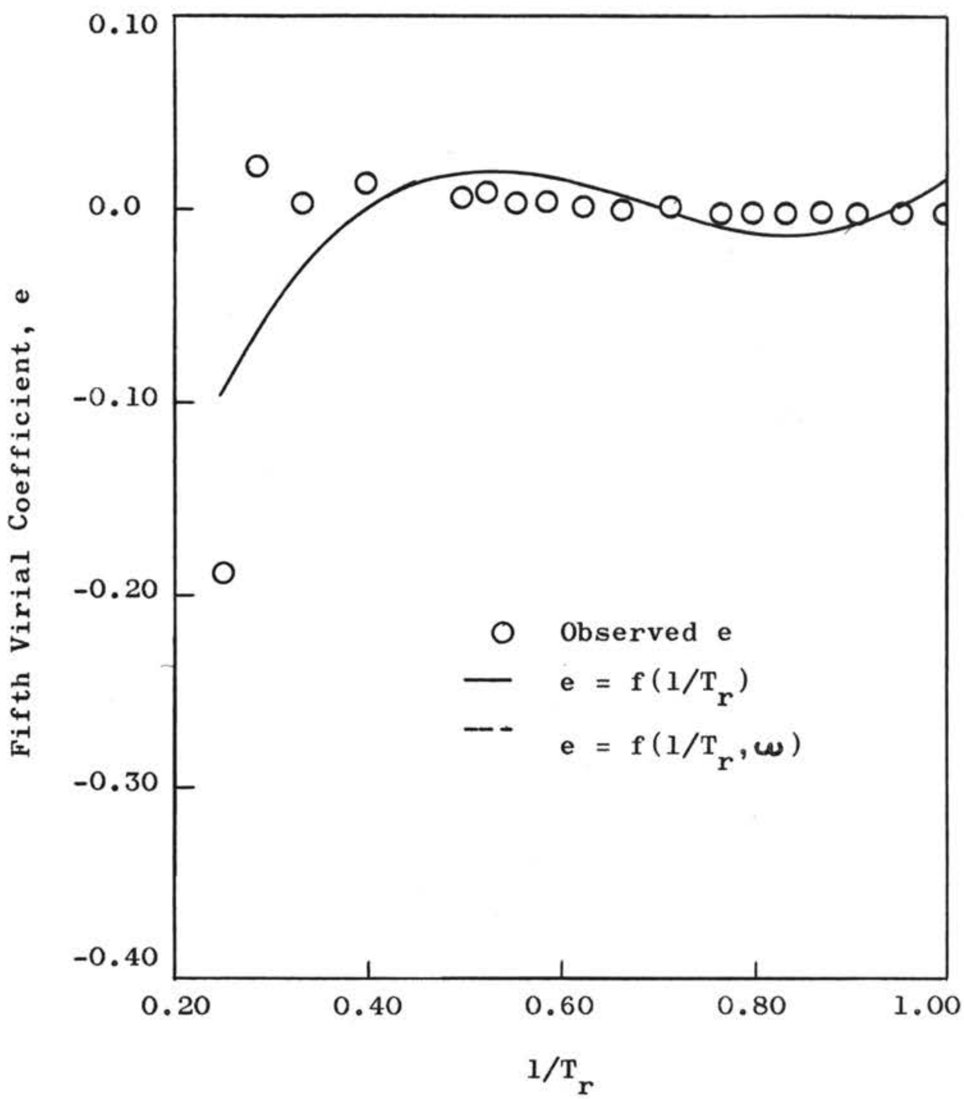


Figure 27

Fifth Virial Coefficient at ω = 0.3

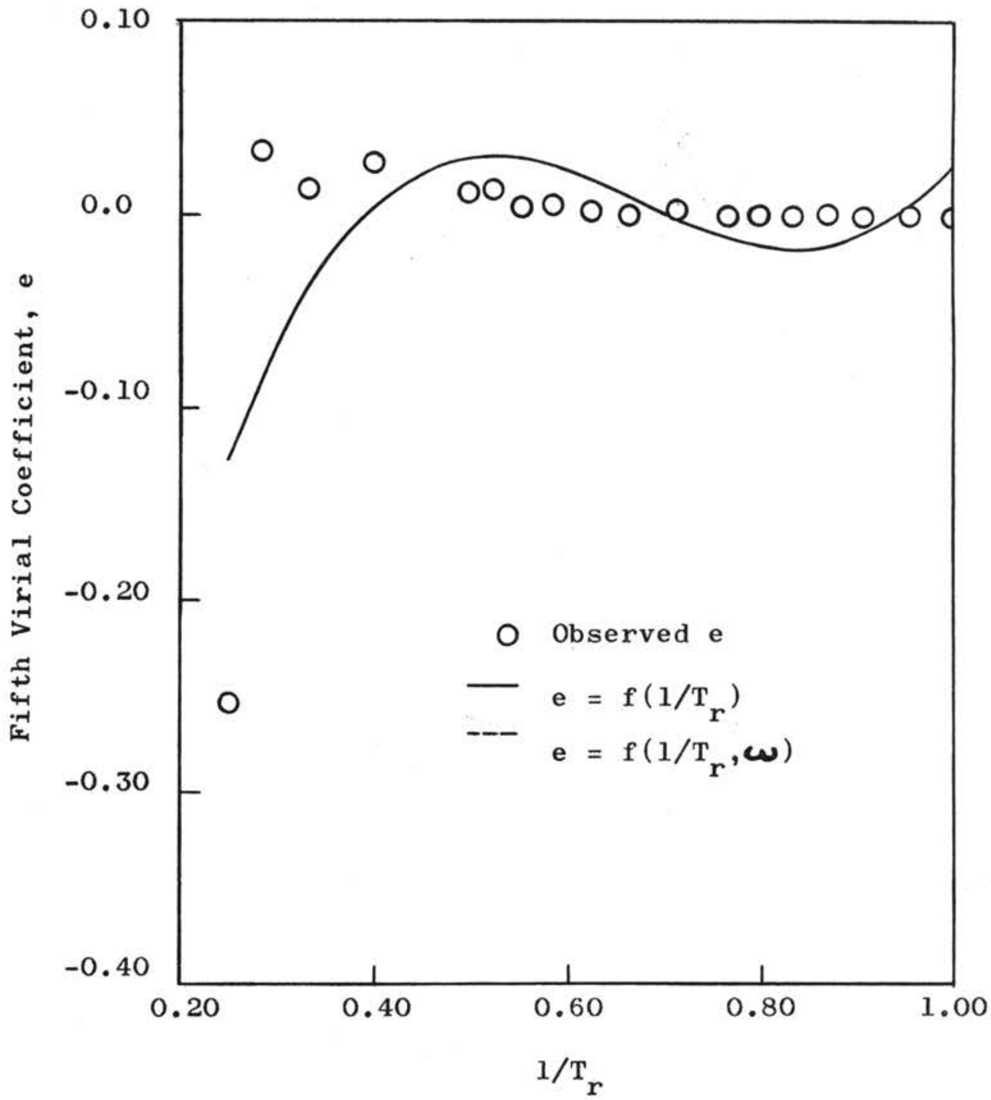


Figure 28

Fifth Virial Coefficient at $\omega = 0.4$

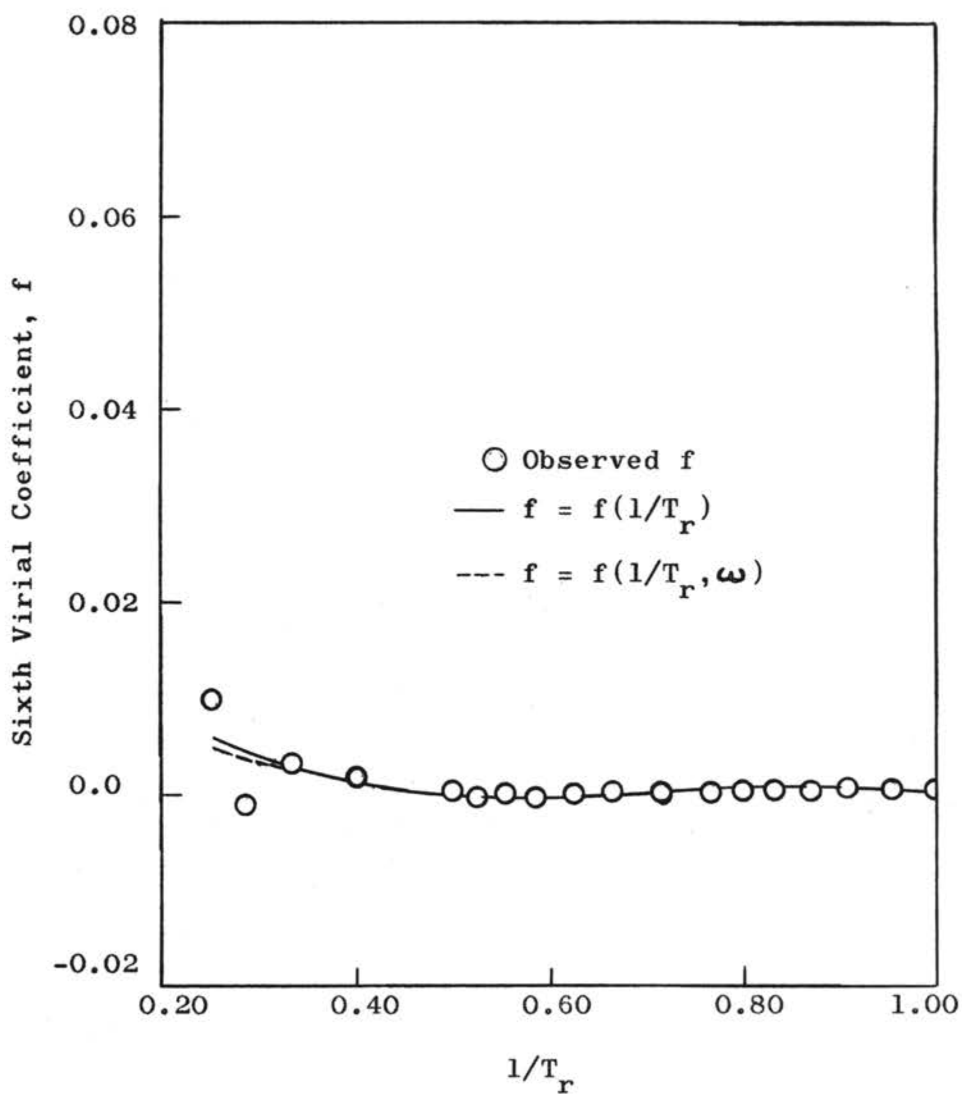


Figure 29

Sixth Virial Coefficient at ω = 0.0

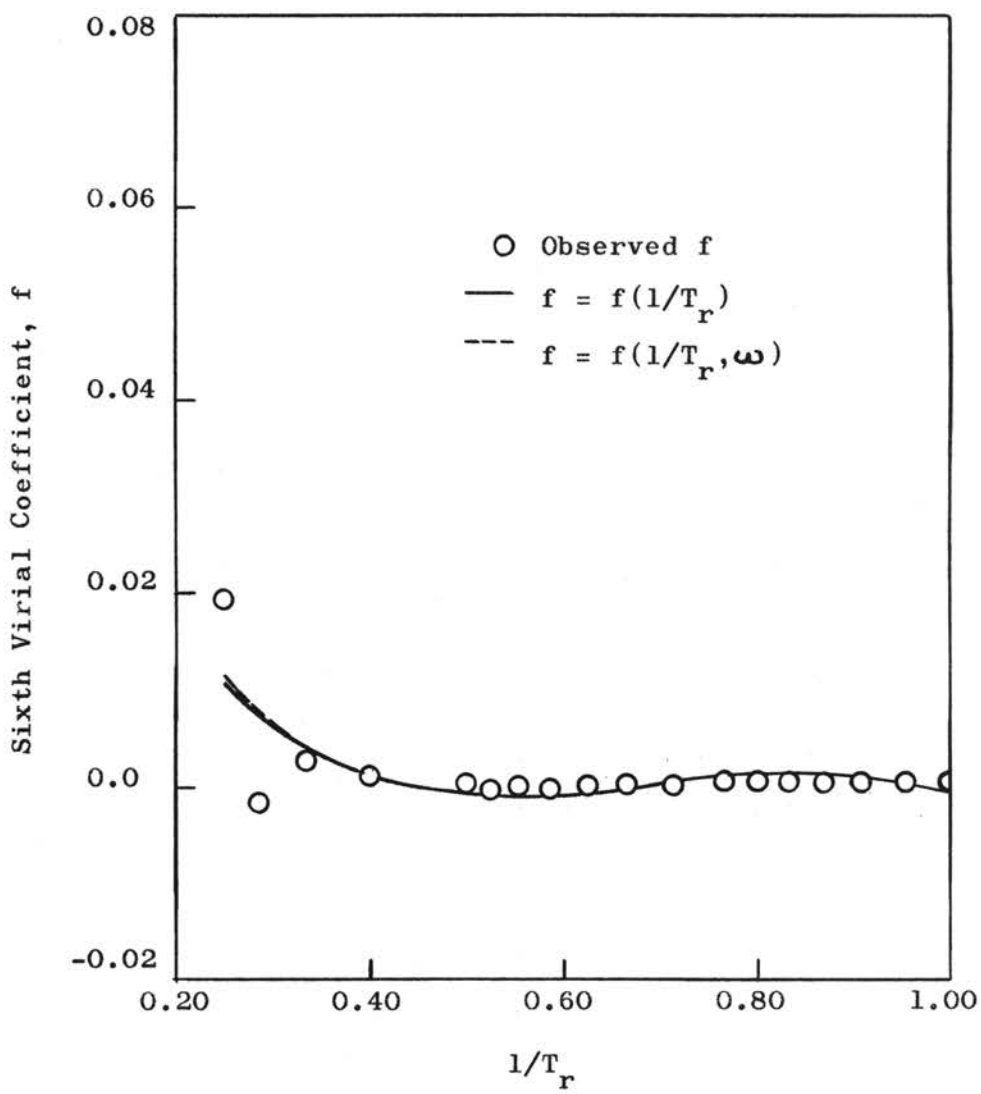


Figure 30

Sixth Virial Coefficient at $\omega = 0.1$

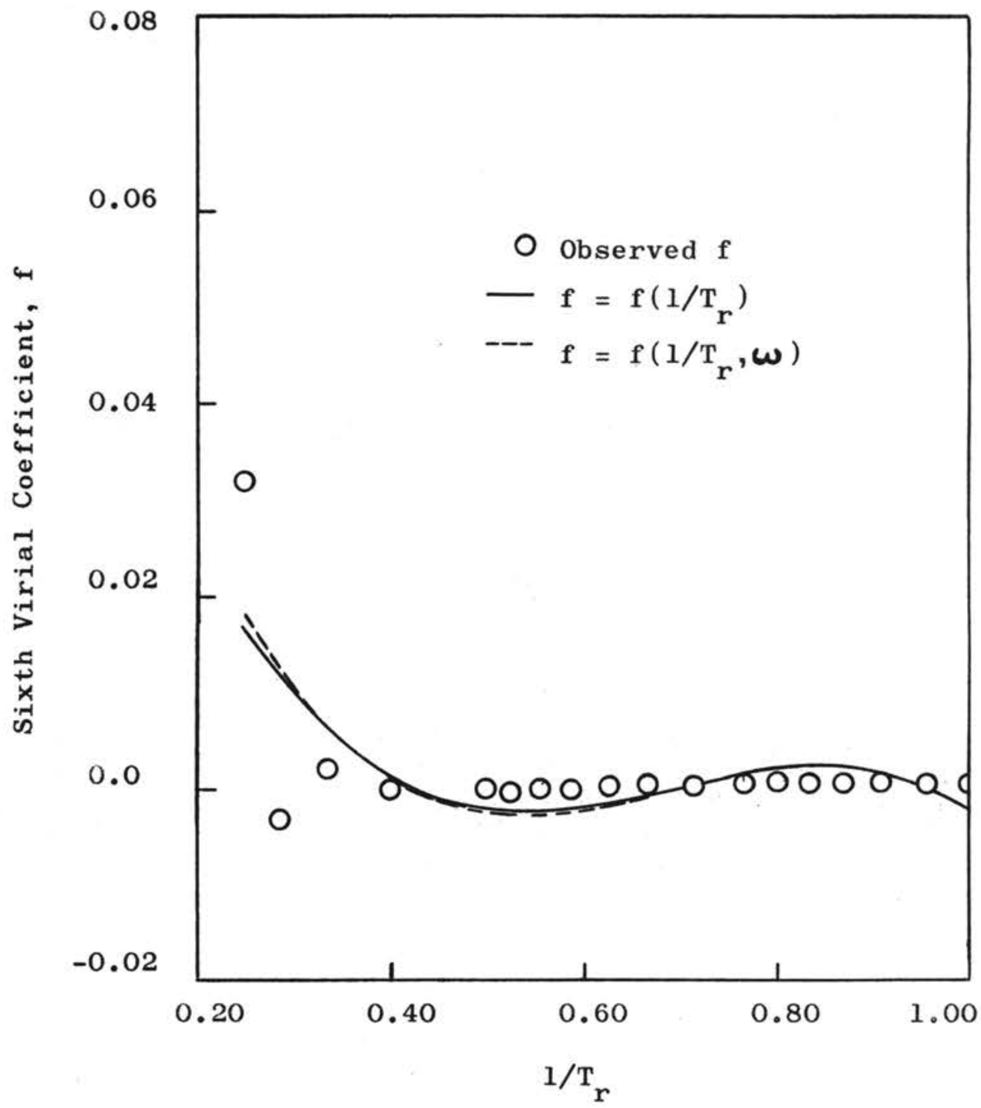


Figure 31

Sixth Virial Coefficient at $\omega = 0.2$

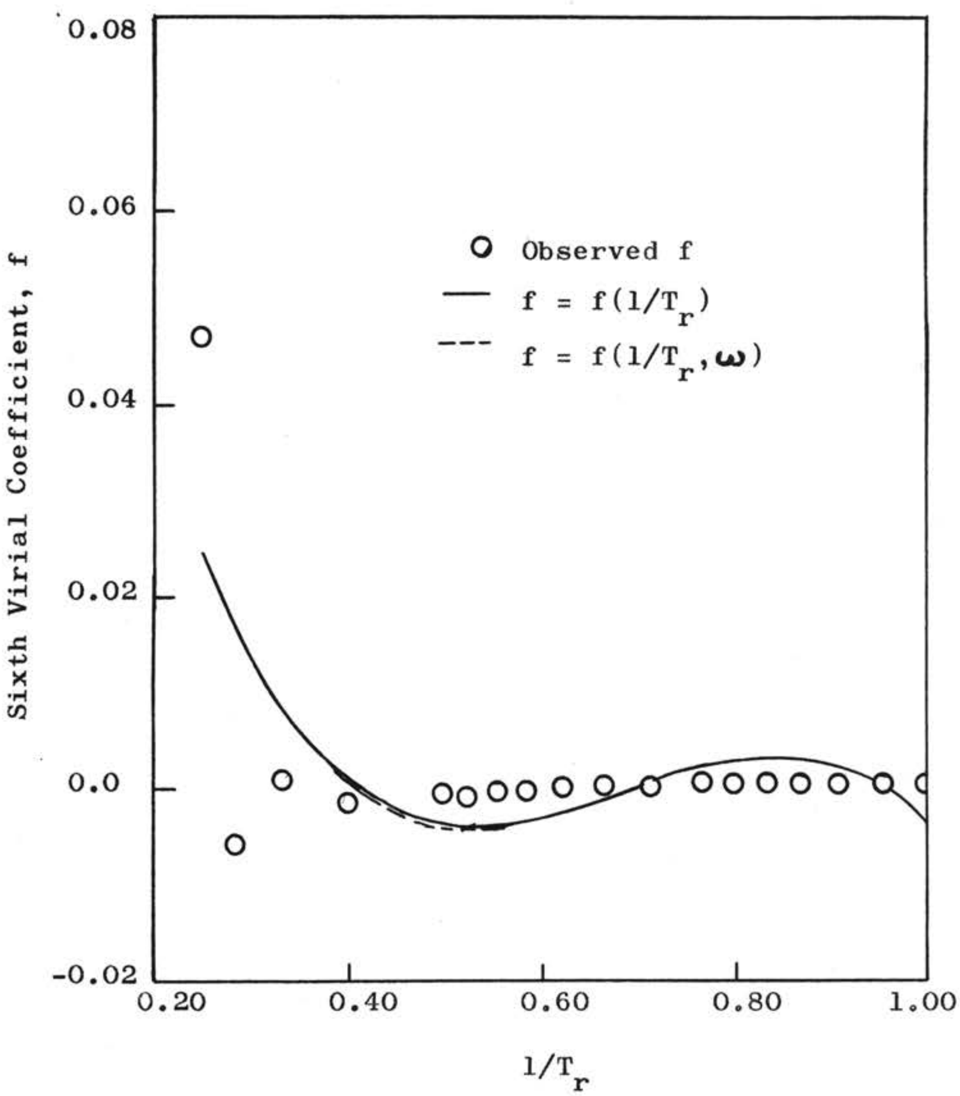


Figure 32

Sixth Virial Coefficient at $\omega = 0.3$

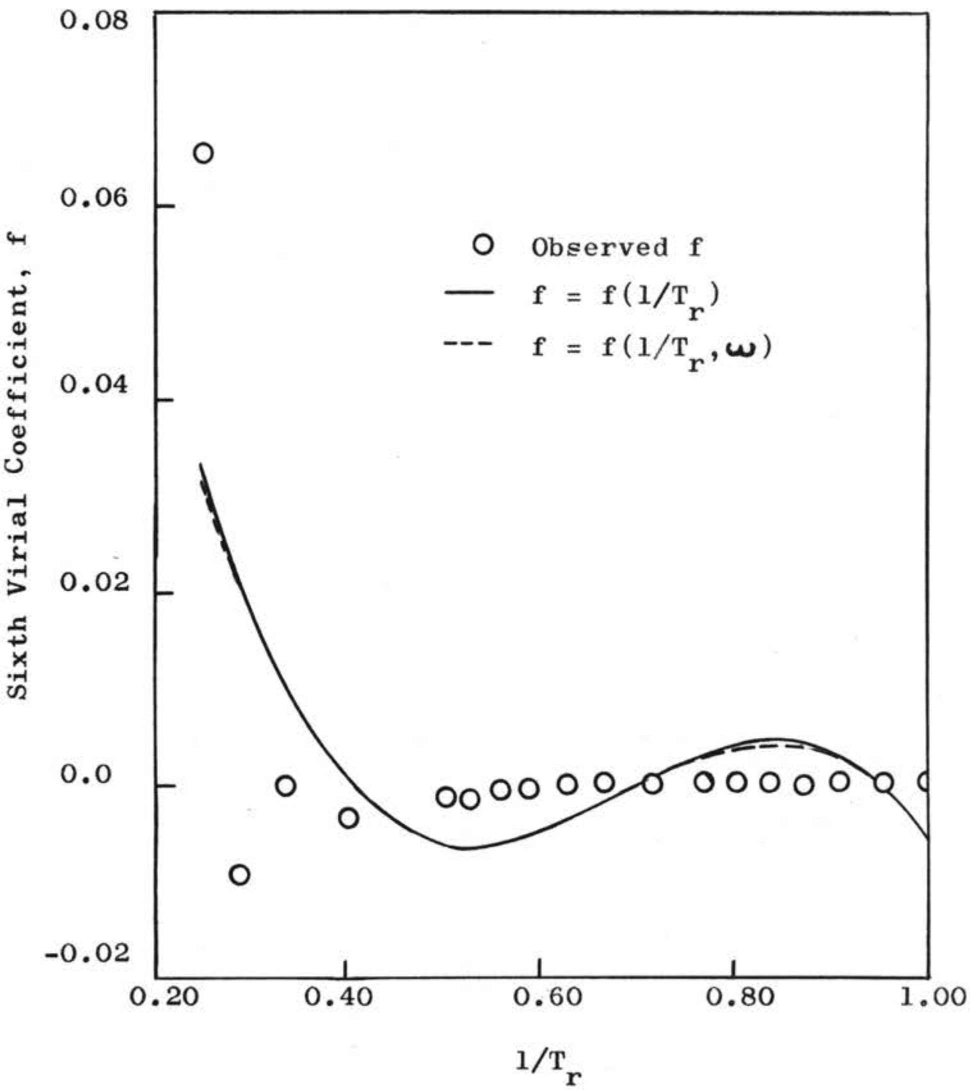


Figure 33

Sixth Virial Coefficient at ω = 0.4

The final step in the derivation of the virial coefficient correlations was to correlate the temperature coefficients of each virial coefficient as a linear function of the acentric factor. The observed values for the virial coefficients were plotted against the acentric factor for a few selected isotherms in Figures 34 to 38 to evaluate the applicability of a linear function in ω. These figures indicate that a linear function in ω is a satisfactory model. This step included a total of 17 regressions for the correlation of 4 temperature coefficients each for the second and third virial coefficients and 3 temperature coefficients each for the fourth, fifth and sixth virial coefficients. The regression of the temperature coefficients completed the derivation of the virial coefficient correlations. The final equations are shown below:

$$b = (0.0059 + 1.3626\omega) + (0.7985 + 9.2397\omega)T_r^{-1} + (-3.350 + 24.7426\omega)T_r^{-2} + (3.7590 - 27.6009\omega)T_r^{-3} + (-1.5531 + 10.6970\omega)T_r^{-4} \quad (24)$$

$$c = (0.1775 - 6.1627\omega) + (-1.8513 + 45.6754\omega)T_r^{-1} + (5.9075 - 117.0395\omega)T_r^{-2} + (-7.2556 + 124.7859\omega)T_r^{-3} + (3.0321 - 47.2971\omega)T_r^{-4} \quad (25)$$

$$d = (0.1851 + 2.2206\omega) + (-0.7741 - 11.6781\omega)T_r^{-1} + (1.0403 + 18.6123\omega)T_r^{-2} + (-0.4292 - 9.2858\omega)T_r^{-3} \quad (26)$$

$$e = (-0.0934 - 1.5872\omega) + (0.3872 + 8.1722\omega)T_r^{-1} + (-0.5186 - 12.8771\omega)T_r^{-2} + (0.2202 + 6.3621\omega)T_r^{-3} \quad (27)$$

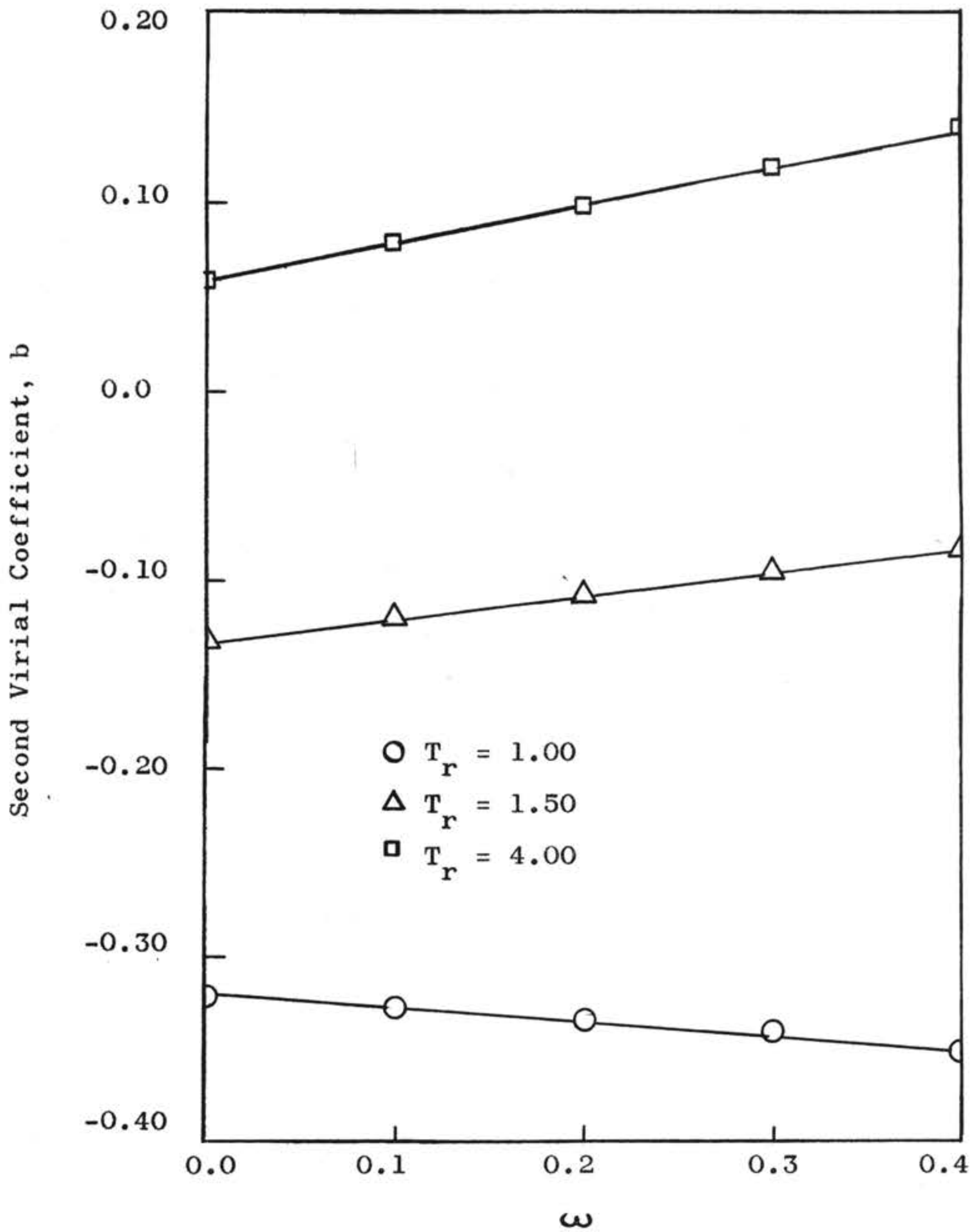


Figure 34

Effect of Acentric Factor
on Second Virial Coefficient

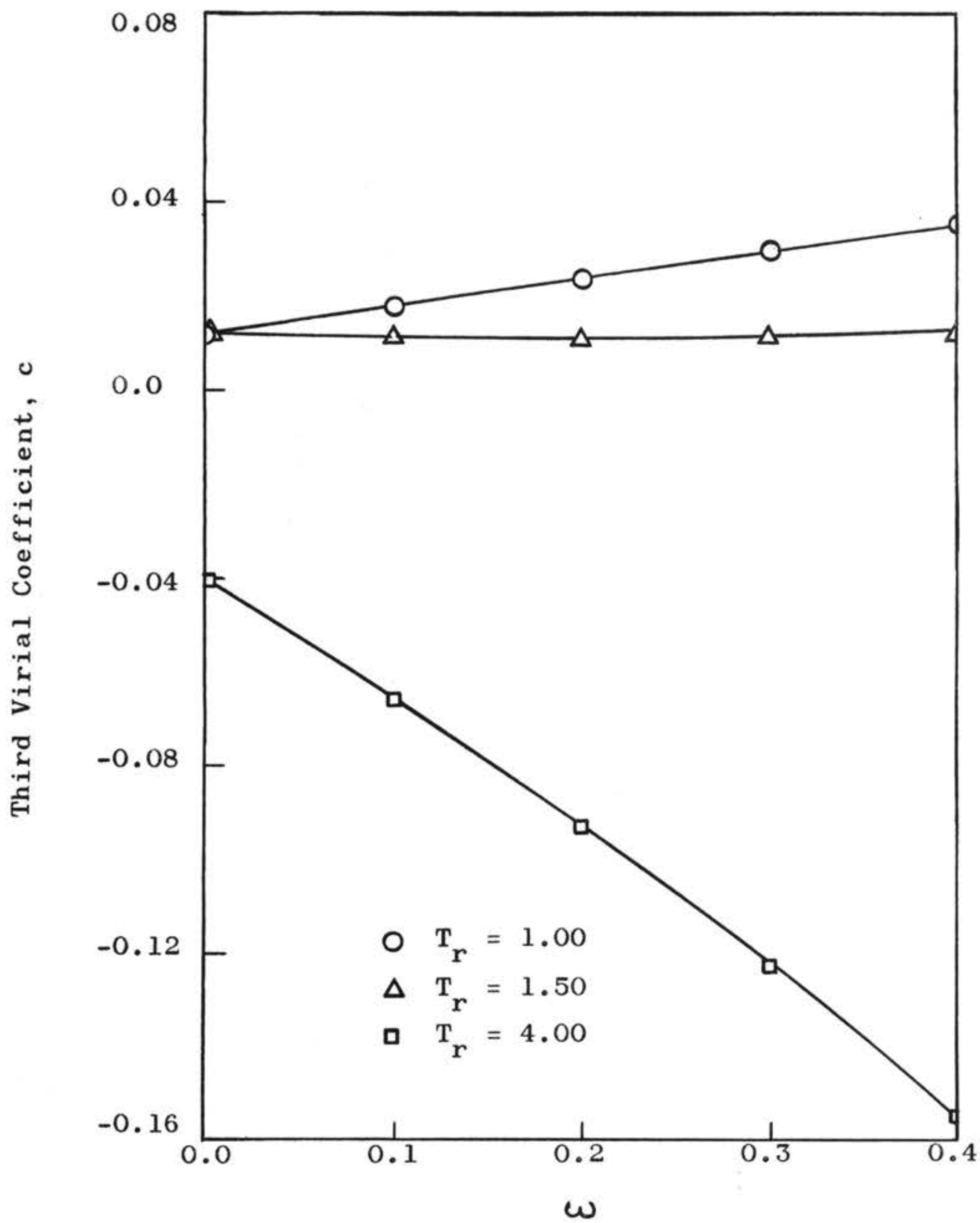


Figure 35

Effect of Acentric Factor
on Third Virial Coefficient

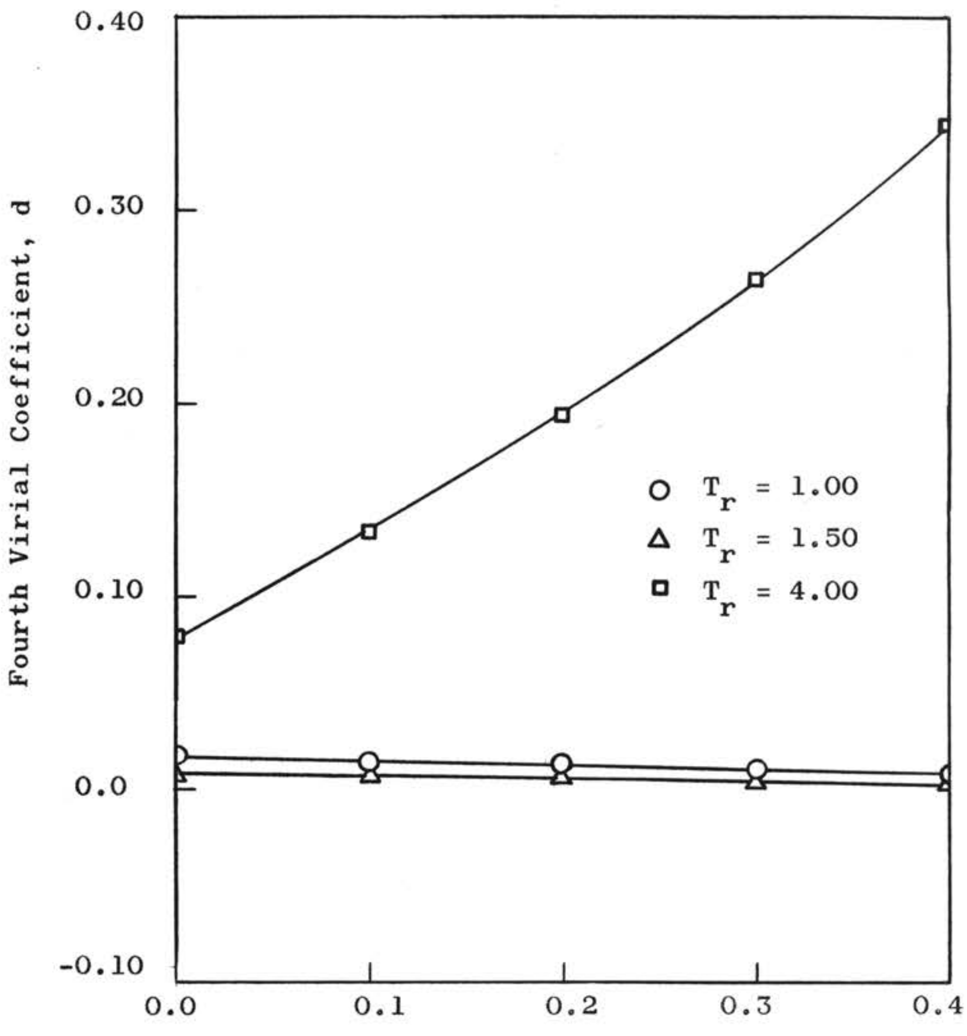


Figure 36

Effect of Acentric Factor
on Fourth Virial Coefficient

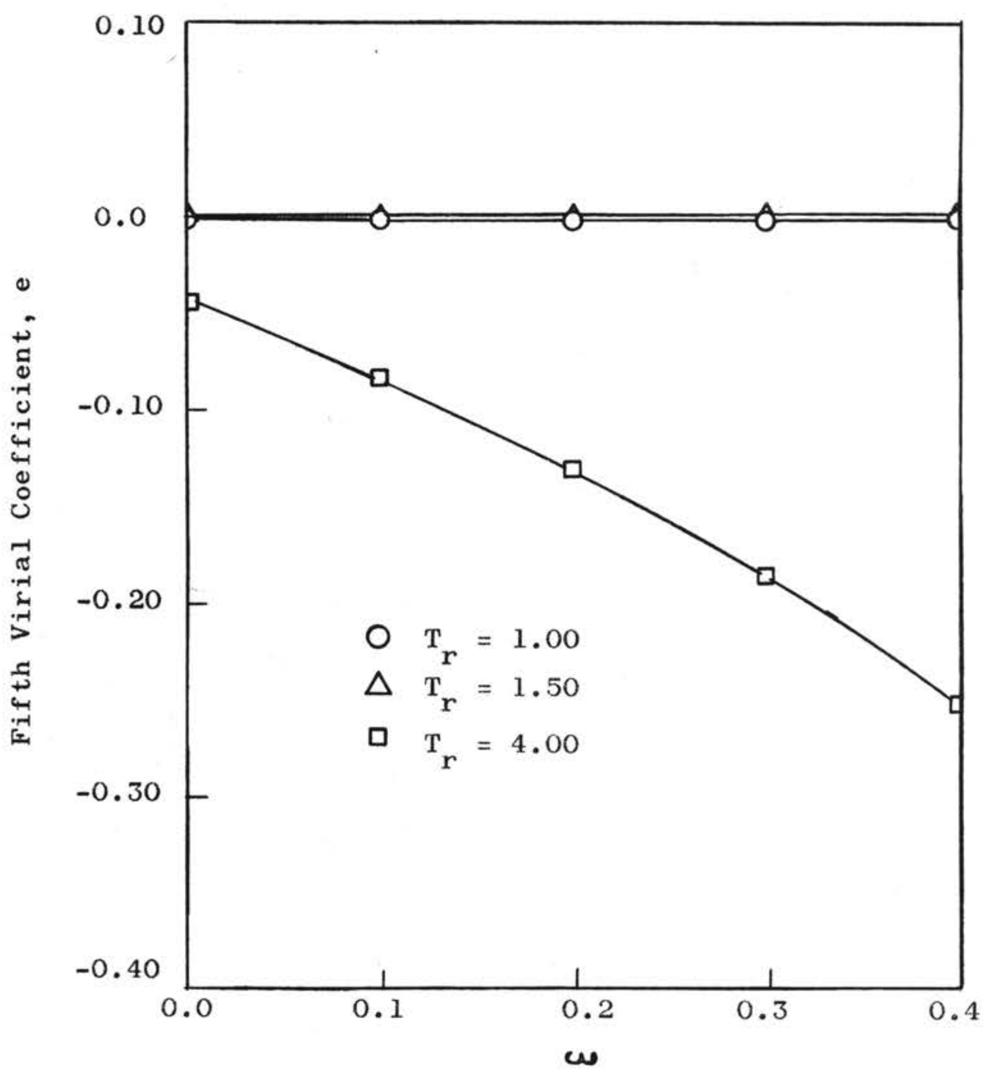


Figure 37

Effect of Acentric Factor
on Fifth Virial Coefficient

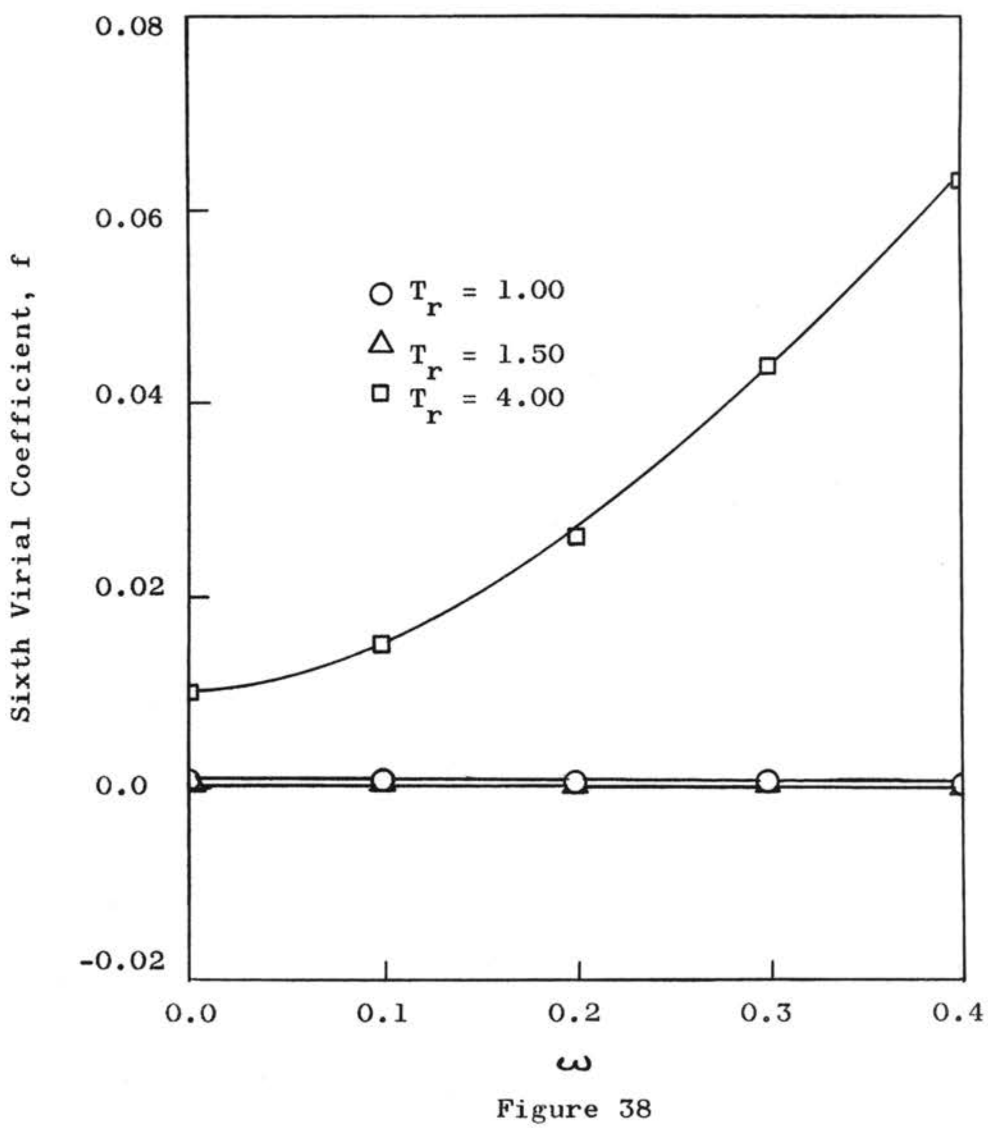


Figure 38

Effect of Acentric Factor on Sixth Virial Coefficient

$$f = (0.0172 + 0.073\omega) + (-0.0718 - 0.0198\omega)T_r^{-1}$$
$$+ (0.0973 + 3.0921\omega)T_r^{-2} + (-0.0425 - 1.5149\omega)T_r^{-3} \quad (28)$$

These equations were used to recalculate virial coefficients and are also shown in Figures 9 to 33. These results agree well with the values calculated with the temperature derived coefficients, which supports the selection of the linear model for correlation with the acentric factor.

A comparison of the second virial coefficient b as calculated from the derived correlation and Pitzer's second virial coefficient is shown for acentric factors of 0.0 and 0.4 in Figures 39 and 40, respectively. These figures indicate a good agreement between the derived second virial coefficient correlation and Pitzer's correlation.

A comparison of virial coefficients calculated from the derived correlations and the observed values derived from the regression of equation (23) can be illustrated in another manner by plotting the calculated values versus the observed values as shown in Figures 41 to 46. Comparisons are shown for the second virial coefficient b at acentric factors of 0.0 and 0.4 and for the remaining virial coefficients at an acentric factor of 0.0.

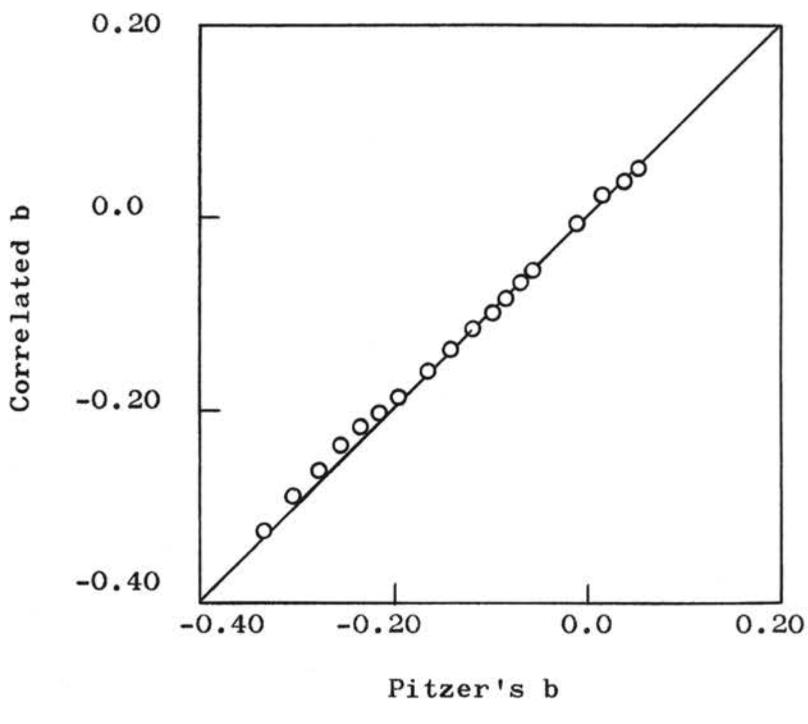


Figure 39

Comparison of Correlated b
and Pitzer's b at $\omega = 0.0$

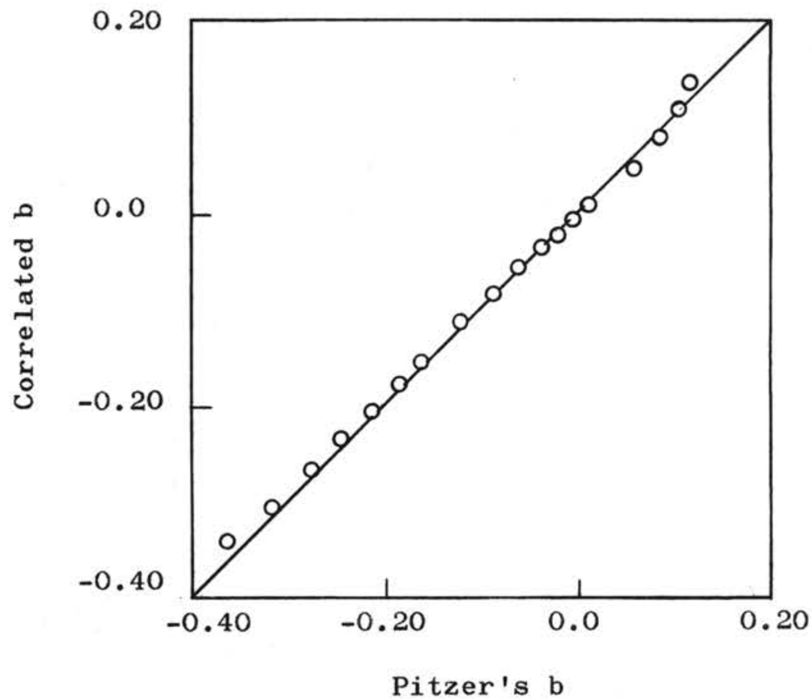


Figure 40

Comparison of Correlated b
and Pitzer's b at ω = 0.4

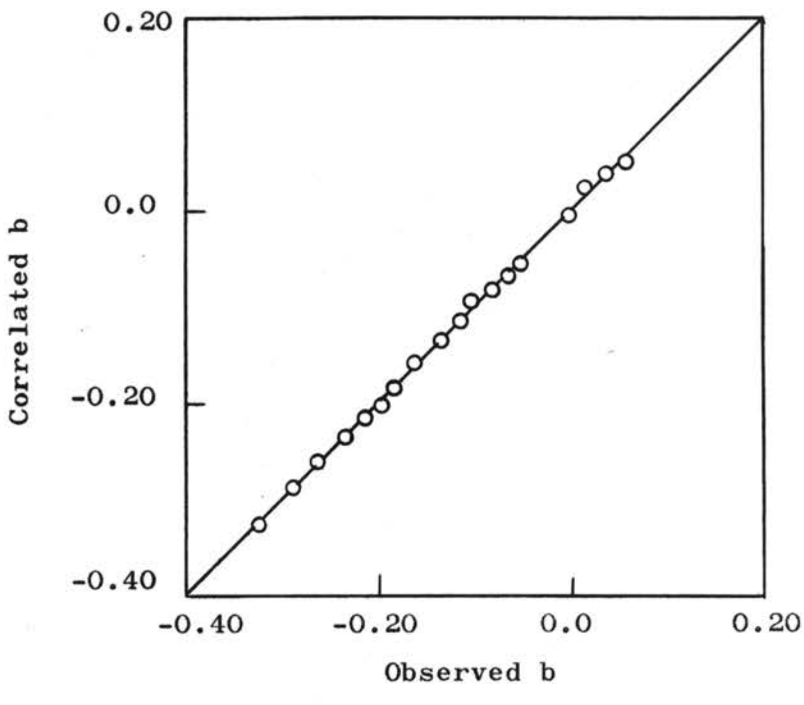


Figure 41

Comparison of Correlated b
and Observed b at ω = 0.0

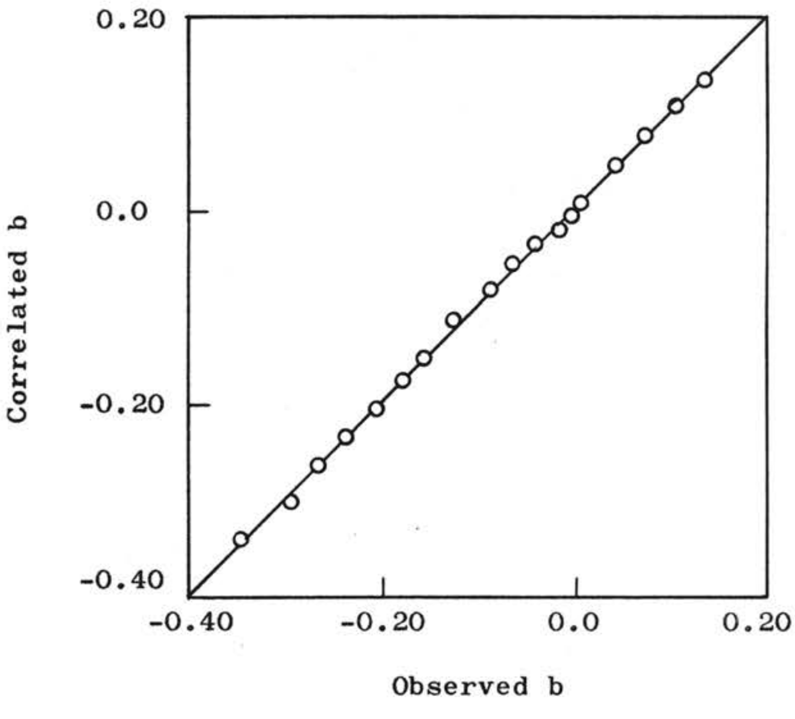


Figure 42

Comparison of Correlated b
and Observed b at ω = 0.4

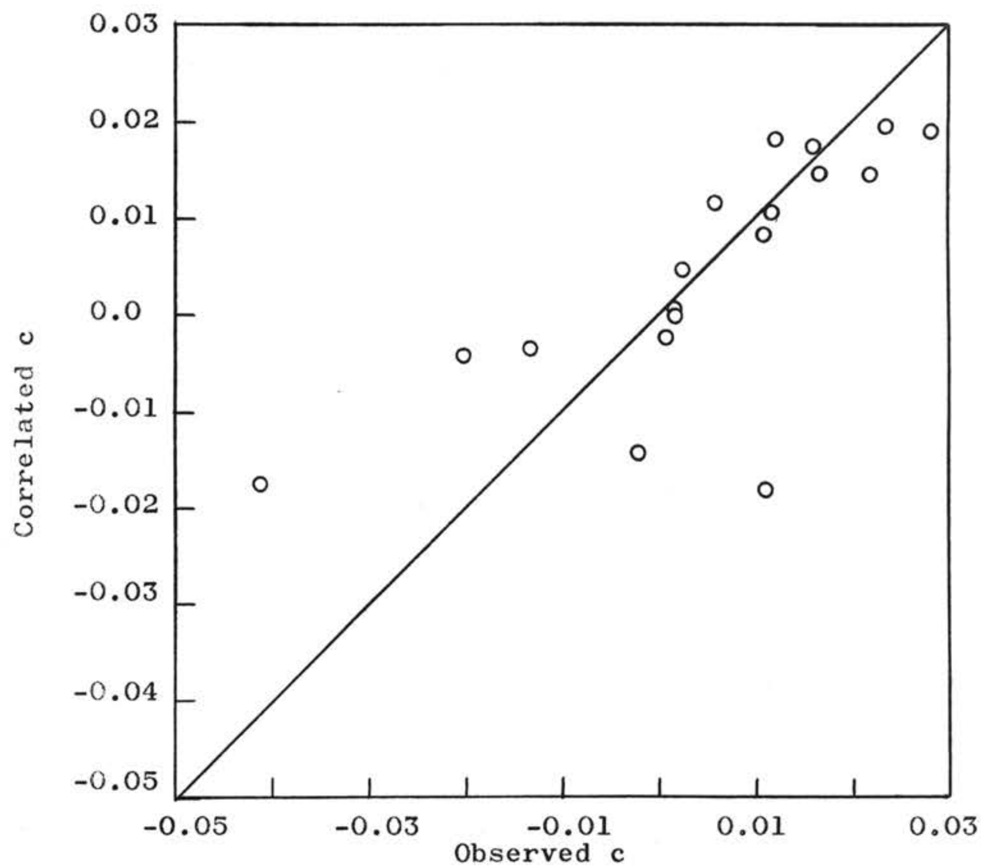


Figure 43

Comparison of Correlated c
and Observed c at ω = 0.0

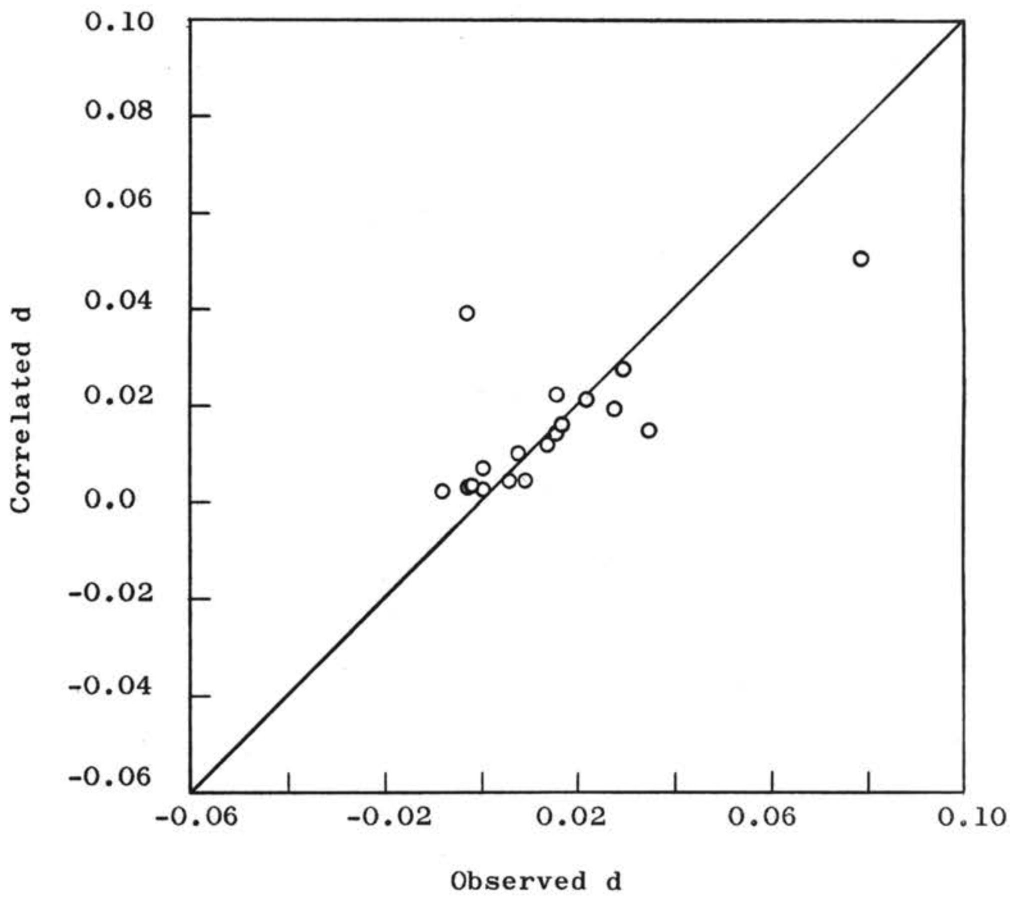


Figure 44

Comparison of Correlated d
and Observed d at $\omega = 0.0$

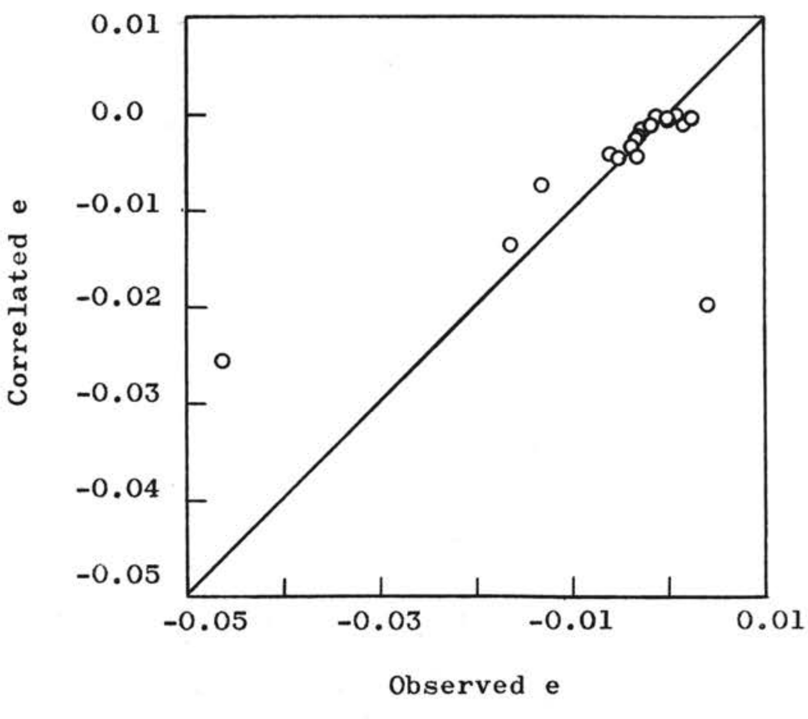


Figure 45

Comparison of Correlated e
and Observed e at $\omega = 0.0$

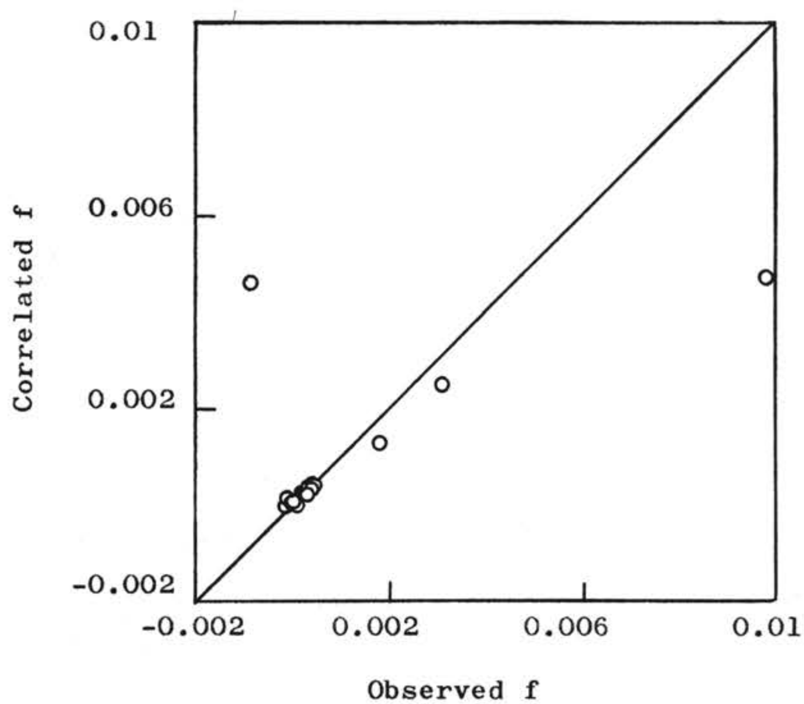


Figure 46

Comparison of Correlated f
and Observed f at ω = 0.0

CHAPTER IV

CALCULATION OF THERMODYNAMIC PROPERTIES

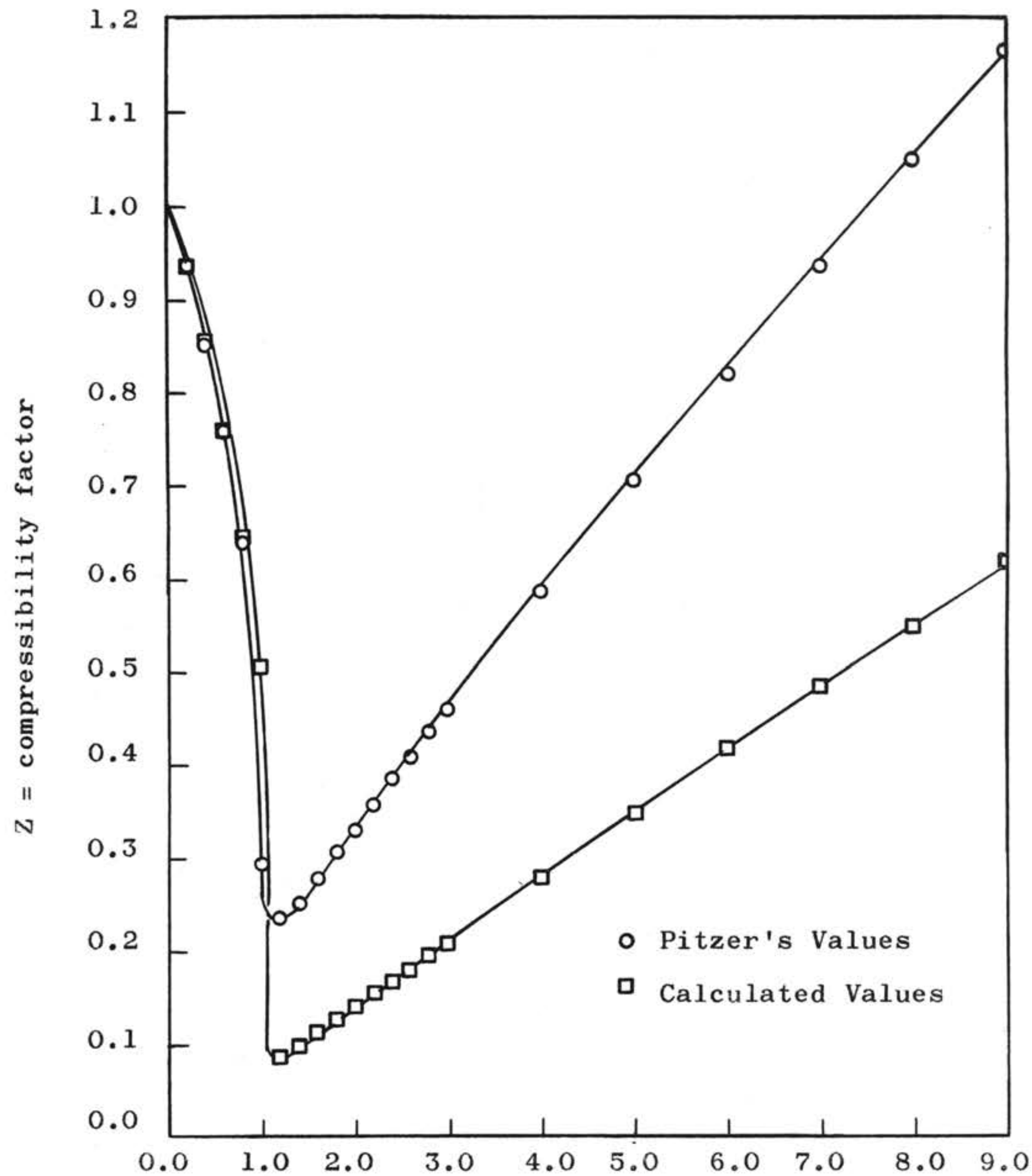
The virial coefficient correlations were tested by calculating generalized compressibility factors with the generalized virial equation of state, equation (7), generalized fugacity coefficients with equation (21) and generalized enthalpies with the following equation:

$$\frac{H^\circ - H}{RT_c} = -T_r \left[\rho_r \left(b - T_r \frac{\partial b}{\partial T_r}\right) + \rho_r^2 \left(c - \frac{T_r}{2} \frac{\partial c}{\partial T_r}\right) + \rho_r^3 \left(d - \frac{T_r}{3} \frac{\partial d}{\partial T_r}\right) + \ldots \right] \qquad (29)$$

The derivation of equation (29) is shown in Appendix H.

The calculation of these thermodynamic properties was made at a reduced temperature of 1.00 and an acentric factor of 0.0. In addition to the generalized compressibility factor and fugacity coefficient tabulations, Pitzer developed a tabulation of generalized enthalpies (12). These enthalpy values were also developed as functions of the acentric factor and are tabulated as a simple fluid term and a deviation term. The compressibility factors, fugacity coefficients, and enthalpies calculated with the derived virial coefficient correlations are compared with Pitzer's values in Figures 47, 48, and 49, respectively.

Figure 47 indicates the virial equation of state is valid at low pressures, but yields compressibility factors which differ



P_r = reduced pressure

Figure 47

Comparison of Calculated Compressibility Factors and Pitzer's Values at T_r = 1.00 and ω = 0.0

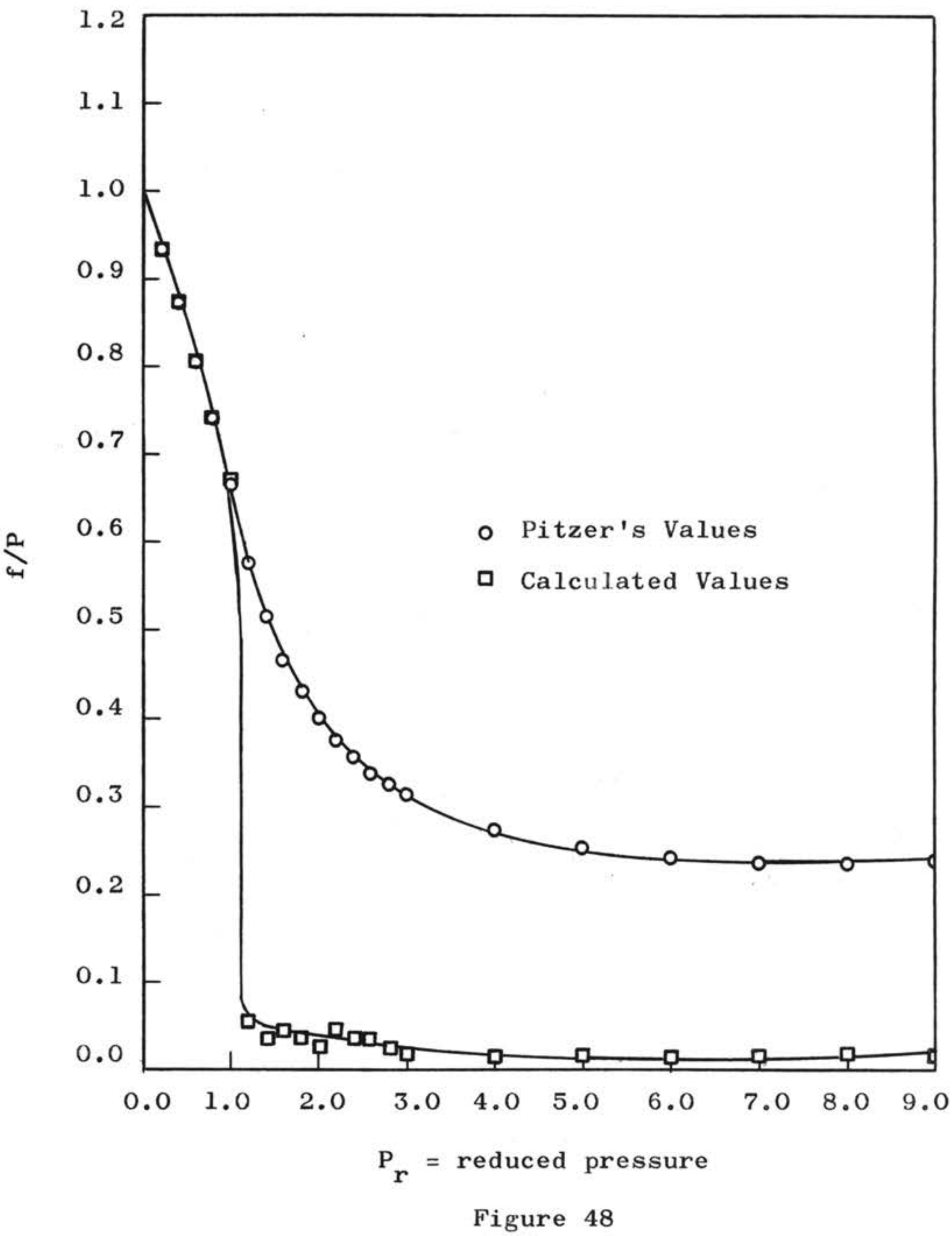


Figure 48

Comparison of Calculated Fugacity Coefficients and Pitzer's Values at T_r = 1.00 and ω = 0.0

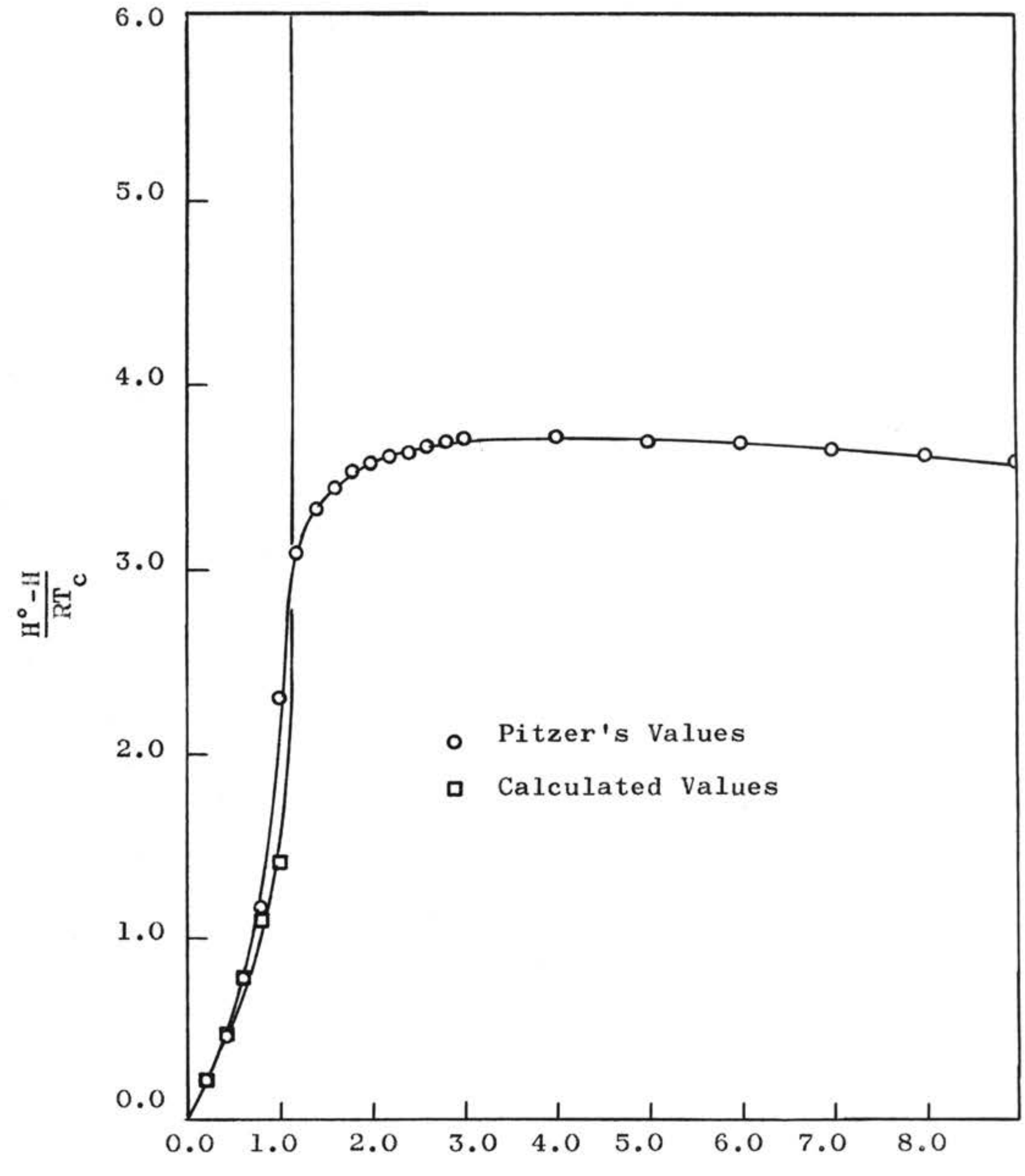


Figure 49

Comparison of Calculated Enthalpies and Pitzer's Values at T_r = 1.00 and ω = 0.0

greatly from Pitzer's values at the critical point and higher pressures. This difference increases with pressure, with the calculated compressibility factor 47% in error at a reduced pressure of 9.0.

Figure 48 also indicates the virial coefficient correlations can be used to calculate fugacity coefficients at low pressures. However, fugacity coefficients calculated at pressures above the critical pressure differ greatly from Pitzer's values. The deviations from Pitzer's values follow the trends in the compressiblity factor results. This result is not surprising since the compressibility factor is used in the calculation of fugacity coefficients.

Generalized enthalpies calculated with equation (29) require a good cross-correlation of virial coefficients with temperature as first temperature derivatives of virial coefficients are used in this calculation. Calculated enthalpies agree with Pitzer's values up to the critical point as shown in Figure 49. However, Pitzer's values can not be reproduced above the critical pressure. These results point up the poor temperature dependency of the third through the sixth generalized virial coefficients.

At low pressures, the virial equation of state can be truncated after the term containing the second virial coefficient b as higher ordered terms tend to zero. As shown previously in Figures 9 to 13, a good correlation was derived for the second virial coefficient. This satisfactory correlation for b substantiates the accurate calculation of thermodynamic properties at low pressures. At the higher pressures, the remaining virial coefficients have a significant effect on the calculation of thermodynamic properties, and, as seen previously, the temperature dependency of the third through the sixth virial coefficients could not be represented satisfactorily with a polynomial function.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Using multiple linear regression of the generalized quantity $(Z-1)/\rho_r$ as a function of ρ_r, the second through the sixth generalized virial coefficients can be derived. The values of the virial coefficients for each individual isotherm can predict accurately the generalized quantity $(Z-1)/\rho_r$ used in their derivation. However, only the generalized second virial coefficient can be correlated satisfactorily with reduced temperature and the acentric factor. Even though the remaining virial coefficients can be used to reproduce accurately the variable used in their derivation, they are not continuous functions of temperature and can not be represented satisfactorily as a polynomial function of reduced temperature.

In addition, the derived virial coefficient correlations can not be used to calculate thermodynamic properties except in regions of low pressure. But in these areas, the second virial coefficient alone is sufficient to predict PVT behavior accurately. A good cross-correlation of virial coefficients with temperature is particularly important in the calculation of enthalpy differences as first temperature derivatives of virial coefficients are used in these calculations.

Some inaccuracy is inherent in transforming specific PVT data into the generalized values. Pitzer states that the data used in the development of the generalized compressibility factors were sparse above $P_r = 3.0$ and $T_r = 2.00$ (18). However, any inaccuracy in the generalized values was not reflected in the correlation as the observed virial coefficients derived from the original regressions were satisfactory as stated above.

The possibility exists that virial coefficients can not be utilized in practical engineering problems and must be restricted to theoretical considerations. The unsatisfactory results obtained with the generalized virial equation of state are in line with the concepts of other workers in the field. Obert and Hirschfelder, et al., state that the virial equation of state is restricted to gases at low to moderate densities (11, 15). Butcher and Dadson indicate that coefficients obtained by regression of PVT data are not necessarily identical with true virial coefficients (4).

The conclusion is made that generalized virial coefficient correlations based on Pitzer's generalized vapor phase compressibility factor tabulations can not be obtained by multiple linear regression. None of the results generated in this work indicates that a surface-fit of these tabulations would be advantageous. Future efforts should be concentrated on the "slope-intercept" or graphical method of deriving virial coefficients. Based on Stuckey's success in developing a correlation for the generalized third virial coefficient c, this correlation and Pitzer's second virial coefficient correlation should be used to investigate additional virial coefficients via the "slope-intercept" technique.

BIBLIOGRAPHY

1. Beattie, J.A. and O. C. Bridgeman, "A New Equation of State for Fluids," Proc. Am. Acad. Arts Sci. 63, 229 (1928).

2. Benedict, M., G. B. Webb, and L. C. Rubin, "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtues. Constants for Twelve Hydrocarbons," Chem. Eng. Progr. 47, 419 (1951).

3. Bush, D. E. and T. E. Short, Private communication, March, 1963.

4. Butcher, E. G. and R. S. Dadson, "The Virial Coefficients of the Carbon Dioxide-Ethylene System. I. Pure Gases," Proc. Roy. Soc. 277, 448 (1964).

5. Dodge, B. F., Chemical Engineering Thermodynamics, McGraw-Hill Book Co., Inc., New York (1944), p. 178.

6. Douslin, D. R., "Pressure-Volume-Temperature Relations and Intermolecular Potentials for Methane and Tetrafluoromethane," Progress in International Research on Thermodynamics and Transport Properties, ASME, New York (1962), p. 153.

7. Edmister, W. C., Applied Hydrocarbon Thermodynamics, Gulf Publishing Company, Houston, Texas (1961), p. 10.

8. Edmister, W. C., "Instructions for Derivation of Generalized Virial Equation of State from Pitzer's Tabulations of Z and Z." Interoffice Memorandum of the School of Chemical Engineering, Oklahoma State University, Stillwater, (1963).

9. Edmister, W. C., "Difference between RK and Pitzer's Reduced Pressued." Interoffice Memorandum of the School of Chemical Engineering, Oklahoma State University, Stillwater (1964).

10. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc., New York (1954), p.2

11. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc. New York (1954), p. 132

12. Lewis, G. N. and M. Randall, Thermodynamics, McGraw-Hill Book Co., Inc., New York (1961), p. 605.

13. Martin, J. J. and C. Y. Hou, "Development of an Equation of State for Gases," A.I.Ch.E. Journal 1, 142 (1955).

14. Milne, E. A., "An Extension of the Theorem of the Virial," Phil. Mag. Ser. 6 50, 409 (1925).

15. Obert, E. F., Concepts of Thermodynamics, McGraw-Hill Book Co., Inc., New York (1960), p. 225.

16. Opfell, J. B., C. J. Pings, and B. H. Sage, Equation of State for Hydrocarbons, Monograph on API Research Project 37, API New York (1959), p. 38.

17. Pitzer, K. S., "The Volumetric and Thermodynamic Properties of Fluids. I. Theoretical Basis and Virial Coefficients," J. Am. Chem. Soc. 77, 3427 (1955).

18. Pitzer, K. S., et al., "The Volumetric and Thermodynamic Properties of Fluids, II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," J. Am. Chem. Soc. 77, 3433 (1955).

19. Pitzer, K. S. and R. F. Curl, Jr., "The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient," J. Am. Chem. Soc. 79, 2369 (1957).

20. Redlich, O. and J. N. S. Kwong, "On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions," Chem. Revs. 44, 233 (1949).

21. Smith, J. M. and H.G. Van Ness, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill Book Co., Inc., New York (1959), p. 90.

22. Steel, R. D. G. and J. H. Torrie, Principles and Procedures of Statistics, McGraw-Hill Book Co., Inc., New York (1960), p. 277.

23. Stuckey, A. N., Jr., "On the Development of an Ideal K-Value Correlation for Hydrocarbons and Associated Gases," M.S. Thesis, Oklahoma State University, Stillwater, (1963).

24. Su, G.-J. and C.-H. Chang, "Generalized Beattie-Bridgeman Equation of State for Real Gases," J. Am. Chem. Soc. 68, 1080 (1946).

APPENDIX A

NOMENCLATURE

a = constant in Redlich-Kwong equation of state

b = generalized second virial coefficient; constant in Redlich-Kwong equation of state

B = second virial coefficient in Leiden virial equation of state

c = generalized third virial coefficient

C = third virial coefficient in Leiden virial equation of state

d = generalized fourth virial coefficient

D = fourth virial coefficient in Leiden virial equation of state

e = generalized fifth virial coefficient

f = generalized sixth virial coefficient; fugacity coefficient

g = generalized seventh virial coefficient

H = enthalpy

P = pressure

R = ideal gas law constant; residual or difference

T = temperature

V = volume

Z = compressibility factor

ρ = density

ω = acentric factor

Superscripts

o = pure component value; ideal gas state value

(o) = universal function of reduced temperature and pressure at = 0

(') = universal function of reduced temperature and pressure that is dependent on the acentric factor

Subscripts

c = critical values

ci = critical ideal values

P = refers to pressure residual

r = reduced values

RK = reduced pressures calculated via Redlich-Kwong equation of state

ri = ideal reduced

APPENDIX B

PITZER'S COMPRESSIBILITY FACTOR TABULATIONS

Pitzer's compressibility factor tabulations for the 18 vapor phase isotherms covering values used in the derivation of the generalized virial coefficients are tabulated here for reference. Table B-I is a tabulation of the simple fluid compressibility factors for an acentric factor of zero. Table B-II is a tabulation of the corrections for deviation from simple fluid behavior.

TABLE B-I

SIMPLE FLUID COMPRESSIBILITY FACTOR, $Z^{(o)}$

	P_r						
T_r	0.2	0.4	0.6	0.8	1.0	1.2	1.4
1.00	0.932	0.849	0.756	0.638	0.291	0.231	0.250
1.05	0.942	0.874	0.800	0.714	0.609	0.470	0.341
1.10	0.950	0.893	0.833	0.767	0.691	0.607	0.512
1.15	0.958	0.908	0.858	0.805	0.746	0.684	0.620
1.20	0.963	0.921	0.879	0.835	0.788	0.737	0.690
1.25	0.968	0.930	0.896	0.858	0.820	0.778	0.740
1.30	0.971	0.940	0.909	0.878	0.846	0.811	0.780
1.40	0.977	0.952	0.929	0.908	0.883	0.859	0.838
1.50	0.982	0.963	0.945	0.927	0.909	0.892	0.875
1.60	0.985	0.971	0.957	0.944	0.930	0.917	0.904
1.70	0.988	0.977	0.966	0.956	0.946	0.936	0.926
1.80	0.991	0.982	0.974	0.966	0.958	0.950	0.944
1.90	0.993	0.986	0.980	0.974	0.968	0.962	0.958
2.00	0.995	0.989	0.984	0.979	0.975	0.971	0.968
2.50	1.000	0.999	0.999	0.998	0.998	0.998	0.998
3.00	1.001	1.002	1.003	1.004	1.005	1.007	1.008
3.50	1.002	1.004	1.006	1.008	1.011	1.013	1.015
4.00	1.003	1.005	1.008	1.010	1.013	1.015	1.017

TABLE B-I (cont'd)

SIMPLE FLUID COMPRESSIBILITY FACTOR, $Z^{(o)}$

	P_r						
T_r	1.6	1.8	2.0	2.2	2.4	2.6	2.8
1.00	0.278	0.304	0.329	0.356	0.381	0.407	0.433
1.05	0.320	0.332	0.350	0.372	0.393	0.417	0.441
1.10	0.442	0.408	0.402	0.405	0.420	0.440	0.462
1.15	0.562	0.514	0.484	0.477	0.478	0.485	0.498
1.20	0.640	0.598	0.568	0.553	0.545	0.544	0.548
1.25	0.702	0.664	0.636	0.618	0.606	0.599	0.597
1.30	0.749	0.718	0.691	0.671	0.657	0.649	0.644
1.40	0.817	0.795	0.777	0.759	0.745	0.734	0.725
1.50	0.859	0.844	0.831	0.819	0.808	0.800	0.794
1.60	0.893	0.882	0.872	0.863	0.855	0.848	0.843
1.70	0.919	0.911	0.903	0.896	0.889	0.883	0.879
1.80	0.937	0.931	0.926	0.921	0.916	0.913	0.910
1.90	0.952	0.948	0.944	0.940	0.936	0.933	0.931
2.00	0.964	0.961	0.959	0.956	0.954	0.953	0.953
2.50	0.997	0.999	1.000	1.001	1.001	1.002	1.004
3.00	1.010	1.012	1.014	1.016	1.019	1.022	1.025
3.50	1.018	1.020	1.022	1.024	1.027	1.030	1.033
4.00	1.020	1.022	1.024	1.026	1.029	1.032	1.035

TABLE B-I (cont'd)

SIMPLE FLUID COMPRESSIBILITY FACTOR, $Z^{(o)}$

	P_r						
T_r	3.0	4.0	5.0	6.0	7.0	8.0	9.0
1.00	0.458	0.582	0.702	0.819	0.932	1.048	1.166
1.05	0.466	0.580	0.700	0.814	0.923	1.032	1.147
1.10	0.484	0.589	0.699	0.810	0.916	1.019	1.129
1.15	0.513	0.600	0.705	0.809	0.911	1.008	1.113
1.20	0.554	0.618	0.714	0.810	0.907	1.000	1.100
1.25	0.598	0.643	0.726	0.816	0.907	0.994	1.088
1.30	0.642	0.668	0.740	0.824	0.910	0.992	1.078
1.40	0.720	0.734	0.781	0.844	0.921	0.994	1.071
1.50	0.790	0.790	0.826	0.877	0.934	1.000	1.070
1.60	0.840	0.835	0.860	0.904	0.953	1.010	1.075
1.70	0.875	0.874	0.895	0.930	0.972	1.023	1.082
1.80	0.908	0.908	0.925	0.955	0.993	1.039	1.091
1.90	0.930	0.934	0.950	0.976	1.010	1.051	1.097
2.00	0.952	0.956	0.972	0.996	1.027	1.064	1.106
2.50	1.006	1.018	1.035	1.055	1.079	1.105	1.136
3.00	1.028	1.041	1.058	1.077	1.100	1.124	1.150
3.50	1.036	1.051	1.067	1.086	1.105	1.126	1.148
4.00	1.038	1.053	1.068	1.086	1.104	1.124	1.143

TABLE B-II

DEVIATION FROM SIMPLE FLUID BEHAVIOR, $Z^{(')}$

T_r	P_r 0.2	0.4	0.6	0.8	1.0	1.2	1.4
1.00	-0.012	-0.016	-0.020	-0.050	-0.080	-0.090	-0.099
1.05	0.000	0.001	0.005	0.015	0.020	0.010	-0.010
1.10	0.002	0.008	0.016	0.030	0.055	0.082	0.110
1.15	0.004	0.012	0.012	0.040	0.064	0.093	0.120
1.20	0.009	0.018	0.028	0.044	0.069	0.100	0.130
1.25	0.011	0.023	0.036	0.050	0.069	0.100	0.130
1.30	0.013	0.027	0.041	0.055	0.072	0.100	0.130
1.40	0.016	0.032	0.049	0.065	0.082	0.100	0.130
1.50	0.017	0.035	0.052	0.070	0.088	0.100	0.130
1.60	0.018	0.036	0.054	0.070	0.080	0.100	0.120
1.70	0.018	0.036	0.054	0.070	0.090	0.100	0.110
1.80	0.018	0.036	0.054	0.070	0.090	0.100	0.110
1.90	0.018	0.035	0.050	0.070	0.090	0.100	0.110
2.00	0.016	0.031	0.050	0.070	0.080	0.100	0.110
2.50	0.010	0.020	0.040	0.050	0.070	0.080	0.100
3.00	0.010	0.020	0.030	0.050	0.060	0.070	0.080
3.50	0.010	0.020	0.030	0.040	0.050	0.060	0.070
4.00	0.010	0.020	0.020	0.030	0.040	0.050	0.060

TABLE B-II (cont'd)

DEVIATION FROM SIMPLE FLUID BEHAVIOR, $Z^{(')}$

T_r	P_r 1.6	1.8	2.0	2.2	2.4	2.6	2.8
1.00	-0.108	-0.115	-0.123	-0.130	-0.130	-0.140	-0.140
1.05	-0.040	-0.060	-0.070	-0.080	-0.090	-0.100	-0.100
1.10	0.082	0.035	0.000	-0.020	-0.030	-0.050	-0.060
1.15	0.140	0.136	0.100	0.070	0.040	0.020	0.000
1.20	0.160	0.170	0.170	0.160	0.140	0.120	0.090
1.25	0.160	0.180	0.190	0.190	0.180	0.160	0.140
1.30	0.160	0.180	0.200	0.200	0.200	0.200	0.190
1.40	0.160	0.180	0.190	0.200	0.210	0.210	0.210
1.50	0.150	0.170	0.180	0.200	0.200	0.210	0.210
1.60	0.140	0.160	0.170	0.180	0.190	0.200	0.200
1.70	0.130	0.150	0.160	0.170	0.180	0.190	0.200
1.80	0.130	0.150	0.160	0.170	0.180	0.190	0.200
1.90	0.130	0.150	0.160	0.170	0.180	0.190	0.200
2.00	0.130	0.140	0.150	0.160	0.170	0.190	0.200
2.50	0.110	0.120	0.130	0.150	0.160	0.180	0.190
3.00	0.090	0.100	0.110	0.130	0.140	0.150	0.160
3.50	0.080	0.080	0.090	0.100	0.110	0.120	0.130
4.00	0.060	0.070	0.080	0.090	0.100	0.100	0.110

TABLE B-II (cont'd)

DEVIATION FROM SIMPLE FLUID BEHAVIOR, $Z^{(')}$

T_r	P_r 3.0	4.0	5.0	6.0	7.0	8.0	9.0
1.00	-0.150	-0.170	-0.200	-0.230	-0.260	-0.300	-0.330
1.05	-0.110	-0.140	-0.170	-0.200	-0.240	-0.280	-0.310
1.10	-0.070	-0.100	-0.130	-0.160	-0.210	-0.250	-0.280
1.15	-0.010	-0.040	-0.080	-0.120	-0.160	-0.200	-0.240
1.20	0.070	0.000	-0.040	-0.080	-0.120	-0.160	-0.190
1.25	0.120	0.050	0.000	-0.030	-0.070	-0.110	-0.130
1.30	0.180	0.100	0.040	0.000	-0.040	-0.070	-0.090
1.40	0.200	0.150	0.110	0.070	0.040	0.010	-0.010
1.50	0.210	0.200	0.170	0.140	0.110	0.090	0.070
1.60	0.210	0.220	0.210	0.190	0.170	0.150	0.140
1.70	0.210	0.240	0.250	0.260	0.250	0.240	0.220
1.80	0.210	0.260	0.290	0.310	0.320	0.320	0.300
1.90	0.210	0.260	0.300	0.350	0.380	0.400	0.400
2.00	0.210	0.260	0.300	0.350	0.400	0.430	0.450
2.50	0.200	0.250	0.300	0.350	0.400	0.450	0.500
3.00	0.170	0.230	0.280	0.340	0.380	0.450	0.500
3.50	0.140	0.190	0.240	0.280	0.330	0.380	0.420
4.00	0.120	0.160	0.200	0.230	0.270	0.310	0.350

APPENDIX C

GENERALIZED QUANTITIES USED FOR CORRELATION

Values of the generalized quantities $(Z-1)/\rho_r$ and ρ_r used for correlation are tabulated for the 18 vapor phase isotherms. These tabulations are shown in Tables C-I, C-II, C-III, C-IV, and C-V for acentric factors of 0.0, 0.1, 0.2, 0.3, and 0.4, respectively.

TABLE C-I

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r					
	0.2		0.4		0.6	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	0.2146	-.3169	0.4711	-.3205	0.7937	-.3074
1.05	0.2022	-.2868	0.4359	-.2891	0.7143	-.2800
1.10	0.1914	-.2613	0.4072	-.2628	0.6548	-.2550
1.15	0.1815	-.2314	0.3831	-.2402	0.6081	-.2335
1.20	0.1731	-.2138	0.3619	-.2183	0.5688	-.2127
1.25	0.1653	-.1936	0.3441	-.2034	0.5357	-.1941
1.30	0.1584	-.1830	0.3273	-.1833	0.5077	-.1792
1.40	0.1462	-.1573	0.3001	-.1599	0.4613	-.1539
1.50	0.1358	-.1326	0.2769	-.1336	0.4233	-.1299
1.60	0.1269	-.1182	0.2575	-.1126	0.3918	-.1097
1.70	0.1191	-.1008	0.2408	-.0955	0.3654	-.0931
1.80	0.1121	-.0803	0.2263	-.0795	0.3422	-.0760
1.90	0.1060	-.0660	0.2135	-.0656	0.3222	-.0621
2.00	0.1005	-.0493	0.2022	-.0544	0.3049	-.0525
2.50	0.0800	.0000	0.1602	-.0062	0.2402	-.0042
3.00	0.0666	.0150	0.1331	.0150	0.1994	.0150
3.50	0.0570	.0351	0.1138	.0351	0.1704	.0352
4.00	0.0499	.0602	0.0995	.0502	0.1483	.0538

TABLE C-I (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r = 0.8		P_r = 1.0		P_r = 1.2	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	1.2539	-.2887	3.4364	-.2063	5.1948	-.1480
1.05	1.0671	-.2680	1.5638	-.2500	2.4316	-.2180
1.10	1.0186	-.2808	1.3156	-.2349	1.7972	-.2187
1.15	0.8642	-.2257	1.1656	-.2179	1.5256	-.2071
1.20	0.7984	-.2067	1.0575	-.2005	1.3569	-.1938
1.25	0.7459	-.1904	0.9756	-.1845	1.2339	-.1799
1.30	0.7009	-.1741	0.9093	-.1694	1.1382	-.1661
1.40	0.6293	-.1462	0.8089	-.1446	0.9978	-.1413
1.50	0.5753	-.1269	0.7334	-.1241	0.8969	-.1204
1.60	0.5297	-.1057	0.6720	-.1042	0.8179	-.1015
1.70	0.4922	-.0894	0.6218	-.0868	0.7541	-.0849
1.80	0.4601	-.0739	0.5799	-.0724	0.7018	-.0712
1.90	0.4323	-.0601	0.5437	-.0589	0.6565	-.0579
2.00	0.4086	-.0514	0.5128	-.0488	0.6179	-.0469
2.50	0.3206	-.0062	0.4008	-.0050	0.4810	-.0042
3.00	0.2656	-.0151	0.3317	-.0151	0.3972	-.0176
3.50	0.2268	-.0353	0.2826	-.0389	0.3385	-.0384
4.00	0.1980	-.0505	0.2468	-.0527	0.2956	-.0508

TABLE C-I (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r					
	1.4		1.6		1.8	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	5.6000	-.1339	5.7554	-.1254	5.9211	-.1175
1.05	3.9101	-.1685	4.7619	-.1428	5.1635	-.1294
1.10	2.4858	-.1963	3.2908	-.1696	4.0107	-.1476
1.15	1.9635	-.1935	2.4756	-.1769	3.0452	-.1596
1.20	1.6908	-.1833	2.0833	-.1728	2.5804	-.1603
1.25	1.5135	-.1718	1.8234	-.1634	2.1687	-.1549
1.30	1.3807	-.1593	1.6432	-.1527	1.9284	-.1462
1.40	1.1933	-.1358	1.3988	-.1308	1.6173	-.1268
1.50	1.0667	-.1172	1.2418	-.1135	1.4218	-.1097
1.60	0.9679	-.0992	1.1198	-.0956	1.2755	-.0925
1.70	0.8893	-.0832	1.0241	-.0791	1.1623	-.0766
1.80	0.8239	-.0680	0.9487	-.0664	1.0741	-.0642
1.90	0.7691	-.0546	0.8846	-.0543	0.9993	-.0520
2.00	0.7231	-.0443	0.8299	-.0434	0.9365	-.0416
2.50	0.5611	-.0036	0.6419	-.0047	0.7207	-.0014
3.00	0.4630	-.0173	0.5281	-.0189	0.5929	-.0202
3.50	0.3941	-.0381	0.4491	-.0401	0.5042	-.0397
4.00	0.3441	-.0494	0.3922	-.0510	0.4403	-.0500

TABLE C-I (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r					
	2.0		2.2		2.4	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.0790	-.1104	6.1798	-.1042	6.2992	-.0983
1.05	5.4422	-.1194	5.6324	-.1115	5.8161	-.1044
1.10	4.5228	-.1322	4.9383	-.1205	5.1948	-.1116
1.15	3.5932	-.1436	4.0106	-.1304	4.3660	-.1196
1.20	2.9343	-.1472	3.3153	-.1348	3.6697	-.1240
1.25	2.5157	-.1447	2.8479	-.1341	3.1683	-.1244
1.30	2.2264	-.1388	2.5221	-.1304	2.8100	-.1221
1.40	1.8386	-.1213	2.0704	-.1164	2.3011	-.1108
1.50	1.6045	-.1053	1.7908	-.1011	1.9802	-.0970
1.60	1.4335	-.0893	1.5933	-.0860	1.7544	-.0827
1.70	1.3208	-.0745	1.4443	-.0720	1.5880	-.0699
1.80	1.1999	-.0617	1.3271	-.0595	1.4556	-.0577
1.90	1.1151	-.0502	1.2318	-.0487	1.3495	-.0474
2.00	1.0428	-.0393	1.1506	-.0382	1.2579	-.0365
2.50	0.8000	.0000	0.8791	.0011	0.9590	.0010
3.00	0.6575	.0213	0.7218	.0222	0.7851	.0242
3.50	0.5591	.0393	0.6138	.0391	0.6677	.0404
4.00	0.4883	.0492	0.5361	.0485	0.5831	.0497

TABLE C-I (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r					
	2.6		2.8		3.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.3882	-.0928	6.4665	-.0877	6.5502	-.0827
1.05	5.9381	-.0982	6.0469	-.0924	6.1312	-.0871
1.10	5.3719	-.1042	5.5096	-.0976	5.6349	-.0916
1.15	4.6616	-.1105	4.8891	-.1027	5.0852	-.0958
1.20	3.9828	-.1145	4.2579	-.1062	4.5126	-.0988
1.25	3.4725	-.1155	3.7521	-.1074	4.0134	-.1002
1.30	3.0817	-.1139	3.3445	-.1064	3.5945	-.0996
1.40	2.5302	-.1051	2.7586	-.0997	2.9762	-.0941
1.50	2.1667	-.0923	2.3510	-.0876	2.5316	-.0830
1.60	1.9163	-.0793	2.0759	-.0756	2.2321	-.0717
1.70	1.7321	-.0675	1.8738	-.0646	2.0168	-.0620
1.80	1.5821	-.0550	1.7094	-.0526	1.8355	-.0501
1.90	1.4667	-.0457	1.5829	-.0436	1.6978	-.0412
2.00	1.3641	-.0345	1.4690	-.0320	1.5756	-.0305
2.50	1.0379	.0019	1.1155	.0036	1.1928	.0050
3.00	0.8480	.0259	0.9106	.0275	0.9728	.0288
3.50	0.7212	.0416	0.7744	.0426	0.8274	.0435
4.00	0.6298	.0508	0.6763	.0518	0.7225	.0526

TABLE C-I (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r					
	4.0		5.0		6.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.8729	-.0608	7.1225	-.0418	7.3260	-.0247
1.05	6.5681	-.0639	6.8027	-.0441	7.0200	-.0265
1.10	6.1738	-.0666	6.5028	-.0463	6.7340	-.0282
1.15	5.7971	-.0690	6.1671	-.0478	6.4492	-.0296
1.20	5.3937	-.0708	5.8357	-.0490	6.1728	-.0308
1.25	4.9767	-.0717	5.5096	-.0497	5.8824	-.0313
1.30	4.6062	-.0721	5.1975	-.0500	5.6012	-.0314
1.40	3.8926	-.0683	4.5729	-.0479	5.0779	-.0307
1.50	3.3755	-.0622	4.0355	-.0431	4.5610	-.0270
1.60	2.9940	-.0551	3.6337	-.0385	4.1482	-.0231
1.70	2.6922	-.0468	3.2862	-.0320	3.7951	-.0184
1.80	2.4474	-.0376	3.0030	-.0250	3.4904	-.0129
1.90	2.2540	-.0293	2.7701	-.0180	3.2355	-.0074
2.00	2.0921	-.0210	2.5720	-.0109	3.0120	-.0013
2.50	1.5717	.0115	1.9324	.0181	2.2749	.0242
3.00	1.2808	.0320	1.5753	.0368	1.8570	.0415
3.50	1.0874	.0469	1.3389	.0500	1.5785	.0545
4.00	0.9497	.0558	1.1704	.0581	1.3812	.0623

TABLE C-I (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.0$

	P_r					
	7.0		8.0		9.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.5107	-.0091	7.6336	.0063	7.7187	.0215
1.05	7.2228	-.0107	7.3828	.0043	7.4729	.0197
1.10	6.9472	-.0121	7.1371	.0027	7.2470	.0178
1.15	6.6816	-.0133	6.9013	.0012	7.0315	.0161
1.20	6.4315	-.0145	6.6667	.0000	6.8182	.0147
1.25	6.1742	-.0151	6.4386	-.0009	6.6176	.0133
1.30	5.9172	-.0152	6.2035	-.0013	6.4221	.0121
1.40	5.4289	-.0146	5.7488	-.0010	6.0024	.0118
1.50	4.9964	-.0132	5.3333	.0000	5.6075	.0125
1.60	4.5908	-.0102	4.9505	.0020	5.2326	.0143
1.70	4.2363	-.0066	4.6001	.0050	4.8929	.0168
1.80	3.9163	-.0018	4.2776	.0091	4.5830	.0199
1.90	3.6477	.0027	4.0062	.0127	4.3180	.0225
2.00	3.4080	.0079	3.7594	.0170	4.0687	.0261
2.50	2.5950	.0304	2.8959	.0363	3.1690	.0429
3.00	2.1212	.0471	2.3725	.0523	2.6087	.0575
3.50	1.8100	.0580	2.0299	.0621	2.2399	.0661
4.00	1.5851	..0656	1.7794	.0697	1.9685	.0726

TABLE C-II

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	0.2		0.4		0.6	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	0.2149	-.3221	0.4720	-.3233	0.7958	-.3091
1.05	0.2022	-.2868	0.4358	-.2889	0.7138	-.2795
1.10	0.1913	-.2603	0.4068	-.2610	0.6536	-.2531
1.15	0.1815	-.2292	0.3826	-.2373	0.6072	-.2319
1.20	0.1729	-.2088	0.3612	-.2137	0.5670	-.2085
1.25	0.1651	-.1872	0.3432	-.1972	0.5336	-.1882
1.30	0.1582	-.1751	0.3264	-.1756	0.5055	-.1719
1.40	0.1460	-.1466	0.2991	-.1498	0.4589	-.1440
1.50	0.1355	-.1203	0.2759	-.1214	0.4210	-.1183
1.60	0.1267	-.1042	0.2565	-.0990	0.3897	-.0965
1.70	0.1189	-.0858	0.2399	-.0809	0.3633	-.7872
1.80	0.1119	-.0643	0.2255	-.0639	0.3403	-.0605
1.90	0.1058	-.0491	0.2128	-.0494	0.3206	-.0468
2.00	0.1003	-.0339	0.2016	-.0392	0.3033	-.0363
2.50	0.0799	.0125	0.1598	.0063	0.2393	.0125
3.00	0.0665	.0301	0.1328	.0301	0.1988	.0302
3.50	0.0570	.0527	0.1136	.0528	0.1699	.0530
4.00	0.0498	.0803	0.0993	.0705	0.1485	.0673

TABLE C-II (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	0.8		1.0		1.2	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	1.2638	-.2904	3.5336	-.2029	5.4054	-.1439
1.05	1.0649	-.2672	1.5587	-.2496	2.4264	-.2180
1.10	1.0143	-.2790	1.3052	-.2325	1.7733	-.2170
1.15	0.8599	-.2221	1.1557	-.2142	1.5051	-.2038
1.20	0.7942	-.2022	1.0483	-.1956	1.3387	-.1890
1.25	0.7416	-.1847	0.9675	-.1789	1.2183	-.1740
1.30	0.6965	-.1673	0.9016	-.1628	1.1243	-.1592
1.40	0.6249	-.1368	0.8015	-.1357	0.9864	-.1328
1.50	0.5710	-.1156	0.7264	-.1132	0.8869	-.1105
1.60	0.5258	-.0932	0.6663	-.0930	0.8091	-.0902
1.70	0.4887	-.0757	0.6160	-.0731	0.7462	-.0724
1.80	0.4568	-.0591	0.5745	-.0574	0.6944	-.0576
1.90	0.4292	-.0443	0.5387	-.0427	0.6498	-.0431
2.00	0.4057	-.0345	0.5086	-.0334	0.6116	-.0311
2.50	0.3190	.0094	0.3980	.0126	0.4771	.0126
3.00	0.2643	.0341	0.3297	.0334	0.3945	.0355
3.50	0.2259	.0531	0.2812	.0569	0.3365	.0565
4.00	0.1974	.0658	0.2458	.0692	0.2941	.0680

TABLE C-II (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	1.4		1.6		1.8	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	5.8309	-.1303	5.9880	-.1224	6.1538	-.1150
1.05	3.9126	-.1683	4.8222	-.1418	5.2585	-.1282
1.10	2.4335	-.1960	3.2309	-.1702	3.9766	-.1480
1.15	1.9263	-.1910	2.4155	-.1755	2.9667	-.1592
1.20	1.6596	-.1790	2.0325	-.1692	2.4390	-.1578
1.25	1.4815	-.1647	1.7827	-.1582	2.1114	-.1506
1.30	1.3580	-.1524	1.6088	-.1461	1.8813	-.1403
1.40	1.1751	-.1268	1.3720	-.1217	1.5814	-.1182
1.50	1.0511	-.1066	1.2204	-.1032	1.3937	-.0997
1.60	0.9552	-.0879	1.1025	-.0844	1.2528	-.0814
1.70	0.8789	-.0717	1.0098	-.0673	1.1434	-.0647
1.80	0.8144	-.0553	0.9357	-.0534	1.0571	-.0511
1.90	0.7604	-.0408	0.8726	-.0401	0.9838	-.0376
2.00	0.7150	-.0294	0.8188	-.0281	0.9231	-.0271
2.50	0.5556	.0144	0.6349	.0126	0.7122	.0154
3.00	0.4593	.0348	0.5234	.0363	0.5871	.0375
3.50	0.3914	.0562	0.4456	.0584	0.5003	.0560
4.00	0.3421	.0672	0.3899	.0667	0.4373	.0663

TABLE C-II (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	2.0		2.2		2.4	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.3151	-.1082	6.4140	-.1024	6.5217	-.0969
1.05	5.5532	-.1183	5.7561	-.1105	5.9524	-.1035
1.10	4.5228	-.1322	4.9628	-.1203	5.2322	-.1114
1.15	3.5205	-.1437	3.9526	-.1305	4.3298	-.1196
1.20	2.8490	-.1457	3.2220	-.1338	3.5778	-.1233
1.25	2.4427	-.1412	2.7630	-.1314	3.0769	-.1222
1.30	2.1638	-.1336	2.4491	-.1262	2.7270	-.1184
1.40	1.7947	-.1137	2.0172	-.1096	2.2380	-.1046
1.50	1.5705	-.0961	1.7481	-.0921	1.9324	-.0890
1.60	1.4061	-.0789	1.5607	-.0762	1.7162	-.0734
1.70	1.2802	-.0633	1.4174	-.0614	1.5565	-.0597
1.80	1.1795	-.0492	1.3030	-.0476	1.4276	-.0462
1.90	1.0965	-.0365	1.2099	-.0355	1.3241	-.0347
2.00	1.0267	-.0253	1.1317	-.0247	1.2358	-.0235
2.50	0.7897	.0165	0.8661	.0185	0.9440	.0180
3.00	0.6504	.0384	0.7127	.0407	0.7744	.0426
3.50	0.5542	.0559	0.6079	.0559	0.6606	.0575
4.00	0.4845	.0660	0.5314	.0659	0.5775	.0675

TABLE C-II (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	2.6		2.8		3.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.6158	-.0918	6.6826	-.0869	6.7720	-.0823
1.05	6.0840	-.0975	6.1872	-.0920	6.2794	-.0868
1.10	5.4336	-.1040	5.5821	-.0975	5.7176	-.0915
1.15	4.6424	-.1105	4.8891	-.1027	5.0951	-.0958
1.20	3.8969	-.1139	4.1891	-.1058	4.4563	-.0985
1.25	3.3821	-.1138	3.6661	-.1061	3.9344	-.0991
1.30	2.7270	-.1184	2.9895	-.1107	3.2486	-.1037
1.40	2.4598	-.0996	2.6810	-.0947	2.8958	-.0898
1.50	2.1112	-.0848	2.2904	-.0808	2.4661	-.0766
1.60	1.8721	-.0705	2.0278	-.0676	2.1777	-.0638
1.70	1.6956	-.0578	1.8321	-.0551	1.9695	-.0528
1.80	1.5498	-.0439	1.6726	-.0419	1.7940	-.0396
1.90	1.4374	-.0334	1.5496	-.0316	1.6603	-.0295
2.00	1.3374	-.0209	1.4388	-.0188	1.5416	-.0175
2.50	1.0196	.0196	1.0948	.0210	1.1696	.0222
3.00	0.8357	.0443	0.8966	.0457	0.9569	.0470
3.50	0.7129	.0589	0.7648	.0601	0.8163	.0612
4.00	0.6238	.0673	0.6692	.0687	0.7143	.0700

TABLE C-II (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	4.0		5.0		6.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.0796	-.0614	7.3314	-.0434	7.5377	-.0271
1.05	6.7306	-.0645	6.9720	-.0455	7.1968	-.0286
1.10	6.2804	-.0670	6.6260	-.0474	6.8697	-.0300
1.15	5.8360	-.0692	6.2379	-.0486	6.5463	-.0310
1.20	5.3937	-.0708	5.8685	-.0494	6.2344	-.0318
1.25	4.9383	-.0713	5.5096	-.0497	5.9041	-.0317
1.30	4.5382	-.0710	5.1696	-.0495	5.6012	-.0314
1.40	3.8146	-.0658	4.5094	-.0461	5.0361	-.0296
1.50	3.2922	-.0577	3.9541	-.0397	4.4893	-.0243
1.60	2.9172	-.0490	3.5471	-.0335	4.0628	-.0190
1.70	2.6202	-.0589	3.1969	-.0250	3.6919	-.0119
1.80	2.3793	-.0277	2.9117	-.0158	3.3807	-.0041
1.90	2.1930	-.0182	2.6853	-.0074	3.1235	.0035
2.00	2.0367	-.0088	2.4950	.0008	2.9098	.0107
2.50	1.5340	.0280	1.8779	.0346	2.2018	.0409
3.00	1.2531	.0511	1.5347	.0560	1.8002	.0617
3.50	1.0681	.0655	1.3094	.0695	1.5389	.0741
4.00	0.9355	.0738	1.1489	.0766	1.3526	.0806

TABLE C-II (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.1$

	P_r					
	7.0		8.0		9.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.7263	-.0122	7.8585	-.0023	7.9435	.0167
1.05	7.4156	-.0136	7.5887	.0005	7.6805	.0151
1.10	7.1102	-.0148	7.3166	-.0008	7.4313	.0136
1.15	6.8011	-.0154	7.0410	-.0017	7.1865	.0124
1.20	6.5177	-.0161	6.7751	-.0024	6.9380	.0117
1.25	6.2222	-.0161	6.5107	-.0026	6.6977	.0112
1.30	5.9433	-.0158	6.2476	-.0024	6.4762	.0107
1.40	5.4054	-.0139	5.7430	-.0009	6.0080	.0117
1.50	4.9383	-.0111	5.2858	.0017	5.5710	.0138
1.60	4.5103	-.0067	4.8780	.0051	5.1653	.0172
1.70	4.1300	-.0007	4.4946	.0105	4.7954	.0217
1.80	3.7940	.0066	4.1498	.0171	4.4603	.0271
1.90	3.5155	.0137	3.8593	.0236	4.1661	.0329
2.00	3.2802	.0204	3.6134	.0296	3.9096	.0386
2.50	2.5022	.0476	2.7826	.0539	3.0354	.0613
3.00	2.0504	.0673	2.2812	.0741	2.5000	.0800
3.50	1.7575	.0785	1.9637	.0835	2.1609	.0879
4.00	1.5473	.0847	1.7316	.0895	1.9100	.0932

TABLE C-III

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	0.2		0.4		0.6	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	0.2151	-.3272	0.4729	-.3261	0.7979	-.3108
1.05	0.2022	-.2868	0.4358	-.2887	0.7134	-.2789
1.10	0.1913	-.2595	0.4065	-.2593	0.6523	-.2511
1.15	0.1814	-.2271	0.3821	-.2345	0.6064	-.2302
1.20	0.1727	-.2038	0.3605	-.2091	0.5652	-.2042
1.25	0.1649	-.1807	0.3424	-.1910	0.5314	-.1821
1.30	0.1580	-.1671	0.3255	-.1678	0.5032	-.1645
1.40	0.1457	-.1359	0.2981	-.1395	0.4565	-.1341
1.50	0.1353	-.1079	0.2749	-.1091	0.4187	-.1065
1.60	0.1264	-.0902	0.2556	-.0853	0.3875	-.0831
1.70	0.1186	-.0708	0.2391	-.0661	0.3613	-.0642
1.80	0.1117	-.0483	0.2246	-.0481	0.3385	-.0449
1.90	0.1056	-.0322	0.2120	-.0330	0.3190	-.0314
2.00	0.1002	-.0180	0.2010	-.0239	0.3018	-.0199
2.50	0.0798	.0250	0.1595	.0188	0.2383	.0294
3.00	0.0665	.0451	0.1325	.0453	0.1982	.0455
3.50	0.0569	.0703	0.1134	.0706	0.1694	.0708
4.00	0.0498	.1005	0.0991	.0908	0.1482	.0810

TABLE C-III (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	0.8		1.0		1.2	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	1.2739	-.2920	3.6364	-.1994	5.6338	-.1397
1.05	1.0626	-.2663	1.5536	-.2491	2.4213	-.2181
1.10	1.0101	-.2772	1.2950	-.2301	1.7499	-.2152
1.15	0.8557	-.2185	1.1460	-.2105	1.4852	-.2002
1.20	0.7901	-.1977	1.0393	-.1907	1.3210	-.1840
1.25	0.7373	-.1790	0.9595	-.1732	1.2030	-.1679
1.30	0.6922	-.1604	0.8940	-.1561	1.1108	-.1521
1.40	0.6204	-.1273	0.7942	-.1267	0.9751	-.1241
1.50	0.5668	-.1041	0.7195	-.1020	0.8772	-.1003
1.60	0.5219	-.0805	0.6607	-.0817	0.8004	-.0787
1.70	0.4851	-.0618	0.6102	-.0590	0.7384	-.0596
1.80	0.4535	-.0441	0.5692	-.0422	0.6873	-.0436
1.90	0.4262	-.0282	0.5338	-.0262	0.6432	-.0280
2.00	0.4028	-.0174	0.5045	-.0178	0.6054	-.0149
2.50	0.3175	.0252	0.3953	.3036	0.4734	.0296
3.00	0.2630	.0532	0.3278	.0519	0.3918	.0536
3.50	0.2250	.0711	0.2798	.0750	0.3345	.0747
4.00	0.1969	.0813	0.2449	.0858	0.2927	.0854

TABLE C-III (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	1.4		1.6		1.8	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.0817	-.1266	6.2402	-.1192	6.4057	-.1122
1.05	3.9331	-.1681	4.8840	-.1409	5.3571	-.1269
1.10	2.3834	-.1955	3.1731	-.1707	3.9430	-.1484
1.15	1.8904	-.1883	2.3581	-.1739	2.8921	-.1586
1.20	1.6294	-.1743	1.9841	-.1653	2.3734	-.1551
1.25	1.4508	-.1572	1.7439	-.1525	2.0571	-.1458
1.30	1.3361	-.1452	1.5759	-.1390	1.8364	-.1340
1.40	1.1574	-.1175	1.3461	-.1122	1.5472	-.1092
1.50	1.0359	-.0956	1.1998	-.0925	1.3667	-.0893
1.60	0.9429	-.0764	1.0858	-.0728	1.2309	-.0699
1.70	0.8687	-.0599	0.9960	-.0552	1.1252	-.0524
1.80	0.8052	-.0422	0.9230	-.0401	1.0406	-.0375
1.90	0.7519	-.0266	0.8610	-.0256	0.9687	-.0227
2.00	0.7071	-.0141	0.8081	-.0124	0.9100	-.0121
2.50	0.5501	.0327	0.6281	.0303	0.7038	.0327
3.00	0.4557	.0527	0.5188	.0540	0.5814	.0550
3.50	0.3887	.0746	0.4421	.0769	0.4964	.0725
4.00	0.3401	.0853	0.3876	.0826	0.4344	.0829

TABLE C-III (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	2.0		2.2		2.4	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.5703	-.1059	6.6667	-.1005	6.7606	-.0954
1.05	5.6689	-.1171	5.8855	-.1094	6.0952	-.1025
1.10	4.5228	-.1322	4.9875	-.1201	5.2701	-.1112
1.15	3.4507	-.1437	3.8962	-.1306	4.2941	-.1197
1.20	2.7685	-.1438	3.1339	-.1324	3.4904	-.1223
1.25	2.3739	-.1373	2.6829	-.1282	2.9907	-.1197
1.30	2.1046	-.1278	2.3802	-.1214	2.6487	-.1144
1.40	1.7528	-.1055	1.9667	-.1022	2.1783	-.0978
1.50	1.5379	-.0865	1.7074	-.0826	1.8868	-.0806
1.60	1.3797	-.0681	1.5295	-.0660	1.6797	-.0637
1.70	1.2583	-.0517	1.3915	-.0503	1.5262	-.0491
1.80	1.1598	-.0362	1.2798	-.0352	1.4006	-.0343
1.90	1.0785	-.0223	1.1888	-.0219	1.2995	-.0215
2.00	1.0111	-.0109	1.1134	-.0108	1.2146	-.0099
2.50	0.7797	.0333	0.8535	.0363	0.9293	.0355
3.00	0.6435	.0559	0.7038	.0596	0.7641	.0615
3.50	0.5495	.0728	0.6021	.0731	0.6537	.0750
4.00	0.4808	.0832	0.5268	.0835	0.5720	.0857

TABLE C-III (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	2.6		2.8		3.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.8602	-.0905	6.9136	-.0861	7.0093	-.0816
1.05	6.2373	-.0967	6.3341	-.0916	6.4350	-.0864
1.10	5.4968	-.1037	5.6566	-.0972	5.8027	-.0913
1.15	4.6235	-.1105	4.8891	-.1027	5.1051	-.0958
1.20	3.8146	-.1133	4.1225	-.1053	4.4014	-.0982
1.25	3.2964	-.1119	3.5840	-.1046	3.8585	-.0980
1.30	2.9028	-.1071	3.1581	-.1007	3.4037	-.0946
1.40	2.3932	-.0936	2.6076	-.0894	2.8195	-.0851
1.50	2.0586	-.0768	2.2329	-.0734	2.4038	-.0699
1.60	1.8300	-.0612	1.9819	-.0590	2.1259	-.0555
1.70	1.6606	-.0476	1.7922	-.0452	1.9244	-.0431
1.80	1.5189	-.0323	1.6374	-.0305	1.7544	-.0285
1.90	1.4093	-.0206	1.5177	-.0191	1.6244	-.0172
2.00	1.3118	-.0069	1.4099	-.0050	1.5091	-.0040
2.50	1.0019	.0379	1.0749	.0391	1.1472	.0401
3.00	0.8238	.0631	0.8830	.0646	0.9416	.0658
3.50	0.7048	.0767	0.7554	.0781	0.8056	.0794
4.00	0.6179	.0842	0.6623	.0861	0.7062	.0878

TABLE C-III (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	4.0		5.0		6.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.2993	-.0619	7.5529	-.0448	7.7620	-.0292
1.05	6.9013	-.0649	7.1500	-.0467	7.3828	-.0306
1.10	6.3908	-.0674	6.7540	-.0484	7.0110	-.0317
1.15	5.8754	-.0694	6.3103	-.0493	6.6464	-.0323
1.20	5.3937	-.0708	5.9018	-.0498	6.2972	-.0327
1.25	4.9005	-.0708	5.5096	-.0497	5.9259	-.0321
1.30	4.4723	-.0698	5.1419	-.0490	5.6012	-.0314
1.40	3.7397	-.0631	4.4476	-.0443	4.9950	-.0284
1.50	3.2129	-.0529	3.8760	-.0361	4.4200	-.0215
1.60	2.8441	-.0425	3.4645	-.0283	3.9809	-.0146
1.70	2.5520	-.0306	3.1124	-.0177	3.5941	-.0050
1.80	2.3148	-.0173	2.8258	-.0060	3.2776	.0052
1.90	2.1352	-.0066	2.6055	.0038	3.0190	.0152
2.00	1.9841	.0040	2.4225	.0132	2.8143	.0235
2.50	1.4981	.0454	1.8265	.0520	2.1333	.0586
3.00	1.2266	.0709	1.4961	.0762	1.7467	.0830
3.50	1.0495	.0848	1.2812	.0898	1.5011	.0946
4.00	0.9217	.0922	1.1282	.0957	1.3251	.0996

TABLE C-III (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.2$

	P_r					
	7.0		8.0		9.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.9545	-.0151	8.0972	-.0015	8.1818	.0122
1.05	7.6190	-.0164	7.8064	-.0031	7.8999	.0108
1.10	7.2810	-.0173	7.5054	-.0041	7.6252	.0096
1.15	6.9249	-.0175	7.1865	-.0045	7.3484	.0088
1.20	6.6063	-.0177	6.8871	-.0046	7.0621	.0088
1.25	6.2710	-.0171	6.5844	-.0043	6.7797	.0091
1.30	5.9696	-.0164	6.2923	-.0035	6.5312	.0092
1.40	5.3821	-.0132	5.7372	-.0007	6.0136	.0115
1.50	4.8815	-.0090	5.2390	.0034	5.5351	.0152
1.60	4.4326	-.0029	4.8077	.0083	5.0997	.0202
1.70	4.0290	.0055	4.3939	.0162	4.7017	.0268
1.80	3.6792	.0155	4.0294	.0256	4.3440	.0348
1.90	3.3925	.0254	3.7228	.0352	4.0245	.0440
2.00	3.1617	.0338	3.4783	.0431	3.7625	.0521
2.50	2.4159	.0658	2.6778	.0728	2.9126	.0810
3.00	1.9841	.0887	2.1966	.0974	2.4000	.1042
3.50	1.7079	.1001	1.9016	.1062	2.0872	.1119
4.00	1.5112	.1046	1.6863	.1103	1.8549	.1148

TABLE C-IV

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	0.2		0.4		0.6	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	0.2154	-.3324	0.4738	-.3288	0.8000	-.3125
1.05	0.2022	-.2868	0.4357	-.2885	0.7129	-.2784
1.10	0.1913	-.2583	0.4061	-.2576	0.6511	-.2491
1.15	0.1813	-.2250	0.3816	-.2317	0.6055	-.2286
1.20	0.1726	-.1987	0.3598	-.2045	0.5634	-.1998
1.25	0.1647	-.1742	0.3416	-.1847	0.5293	-.1761
1.30	0.1578	-.1590	0.3245	-.1599	0.5010	-.1571
1.40	0.1455	-.1251	0.2971	-.1292	0.4541	-.1240
1.50	0.1351	-.0955	0.2739	-.0967	0.4164	-.0946
1.60	0.1262	-.0761	0.2546	-.0714	0.3853	-.0696
1.70	0.1184	-.0557	0.2382	-.0512	0.3593	-.0495
1.80	0.1115	-.0323	0.2238	-.0322	0.3366	-.0292
1.90	0.1054	-.0152	0.2113	-.0166	0.3174	-.0158
2.00	0.1000	-.0020	0.2003	-.0085	0.3003	-.0033
2.50	0.0798	.0376	0.1592	.0314	0.2374	.0463
3.00	0.0664	.0602	0.1323	.0605	0.1976	.0607
3.50	0.0569	.0879	0.1132	.0884	0.1689	.0888
4.00	0.0497	.1207	0.0989	.1112	0.1479	.0946

TABLE C-IV (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	0.8		1.0		1.2	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	1.2481	-.2936	3.7453	-.1957	5.8824	-.1353
1.05	1.0604	-.2655	1.5486	-.2486	2.4162	-.2181
1.10	1.0059	-.2754	1.2849	-.2276	1.7272	-.2133
1.15	0.8515	-.2149	1.1364	-.2066	1.4658	-.1966
1.20	0.7860	-.1931	1.0305	-.1856	1.3038	-.1787
1.25	0.7331	-.1732	0.9516	-.1674	1.1881	-.1616
1.30	0.6880	-.1534	0.8866	-.1493	1.0976	-.1449
1.40	0.6161	-.1177	0.7870	-.1174	0.9642	-.1151
1.50	0.5626	-.9243	0.7127	-.0906	0.8677	-.0899
1.60	0.5181	-.0676	0.6551	-.0702	0.7920	-.0670
1.70	0.4817	-.0478	0.6046	-.0447	0.7307	-.0465
1.80	0.4503	-.0289	0.5640	-.0266	0.6803	-.0294
1.90	0.4232	-.0118	0.5290	-.0095	0.6367	-.0126
2.00	0.4000	.0000	0.5005	-.0020	0.5994	.0017
2.50	0.3159	.0412	0.3925	.0484	0.4697	.0468
3.00	0.2617	.0726	0.3258	.0705	0.3891	.0720
3.50	0.2241	.0893	0.2785	.0934	0.3325	.0932
4.00	0.1963	.0968	0.2439	.1025	0.2913	.1030

TABLE C-IV (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	1.4		1.6		1.8	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.3550	-.1227	6.5147	-.1158	6.6790	-.1094
1.05	3.9448	-.1673	4.9474	-.1399	5.4595	-.1257
1.10	2.3353	-.1948	3.1173	-.1711	3.9101	-.1487
1.15	1.8558	-.1854	2.3035	-.1719	2.8212	-.1578
1.20	1.6004	-.1693	1.9380	-.1610	2.3112	-.1519
1.25	1.4213	-.1492	1.7067	-.1465	2.0056	-.1406
1.30	1.3149	-.1377	1.5443	-.1315	1.7935	-.1271
1.40	1.1403	-.1079	1.3212	-.1022	1.5144	-.0998
1.50	1.0212	-.0842	1.1799	-.0814	1.3408	-.0783
1.60	0.9309	-.0645	1.0695	-.0608	1.2097	-.0579
1.70	0.8587	-.0477	0.9824	-.0428	1.1076	-.0397
1.80	0.7961	-.0289	0.9107	-.0264	1.0246	-.0234
1.90	0.7435	-.0121	0.8498	-.0106	0.9540	-.0073
2.00	0.6993	.0014	0.7976	.0038	0.8973	.0033
2.50	0.5447	.0514	0.6214	.0483	0.6957	.0503
3.00	0.4522	.0708	0.5143	.0719	0.5758	.0729
3.50	0.3861	.0932	0.4387	.0957	0.4926	.0893
4.00	0.3382	.1035	0.3854	.0986	0.4314	.0997

TABLE C-IV (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	2.0		2.2		2.4	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.8470	-.1034	6.9401	-.0984	7.0175	-.0938
1.05	5.7895	-.1159	6.0208	-.1083	6.2451	-.1015
1.10	4.5228	-.1322	5.0125	-.1199	5.3086	-.1110
1.15	3.5835	-.1436	3.8415	-.1307	4.2591	-.1197
1.20	2.6925	-.1415	3.0505	-.1308	3.4072	-.1212
1.25	2.3088	-.1330	2.6074	-.1246	2.9091	-.1169
1.30	2.0486	-.1215	2.3151	-.1162	2.5748	-.1099
1.40	1.7129	-.0969	1.9187	-.0943	2.1216	-.0905
1.50	1.5066	-.0763	1.6686	-.0725	1.8433	-.0716
1.60	1.3543	-.0569	1.4995	-.0554	1.6447	-.0535
1.70	1.2371	-.0396	1.3665	-.0388	1.4971	-.0381
1.80	1.1408	-.0228	1.2574	-.0223	1.3746	-.0218
1.90	1.0611	-.0075	1.1604	-.0077	1.2759	-.0078
2.00	0.9960	.0040	1.0956	.0037	1.1940	.0042
2.50	0.7700	.0507	0.8413	.0547	0.9152	.0535
3.00	0.6367	.0738	0.6951	.0791	0.7540	.0809
3.50	0.5447	.0900	0.5964	.0905	0.6469	.0928
4.00	0.4771	.1006	0.5223	.1015	0.5666	.1041

TABLE C-IV (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	2.6		2.8		3.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.1233	-.0891	7.1611	-.0850	7.2639	-.0808
1.05	6.3984	-.0958	6.4482	-.0909	6.5985	-.0859
1.10	5.5615	-.1034	5.7330	-.0970	5.8904	-.0912
1.15	4.6046	-.1105	4.8891	-.1027	5.1151	-.0958
1.20	3.7356	-.1124	4.0580	-.1047	4.3478	-.0978
1.25	3.2148	-.1098	3.5055	-.1030	3.7855	-.0967
1.30	2.8209	-.1032	3.0725	-.0973	3.3156	-.0917
1.40	2.3302	-.0871	2.5381	-.0835	2.7473	-.0801
1.50	2.0085	-.0682	2.1781	-.0656	2.3447	-.0627
1.60	1.7896	-.0514	1.9380	-.0501	2.0764	-.0467
1.70	1.6270	-.0369	1.7541	-.0348	1.8813	-.0330
1.80	1.4891	-.0201	1.6037	-.0187	1.7164	-.0169
1.90	1.3822	-.0072	1.4871	-.0061	1.5901	-.0044
2.00	1.2871	-.0078	1.3820	.0094	1.4778	.0102
2.50	0.9848	.0569	1.0556	.0578	1.1257	.0586
3.00	0.8122	.0825	0.8698	.0839	0.9268	.0852
3.50	0.6969	.0947	0.7463	.0965	0.7951	.0981
4.00	0.6121	.1013	0.6554	.1037	0.6983	.1060

TABLE C-IV (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	4.0		5.0		6.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.5330	-.0623	7.7882	-.0460	8.0000	-.0312
1.05	7.0809	-.0652	7.3373	-.0478	7.5786	-.0325
1.10	6.5051	-.0678	6.8871	-.0494	7.1582	-.0332
1.15	5.9154	-.0696	6.3845	-.0500	6.7495	-.0336
1.20	5.3937	-.0708	5.9354	-.0502	6.3613	-.0336
1.25	4.8632	-.0703	5.5096	-.0497	5.9480	-.0324
1.30	4.4082	-.0685	5.1146	-.0485	5.6012	-.0314
1.40	3.6677	-.0603	4.3875	-.0424	4.9546	-.0272
1.50	3.1375	-.0478	3.8008	-.0323	4.3526	-.0186
1.60	2.7747	-.0357	3.3857	-.0227	3.9022	-.0100
1.70	2.4873	-.0217	3.0321	-.0099	3.5014	-.0023
1.80	2.2538	-.0062	2.7448	.0044	3.1807	.0151
1.90	2.0803	.0058	2.5304	.0158	2.9213	.0277
2.00	1.9342	.0176	2.3540	.0263	2.7248	.0371
2.50	1.4639	.0635	1.7778	.0703	2.0690	.0773
3.00	1.2012	.0916	1.4594	.0973	1.6964	.1055
3.50	1.0315	.1047	1.2542	.1108	1.4652	.1160
4.00	0.9083	.1112	1.1082	.1155	1.2987	.1194

TABLE C-IV (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.3$

	P_r					
	7.0		8.0		9.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	8.1967	-.0178	8.3507	-.0050	8.4349	.0079
1.05	7.8339	-.0190	8.0370	-.0065	8.1323	.0066
1.10	7.4603	-.0197	7.7042	-.0073	7.8295	.0057
1.15	7.0533	-.0194	7.3381	-.0071	7.5179	.0055
1.20	6.6973	-.0193	7.0028	-.0069	7.1908	.0060
1.25	6.3205	-.0180	6.6597	-.0059	6.8637	.0071
1.30	5.9962	-.0170	6.3376	-.0046	6.5871	.0077
1.40	5.3591	-.0125	5.7315	-.0005	6.0193	.0113
1.50	4.8259	-.0058	5.1931	.0052	5.4995	.0165
1.60	4.3576	.0009	4.7393	.0116	5.0358	.0232
1.70	3.9328	.0120	4.2976	.0221	4.6116	.0321
1.80	3.5711	.0249	3.9158	.0345	4.2337	.0428
1.90	3.2778	.0378	3.5957	.0475	3.8922	.0558
2.00	3.0514	.0482	3.3529	.0576	3.6261	.0665
2.50	2.3353	.0852	2.5806	.0930	2.7994	.1022
3.00	1.9220	.1113	2.1181	.1223	2.3077	.1300
3.50	1.6611	.1228	1.8433	.1302	2.0184	.1358
4.00	1.4768	.1253	1.6434	.1320	1.8029	.1376

TABLE C-V

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.4$

	P_r					
	0.2		0.4		0.6	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	0.2157	-.3375	0.4747	-.3316	0.8021	-.3142
1.05	0.2022	-.2868	0.4357	-.2883	0.7125	-.2779
1.10	0.1912	-.2573	0.4058	-.2558	0.6498	-.2471
1.15	0.1812	-.2229	0.3811	-.2288	0.6047	-.2269
1.20	0.1724	-.1937	0.3591	-.1999	0.5617	-.1955
1.25	0.1645	-.1677	0.3407	-.1784	0.5272	-.1699
1.30	0.1576	-.1510	0.3236	-.1520	0.4987	-.1496
1.40	0.1453	-.1145	0.2961	-.1189	0.4518	-.1138
1.50	0.1348	-.0831	0.2729	-.0845	0.4142	-.0826
1.60	0.1260	-.0619	0.2537	-.0575	0.3832	-.0558
1.70	0.1182	-.0406	0.2373	-.0362	0.3574	-.0347
1.80	0.1113	-.0162	0.2230	-.0161	0.3348	-.0131
1.90	0.1052	.0019	0.2105	.0000	0.3158	.0000
2.00	0.0999	.0140	0.1997	.0070	0.2988	.0134
2.50	0.0797	.0502	0.1589	.0441	0.2365	.0634
3.00	0.0663	.0754	0.1320	.0758	0.1970	.0761
3.50	0.0568	.1056	0.1129	.1065	0.1684	.1069
4.00	0.0497	.1410	0.0987	.1317	0.1479	.1084

TABLE C-V (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.4$

	P_r					
	0.8		1.0		1.2	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	1.2945	-.2951	3.8610	-.1919	6.1538	-.1308
1.05	1.0582	-.2646	1.5436	-.2481	2.4111	-.2182
1.10	1.0018	-.2735	1.2750	-.2251	1.7051	-.2113
1.15	0.8473	-.2113	1.1270	-.2027	1.4469	-.1927
1.20	0.7819	-.1885	1.0217	-.1805	1.2870	-.1733
1.25	0.7289	-.1674	0.9438	-.1615	1.1736	-.1551
1.30	0.6838	-.1462	0.8795	-.1424	1.0847	-.1374
1.40	0.6118	-.1079	0.7800	-.1080	0.9534	-.1059
1.50	0.5585	-.0806	0.7061	-.0790	0.8584	-.0792
1.60	0.5144	-.0544	0.6497	-.0585	0.7837	-.0549
1.70	0.4782	-.0335	0.5990	-.0300	0.7232	-.0332
1.80	0.4471	-.0134	0.5589	-.0107	0.6734	-.0148
1.90	0.4202	.0048	0.5242	.0076	0.6303	.0032
2.00	0.3972	.0176	0.4965	.0141	0.5935	.0185
2.50	0.3143	.0573	0.3899	.0667	0.4660	.0644
3.00	0.2604	.0922	0.3239	.0896	0.3865	.0906
3.50	0.2232	.1075	0.2771	.1119	0.3306	.1119
4.00	0.1957	.1124	0.2430	.1194	0.2899	.1208

TABLE C-V (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.4$

	P_r					
	1.4		1.6		1.8	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	6.6540	-.1187	6.8143	-.1123	6.9767	-.1064
1.05	3.9565	-.1676	5.0125	-.1389	5.5659	-.1243
1.10	2.2891	-.1940	3.0635	-.1714	3.8776	-.1491
1.15	1.8224	-.1822	2.2513	-.1697	2.7537	-.1567
1.20	1.5723	-.1641	1.8939	-.1563	2.2523	-.1483
1.25	1.3930	-.1407	1.6710	-.1400	1.9565	-.1349
1.30	1.2944	-.1298	1.5139	-.1235	1.7527	-.1198
1.40	1.1236	-.0979	1.2972	-.0917	1.4829	-.0897
1.50	1.0068	-.0725	1.1607	-.0698	1.3158	-.0669
1.60	0.9191	-.0522	1.0537	-.0484	1.1892	-.0454
1.70	0.8490	-.0353	0.9693	-.0299	1.0904	-.0266
1.80	0.7872	-.0152	0.8988	-.0122	1.0091	-.0089
1.90	0.7354	.0027	0.8388	.0048	0.9398	.0085
2.00	0.6917	.0173	0.7874	.0203	0.8850	.0192
2.50	0.5395	.0704	0.6148	.0667	0.6877	.0683
3.00	0.4487	.0891	0.5099	.0902	0.5703	.0912
3.50	0.3835	.1121	0.4354	.1148	0.4889	.1064
4.00	0.3362	.1219	0.3831	.1148	0.4286	.1167

TABLE C-V (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.4$

	P_r					
	2.0		2.2		2.4	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.1480	-.1008	7.2368	-.0962	7.2948	-.0920
1.05	5.9154	-.1146	6.1625	-.1071	6.4026	-.1004
1.10	4.5228	-.1322	5.0378	-.1197	5.3476	-.1107
1.15	3.3190	-.1434	3.7882	-.1307	4.2246	-.1198
1.20	2.6205	-.1389	2.9714	-.1289	3.3278	-.1199
1.25	2.2472	-.1282	2.5360	-.1207	2.8319	-.1137
1.30	1.9954	-.1148	2.2534	-.1105	2.5050	-.1050
1.40	1.6748	-.0878	1.8730	-.0860	2.0679	-.0827
1.50	1.3158	-.0669	1.4766	-.0657	1.6314	-.0619
1.60	1.3298	-.0451	1.4706	-.0442	1.6112	-.0428
1.70	1.2166	-.0271	1.3424	-.0268	1.4691	-.0265
1.80	1.1223	-.0089	1.2358	-.0089	1.3495	-.0089
1.90	1.0443	.0077	1.1487	.0070	1.2531	.0064
2.00	0.9814	.0194	1.0784	.0185	1.1742	.0187
2.50	0.7605	.0684	0.8294	.0735	0.9014	.0721
3.00	0.6301	.0920	0.6866	.0990	0.7442	.1008
3.50	0.5401	.1074	0.5908	.1083	0.6403	.1109
4.00	0.4735	.1183	0.5179	.1197	0.5613	.1229

TABLE C-V (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT ω = 0.4

	P_r					
	2.6		2.8		3.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.4074	-.0876	7.4271	-.0839	7.5377	-.0799
1.05	6.5681	-.0949	6.6500	-.0901	6.7705	-.0854
1.10	5.6277	-.1031	5.8115	-.0967	5.9809	-.0910
1.15	4.5859	-.1106	4.8891	-.1027	5.1251	-.0958
1.20	3.6599	-.1115	3.9954	-.1041	4.2955	-.0973
1.25	3.1373	-.1074	3.4303	-.1012	3.7152	-.0953
1.30	2.7435	-.0988	2.9915	-.0936	3.2321	-.0885
1.40	2.2703	-.0802	2.4722	-.0773	2.6786	-.0747
1.50	1.9608	-.0592	2.1260	-.0574	2.2883	-.0551
1.60	1.7511	-.0411	1.8960	-.0406	2.0292	-.0375
1.70	1.5948	-.0257	1.7175	-.0239	1.8402	-.0223
1.80	1.4605	-.0075	1.5713	-.0064	1.6801	-.0048
1.90	1.3562	-.0066	1.4576	-.0075	1.5571	-.0090
2.00	1.2634	.0230	1.3553	.0243	1.4479	.0249
2.50	0.9683	.0764	1.0370	.0771	1.1050	.0778
3.00	0.8010	.1024	0.8571	.1038	0.9124	.1052
3.50	0.6891	.1132	0.7373	.1153	0.7849	.1172
4.00	0.6063	.1187	0.6487	.1218	0.6906	.1245

TABLE C-V (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.4$

	P_r					
	4.0		5.0		6.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	7.7821	-.0625	8.0386	-.0470	8.2531	-.0331
1.05	7.2701	-.0655	7.5347	-.0488	7.7851	-.0342
1.10	6.6236	-.0681	7.0254	-.0502	7.3117	-.0347
1.15	5.9559	-.0698	6.4604	-.0506	6.8560	-.0349
1.20	5.3937	-.0708	5.9694	-.0506	6.4267	-.0345
1.25	4.8265	-.0698	5.5096	-.0497	5.9701	-.0328
1.30	4.3459	-.0672	5.0875	-.0480	5.6012	-.0314
1.40	3.5984	-.0572	4.3290	-.0404	4.9148	-.0260
1.50	3.0651	-.0424	3.7286	-.0284	4.2872	-.0156
1.60	2.7086	-.0284	3.3104	-.0169	3.8265	-.0052
1.70	2.4257	-.0124	2.9560	-.0017	3.4134	.0100
1.80	2.1959	.0055	2.6684	.0154	3.0893	.0256
1.90	2.0282	.0187	2.4594	.0285	2.8297	.0410
2.00	1.8868	.0318	2.2894	.0402	2.6408	.0515
2.50	1.4311	.0825	1.7316	.0895	2.0084	.0971
3.00	1.1768	.1130	1.4245	.1193	1.6488	.1292
3.50	1.0141	.1252	1.2284	.1327	1.4310	.1384
4.00	0.8953	.1307	1.0889	.1359	1.2733	.1398

TABLE C-V (cont'd)

GENERALIZED QUANTITIES $(Z-1)/\rho_r$ AND ρ_r AT $\omega = 0.4$

	P_r					
	7.0		8.0		9.0	
T_r	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$	ρ_r	$\frac{Z-1}{\rho_r}$
1.00	8.4541	-.0203	8.6207	-.0084	8.7041	.0039
1.05	8.0613	-.0215	8.2816	-.0097	8.3787	.0027
1.10	7.6486	-.0220	7.9137	-.0102	8.0451	.0021
1.15	7.1865	-.0213	7.4963	-.0096	7.6953	.0022
1.20	6.7908	-.0208	7.1225	-.0090	7.3242	.0033
1.25	6.3709	-.0190	6.7368	-.0074	6.9498	.0052
1.30	6.0231	-.0176	6.3837	-.0056	6.6440	.0063
1.40	5.3362	-.0118	5.7257	-.0003	6.0249	.0111
1.50	4.7716	-.0046	5.1480	.0070	5.4645	.0179
1.60	4.2850	.0049	4.6729	.0150	4.9735	.0263
1.70	3.8411	.0187	4.2054	.0283	4.5249	.0376
1.80	3.4691	.0349	3.8084	.0439	4.1288	.0511
1.90	3.1706	.0511	3.4769	.0607	3.7684	.0682
2.00	2.9486	.0634	3.2362	.0729	3.4992	.0817
2.50	2.2599	.1058	2.4903	.1144	2.6946	.1247
3.00	1.8637	.1352	2.0450	.1487	2.2222	.1575
3.50	1.6168	.1466	1.7885	.1554	1.9540	.1617
4.00	1.4439	.1468	1.6026	.1548	1.7537	.1614

APPENDIX D

MATHEMATICS OF MULTIPLE LINEAR REGRESSION

Multiple linear regression or least-mean-square regression is used in this work to generate virial coefficient and to correlate these coefficients with other variables. A description of multiple linear regression and the associated mathematics is given below.

When using multiple linear regression, a regression model is selected first. The model is some equation which is postulated to describe the behavior between a dependent variable and one or more independent variables. Regression coefficients for this model are then derived using a specific set of known values for the variables under consideration. These regression coefficients, when used in the regression model, define a regession equation. A graphical representation of the regression equation is referred to as a regression curve. These regression coefficients are derived such that the sum of the squares of the deviations of the known values of the dependent variable from those values of the dependent variable as generated by the regression equation is a minimum. Stated in another way, any equation other than the regression equation will yield a greater sum of squares of deviations than that sum obtained using the regression equation.

Consider some dependent variable Y_i related to an independent variable X_i. The relationship between X_i and Y_i can be expressed in terms of a linear function. For example, if the relationship between X_i and Y_i is a polynomial function:

$$Y_i = b_0 + b_1 X_i + b_2 X_i^2 + \ldots\ldots + b_k X_i^k \qquad \text{(D-1)}$$

this relationship can be written as a linear function:

$$Y_i = b_0 + b_1 X_{1i} + b_2 X_{2i} + \ldots\ldots + b_k X_{ki} \qquad \text{(D-2)}$$

where:

$$X_{1i} = X_i \qquad \text{(D-3)}$$

$$X_{2i} = X_i^2 \qquad \text{(D-4)}$$

$$\vdots$$

$$X_{ki} = X_i^k \qquad \text{(D-5)}$$

Note the first subscript on the term X in equation (D-2) refers to a specific linear variable, and the second subscript refers to a specific value for the independent variable X_i.

For n pairs of values of X_i and Y_i, a set of equations referred to as the normal equations are written as follows:

$$
\begin{aligned}
b_0 n + b_1 \sum X_{1i} + b_2 \sum X_{2i} + \ldots\ldots + b_k \sum X_{ki} &= \sum Y_i \\
b_0 \sum X_{1i} + b_2 \sum X_{1i}^2 + b_2 \sum X_{1i} X_{2i} + \ldots\ldots + b_k \sum X_{1i} X_{ki} &= \sum X_{1i} Y_i \\
b_0 \sum X_{2i} + b_1 \sum X_{1i} X_{2i} + b_2 \sum X_{2i}^2 + \ldots\ldots + b_k \sum X_{2i} X_{ki} &= \sum X_{2i} Y_i \\
&\vdots \qquad \text{(D-6)} \\
b_0 \sum X_{ki} + b_1 \sum X_{1i} X_{ki} + b_2 \sum X_{2i} X_{ki} + \ldots\ldots + b_k \sum X_{ki}^2 &= \sum X_{ki} Y_i
\end{aligned}
$$

The normal equations are solved simultaneously for the regression coefficients b_0, b_1,b_2, ...,b_k. The computer program of Bush and Short solves the normal equations via Cholesky's method for matrix solution.

The standard error of estimate is used as a test for selection of regression models. The standard error of estimate is an estimate of the deviation of the actual value of Y_i from that value calculated with the regression equation. Letting d represent this deviation, the standard error of estimate is calculated as follows:

$$\text{standard error of estimate} = \sqrt{\frac{d^2}{n - 2}} \qquad \text{(D-7)}$$

Again, n is the number of pairs of values of X_i and Y_i used in the regression.

APPENDIX E

DERIVATION OF GENERALIZED FREE ENERGY EQUATION

The change in free energy can be expressed in differential form as:

$$dF = VdP \tag{E-1}$$

The volume V can be expressed as follows:

$$V = \frac{ZRT}{P} \tag{E-2}$$

From the definitions of reudced quantities, equation (E-2) can be written as follows:

$$V = \frac{ZRT_cT_r}{P_cP_r} = \frac{RT_c}{P_c}\left(\frac{1}{P_r/ZT_r}\right) = \frac{RT_c}{P_c}\left(\frac{1}{\rho_r}\right) \tag{E-3}$$

The pressure P can be written as follows:

$$P = P_cP_r = P_c\rho_rZT_r \tag{E-4}$$

Taking the total differential of equation (E-4) at constant temperature

$$dP = P_cT_r\left[Zd\rho_r + \rho_rdZ\right] \tag{E-5}$$

Using equations (E-3) and (E-5), the differential change in free energy can be expressed as follows:

$$VdP = \left[\frac{RT_c}{P_c}\left(\frac{1}{\rho_r}\right)\right]\left[P_cT_r(Zd\rho_r + \rho_rdZ)\right] \tag{E-6}$$

Rearrangement of equation (E-6) yields:

$$\frac{1}{RT_cT_r}Vdp = \frac{1}{RT}VdP = \frac{Z}{\rho_r}d\rho_r + dZ \tag{E-7}$$

The term Z/ρ_r can be written as follows:

$$\frac{Z}{\rho_r} = \frac{Z - 1}{\rho_r} + \frac{1}{\rho_r} \tag{E-8}$$

Substituting equation (E-8) into equation (E-7):

$$\frac{1}{RT} VdP = \frac{Z-1}{\rho_r} d\rho_r + \frac{d\rho_r}{\rho_r} + dZ \tag{E-9}$$

Integration of equation (E-9) across the two-phase region, where the change in free energy is zero, yields the following expression:

$$\frac{1}{RT} \int_1^2 VdP = \int_1^2 \left(\frac{Z - 1}{\rho_r}\right) d\rho_r + \ln\left(\frac{\rho_{r2}}{\rho_{r1}}\right) + (Z_2 - Z_1) = 0 \tag{E-10}$$

Equation (E-10) forms the basis for postulating a continuous, hypothetical isotherm across the two-phase region.

APPENDIX F

CONVERSION OF REDLICH-KWONG EQUATION OF STATE INTO GENERALIZED TERMS

The Redlich-Kwong equation of state can be written as follows:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \qquad \text{(F-1)}$$

The constants a and b are defined as follows:

$$a = 0.4278 \frac{R^2T_c^{2.5}}{P_c} \qquad \text{(F-2)}$$

$$b = 0.0867 \frac{RT_c}{P_c} \qquad \text{(F-3)}$$

From the definitions of reduced quantities, the following expressions can be written:

$$P = P_cP_r \qquad \text{(F-4)}$$

$$T = T_cT_r \qquad \text{(F-5)}$$

$$V = V_{ci}V_{ri} = \left(\frac{RT_c}{P_c}\right) V_{ri} \qquad \text{(F-6)}$$

Substituting equations (F-2), (F-3), (F-4), (F-5), and (F-6) into equation (F-1) yields:

$$P_cP_r = \frac{RT_cT_r}{\frac{RT_c}{P_c}V_{ri} - 0.0867\frac{RT_c}{P_c}} - \frac{0.4278\frac{R^2T_c^{2.5}}{P_c}}{T_c^{0.5}T_r^{0.5}\frac{RT_c}{P_c}V_{ri}\left(\frac{RT_c}{P_c}V_{ri}+0.0867\frac{R}{I}\right.}$$

$$= \frac{RT_cT_r}{\frac{RT_c}{P_c}(V_{ri}-0.0867)} - \frac{0.4278\frac{R^2\ T_c^{2.5}}{P_c}}{T_c^{2.5}T_r^{0.5}\frac{R^2}{P_c^2}V_{ri}(V_{ri}+0.0867)}$$

(Equation continued)

$$= \frac{P_c T_r}{V_{ri} - 0.0867} - \frac{0.4278\ P_c}{T_r^{0.5} V_{ri}\,(V_{ri} + 0.0867)} \qquad \text{(F-7)}$$

Solving equation (F-7) for P_r:

$$P_r = \frac{T_r}{V_{ri} - 0.0867} - \frac{0.4278}{T_r^{0.5}\ V_{ri}(V_{ri} + 0.0867)} \qquad \text{(F-8)}$$

Equation (F-8) is the Redlich-Kwong equation of state in generalized terms.

APPENDIX G

DERIVATION OF GENERALIZED FUGACITY COEFFICIENT EQUATION

The calculation of fugacity coefficients can be made through the use of virial coefficients. Comparison with Pitzer's generalized tabulations of fugacity coefficients provides one test of the virial coefficient correlations. Recalling the definition of the fugacity coefficient:

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_0^P \left(V - \frac{RT}{P}\right) dP = \frac{1}{RT}\int_0^P VdP - \int_0^P d(\ln P) \qquad \text{(G-1)}$$

The differential of the product PV is given as:

$$d(PV) = VdP + PdV \qquad \text{(G-2)}$$

Rearranging equation (G-2):

$$VdP = d(PV) - PdV \qquad \text{(G-3)}$$

Substituting equation (G-3) into the first integral on the right-hand side of equation (G-1):

$$\frac{1}{RT}\int_0^P VdP = \frac{1}{RT}\int_0^P d(PV) - \frac{1}{RT}\int_\infty^V PdV \qquad \text{(G-4)}$$

Integrating the first integral on the right-hand side of equation (G-4) yields the following for equation (G-4):

$$\frac{1}{RT}\int_0^P VdP = \left[PV\right]_0^P - \frac{1}{RT}\int_\infty^V PdV = \frac{1}{RT}\left[PV - RT\right] - \frac{1}{RT}\int_\infty^V PdV$$

$$= \frac{PV}{RT} - 1 + \frac{1}{RT}\int_V^\infty PdV \qquad \text{(G-5)}$$

Recalling the Leiden form of the virial equation of state:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \qquad \text{(G-6)}$$

Solving equation (G-6) explicitly in terms of pressure:

$$P = \frac{RT}{V} + \frac{BRT}{V^2} + \frac{CRT}{V^3} + \frac{DRT}{V^4} + \ldots \qquad \text{(G-7)}$$

Substituting equation (G-7) into the integral on the right-hand side of equation (G-5):

$$\frac{1}{RT}\int_0^P VdP = \frac{PV}{RT} - 1 + \int_V^{\infty}\left(\frac{1}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^4} \ldots\right)dV \qquad \text{(G-8)}$$

Integrating the integral in equation (G-8):

$$\frac{1}{RT}\int_0^P VdP = \frac{PV}{RT} - 1 + \left[\ln V - \frac{B}{V} - \frac{C}{2V^2} - \frac{D}{3V^3} - \ldots\right]_V^{\infty}$$

$$= \frac{PV}{RT} - 1 + \ln V^{\infty} - \ln V + \frac{B}{V} + \frac{C}{2V^2} + \frac{D}{3V^3} + \ldots \qquad \text{(G-9)}$$

Integrating the second integral on the right-hand side of equation (G-1):

$$-\int_0^P d(\ln P) = -\left[\ln P\right]_o^P = \ln P^\circ - \ln P \qquad \text{(G-10)}$$

Adding equations (G-9) and (G-10):

$$\ln\left(\frac{f}{P}\right) = \frac{PV}{RT} - 1 + \ln(P^\circ V^{\infty}) - \ln(PV) + \frac{B}{V} + \frac{C}{2V^2} + \frac{D}{3V^3} + \ldots \qquad \text{(G-11)}$$

Rearranging equation (G-6):

$$\frac{PV}{RT} - 1 = \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \qquad \text{(G-12)}$$

Also:

$$\ln(P^\circ V^{\infty}) = \ln(RT) \qquad \text{(G-13)}$$

Substituting equations (G-12) and G-13) into equation (G-11):

$$\ln\left(\frac{f}{P}\right) = \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots + \ln(RT) - \ln(PV) + \frac{B}{V} + \frac{C}{2V^2} + \frac{D}{3V^3} + \ldots \qquad \text{(G-14)}$$

Collecting terms:

$$\ln\left(\frac{f}{P}\right) = \frac{2B}{V} + \frac{3C}{2V^2} + \frac{4D}{3V^3} + \ldots - \ln Z \qquad \text{(G-15)}$$

Recalling the derivation of the generalized virial equation of state:

$$\frac{B}{V} = b\rho_r \qquad \text{(C-16)}$$

$$\frac{C}{V^2} = c\rho_r^2 \qquad \text{(G-17)}$$

$$\frac{D}{V^3} = d\rho_r^3 \qquad \text{(G-18)}$$

Substituting these terms into equation (G-15):

$$\ln\left(\frac{f}{P}\right) = 2b\rho_r + \frac{3}{2}\,d\rho_r^2 + \frac{4}{3}\,d\rho_r^3 + \ldots - \ln Z \qquad \text{(C-19)}$$

Equation (G-19) is used to calculate fugacity coefficients via the generalized virial coefficient correlations. A rearrangement of equation (G-19) is tested as a regression model for generating virial coefficients

APPENDIX H

DERIVATION OF GENERALIZED ENTHALPY EQUATION

The calculation of enthalpies can be made through the use of virial coefficients. Comparison with Pitzer's generalized tabulations provides one test of the virial coefficient correlations. If enthalpy is defined as a function of temperature and pressure, a differential change in enthalpy is given as follows:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \text{(H-1)}$$

Edmister and many others show that this differential change in enthalpy can be evaluated with the following relation:

$$dH = C_p dT + VdP - T \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{(H-2)}$$

Assuming constant temperature, $C_p dT$ is zero and:

$$dH = VdP - T \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{(H-3)}$$

Recalling the rearranged form of the differential (PV):

$$VdP = d\ (PV) - PdV \qquad \text{(H-4)}$$

At constant temperature, the following relation can be obtained from the definitions of entropy:

$$\left(\frac{\partial V}{\partial T}\right)_P dP = - \left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{(H-5)}$$

Substituting equations (H-4) and (H-5) into equation (H-3):

$$dH = -PdV + d(PV) + T \left(\frac{\partial P}{\partial T}\right)_V dV = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV + d(PV) \qquad \text{(H-6)}$$

Recalling the pressure-explicit form of the Leiden virial equation of state:

$$P = \frac{RT}{V} + \frac{BRT}{V^2} + \frac{CRT}{V^3} + \frac{DRT}{V^4} + \ldots \qquad \text{(H-7)}$$

Differentiating equation (H-7) with respect to temperature at constant volume:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} + \frac{R}{V^2}\left[B + T\left(\frac{\partial B}{\partial T}\right)\right] + \frac{R}{V^3}\left[C + T\left(\frac{\partial C}{\partial T}\right)\right] + \frac{R}{V^4}\left[D + T\left(\frac{\partial D}{\partial T}\right)\right] + \ldots \qquad \text{(H-8)}$$

Substituting equation (H-8) into the first term of equation (H-6):

$$\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] = \frac{RT}{V} + \frac{BRT}{V^2} + \frac{RT^2}{V^2}\left(\frac{\partial B}{\partial T}\right) + \frac{CRT}{V^3} + \frac{RT^2}{V^3}\left(\frac{\partial C}{\partial T}\right) + \frac{DRT}{V^4} + \frac{RT^2}{V^4}\left(\frac{\partial D}{\partial T}\right) + \ldots - \frac{RT}{V} - \frac{BRT}{V^2} - \frac{CRT}{V^3} - \frac{DRT}{V^4} - \ldots$$

$$= \frac{RT^2}{V^2}\left(\frac{\partial B}{\partial T}\right) + \frac{RT^2}{V^3}\left(\frac{\partial C}{\partial T}\right) + \frac{RT^2}{V^4}\left(\frac{\partial D}{\partial T}\right) + \ldots \qquad \text{(H-9)}$$

Integrating equation (H-9) between infinite volume (zero pressure) and a finite volume V:

$$\int_{\infty}^{V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV = \left[-\frac{RT^2}{V}\left(\frac{\partial B}{\partial T}\right) - \frac{RT^2}{2V^2}\left(\frac{\partial C}{\partial T}\right) - \frac{RT^2}{3V^3}\left(\frac{\partial D}{\partial T}\right) - \ldots\right]_{\infty}^{V} = -\frac{RT^2}{V}\left(\frac{\partial B}{\partial T}\right) - \frac{RT^2}{2V^2}\left(\frac{\partial C}{\partial T}\right) - \frac{RT^2}{3V^3}\left(\frac{\partial D}{\partial T}\right) - \ldots$$

(H-10)

Integrating the d(PV) term in equation (H-6):

$$\Delta(PV) = PV - RT = \frac{B}{V}RT + \frac{C}{V^2}RT + \frac{D}{V^3}RT + \ldots \qquad \text{(H-11)}$$

Adding equations (H-10) and (H-11):

$$H - H^{\circ} = RT \left[\frac{1}{V} (B-T \frac{\partial B}{\partial T}) + \frac{1}{V^2} (C - \frac{T}{2} \frac{\partial C}{\partial T}) + \frac{1}{V^3} (D - \frac{T}{3} \frac{\partial D}{\partial T}) + \ldots\right] \quad \text{(H-12)}$$

$$\frac{H-H^{\circ}}{RT} = \frac{1}{V} (B-T \frac{\partial B}{\partial T}) + \frac{1}{V^2} (C - \frac{T}{2} \frac{\partial C}{\partial T}) + \frac{1}{V^3} (D- \frac{T}{3} \frac{\partial D}{\partial T}) + \ldots \quad \text{(H-13)}$$

Transforming equation (H-13) into generalized terms:

$$\frac{H-H^{\circ}}{RT_c} = T_r \left[\left(\frac{P_c}{RT_c}\right)\left(\frac{P_r}{ZT_r}\right)(B - T_r \frac{\partial B}{\partial T_r}) + \left(\frac{P_c}{RT_c}\right)^2 \left(\frac{P_r}{ZT_r}\right)^2 (C - \frac{T_r}{2} \frac{\partial C}{\partial T_r}) + \left(\frac{P_c}{RT_c}\right)^3 \left(\frac{P_r}{ZT_r}\right)^3 (D - \frac{T_r}{3} \frac{\partial D}{\partial T_r}) + \ldots\right] \quad \text{(H-14)}$$

$$\frac{H-H^{\circ}}{RT_c} = T_r \left[\rho_r (b-T_r \frac{\partial b}{\partial T_r}) + \rho_r^2 (c- \frac{T_r}{2} \frac{\partial c}{\partial T_r}) + \rho_r^3 (d - \frac{T_r}{3} \frac{\partial d}{\partial T_r}) + \ldots\right] \quad \text{(H-15)}$$

$$\frac{H-H^{\circ}}{RT_c} = - T_r \left[\rho_r (b-T_r \frac{\partial b}{\partial T_r}) + \rho_r^2 (c - \frac{T_r}{2} \frac{\partial c}{\partial T_r}) + \rho_r^3 (d - \frac{T_r}{3} \frac{\partial d}{\partial T_r}) + \ldots\right] \quad \text{(H-16)}$$

Equation (H-16) is used to calculate generalized enthalpies via the generalized virial coefficient correlations.

VITA

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Master of Science

Thesis: A GENERALIZED VIRIAL EQUATION OF STATE

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