EXTENSION TO THE THREE-PARAMETER GENERALIZED CORRELATION
AND
SOME APPLICATIONS TO THE VIRIAL EQUATION OF STATE

by

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To Julie, my beloved wife

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LIST OF NOMENCLATURE

A	coefficients in equations (23) and (25)
a	radius of the spherical core in the Lennard-Jones potential model
B	second virial coefficient; also as coefficients in equations (24), (26), (28) and (29)
$B_{ij}(B_{12})$	cross second virial coefficient
C	third virial coefficient; also as coefficients in equations (28) and (30)
C_p	isobaric heat capacity
C_v	isochoric heat capacity
D	coefficients in equations (28) and (31)
b,c,d	coefficients in equations (28) to (31)
f	fugacity
H	enthalpy
k	Boltzmann's constant
$k_{ij}(k_{12})$	binary interaction parameter
N	Avogadro's number
n	number of components in a mixture
P	pressure
R	universal gas constant; also as the reduced well width in the square-well potential model
r	distance between molecular centers
r_0	the intermolecular distance at the minimum potential in the Lennard-Jones model
S	entropy
T	temperature
u	defined by equation (72) for the collision diameter of the binary mixture

V	volume (molal or specific)
W	potential energy between molecules
y	gas phase mole fraction
Z	compressibility factor

GREEK LETTERS

β	isothermal coefficient of bulk compressibility; also as coefficient in equation (28)
γ	coefficient in equation (28)
ε	depth of the energy well (at the minimum potential energy)
μ	Joule-Thomson coefficient
ρ	density
ρ'	the shortest distance between the cores in the Lennard-Jones potential model
ρ'_0	the ρ' distance at the potential minimum
σ	molecular separation defined by equation (63)
ω	acentric factor

SUPERSCRIPTS

0	simple fluid properties
1,2,3	order of deviation functions
L	liquid phase
r	reference fluid property
V	vapor phase
'	denoting difference; such as B' in equation (28) is different from B in equation (7)
*	ideal gas state

SUBSCRIPTS

0,1,2,3,4	denoting coefficients in equations (23) to (26), (29), (30) and (31)
11,22	denoting pure components in a binary mixture
c	critical property
calc.	calculated value
expt.	experimental value
i,j	component identification
J.T.	Joule-Thomson coefficient
m	mixture property
P	constant pressure
r	reduced property
sat.	saturated property
T	constant temperature

ABSTRACT

The three-parameter generalized correlation (acentric-factor correlation) of Pitzer et al.{128} (1955) for calculating the compressibility factor of pure compounds in the T_r and P_r regions of $0.8 \leq T_r \leq 4.0$ and $0 \leq P_r \leq 9.0$ has been thoroughly examined and then extended to wider ranges. By collecting the P-V-T data of 57 compounds available in the literature with data points in the proximity of 15,000, the proposed form $Z = Z^{(0)} + \omega Z^{(1)}$ of Pitzer's correlation was found to be appropriate. As a result, values of $Z^{(0)}$ and $Z^{(1)}$ were tabulated at regular intervals of T_r and P_r and with the ranges of applicability extended to $0.2 \leq T_r \leq 5.0$ and $0 \leq P_r \leq 12.0$. However, in the final correlation, through verifications, four compounds (hydrogen, helium, ammonia and water) were deleted from this correlation so that the necessity of excluding these compounds with quantum or highly polar nature was also confirmed. This correlation was further tested by first comparing the calculated compressibility factors with the experimental compressibility factor data for 12 compounds with 1,556 data points, and again tested by checking the satisfaction of the boundary condition of this correlation. It was shown that this presentation is not only adequate but also more accurate with improving precision for compressibility factor calculations, when compared with published works.

The binary interaction coefficients of binary mixtures have also been studied by the use of the second virial coefficient approach. Using appropriate mixing rules to the second virial coefficient correlation proposed by Pitzer and Curl{129} (1957) for pure compounds in terms of the acentric factor, 493 values of the binary interaction parameters for 121 binary systems were obtained. These values indicate themselves well with the fact that the binary interaction constant is a function of temperature, not universal constant.

CHAPTER I

INTRODUCTION AND OBJECTIVES

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A. Examination and Extension of the Pitzer Generalized Correlation

For pure compounds, the quantitative representation of the volumetric behaviour and thermodynamic properties of fluids over both gas and liquid regions has proven to be of primary importance in process engineering calculations. It is now over one hundred years since van der Waals first proposed his equation of state {161} (1873), yet still we are in need of improvements in the prediction and correlation of the volumetric properties of normal fluids. This situation is in marked contrast to the extensive theoretical advances with respect to the thermodynamic properties of ideal gases. In order to study the volumetric properties of the pure fluids, the compressibility factor

$$Z = \frac{PV}{RT} \tag{1}$$

is chosen to be the basis for this study. The reason for this choice lies in two aspects: first, for this compressibility factor, Z, its value is unity for an ideal gas and hence the deviation from unity compressibility factor will denote the extent to which the volume of the gas molecules and the molecular interactions are relevant. Secondly, whenever we have a complete set of generalized correlations for the compressibility factors, then we will be able to learn many useful thermodynamic properties of the pure compounds with interest.

For the thermodynamic properties of pure compounds, most contain partial derivatives of the three properties P, V, T, such as $(\partial V/\partial P)_T$ or $(\partial V/\partial T)_P$, (Reid and Sherwood {143} (1966)). However, when we have the compressibility factor data Z calculated on hand, we can first establish the derivative compressibility factors defined by

$$Z_P = Z - P_r\left(\frac{\partial Z}{\partial P_r}\right)_{T_r} \qquad (2)$$

$$Z_T = Z + T_r\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \qquad (3)$$

and then obtain the partial derivatives by

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{RZ_T}{P} \qquad (4)$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RTZ_P}{P^2} \qquad (5)$$

it is then a very simple task to express useful equilibrium properties in terms of these generalized functions. This application as to the derivative compressibility factors will be further discussed in Chapter VIII. Hence, the importance of studying the compressibility factor for pure compounds cannot be over-emphasized.

Also the demand for the volumetric properties of normal fluids has been increased rapidly in the natural gas and petrochemical industries, and this demand will grow even greater in the future. However, the needed volumetric properties are frequently not available at the desired temperature and pressure, especially at the extreme conditions. For this purpose, the three-parameter correlation of Pitzer et al.{128} (1955) has found wide acceptance and is used more and more extensively in predicting such properties in the T_r and P_r regions of $0.8 \leq T_r \leq 4.0$ and $0 \leq P_r \leq 9.0$. It was further extended to the low temperature region of $0.5 \leq T_r \leq 0.8$ and $0 \leq P_r \leq 9.0$ by Lu et al.{103} (1973), by using the isothermal coefficient of bulk compressibility values compiled by Rowlinson {149} (1969). Then Lee and Kesler {96} (1975) presented $Z^{(0)}$ and $Z^{(1)}$ values in the regions of $0.3 \leq T_r \leq 4.0$ and $0 \leq P_r \leq 10.0$ based on a modified equation of state proposed by Benedict, Webb and Rubin {8} (1940). This investigation attempted to examine and then verify the validity of this generalized correlation in the form of $Z = Z^{(0)} + \omega Z^{(1)}$ through correlating more extensive and more up-to-date literature data, together with reaching the confirmation that compounds with quantum or highly polar nature must be excluded from this acentric-factor correlation.

The Pitzer three-parameter generalized correlation employed the acentric factor in addition to the reduced temperature and reduced pressure, which were originally covered by the hypothesis of corresponding states proposed by van der Waals. This acentric factor correlation is the most frequently used third parameter, therefore Pitzer's tables of $Z^{(0)}$ and $Z^{(1)}$ values have been widely quoted, notwithstanding that there are some limitations in the original presentation. These limitations include the number of compounds used as the basis for correlational purpose may be too few, the applicable ranges of T_r and P_r may be limited, and therefore the assumed linear relationship of $Z = Z^{(0)} + \omega Z^{(1)}$ may not be appropriate. Hence the need of a revised and more up-to-date presentation of this three-parameter generalized correlation is apparent. It is then the objective of this study (i) first, to examine whether the first-order truncation of the compressibility factor function expanded by means of a power series in the acentric factor

$$Z = Z^{(0)} + \omega Z^{(1)} + \ldots \qquad (6)$$

is appropriate; and (ii) secondly, if it is verifiable, to extend the T_r and P_r regions to cover wider ranges of interest, especially in the extreme conditions; such as the volumetric properties at both high temperature and high pressure conditions at which the demand of such properties and knowledge is growing in recent natural gas and petroleum industries.

B. Evaluation of the Binary Interaction Parameter from the Second Virial Coefficient Approach

In parallel to the objective of the compressibility-factor correlation study for the pure compounds, which is to learn many useful thermodynamic properties of pure compounds of interest, attention has also been focused on the study and understanding of the properties of mixtures as well as the excess thermodynamic properties due to mixing processes. One of the most common methods of predicting mixture properties is to select a suitable equation of state together with appropriate thermodynamic relationships and mixing rules, due to the lack of experimental data often encountered. This is most useful for predicting excess thermodynamic properties and phase equilibria data in mixtures. Due to the fact that these data and properties are more plentiful for binary systems than that for ternary systems, and are most frequently not available for multi-component systems, it is therefore not only desirable but also necessary to estimate multi-component data from binary data. Hence the binary interaction coefficients which are the key factor in predicting binary mixture properties are generally incorporated in the mixing rules of an equation of state, in order for evaluating the parameters used in the prediction of the properties on binary systems. These coefficients are needed for further calculating the properties for ternary and higher solutions from data for the behaviour of the constituent binary mixtures.

Furthermore, as far as the realm of the equation of state is concerned, the only equation of state having exact physical significance on a molecular scale and thoroughly sound theoretical foundation is the virial equation of state:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots = 1 + B\rho + C\rho^2 + \ldots \qquad (7)$$

where B, C, ... etc., are the second, third, ... virial coefficients. The physical significance as represented by this equation of state is to reflect the molecular interactions of particular numbers of molecules. Thus, for the second virial coefficient:

$$B = \lim_{\frac{1}{V} \to 0} (Z - 1)V \tag{8}$$

it accounts for the interactions between pairs of molecules. However, virtually nothing is known about the virial coefficients beyond the third. Fortunately, the virial equation when truncated to the second term is a highly reliable equation of state at low pressures. The second term of the virial equation represents no more than a first-order correction to the ideal-gas law, and as such provides an entirely suitable extension to the simplest of P-V-T expressions for low pressures. Furthermore, the virial equation, when truncated to three terms, represents data accurately and is, therefore, entirely adequate for the vast majority of engineering applications (Van Ness {163} (1964), p. 47).

For obtaining the information and properties of binary mixtures, the binary interaction parameters as proposed by Chueh and Prausnitz {23} (1967) as well as by Zudkevitch et al.{80}{170} (1970) have played a key role as far as the modified mixing rules of the Redlich-Kwong equation of state {141} (1949) are concerned. A direct relationship was established between these binary interaction parameters by Kato et al.{84} (1976). These parameters lie in the correction term to the characteristic energy parameter for a binary interaction, derived from the geometric mean of the pure component parameters, by a coefficient(1 - k_{ij}). This correction factor was also demonstrated by Hiza and Duncan {71} (1970). When we insert this binary interaction constant k_{ij} into the mixing rules of an equation of state, an excellent representation of the mixture data can be obtained, as a contrast to the rather poor predicted result when using the mixing rules without this correction parameter, i.e., when $k_{ij} = 0$. References in these aspects concerning the binary mixture behaviour involves the compressibility factor, fugacity coefficients, saturated liquid volume and critical pressure for binary mixtures (Chueh and Prausnitz {23}{24}{25} (1967)); cross second virial coefficients (Hiza and Duncan {71} (1970)); isothermal enthalpy departures (Sugie and Lu {160} (1971)) and the solid-vapor equilibrium data (Robinson and Hiza {147} (1975)). Also, good agreements of the activity coefficients and the excess Gibbs free energy of mixing data with the experimental values were obtained by applying the binary interaction constants (Hamam and Lu {65} (1976)). Furthermore a few treatments of the k_{ij} values have been provided by means of the excess molal volume of mixing (Chang and Lu {17} (1970)), the excess volume, enthalpy and Gibbs free energy of mixing (Chang and Lu {18} (1971)) and from the binary isothermal vapor-liquid equilibria data by minimizing the deviations between the calculated and experimental total pressure or the vapor-phase composition (Kato et al.{84} (1976)).

The objective of this study is to obtain the k_{ij} values as they are characteristic constants of the i-j interactions, so as to obtain the useful information and property behaviour of the binary mixtures, especially for the vapor-liquid equilibria and excess thermodynamic properties of mixing as stated thus far. Also, interest has been drawn on the argument claimed by Chueh and Prausnitz {23} (1967) that the k_{ij} values are independent of temperature, density and compositions.

In this investigation, the second virial coefficient correlation in terms of the acentric factor proposed by Pitzer and Curl {129} (1957) for pure compounds was employed, together with adopting the mixing rules proposed by Guggenheim and McGlashan {62} (1951), followed by Prausnitz and Gunn {130} (1958), as well as by Chueh and Prausnitz {23} (1967), the binary interaction constants for binary mixtures were calculated. These binary interaction constants so evaluated do show themselves to be a function of temperature and are comparable with those developed by other published works concerning the temperature-dependence of k_{ij}, such as partly shown by Chang and Lu {17}{18} (1970, 1971), Lu et al.{104} (1974), Hamam and Lu {63}{64}{65} (1974, 1976), Kato et al. {83}{84} (1975,1976) and Hamam et al.{66} (1977). Hence this work offers a strong support for the fact that k_{ij} is a function of temperature, not universal constant, and furthermore, these binary interaction constants do fit in the trend of the k_{ij}-temperature relationships as established by the k_{ij} values obtained through using the binary vapor-liquid equilibria data.

CHAPTER II

REVIEW OF PAST WORK

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A. The Principle of Corresponding States and Pitzer's Original Work

In a series of papers, Pitzer and co-workers presented studies under the title of "The Volumetric and Thermodynamic Properties of Fluids" {127}{128}{129}{34} (1955, 1957, 1958). These papers developed a corresponding states principle with theoretical basis in relation to the statistical mechanical proof of the theory of corresponding states, together with rigorous theoretical tests made for the second virial coefficients. They suggested that the compressibility factor of a normal fluid in either gas or liquid state should be expressible with precision as a function of just one parameter in addition to the reduced temperature and reduced pressure, which were involved in the original hypothesis of corresponding states from van der Waals. The additional parameter is defined in terms of the vapor pressure at $T_r = 0.7$. This third parameter is required because the intermolecular force in complex molecules is a sum of interactions between various parts of the molecules - not just their centers - hence the name "acentric factor" is suggested. The theory requires that any group of substances with equal values of the acentric factor should conform among themselves to the principle of corresponding states. This result is verified with relatively high accuracy, according to Pitzer et al.{128} (1955). They defined the acentric factor as

$$\omega = -\log\left(\frac{P_{sat.}}{P_c}\right)_{T_r=0.7} - 1.000 \qquad (9)$$

Then they used the power series expression in the acentric factor

$$Z = Z^{(0)} + \omega Z^{(1)} + \ldots \qquad (6)$$

where the coefficients $Z^{(0)}$, $Z^{(1)}$, ... etc., are each functions of T_r and P_r. Hence the compressibility factor is expressed as a function of three variables shown by

$$Z = \frac{PV}{RT} = Z(T_r, P_r, \omega) \qquad (10)$$

and the generalized correlation of the tabulated coefficients of equation (6) is often called the three-parameter correlation or the acentric-factor correlation.

For the power series expansion of the compressibility factor shown in equation (6), Pitzer and co-workers reported that in almost all regions, the first two terms are sufficient, hence their correlations were essentially of the form

$$Z = Z^{(0)} + \omega Z^{(1)} \qquad (11)$$

and furthermore, they found that this linear relationship in the acentric factor was also adequate for the other thermodynamic properties of pure fluids as far as the application of the compressibility factor is concerned {129}{34} (1957, 1958), such as the second virial coefficient, obtained by the equation

$$B = \lim_{\frac{1}{V}\to 0} (Z - 1)V \tag{8}$$

and interpreted in terms of the acentric factor as

$$\frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega\frac{B^{(1)}P_c}{RT_c} \tag{12}$$

Likewise, for the fugacity, enthalpy and entropy functions, they were obtained by

$$\ell n(\tfrac{f}{P}) = \int_0^{P_r} \frac{(Z - 1)}{P_r}\, dP_r \tag{13}$$

$$\left(\frac{H^*-H}{RT_c}\right) = T_r^{\,2} \int_0^{P_r} \left(\frac{1}{P_r}\right)\left(\frac{\partial Z}{\partial T_r}\right) dP_r \tag{14}$$

$$\left(\frac{S^*-S}{R}\right) = \int_0^{P_r} \left(Z-1 + T\frac{\partial Z}{\partial T}\right)\left(\frac{1}{P_r}\right) dP_r \tag{15}$$

and interpreted by

$$\log(\tfrac{f}{P}) = \left[\log(\tfrac{f}{P})\right]^{(0)} + \omega\left[\log(\tfrac{f}{P})\right]^{(1)} \tag{16}$$

$$\left(\frac{H^*-H}{RT_c}\right) = \left(\frac{H^*-H}{RT_c}\right)^{(0)} + \omega\left(\frac{H^*-H}{RT_c}\right)^{(1)} \tag{17}$$

$$\left(\frac{S^*-S}{R}\right) = \left(\frac{S^*-S}{R}\right)^{(0)} + \omega\left(\frac{S^*-S}{R}\right)^{(1)} \tag{18}$$

also these three functions are interrelated by the relationship

$$\left(\frac{S^*-S}{R}\right) = \left(\frac{H^*-H}{RT_c}\right)\left(\frac{1}{T_r}\right) + \ell n(\tfrac{f}{P}) \tag{19}$$

These functions were evaluated by graphical differentiation and integration of the $Z^{(0)}$ and $Z^{(1)}$ values with respect to T_r and P_r, respectively.

Also in their works, Pitzer et al. showed that this three-parameter generalized correlation is applicable to the compounds categorized as the "normal" fluids, with emphasis on the simplest class of such substances following the corresponding states behaviour as comprising the heavier rare gases (Ar, Kr and Xe) and termed as "simple fluids". For these simple fluids, their acentric factor values are taken to be zero based on the definition shown in equation (9). The properties of the "normal" fluids as well as the "simple" fluids will be discussed in Chapter X, Appendix B. For this reason, the compounds with quantum effects or highly polar nature were excluded from Pitzer's original correlations, and the values of $Z^{(0)}$ and $Z^{(1)}$ as defined by equation (11) were presented in tabular forms for compressibility factor calculations {128} (1955).

B. Earlier Extensions of the Pitzer Correlation

Following the three-parameter correlations proposed by Pitzer and co-workers, a number of authors have recently extended the correlations to lower temperatures. Chao et al. {20}{21} (1971) presented correlations for the enthalpy, entropy, fugacity and vapor pressure of non-polar liquids at low temperatures. Carruth and Kobayashi {16} (1972) again reported an extension to low reduced temperatures of the three-parameter corresponding states for vapor pressures, enthalpies and entropies of vaporization and liquid fugacity coefficients. For the compressibility factor correlation, which is of prime interest in this work as well as in understanding the thermodynamic properties of pure compounds, Lu and co-workers {103}{74}{75} (1973, 1974) extended the generalized $Z^{(0)}$ and $Z^{(1)}$ values to the low temperature region of $0.5 \leqq T_r \leqq 0.8$ and $0 \leqq P_r \leqq 9.0$ by using the isothermal coefficient of bulk compressibility, β_T, compiled by Rowlinson {149} (1969) and defined by

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{20}$$

to evaluate the Z values of liquids. The Z values for the gas phase were obtained from the generalized second virial coefficients reported (Chang and Lu {19} (1972)). The working functions are

$$\int_{P_1}^{P_2} \beta_T \, dP = -\int_{P_1}^{P_2} \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T dP \tag{21}$$

and

$$\beta_T(P_2-P_1) = \ln\left(\frac{V_1}{V_2}\right) \tag{22}$$

under the assumption that β_T was preliminarily treated as constant independent of pressure at a given temperature.

Using the $Z^{(0)}$ and $Z^{(1)}$ values presented in tabular form, the correlation for the compressibility factors were further expressed by an analytical form expressed by means of the following equations:

$$\frac{Z^{(0)}}{P_r} = A_0(T_r) + A_1(T_r)P_r + A_2(T_r)P_r^2 + A_3(T_r)P_r^3 \qquad (23)$$

$$\frac{Z^{(1)}}{P_r} = B_0(T_r) + B_1(T_r)P_r + B_2(T_r)P_r^{\frac{1}{2}} + B_3(T_r)P_r^{\frac{1}{3}} \qquad (24)$$

in which A_i and B_i are functions of T_r and were further correlated by equations as

$$A_i(T_r) = A_{i0} + A_{i1}T_r + A_{i2}T_r^2 + A_{i3}T_r^3 + A_{i4}T_r^4 \qquad (25)$$

$$B_i(T_r) = B_{i0} + B_{i1}T_r^{-1} + B_{i2}T_r^{-2} + B_{i3}T_r^{-3} + B_{i4}T_r^{-4} \qquad (26)$$

hence the coefficients of equations (25) and (26) were obtained. Furthermore, for the application of the extended correlation to the low temperatures, generalized $(\frac{f}{P})$, Z_T, Z_P and enthalpy departure values for liquids at these low reduced temperatures were also presented based on the compressibility factor correlation.

Lee and Kesler {96} (1975) demonstrated Pitzer's three-parameter generalized correlation together with their applications by the use of a modified equation of state originally proposed by Benedict et al. (BWR equation of state) {8} (1940). They chose n-Octane as a reference fluid and expressed the compressibility factor as

$$Z = Z^{(0)} + \omega Z^{(1)} \qquad (11)$$

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} (Z^{(r)} - Z^{(0)}) \qquad (27)$$

where (r) denotes reference fluid. The equation of state is

$$Z = \left(\frac{P_r V_r}{T_r}\right) = 1 + \frac{B'}{V_r} + \frac{C'}{V_r^2} + \frac{D'}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta' + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \tag{28}$$

where

$$B' = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \tag{29}$$

$$C' = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \tag{30}$$

$$D' = d_1 + \frac{d_2}{T_r} \tag{31}$$

the constants B', C', D' and β' are different from the notations of B, C, D and β used thus far in this work. In order to determine the constants in equations (28) to (31), the compressibility factor data of four compounds and the enthalpy data of five compounds were correlated by use of the following constraints:

$$f^V = f^L \text{ (at saturated condition)} \tag{32}$$

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = \left(\frac{\partial^2 P_r}{\partial V_r^2}\right)_{T_r} = 0 \quad \text{(at critical point)} \tag{33}$$

where f is the fugacity. Then properties such as fugacity coefficient, enthalpy departure, entropy departure, isochoric and isobaric heat capacity departures were evaluated by means of thermodynamic relationships and the constants obtained from equations (28) to (31). Also an expression for the acentric factor evaluation was proposed. A comparison between the calculated compressibility factors and the literature data for 12 compounds was also presented which serves further as the source for the comparing and testing purpose for this presentation (see Chapter VI).

C. Literature Survey of the P-V-T and Second Virial Coefficient Data

The limitations of the Pitzer correlation {128} (1955) as described earlier (see Chapter I, Part A), also as shown by the statements quoted from Pitzer's original work {128} (1955), (see Chapter III, Part C), indicate that the data sources chosen as the correlation basis will be the key factor as far as the precision and applicability of this generalized correlation are concerned. Hence, ample efforts were made to collect appropriate data. At first, all the data used by Pitzer et al.{128} (1955) were collected. It was obvious that the data of Sage et al.{150}{123}{28}{137}{151}{138} (1937, 1943, 1945, 1950, 1951) played a very important role in Pitzer's original work, especially for temperatures near $T_r = 0.8$. For the gas phase data, the ones reported by Michels and co-workers were also chosen {112}{113}{110}{111} {114}{115} (1935, 1936, 1937, 1949) extensively. The number of compounds chosen is 15.

In this work, compressibility factor data for 57 compounds available in the literature have been selected which cover adequately the T_r and P_r regions of $0.5 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 12.0$. Due to the credibility of the authors, the data of A. Michels and co-workers, {109}{110}{111}{112}{113}{114}{115}{116}{117}{118}{119} (1934, 1935, 1936, 1937, 1949, 1951, 1953, 1958, 1966), also of Sage et al.{150}{123}{124}{28}{137}{151}{152}{138}{140} (1937, 1943, 1944, 1945, 1950, 1951, 1955, 1957) were used. Extensive data were taken from the Journal of Chemical and Engineering Data series. The overall number of compounds chosen is 57 from 66 data sources. (see Table 2 and Chapter IX). The literature data used by Lu et al.{103} (1973) and by Lee and Kesler {96} (1975) were also covered.

For the virial equation of state, it really has not suffered from lack of treatment and study. In principle, the determination of virial coefficients experimentally is straightforward. It is only necessary to measure P, V, and T accurately and then to extract the virial coefficients. For example, the second virial coefficients can be obtained from equation (8):

$$B = \lim_{\frac{1}{V}\to 0} (Z - 1)V \tag{8}$$

which has drawn extensive attention due to the simplicity in form and significance in theoretical considerations. Also, it provides valuable criteria for smoothing the P-V-T data. The virial coefficients depend only on the temperature and on the particular gas, but are independent of density or pressure. For pure compounds, the virial coefficients have been compiled by Dymond and Smith {48} (1969) as well as by Mason and Spurling {106} (1969). The second virial coefficients of mixtures, through which binary interaction parameters will be evaluated in this work, is shown exactly by

$$B = \sum_{i}^{n} \sum_{j}^{n} y_i y_j B_{ij} \qquad (34)$$

where n is the number of constituents in the gaseous solution. For a binary solution consisting of constituents 1 and 2, this equation becomes:

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (35)$$

where y is the mole fraction in the system and B_m denotes the second virial coefficient of the binary mixture. The coefficients B_{11} and B_{22} are the second virial coefficients for the pure gases 1 and 2 at the temperature of the solution, and B_{12} is the interaction or cross coefficient, which is a function of temperature only. Experimental values of B_{12} are usually calculated from equation (35). Usually these second virial coefficients data are presented in the way of solubility or phase equilibria, for which a compilation work was done by Mason and Spurling {106} (1969). In this investigation, data for 121 binary systems were collected and special attention has been given to compounds which are the constituents of natural gas or petroleum gas, such as hydrocarbons (both paraffinic and olefinic) ranging from methane to n-Octane, nitrogen, carbon dioxide and hydrogen sulfide.

CHAPTER III

PROCEDURE OF EXAMINING AND EXTENDING THE PITZER CORRELATION

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In this Chapter, we first reviewed the validity of Pitzer's acentric-factor correlation and then extended the $Z^{(0)}$ and $Z^{(1)}$ values to wider ranges. Data for 57 compounds were collected for correlation and cross-plotting technique was adopted for the review and extension purposes.

A. Compressibility Factor Data of Pure Compound from Literature

Pitzer and co-workers {128} (1955) expanded the compressibility factor function by means of a power series in the acentric factor :

$$Z = Z^{(0)} + \omega Z^{(1)} \quad \ldots \qquad (6)$$

where $Z^{(0)}$, $Z^{(1)}$, ... etc., are each functions of T_r and P_r. In this work, we carefully collected the P-V-T data from literature and used the assumptions of Pitzer et al.{128}(1955) that, in a homogeneous region, the Z, $Z^{(0)}$ and $Z^{(1)}$ ... values are all single-valued and continuous functions of T_r and P_r and that the derivatives with respect to T_r and P_r are also continuous. Hence for the same compound, the data source for which the compressibility factor data was a continuous function of T_r and P_r to the utmost degree was chosen, and the choices depended on the credibility of the author. Also the test for the smoothness of the P-V-T data provided by the second virial coefficient consideration (see Chapter IV, Part C) was employed whenever necessary. The data used by Pitzer et al.{128} (1955) were also included. Due to the fact that Pitzer's original data were mostly in the vapor phase, the data of 55 compounds collected as the correlational basis were also covering the T_r and P_r ranges in the vapor phase originally as shown in Table 1. Then, in the subsequent efforts, data in the liquid phase were again chosen extensively to cover the whole ranges of $0.5 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 12.0$ as applicable for both the liquid and vapor phases. At this time 2,3-Di-methylbutane and water were included and made up the data for the pure compounds numbered 57, and the data sources reported by Lu et al.{103} (1973) and Lee and Kesler {96} (1975) were all covered. All the data used in this work together with their T_r and P_r ranges are listed in Table 2. The data were in the form of isotherms and presented as temperature-pressure-specific volume (or compressibility factor or density) relationships and the compressibility factors were calculated using appropriate universal gas constants. For the data of methane by Vennix et al.{165} (1970) for which the presentation was neither in the form of isotherms nor in the form of isobars, reference was made to the original work in which the data was adjusted into the form of isotherms (Vennix {164} (1966)). Hence we have a set of calculated Z-T_r-P_r results for each reference,

TABLE 1 Literature Data Used in This Work (1)

Compound	Pr Range	Tr Range	Reference
Argon	0-60.186	0.850-2.802	Michels et al. (1949); (1958)
Krypton	0- 1.917	1.358-2.438	International Critical Tables (1928)
Xenon	0- 7.002	1.000-1.978	Beattie et al. (1951)
Methane	0- 8.472	1.434-2.221	Michels and Nederbragt (1936)
Ethane	0- 4.944	0.964-1.291	Sage et al. (1937)
Propane	0- 7.291	1.000-1.482	Beattie et al. (1937)
n-Butane	0-18.155	0.732-1.202	Olds et al. (1944)
2-Methylpropane (isobutane)	0- 9.448	0.803-1.252	Sage and Lacey (1950)
n-Pentane	0-20.459	0.804-1.088	Sage and Lacey (1950)
2-Methylbutane (isopentane)	0- 1.815	0.702-1.028	Silberberg et al. (1959)
2,2-Dimethylpropane (neopentane)	0- 9.883	0.791-1.148	Dawson et al. (1973)
n-Hexane	0-10.163	1.031-1.080	Kelso and Felsing (1940)
2-Methylpentane	0- 8.187	1.052-1.102	Kelso and Felsing (1940)
3-Methylpentane	0-10.113	0.690-1.087	Day and Felsing (1952)
2,2-Dimethylbutane	0- 1.501	1.009-1.173	Griskey and Canjar (1964)
n-Heptane	0- 9.469	1.015-1.153	Smith et al. (1937)
n-Octane	0-12.225	0.656-0.694	Felsing and Watson (1942)
2,2,4-Trimethylpentane	0-11.844	0.686-0.961	Felsing and Watson (1943)
2,2,3,3-Tetramethylbutane	0-10.601	0.674-0.956	Felsing et al. (1947)
n-Nonane	0-21.642	0.510-0.964	Doolittle (1964)
n-Decane	0- 0.048	0.414-0.783	Rossini et al. (1953)
n-Undecane	0-15.271	0.474-0.897	Doolittle (1964)
n-Dodecane	0- 0.056	0.388-0.734	Rossini et al. (1953)
n-Tridecane	0-17.409	0.448-0.848	Doolittle (1964)
n-Heptadecane	0-15.191	0.440-0.781	Doolittle (1964)
n-Eicosane	0-17.911	0.486-0.747	Doolittle (1964)
Cyclopropane	0- 5.753	0.737-1.189	Lin et al. (1970)
Cyclohexane	0-16.922	0.562-0.923	Reamer and Sage (1957)
Ethene (ethylene)	0-19.873	0.967-1.499	Din (1956)
Propene (propylene)	0-14.951	0.944-1.401	Sage and Lacey (1955)

TABLE 1 (continued)

Compound	Pr Range	Tr Range	Reference
1-Butene	0-17.135	0.900-1.059	Sage and Lacey (1955)
1-Pentene	0- 7.796	0.760-1.072	Day and Felsing (1951)
Ethyne (acetylene)	0- 1.650	0.584-1.038	Din (1956)
Benzene	0- 1.300	0.920-1.120	Gornowski et al. (1947)
Neon	0- 7.435	0.674-6.742	McCarty and Stewart (1965)
Nitrogen	0-22.930	0.975-3.352	Michels et al. (1951)
Oxygen	0-19.944	0.779-3.054	International Critical Tables (1928)
Hydrogen sulfide	0- 7.652	0.744-1.190	Reamer et al. (1950); Sage and Lacey (1955)
Carbon dioxide	0-24.600	0.898-1.392	Michels and Michels (1936); Michels et al. (1936)
Carbon monoxide	0-20.272	0.626-5.064	Din (1956)
Sulfur dioxide	0- 4.054	0.657-1.215	Kang et al. (1961)
Nitrogen monoxide	0- 2.500	1.081-1.568	International Critical Tables (1928)
Nitrous oxide	0- 4.393	0.785-1.366	Couch et al. (1961)
Difluoromethane	0- 3.448	0.848-1.346	Malbrunot et al. (1968)
Perfluoromethane (tetrafluoromethane)	0-10.667	1.200-2.738	Douslin (1962)
Chlorodifluoromethane (Freon 22)	0- 7.035	0.821-1.282	Zander (1968)
Chlorotrifluoromethane (Freon 13)	0- 9.819	0.987-1.401	Michels et al. (1966)
Dichlorodifluoromethane (Freon 12)	0- 1.965	0.839-1.099	Michels et al. (1966)
Chloromethane (methyl chloride)	0- 0.617	0.824-0.932	International Critical Tables (1928)
Dichloromethane (methylene chloride)	0- 3.333	0.784-1.470	Seshadri et al. (1967)
Trichloromethane (chloroform)	0- 3.704	0.783-1.398	Seshadri et al. (1968)
Perchloromethane (carbon tetrachloride)	0- 4.444	0.755-1.348	Seshadri et al. (1966)
Hydrogen	0-23.438	0.879-5.092	International Critical Tables (1928)
Helium	0-24.898	0.496-5.650	International Critical Tables (1928)
Ammonia	0- 1.172	0.796-1.474	Beattie and Lawrence (1930)

TABLE 2 - LITERATURE DATA USED IN THIS WORK (2)

Compound	Pr Range	Tr Range	Reference
Argon	0-2.193	1.147-4.458	Holborn and Otto (1925)
	0-1.302	0.818-1.944	International Critical Tables (1928)
	0-104.167	0.596-3.974	Din (1956)
	0-60.186	0.850-2.802	Michels et al. (1949); (1958)
Krypton	0-1.917	1.358-2.438	International Critical Tables (1928)
Xenon	0-1.768	0.981-1.762	International Critical Tables (1928)
	0-7.002	1.000-1.978	Beattie et al. (1951)
Methane	0-7.097	1.434-2.483	International Critical Tables (1928)
	0-8.472	1.434-2.221	Michels and Nederbragt (1935); (1936)
	0-2.100	0.671-1.545	Corcoran et al. (1945)
	0-14.997	1.545-2.682	Sage and Lacey (1950)
	0-22.046	0.682-2.467	Din (1961)
	0-8.832	1.434-3.271	Douslin et al. (1964)
	0-66.138	1.699-2.231	Deffet and Ficks (1965)
	0-15.232	0.789-1.444	Vennix et al. (1970)
Ethane	0-4.944	0.964-1.291	Sage et al. (1937)
	0-14.125	1.019-1.673	Sage and Lacey (1950)
	0-10.382	0.655-1.637	Din (1961)
	0-14.000	0.500-2.000	Phillips and Thodos (1962)
Propane	0-7.291	1.000-1.482	Beattie et al. (1937)
	0-16.220	0.841-1.382	Sage and Lacey (1950)
	0-14.306	0.622-1.622	Din (1956)
n-Butane	0-18.155	0.732-1.202	Olds et al. (1944); Sage and Lacey(1950)
2-Methylpropane (isobutane)	0-9.448	0.762-1.252	Sage and Lacey (1950)
	0-15.117	0.762-1.252	Gonzalez and Lee (1966)
n-Pentane	0-20.459	0.662-1.088	Sage and Lacey (1950)
2-Methylbutane (isopentane)	0-1.815	0.702-1.028	Silberberg et al. (1959)
	0-5.453	0.973-1.028	Vohra and Kobe (1959)
2,2-Dimethylpropane (neopentane)	0-17.238	0.717-1.024	Gonzalez and Lee (1968)
	0-9.883	0.791-1.148	Dawson et al. (1973)
n-Hexane	0-10.488	0.735-1.080	Kelso and Felsing (1940); (1942)
2-Methylpentane	0-10.495	0.750-1.102	Kelso and Felsing (1940); (1942)
	0-1.357	1.011-1.152	Griskey and Canjar (1964)

....2

Compound	Pr Range	Tr Range	Reference
3-Methylpentane	0-10.113	0.690-1.087	Day and Felsing (1952)
2,2-Dimethylbutane	0-9.868	0.764-1.122	Felsing and Watson (1943)
	0-1.501	1.009-1.173	Griskey and Canjar (1964)
2,3-Dimethylbutane	0-10.157	0.746-1.096	Kelso and Felsing (1942)
n-Heptane	0-13.018	0.561-1.153	Smith et al. (1937)
	0-182.764	0.506-1.061	Doolittle (1963); (1964)
n-Octane	0-12.225	0.656-0.964	Felsing and Watson (1942)
	0-8.496	0.454-0.524	Benson and Winnick (1971)
	0-0.041	0.432-0.696	Chappelow et al. (1971)
2,2,4-Trimethylpentane	0-11.844	0.686-0.961	Felsing and Watson (1943)
2,2,3,3-Tetramethylbutane	0-10.601	0.674-0.956	Felsing et al. (1947)
n-Nonane	0-13.545	0.523-0.860	Sage and Lacey (1955)
	0-218.341	0.510-0.964	Doolittle (1964)
n-Decane	0-32.863	0.504-0.828	Sage and Lacey (1950)
	0-0.048	0.396-0.729	Rossini et al. (1953)
n-Undecane	0-254.513	0.474-0.897	Doolittle (1964)
n-Dodecane	0-0.056	0.396-0.734	Rossini et al. (1953)
n-Tridecane	0-290.145	0.448-0.848	Doolittle (1964)
n-Heptadecane	0-379.781	0.440-0.781	Doolittle (1964)
n-Eicosane	0-447.777	0.486-0.747	Doolittle (1964)
Cyclopropane	0-5.753	0.737-1.189	Lin et al. (1970)
Cyclohexane	0-16.922	0.562-0.923	Reamer and Sage (1957)
Ethene (ethylene)	0-20.137	0.967-1.670	International Critical Tables (1928)
	0-49.683	0.967-1.499	Din (1956)
Propene (propylene)	0-14.951	0.762-1.401	Sage and Lacey (1955)
1-Butene	0-17.135	0.742-1.059	Sage and Lacey (1955)
1-Pentene	0-7.796	0.760-1.072	Day and Felsing (1951)
Ethyne (acetylene)	0-0.198	0.886-0.967	International Critical Tables (1928)
	0-1.650	0.519-1.038	Din (1956)
Benzene	0-1.300	0.920-1.120	Gornowski et al. (1947)
	0-14.073	0.553-0.909	Sage and Lacey (1955)

....3

Compound	Pr Range	Tr Range	Reference
Neon	0-7.435	0.562-6.742	McCarty and Stewart (1965)
Nitrogen	0-3.164	0.975-5.332	Holborn and Otto (1925)
	0-90.171	0.987-5.332	International Critical Tables (1928)
	0-2.555	2.164-3.352	Michels et al. (1934)
	0-30.670	2.024-5.544	Sage and Lacey (1950)
	0-237.297	0.975-3.352	Michels et al. (1951)
	0-300.571	0.634-5.544	Din (1961)
Oxygen	0-2.115	1.767-2.414	Holborn and Otto (1925)
	0-59.832	0.779-3.054	International Critical Tables (1928)
Hydrogen sulfide	0-7.652	0.744-1.190	Reamer et al. (1950); Sage and Lacey (1955)
	0-18.943	0.998-1.320	Lewis and Fredericks (1968)
Carbon dioxide	0-1.307	0.776-0.996	Jenkin (1920)
	0-13.727	0.898-1.746	International Critical Tables (1928)
	0-42.786	0.898-1.392	Michels and Michels (1936); Michels et al. (1936)
	0-1.351	0.907-1.030	Michels et al. (1937)
	0-9.338	0.913-1.680	Sage and Lacey (1955)
	0-50.000	0.712-20.000	Kennedy and Thodos (1960)
	0-2.059	0.898-2.870	Van Huff et al. (1963)
Carbon monoxide	0-34.752	0.550-5.064	Din (1956)
Sulfur dioxide	0-4.054	0.657-1.215	Kang et al. (1961)
Nitrogen monoxide	0-2.500	1.081-1.568	International Critical Tables (1928)
Nitrous oxide	0-4.393	0.785-1.366	Couch et al. (1961)
Difluoromethane	0-3.448	0.706-1.346	Malbrunot et al. (1968)
Perfluoromethane (tetrafluoromethane)	0-10.667	1.200-2.738	Douslin (1962)
Chlorodifluoromethane (Freon 22)	0-7.035	0.821-1.282	Zander (1968)
Chlorotrifluoromethane (Freon 13)	0-11.370	0.987-1.401	Michels et al. (1966)
Dichlorodifluoromethane (Freon 12)	0-1.965	0.839-1.099	Michels et al. (1966)
Chloromethane (methyl chloride)	0-0.617	0.824-0.932	International Critical Tables (1928)
	0-4.732	0.740-1.197	Hsu and McKetta (1964)
Dichloromethane (methylene chloride)	0-3.333	0.549-1.470	Seshadri et al. (1967)

......4

Compound	Pr Range	Tr Range	Reference
Trichloromethane (chloroform)	0-3.704	0.522-1.398	Seshadri et al. (1968)
Perchloromethane (carbon tetrachloride)	0-4.444	0.539-1.348	Seshadri et al. (1966)
Hydrogen	0-226.562	0.879-20.194	International Critical Tables (1928)
Helium	0-24.898	0.496-44.481	International Critical Tables (1928)
Ammonia	0-1.172	0.796-1.474	Beattie and Lawrence (1930)
Water	0-1.000	0.422-1.425	Steam Tables (1940)

and the sources of the critical constants and the molecular weights are given in Chapter X, Appendix A.

B. Cross-Plotting Technique for Each Pure Compound

First we draw graphs of the compressibility factor, Z, versus reduced pressure at constant reduced temperature conditions, that is, isotherms. These drawings were made all on large graphic papers to facilitate the readings in order to obtain highly precise compressibility factor values. Sample drawings of this nature were shown in Figures 1 to 4 for ethane (Sage et al.{150} (1937)), neopentane (Dawson et al.{36} (1973)), n-Octane (Felsing and Watson {52} (1942)) and n-Heptadecane (Doolittle {44} (1964)). Heavy hydrocarbons such as n-Decane or further have sufficiently low vapor pressures such that essentially, no experimental information appears to be available concerning the volumetric and compressibility factor characteristics of the gas phase. Care was taken not to extrapolate the available data and special attention was focused on the regions near the two-phase zone, that is, around the critical point where the liquid and vapor phases coexist.

Secondly, cross-plotting technique was employed and the Z versus T_r using P_r as the parameters were drawn on large graphs this time. These graphs were made from the information of the Z versus P_r at constant T_r drawings as described in the first step. Typical examples were shown in Figures

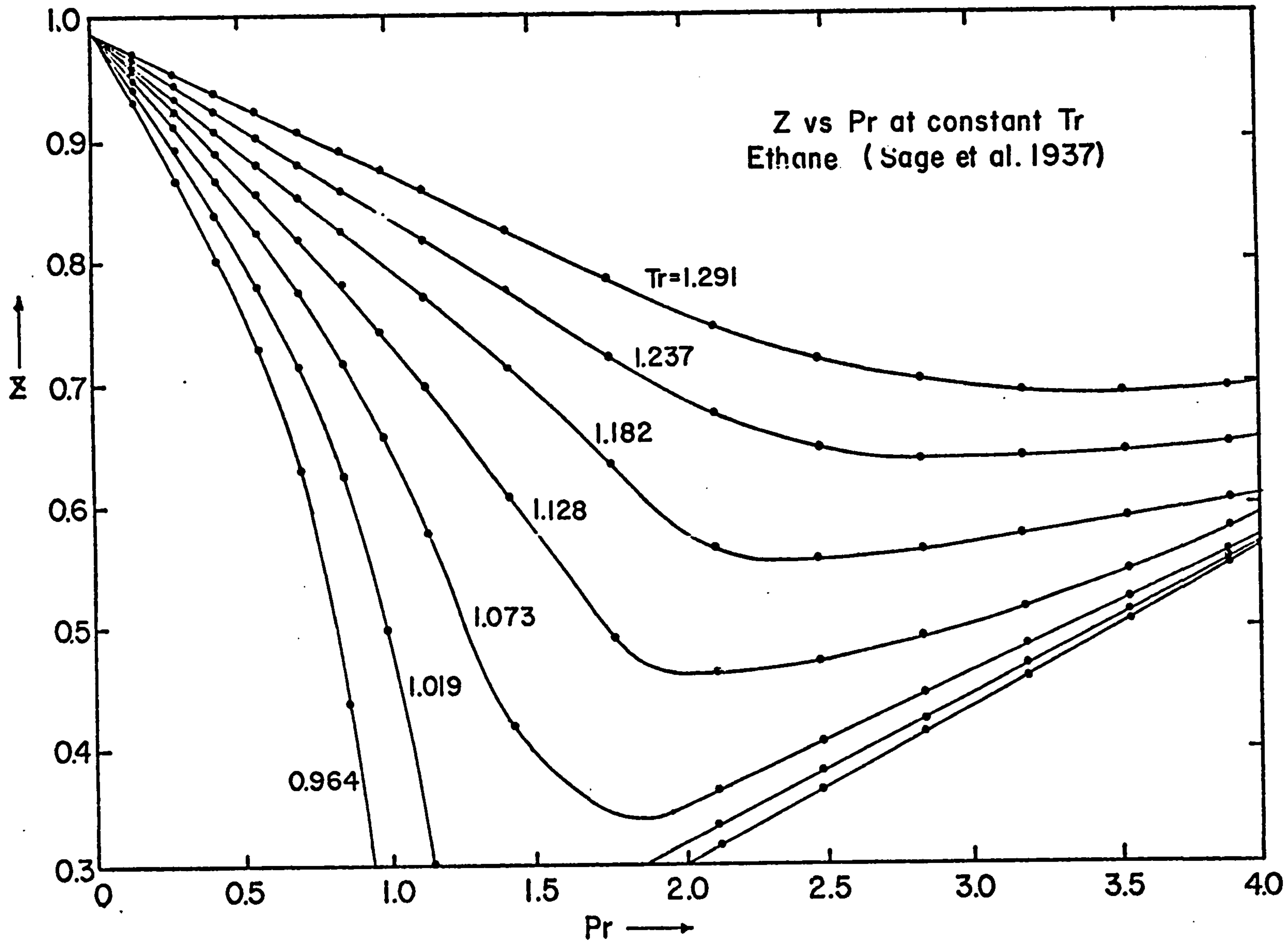

Figure 1. Z vs Pr at Constant Tr for Ethane

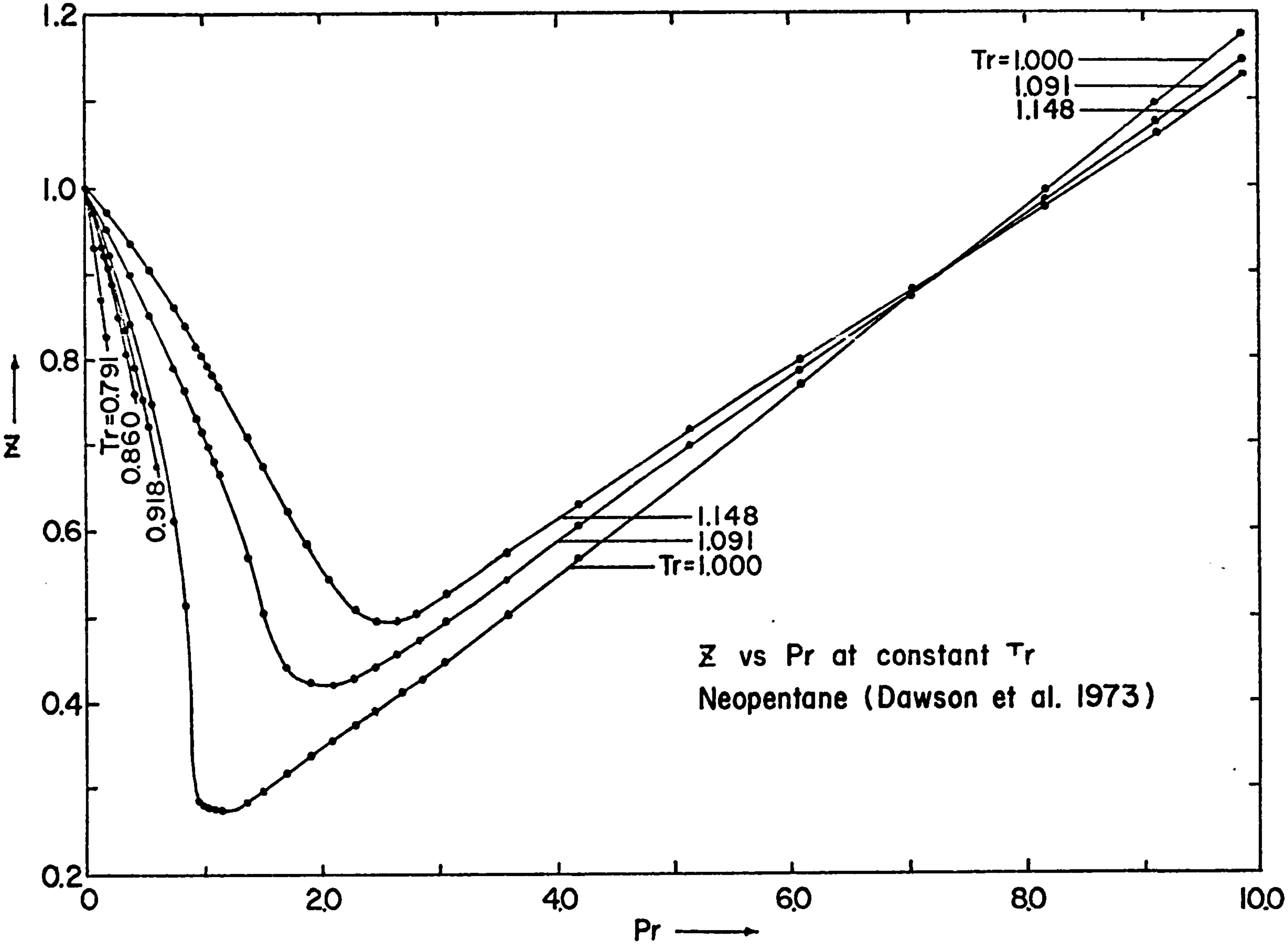

Figure 2. Z vs Pr at Constant Tr for Neopentane

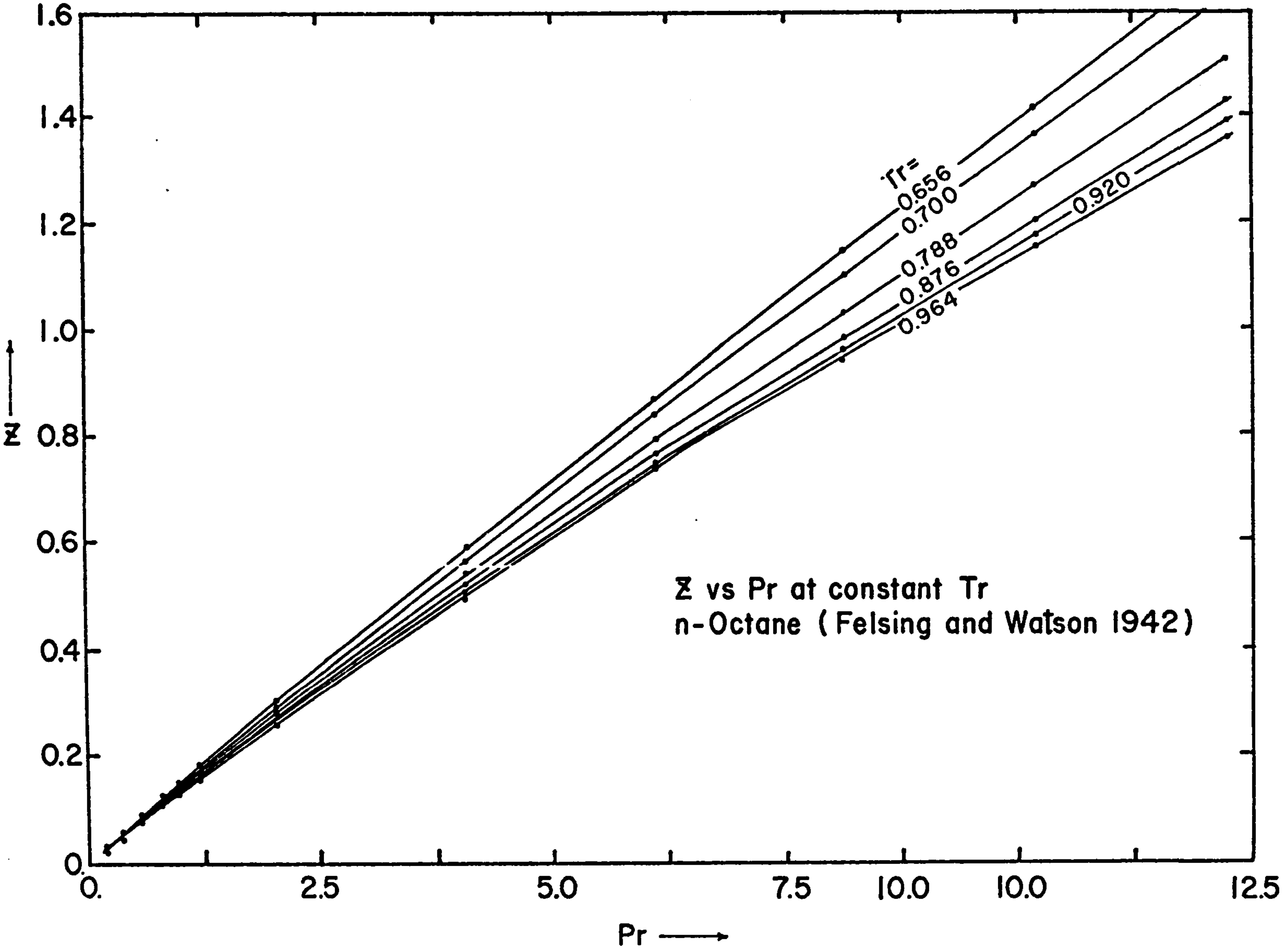

Figure 3. Z vs Pr at Constant Tr for n-Octane

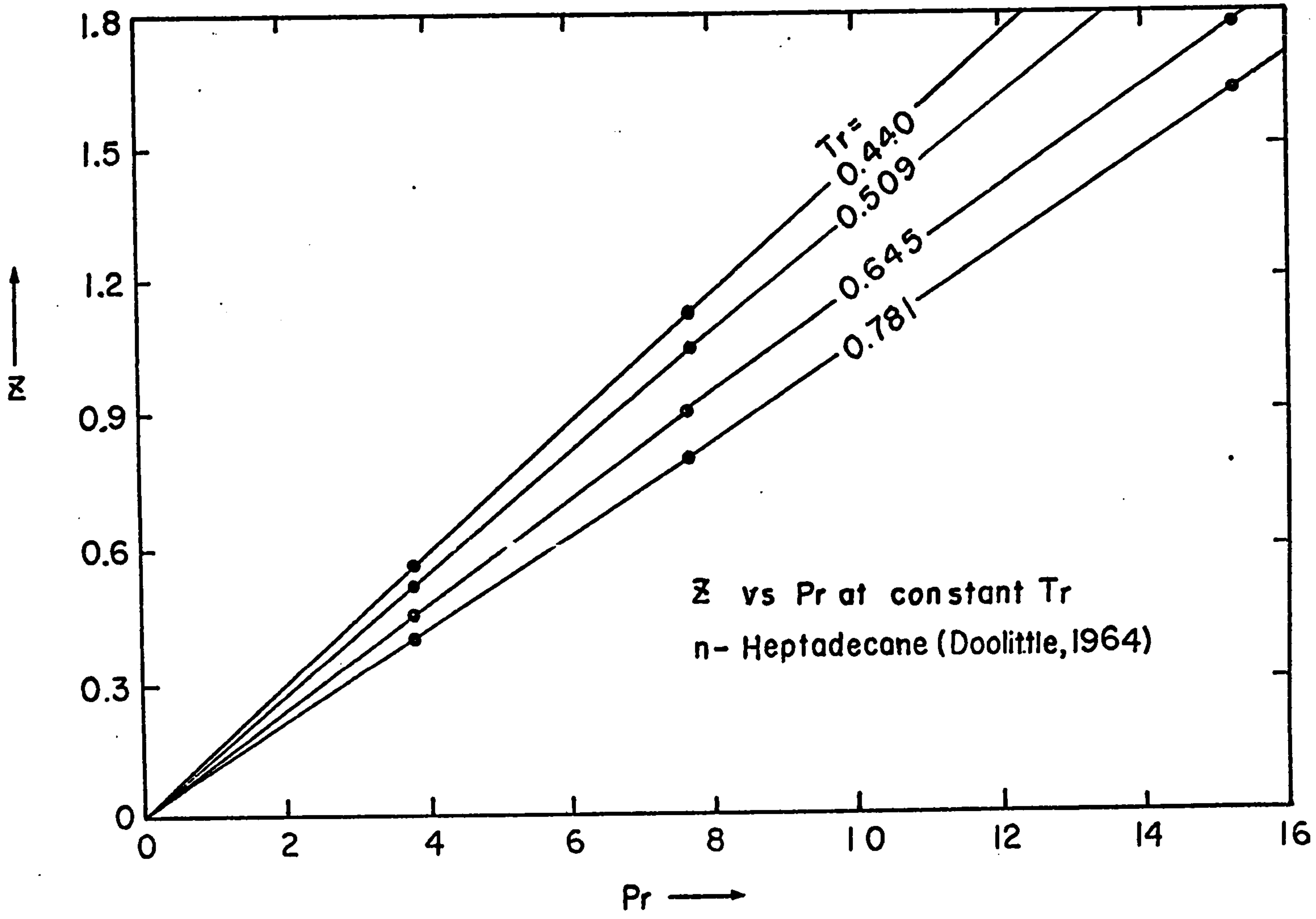

Figure 4. Z vs Pr at Constant Tr for n-Heptadecane

5 to 8, obtained from Figures 1 to 4. Again, special care was taken on the critical region as well as on the prohibition of extrapolation.

Having obtained these two kinds of drawings, namely the Z versus P_r at constant T_r and the Z versus T_r at constant P_r, it was then possible to obtain tables of the compressibility factor as a function of P_r and T_r at regular intervals for each compound, thus formed a cross-plotting procedure. These tables were examplified by the four compounds ethane, neopentane, n-Octane and n-Heptadecane, shown in Tables 3 to 6, as obtained from Figures 1 to 8.

C. Correlation of the $Z^{(0)}$ and $Z^{(1)}$ Values

Now we are ready for the extension and review of Pitzer's generalized correlation. The motivation and incentive for this examination, as stated in Chapter I, Part A and Chapter II, Part C, came essentially from the following quotation from the original work of Pitzer et al.{128} (1955, p.3435): "In certain regions either the data are poor or more commonly the data deviate from the linear correlation in ω. In such regions values are given to only the second decimal place and correspondingly lower accuracy must be expected in the calculated results". From these key comments, it is obvious that the accuracy of the $Z^{(0)}$ and $Z^{(1)}$ values presented by the linear correlation for the compressibility factor calculations must depend on the data used as the correlation

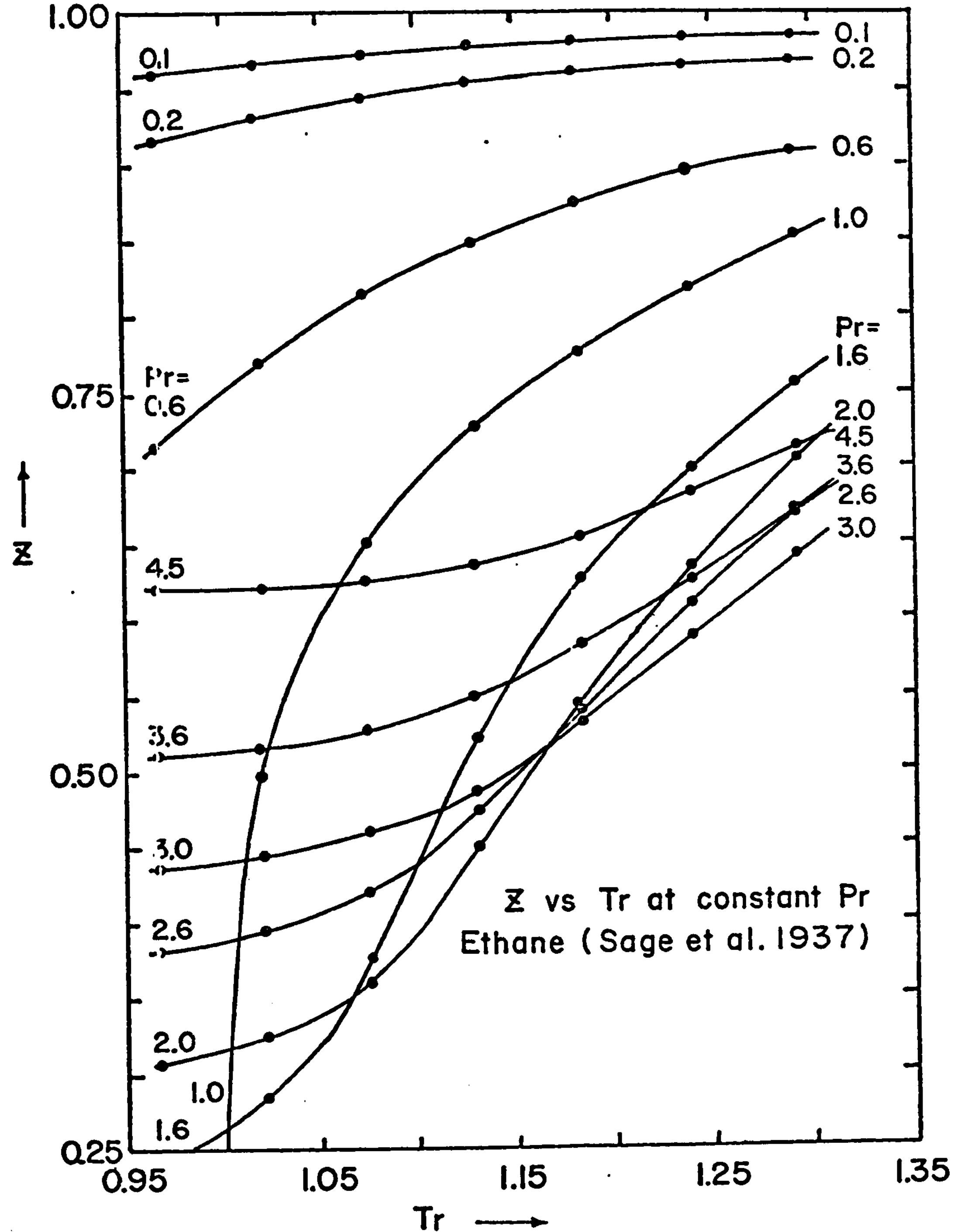

Figure 5. Z vs Tr at Constant Pr for Ethane

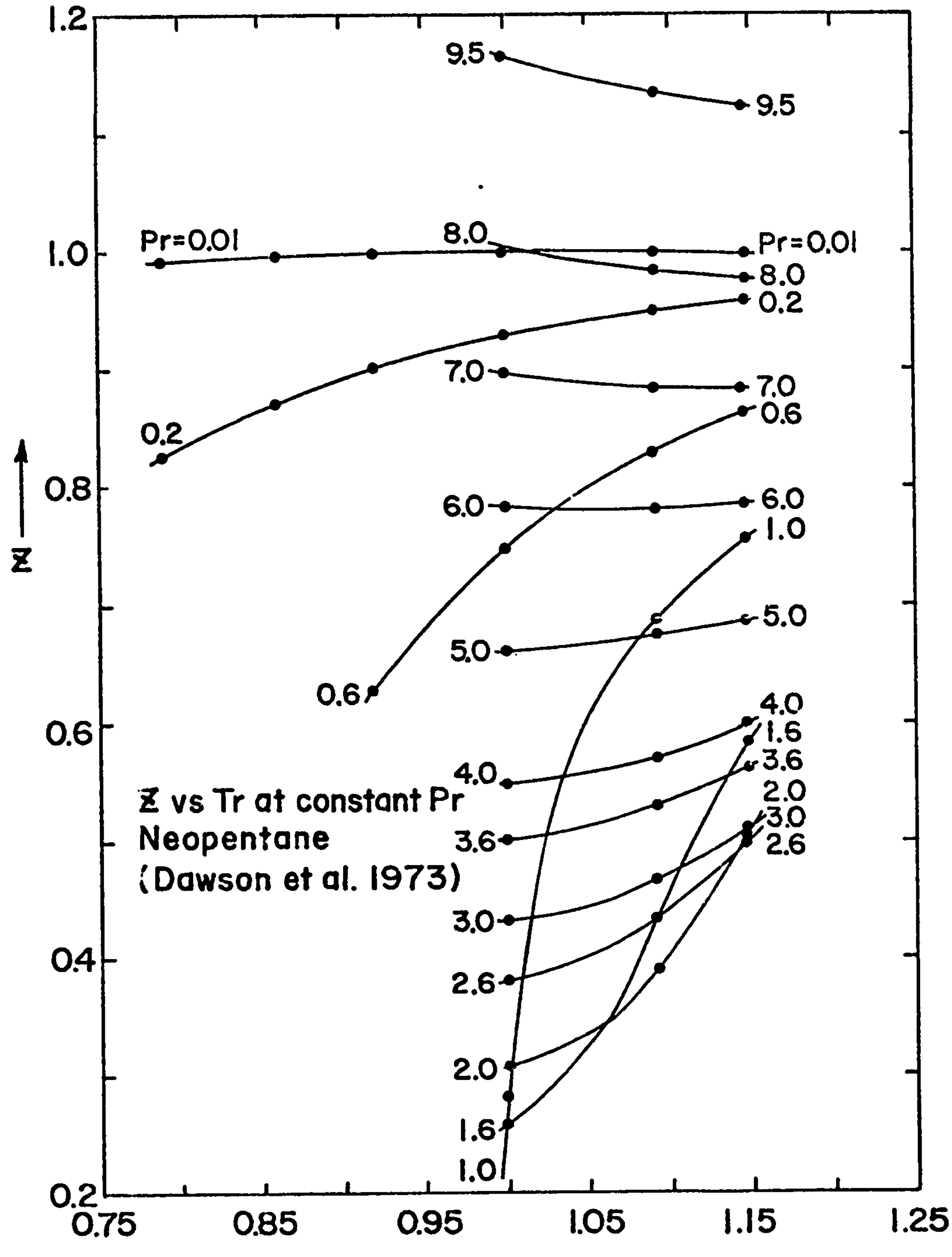

Figure 6. Z̄ vs Tr at Constant Pr for Neopentane

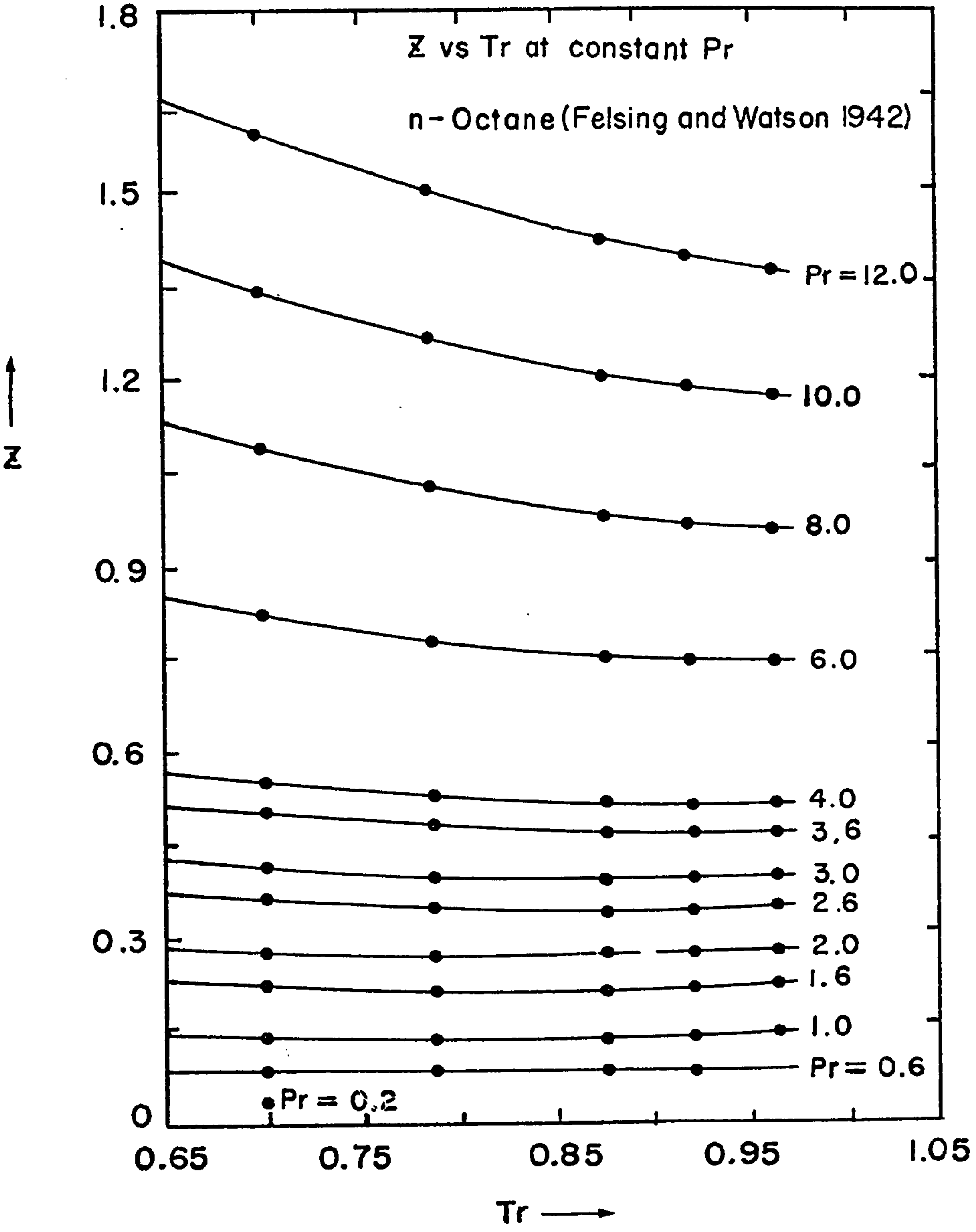

Figure 7. Z vs Tr at Constant Pr for n-Octane

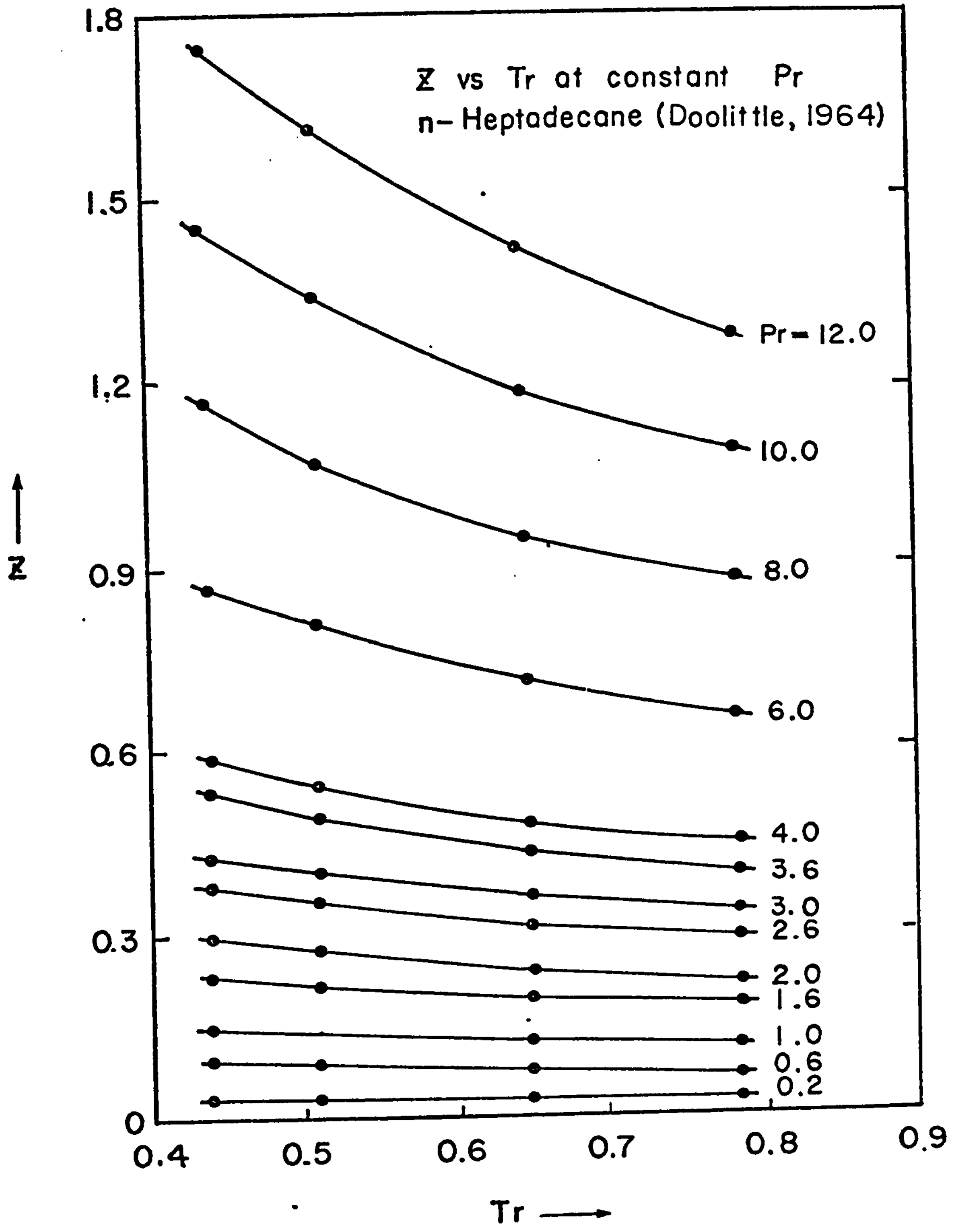

Figure 8. Z vs Tr at Constant Pr for n-Heptadecane

TABLE 3. Z-Tr-Pr Table for Ethane from Cross Plotting

Tr \ Pr	0.01	0.05	0.1	0.15	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.5
1.0	.9960	.9825	.9644	.9461	.9280	.8464	.7530	.6290	.2822	.2182	.2432	.2671	.2921	.3162	.3414	.3665	.3912	.4163	.4407	.4651	.4890	.5131	.5370	.5607	.6220
1.05	.9965	.9847	.9692	.9541	.9391	.8730	.7993	.7135	.6058	.4505	.3620	.3220	.3315	.3395	.3625	.3842	.4070	.4289	.4510	.4740	.4972	.5206	.5436	.5671	.6241
1.1	.9969	.9859	.9739	.9614	.9502	.8946	.8331	.7665	.6938	.6070	.5136	.4527	.4253	.3954	.4106	.4255	.4403	.4560	.4706	.4920	.5136	.5343	.5561	.5770	.6308
1.15	.9972	.9889	.9791	.9675	.9555	.9109	.8593	.8087	.7503	.6881	.6227	.5700	.5300	.4886	.4916	.4941	.4965	.5005	.5023	.5211	.5400	.5593	.5782	.5972	.6437
1.2	.9975	.9901	.9805	.9705	.9611	.9214	.8820	.8393	.7910	.7432	.6940	.6505	.6134	.5761	.5703	.5647	.5603	.5541	.5482	.5638	.5788	.5941	.6091	.6243	.6642
1.25	.9978	.9912	.9830	.9746	.9665	.9321	.8983	.8602	.8249	.7845	.7462	.7105	.6792	.6470	.6375	.6281	.6186	.6082	.5991	.6110	.6231	.6348	.6460	.6580	.6890

TABLE 4. Z-Tr-Pr Table for Neopentane from Cross Plotting

Tr \ Pr	0.01	0.05	0.1	0.15	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8
0.8	.9930	.9604	.9210	.8528	.8318													
0.85	.9939	.9665	.9372	.9014	.8660													
0.9	.9945	.9730	.9500	.9210	.8912	.7575												
0.95	.9951	.9783	.9570	.9342	.9115	.8075	.6726											
1.0	.9959	.9819	.9635	.9445	.9266	.8435	.7480	.6230	.2730	.2122	.2365	.2600	.2840	.3077	.3325	.3572	.3810	.4057
1.05	.9965	.9845	.9688	.9536	.9385	.8720	.7985	.7135	.6080	.4583	.3680	.3255	.3310	.3355	.3573	.3785	.4000	.4213
1.1	.9969	.9857	.9740	.9616	.9500	.8950	.8343	.7690	.6984	.6165	.5267	.4658	.4350	.4032	.4160	.4285	.4412	.4545
1.15	.9971	.9890	.9793	.9677	.9560	.9120	.8617	.8130	.7567	.6983	.6368	.5865	.5470	.5067	.5064	.5061	.5061	.5062

Tr \ Pr	3.0	3.2	3.4	3.6	3.8	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
0.8																	
0.85																	
0.9																	
0.95																	
1.0	.4294	.4530	.4765	.5000	.5233	.5466	.6066	.6661	.7235	.7811	.8383	.8955	.9487	1.0016	1.0558	1.1096	1.1637
1.05	.4423	.4649	.4876	.5103	.5330	.5558	.6113	.6669	.7226	.7780	.8328	.8878	.9394	.9908	1.0423	1.0940	1.1460
1.1	.4670	.4875	.5085	.5288	.5497	.5700	.6220	.6734	.7263	.7792	.8315	.8830	.9323	.9820	1.0325	1.0831	1.1324
1.15	.5065	.5236	.5414	.5598	.5780	.5960	.6400	.6839	.7338	.7835	.8318	.8796	.9271	.9747	1.0226	1.0705	1.1189

TABLE 5. Z-Tr-Pr Table for n-Octane from Cross Plotting

Tr \ Pr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
0.7	.0290	.0574	.0845	.1116	.1405	.1700	.1975	.2250	.2520	.2795	.3075	.3357	.3636	.3920	.4202	.4470	.4745	.5017
0.8		.0541	.0831	.1089	.1373	.1640	.1908	.2173	.2445	.2710	.2970	.3230	.3497	.3760	.4016	.4271	.4527	.4781
0.85		.0551	.0827	.1092	.1376	.1638	.1900	.2166	.2425	.2690	.2945	.3196	.3446	.3703	.3958	.4202	.4452	.4700
0.9			.0840	.1111	.1401	.1660	.1916	.2177	.2433	.2690	.2943	.3194	.3451	.3702	.3957	.4200	.4438	.4675
0.95				.1186	.1455	.1729	.1986	.2247	.2504	.2764	.3012	.3250	.3498	.3742	.3980	.4206	.4436	.4665

Tr \ Pr	3.8	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0
0.7	.5290	.5560	.6223	.6895	.7572	.8247	.8933	.9613	1.0260	1.0910	1.1540	1.2170	1.2821	1.3469	1.4112	1.4760	1.5414	1.6070
0.8	.5031	.5290	.5910	.6523	.7153	.7788	.8410	.9030	.9634	1.0231	1.0830	1.1431	1.2013	1.2602	1.3191	1.3773	1.4370	1.4963
0.85	.4944	.5191	.5806	.6422	.7030	.7642	.8238	.8821	.9400	.9970	1.0541	1.1110	1.1682	1.2262	1.2842	1.3421	1.4000	1.4581
0.9	.4915	.5158	.5753	.6341	.6927	.7492	.8085	.8667	.9227	.9780	1.0320	1.0862	1.1433	1.2000	1.2561	1.3130	1.3685	1.4250
0.95	.4900	.5127	.5727	.6313	.6866	.7427	.7994	.8566	.9102	.9631	1.0176	1.0713	1.1241	1.1773	1.2310	1.2842	1.3371	1.3900

TABLE 6. Z-Tr-Pr Table for n-Heptadecane from Cross Plotting

Tr \ Pr	0.01	0.05	0.1	0.15	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4
0.5	.0019	.0069	.0130	.0203	.0268	.0560	.0835	.1097	.1365	.1642	.1920	.2193	.2476	.2751	.3022	.3292	.3565	.3838	.4105	.4377	.4650
0.6		.0063	.0123	.0183	.0233	.0498	.0726	.0977	.1240	.1471	.1714	.1955	.2200	.2440	.2691	.2935	.3176	.3433	.3680	.3919	.4165
0.7				.0174	.0230	.0461	.0674	.0898	.1136	.1375	.1607	.1830	.2047	.2272	.2510	.2743	.2974	.3215	.3450	.3679	.3907

Tr \ Pr	3.6	3.8	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0
0.5	.4916	.5186	.5459	.6142	.6825	.7505	.8184	.8873	.9571	1.0233	1.0895	1.1561	1.2230	1.2913	1.3593	1.4271	1.4962	1.5640	1.6331
0.6	.4404	.4647	.4888	.5501	.6113	.6738	.7357	.7952	.8543	.9156	.9772	1.0370	1.0981	1.1571	1.2165	1.2760	1.3355	1.3957	1.4546
0.7	.4132	.4363	.4593	.5145	.5702	.6281	.6855	.7440	.8015	.8562	.9123	.9663	1.0192	1.0755	1.1301	1.1856	1.2402	1.2965	1.3530

basis, and more basically, on the validity of the linear truncation of equation (6), i.e., in the form of

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{11}$$

In this investigation, attempts have been made to verify this linear correlation in ω.

Following the procedures of Parts A and B, we obtained the Z-P_r-T_r values represented by tables in regular intervals of T_r and P_r for the 55 compounds as chosen in the first stage shown in Table 1. The data used in this study were further expanded to cover lower temperature regions for liquid phase as shown in Table 2, hence this presentation was founded on an extensive and more up-to-date literature data basis for correlational purpose. In the first place, we gathered all the compressibility factor data available at one reduced pressure and one reduced temperature, then plotted all the compressibility factor data for the various compounds as a function of their corresponding acentric factors at this specified P_r and T_r, then repeating this for all pairs of P_r-T_r conditions. The sources of all the acentric factor values used in this work are given in Chapter X, Appendix A. In plotting these graphs of Z versus ω for the corresponding T_r and P_r conditions, it was obvious that the existence of the quadratic and further terms in the equation

$$Z = Z^{(0)} + \omega Z^{(1)} + \ldots \tag{6}$$

is not necessary. Furthermore, when we excluded the data points of the quantum and highly polar compounds such as hydrogen, helium, ammonia and water from the figures, the linear correlation was obviously shown. A sample graph of this nature was shown in Figure 9 for $T_r = 1.4$, $P_r = 1.0$ conditions. The exclusion of quantum and highly polar compounds from this generalized correlation for normal fluids will be further verified later in this part. Moreover, after employing the least-squares regression method on the second and even third order forms of equation (6), it was found that the $Z^{(2)}$, $Z^{(3)}$ terms showed such scattered and irregular behaviour that there arose considerable doubt as to their validity and hence there was little ground to claim that they are functions of T_r and P_r, letting alone reasonably smooth ones. Therefore, this acentric-factor correlation with the linear form

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{11}$$

is verified to be appropriate.

Thus far we have verified the validity of the linear correlation for compressibility factor data proposed by Pitzer and co-workers {128} (1955), namely, equation (11). Based on the more extensive P-V-T data obtained from the literature as shown in Table 1, an attempt was made to extend Pitzer's original work to wider ranges. By using the least-squares regression method again, all the compressibility factor-acentric factor data were correlated on all the conditions of P_r and T_r, in the linear form of the acentric factor. Thus, we obtained tables of $Z^{(0)}$ and $Z^{(1)}$ values well covering the regions of $0.5 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 11.0$, all

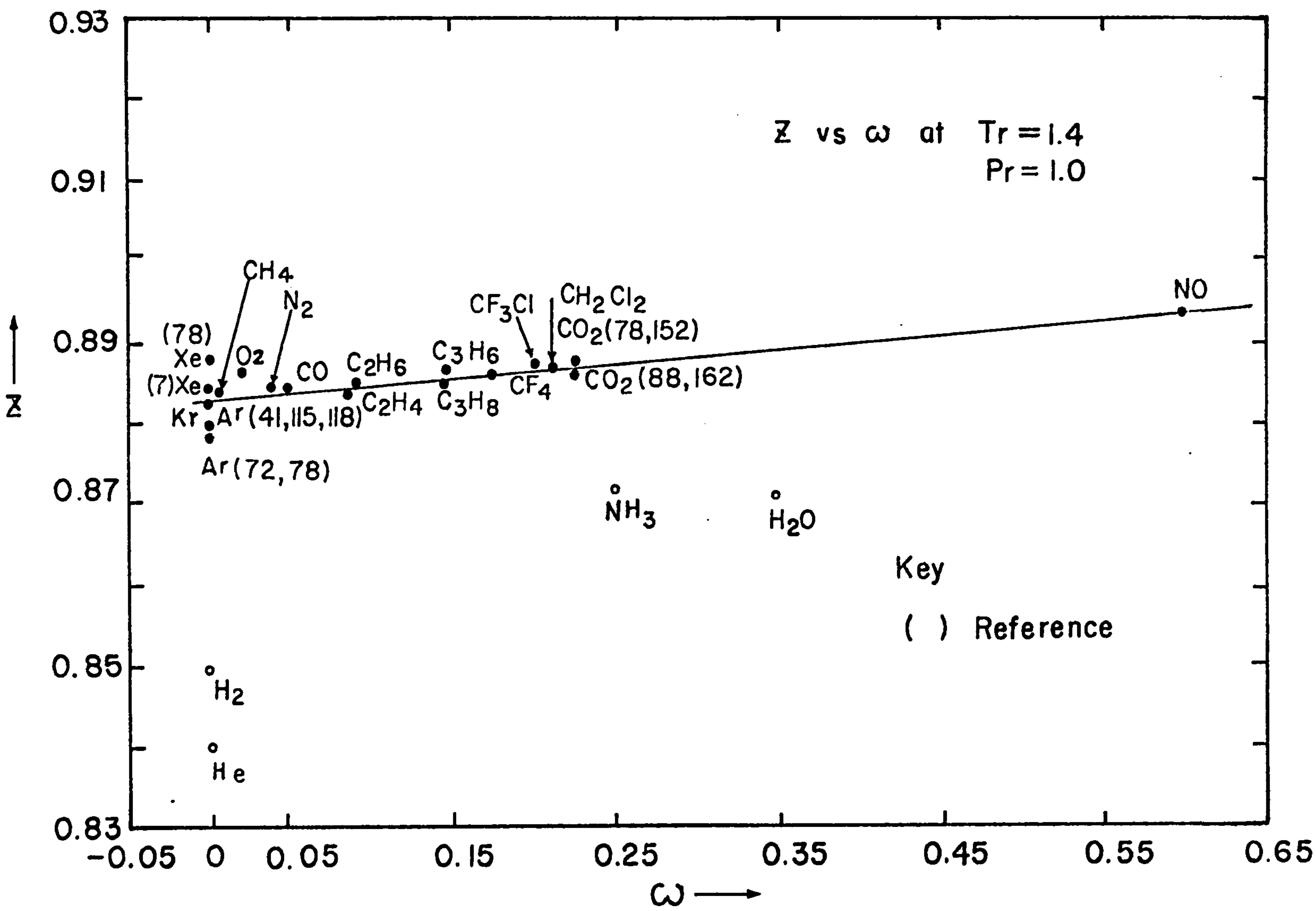

Figure 9. Compressibility Factor as a Function of the Acentric Factor

based on the compressibility factor data as shown in Table 1. These values were presented in Tables 7 and 8. They had well extended the regions of $0.8 \leqq T_r \leqq 4.0$ and $0 \leqq P_r \leqq 9.0$ originally presented by Pitzer et al.{128}(1955). For the $Z^{(0)}$ and $Z^{(1)}$ values shown in Tables 7 and 8, the low-temperature data were not presented mainly because for all the references used in Table 1, the data sources for such low temperatures at $T_r = 0.5$ to 0.7 were rather few, as shown by the T_r ranges for the various references in Table 1. These low temperature data may not be enough for correlation purposes. Therefore efforts were again made to collect and to amplify the literature data available to cover the low temperature region for which most of the data were in the liquid phase. This time, the highly polar compound water was included since it was used in Pitzer's original work. Also we were able to collect data for one more compound, 2,3-Dimethylbutane, hence made the total number of compounds for which compressibility factor data were collected to be 57. All the data sources together with their T_r and P_r ranges are given in Table 2. Now, the literature data are enough for the correlation work to be applied to the whole T_r and P_r ranges of $0.5 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 12.0$. Based on these data sources, values of $Z^{(0)}$ and $Z^{(1)}$ were obtained by the linear correlation program as shown in Chapter X, Appendix C (for $T_r = 1.4$ and $P_r = 1.0$ conditions).

Up to this point, we are ready to make our final presentations of the $Z^{(0)}$ and $Z^{(1)}$ values tabulated as was done

TABLE 7

Values of $Z^{(0)}$ Obtained From All Compounds Listed in Table 1

Tr \ Pr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0.5									
0.6									
0.7									
0.8	.8370	.7126	.1968	.2573	.3172	.3512	.4421	.5131	.5676
0.85	.8822	.7399	.2045	.2656	.3135	.3599	.4342	.5110	.5722
0.9	.9015	.7829	.6461	.2816	.3283	.1603	.2105	.2327	.2680
0.95	.9158	.8189	.7085	.5222	.3219	.1892	.2300	.2457	.2810
1.0	.9273	.8454	.7570	.6425	.3941	.2913	.2551	.2784	.3029
1.05	.9369	.8689	.7991	.7098	.5986	.4596	.3609	.3475	.3444
1.1	.9440	.8866	.8292	.7631	.6826	.5998	.5052	.4395	.4113
1.15	.9513	.9012	.8550	.8020	.7428	.6792	.6154	.5529	.5057
1.2	.9566	.9134	.8747	.8315	.7858	.7360	.6868	.6404	.5934
1.25	.9620	.9244	.8914	.8540	.8190	.7776	.7381	.6993	.6628
1.3	.9663	.9336	.9051	.8737	.8421	.8093	.7778	.7441	.7153
1.35	.9719	.9449	.9216	.8938	.8666	.8388	.8140	.7853	.7623
1.4	.9746	.9493	.9287	.9042	.8801	.8551	.8316	.8096	.7908
1.45	.9775	.9551	.9363	.9148	.8933	.8718	.8510	.8381	.8154
1.5	.9797	.9595	.9434	.9241	.9047	.8899	.8713	.8592	.8432
1.55	.9815	.9635	.9496	.9320	.9146	.9020	.8868	.8738	.8600
1.6	.9835	.9672	.9546	.9388	.9237	.9088	.8940	.8812	.8695
1.65	.9851	.9706	.9595	.9456	.9315	.9181	.9051	.8939	.8840
1.7	.9865	.9735	.9638	.9512	.9387	9273	.9149	.9051	.8965
1.75	.9868	.9764	.9678	.9563	.9453	.9350	.9250	.9161	.9087
1.8	.9893	.9788	.9713	.9624	.9514	.9415	.9329	.9248	.9189
1.85	.9905	.9811	.9746	.9655	.9566	.9579	.9402	.9322	.9280
1.9	.9915	.9832	.9774	.9696	.9612	.9533	.9467	.9404	.9361
1.95	.9928	.9851	.9801	.9730	.9655	.9589	.9525	.9473	.9437
2.0	.9937	.9871	.9826	.9767	.9696	.9635	.9573	.9534	.9511
2.25	.9968	.9935	.9907	.9878	.9856	.9827	.9795	.9781	.9780
2.5	.9993	.9983	.9986	.9990	.9987	.9969	.9961	.9968	.9975
2.75	.9995	.9992	.9986	.9986	.9989	.9996	.9988	.9987	.9991
3.0	1.0004	1.0005	1.0013	1.0018	1.0019	1.0020	1.0020	1.0023	1.0030
3.25	1.0003	.9998	.9997	1.0006	1.0011	1.0016	1.0024	1.0020	1.0030
3.5	1.0013	1.0009	1.0014	1.0024	1.0034	1.0039	1.0051	1.0052	1.0069
3.75	1.0016	1.0018	1.0024	1.0037	1.0045	1.0060	1.0069	1.0081	1.0090
4.0	1.0013	1.0022	1.0028	1.0046	1.0055	1.0067	1.0082	1.0095	1.0105
4.25	1.0026	1.0050	1.0061	1.0090	1.0104	1.0134	1.0159	1.0182	1.0200
4.5	1.0026	1.0054	1.0074	1.0098	1.0118	1.0143	1.0168	1.0188	1.0210
4.75	1.0036	1.0058	1.0080	1.0100	1.0129	1.0150	1.0172	1.0192	1.0220
5.0	1.0035	1.0058	1.0082	1.0106	1.0134	1.0157	1.0181	1.0198	1.0222

Tr \ Pr	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
0.5					.1893	.1798	.2096	.2220	.4564
0.6		.4905	.4478	.4968	.4921	.5264	.5584	.6216	.6178
0.7	.3500	.3859	.3998	.4356	.4550	.4829	.5190	.5337	.5788
0.8	.3318	.3593	.4150	.4475	.4780	.5067	.5435	.5752	.6034
0.85	.2930	.3253	.4006	.4368	.4730	.5012	.5363	.5688	.5977
0.9	.2894	.3192	.3705	.3936	.4233	.4547	.4830	.5097	.5372
0.95	.3102	.3391	.3684	.3932	.4204	.4465	.4740	.5002	.5247
1.0	.3255	.3500	.3748	.4007	.4246	.4486	.4727	.4954	.5195
1.05	.3624	.3807	.4031	.4228	.4454	.4688	.4915	.5148	.5380
1.1	.4086	.4154	.4289	.4493	.4626	.4839	.5042	.5259	.5773
1.15	.4760	.4636	.4661	.4792	.4926	.5080	.5260	.5420	.5617
1.2	.5570	.5342	.5252	.5285	.5292	.5379	.5537	.5643	.5814
1.25	.6304	.6074	.5903	.5860	.5802	.5792	.5831	.5978	.6091
1.3	.6895	.6657	.6490	.6389	.6304	.6266	.6305	.6349	.6361
1.35	.7423	.7146	.6999	.6880	.6774	.6708	.6708	.6707	.6692
1.4	.7732	.7517	.7451	.7286	.7166	.7099	.7083	.7054	.7055
1.45	.7995	.7841	.7733	.7714	.7538	.7473	.7448	.7449	.7403
1.5	.8308	.8210	.8111	.8045	.7853	.7796	.7756	.7746	.7704
1.55	.8490	.8436	.8340	.8301	.8104	.8054	.7999	.7985	.7972
1.6	.8594	.8560	.8470	.8439	.8334	.8280	.8242	.8224	.8211
1.65	.8752	.8735	.8664	.8630	.8534	.8487	.8449	.8432	.8426
1.7	.8890	.8886	.8825	.8794	.8710	.8667	.8634	.8613	.8614
1.75	.9028	.9026	.8977	.8957	.8891	.8849	.8825	.8804	.8816
1.8	.9139	.9153	.9106	.9090	.9033	.8998	.8977	.8956	.8973
1.85	.9239	.9262	.9222	.9208	.9161	.9130	.9115	.9097	.9111
1.9	.9327	.9354	.9322	.9310	.9274	.9248	.9240	.9219	.9234
1.95	.9409	.9438	.9415	.9402	.9373	.9356	.9354	.9333	.9344
2.0	.9483	.9480	.9497	.9484	.9463	.9453	.9452	.9435	.9442
2.25	.9785	.9794	.9796	.9801	.9798	.9800	.9805	.9793	.9811
2.5	1.0000	.9960	.9950	.9959	.9981	.9989	1.0000	1.0010	1.0024
2.75	.9995	1.0004	.9993	1.0016	1.0020	1.0026	1.0036	1.0036	1.0051
3.0	1.0048	1.0047	1.0063	1.0055	1.0084	1.0098	1.0098	1.0098	1.0108
3.25	1.0033	1.0047	1.0049	1.0061	1.0065	1.0078	1.0094	1.0087	1.0103
3.5	1.0073	1.0086	1.0095	1.0108	1.0123	1.0132	1.0149	1.0149	1.0168
3.75	1.0101	1.0111	1.0126	1.0142	1.0157	1.0174	1.0184	1.0194	1.0213
4.0	1.0117	1.0130	1.0145	1.0160	1.0178	1.0194	1.0209	1.0221	1.0242
4.25	1.0216	1.0238	1.0258	1.0284	1.0314	1.0338	1.0354	1.0372	1.0399
4.5	1.0229	1.0248	1.0271	1.0294	1.0326	1.0349	1.0371	1.0380	1.0410
4.75	1.0239	1.0260	1.0279	1.0302	1.0330	1.0352	1.0382	1.0384	1.0413
5.0	1.0244	1.0264	1.0289	1.0309	1.0327	1.0350	1.0378	1.0390	1.0413

Tr \ Pr	3.8	4.0	4.5	5.0	5.5	6.0	6.5	7.0
0.5	.4916	.5122	.6988	.7636	.8291	.8796	.9337	.9939
0.6	.6398	.6740	.7622	.8428	.9381	1.0058	1.0754	1.1563
0.7	.6059	.6426	.7349	.8073	.8842	.9586	1.0287	1.1032
0.8	.6404	.6733	.7533	.8338	.9130	.9901	1.0653	1.1417
0.85	.6328	.6676	.7458	.8188	.8926	.9687	1.0436	1.1188
0.9	.5688	.6019	.6622	.7253	.7916	.8595	.9284	1.0482
0.95	.5472	.5717	.6188	.6822	.7411	.7994	.8544	.8696
1.0	.5436	.5672	.6209	.6790	.7340	.7885	.8483	.9002
1.05	.5635	.5873	.6426	.7016	.7609	.8170	.8778	.9338
1.1	.5706	.5939	.6454	.7018	.7581	.8125	.8678	.9207
1.15	.5822	.6047	.6535	.7051	.7587	.8112	.8692	.9126
1.2	.5985	.6190	.6652	.7112	.7624	.8125	.8616	.9097
1.25	.6232	.6434	.6838	.7286	.7738	.8236	.8672	.9140
1.3	.6478	.6660	.7051	.7443	.7871	.8332	.8724	.9159
1.35	.6765	.6909	.7288	.7628	.8005	.8420	.8784	.9192
1.4	.7102	.7187	.7420	.7825	.8162	.8536	.8879	.9251
1.45	.7424	.7444	.7631	.8015	.8316	.8648	.8963	.9317
1.5	.7703	.7706	.7848	.8216	.8487	.8771	.9089	.9430
1.55	.7984	.7693	.8066	.8393	.8630	.8937	.9224	.9544
1.6	.8214	.8215	.8292	.8587	.8790	.9032	.9335	.9642
1.65	.8567	.8427	.8486	.8771	.8947	.9160	.9448	.9734
1.7	.8605	.8612	.8668	.8941	.9104	.9289	.9516	.9827
1.75	.8799	.8806	.9005	.9115	.9268	.9342	.9640	.9917
1.8	.8954	.8960	.9151	.9255	.9401	.9556	.9746	1.0006
1.85	.9092	.9101	.9288	.9386	.9518	.9659	.9847	1.0087
1.9	.9220	.9223	.9413	.9504	.9633	.9764	.9944	1.0164
1.95	.9332	.9337	.9525	.9610	.9733	.9862	1.0024	1.0235
2.0	.9560	.9442	.9632	.9712	.9832	.9952	1.0109	1.0298
2.25	.9818	.9826	1.0032	1.0116	1.0212	1.0337	1.0451	1.0595
2.5	1.0044	1.0060	1.0269	1.0353	1.0453	1.0558	1.0673	1.0795
2.75	1.0057	1.0104	1.0187	1.0256	1.0328	1.0410	1.0500	1.0594
3.0	1.0121	1.0139	1.0235	1.0304	1.0360	1.0420	1.0511	1.0606
3.25	1.0120	1.0132	1.0177	1.0217	1.0262	1.0315	1.0362	1.0426
3.5	1.0194	1.0204	1.0240	1.0284	1.0329	1.0383	1.0435	1.0492
3.75	1.0238	1.0245	1.0281	1.0326	1.0376	1.0406	1.0480	1.0543
4.0	1.0260	1.0275	1.0304	1.0352	1.0402	1.0454	1.0512	1.0574
4.25	1.0436	1.0462	1.0660	1.0738	1.0421	1.0474	1.0528	1.0588
4.5	1.0442	1.0474	1.0658	1.0738	1.0433	1.0486	1.0543	1.0592
4.75	1.0445	1.0472	1.0658	1.0740	1.0807	1.0882	1.0960	1.1028
5.0	1.0446	1.0468	1.0660	1.0738	1.0798	1.0878	1.0940	1.1019

Pr / Tr	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
0.5	1.0385	1.0942	1.1518	1.1947	1.2495	1.3081	1.3751	1.4248
0.6	1.2296	1.3090	1.3750	1.4522	1.3252	1.3922	1.4581	1.5268
0.7	1.1728	1.2416	1.3158	1.3850	1.4518	1.5239	1.5314	1.6057
0.8	1.2213	1.2958	1.3087	1.3834	1.4555	1.5215	1.8332	1.9163
0.85	1.1947	1.2709	1.2895	1.3507	1.4257	1.4987	2.3986	2.5093
0.9	1.1210	1.1923	1.1880	1.2442	1.3098	1.3730	3.8414	4.0973
0.95	.9193	.9877	.5426	.5472	.5702	.5874		
1.0	.9514	.9530	.9606	.8456	.8942	.9100	1.0614	
1.05	.9891	1.0309	1.0798	1.1249	1.1758	1.2306	1.3491	
1.1	.9751	1.0151	1.0656	1.1104	1.1613	1.2090	1.3143	
1.15	.9646	1.0038	1.0521	1.0960	1.1413	1.1886	1.2689	
1.2	.9552	.9938	1.0377	1.0772	1.1307	1.1759	1.2352	
1.25	.9572	.9886	1.0305	1.0754	1.1186	1.1639		
1.3	.9585	.9877	1.0266	1.0683	1.1074	1.1502		
1.35	.9590	.9881	1.0249	1.0637	1.1003	1.1430		
1.4	.9638	.9905	1.0249	1.0620	1.0958	1.1380	.9972	
1.45	.9669	.9883	1.0233	1.0590	1.0897	1.1316	.9964	
1.5	.9752	.9955	1.0272	1.0616	1.0923	1.1301	1.1720	
1.55	.9845	1.0045	1.0354	1.0673	1.0997	1.1355	1.1760	
1.6	.9923	1.0112	1.0406	1.0703	1.1022	1.1355	1.1787	
1.65	1.0008	1.0189	1.0457	1.0733	1.1045	1.1349	1.1801	
1.7	1.0085	1.0270	1.0512	1.0770	1.1073	1.1344	1.1855	
1.75	1.0162	1.0366	1.0606	1.0854	1.1138	1.1387	1.1813	
1.8	1.0239	1.0432	1.0657	1.0892	1.1161	1.1396	1.1803	
1.85	1.0310	1.0495	1.0710	1.0935	1.1188	1.1405	1.1815	
1.9	1.0375	1.0552	1.0762	1.0974	1.1213	1.1414	1.1808	
1.95	1.0435	1.0606	1.0814	1.1017	1.1238	1.1425	1.1807	
2.0	1.0495	1.0656	1.0857	1.1055	1.1266	1.1439	1.1806	
2.25	1.0768	1.0908	1.1704	1.1239	1.1422	1.1574	1.1804	
2.5	1.0928	1.1058	1.1220	1.1375	1.1521	1.1675	1.1816	
2.75	1.0700	1.0708	1.1304	1.1442	1.1574	1.1724	1.1811	
3.0	1.0688	1.0575	1.1355	1.1490	1.1590	1.1676		
3.25	1.0486	.9871	.9904	.9922	.9971	1.0025		
3.5	1.0564	.9975	1.0006	1.0054	1.0100	1.0139		
3.75	1.0610	1.0072	1.0111	1.0159	1.0204	1.0244	1.0287	1.0346
4.0	1.0632	1.0145	1.0188	1.0237	1.0272	1.0316	1.0364	1.0415
4.25	1.0646	1.0192	1.0230	1.0272	1.0314	1.0363	1.0413	1.0468
4.5	1.0656	1.0219	1.0258	1.0294	1.0342	1.0391	1.0447	1.0496
4.75	1.1111							
5.0	1.1091							

TABLE 8

Values of $Z^{(1)}$ Obtained From All Compounds Listed in Table 1

Tr \ Pr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0.5									
0.6									
0.7									
0.8	-.0245	-.3400	-.4067	-.5200	-.6367	-.6467	-.8800	-1.0433	-1.1433
0.85	-.0967	-.1992	-.4367	-.5533	-.6233	-.6833	-.8500	-1.0367	-1.1633
0.9	-.0646	-.1345	-.4595	-.6067	-.6667	.0942	.0121	.0298	.0022
0.95	-.0366	-.0726	-.1391	-.2730	-.6000	.0137	-.0384	-.0278	-.0444
1.0	-.0228	-.0209	-.0533	-.0891	-.1947	-.3615	-.1256	-.1248	-.1164
1.05	-.0068	-.0061	-.0305	-.0183	.0285	.0141	-.0810	-.1450	-.1133
1.1	.0096	.0214	.0108	.0173	.0637	.0945	.1442	.0921	.0038
1.15	.0088	.0291	.0142	.0222	.0481	.0887	.1257	.1574	.1234
1.2	.0102	.0344	.0266	.0302	.0438	.0773	.1056	.1533	.1584
1.25	.0080	.0321	.0302	.0388	.0274	.0701	.0933	.1468	.1453
1.3	.0070	.0318	.0276	.0336	.0457	.0626	.0830	.1441	.1394
1.35	.0031	.0076	-.0048	.0063	.0237	.0415	-.0774	.1121	.0990
1.4	.0093	.0303	.0257	.0458	.0654	.0905	.1156	.1650	.1444
1.45	.0166	.0324	.0332	.0602	.0827	.1088	.1482	.0977	.1686
1.5	.0194	.0405	.0447	.0686	.0885	.0439	.0465	.0534	.0540
1.55	.0244	.0516	.0518	.0911	.1246	-.0160	-.0014	-.0054	-.0006
1.6	.0269	.0554	.0570	.0948	.1275	.1757	.2083	.2812	.2726
1.65	.0284	.0557	.0606	.0934	.1348	.1769	.2094	.2732	.2674
1.7	.0283	.0568	.0630	.0940	.1342	.1735	.2090	.2641	.2628
1.75	.0358	.0553	.0636	.0951	.1332	.1696	.2045	.2549	.2599
1.8	.0257	.0525	.0629	.0838	.1321	.1692	.2011	.2500	.2556
1.85	.0237	.0552	.0599	.0922	.1313	.1657	.1981	.2480	.2542
1.9	.0221	.0511	.0581	.0908	.1282	.1669	.1969	.2382	.2514
1.95	.0206	.0482	.0602	.0872	.1256	.1604	.1913	.2287	.2392
2.0	.0182	.0431	.0558	.0808	.1202	.1561	.1943	.2232	.2309
2.25	.0177	.0396	.0566	.0802	.0932	.1233	.1511	.1647	.1867
2.5	.0144	.0319	.0082	.0432	.0617	.0854	.1090	.1068	.1299
2.75	.0194	.0416	.0645	.0845	.1012	.1212	.1456	.1492	.1911
3.0	.0258	.0681	.0841	.1334	.1750	.2807	.2734	.3372	.3870
3.25	.0401	.0803	.1278	.1680	.2370	.3308	.3671	.4048	.4381
3.5	.0265	.0925	.1456	.2898	.2163	.2646	.3258	.3803	.4109
3.75	.0503	.0680	.1286	.1789	.2143	.2633	.3197	.3741	.4061
4.0	.0612	.0864	.1204	.1687	.2333	.2510	.3054	.3701	.3871
4.25	.0306	.0286	.0551	.0786	.1296	.1459	.1490	.1969	.2326
4.5	.0337	.0296	.0388	.0643	.1051	.1592	.1357	.2092	.2245
4.75	.0153	.0235	.0480	.0582	.1204	.1204	.1571	.2051	.2388
5.0	-.0061	.0173	.0500	.0418	.1102	.1102	.1306	.1980	.2010

Tr \ Pr	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
0.5					.4229	.4905	.4864	.5172	.1099
0.6		-.4653	-.2428	-.2840	-.1981	-.2136	-.2224	-.3181	-.2266
0.7	-.1950	-.2140	-.1658	-.1899	-.1632	-.1696	-.1904	-.1728	-.2060
0.8	-.1142	-.1038	-.1942	-.2078	-.2139	-.2151	-.2455	-.2540	-.2591
0.85	.0285	.0140	-.1505	-.1716	-.2000	-.1996	-.2235	-.2385	-.2479
0.9	.0544	.0546	-.0636	-.0558	-.0672	-.0690	-.0762	-.0841	-.0772
0.95	-.0078	.0024	-.0059	.0038	.0025	.0106	.0172	.0214	.0365
1.0	-.0676	-.0608	-.0580	-.0535	-.0467	-.0449	-.0417	-.0280	-.0293
1.05	-.1150	-.1117	-.1466	-.1093	-.1128	-.1186	-.1228	-.1285	-.1333
1.1	-.0265	-.0430	-.0546	-.0882	-.0637	-.0801	-.0853	-.0947	- 2028
1.15	.1085	.0804	.0494	-.0023	-.0240	-.0403	-.0587	-.0328	-.0427
1.2	.1747	.1562	.1213	.0833	.0810	.0630	.0278	.0646	.0367
1.25	.1711	.1670	.1622	.1328	.1160	.1289	.1176	.0674	.1230
1.3	.1574	.1766	.1736	.1464	.1374	.1384	.0980	.0720	.2176
1.35	.1049	.1640	.1609	.1582	.1649	.1742	.1462	.1321	.2757
1.4	.1541	.1951	.1094	.1985	.2246	.2255	.2119	.2153	.2821
1.45	.1824	.2100	.2071	.0955	.2214	.2095	.1924	.1607	.3307
1.5	.0542	.0500	.0502	.0432	.2303	.2261	.2165	.1959	.3677
1.55	-.0024	-.0089	-.0062	-.0136	.3508	.3802	.3960	.4040	.4179
1.6	.2934	.2746	.3041	.2952	.3440	.3723	.3939	.4144	.4213
1.65	.2923	.2675	.2844	.2909	.3400	.3646	.3878	.4092	.4167
1.7	.2826	.2598	.2745	.2852	.3323	.3569	.3801	.4072	.4124
1.75	.2763	.2507	.2670	.2738	.3143	.3410	.3620	.3870	.3938
1.8	.2692	.2369	.2613	.2651	.3028	.3321	.3522	.3808	.3378
1.85	.2656	.2291	.2488	.2606	.2914	.3220	.3420	.3748	.3802
1.9	.2609	.2302	.2422	.2590	.2816	.3114	.3333	.3719	.3749
1.95	.2571	.2265	.2394	.2562	.2779	.3050	.3266	.3661	.3700
2.0	.2488	.2577	.2335	.2478	.2748	.2986	.3164	.3567	.3669
2.25	.2005	.1990	.2116	.2236	.2457	.2670	.2833	.3218	.3340
2.5	.1277	.1805	.2031	.2251	.2427	.2566	.2774	.2971	.3224
2.75	.2066	.2233	.2475	.2667	.2959	.3166	.3410	.3741	.3913
3.0	.3842	.4601	.4614	.5578	.6739	.6660	.6944	.7771	.8277
3.25	.4919	.5184	.5402	.6193	.6957	.7554	.7780	.8762	.9184
3.5	.4619	.5075	.5537	.5918	.6462	.6973	.7272	.8116	.8592
3.75	.4776	.5048	.5503	.6034	.6238	.6762	.7109	.7639	.8027
4.0	.4571	.5082	.5653	.6184	.6197	.6850	.6932	.7381	.7857
4.25	.2622	.2949	.3367	.3357	.3500	.3837	.4367	.4500	.4735
4.5	.2673	.2765	.3143	.3184	.3582	.3735	.4020	.4612	.4582
4.75	.2510	.2500	.3326	.3235	.3490	.3745	.3806	.4571	.4449
5.0	.2449	.2469	.3041	.3102	.3592	.3755	.3888	.4449	.4571

Tr \ Pr	3.8	4.0	4.5	5.0	5.5	6.0	6.6	7.0
0.5	.0978	.1063	-.1056	-.0970	-.0890	-.0624	-.0389	-.0198
0.6	-.2188	-.2314	-.2758	-.2983	-.3392	-.3428	-.3506	-.3709
0.7	-.2098	-.2306	-.2846	-.3025	-.3265	-.3475	-.3640	-.3822
0.8	-.2843	-.2992	-.3361	-.3670	-.4031	-.4287	-.4544	-.4876
0.85	-.2699	-.2876	-.3220	-.3404	-.3630	-.3886	-.4201	-.4528
0.9	-.0948	-.1071	-.0952	-.0880	-.1001	-.1051	-.1193	-.2566
0.95	.0558	.0611	.1323	.1572	.1866	.2169	.2600	.4276
1.0	-.0243	-.0244	.0202	.0457	.0695	.0866	.1198	.1520
1.05	-.1476	-.1538	-.1483	-.1664	-.1880	-.2002	-.2320	-.2342
1.1	-.1135	-.1245	-.1200	-.1437	- 1636	-.1795	-.1940	-.2074
1.15	-.0573	-.0767	-.0812	-.1022	-.1177	-.1421	-.1497	-.1620
1.2	.0242	.0000	-.0204	-.0195	-.0558	-.0781	-.0913	-.1016
1.25	.1112	.0400	.0215	-.0050	-.0254	-.0692	-.0761	-.0900
1.3	.1985	.1186	.0549	.0256	-.0021	-.0409	-.0430	-.0537
1.35	.2402	.2010	.1147	.0922	.0595	.0265	.0258	.0058
1.4	.2771	.2423	.2132	.1276	.1052	.0694	.0620	.0539
1.45	.3277	.3362	.3147	.1946	.1677	.1406	.1322	.1115
1.5	.3772	.4061	.3877	.2421	.2229	.2097	.1784	.1460
1.55	.4166	.4569	.4692	.3368	.3276	.2896	.2888	.2682
1.6	.4319	.4510	.4709	.3482	.3509	.3451	.3188	.2984
1.65	-.1010	.4550	.4805	.3638	.3660	.3656	.3434	.3228
1.7	.4391	.4558	.4826	.3704	.3748	.3797	.3951	.3386
1.75	.4302	.4428	.3562	.3665	.3675	.9019	.3958	.3553
1.8	.4242	.4379	.3574	.3673	.3715	.3831	.4012	.3535
1.85	.4136	.4289	.3475	.3663	.3754	.3935	.4051	.3764
1.9	.4047	.4260	.3433	.3637	.3762	.3980	.4043	.3893
1.95	.4001	.4129	.3397	.3638	.3788	.3993	.4135	.3997
2.0	.0133	.4042	.3282	.3555	.3702	.3975	.4076	.4066
2.25	.3545	.3771	.2898	.3133	.3441	.3550	.3840	.3982
2.5	.3333	.3511	.2703	.2948	.3202	.3389	.3618	.3746
2.75	.4152	.2328	.4321	.4765	.5192	.5572	.5883	.6376
3.0	.8433	.9052	.9092	.9644	1.1102	1.2098	1.2527	1.3080
3.25	.9330	1.0212	1.1193	1.2382	1.3631	1.4863	1.6199	1.7125
3.5	.8496	.9150	1.0551	1.1357	1.2286	1.3204	1.4245	1.5051
3.75	.8490	.8782	1.0143	1.1031	1.1592	1.3592	1.3806	1.4631
4.0	.8435	.8592	1.0102	1.0826	1.1867	1.3316	1.3582	1.4480
4.25	.4826	.5163	.2837	.2959	1.1571	1.2714	1.3235	1.4112
4.5	.4826	.5000	.2878	.3041	1.1408	1.2398	1.3020	1.3765
4.75	.5082	.5031	.2878	.3347	.3776	.4305	.4469	.4755
5.0	.5071	.5378	.2837	.3082	.3878	.9510	.4837	.4980

Tr \ Pr	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
0.5	.0177	.0387	.0562	.0952	.1171	.1318	.1313	.1567
0.6	-.3851	-.4055	-.4090	-.4289	-.1686	-.1749	-.1782	-.1910
0.7	-.3951	-.4075	-.4269	-.4460	-.4531	-.4751	-.4013	-.4236
0.8	-.5273	-.3529	-.4833	-.5139	-.5391	-.5499	-.9606	-1.0024
0.85	-.4844	-.5194	-.4507	-.4523	-.4787	-.5084	-2.0288	-2.1246
0.9	-.2884	-.3115	-.1744	-.1648	-.1743	-.1755	-4.9956	-5.3849
0.95	.4742	.5093	1.8548	2.0290	2.1375	2.2733		
1.0	.1842	.4756	.6572	1.2788	1.3451	1.4709	1.4875	
1.05	-.2487	-.2025	-.2162	-.1735	-.1706	-.1910	-.5964	
1.1	-.2174	-.1755	-.1783	-.1460	-.1569	-.1501	-.4856	
1.15	-.1663	-.1307	-.1339	-.1020	-.0770	-.0709	-.2971	
1.2	-.0905	-.0681	-.0596	-.0328	-.0763	-.0913	-.1508	
1.25	-.0889	-.0244	-.0228	-.0373	-.0252	-.0682		
1.3	-.0386	.0421	.0421	.0440	.0888	.0831		
1.35	.0003	.0659	.0503	.1147	.1306	.1123		
1.4	.0338	.1028	.0881	.1462	.1645	.1372	1.2966	
1.45	.1149	.2405	.2436	.2281	.2708	.2059	1.3080	
1.5	.1407	.2858	.2905	.2862	.2977	.2830	.3056	
1.55	.2620	.3384	.3393	.3360	.3351	.3272	.2936	
1.6	.2925	.3635	.3616	.3661	.3589	.3558	.2888	
1.65	.3152	.3857	.3848	.3908	.3797	.3878	.2960	
1.7	.3356	.3944	.4033	.4060	.3985	.4212	.2064	
1.75	.3534	.3891	.3926	.3933	.3924	.4254	.3256	
1.8	.3668	.3983	.4065	.4092	.4108	.4443	.3504	
1.85	.3793	.4077	.4141	.4216	.4230	.4635	.3632	
1.9	.3912	.4161	.4206	.4372	.4396	.4813	.3840	
1.95	.3973	.4172	.4259	.4427	.4516	.5007	.3984	
2.0	.4012	.4249	.4227	.4477	.4618	.5114	.4144	
2.25	.3933	.4213	.4312	.4470	.4532	.4983	.4768	
2.5	.3888	.4076	.4172	.4303	.4480	.4762	.4968	
2.75	.6596	.7683	.4098	.4262	.4408	.4530	.5064	
3.0	1.4070	1.9766	.4104	.3642	.4304	.5782		
3.25	1.8449	3.4710	3.6688	3.5898	3.7510	3.9102		
3.5	1.5990	3.0326	3.2388	3.3592	3.5571	3.7041		
3.75	1.5418	2.8939	3.0326	3.1367	3.3531	3.4857	3.6592	3.7571
4.0	1.5398	2.7490	2.9143	2.9469	3.1673	3.3000	3.4163	3.5388
4.25	1.5031	2.6531	2.7898	2.8796	3.0082	3.1184	3.2347	3.3367
4.5	1.4582	2.5592	2.6898	2.7917	2.9122	3.0184	3.0755	3.1980
4.75	.5163							
5.0	.5102							

by Pitzer et al.{128} (1955). Yet we have two sets of literature data upon which correlational work can be done, listed in Tables 1 and 2. Essentially, the former is part of the latter, therefore, by first reasoning the extenion of Pitzer's generalized three-parameter correlation seemingly will be better if based on the data sources of Table 2. However, due to the fact that the original work of Pitzer et al.{128} (1955) also used very limited data sources for the low temperature regions as the correlation basis, with which the situation of Table 1 is very similar, it was decided that the correlation work be done on the basis of both Tables 1 and 2 respectively, and then tested the two presentations with the experimental compressibility factor data, as is done in Chapter VI. It will be further concluded in Chapter VI that the $Z^{(0)}$ and $Z^{(1)}$ values as obtained from the literature data of Table 2 are more precise and adequate, hence the essence of this generalized correlation which requires that the data used as correlational basis be more extensive is demonstrated. The final $Z^{(0)}$ and $Z^{(1)}$ values presented in Tables 9 and 10 were obtained from literature data of Table 1; while those of Tables 11 and 12 were from data of Table 2.

When we carefully examined the tables of $Z^{(0)}$ and $Z^{(1)}$ obtained after the least-squares correlation programming, also after deliberately plotting $Z^{(0)}$ and $Z^{(1)}$ values as functions of T_r (at certain P_r) as well as functions of P_r (at certain T_r), some showed abnormal discontinuity in certain ranges of T_r and P_r. Such deviations from the general

TABLE 9

$Z^{(0)}$ Values for Compressibility Factor Calculation (1)

Tr \ Pr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0.2	.0818	.1526	.2235	.2949	.3660	.4379	.5096	.5817	.6534
0.3	.0650	.1229	.1809	.2388	.2965	.3543	.4120	.4697	.5273
0.4	.0528	.1005	.1482	.1958	.2431	.2906	.3379	.3852	.4326
0.5	.0446	.0859	.1218	.1680	.2089	.2497	.2905	.3316	.3724
0.6	.0393	.0765	.1129	.1497	.1864	.2231	.2592	.2955	.3317
0.7	.0356	.0700	.1039	.1378	.1719	.2052	.2387	.2713	.3049
0.8	.8553	.0879	.1312	.1572	.1752	.1947	.2407	.2716	.2968
0.85	.8837	.0878	.1200	.1453	.1738	.1923	.2297	.2550	.2834
0.9	.9018	.7806	.1276	.1603	.1801	.1939	.2321	.2588	.2836
0.95	.9166	.8210	.7016	.1667	.1876	.1966	.2389	.2631	.2922
1.0	.9286	.8483	.7558	.6419	.2943	.2287	.2530	.2760	.3006
1.05	.9387	.8716	.7990	.7100	.5993	.4615	.3705	.3542	.3464
1.1	.9462	.8896	.8291	.7628	.6832	.6032	.5119	.4516	.4719
1.15	.9538	.9039	.8555	.8022	.7444	.6831	.6189	.5565	.5115
1.2	.9590	.9162	.8754	.8323	.7878	.7391	.6911	.6466	.6005
1.25	.9649	.9281	.8926	.8552	.8207	.7812	.7428	.7054	.6703
1.3	.9692	.9378	.9066	.8750	.8444	.8128	.7827	.7504	.7235
1.35	.9749	.9499	.9236	.8958	.8691	.8421	.8189	.7915	.7701
1.4	.9775	.9544	.9306	.9058	.8822	.8579	.8352	.8139	.7965
1.45	.9800	.9593	.9379	.9162	.8951	.8740	.8538	.8366	.8199
1.5	.9821	.9635	.9450	.9255	.9064	.8921	.8756	.8621	.8472
1.55	.9839	.9677	.9469	.9335	.9162	.9043	.8894	.8766	.8641
1.6	.9850	.9683	.9515	.9353	.9218	.9091	.8979	.8889	.8786
1.65	.9862	.9715	.9587	.9462	.9353	.9246	.9139	.9039	.8938
1.7	.9873	.9729	.9612	.9512	.9424	.9334	.9240	.9162	.9086
1.75	.9883	.9747	.9652	.9563	.9481	.9399	.9322	.9247	.9188
1.8	.9894	.9821	.9719	.9637	.9555	.9484	.9418	.9353	.9290
1.85	.9905	.9829	.9748	.9677	.9612	.9555	.9498	.9443	.9395
1.9	.9916	.9840	.9778	.9717	.9656	.9601	.9556	.9511	.9464
1.95	.9930	.9867	.9807	.9758	.9703	.9663	.9622	.9584	.9550
2.0	.9951	.9899	.9837	.9803	.9759	.9718	.9684	.9655	.9623
2.25	.9980	.9952	.9924	.9904	.9886	.9867	.9856	.9854	.9845
2.5	1.0004	1.0002	.9993	.9990	.9990	.9990	.9991	.9995	1.0004
2.75	1.0006	1.0013	1.0024	1.0027	1.0040	1.0050	1.0062	1.0074	1.0089
3.0	1.0018	1.0030	1.0045	1.0057	1.0075	1.0089	1.0106	1.0125	1.0142
3.25	1.0022	1.0041	1.0058	1.0080	1.0099	1.0115	1.0133	1.0156	1.0178
3.5	1.0025	1.0042	1.0072	1.0084	1.0114	1.0140	1.0165	1.0187	1.0220
3.75	1.0028	1.0045	1.0075	1.0100	1.0125	1.0160	1.0186	1.0210	1.0239
4.0	1.0031	1.0050	1.0079	1.0112	1.0140	1.0167	1.0200	1.0220	1.0254
4.25	1.0033	1.0055	1.0080	1.0116	1.0142	1.0172	1.0202	1.0226	1.0257
4.5	1.0037	1.0060	1.0083	1.0121	1.0144	1.0178	1.0205	1.0228	1.0260
4.75	1.0039	1.0062	1.0086	1.0122	1.0147	1.0180	1.0207	1.0230	1.0261
5.0	1.0040	1.0067	1.0087	1.0124	1.0154	1.0182	1.0210	1.0234	1.0263

Tr \ Pr	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
0.2	.7256	.7982	.8710	.9443	1.0168	1.0897	1.1625	1.2354	1.3080
0.3	.5849	.6423	.6998	.7572	.8145	.8721	.9291	.9868	1.0435
0.4	.4798	.5266	.5735	.6208	.6677	.7148	.7614	.8082	.8548
0.5	.4131	.4535	.4940	.5343	.5748	.6152	.6550	.6947	.7345
0.6	.3679	.4036	.4395	.4752	.5110	.5469	.5820	.6172	.6524
0.7	.3379	.3708	.4033	.4361	.4689	.5013	.5329	.5643	.5960
0.8	.3224	.3554	.3802	.4133	.4379	.4637	.4962	.5206	.5536
0.85	.3138	.3400	.3677	.3950	.4244	.4509	.4806	.5051	.5359
0.9	.3135	.3363	.3646	.3889	.4167	.4455	.4690	.4965	.5207
0.95	.3151	.3391	.3668	.3793	.4066	.4335	.4575	.4841	.5168
1.0	.3228	.3469	.3713	.3975	.4207	.4443	.4680	.4900	.5139
1.05	.3640	.3816	.4033	.4229	.4449	.4683	.4906	.5135	.5345
1.1	.4144	.4191	.4313	.4484	.4638	.4849	.5045	.5251	.5422
1.15	.4847	.4694	.4706	.4787	.4968	.5115	.5287	.5425	.5624
1.2	.5658	.5445	.5342	.5305	.5367	.5440	.5593	.5670	.5841
1.25	.6400	.6169	.6004	.5923	.5896	.5879	.5915	.6042	.6160
1.3	.6973	.6764	.6588	.6475	.6406	.6360	.6394	.6452	.6518
1.35	.7500	.7251	.7097	.6966	.6875	.6817	.6785	.6780	.6812
1.4	.7793	.7603	.7478	.7348	.7268	.7203	.7173	.7164	.7176
1.45	.8045	.7911	.7800	.7702	.7632	.7570	.7533	.7506	.7510
1.5	.8363	.8272	.8160	.8061	.7973	.7904	.7845	.7818	.7808
1.55	.8537	.8444	.8359	.8273	.8195	.8149	.8106	.8080	.8078
1.6	.8703	.8622	.8544	.8482	.8416	.8370	.8343	.8318	.8316
1.65	.8860	.8791	.8731	.8669	.8614	.8575	.8546	.8526	.8506
1.7	.9011	.8944	.8888	.8834	.8790	.8755	.8727	.8710	.8693
1.75	.9126	.9076	.9037	.8998	.8963	.8927	.8910	.8895	.8878
1.8	.9242	.9204	.9166	.9134	.9104	.9076	.9050	.9048	.9044
1.85	.9344	.9313	.9281	.9254	.9232	.9207	.9200	.9191	.9192
1.9	.9433	.9403	.9380	.9358	.9342	.9324	.9322	.9315	.9318
1.95	.9516	.9488	.9473	.9452	.9439	.9429	.9422	.9422	.9430
2.0	.9593	.9570	.9553	.9535	.9528	.9525	.9517	.9521	.9533
2.25	.9850	.9853	.9857	.9860	.9873	.9878	.9895	.9902	.9922
2.5	1.0008	1.0024	1.0033	1.0045	1.0052	1.0077	1.0096	1.0121	1.0149
2.75	1.0110	1.0127	1.0145	1.0166	1.0183	1.0202	1.0226	1.0253	1.0280
3.0	1.0164	1.0183	1.0208	1.0232	1.0251	1.0283	1.0305	1.0333	1.0362
3.25	1.0204	1.0225	1.0251	1.0277	1.0307	1.0337	1.0375	1.0398	1.0428
3.5	1.0248	1.0275	1.0300	1.0323	1.0352	1.0380	1.0420	1.0444	1.0467
3.75	1.0260	1.0296	1.0323	1.0356	1.0381	1.0417	1.0440	1.0472	1.0496
4.0	1.0277	1.0315	1.0340	1.0365	1.0398	1.0420	1.0457	1.0491	1.0517
4.25	1.0281	1.0317	1.0341	1.0372	1.0409	1.0438	1.0460	1.0492	1.0518
4.5	1.0288	1.0320	1.0350	1.0381	1.0410	1.0440	1.0468	1.0500	1.0525
4.75	1.0295	1.0326	1.0358	1.0384	1.0410	1.0445	1.0472	1.0499	1.0524
5.0	1.0298	1.0328	1.0360	1.0385	1.0414	1.0444	1.0471	1.0498	1.0523

Tr \ Pr	3.8	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5
0.2	1.3808	1.4537	1.6356	1.8177	1.9999	2.1820	2.3641	2.5463	2.7285
0.3	1.1009	1.1581	1.3010	1.4441	1.5863	1.7282	1.8704	2.0125	2.1537
0.4	.9017	.9481	1.0647	1.1813	1.2966	1.4121	1.5276	1.6427	1.7566
0.5	.7742	.8144	.9139	1.0135	1.1117	1.2099	1.3076	1.4059	1.5023
0.6	.6873	.7226	.8105	.8984	.9842	1.0703	1.1565	1.2422	1.3263
0.7	.6277	.6595	.7386	.8177	.8946	.9719	1.0490	1.1259	1.2008
0.8	.5782	.6040	.6740	.7448	.8156	.8859	.9572	1.0276	1.0977
0.85	.5614	.5919	.6593	.7283	.7999	.8679	.9373	1.0074	1.0772
0.9	.5489	.5738	.6402	.7059	.7711	.8388	.9043	.9723	1.0358
0.95	.5398	.5617	.6284	.9646	.7556	.8226	.8878	.9547	1.0191
1.0	.5375	.5612	.6261	.6818	.7419	.7989	.8707	.8185	.9795
1.05	.5570	.5784	.6253	.6805	.7482	.8042	.8618	.9150	.9682
1.1	.5690	.5906	.6432	.6800	.7478	.8031	.8609	.9124	.9577
1.15	.5821	.6021	.6535	.7051	.7543	.8015	.8545	.9021	.9562
1.2	.6055	.6177	.6652	.7112	.7609	.8177	.8615	.8998	.9547
1.25	.6299	.6457	.6876	.7318	.7738	.8236	.8654	.9025	.9508
1.3	.6600	.6716	.7051	.7419	.7831	.8258	.8692	.9077	.9521
1.35	.6880	.6982	.7288	.7609	.7968	.8331	.8720	.9108	.9538
1.4	.7207	.7285	.7550	.7865	.8172	.8494	.8849	.9187	.9549
1.45	.7527	.7569	.7758	.8015	.8316	.8648	.8954	.9300	.9632
1.5	.7813	.7847	.7988	.8216	.8487	.8771	.9089	.9363	.9671
1.55	.8070	.8109	.8223	.8393	.8630	.8882	.9172	.9468	.9783
1.6	.8320	.8332	.8432	.8587	.8801	.9032	.9299	.9543	.9826
1.65	.8507	.8536	.8633	.8771	.8947	.9160	.9385	.9625	.9900
1.7	.8704	.8721	.8822	.8941	.9104	.9289	.9516	.9738	.9986
1.75	.8896	.8911	.9005	.9115	.9268	.9431	.9640	.9857	1.0093
1.8	.9051	.9068	.9151	.9255	.9401	.9556	.9746	.9948	1.0168
1.85	.9198	.9210	.9288	.9386	.9518	.9659	.9847	1.0033	1.0254
1.9	.9328	.9336	.9413	.9504	.9633	.9764	.9923	1.0100	1.0306
1.95	.9444	.9451	.9525	.9610	.9733	.9862	1.0024	1.0216	1.0406
2.0	.9538	.9557	.9632	.9723	.9832	.9952	1.0109	1.0272	1.0469
2.25	.9940	.9968	1.0032	1.0116	1.0212	1.0322	1.0451	1.0595	1.0731
2.5	1.0175	1.0198	1.0269	1.0352	1.0453	1.0558	1.0673	1.0795	1.0928
2.75	1.0299	1.0338	1.0416	1.0501	1.0600	1.0700	1.0811	1.0925	1.1051
3.0	1.0394	1.0427	1.0511	1.0588	1.0690	1.0790	1.0903	1.1018	1.1140
3.25	1.0460	1.0483	1.0570	1.0657	1.0739	1.0839	1.0930	1.1038	1.1155
3.5	1.0503	1.0532	1.0608	1.0696	1.0784	1.0879	1.0972	1.1072	1.1177
3.75	1.0538	1.0553	1.0643	1.0721	1.0810	1.0892	1.0981	1.1080	1.1180
4.0	1.0545	1.0584	1.0658	1.0740	1.0820	1.0904	1.0980	1.1065	1.1160
4.25	1.0555	1.0586	1.0660	1.0740	1.0820	1.0900	1.0980	1.1060	1.1140
4.5	1.0560	1.0590	1.0659	1.0738	1.0812	1.0890	1.0975	1.1056	1.1133
4.75	1.0559	1.0585	1.0658	1.0732	1.0807	1.0882	1.0969	1.1047	1.1125
5.0	1.0558	1.0577	1.0654	1.0726	1.0798	1.0878	1.0962	1.1038	1.1118

Tr \ Pr	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0
0.2	2.9103	3.0923	3.2745	3.4566	3.6387	3.8210	4.0028	4.1851	4.3667
0.3	2.2943	2.4356	2.5768	2.7179	2.8588	2.9956	3.1329	3.2700	3.4067
0.4	1.8709	1.9850	2.0992	2.2133	2.3271	2.4407	2.5544	2.6681	2.7818
0.5	1.5988	1.6951	1.7915	1.8879	1.9845	2.0792	2.1738	2.2683	2.3630
0.6	1.4105	1.4946	1.5789	1.6625	1.7465	1.8298	1.9131	1.9964	2.0797
0.7	1.2756	1.3505	1.4257	1.5004	1.5751	1.6489	1.7227	1.7965	1.8702
0.8	1.1684	1.2398	1.3084	1.3803	1.4470	1.5139	1.5832	1.6561	1.7254
0.85	1.1450	1.2186	1.2868	1.3565	1.4282	1.4956	1.5612	1.6316	1.7002
0.9	1.1053	1.1698	1.2372	1.3033	1.3684	1.4359	1.4995	1.5688	1.6329
0.95	1.0819	1.1477	1.2139	1.2791	1.3463	1.4081	1.4734	1.5381	1.6024
1.0	1.0386	1.0993	1.1590	1.2192	1.2778	1.3357	1.3967	1.4564	1.5157
1.05	1.0214	1.0740	1.1249	1.1816	1.2306	1.2834	1.3343	1.3870	1.4394
1.1	1.0087	1.0606	1.1104	1.1613	1.2090	1.2532	1.3036	1.3510	1.3968
1.15	1.0003	1.0480	1.0960	1.1413	1.1886	1.2360	1.2844	1.3332	1.3826
1.2	.9938	1.0377	1.0836	1.1307	1.1759	1.2170	1.2579	1.3014	1.3445
1.25	.9935	1.0371	1.0754	1.1186	1.1639	1.2116	1.2500	1.2946	1.3391
1.3	.9909	1.0325	1.0726	1.1130	1.1562	1.1974	1.2373	1.2801	1.3205
1.35	.9871	1.0276	1.0674	1.1066	1.1497	1.1903	1.2294	1.2688	1.3188
1.4	.9914	1.0275	1.0638	1.1007	1.1388	1.1766	1.2156	1.2547	1.3176
1.45	.9959	1.0283	1.0593	1.0920	1.1381	1.1751	1.2134	1.2505	1.3068
1.5	.9977	1.0289	1.0578	1.0886	1.1376	1.1738	1.2102	1.2463	1.2858
1.55	1.0074	1.0382	1.0705	1.0869	1.1371	1.1723	1.2071	1.2420	1.2773
1.6	1.0112	1.0426	1.0730	1.1022	1.1355	1.1714	1.2054	1.2380	1.2760
1.65	1.0189	1.0469	1.0758	1.1074	1.1388	1.1702	1.2030	1.2343	1.2746
1.7	1.0253	1.0512	1.0802	1.1110	1.1393	1.1709	1.2010	1.2295	1.2730
1.75	1.0347	1.0606	1.0874	1.1133	1.1399	1.1718	1.1979	1.2255	1.2552
1.8	1.0394	1.0634	1.0892	1.1153	1.1405	1.1725	1.1986	1.2201	1.2531
1.85	1.0495	1.0710	1.0935	1.1188	1.1458	1.1731	1.1998	1.2258	1.2511
1.9	1.0521	1.0749	1.0998	1.1243	1.1481	1.1740	1.2008	1.2266	1.2530
1.95	1.0606	1.0806	1.1017	1.1252	1.1499	1.1766	1.2018	1.2271	1.2561
2.0	1.0667	1.0857	1.1055	1.1266	1.1518	1.1783	1.2033	1.2280	1.2583
2.25	1.0885	1.1056	1.1239	1.1422	1.1605	1.1804	1.2049	1.2289	1.2550
2.5	1.1067	1.1220	1.1375	1.1521	1.1675	1.1821	1.2072	1.2273	1.2532
2.75	1.1181	1.1315	1.1460	1.1600	1.1749	1.1901	1.2063	1.2245	1.2505
3.0	1.1261	1.1407	1.1557	1.1695	1.1855	1.1885	1.2040	1.2222	1.2493
3.25	1.1285	1.1420	1.1572	1.1736	1.1833	1.1862	1.2003	1.2192	1.2477
3.5	1.1300	1.1434	1.1555	1.1720	1.1809	1.1834	1.1972	1.2092	1.2470
3.75	1.1289	1.1399	1.1515	1.1648	1.1788	1.1803	1.1946	1.2050	1.2412
4.0	1.1257	1.1351	1.1455	1.1560	1.1667	1.1786	1.1904	1.2025	1.2160
4.25	1.1230	1.1337	1.1424	1.1530	1.1646	1.1764	1.1886	1.2011	1.2144
4.5	1.1226	1.1322	1.1417	1.1518	1.1619	1.1731	1.1851	1.1966	1.2089
4.75	1.1199	1.1301	1.1391	1.1483	1.1588	1.1697	1.1731	1.1827	1.1927
5.0	1.1195	1.1286	1.1372	1.1457	1.1542	1.1637	1.1722	1.1816	1.1903

TABLE 10

$Z^{(1)}$ Values for Compressibility Factor Calculation (1)

Tr \ Pr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0.2	-.0247	-.0425	-.0590	-.0762	-.0885	-.1047	-.1222	-.1363	-.1509
0.3	-.0317	-.0489	-.0660	-.0833	-.1007	-.1174	-.1351	-.1491	-.1630
0.4	-.0351	-.0544	-.0685	-.0885	-.1088	-.1217	-.1426	-.1653	-.1817
0.5	-.0340	-.0523	-.0676	-.0864	-.1050	-.1198	-.1388	-.1572	-.1735
0.6	-.0321	-.0492	-.0663	-.0834	-.1004	-.1168	-.1340	-.1473	-.1638
0.7	-.0295	-.0439	-.0605	-.0754	-.0907	-.1038	-.1163	-.1300	-.1442
0.8	-.0984	-.0294	-.0431	-.0545	-.0684	-.0792	-.0928	-.1044	-.1161
0.85	-.0689	-.0358	-.0482	-.0618	-.0704	-.0806	-.0930	-.1016	-.1123
0.9	-.0442	-.0863	-.0612	-.0695	-.0777	-.0860	-.0932	-.1006	-.1088
0.95	-.0359	-.0452	-.0992	-.0616	-.0706	-.0792	-.0871	-.0945	-.1007
1.0	-.0282	-.0391	-.0507	-.0605	-.0684	-.0763	-.0838	-.0913	-.0986
1.05	-.0231	-.0135	-.0049	.0067	.0231	.0410	.0299	.0003	-.0211
1.1	-.0044	.0010	.0065	.0159	.0290	.0442	.0462	.1069	.0653
1.15	.0004	.0079	.0179	.0330	.0515	.0750	.1048	.1261	.1400
1.2	.0010	.0094	.0195	.0371	.0592	.0841	.1177	.1405	.1587
1.25	.0015	.0108	.0254	.0422	.0667	.0896	.1206	.1431	.1647
1.3	.0020	.0120	.0296	.0488	.0728	.0991	.1234	.1446	.1666
1.35	.0048	.0147	.0308	.0495	.0737	.1005	.1244	.1453	.1673
1.4	.0087	.0185	.0332	.0503	.0742	.1018	.1259	.1461	.1611
1.45	.0115	.0233	.0392	.0588	.0801	.1028	.1235	.1417	.1593
1.5	.0124	.0278	.0441	.0631	.0834	.1035	.1215	.1385	.1548
1.55	.0141	.0302	.0489	.0658	.0837	.1019	.1182	.1333	.1490
1.6	.0156	.0331	.0524	.0687	.0840	.1002	.1153	.1288	.1426
1.65	.0157	.0328	.0517	.0684	.0836	.1000	.1142	.1284	.1415
1.7	.0157	.0325	.0506	.0680	.0831	.0998	.1131	.1278	.1403
1.75	.0155	.0323	.0501	.0673	.0819	.0980	.1115	.1251	.1379
1.8	.0154	.0320	.0498	.0666	.0804	.0965	.1097	.1232	.1357
1.85	.0152	.0315	.0490	.0654	.0791	.0943	.1068	.1205	.1333
1.9	.0150	.0311	.0481	.0638	.0777	.0929	.1042	.1187	.1294
1.95	.0148	.0306	.0473	.0627	.0765	.0911	.1023	.1166	.1269
2.0	.0145	.0300	.0459	.0615	.0749	.0892	.1001	.1142	.1241
2.25	.0135	.0278	.0424	.0568	.0689	.0853	.0960	.1115	.1181
2.5	.0123	.0255	.0396	.0523	.0632	.0811	.0925	.1069	.1125
2.75	.0114	.0239	.0367	.0489	.0590	.0753	.0864	.1002	.1066
3.0	.0102	.0218	.0338	.0450	.0539	.0704	.0798	.0935	.0998
3.25	.0096	.0200	.0318	.0426	.0505	.0667	.0759	.0882	.0951
3.5	.0087	.0191	.0297	.0393	.0473	.0622	.0717	.0828	.0899
3.75	.0081	.0182	.0282	.0374	.0446	.0593	.0681	.0795	.0859
4.0	.0075	.0168	.0263	.0351	.0418	.0561	.0640	.0759	.0818
4.25	.0069	.0157	.0248	.0335	.0394	.0532	.0610	.0722	.0779
4.5	.0064	.0147	.0234	.0316	.0368	.0516	.0583	.0698	.0749
4.75	.0059	.0137	.0222	.0300	.0347	.0496	.0560	.0671	.0717
5.0	.0055	.0129	.0210	.0286	.0329	.0478	.0539	.0648	.0691

Tr \ Pr	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
0.2	-.1649	-.1790	-.1929	-.2072	-.2208	-.2347	-.2491	-.2633	-.2777
0.3	-.1782	-.1965	-.2116	-.2267	-.2414	-.2601	-.2750	-.2901	-.3085
0.4	-.2006	-.2240	-.2388	-.2624	-.2831	-.3086	-.3264	-.3400	-.3563
0.5	-.1913	-.2094	-.2259	-.2433	-.2620	-.2807	-.2966	-.3140	-.3291
0.6	-.1801	-.1930	-.2084	-.2212	-.2360	-.2494	-.2639	-.2771	-.2892
0.7	-.1553	-.1684	-.1818	-.1929	-.2062	-.2164	-.2273	-.2491	-.2508
0.8	-.1291	-.1402	-.1510	-.1617	-.1724	-.1806	-.1912	-.2013	-.2116
0.85	-.1222	-.1319	-.1415	-.1512	-.1608	-.1705	-.1799	-.1894	-.1986
0.9	-.1166	-.1233	-.1310	-.1387	-.1453	-.1533	-.1600	-.1676	-.1760
0.95	-.1085	-.1161	-.1225	-.1292	-.1357	-.1421	-.1477	-.1546	-.1604
1.0	-.1059	-.1126	-.1186	-.1254	-.1310	-.1374	-.1433	-.1484	-.1533
1.05	-.0401	-.0530	-.0626	-.0724	-.0811	-.0890	-.0956	-.1018	-.1071
1.1	.0372	.0122	-.0032	-.0155	-.0260	-.0365	-.0466	-.0544	-.0636
1.15	.1262	.1007	.0753	.0461	.0239	.0066	-.0052	-.0152	-.0243
1.2	.1781	.1654	.1458	.1267	.1085	.0902	.0735	.0592	.0461
1.25	.1832	.1985	.1856	.1666	.1467	.1288	.1146	.1063	.0944
1.3	.1875	.2118	.2198	.2072	.1935	.1759	.1594	.1448	.1317
1.35	.1841	.2119	.2202	.2218	.2201	.2106	.1989	.1836	.1776
1.4	.1826	.2120	.2206	.2269	.2223	.2138	.2061	.1989	.1914
1.45	.1764	.1988	.2114	.2205	.2238	.2201	.2189	.2143	.2096
1.5	.1706	.1844	.1982	.2118	.2253	.2332	.2322	.2264	.2219
1.55	.1613	.1755	.1861	.1984	.2102	.2193	.2204	.2229	.2240
1.6	.1557	.1671	.1770	.1870	.1962	.2051	.2126	.2203	.2265
1.65	.1543	.1663	.1767	.1865	.1959	.2046	.2122	.2196	.2278
1.7	.1528	.1651	.1762	.1860	.1953	.2039	.2118	.2188	.2289
1.75	.1499	.1629	.1734	.1833	.1916	.1999	.2088	.2151	.2256
1.8	.1469	.1603	.1703	.1798	.1860	.1944	.2059	.2133	.2229
1.85	.1437	.1571	.1675	.1754	.1807	.1903	.2021	.2115	.2194
1.9	.1402	.1538	.1641	.1726	.1789	.1867	.1989	.2060	.2167
1.95	.1375	.1515	.1619	.1691	.1742	.1829	.1957	.2032	.2136
2.0	.1349	.1487	.1583	.1660	.1707	.1789	.1920	.1998	.2105
2.25	.1277	.1372	.1459	.1533	.1589	.1608	.1771	.1862	.1963
2.5	.1195	.1267	.1328	.1399	.1434	.1475	.1588	.1695	.1807
2.75	.1118	.1179	.1231	.1285	.1323	.1363	.1442	.1551	.1602
3.0	.1033	.1078	.1129	.1173	.1202	.1244	.1315	.1399	.1454
3.25	.1019	.1048	.1087	.1110	.1135	.1167	.1203	.1272	.1341
3.5	.0995	.1015	.1043	.1059	.1067	.1072	.1144	.1253	.1336
3.75	.0957	.0976	.1008	.1023	.1032	.1043	1.1116	.1214	.1287
4.0	.0916	.0938	.0967	.0985	.0996	.1007	.1082	.1195	.1248
4.25	.0881	.0902	.0932	.0951	.0963	.0978	.1052	.1171	.1206
4.5	.0853	.0877	.0906	.0925	.0937	.0956	.1032	.1150	.1175
4.75	.0824	.0848	.0877	.0899	.0911	.0932	.1007	.1122	.1139
5.0	.0802	.0826	.0859	.0877	.0890	.0915	.0989	.1099	.1107

Tr \ Pr	3.8	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5
0.2	-.2910	-.3041	-.3402	-.3768	-.4089	-.4397	-.4735	-.5018	-.5357
0.3	-.3239	-.3388	-.3805	-.4160	-.4564	-.4924	-.5290	-.5682	-.6038
0.4	-.3821	-.3892	-.4319	-.4717	-.5116	-.5517	-.5864	-.6215	-.6590
0.5	-.3470	-.3619	-.4018	-.4385	-.4765	-.5134	-.5488	-.5870	-.6209
0.6	-.3047	-.3172	-.3513	-.3845	-.4141	-.4469	-.4767	-.5052	-.5337
0.7	-.2605	-.2733	-.2998	-.3268	-.3521	-.3782	-.4020	-.4237	-.4484
0.8	-.2199	-.2301	-.2520	-.2746	-.2986	-.3173	-.3379	-.3563	-.3737
0.85	-.2063	-.2150	-.2352	-.2539	-.2724	-.2886	-.3056	-.3207	-.3362
0.9	-.1844	-.1911	-.2094	-.2264	-.2429	-.2576	-.2734	-.2877	-.3006
0.95	-.1660	-.1731	-.1867	-.2016	-.2152	-.2284	-.2411	-.2535	-.2644
1.0	-.1582	-.1627	-.1735	-.1835	-.1934	-.2017	-.2108	-.2188	-.2278
1.05	-.1126	-.1187	-.1319	-.1443	-.1551	-.1675	-.1781	-.1880	-.1973
1.1	-.0715	-.0784	-.0961	-.1130	-.1274	-.1404	-.1520	-.1626	-.1731
1.15	-.0322	-.0401	-.0570	-.0722	-.0850	-.0977	-.1078	-.1172	-.1260
1.2	.0342	.0222	-.0029	-.0207	-.0363	-.0493	-.0617	-.0736	-.0835
1.25	.0799	.0633	.0398	.0187	.0091	-.0126	-.0315	-.0455	-.0577
1.3	.1187	.1080	.0698	.0586	.0392	.0228	.0080	-.0038	-.0133
1.35	.1595	.1487	.1256	.0995	.0816	.0667	.0522	.0406	.0289
1.4	.1848	.1775	.1613	.1452	.1300	.1158	.1029	.0904	.0794
1.45	.2005	.1980	.1896	.1699	.1580	.1497	.1389	.1255	.1090
1.5	.2171	.2123	.2009	.1910	.1804	.1706	.1601	.1502	.1407
1.55	.2253	.2239	.2201	.2187	.2100	.2052	.1985	.1896	.1799
1.6	.2326	.2398	.2541	.2512	.2433	.2368	.2284	.2200	.2111
1.65	.2340	.2414	.2546	.2601	.2567	.2518	.2470	.2387	.2312
1.7	.2356	.2423	.2552	.2672	.2735	.2698	.2643	.2582	.2518
1.75	.2324	.2401	.2549	.2681	.2753	.2755	.2743	.2702	.2677
1.8	.2300	.2378	.2547	.2688	.2769	.2802	.2828	.2811	.2792
1.85	.2278	.2357	.2535	.2690	.2774	.2813	.2836	.2849	.2839
1.9	.2251	.2333	.2519	.2692	.2781	.2822	.2845	.2885	.2999
1.95	.2227	.2318	.2507	.2678	.2769	.2812	.2839	.2889	.3006
2.0	.2194	.2305	.2492	.2661	.2754	.2800	.2833	.2892	.3014
2.25	.2081	.2203	.2384	.2498	.2616	.2695	.2786	.2907	.3025
2.5	.1946	.2100	.2261	.2342	.2468	.2589	.2711	.2844	.3033
2.75	.1763	.1896	.1995	.2201	.2345	.2482	.2614	.2733	.2930
3.0	.1596	.1765	.1888	.2066	.2221	.2378	.2523	.2611	.2828
3.25	.1539	.1682	.1833	.1951	.2100	.2242	.2371	.2497	.2603
3.5	.1487	.1599	.1775	.1842	.1989	.2098	.2225	.2380	.2555
3.75	.1433	.1548	.1738	.1795	.1972	.2021	.2169	.2297	.2447
4.0	.1401	.1516	.1679	.1733	.1855	.1963	.2106	.2220	.2341
4.25	.1362	.1464	.1635	.1687	.1783	.1896	.2048	.2141	.2233
4.5	.1331	.1441	.1599	.1631	.1735	.1840	.2006	.2080	.2145
4.75	.1295	.1400	.1557	.1579	.1686	.1782	.1933	.2016	.2082
5.0	.1274	.1370	.1525	.1625	.1741	.1917	.1974	.2033	.2108

Tr \ Pr	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0
0.2	-.5648	-.5937	-.6220	-.6515	-.6808	-.7094	-.7361	-.7634	-.7887
0.3	-.6381	-.6731	-.7075	-.7394	-.7755	-.8138	-.8475	-.8799	-.9128
0.4	-.6915	-.7236	-.7564	-.7896	-.8209	-.8518	-.8834	-.9128	-.9405
0.5	-.6583	-.6922	-.7273	-.7625	-.7953	-.8276	-.8595	-.8907	-.9193
0.6	-.5623	-.5917	-.6204	-.6486	-.6770	-.7050	-.7333	-.7610	-.7846
0.7	-.4714	-.4949	-.5183	-.5386	-.5615	-.5861	-.6014	-.6233	-.6430
0.8	-.3892	-.4086	-.4213	-.4366	-.4506	-.4645	-.4789	-.4931	-.5044
0.85	-.3494	-.3625	-.3758	-.3881	-.4002	-.4108	-.4230	-.4343	-.4454
0.9	-.3131	-.3244	-.3356	-.3468	-.3577	-.3667	-.3768	-.3859	-.3944
0.95	-.2751	-.2870	-.2974	-.3086	-.3170	-.3268	-.3370	-.3450	-.3533
1.0	-.2356	-.2431	-.2509	-.2585	-.2661	-.2735	-.2810	-.2886	-.2948
1.05	-.2046	-.2120	-.2194	-.2248	-.2308	-.2346	-.2396	-.2440	-.2474
1.1	-.1809	-.1879	-.1944	-.2009	-.2053	-.2112	-.2149	-.2181	-.2208
1.15	-.1330	-.1397	-.1460	-.1522	-.1579	-.1625	-.1682	-.1724	-.1778
1.2	-.0932	-.1021	-.1109	-.1175	-.1237	-.1300	-.1363	-.1423	-.1484
1.25	-.0633	-.0741	-.0802	-.0886	-.0924	-.0998	-.1075	-.1163	-.1215
1.3	-.0212	-.0299	-.0356	-.0423	-.0475	-.0539	-.0592	-.0643	-.0692
1.35	.0205	.0152	.0043	-.0093	-.0156	-.0283	-.0337	-.0432	-.0503
1.4	.0687	.0577	.0482	.0386	.0300	.0216	.0142	.0064	-.0015
1.45	.0967	.0883	.0756	.0634	.0582	.0494	.0413	.0375	.0304
1.5	.1314	.1224	.1135	.1053	.0962	.0874	.0786	.0700	.0623
1.55	.1684	.1588	.1492	.1366	.1243	.1170	.1066	.0993	.0898
1.6	.2015	.1922	.1814	.1702	.1595	.1479	.1365	.1232	.1112
1.65	.2283	.2195	.2098	.2002	.1887	.1781	.1655	.1577	.1493
1.7	.2445	.2364	.2289	.2206	.2115	.2022	.1930	.1835	.1711
1.75	.2608	.2549	.2473	.2401	.2338	.2275	.2181	.2095	.1955
1.8	.2766	.2721	.2684	.2646	.2520	.2434	.2340	.2234	.2139
1.85	.2813	.2799	.2751	.2703	.2674	.2602	.2554	.2478	.2382
1.9	.2891	.2874	.2859	.2847	.2833	.2801	.2735	.2693	.2604
1.95	.2983	.2966	.2933	.2902	.2877	.2863	.2804	.2745	.2689
2.0	.3045	.3089	.3041	.3014	.2989	.2974	.2902	.2833	.2768
2.25	.3081	.3153	.3222	.3260	.3237	.3210	.3189	.3134	.3077
2.5	.3128	.3206	.3399	.3428	.3445	.3443	.3431	.3415	.3388
2.75	.3067	.3145	.3313	.3379	.3402	.3420	.3425	.3419	.3402
3.0	.2955	.3069	.3267	.3321	.3363	.3389	.3401	.3422	.3419
3.25	.2827	.2967	.3125	.3234	.3285	.3311	.3343	.3361	.3378
3.5	.2707	.2874	.2997	.3088	.3172	.3224	.3255	.3301	.3336
3.75	.2602	.2768	.2890	.2968	.3071	.3177	.3252	.3273	.3304
4.0	.2498	.2667	.2788	.2853	.2965	.3102	.3178	.3218	.3289
4.25	.2406	.2566	.2673	.2751	.2868	.3044	.3141	.3172	.3270
4.5	.2327	.2487	.2598	.2677	.2785	.2992	.3113	.3156	.3249
4.75	.2156	.2398	.2506	.2596	.2702	.2924	.3075	.3132	.3231
5.0	.2108	.2339	.2437	.2531	.2636	.2873	.3044	.3111	.3218

trend will cause serious error should compressibility factor calculations be made based on these $Z^{(0)}$ and $Z^{(1)}$ values. Having carefully reviewed the compressibility factor-acentric factor graphs plotted, it was concluded that the data points of hydrogen, helium and ammonia (also with water) were of prime responsibility for these deviations and discontinuity.

Once we excluded all the data points of hydrogen, helium, ammonia and water, the $Z^{(0)}$ and $Z^{(1)}$ values as calculated from and comprised of all the remaining compounds became coordinated with each other much better and prevailed extraordinarily improving quality as far as continuity and smoothness are concerned. Sample drawings for $Z^{(0)}$ and $Z^{(1)}$ showing this smoothing technology were depicted in Figures 10 and 11 for $T_r = 1.4$ condition. From this approach, it had again verified that compounds with quantum or highly polar nature must be excluded from this correlation. It was also attempted to try to exclude the seemingly less relevant and slightly polar compounds such as difluoromethane, Freon 22, etc., all for which with the common nature of halogenated methane, yet the results proved to be more diverse. Hence this generalized correlation was essentially composed of data from 53 compounds (Table 2) after careful and extensive study of their accuracy and applicability. These compounds can be categorized as in the realm of normal fluids in this correlation.

The $Z^{(0)}$ and $Z^{(1)}$ values thus obtained for compressibility factor calculations were therefore well correlated.

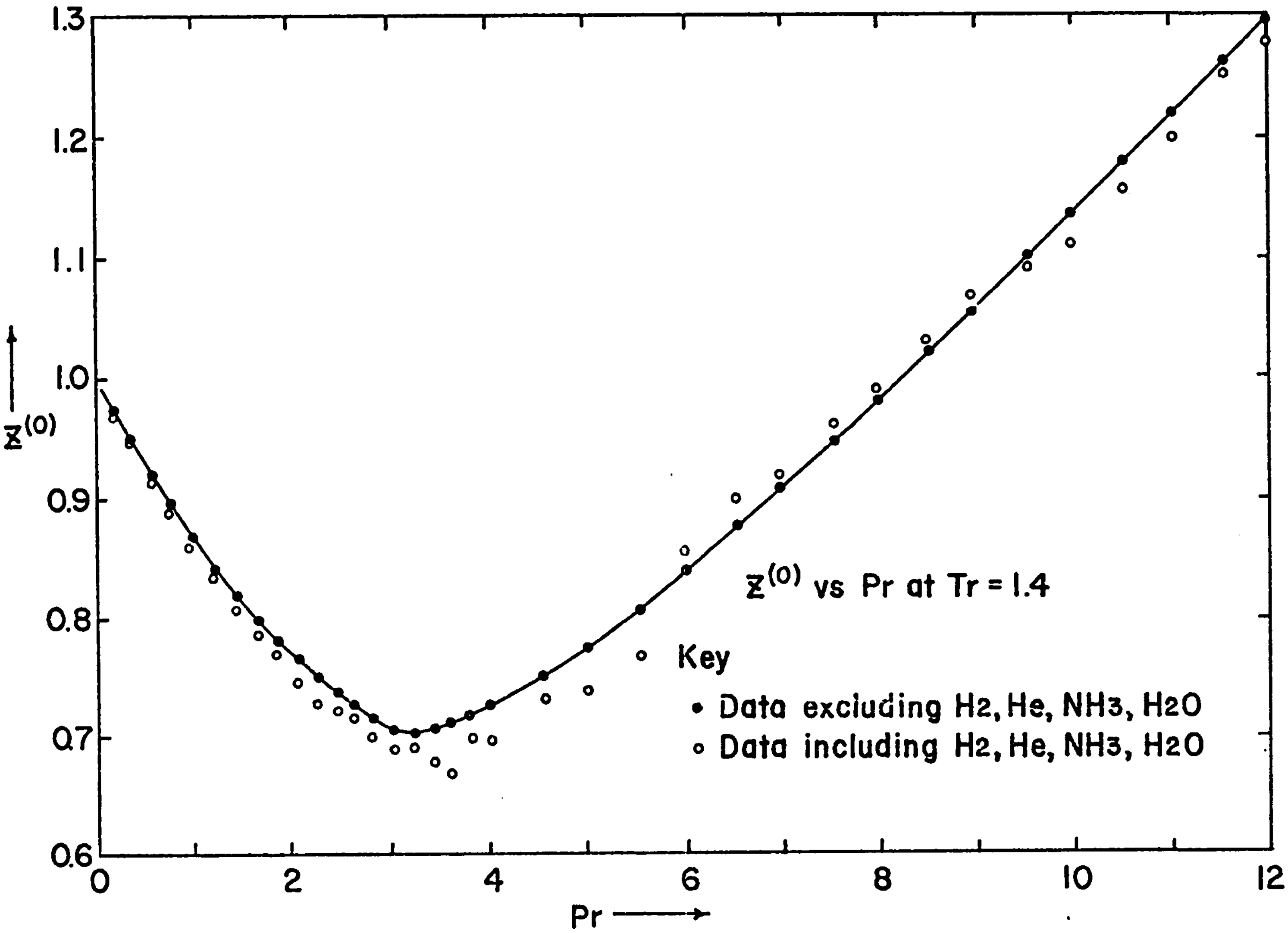

Figure 10. $\bar{Z}^{(0)}$ as a Function of Pr at Tr = 1.4

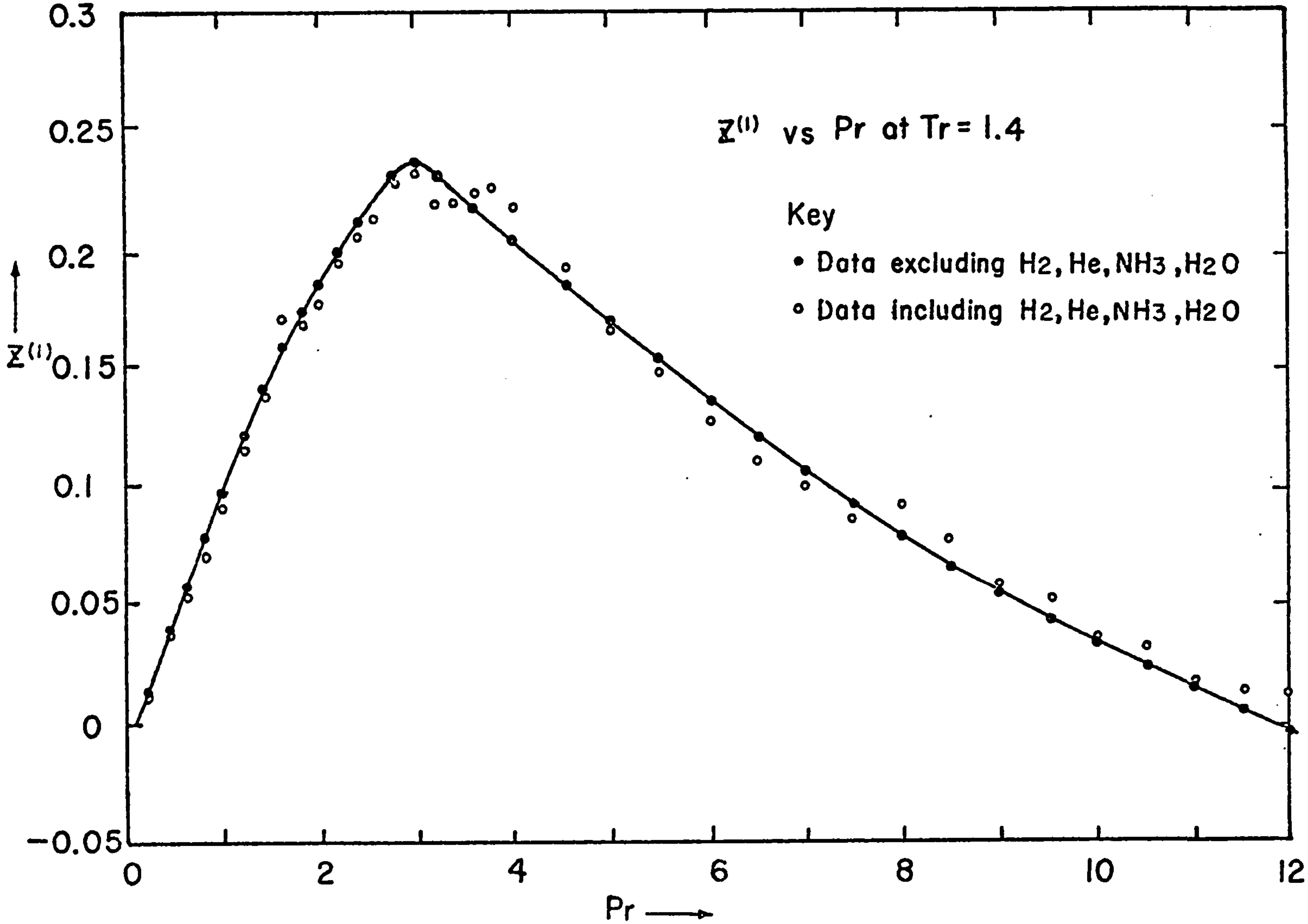

Figure 11. $Z^{(1)}$ as a Function of Pr at Tr = 1.4

The $Z^{(0)}$ values were found to be continuous and smooth functions of T_r and P_r themselves and needed essentially no further adjustment. The $Z^{(1)}$ values were also continuous and smooth, only to a lesser extent, yet still within the limits of experimental error. Nevertheless, in order to obtain a high precision and accuracy in the presentation and in the compressibility factor calculation, the cross-plotting technique was again applied to the tables of $Z^{(0)}$ and $Z^{(1)}$ values thus far obtained. Plotting the $Z^{(0)}$ and $Z^{(1)}$ values as functions of both T_r and P_r conditions, then re-examined the tables obtained, if not totally satisfactory, such as this case indicated, we repeated the cross-plotting technique all over again. Also during this procedure, adjustment was made in reference to the Z versus ω graphs whenever necessary. In doing so, we finally were able to obtain tables of $Z^{(0)}$ and $Z^{(1)}$, which were continuous and reasonably smooth functions of temperature and pressure, viewed for both cases of constant T_r and constant P_r. Furthermore, at the same time of pursuing cross-plotting, it appeared that at constant P_r, the curves showed a regular shape of trend for $T_r < 0.5$ (in this investigation, the data in Table 2 well covered the ranges of $0.5 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 12.0$); hence efforts were made to try to extrapolate the temperature ranges to $T_r = 0.2$, using the few data points available, again the smoothing technique was employed all the way through. The final results of $Z^{(0)}$ and $Z^{(1)}$ values obtained from this study are tabulated in Tables 11 and 12 (also in Tables 9 and 10 as from the data of Table 1).

CHAPTER IV

APPLICATION OF THE PITZER CORRELATION TO THE VIRIAL EQUATION OF STATE

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APPLICATION OF THE PITZER CORRELATION TO THE VIRIAL EQUATION OF STATE

One of the applications of the generalized compressibility factor correlation presented by Pitzer et al.{129} (1957) which has drawn intensive attention in this study is the second virial coefficient. Applying appropriate mixing rules to this correlation originally proposed for pure compounds in terms of the acentric factor, this correlation was extended to the realm of mixtures and values of the binary interaction parameters were thus obtained.

A. Correlation of Pitzer and Curl for Pure Compound

The second virial coefficient as obtained by the P-V-T data

$$B = \lim_{\frac{1}{V}\to 0} (Z - 1)V \tag{8}$$

is usually used as a theoretical guide and rigorous test for the smoothing of the P-V-T data. In the work by Pitzer and Curl {129} (1957) as part of the series following the introduction of the acentric factor, they presented an equation for the second virial coefficient in reduced form which included linear dependence on the acentric factor:

$$\frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega \frac{B^{(1)}P_c}{RT_c} \tag{12}$$

where $B^{(0)}$ and $B^{(1)}$ are functions of the reduced temperature. Based on the fact that for the simple fluids of zero acentric factor (the heavier inert gases Ar, Kr and Xe), their properties are quite well represented by a Lennard-Jones intermolecular potential (see Chapter VIII), hence the equation of Beattie and Stockmayer {4}{5}{6} (1941,1942) was taken as a point of departure. This was converted from the molecular potential constants to the macroscopic critical constants and then modified to obtain the equations for correlated $B^{(0)}$ and $B^{(1)}$:

$$\frac{B^{(0)}P_c}{RT_c} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^{\,2}} - \frac{0.0121}{T_r^{\,3}} \qquad (36)$$

$$\frac{B^{(1)}P_c}{RT_c} = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^{\,2}} - \frac{0.097}{T_r^{\,3}} - \frac{0.0073}{T_r^{\,8}} \qquad (37)$$

where the small terms of high power T_r^{-3} and T_r^{-8} were required to fit the data at low temperatures. Also from thermodynamic relationship yields the equation

$$\lim_{P\to 0}\left(\frac{\partial C_p}{\partial p}\right)_T = -\,T\frac{\partial^2 B}{\partial T^2} \qquad (38)$$

consequently, the pressure dependence of the heat capacity offers a very sensitive test of any equation for the second virial coefficient. Pitzer and Curl reported that this second virial coefficient correlation yielded agreement with measured values of the pressure derivative of the gas heat capacity and therefore is valuable for the estimation of gas imperfection corrections to various data on gases at low pressures. Again the substances which can be expected to conform are the normal fluids.

B. Mixing Rules

When we develop a correlation function of the second virial coefficient for mixtures based on the acentric-factor correlation by Pitzer and Curl shown in equations (12), (36) and (37), we need a set of mixing rules. The mixing rules which were first proposed concerning the second virial coefficients of mixtures of slightly imperfect gases in terms of the properties of the constituents through the principle of corresponding states were first from Guggenheim and McGlashan {62} (1951). They developed a reduced equation of state for the second virial coefficients of mixtures from the point of view of Lennard-Jones potential function and interpreted it as a function of reduced temperature. Then Prausnitz and Gunn {130} (1958) demonstrated a mixing function of the second virial coefficients for mixtures in terms of the acentric-factor correlation of Pitzer and Curl {129} (1957) based on the work of Guggenheim and McGlashan {62} (1951). This work adopts these mixing rules for the second virial coefficients and the mixing rules for the physical properties of the binary system proposed by Chueh and Prausnitz {23} (1967) as they are widely accepted.

The mixing functions are all summarized as follows:

$$\frac{B_{ij}P_{c_{ij}}}{R\,T_{c_{ij}}} = \frac{B_{ij}Z_{c_{ij}}}{V_{c_{ij}}} = f^{(0)}(T_{r_{ij}}) + \omega_{ij}f^{(1)}(T_{r_{ij}}) \qquad (39)$$

where

$$f^{(0)}(T_{r_{ij}}) = 0.1445 - \frac{0.330}{T_{r_{ij}}} - \frac{0.1385}{T_{r_{ij}}^{2}} - \frac{0.0121}{T_{r_{ij}}^{3}} \qquad (40)$$

$$f^{(1)}(T_{r_{ij}}) = 0.073 + \frac{0.46}{T_{r_{ij}}} - \frac{0.50}{T_{r_{ij}}^{2}} - \frac{0.097}{T_{r_{ij}}^{3}} - \frac{0.0073}{T_{r_{ij}}^{8}} \qquad (41)$$

$$Z_{c_{ij}} = 0.291 - 0.08\omega_{ij} \qquad (42)$$

$$\omega_{ij} = 0.5(\omega_i + \omega_j) \qquad (43)$$

$$V_{c_{ij}} = \frac{1}{8}(V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}})^{3} \qquad (44)$$

$$T_{r_{ij}} = \frac{T}{T_{c_{ij}}} \qquad (45)$$

$$T_{c_{ij}} = (T_{c_i}T_{c_j})^{\frac{1}{2}}\,(1 - k_{ij}) \qquad (46)$$

The k_{ij} in equation (46) is called the binary interaction coefficient. This equation provides the definition of k_{ij}.

C. Calculation of the Binary Interaction Constant

When we substitute equations (40) to (46) into (39), after rearranging, we obtain the following equation:

$$\frac{B_{ij}}{V_{c_{ij}}}(0.291 - 0.08\omega_{ij})T_{r_{ij}}{}^{8} - (0.1445 + 0.073\omega_{ij})T_{r_{ij}}{}^{8}$$

$$- (0.46\omega_{ij} - 0.33)T_{r_{ij}}{}^{7} + (0.1385 + 0.5\omega_{ij})T_{r_{ij}}{}^{6}$$

$$+ (0.0121 + 0.097\omega_{ij})T_{r_{ij}}{}^{5} + 0.0073\omega_{ij} = 0 \qquad (47)$$

This equation consists merely of B_{ij}, the cross coefficient, T, the temperature of the system, k_{ij}, the binary interaction constant, and the physical properties of the two constituents, i.e., critical volumes, acentric factors and critical temperatures. The critical temperature characterizes the intermolecular interaction energy and the acentric factor takes into account the intermolecular forces in complex molecules to be the sum of interactions between various parts of the molecules, not just their centers but non-central portions, too. For the critical volume, it is a simple measure related to intermolecular distance. Nevertheless, it is unsatisfactory from the empirical viewpoint, the differential compressibility is infinite at the critical point and consequently the critical volume is not directly measurable with high accuracy and extrapolation is commonly employed to obtain such data. For pure compounds, the critical pressure is a much more accurately determinable quantity and is usually used for correlation purposes. However, for mixtures, the mixing rule which governs the critical pressure of the mixture from those of the pure components is given by

$$P_{c_{ij}} = \frac{Z_{c_{ij}} RT_{c_{ij}}}{V_{c_{ij}}} \tag{48}$$

Hence the critical volume $V_{c_{ij}}$ is adopted in equation (47) as calculated from equation (44), the Lorentz combination.

As to the cross second virial coefficient, B_{ij} (or written as B_{12}), usually it is available in the literature as calculated from the equation

$$B_m = y_1{}^2 B_{11} + 2y_1 y_2 B_{12} + y_2{}^2 B_{22} \tag{35}$$

However, very often we have only the P-V-T data for the binary mixture in the form of isotherms and we obtain the B_m for the mixture using the equation

$$B = \lim_{\frac{1}{V}\to 0} (Z - 1)V \tag{8}$$

as this is clearly shown when we truncate the original virial equation of state

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots = 1 + B\rho + C\rho^2 + \ldots \tag{7}$$

to the first three terms and rearrange it as follows

$$(Z - 1)(V) = B + \frac{C}{V} \tag{49}$$

This truncation after the third term of equation (7) is highly recommended and dependable, for the reason that equation (49) is known from both theory and experience to be a reliable guide as mentioned earlier (see Chapter I, Part B). Hence from equation (8) it is clear that when we draw the values of $(Z - 1)(V)$ versus $\frac{1}{V}$ for a binary system at certain temperature, the second virial coefficient B_m is the intercept at $\frac{1}{V} = 0$, as we see from equation (49) that this plot must be a straight line. Experience with reliable data shows that equation (49) is in fact valid up to moderate pressures and the function (Z - 1)(V) is a particularly valuable one for smoothing P-V-T data and for extrapolation of data to zero pressure, i.e., to $\frac{1}{V} = 0$. It seems safe to say that data which do not approach linearity on a (Z - 1)V versus 1/V plot as 1/V becomes small are incorrect (Van Ness,{163} (1964)). However, as 1/V or P approaches zero, the quantity (Z - 1)(V) becomes very sensitive to small experimental error, hence data for very low pressures can be expected to scatter, and thus throws greater weight on the data at higher pressures. Two typical examples are depicted in Figures 12 and 13, one is for the system methane-nitrogen and the other is for n-Pentane-Hydrogen sulfide at the specified compositions and temperatures. Once we obtained the B_m value for the binary system we were able to evaluate the cross coefficient B_{12} of this system by equation (35), using the second virial coefficients of the pure components such as compiled by Dymond and Smith {48} (1969) and Mason and Spurling {106} (1969), or obtained from the P-V-T data of the pure components.

From equation (47) it is clear that for a binary system at certain temperature, whenever we have the cross coefficient B_{ij}, we can calculate the $T_{r_{ij}}$ value and hence obtain the k_{ij} value by equations (45) and (46). This program is

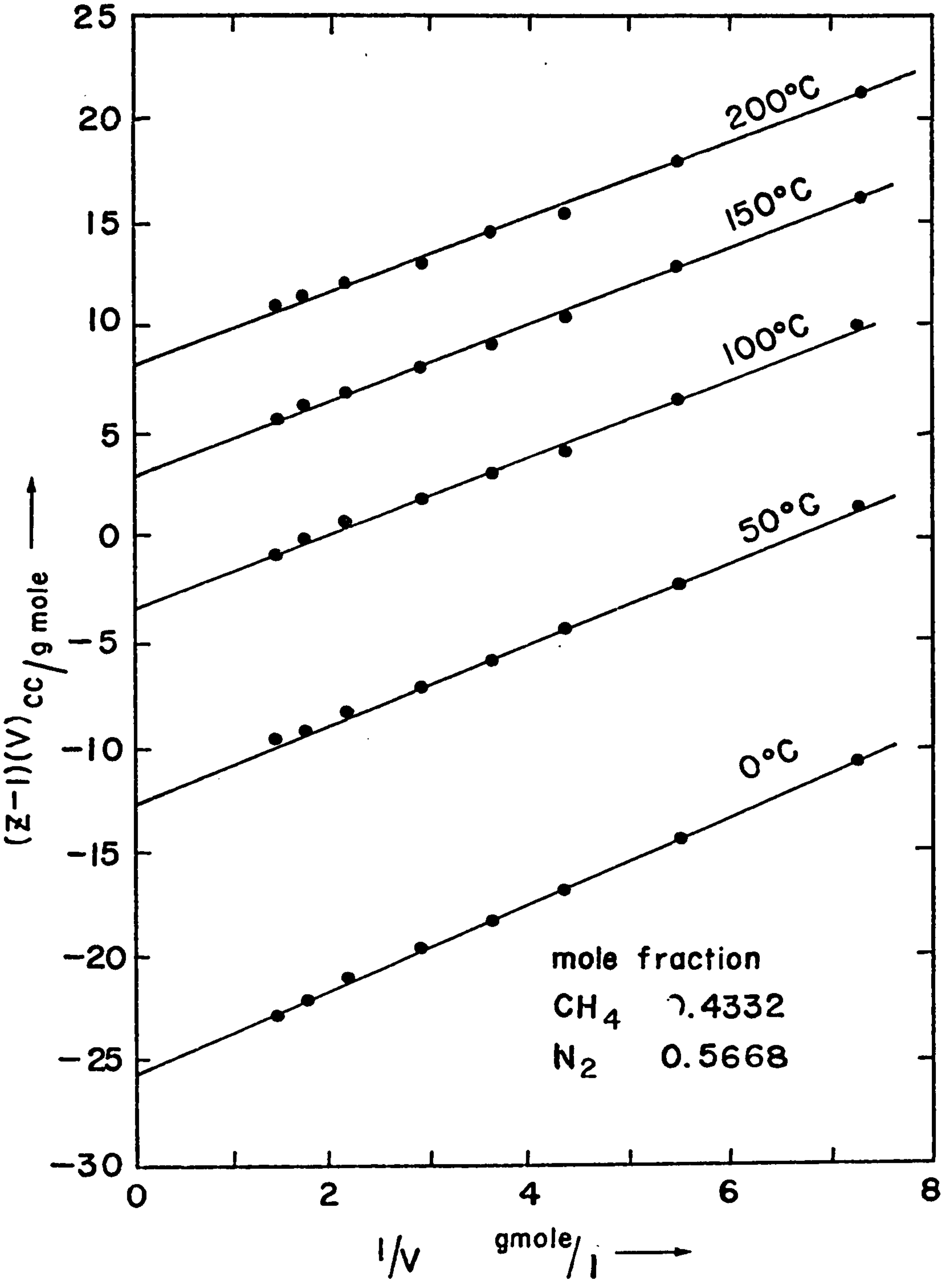

Figure 12. Determination of Bm for CH_4−N_2 System
(Keyes and Burks, 1928)

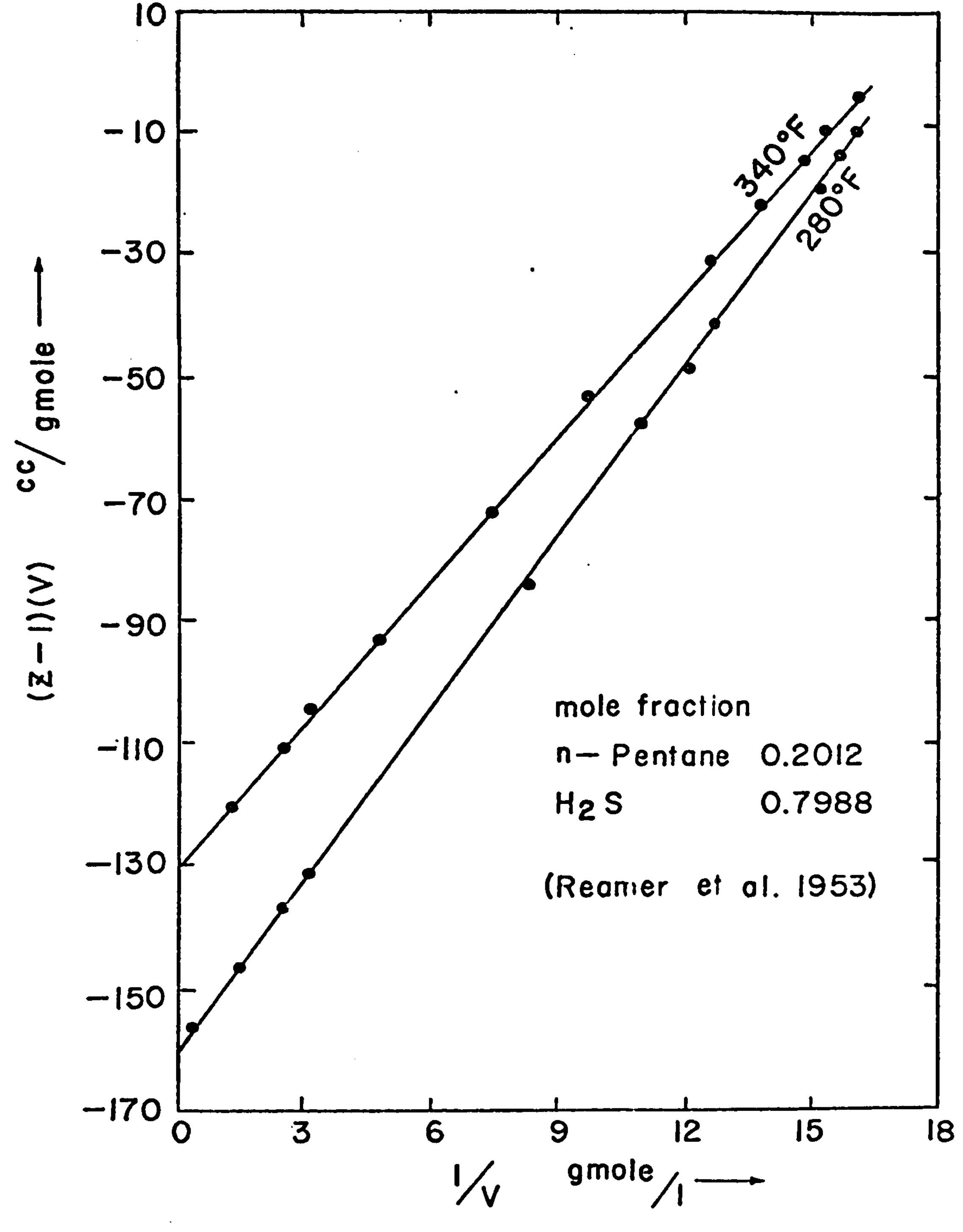

Figure 13. Determination of Bm for $n-C_5H_{12}-H_2S$ System

shown in Chapter X, Appendix D. There were eight roots evaluated from equation (47) as this equation was of the eighth order. The root which made the difference between the coefficients of equation (47) and the calculated ones (using the eight roots obtained) minimum was chosen, preferably the difference should be zero. By doing this, 493 values of the binary interaction constants for 121 binary systems were evaluated at specified temperatures.

CHAPTER V

RESULTS AND DISCUSSION

Extension of the Three-Parameter Correlation

Pitzer's three-parameter generalized correlation has been verified and then extended to $0.2 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 12.0$ in this investigation, as compared to the ranges of $0.8 \leqq T_r \leqq 4.0$ and $0 \leqq P_r \leqq 9.0$ presented in the original work (Pitzer et al.{128} (1955)). The final tabulated $Z^{(0)}$ and $Z^{(1)}$ values are presented in Tables 11 and 12 based on the literature data listed in Table 2. They are depicted as functions of T_r at constant P_r in Figures 14 and 15 for the ranges specified. These figures serve further for the comparison and testing purposes in Chapter VI.

The values of $Z^{(0)}$ and $Z^{(1)}$ re-tabulated are in regular intervals and the regions of applicability are extended to cover wider ranges of interest. These tables are well subdivided for interpolation to the T_r and P_r conditions at which the desired compressibility factor is to be calculated. In comparison with other published works, the volumetric data for 53 compounds were used in this work as correlational basis, while Pitzer et al.{128} (1955) used 15 and Lee and Kesler {96} (1975) used only 4. The range of the acentric factor values used in this work (-0.002 to 0.9065)

TABLE 11

$Z^{(0)}$ Values for Compressibility Factor Calculation (2)

Tr \ Pr	0.01	0.05	0.1	0.15	0.2	0.4	0.6	0.8
0.2	.0043	.0180	.0380	.0530	.0685	.1388	.2059	.2742
0.3	.0035	.0150	.0312	.0450	.0583	.1160	.1757	.2317
0.4	.0028	.0120	.0254	.0378	.0503	.0955	.1455	.1908
0.5	.0025	.0106	.0205	.0307	.0405	.0841	.1253	.1655
0.6	.9856	.0098	.0190	.0280	.0365	.0753	.1105	.1480
0.7	.9893	.9497	.8950	.0263	.0350	.0692	.1020	.1345
0.8	.9940	.9648	.9305	.8756	.8545	.0650	.0990	.1296
0.85	.9945	.9695	.9435	.9115	.8800	.0657	.0985	.1293
0.9	.9950	.9750	.9540	.9271	.8995	.7792	.0998	.1310
0.95	.9955	.9795	.9595	.9380	.9170	.8193	.6943	.1395
1.0	.9960	.9828	.9650	.9470	.9295	.8490	.7570	.6345
1.05	.9965	.9850	.9695	.9545	.9395	.8741	.8005	.7140
1.1	.9969	.9858	.9740	.9615	.9500	.8942	.8323	.7644
1.15	.9972	.9889	.9788	.9670	.9550	.9082	.8570	.8050
1.2	.9976	.9900	.9800	.9700	.9603	.9198	.8792	.8350
1.25	.9978	.9910	.9825	.9740	.9657	.9300	.8950	.8554
1.3	.9980	.9921	.9846	.9770	.9700	.9395	.9095	.8752
1.35	.9982	.9929	.9860	.9800	.9742	.9454	.9214	.8948
1.4	.9984	.9938	.9878	.9815	.9755	.9546	.9290	.9050
1.45	.9986	.9944	.9890	.9835	.9776	.9596	.9350	.9150
1.5	.9988	.9950	.9900	.9854	.9805	.9648	.9445	.9290
1.55	.9989	.9955	.9913	.9868	.9822	.9685	.9507	.9360
1.6	.9990	.9960	.9922	.9882	.9841	.9724	.9565	.9429
1.65	.9991	.9963	.9931	.9893	.9855	.9755	.9610	.9510
1.7	.9992	.9967	.9940	.9906	.9873	.9775	.9657	.9572
1.75	.9993	.9969	.9945	.9914	.9884	.9798	.9693	.9615
1.8	.9994	.9972	.9950	.9924	.9898	.9812	.9730	.9665
1.85	.9994	.9975	.9955	.9931	.9907	.9850	.9757	.9701
1.9	.9995	.9979	.9960	.9940	.9920	.9859	.9788	.9740
1.95	.9995	.9981	.9964	.9946	.9928	.9885	.9811	.9773
2.0	.9996	.9982	.9968	.9952	.9936	.9900	.9835	.9800
2.25	.9996	.9987	.9974	.9965	.9957	.9943	.9900	.9886
2.5	.9997	.9992	.9980	.9980	.9981	.9985	.9968	.9972
2.75	.9997	.9997	.9988	.9989	.9991	1.0004	.9996	1.0008
3.0	.9998	1.0002	.9995	.9999	1.0003	1.0022	1.0025	1.0045
3.25	.9998	1.0003	.9998	1.0003	1.0009	1.0030	1.0038	1.0060
3.5	.9999	1.0004	1.0002	1.0008	1.0015	1.0038	1.0051	1.0075
3.75	.9999	1.0005	1.0005	1.0012	1.0018	1.0041	1.0056	1.0081
4.0	1.0000	1.0006	1.0008	1.0014	1.0020	1.0045	1.0062	1.0088
4.25	1.0000	1.0007	1.0011	1.0016	1.0021	1.0048	1.0066	1.0092
4.5	1.0001	1.0008	1.0013	1.0017	1.0022	1.0050	1.0071	1.0095
4.75	1.0001	1.0008	1.0014	1.0018	1.0023	1.0052	1.0074	1.0097
5.0	1.0002	1.0009	1.0015	1.0019	1.0024	1.0053	1.0076	1.0098

Pr Tr	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
0.2	.3426	.4110	.4793	.5475	.6157	.6837	.7520	.8200
0.3	.2895	.3475	.4055	.4630	.5208	.5785	.6359	.6935
0.4	.2382	.2860	.3335	.3810	.4280	.4755	.5225	.5695
0.5	.2060	.2470	.2880	.3285	.3700	.4107	.4510	.4905
0.6	.1855	.2215	.2575	.2935	.3294	.3653	.4015	.4370
0.7	.1693	.2043	.2370	.2695	.3020	.3345	.3675	.4000
0.8	.1631	.1945	.2255	.2570	.2881	.3193	.3495	.3790
0.85	.1623	.1930	.2230	.2535	.2836	.3140	.3430	.3719
0.9	.1640	.1936	.2225	.2520	.2812	.3103	.3390	.3675
0.95	.1695	.1995	.2280	.2570	.2855	.3142	.3415	.3680
1.0	.2903	.2243	.2496	.2740	.2993	.3240	.3497	.3755
1.05	.6037	.4445	.3572	.3196	.3323	.3440	.3675	.3904
1.1	.6891	.5991	.5033	.4422	.4166	.3900	.4070	.4236
1.15	.7443	.6796	.6113	.5566	.5158	.4740	.4795	.4842
1.2	.7848	.7345	.6823	.6366	.5980	.5585	.5546	.5505
1.25	.8181	.7752	.7345	.6969	.6634	.6291	.6200	.6115
1.3	.8442	.8095	.7757	.7441	.7162	.6870	.6755	.6645
1.35	.8645	.8392	.8088	.7816	.7603	.7381	.7257	.7125
1.4	.8830	.8590	.8344	.8123	.7937	.7740	.7620	.7505
1.45	.8943	.8745	.8542	.8351	.8175	.7992	.7895	.7793
1.5	.9075	.8930	.8754	.8592	.8449	.8293	.8200	.8115
1.55	.9197	.9052	.8916	.8776	.8641	.8505	.8425	.8346
1.6	.9302	.9178	.9060	.8943	.8830	.8713	.8645	.8577
1.65	.9380	.9270	.9167	.9068	.8967	.8866	.8807	.8748
1.7	.9457	.9363	.9276	.9192	.9105	.9020	.8971	.8920
1.75	.9516	.9436	.9360	.9286	.9211	.9136	.9095	.9053
1.8	.9578	.9509	.9446	.9381	.9318	.9255	.9221	.9187
1.85	.9625	.9565	.9511	.9454	.9397	.9343	.9316	.9289
1.9	.9670	.9622	.9575	.9530	.9482	.9436	.9415	.9393
1.95	.9712	.9667	.9628	.9585	.9548	.9508	.9492	.9477
2.0	.9751	.9714	.9680	.9647	.9614	.9580	.9571	.9560
2.25	.9855	.9840	.9823	.9810	.9796	.9781	.9783	.9785
2.5	.9964	.9965	.9969	.9972	.9976	.9980	.9995	1.0010
2.75	1.0010	1.0019	1.0030	1.0040	1.0051	1.0062	1.0082	1.0102
3.0	1.0055	1.0074	1.0091	1.0108	1.0124	1.0141	1.0166	1.0193
3.25	1.0075	1.0098	1.0117	1.0136	1.0156	1.0175	1.0200	1.0230
3.5	1.0095	1.0122	1.0146	1.0169	1.0192	1.0216	1.0244	1.0271
3.75	1.0103	1.0133	1.0157	1.0182	1.0206	1.0230	1.0257	1.0286
4.0	1.0114	1.0142	1.0168	1.0194	1.0219	1.0245	1.0273	1.0301
4.25	1.0121	1.0146	1.0172	1.0200	1.0226	1.0253	1.0282	1.0312
4.5	1.0129	1.0150	1.0178	1.0206	1.0233	1.0261	1.0292	1.0322
4.75	1.0134	1.0152	1.0180	1.0208	1.0237	1.0265	1.0297	1.0329
5.0	1.0140	1.0154	1.0183	1.0212	1.0241	1.0270	1.0303	1.0335

Pr Tr	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0
0.2	.8881	.9560	1.0241	1.0921	1.1597	1.2273	1.2950	1.3628
0.3	.7507	.8081	.8655	.9226	.9796	1.0365	1.0938	1.1507
0.4	.6160	.6630	.7100	.7565	.8030	.8493	.8960	.9422
0.5	.5307	.5709	.6107	.6505	.6905	.7300	.7698	.8096
0.6	.4730	.5093	.5451	.5800	.6150	.6500	.6852	.7198
0.7	.4330	.4660	.4990	.5305	.5625	.5943	.6260	.6578
0.8	.4096	.4397	.4693	.4988	.5280	.5575	.5863	.6160
0.85	.4005	.4296	.4588	.4865	.5150	.5430	.5713	.5992
0.9	.3960	.4245	.4530	.4800	.5069	.5335	.5607	.5878
0.95	.3957	.4227	.4492	.4745	.5000	.5255	.5516	.5767
1.0	.4008	.4266	.4515	.4762	.5008	.5253	.5497	.5742
1.05	.4137	.4365	.4590	.4826	.5065	.5303	.5540	.5780
1.1	.4405	.4579	.4745	.4965	.5187	.5405	.5627	.5843
1.15	.4895	.4950	.5000	.5196	.5395	.5596	.5795	.5993
1.2	.5470	.5432	.5391	.5556	.5720	.5884	.6045	.6210
1.25	.6026	.5930	.5842	.5975	.6105	.6236	.6363	.6495
1.3	.6530	.6416	.6305	.6400	.6497	.6592	.6690	.6790
1.35	.7000	.6870	.6744	.6819	.6890	.6965	.7040	.7115
1.4	.7383	.7265	.7142	.7200	.7261	.7316	.7373	.7430
1.45	.7695	.7596	.7500	.7547	.7583	.7617	.7665	.7700
1.5	.8026	.7935	.7841	.7875	.7900	.7934	.7963	.7994
1.55	.8265	.8187	.8106	.8131	.8157	.8183	.8208	.8234
1.6	.8508	.8440	.8372	.8392	.8412	.8431	.8450	.8471
1.65	.8689	.8630	.8571	.8589	.8605	.8626	.8644	.8662
1.7	.8872	.8821	.8773	.8790	.8805	.8823	.8840	.8856
1.75	.9012	.8970	.8929	.8945	.8962	.8980	.8997	.9014
1.8	.9153	.9119	.9085	.9102	.9119	.9137	.9154	.9171
1.85	.9261	.9234	.9207	.9225	.9243	.9262	.9280	.9298
1.9	.9372	.9350	.9329	.9347	.9367	.9386	.9405	.9424
1.95	.9461	.9446	.9430	.9450	.9469	.9489	.9508	.9528
2.0	.9549	.9540	.9530	.9551	.9570	.9592	.9612	.9633
2.25	.9788	.9790	.9792	.9817	.9842	.9866	.9891	.9916
2.5	1.0025	1.0040	1.0055	1.0086	1.0115	1.0144	1.0173	1.0204
2.75	1.0121	1.0140	1.0161	1.0192	1.0224	1.0255	1.0287	1.0318
3.0	1.0217	1.0245	1.0270	1.0303	1.0336	1.0369	1.0401	1.0435
3.25	1.0258	1.0285	1.0312	1.0345	1.0379	1.0413	1.0446	1.0480
3.5	1.0300	1.0327	1.0355	1.0389	1.0423	1.0458	1.0492	1.0526
3.75	1.0315	1.0342	1.0370	1.0403	1.0436	1.0470	1.0502	1.0536
4.0	1.0330	1.0357	1.0386	1.0418	1.0450	1.0483	1.0515	1.0547
4.25	1.0341	1.0371	1.0400	1.0431	1.0462	1.0494	1.0525	1.0556
4.5	1.0353	1.0383	1.0414	1.0444	1.0475	1.0505	1.0536	1.0566
4.75	1.0361	1.0393	1.0425	1.0454	1.0484	1.0513	1.0543	1.0572
5.0	1.0368	1.0400	1.0433	1.0462	1.0491	1.0520	1.0549	1.0578

Pr Tr	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
0.2	1.5315	1.7014	1.8702	2.0400	2.2095	2.3782	2.5451	2.7130
0.3	1.2936	1.4360	1.5796	1.7226	1.8657	2.0080	2.1485	2.2891
0.4	1.0590	1.1755	1.2910	1.4060	1.5236	1.6400	1.7541	1.8680
0.5	.9095	1.0097	1.1080	1.2062	1.3056	1.4055	1.5010	1.5962
0.6	.8085	.8962	.9835	1.0712	1.1565	1.2420	1.3265	1.4120
0.7	.7360	.8145	.8925	.9708	1.0500	1.1290	1.2035	1.2782
0.8	.6875	.7592	.8305	.9020	.9725	1.0430	1.1115	1.1790
0.85	.6695	.7403	.8081	.8763	.9431	1.0090	1.0735	1.1381
0.9	.6545	.7215	.7858	.8496	.9150	.9800	1.0420	1.1038
0.95	.6426	.7078	.7692	.8313	.8940	.9569	1.0162	1.0750
1.0	.6368	.6990	.7590	.8194	.8790	.9388	.9945	1.0500
1.05	.6360	.6943	.7523	.8100	.8670	.9243	.9780	1.0314
1.1	.6395	.6940	.7490	.8042	.8585	.9123	.9635	1.0151
1.15	.6480	.6964	.7485	.8006	.8510	.9012	.9509	1.0002
1.2	.6637	.7050	.7528	.8000	.8483	.8960	.9423	.9901
1.25	.6833	.7165	.7610	.8050	.8507	.8950	.9400	.9844
1.3	.7064	.7335	.7744	.8150	.8559	.8965	.9392	.9806
1.35	.7312	.7516	.7885	.8250	.8630	.9008	.9415	.9830
1.4	.7578	.7713	.8058	.8400	.8748	.9091	.9473	.9850
1.45	.7808	.7911	.8233	.8550	.8875	.9194	.9547	.9901
1.5	.8072	.8150	.8439	.8722	.9015	.9301	.9636	.9962
1.55	.8298	.8363	.8625	.8887	.9150	.9412	.9725	1.0040
1.6	.8520	.8570	.8808	.9045	.9282	.9520	.9816	1.0110
1.65	.8708	.8753	.8973	.9195	.9414	.9633	.9911	1.0189
1.7	.8898	.8939	.9140	.9342	.9545	.9746	1.0007	1.0268
1.75	.9057	.9100	.9289	.9478	.9667	.9855	1.0102	1.0350
1.8	.9214	.9257	.9433	.9610	.9786	.9962	1.0195	1.0431
1.85	.9343	.9388	.9556	.9723	.9889	1.0056	1.0280	1.0503
1.9	.9472	.9519	.9678	.9837	.9996	1.0155	1.0367	1.0580
1.95	.9577	.9626	.9780	.9933	1.0086	1.0240	1.0443	1.0646
2.0	.9684	.9736	.9884	1.0032	1.0180	1.0328	1.0522	1.0717
2.25	.9978	1.0041	1.0179	1.0317	1.0455	1.0593	1.0764	1.0935
2.5	1.0278	1.0352	1.0478	1.0606	1.0733	1.0860	1.1007	1.1155
2.75	1.0396	1.0475	1.0598	1.0720	1.0842	1.0965	1.1102	1.1240
3.0	1.0518	1.0600	1.0718	1.0836	1.0955	1.1072	1.1199	1.1327
3.25	1.0564	1.0648	1.0762	1.0875	1.0989	1.1103	1.1224	1.1345
3.5	1.0611	1.0696	1.0805	1.0916	1.1025	1.1134	1.1249	1.1364
3.75	1.0619	1.0702	1.0810	1.0918	1.1026	1.1133	1.1243	1.1354
4.0	1.0628	1.0708	1.0814	1.0920	1.1027	1.1133	1.1238	1.1344
4.25	1.0635	1.0712	1.0815	1.0918	1.1021	1.1124	1.1224	1.1325
4.5	1.0643	1.0717	1.0816	1.0916	1.1016	1.1115	1.1210	1.1305
4.75	1.0647	1.0720	1.0817	1.0914	1.1012	1.1109	1.1196	1.1284
5.0	1.0650	1.0722	1.0817	1.0912	1.1007	1.1102	1.1182	1.1263

Pr Tr	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0
0.2	2.8801	3.0470	3.2139	3.3831	3.5528	3.7219	3.8900	4.0585
0.3	2.4300	2.5708	2.7115	2.8522	2.9933	3.1339	3.2741	3.4145
0.4	1.9825	2.0972	2.2110	2.3250	2.4390	2.5533	2.6676	2.7805
0.5	1.6915	1.7870	1.8845	1.9820	2.0792	2.1773	2.2745	2.3726
0.6	1.4965	1.5811	1.6643	1.7480	1.8320	1.9155	1.9990	2.0820
0.7	1.3516	1.4250	1.5002	1.5750	1.6495	1.7243	1.7795	1.8750
0.8	1.2470	1.3148	1.3810	1.4475	1.5142	1.5800	1.6466	1.7138
0.85	1.2020	1.2665	1.3305	1.3956	1.4610	1.5253	1.5905	1.6560
0.9	1.1645	1.2250	1.2880	1.3505	1.4133	1.4758	1.5379	1.5995
0.95	1.1345	1.1932	1.2515	1.3100	1.3687	1.4273	1.4855	1.5431
1.0	1.1065	1.1630	1.2190	1.2745	1.3306	1.3852	1.4405	1.4959
1.05	1.0855	1.1390	1.1935	1.2482	1.3030	1.3575	1.4126	1.4670
1.1	1.0675	1.1200	1.1710	1.2216	1.2720	1.3223	1.3735	1.4251
1.15	1.0500	1.0998	1.1496	1.1986	1.2475	1.2968	1.3456	1.3948
1.2	1.0383	1.0852	1.1327	1.1812	1.2300	1.2785	1.3264	1.3740
1.25	1.0300	1.0750	1.1218	1.1679	1.2143	1.2600	1.3060	1.3515
1.3	1.0255	1.0694	1.1128	1.1555	1.1985	1.2410	1.2831	1.3253
1.35	1.0243	1.0650	1.1062	1.1470	1.1875	1.2290	1.2695	1.3104
1.4	1.0236	1.0636	1.1022	1.1399	1.1778	1.2155	1.2530	1.2932
1.45	1.0275	1.0648	1.0996	1.1338	1.1680	1.2016	1.2367	1.2728
1.5	1.0309	1.0649	1.0978	1.1625	1.1300	1.1941	1.2266	1.2585
1.55	1.0353	1.0665	1.0981	1.1295	1.1610	1.1923	1.2235	1.2549
1.6	1.0405	1.0700	1.0995	1.1290	1.1584	1.1881	1.2176	1.2470
1.65	1.0467	1.0746	1.1024	1.1302	1.1581	1.1857	1.2135	1.2412
1.7	1.0529	1.0790	1.1052	1.1313	1.1574	1.1835	1.2097	1.2357
1.75	1.0597	1.0843	1.1092	1.1339	1.1586	1.1832	1.2080	1.2328
1.8	1.0663	1.0897	1.1130	1.1365	1.1600	1.1833	1.2072	1.2307
1.85	1.0726	1.0950	1.1174	1.1397	1.1621	1.1844	1.2065	1.2285
1.9	1.0792	1.1006	1.1218	1.1430	1.1643	1.1855	1.2066	1.2275
1.95	1.0851	1.1055	1.1260	1.1463	1.1667	1.1870	1.2071	1.2272
2.0	1.0912	1.1107	1.1302	1.1496	1.1690	1.1883	1.2078	1.2273
2.25	1.1106	1.1278	1.1449	1.1620	1.1791	1.1962	1.2133	1.2305
2.5	1.1302	1.1450	1.1598	1.1745	1.1892	1.2039	1.2185	1.2335
2.75	1.1377	1.1515	1.1652	1.1790	1.1928	1.2065	1.2204	1.2343
3.0	1.1455	1.1581	1.1709	1.1836	1.1963	1.2090	1.2217	1.2344
3.25	1.1467	1.1588	1.1710	1.1831	1.1952	1.2073	1.2194	1.2315
3.5	1.1478	1.1594	1.1709	1.1824	1.1939	1.2054	1.2169	1.2283
3.75	1.1463	1.1574	1.1684	1.1794	1.1905	1.2013	1.2122	1.2233
4.0	1.1449	1.1554	1.1660	1.1765	1.1871	1.1975	1.2079	1.2182
4.25	1.1423	1.1525	1.1626	1.1725	1.1823	1.1922	1.2023	1.2124
4.5	1.1399	1.1494	1.1589	1.1684	1.1780	1.1873	1.1968	1.2062
4.75	1.1371	1.1458	1.1546	1.1633	1.1720	1.1807	1.1894	1.1980
5.0	1.1344	1.1423	1.1505	1.1585	1.1664	1.1746	1.1825	1.1906

TABLE 12

$Z^{(1)}$ Values for Compressibility Factor Calculation (2)

Tr \ Pr	0.01	0.05	0.1	0.15	0.2	0.4	0.6	0.8
0.2	-.0008	-.0040	-.0072	-.0104	-.0140	-.0261	-.0385	-.0530
0.3	-.0009	-.0045	-.0088	-.0130	-.0176	-.0317	-.0490	-.0651
0.4	-.0009	-.0050	-.0100	-.0151	-.0196	-.0376	-.0575	-.0763
0.5	-.0008	-.0048	-.0098	-.0135	-.0178	-.0364	-.0543	-.0724
0.6	-.0206	-.0045	-.0087	-.0126	-.0171	-.0330	-.0491	-.0651
0.7	-.0099	-.0503	-.1172	-.0115	-.0151	-.0300	-.0450	-.0581
0.8	-.0050	-.0225	-.0478	-.1157	-.1150	-.0276	-.0398	-.0525
0.85	-.0029	-.0150	-.0317	-.0513	-.0714	-.0273	-.0395	-.0511
0.9	-.0025	-.0100	-.0200	-.0311	-.0418	-.1109	-.0397	-.0500
0.95	-.0021	-.0060	-.0125	-.0194	-.0268	-.0598	-.1103	-.0525
1.0	-.0003	-.0044	-.0075	-.0113	-.0146	-.0282	-.0450	-.0581
1.05	-.0001	-.0025	-.0031	-.0038	-.0050	-.0098	-.0099	-.0023
1.1	-.0000	.0000	.0000	.0002	.0005	.0037	.0100	.0227
1.15	.0001	.0010	.0024	.0036	.0050	.0124	.0241	.0400
1.2	.0004	.0024	.0045	.0064	.0078	.0194	.0328	.0500
1.25	.0005	.0029	.0050	.0076	.0101	.0238	.0393	.0560
1.3	.0007	.0035	.0060	.0093	.0125	.0272	.0425	.0610
1.35	.0008	.0038	.0070	.0101	.0131	.0297	.0450	.0649
1.4	.0008	.0041	.0073	.0110	.0145	.0302	.0475	.0659
1.45	.0009	.0044	.0077	.0114	.0150	.0321	.0487	.0667
1.5	.0009	.0048	.0080	.0117	.0154	.0325	.0500	.0675
1.55	.0009	.0049	.0083	.0120	.0157	.0329	.0503	.0676
1.6	.0009	.0050	.0085	.0122	.0160	.0333	.0506	.0675
1.65	.0010	.0050	.0087	.0124	.0161	.0333	.0504	.0667
1.7	.0010	.0050	.0088	.0125	.0162	.0332	.0500	.0664
1.75	.0010	.0050	.0088	.0126	.0163	.0330	.0495	.0655
1.8	.0010	.0050	.0088	.0125	.0162	.0328	.0490	.0647
1.85	.0010	.0050	.0087	.0122	.0157	.0324	.0485	.0636
1.9	.0010	.0050	.0085	.0120	.0154	.0321	.0481	.0629
1.95	.0010	.0049	.0084	.0118	.0152	.0317	.0475	.0619
2.0	.0010	.0048	.0084	.0116	.0149	.0314	.0470	.0610
2.25	.0010	.0045	.0080	.0110	.0139	.0291	.0436	.0564
2.5	.0009	.0040	.0075	.0102	.0128	.0275	.0405	.0521
2.75	.0009	.0039	.0070	.0095	.0118	.0254	.0380	.0484
3.0	.0008	.0038	.0064	.0086	.0109	.0238	.0352	.0450
3.25	.0008	.0035	.0061	.0082	.0102	.0225	.0333	.0420
3.5	.0007	.0032	.0058	.0076	.0095	.0206	.0314	.0394
3.75	.0007	.0030	.0055	.0072	.0090	.0198	.0299	.0370
4.0	.0006	.0027	.0053	.0069	.0085	.0185	.0280	.0350
4.25	.0006	.0024	.0050	.0066	.0081	.0175	.0265	.0322
4.5	.0005	.0022	.0048	.0063	.0078	.0167	.0254	.0300
4.75	.0005	.0020	.0045	.0060	.0075	.0160	.0243	.0275
5.0	.0005	.0018	.0042	.0057	.0072	.0153	.0234	.0255

Tr \ Pr	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
0.2	-.0664	-.0802	-.0930	-.1067	-.1199	-.1327	-.1452	-.1584
0.3	-.0813	-.0960	-.1123	-.1285	-.1450	-.1611	-.1767	-.1920
0.4	-.0950	-.1129	-.1315	-.1500	-.1690	-.1878	-.2060	-.2240
0.5	-.0900	-.1075	-.1245	-.1420	-.1590	-.1759	-.1930	-.2095
0.6	-.0800	-.0966	-.1120	-.1273	-.1422	-.1575	-.1721	-.1862
0.7	-.0725	-.0864	-.0991	-.1125	-.1262	-.1390	-.1515	-.1631
0.8	-.0650	-.0769	-.0885	-.0998	-.1113	-.1225	-.1325	-.1420
0.85	-.0625	-.0735	-.0837	-.0936	-.1043	-.1141	-.1229	-.1327
0.9	-.0600	-.0700	-.0785	-.0870	-.0962	-.1048	-.1130	-.1215
0.95	-.0602	-.0675	-.0742	-.0813	-.0885	-.0955	-.1022	-.1090
1.0	-.0875	-.0615	-.0667	-.0720	-.0771	-.0825	-.0880	-.0927
1.05	.0223	.0700	.0553	.0295	-.0070	-.0436	-.0515	-.0605
1.1	.0475	.0887	.1186	.1200	.0930	.0669	.0454	.0246
1.15	.0628	.0950	.1298	.1513	.1589	.1659	.1392	.1118
1.2	.0722	.0996	.1312	.1570	.1776	.1975	.1792	.1618
1.25	.0776	.1025	.1308	.1556	.1787	.2012	.1948	.1887
1.3	.0825	.1050	.1306	.1538	.1753	.1975	.1991	.2006
1.35	.0850	.1070	.1282	.1506	.1716	.1925	.1992	.2068
1.4	.0854	.1072	.1276	.1473	.1678	.1875	.1973	.2074
1.45	.0865	.1062	.1256	.1445	.1637	.1825	.1943	.2057
1.5	.0876	.1050	.1237	.1420	.1605	.1782	.1909	.2033
1.55	.0869	.1040	.1215	.1394	.1570	.1746	.1870	.1998
1.6	.0865	.1030	.1201	.1373	.1542	.1715	.1841	.1969
1.65	.0855	.1015	.1180	.1346	.1515	.1680	.1806	.1933
1.7	.0847	.1004	.1165	.1324	.1487	.1646	.1772	.1899
1.75	.0835	.0987	.1143	.1300	.1455	.1611	.1736	.1860
1.8	.0824	.0975	.1127	.1279	.1430	.1580	.1704	.1828
1.85	.0812	.0957	.1105	.1255	.1402	.1550	.1671	.1795
1.9	.0800	.0944	.1087	.1233	.1377	.1521	.1642	.1763
1.95	.0785	.0926	.1068	.1209	.1350	.1492	.1611	.1730
2.0	.0773	.0913	.1051	.1190	.1323	.1467	.1583	.1699
2.25	.0715	.0841	.0968	.1096	.1225	.1351	.1460	.1568
2.5	.0660	.0780	.0895	.1010	.1123	.1239	.1338	.1440
2.75	.0612	.0722	.0830	.0938	.1045	.1153	.1247	.1341
3.0	.0570	.0673	.0773	.0870	.0971	.1069	.1158	.1246
3.25	.0535	.0630	.0722	.0816	.0908	.1002	.1087	.1172
3.5	.0502	.0594	.0680	.0768	.0855	.0941	.1020	.1101
3.75	.0472	.0560	.0642	.0725	.0808	.0890	.0966	.1043
4.0	.0447	.0531	.0610	.0688	.0766	.0844	.0915	.0988
4.25	.0422	.0501	.0575	.0651	.0727	.0802	.0875	.0940
4.5	.0401	.0480	.0553	.0624	.0695	.0767	.0835	.0900
4.75	.0385	.0462	.0530	.0600	.0665	.0733	.0801	.0869
5.0	.0372	.0447	.0510	.0575	.0643	.0705	.0770	.0835

Tr \ Pr	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0
0.2	-.1710	-.1843	-.1970	-.2115	-.2253	-.2397	-.2535	-.2678
0.3	-.2075	-.2230	-.2382	-.2540	-.2700	-.2861	-.3019	-.3178
0.4	-.2415	-.2600	-.2775	-.2955	-.3140	-.3320	-.3500	-.3676
0.5	-.2265	-.2430	-.2600	-.2765	-.2930	-.3095	-.3260	-.3425
0.6	-.2016	-.2152	-.2300	-.2443	-.2578	-.2722	-.2862	-.3000
0.7	-.1760	-.1878	-.2000	-.2112	-.2233	-.2349	-.2460	-.2581
0.8	-.1520	-.1615	-.1716	-.1818	-.1910	-.2015	-.2111	-.2208
0.85	-.1419	-.1504	-.1598	-.1681	-.1770	-.1855	-.1951	-.2032
0.9	-.1290	-.1376	-.1453	-.1521	-.1600	-.1675	-.1755	-.1825
0.95	-.1165	-.1231	-.1300	-.1366	-.1431	-.1496	-.1561	-.1624
1.0	-.1006	-.1059	-.1122	-.1172	-.1235	-.1291	-.1341	-.1400
1.05	-.0686	-.0769	-.0847	-.0900	-.0958	-.1016	-.1066	-.1125
1.1	.0037	-.0172	-.0380	-.0445	-.0516	-.0589	-.0658	-.0725
1.15	.0843	.0570	.0301	.0203	.0105	.0012	-.0075	-.0172
1.2	.1432	.1258	.1075	.0952	.0828	.0706	.0577	.0450
1.25	.1818	.1757	.1694	.1563	.1423	.1297	.1155	.1025
1.3	.2020	.2037	.2051	.1933	.1815	.1696	.1574	.1455
1.35	.2137	.2207	.2275	.2176	.2080	.1985	.1889	.1790
1.4	.2177	.2278	.2376	.2307	.2235	.2173	.2104	.2033
1.45	.2171	.2285	.2400	.2363	.2324	.2283	.2242	.2205
1.5	.2155	.2279	.2401	.2386	.2375	.2363	.2346	.2334
1.55	.2122	.2247	.2373	.2380	.2386	.2393	.2399	.2406
1.6	.2096	.2223	.2350	.2376	.2402	.2428	.2454	.2480
1.65	.2059	.2187	.2312	.2350	.2388	.2425	.2463	.2501
1.7	.2026	.2150	.2278	.2327	.2376	.2425	.2474	.2523
1.75	.1985	.2110	.2235	.2291	.2347	.2401	.2458	.2514
1.8	.1952	.2076	.2200	.2262	.2325	.2387	.2450	.2512
1.85	.1916	.2038	.2160	.2227	.2293	.2360	.2425	.2492
1.9	.1884	.2003	.2125	.2196	.2267	.2336	.2407	.2478
1.95	.1848	.1967	.2086	.2159	.2231	.2304	.2376	.2450
2.0	.1815	.1932	.2048	.2124	.2200	.2275	.2350	.2426
2.25	.1677	.1786	.1895	.1972	.2049	.2126	.2203	.2280
2.5	.1539	.1642	.1741	.1820	.1898	.1977	.2057	.2136
2.75	.1436	.1531	.1625	.1702	.1778	.1855	.1931	.2008
3.0	.1335	.1423	.1512	.1587	.1660	.1736	.1810	.1885
3.25	.1256	.1340	.1426	.1498	.1569	.1641	.1712	.1784
3.5	.1182	.1262	.1343	.1412	.1480	.1551	.1619	.1688
3.75	.1119	.1195	.1272	.1339	.1405	.1472	.1538	.1606
4.0	.1060	.1134	.1206	.1270	.1334	.1399	.1462	.1527
4.25	.1012	.1085	.1153	.1211	.1272	.1335	.1396	.1455
4.5	.0968	.1035	.1105	.1160	.1221	.1279	.1335	.1392
4.75	.0935	.1001	.1070	.1125	.1177	.1230	.1286	.1339
5.0	.0903	.0970	.1035	.1085	.1131	.1180	.1232	.1281

Tr \ Pr	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
0.2	-.3030	-.3386	-.3727	-.4070	-.4409	-.4750	-.5105	-.5461
0.3	-.3573	-.3975	-.4370	-.4768	-.5165	-.5561	-.5950	-.6340
0.4	-.4130	-.4583	-.5030	-.5472	-.5900	-.6350	-.6780	-.7218
0.5	-.3835	-.4248	-.4640	-.5034	-.5430	-.5825	-.6200	-.6581
0.6	-.3353	-.3700	-.4025	-.4357	-.4692	-.5032	-.5334	-.5645
0.7	-.2877	-.3170	-.3431	-.3705	-.3975	-.4253	-.4504	-.4750
0.8	-.2451	-.2700	-.2909	-.3126	-.3335	-.3550	-.3758	-.3955
0.85	-.2254	-.2478	-.2665	-.2845	-.3025	-.3218	-.3388	-.3569
0.9	-.2009	-.2204	-.2370	-.2548	-.2701	-.2875	-.3027	-.3182
0.95	-.1773	-.1933	-.2095	-.2247	-.2400	-.2545	-.2688	-.2820
1.0	-.1532	-.1675	-.1800	-.1932	-.2060	-.2200	-.2327	-.2450
1.05	-.1253	-.1392	-.1507	-.1625	-.1731	-.1848	-.1959	-.2065
1.1	-.0881	-.1046	-.1150	-.1265	-.1372	-.1481	-.1582	-.1678
1.15	-.0400	-.0627	-.0741	-.0865	-.0986	-.1100	-.1196	-.1284
1.2	.0144	-.0158	-.0297	-.0426	-.0572	-.0700	-.0785	-.0877
1.25	.0684	.0350	.0192	.0042	-.0112	-.0275	-.0375	-.0464
1.3	.1150	.0850	.0678	.0500	.0325	.0158	.0055	-.0044
1.35	.1556	.1312	.1133	.0946	.0764	.0590	.0486	.0375
1.4	.1864	.1702	.1522	.1349	.1166	.0987	.0879	.0766
1.45	.2117	.2025	.1860	.1697	.1539	.1375	.1262	.1144
1.5	.2306	.2275	.2132	.1986	.1846	.1700	.1586	.1475
1.55	.2423	.2440	.2321	.2204	.2085	.1967	.1861	.1758
1.6	.2545	.2610	.2518	.2425	.2332	.2240	.2142	.2043
1.65	.2596	.2690	.2624	.2558	.2491	.2425	.2338	.2250
1.7	.2646	.2768	.2730	.2692	.2653	.2615	.2540	.2464
1.75	.2653	.2793	.2778	.2764	.2749	.2734	.2672	.2609
1.8	.2668	.2825	.2834	.2842	.2851	.2860	.2811	.2760
1.85	.2659	.2825	.2851	.2878	.2904	.2931	.2895	.2857
1.9	.2655	.2830	.2874	.2918	.2963	.3007	.2978	.2950
1.95	.2633	.2815	.2872	.2930	.2987	.3044	.3032	.3021
2.0	.2614	.2803	.2872	.2946	.3018	.3090	.3089	.3089
2.25	.2472	.2665	.2767	.2865	.2963	.3065	.3100	.3133
2.5	.2334	.2531	.2658	.2787	.2914	.3041	.3111	.3180
2.75	.2197	.2392	.2525	.2658	.2792	.2925	.3007	.3089
3.0	.2070	.2258	.2396	.2535	.2674	.2812	.2907	.3001
3.25	.1965	.2142	.2280	.2417	.2555	.2694	.2792	.2890
3.5	.1861	.2033	.2171	.2308	.2446	.2585	.2686	.2787
3.75	.1773	.1940	.2074	.2207	.2342	.2476	.2578	.2681
4.0	.1688	.1848	.1980	.2110	.2241	.2374	.2477	.2582
4.25	.1610	.1762	.1890	.2021	.2152	.2280	.2381	.2485
4.5	.1538	.1683	.1810	.1935	.2063	.2189	.2290	.2394
4.75	.1471	.1605	.1727	.1855	.1977	.2101	.2200	.2297
5.0	.1405	.1532	.1655	.1776	.1895	.2020	.2114	.2210

Tr \ Pr	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0
0.2	-.5817	-.6172	-.6526	-.6882	-.7235	-.7597	-.7956	-.8310
0.3	-.6726	-.7115	-.7506	-.7895	-.8287	-.8675	-.9059	-.9442
0.4	-.7640	-.8070	-.8490	-.8915	-.9340	-.9770	-1.0200	-1.0630
0.5	-.6950	-.7325	-.7700	-.8082	-.8465	-.8850	-.9230	-.9600
0.6	-.5963	-.6275	-.6590	-.6903	-.7221	-.7529	-.7842	-.8145
0.7	-.5006	-.5267	-.5523	-.5775	-.6029	-.6281	-.6533	-.6780
0.8	-.4152	-.4344	-.4541	-.4734	-.4930	-.5123	-.5310	-.5498
0.85	-.3740	-.3920	-.4091	-.4275	-.4462	-.4641	-.4827	-.5007
0.9	-.3340	-.3500	-.3651	-.3807	-.3965	-.4122	-.4276	-.4426
0.95	-.2953	-.3080	-.3218	-.3350	-.3482	-.3618	-.3749	-.3870
1.0	-.2571	-.2700	-.2806	-.2920	-.3037	-.3151	-.3275	-.3396
1.05	-.2173	-.2275	-.2380	-.2485	-.2586	-.2689	-.2804	-.2925
1.1	-.1773	-.1875	-.1972	-.2075	-.2175	-.2283	-.2386	-.2490
1.15	-.1383	-.1475	-.1572	-.1660	-.1750	-.1836	-.1926	-.2007
1.2	-.0975	-.1070	-.1166	-.1250	-.1331	-.1413	-.1505	-.1592
1.25	-.0559	-.0650	-.0742	-.0841	-.0945	-.1043	-.1136	-.1225
1.3	-.0140	-.0238	-.0343	-.0442	-.0545	-.0642	-.0738	-.0830
1.35	.0276	.0168	.0056	-.0050	-.0159	-.0263	-.0375	-.0497
1.4	.0654	.0550	.0445	.0334	.0232	.0138	.0037	-.0063
1.45	.1037	.0922	.0808	.0695	.0585	.0470	.0353	.0241
1.5	.1368	.1257	.1145	.1032	.0916	.0808	.0695	.0583
1.55	.1653	.1549	.1442	.1340	.1237	.1136	.1035	.0934
1.6	.1944	.1845	.1747	.1648	.1550	.1451	.1348	.1249
1.65	.2163	.2077	.1990	.1903	.1816	.1730	.1642	.1554
1.7	.2388	.2312	.2237	.2162	.2085	.2011	.1937	.1863
1.75	.2547	.2485	.2422	.2360	.2298	.2239	.2175	.2112
1.8	.2712	.2662	.2610	.2561	.2514	.2465	.2411	.2360
1.85	.2820	.2785	.2747	.2710	.2672	.2637	.2600	.2563
1.9	.2921	.2892	.2920	.2863	.2807	.2750	.2691	.2635
1.95	.3008	.2996	.2984	.2972	.2960	.2945	.2933	.2927
2.0	.3088	.3087	.3086	.3085	.3084	.3082	.3080	.3079
2.25	.3167	.3202	.3236	.3270	.3304	.3335	.3371	.3410
2.5	.3249	.3318	.3387	.3458	.3530	.3601	.3672	.3739
2.75	.3170	.3252	.3334	.3416	.3498	.3580	.3665	.3745
3.0	.3096	.3190	.3285	.3380	.3475	.3570	.3665	.3760
3.25	.2988	.3087	.3186	.3283	.3380	.3476	.3576	.3675
3.5	.2889	.2990	.3090	.3192	.3296	.3402	.3505	.3607
3.75	.2784	.2886	.2988	.3091	.3195	.3297	.3400	.3502
4.0	.2685	.2789	.2895	.2997	.3100	.3203	.3302	.3401
4.25	.2588	.2690	.2793	.2894	.2998	.3095	.3193	.3292
4.5	.2496	.2597	.2698	.2797	.2896	.2993	.3095	.3195
4.75	.2395	.2492	.2591	.2691	.2794	.2896	.2986	.3080
5.0	.2306	.2402	.2497	.2592	.2688	.2781	.2875	.2973

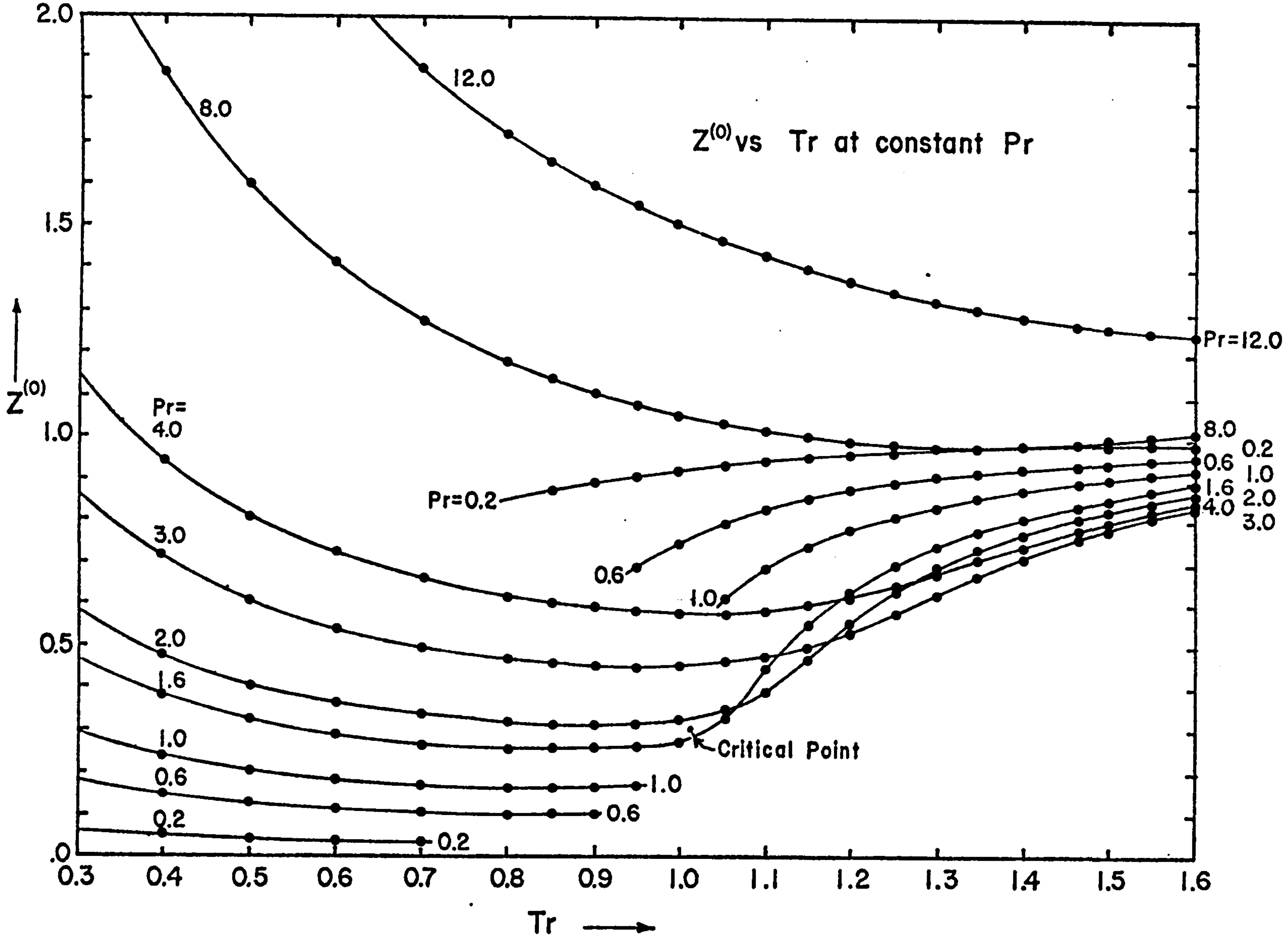

Figure 14. Generalized Plot of Z$^{(0)}$ Values

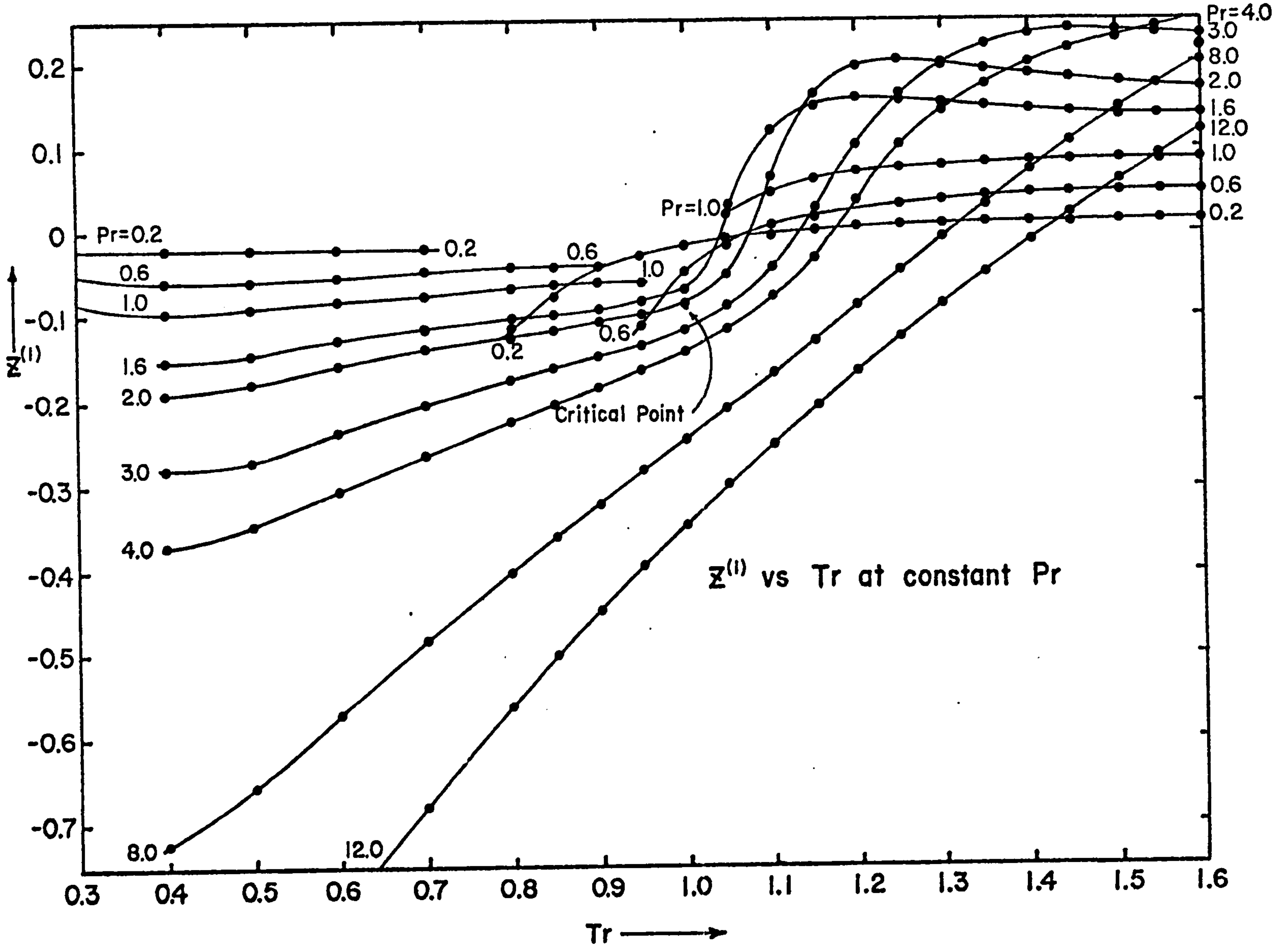

Figure 15. Generalized Plot of $\bar{Z}^{(1)}$ Values

is wider than those used by Pitzer et al. (-0.002 to 0.352) and by Lee and Kesler (0.0072 to 0.4902).

For the purpose of testing the $Z^{(0)}$ and $Z^{(1)}$ values obtained, (see Chapter VI), the experimental compressibility factor data for 12 compounds reported by Lee and Kesler {96} (1975) were again compared based on $Z^{(0)}$ and $Z^{(1)}$ values of this work. With the same T_r and P_r ranges, the total number of experimental points included in the comparison is 1,556 in this work (while Lee and Kesler reported 280) with the overall average absolute deviation of 1.38% (compared to 1.41% by Lee and Kesler). If we exclude 1-Pentene from the comparison, the overall average absolute deviation reduces to 1.07% in this work (with data points of 1,480) and 1.35% by Lee and Kesler's presentation (with 263 data points). The comparison results are tabulated in Table 13. It is obviously shown that this study is more precise when comparing with the experimental compressibility factor data for both the liquid and vapor phases. Furthermore, the boundary condition of this generalized correlation at acentric factor equals to zero for simple fluids was also applied to this study to test if this work satisfies this boundary condition. Through testing with the experimental compressibility factor data for simple fluids defined by Pitzer {127} (1955), this work provided testing results mostly compatible with the work by Pitzer et al.{128} (1955), as well as by Lu et al. {103} (1973) and very often with lesser extent of deviations. Hence this presentation has proved to be able to satisfy the boundary condition of this correlation with improving applicability.

TABLE 13 - COMPARISON OF THE CALCULATED COMPRESSIBILITY FACTORS BASED ON THIS WORK WITH LEE AND KESLER'S (1975)

Compound	No. of Points		T_r Range		P_r Range		Ave. Abs. Dev., %		Reference
	L.-K.	This work	L.-K.	This work	L.-K.	This work	L.-K.	This work	
Subcooled liquid and dense phase									
Methane	21	221	0.79-1.44	0.789-1.444	0.32-10.0	0.321-10.968	1.06	1.14	Vennix et al. (1970)
1-Butene	16	85	0.74-1.06	0.742-1.059	0.34- 8.5	0.343- 8.568	1.06	0.75	Sage and Lacey (1955)
Neopentane	18	184	1.0 -1.15	1.000-1.148	1.05- 9.5	1.045- 9.503	1.17	1.09	Dawson et al. (1973)
1-Pentene	17	76	0.76-1.07	0.76 -1.072	0.16- 8.9	0.14 - 7.796	2.22	7.42	Day and Felsing (1951)
n-Octane	12	73	0.66-0.96	0.656-0.964	0.2 - 8.2	0.204- 8.150	1.87	1.50	Felsing and Watson (1942)
n-Nonane	13	221	0.52-0.86	0.523-0.860	0.6 -15.0	0.602-15.050	1.09	0.94	Sage and Lacey (1955)
Cyclohexane	14	117	0.56-0.92	0.562-0.923	0.34- 8.5	0.338- 8.461	0.43	0.35	Reamer and Sage (1957)
Benzene	17	117	0.55-0.91	0.553-0.909	0.28- 7.0	0.281- 7.036	3.15	2.35	Sage and Lacey (1955)
Hydrogen sulfide	12	65	0.74-0.92	0.744-0.922	0.16- 7.7	0.153- 7.652	1.12	0.78	Sage and Lacey (1955)
n-Octane	9	27	0.46-0.70	0.457-0.696	0.04	0.041	1.26	1.30	Chappelow et al. (1971)
n-Decane	9	35	0.41-0.72	0.414-0.720	0.05	0.048	0.99	1.06	Rossini et al. (1953)
n-Dodecane	9	38	0.41-0.72	0.405-0.717	0.06	0.056	1.14	1.15	Rossini et al. (1953)
n-Heptadecane	15	24	0.44-0.78	0.44 -0.781	0-23	0-22.787	2.82	2.26	Doolittle (1964)
Total, with 1-Pentene	182	1283					1.54	1.51	
Total, without 1-Pentene	165	1207					1.47	1.14	
Superheated Vapor									
Methane	16	16	1.09-1.17	1.087-1.174	1.3 - 2.0	1.313- 2.035	0.30	0.20	Vennix et al. (1970)
Neopentane	24	54	0.8 -1.15	0.802-1.148	0.05- 0.76	0.048- 0.760	0.44	0.36	Dawson et al. (1973)
Hydrogen sulfide	20	139	0.74-1.19	0.744-1.190	0.01- 7.7	0.011- 7.652	0.41	0.40	Sage and Lacey (1955)
Total	60	209					0.39	0.38	

TABLE 13 - (continued)

Compound	No. of Points		T_r Range		P_r Range		Ave. Abs. Dev.,%		Reference
	L.-K.	This work	L.-K.	This work	L.-K.	This work	L.-K.	This work	
Saturated Liquid									
1-Butene	6	11	0.78-1.00	0.785-1.002	0.17-1.00	0.171-1.008	1.55	1.45	Sage and Lacey (1955)
n-Nonane	5	9	0.63-0.86	0.635-0.860	0.01-0.30	0.011-0.287	1.36	1.41	Sage and Lacey (1955)
Benzene	7	7	0.55-0.91	0.553-0.909	0.00-0.51	0.004-0.512	3.15	3.13	Sage and Lacey (1955)
Hydrogen sulfide	7	13	0.76-1.00	0.76 -1.000	0.15-1.00	0.153-1.000	1.96	2.42	Sage and Lacey (1955)
Total	25	40					2.07	2.05	
Saturated Vapor									
1-Butene	6	11	0.78-1.0	0.785-1.002	0.17-1.0	0.171-1.008	1.51	1.42	Sage and Lacey (1955)
Hydrogen sulfide	7	13	0.76-1.0	0.76 -1.000	0.15-1.0	0.153-1.000	4.12	2.89	Sage and Lacey (1955)
Total	13	24					2.92	2.22	
Overall, with 1-Pentene	280	1556					1.41	1.38	
Overall, without 1-Pentene	263	1480					1.35	1.07	

The Binary Interaction Parameters

The binary interaction constants obtained from the correlation of second virial coefficient for 121 systems have been presented in Tables 14 and 15. Table 14 presents the k_{ij} values for systems composed of compounds which are of prime interest as the constituents of natural or petroleum gas including hydrocarbons of methane to n-Octane, nitrogen, carbon dioxide and hydrogen sulfide, etc., while Table 15 presents k_{ij} values for other binary systems reserved for possible future use. Twenty-four values for Methane-n-Butane system and five values for Nitrogen-Ethane system are depicted in Figures 16 and 17.

From Figures 16 and 17, it is clearly shown that the binary interaction coefficient is a function of temperature. Also demonstrated in these figures are the k_{ij} values proposed by other authors, which are compatible with the values presented here. The comparison of the k_{ij} values will be discussed in Chapter VI. Moreover, for the temperature dependence of the k_{ij} values, Figures 16 and 17 show a trend represented by a second-order correlation for these two binary systems. However, if we cut the curves around certain temperatures, such as $400^{\circ}K$ for methane-n-butane system or $450^{\circ}K$ for nitrogen-ethane system, we have a linear correlation, i.e., first-order curve. This trend of temperature dependence for the binary interaction coefficients will be further discussed in Chapter VI.

TABLE 14. kij Values for Systems Containing Hydrocarbons, Nitrogen, Carbon Dioxide and Hydrogen Sulfide

System	Temperature (°K)	kij	Reference
Methane-Ethane	273.00	-0.0037	Guggenheim and McGlashan (1951)
	298.00	-0.0019	
	323.00	0.0016	
	273.20	-0.0035	Huff and Reed (1963)
	298.20	-0.0019	
	323.20	0.0017	
	298.00	-0.0060	Dantzler et al. (1968)
	323.00	-0.0161	
	348.00	-0.0296	
	373.00	-0.0248	
Methane-Propane	310.90	0.0024	Huff and Reed (1963)
	344.30	-0.0066	
	377.60	-0.0167	
	444.30	-0.0480	
	510.90	-0.0578	
	298.00	-0.0123	Dantzler et al. (1968)
	323.00	-0.0119	
	348.00	0.0067	
	373.00	0.0208	
Methane-n-Butane	423.15	-0.0235	Beattie and Stockmayer (1942)
	448.15	-0.0256	
	473.15	-0.0362	
	498.15	-0.0395	
	523.15	-0.0406	
	548.15	-0.0419	
	573.15	-0.0431	
	423.00	-0.0252	Guggenheim and McGlashan (1951)
	448.00	-0.0237	
	473.00	-0.0341	
	498.00	-0.0334	
	523.00	-0.0397	
	548.00	-0.0406	
	573.00	-0.0467	
	344.30	0.0075	Huff and Reed (1963)
	377.60	0.0230	
	410.90	0.0166	
	444.30	0.0138	
	477.60	0.0112	
	510.90	0.0074	
	298.00	-0.0056	Dantzler et al. (1968)
	323.00	0.0035	
	348.00	0.0170	
	373.00	0.0270	
Methane-Isobutane	344.30	0.0032	Huff and Reed (1963)
	377.60	0.0157	
	410.90	0.0216	
	444.30	0.0125	
	477.60	0.0037	
	510.90	-0.0148	
Methane-n-Pentane	310.90	0.0220	Huff and Reed (1963)
	344.20	0.0561	
	377.50	0.0722	
	410.90	0.0755	
	444.20	0.0651	
	477.50	0.0489	
	510.80	0.0270	
	298.00	0.0087	Dantzler et al. (1968)
	323.00	0.0191	
	348.00	0.0294	
	373.00	0.0368	

TABLE 14 (continued)

System	Temperature (°K)	kij	Reference
Methane-Neopentane	303.16	0.0765	Hamann et al. (1955)
	323.16	0.0879	
	333.16	0.0895	
	343.16	0.0910	
	353.16	0.0802	
	363.16	0.0770	
	383.16	0.0720	
	403.16	0.0673	
	303.20	0.0764	Huff and Reed (1963)
	323.20	0.0878	
	333.20	0.0898	
	343.20	0.0909	
	353.20	0.0801	
	363.20	0.0769	
	383.20	0.0719	
	403.20	0.0676	
Methane-n-Hexane	298.00	0.0321	Dantzler et al. (1968)
	323.00	0.0175	
	348.00	0.0368	
	373.00	0.0526	
Ethane-Propane	298.00	0.0020	Dantzler et al. (1968)
	323.00	0.0041	
	348.00	0.0100	
	373.00	0.0102	
Ethane-n-Butane	298.00	0.0066	Dantzler et al. (1968)
	323.00	0.0032	
	348.00	0.0087	
	373.00	0.0206	
Ethane-n-Pentane	298.00	0.0144	Dantzler et al. (1968)
	323.00	0.0130	
	348.00	0.0197	
	373.00	0.0254	
Ethane-n-Hexane	298.00	0.0283	Dantzler et al. (1968)
	323.00	0.0221	
	348.00	0.0298	
	373.00	0.0377	
Ethane-Propylene	377.60	0.0180	Huff and Reed (1963)
	410.90	0.0127	
	444.30	-0.0019	
	477.60	0.0065	
Propane-n-Butane	298.00	-0.0029	Dantzler et al. (1968)
	323.00	0.0035	
	348.00	0.0117	
	373.00	0.0171	
Propane-n-Pentane	298.00	0.0050	Dantzler et al. (1968)
	323.00	0.0067	
	348.00	0.0129	
	373.00	0.0126	
Propane-n-Hexane	298.00	0.0128	Dantzler et al. (1968)
	323.00	0.0053	
	348.00	-0.0301	
	373.00	-0.0281	

TABLE 14 (continued)

System	Temperature (°K)	kij	Reference
n-Butane-n-Pentane	298.00	-0.0060	Dantzler et al. (1968)
	323.00	-0.0035	
	348.00	0.0029	
	373.00	0.0048	
n-Butane-n-Hexane	298.00	0.0128	Dantzler et al. (1968)
	323.00	0.0001	
	348.00	0.0091	
	373.00	0.0156	
n-Butane-Isobutane	344.26	0.5924	Connolly (1962)
	360.93	0.5765	
	377.59	0.5605	
	394.26	0.5443	
	406.87	0.5319	
	410.93	0.5281	
	444.26	0.4956	
n-Pentane-n-Hexane	298.00	-0.0055	Dantzler et al. (1968)
	323.00	-0.0099	
	348.00	-0.0116	
	373.00	0.0041	
Cyclohexane-Benzene	328.15	-0.0008	Waelbroeck (1955)
	333.15	-0.0005	
	338.15	0.0011	
	343.15	0.0021	
	348.15	0.0002	
	373.15	-0.0037	Cox and Stubley (1960)
	308.20	0.0340	Huff and Reed (1963)
	323.20	0.0256	
	343.20	0.0272	
Nitrogen-Methane	273.15	0.0378	Keyes and Burks (1928)
	323.15	0.0328	
	373.15	0.0262	
	423.15	0.0146	
	473.15	0.0097	
	273.15	-0.1232	Kritschewsky and Levenhenko (1941)
	323.15	-0.1844	
	373.15	-0.2745	
	423.15	-0.2993	
	473.15	-0.3326	
	173.15	0.2316	Bol'shakov et al. (1967)
	198.15	0.1645	
	223.15	0.1095	
	248.15	0.0674	
	273.15	0.0332	
Nitrogen-Ethane	277.60	-0.0106	Huff and Reed (1963)
	310.90	0.0043	
	377.60	0.0259	
	444.30	0.0447	
	510.90	0.0400	
Nitrogen-n-Butane	427.60	0.1000	Huff and Reed (1963)
	444.30	0.1001	
	460.90	0.1085	
	477.60	0.1138	
	308.15	0.0609	Cruickshank et al. (1968)
	303.00	0.1003	Hicks and Young (1968)
	323.00	0.0795	
Nitrogen-n-Pentane	298.15	0.1001	Cruickshank et al. (1966)
	308.15	0.1295	Cruickshank et al. (1968)
	313.00	0.1090	Hicks and Young (1968)
	330.00	0.0993	

TABLE 14 (continued)

System	Temperature (°K)	kij	Reference
Nitrogen-n-Hexane	298.15	0.1426	Cruickshank et al. (1966)
	303.15	0.1526	
	323.15	0.1685	
	308.15	0.1111	Cruickshank et al. (1968)
	303.00	0.1440	Hicks and Young (1968)
	313.00	0.1384	
	333.00	0.1302	
Nitrogen-2,2-Dimethylbutane	298.15	0.1732	Cruickshank et al. (1966)
Nitrogen-n-Heptane	308.15	0.4318	Cruickshank et al. (1968)
	313.00	0.4550	Hicks and Young (1968)
Nitrogen-n-Octane	308.15	0.1392	Cruickshank et al. (1968)
Nitrogen-Isooctane	323.15	0.2267	Prausnitz and Benson (1959)
	348.15	0.2254	
Nitrogen-n-Decane	323.15	0.1677	Prausnitz and Benson (1959)
	348.15	0.1593	
Nitrogen-Cyclohexane	308.15	0.0914	Cruickshank et al. (1968)
Nitrogen-Benzene	303.15	0.0776	Cruickshank et al. (1966)
	313.15	0.0905	
	308.15	0.1181	Cruickshank et al. (1968)
Nitrogen-Toluene	323.15	0.2267	Prausnitz and Benson (1959)
	348.15	0.2254	
Carbon dioxide-Methane	310.90	0.0080	Huff and Reed (1963)
	344.20	0.0073	
	377.50	0.0065	
	410.90	0.0034	
	444.20	0.0016	
	477.50	-0.0015	
	510.80	-0.0049	
Carbon dioxide-Ethane	310.90	0.1271	Huff and Reed (1963)
	344.20	0.0941	
	377.50	0.0701	
	410.90	0.0537	
	444.20	0.0475	
	477.50	0.0483	
	510.80	0.0624	
Carbon dioxide-Propane	310.90	0.0896	Huff and Reed (1963)
	344.30	0.1056	
	377.60	0.1287	
	444.30	0.1113	
	477.60	0.0930	
	510.90	0.0769	
Carbon dioxide-n-Butane	377.60	0.1265	Huff and Reed (1963)
	410.90	0.1355	
	444.30	0.1297	
	477.60	0.1220	
Carbon dioxide-Isooctane	323.15	0.2345	Prausnitz and Benson (1959)
	348.15	0.2308	
Carbon dioxide-n-Decane	323.15	0.2262	Prausnitz and Benson (1959)
	348.15	0.2439	

TABLE 14 (continued)

System	Temperature (°K)	kij	Reference
Carbon dioxide-Toluene	323.15	0.2177	Prausnitz and Benson (1959)
	348.15	0.2129	
Carbon dioxide-Nitrogen	303.13	-0.0296	Gorski and Miller (1953)
	303.15	-0.0362	Cottrell et al. (1956)
	333.15	-0.0899	
	363.15	-0.1118	
	298.00	-0.0209	Prausnitz and Myers (1963)
	303.00	-0.0355	
Hydrogen Sulfide-Methane	311.11	0.1846	Reamer et al. (1951)
	344.44	0.1133	
	377.78	0.1006	
	411.11	0.1475	
	444.44	0.4671	
Hydrogen Sulfide-n-Pentane	411.11	-0.0038	Reamer et al. (1953)
	444.44	0.0259	

TABLE 15. kij Values for 78 Miscellaneous Binary Systems

System	Temperature (°K)	kij	Reference
Naphthalene-Methane	296.15	0.5933	King and Robertson (1962)
	342.15	0.6047	
	348.15	0.6110	
	294.00	0.5767	Najour and King (1966)
	307.00	0.5794	
	327.00	0.5861	
	333.00	0.5867	
	341.00	0.5768	
Naphthalene-Ethylene	296.15	0.0932	King and Robertson (1962)
	337.15	0.0995	
	296.50	0.0761	Najour and King (1966)
	298.00	0.0786	
	308.00	0.0806	
	312.50	0.1025	
	326.00	0.0914	
	333.00	0.0873	
	342.50	0.0776	
Naphthalene-Nitrogen	295.15	0.1927	King and Robertson (1962)
	345.15	0.1973	
Naphthalene-Carbon dioxide	297.00	0.1618	Najour and King (1966)
	299.00	0.1694	
	309.00	0.1763	
	323.50	0.2156	
	328.00	0.2196	
	332.00	0.2299	
	333.00	0.2421	
	337.00	0.2321	
	346.00	0.2256	
Carbon dioxide-Carbon monoxide	303.15	0.0466	Cottrell et al. (1956)
	333.15	-0.0654	
	363.15	-0.0542	
	298.00	-0.0017	Prausnitz and Myers (1963)
	303.00	0.0400	
Carbon dioxide-Oxygen	303.15	0.0311	Gorski and Miller (1953)
	303.15	0.0694	Cottrell et al. (1956)
	333.15	0.0552	
	363.15	-0.0007	
	303.00	0.0702	Prausnitz and Myers (1963)
Carbon monoxide-n-Octane	373.15	0.0798	Connolly (1964)
Carbon monoxide-Benzene	323.15	0.0677	Connolly (1964)
	373.15	0.0488	
Carbon monoxide-Nitrogen	298.00	-0.0166	Prausnitz and Myers (1963)
Methane-Carbon tetrafluoride	273.15	0.0722	Douslin et al. (1967)
	298.15	0.0666	
	303.15	0.0655	
	323.15	0.0619	
	348.15	0.0566	
	373.15	0.0540	
	398.15	0.0493	
	423.15	0.0459	
	448.15	0.0450	
	473.15	0.0413	
	498.15	0.0401	
	523.15	0.0371	
	548.15	0.0360	
	573.15	0.0336	
	598.15	0.0314	
	623.15	0.0310	

TABLE 15 (continued)

System	Temperature (^{o}K)	kij	Reference
Methane-Sulfur hexafluoride	313.16	0.0606	Hamann et al. (1955)
	333.16	0.0685	
	353.16	0.0743	
	373.16	0.0862	
	393.16	0.1078	
Methyl chloride-Propane	198.00	0.0844	Kappalo and Schafer (1962)
	203.00	0.0862	
	208.00	0.0886	
	218.00	0.0910	
	223.00	0.0949	
	228.00	0.0968	
	233.00	0.1010	
	293.00	0.1455	
	193.00	-0.0037	O'Connell and Prausnitz (1967)
	213.00	-0.0015	
Methyl bromide-Propane	193.00	0.1148	O'Connell and Prausnitz (1967)
	213.00	0.0961	
	233.00	0.0860	
	244.00	0.0845	
	273.00	0.0825	
	293.00	0.0811	
	297.00	0.0802	
	321.00	0.0763	
Methyl bromide-n-Butane	244.00	0.0547	O'Connell and Prausnitz (1967)
	321.00	0.0741	
Methyl bromide-n-Pentane	313.00	-0.0152	O'Connell and Prausnitz (1967)
Ethyl bromide-n-Pentane	293.00	0.0686	Ratsch and Bittrich (1965)
	313.20	0.0043	
Chloroform-n-Hexane	326.20	0.0058	Fox and Lambert (1952)
	352.00	0.0163	
Chloroform-n-Heptane	352.00	0.0909	O'Connell and Prausnitz (1967)
Chloroform-Benzene	333.70	-0.0063	O'Connell and Prausnitz (1967)
Nitrogen-Carbon tetrachloride	323.15	0.2131	Prausnitz and Benson (1959)
	348.15	0.1921	
Carbon dioxide-Carbon tetrachloride	323.15	0.1906	Prausnitz and Benson (1959)
	348.15	0.2073	
Methyl bromide-Ethyl bromide	293.10	-0.1111	O'Connell and Prausnitz (1967)
	313.20	-0.1159	
Methyl chloride-Carbon disulfide	323.15	0.1046	Bottomley and Spurling (1967)
	325.85	0.0974	
	349.56	0.0805	
	377.43	0.0922	
	402.43	0.0999	
	430.01	0.1503	
Chloroform-Carbon tetrachloride	315.70	-0.0518	O'Connell and Prausnitz (1967)
	343.20	-0.0706	
Argon-Nitrogen	90.00	0.0044	Prausnitz and Myers (1963)
Argon-Oxygen	90.00	-0.0272	Prausnitz and Myers (1963)

TABLE 15 (continued)

System	Temperature (°K)	kij	Reference
Nitrogen-Oxygen	273.00	-0.0458	Guggenheim and McGlashan (1951)
	323.00	-0.0533	
	373.00	-0.0684	
	423.00	-0.0927	
	473.00	-0.1017	
	303.15	-0.0054	Gorski and Miller (1953)
	90.00	-0.0352	Prausnitz and Myers (1963)
Neon-Ethylene	122.00	-0.3154	Hiza and Duncan (1970)
Neon-Argon	90.00	0.0901	Prausnitz and Myers (1963)
Neon-Nitrogen	90.00	0.0480	Prausnitz and Myers (1963)
Neon-Oxygen	90.00	-0.0286	Prausnitz and Myers (1963)
Neon-Hydrogen	90.00	-0.0294	Prausnitz and Myers (1963)
Neon-Helium	273.00	-0.2920	Guggenheim and McGlashan (1951)
	373.00	-0.3062	
	473.00	-0.3130	
	573.00	-0.3187	
	673.00	-0.3305	
	90.00	-0.2463	Prausnitz and Myers (1963)
Hydrogen-n-Pentane	298.15	0.0055	Cruickshank et al. (1966)
Hydrogen-n-Hexane	298.15	0.0536	Cruickshank et al. (1966)
Hydrogen- 2,2-dimethyl butane	298.15	0.0755	Cruickshank et al. (1966)
Hydrogen-Isooctane	323.15	0.1984	Prausnitz and Benson (1959)
	348.15	0.2882	
Hydrogen-n-Decane	323.15	0.4288	Prausnitz and Benson (1959)
Hydrogen-Ethylene	298.00	-0.1435	Prausnitz and Myers (1963)
	102.00	0.0063	Hiza and Duncan (1970)
Hydrogen-Toluene	323.15	0.1935	Prausnitz and Benson (1959)
	348.15	0.3267	
Hydrogen-Naphthalene	295.15	0.0441	King and Robertson (1962)
	343.15	-0.0297	
Hydrogen-Nitrogen	273.00	-0.1679	Guggenheim and McGlashan (1951)
	293.00	-0.1956	
	298.15	-0.2504	Prausnitz and Myers (1963)
Hydrogen-Carbon dioxide	298.15	-0.2631	Prausnitz and Myers (1963)
	303.00	-0.2995	
Hydrogen-Carbon monoxide	273.00	-0.1917	Guggenheim and McGlashan (1951)
	290.00	-0.1679	
	298.00	-0.2366	Prausnitz and Myers (1963)
Hydrogen-Argon	298.00	-0.2516	Guggenheim and McGlashan (1951)
	323.00	-0.3069	
	348.00	-0.3245	
	373.00	-0.3397	
	398.00	-0.3547	
	423.00	-0.3720	
	447.00	-0.3908	
	90.00	-0.0762	Prausnitz and Myers (1963)

TABLE 15 (continued)

System	Temperature (°K)	kij	Reference
Hydrogen-Carbon tetrachloride	348.15	-0.0434	Prausnitz and Benson (1959)
Helium-Ethylene	122.00	0.0760	Hiza and Duncan (1970)
Helium-Nitrogen	90.00	-0.2928	Prausnitz and Myers (1963)
Helium-Carbon dioxide	303.00	-0.6500	Prausnitz and Myers (1963)
Helium-Oxygen	90.00	-0.7680	Prausnitz and Myers (1963)
Helium-Argon	298.00	-0.8795	Guggenheim and McGlashan (1951)
	323.00	-0.9843	
	348.00	-1.0664	
	373.00	-1.1533	
	398.00	-1.2151	
	423.00	-1.2839	
	447.00	-1.3762	
	90.00	-0.1836	Prausnitz and Myers (1963)
	298.00	-0.7203	
Helium-Hydrogen	298.00	-0.3042	Guggenheim and McGlashan (1951)
	323.00	-0.3085	
	348.00	-0.5651	
	373.00	-0.3136	
	398.00	-0.1932	
	423.00	-0.1770	
	448.00	-0.1469	
	90.00	-0.2127	Prausnitz and Myers (1963)
Acetone-n-Butane	282.30	0.0869	O'Connell and Prausnitz (1967)
	321.00	0.1479	
Acetone-n-Hexane	343.00	0.0947	O'Connell and Prausnitz (1967)
Acetone-Cyclohexane	326.00	0.0327	Lambert et al. (1954)
	349.00	0.0336	
	353.00	0.1584	O'Connell and Prausnitz (1967)
Acetone-Benzene	363.15	-0.0148	Zaalishvili and Belousova (1964)
	373.15	-0.0036	
	333.00	0.0023	O'Connell and Prausnitz (1967)
	353.20	-0.0356	
	383.20	-0.0159	
Acetone-Methyl chloride	323.15	-0.1102	Bottomley and Spurling (1967)
	327.05	-0.1093	
	352.49	-0.0789	
	376.37	-0.0764	
	400.72	-0.0667	
	427.78	-0.0658	
Acetone-Methylene chloride	323.00	-0.1780	O'Connell and Prausnitz (1967)
	333.00	-0.1714	
	343.00	-0.1642	
	353.00	-0.1516	
	363.00	-0.1359	
Acetone-Chloroform	333.20	-0.0143	O'Connell and Prausnitz (1967)
	343.20	-0.0195	
	353.20	-0.0087	
	363.20	-0.0007	

TABLE 15 (continued)

System	Temperature (°K)	kij	Reference
Acetone-Carbon disulfide	323.15	0.0932	Bottomley and Spurling (1967)
	324.84	0.0963	
	349.85	0.1058	
	378.84	0.1109	
	407.38	0.0899	
	432.09	0.0791	
Acetone-Nitromethane	318.15	-0.3945	Brown and Smith (1960)
	323.20	-0.3151	O'Connell and Prausnitz (1967)
Acetone-Acetonitrile	318.15	-0.3914	Brown and Smith (1960)
Acetone-Ether	333.20	0.0433	O'Connell and Prausnitz (1967)
	343.20	0.0701	
Ether-n-Hexane	326.20	-0.0094	O'Connell and Prausnitz (1967)
	352.00	-0.0096	
Ether-Methyl bromide	293.00	0.0059	Ratsch and Bittrich (1965)
	313.00	0.0082	
Ether-Methyl iodide	313.20	-0.0821	O'Connell and Prausnitz (1967)
	328.20	-0.0689	
	343.20	-0.0467	
	358.20	-0.0383	
Ether-Ethyl bromide	293.10	-0.0929	O'Connell and Prausnitz (1967)
	313.20	-0.1045	
Ether-Chloroform	326.20	-0.2179	O'Connell and Prausnitz (1967)
	338.20	-0.1923	
	352.00	-0.1389	
	363.00	-0.0962	
Diethyl ether-Chloroform	393.00	0.0669	Fox and Lambert (1952)
Chloroform-Methyl formate	323.00	0.0465	Lambert et al. (1959)
	350.00	0.0389	
	368.00	0.0357	
Chloroform-n-Propyl formate	324.00	0.0502	Lambert et al. (1959)
	335.00	0.0450	
	353.00	0.0385	
	368.00	0.0340	
Chloroform-Methyl acetate	323.00	0.0500	Lambert et al. (1959)
	338.00	0.0435	
	353.00	0.0382	
	368.00	0.0329	
Chloroform-Ethyl acetate	323.00	0.0515	Lambert et al. (1959)
	338.00	0.0449	
	353.00	0.0396	
	368.00	0.0348	
Chloroform-Diethyl amine	323.00	0.0238	Lambert et al. (1959)
	337.00	0.0072	
Cyclohexane-Diethyl amine	349.00	0.0265	Lambert et al. (1954)
Cyclohexane-Acetonitrile	326.00	0.0297	Lambert et al. (1954)
Benzene-Nitromethane	323.15	-0.0260	Bottomley and Spurling (1963)
Acetonitrile-Acetaldehyde	313.15	-0.7708	Prausnitz and Carter (1960)
	333.15	-0.7821	
	353.25	-0.7030	
	373.55	-0.6692	

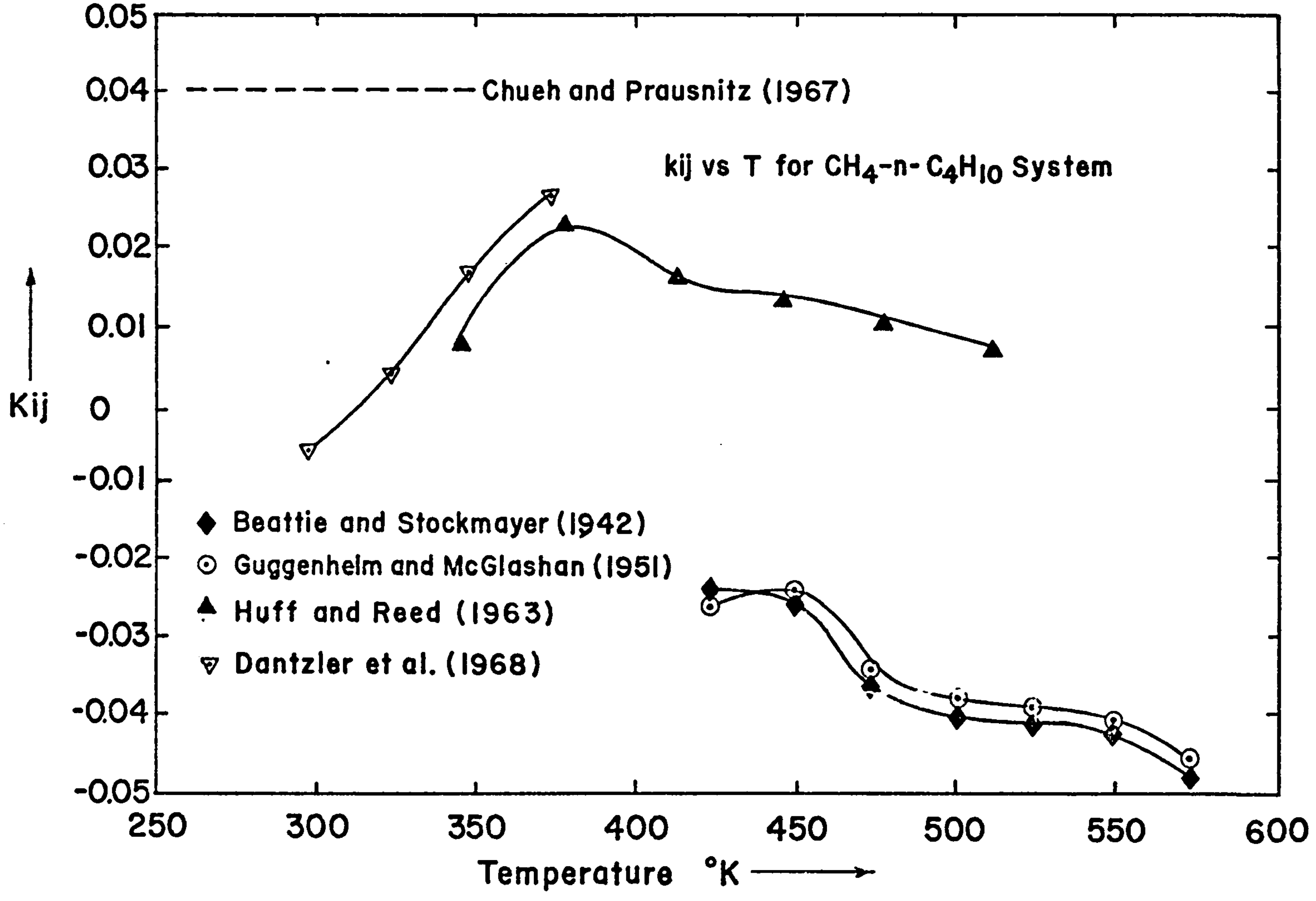

Figure 16. kij as a Function of Temperature for Methane-n-Butane System

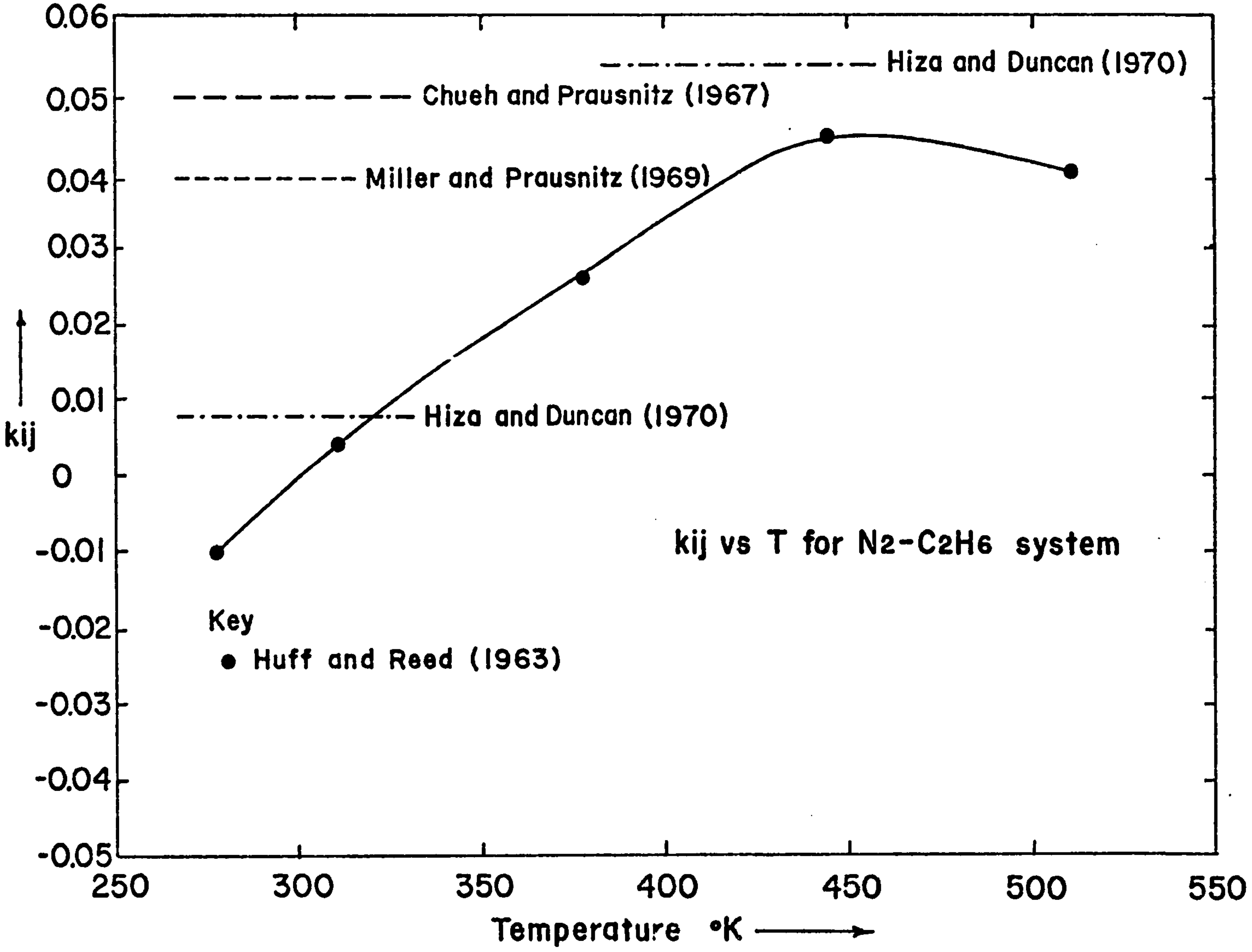

Figure 17. kij as a Function of Temperature for Nitrogen-Ethane System

CHAPTER VI

TESTING AND COMPARISON WITH PUBLISHED WORKS

Having obtained the $Z^{(0)}$ and $Z^{(1)}$ values for the extension of the Pitzer's generalized correlation as well as the binary interaction coefficients characteristic of the interactions between pairs of molecules, we can try to derive further understanding about the behaviour and properties of pure compounds and binary mixtures. However, for the compressibility factor correlations, due to the existence of several published works with the same topic and essence, attempts have been made to compare among the results with the experimental data since the experimental data are the most impartial bases we can turn to for testing and comparison purposes. For this comparison, it will be the precision and accuracy which count most. As to the binary interaction parameters, since there is very little work done in this aspect, an attempt was made to compare the values obtained in this investigation with the few others published using other ways of approach. In this case it is the temperature dependence of the k_{ij} values as well as the trend of this dependence, which are of prime interest.

Extension of the Three-Parameter Correlation

Since Pitzer and co-workers demonstrated their famous acentric-factor correlation for the compressibility factor calculation {128} (1955), Lu et al.{103} (1973) and Lee and Kesler {96} (1975) presented extensions of the original work by different approaches described in Chapter II, Part B. Also included in these works were tables of the deviations of calculated compressibility factors from the literature values as a comparison result. Hence, similar efforts have been made on this presentation.

For testing the applicability of this study, at first we compared the calculated compressibility factors based on this work with the literature data, at the same time compared the deviations of these results with the deviations reported in the published works, assuming that the average absolute percentage deviations reported in those works are representative of all the data points involved in the specified T_r and P_r ranges. For this testing and comparison purposes 12 compounds chosen by Lee and Kesler {96} (1975) were also employed to this investigation with the same references and T_r and P_r ranges because of its more extensive covering of the T_r and P_r ranges which are more representative of the presentation - not for low temperatures only. By plotting $Z^{(0)}$ and $Z^{(1)}$ values of this work on large graphs and then interpolating to the experimental P_r and T_r conditions of each data point, the calculated compressibility factors were obtained. However, for the data points at which the T_r and P_r conditions were in the boundary between gas and liquid phases, extrapolation following the trend of the curves as examplified by the P_r = 1.0 curve was used. The sourses of the acentric factors used in this study are given in Chapter X, Appendix A. The calculated compressibility factor values were then compared with the literature values and we evaluated the percentage absolute average deviation defined by $100[Z_{calc} - Z_{expt}]/Z_{expt}$. The comparison results are presented in Table 13. The criteria concerning the work by Lee and Kesler's were extracted from their published report (Lee and Kesler {96} (1975)). From Table 13 it is clearly shown that this investigation is not only adequate but also more accurate in all the four categories of both saturated and unsaturated liquid and gas phases, with or without the compound 1-Pentene. For 1-Pentene, Lu et al.{103} (1973) reported an absolute average deviation of 11.29% for 20 points in low-temperature liquid phase using the same data reference (Day and Felsing {37} (1951)). It should be mentioned that the number of points reported in Table 13 for this study includes all the data points available from the same reference at the same T_r and P_r conditions as used by Lee and Kesler {96} (1975), the overall number of points is 1,556 in this work as compared to 280 reported by Lee and Kesler. As a comparison, Lu et al.{103} (1973) reported the comparison results for low temperature compressibility factor calculations of 21 compounds with 463 data points as having an overall average absolute deviation of 1.53% (reduced to 1.09% if 1-Pentene was excluded). This work provides a testing result for compressibility factor calculations of 12 compounds with

1,556 data points as having an overall average absolute deviation of 1.38% (reduced to 1.07% if we exclude 1-Pentene).

For further testing the applicability of this presentation, attention was drawn to the boundary condition of this acentric-factor correlation. This boundary condition complies with the definition of the acentric factor such that this third parameter is chosen to make $\omega = 0$ for the simple fluids Ar, Kr and Xe, with simple spherical molecules (see Chapter X, Appendix B). Therefore, for Ar, Kr and Xe the generalized $Z^{(0)}$ values should not be too far from their compressibility factors at the same T_r and P_r,whenever the literature data should be available; since the compressibility factor correction term for deviation from simple fluid, namely $Z^{(1)}$, does not play a significant role at all. Hence this boundary condition can be served as a pertinent test for the $Z^{(0)}$ values obtained from generalized compressibility factor correlations. The compressibility factor values of the simple fluids available in the literature were thus interpolated at regular intervals of T_r and P_r and compared graphically with the $Z^{(0)}$ values obtained in this work together with those obtained from the Pitzer's correlation{128} (1955). Qualitatively, the agreement between the correlated and experimental Z values is very good, and in a number of instances, the deviations between the calculated and the experimental Z values obtained by the proposed correlation are smaller than those obtained by the Pitzer correlation. Therefore this work provides an improving correlation for the $Z^{(0)}$ values as far as this testing procedure is concerned. It should be mentioned that the references for Ar, Kr and Xe listed in Table 2 also include the ones used by Pitzer et al.{128} (1955). The $Z^{(1)}$ values obtained in this work, when plotted as functions of T_r (or P_r) at constant P_r (or T_r), reveal curves of shape mostly compatible with those by Pitzer et al.{128} (1955), while the numerical values are of prominent difference.

It was further noticed that for the $Z^{(0)}$ values at $T_r = 0.8$ (where the $Z^{(0)}$ values presented by Lu et al.{103} (1973) were essentially the same as those of Pitzer et al. {128} (1955)), an evident difference existed between the values of this study and the ones presented by Lu et al. {103} (1973), up to about 2 to 3%, especially at the high pressure conditions. Therefore the boundary condition testing of the acentric-factor correlation at $\omega = 0$ was again applied to the work by Lu et al.{103} (1973) which was in the low temperature region ($0.5 \leqq T_r \leqq 0.8$, $0 \leqq P_r \leqq 9.0$), as well as to the present study. However, the experimental data for the simple fluids at such low temperatures are not easy to find. The one found available for the boundary condition testing purpose was given by Din {41} (1956) for argon, which gave the experimental compressibility factor data in the T_r ranges from 0.596 to 0.795 and P_r ranges from 0.021 to 6.250 with 36 data points. Hence the $Z^{(0)}$ values of this study and of Lu et al.{103} (1973) were again interpolated to the T_r and P_r conditions of the experimental data at each point, and then compared the values obtained with the experimental compressibility factor data given by Din {41} (1956). The overall average absolute deviation was 0.51% in this investigation and 0.87% by Lu et al.{103} (1973) (in the original work, they reported a deviation of 0.70% for 23 points with the same reference and T_r and P_r regions) for a total number of data points 36. This reference of Din {41} (1956) for argon has been used for correlational basis by both investigations.

Following these testing and comparison procedures, it was also found that the $Z^{(0)}$ and $Z^{(1)}$ values presented in Tables 11 and 12 as obtained by using the literature data of Table 2 provided better results than the $Z^{(0)}$ and $Z^{(1)}$ values of Tables 9 and 10 as from the data sources of Table 1. Hence Tables 11 and 12 are the final results of the $Z^{(0)}$ and $Z^{(1)}$ values of this investigation and they have been used in the testing processes of this chapter. Through this, we have verified the fact that this three-parameter (acentric-factor) generalized correlation for compressibility factor calculation must be correlated based on appropriate data sources. The more extensive and more up-to-date the data can be, the better and more accurate correlations can be obtained.

The Binary Interaction Parameters

In this study, 493 values of the binary interaction coefficients for 121 binary systems have been obtained. For these systems, the k_{ij} values clearly demonstrate themselves to be functions of temperature, as well shown by Tables 14 and 15, and Figures 16 and 17. However, in the literature there were several works presenting values of the binary interaction coefficients and which sufficed just as well for comparison purposes, due to the lack of testing technique and experimental information available for these k_{ij} values. These works include Chueh and Prausnitz {23} (1967), Miller and Prausnitz {120} (1969), Hiza and Duncan {71}(1970) and partly shown by a series of papers by Lu and co-workers (Chang and Lu {17}{18} (1970, 1971); Hsi and Lu {73} (1972); Lu et al.{104} (1974); Hamam and Lu {64}{65} (1976)). For the works by Prausnitz et al., the k_{ij} values were treated as true constants independent of temperature, while its temperature dependence was shown in the works by Hiza and Duncan as well as by Lu et al.

For the binary interaction constants evaluated in this work based on the second virial coefficient approach, extensive comparison has been made between the presentations of this study and the above-mentioned published works. For all the binary systems included in this investigation, the k_{ij} values of 15 hydrocarbon-hydrocarbon systems, two nitrogen-hydrocarbon systems and four carbon dioxide-hydrocarbon systems were compatible with those presented by Chueh and Prausnitz {23} (1967) and by Miller and Prausnitz {120} (1969) in which the binary interaction constants were assumed to be universal constants; and the k_{ij} values of nitrogen-ethane system were comparable with the one by Hiza and

Duncan {71} (1970) which was essentially evaluating k_{ij} values for systems containing inert and elementary gases. Also the k_{ij} values of five hydrocarbon-hydrocarbon systems, two carbon dioxide-hydrocarbon systems and one nitrogen-hydrocarbon system were in agreement with the presentations by Lu and co-workers for the published works which reflected the temperature-dependence of the binary interaction coefficients. Twenty-nine k_{ij} values for two systems studied in this work together with the k_{ij} values of the published efforts were depicted in Figures 16 and 17. From these figures it is clearly shown that k_{ij} is a function of temperature; however, the trend of this temperature dependence of k_{ij} values is not regular and clear enough for correlation purposes. Nevertheless, based on the calculation of the k_{ij} values through vapor-liquid equilibria considerations and with subsequent correlations of k_{ij} as functions of temperatures and systems, this work copes itself very well with the trend developed thereof and hence is able to offer valuable information on the properties of binary mixtures. These k_{ij} values as obtained from the binary isothermal vapor-liquid equilibria data were evaluated by minimizing the deviation between the calculated and experimental total pressure or the vapor-phase composition. The correlation established for the binary interaction coefficients as function of temperature and the binary system is

$$k_{12} = 0.0135 + 0.3435\omega_2 + (-0.000226 + 0.00007156\omega_2)T \tag{50}$$

where ω_2 is the acentric factor of the constituent in the binary mixture with higher critical temperature. The T(temperature) in equation (50) refers to $120^\circ K \leqq T \leqq 260^\circ K$ for methane-ethane system, $120^\circ K \leqq T \leqq 300^\circ K$ for methane-propane system, $150^\circ K \leqq T \leqq 360^\circ K$ for methane-n-butane system and $183^\circ K \leqq T \leqq 411^\circ K$ for methane-n-pentane system. Presented in Table 15 is also a table for 250 k_{ij} values of 78 binary systems. Due to the fact that most of the constituents in the systems presented are of molar or quantum nature, for which the original second virial coefficient correlation proposed by Pitzer and Curl {129} (1957) will require possible modification, this presentation is reserved for reference, hopefully possible future use.

CHAPTER VII

CONCLUSION

Extension of the Three-Parameter Correlation

In this investigation, the Pitzer generalized three-parameter correlation in terms of the linear relationship of acentric-factor has been verified to be adequate. By collecting more extensive and more up to date literature data used as the correlational basis, this correlation has been extended to wider ranges of applicability. The necessity of using more extensive data sources to obtain improving and more precise correlations has also been verified, by which this study obviously provides results on a much more sound basis than earlier published efforts. Through testing and comparison with the literature compressibility factor values, the $Z^{(0)}$ and $Z^{(1)}$ tables of this work provide a calculated compressibility factor results better than those of Lee and Kesler's {96} (1975) in all the saturated and unsaturated liquid and vapor phases. Furthermore, this work also demonstrated a much more accurate and more precise capability as far as the satisfaction of the boundary condition of the acentric-factor correlation at $\omega = 0$ is concerned. For the $Z^{(0)}$ values, this proposed correlation satisfies the experimental compressibility factor data of simple fluids with much lesser extent of deviations than those proposed by Pitzer et al. {128} (1955) as well as by Lu et al. {103} (1973), especially at the low temperature conditions. For the $Z^{(1)}$ values, the proposed correlation reveals a trend as a function of T_r and P_r mostly compatible with the earlier works mentioned above. Therefore it can be concluded that this investigation offers a correlation result with much improving quality for the compressibility factor calculations as well as for the satisfaction of the boundary conditions, when compared with published works (Pitzer et al. {128} (1955), Lu et al. {103} (1973), Lee and Kesler {96} (1975)).

The $Z^{(0)}$ and $Z^{(1)}$ values proposed also lend themselves readily for further study of the properties of normal fluids in terms of the generalized derivative compressibility factor functions described in Chapter I, Part A; these properties include fugacity coefficients, enthalpy departures, Joule-Thomson coefficients and the difference between isobaric and isochoric heat capacities, etc. By doing this, we will be able to obtain many useful equilibrium thermodynamic properties of pure compounds of interest.

The Binary Interaction Parameters

The binary interaction coefficients of 493 values for 121 binary systems are evaluated in this work, based on the second virial coefficient approach due to its theoretical founding basis. These values compare themselves very well with the values calculated by other ways of approach, such as vapor-liquid equilibria, and as a consequence offer a very strong support for the fact that k_{ij} is a function of temperature, not universal constants; again further fit in the trend of the binary interaction constants-temperature correlations developed. Hence this study offers a valuable information about the deviations from the geometric mean values for binary inter-energy parameters, which serves as the starting and crucial point for understanding the intermolecular interactions as well as the behaviour and properties of the binary systems, which further is necessary for the understanding of the properties of multi-component mixture systems.

CHAPTER VIII

SUGGESTIONS FOR FURTHER WORK

Extension of the Three-Parameter Correlation

Having obtained the generalized compressiblity factor correlations $Z^{(0)}$ and $Z^{(1)}$ as functions of T_r and P_r, we are able to calculate the other equilibrium properties for pure compounds as applications of this fundamental investigation.

It is suggested that similar efforts be made to pursue further study based on this work for the ranges of $0.2 \leqq T_r \leqq 5.0$ and $0 \leqq P_r \leqq 12.0$ as the published works by Hsi and Lu {74} (1974) as originally for low temperature regions. By use of the generalized derivative compressibility factor functions defined by equations (2) and (3) as discussed in Chapter I, Part A, after further rearranging into:

$$Z_P = -P_r^2\left[\frac{\partial(Z/P_r)}{\partial P_r}\right]_{T_r} \tag{51}$$

$$Z_T = \left[\frac{\partial(ZT_r)}{\partial T_r}\right]_{P_r} \tag{52}$$

or applying the linear relationship in the acentric factor:

$$Z_P = Z_P^{(0)} + \omega Z_P^{(1)} \tag{53}$$

$$Z_T = Z_T^{(0)} + \omega Z_T^{(1)} \tag{54}$$

where

$$Z_P^{(0)} = Z^{(0)} - P_r\left(\frac{\partial Z^{(0)}}{\partial P_r}\right)_{T_r} \qquad (55)$$

$$Z_P^{(1)} = Z^{(1)} - P_r\left(\frac{\partial Z^{(1)}}{\partial P_r}\right)_{T_r} \qquad (56)$$

$$Z_T^{(0)} = Z^{(0)} + T_r\left(\frac{\partial Z^{(0)}}{\partial T_r}\right)_{P_r} \qquad (57)$$

$$Z_T^{(1)} = Z^{(1)} + T_r\left(\frac{\partial Z^{(1)}}{\partial T_r}\right)_{P_r} \qquad (58)$$

we are able to obtain the $Z_T^{(0)}$, $Z_T^{(1)}$, $Z_P^{(0)}$ and $Z_P^{(1)}$ generalized correlations as functions of T_r and P_r. Once we obtain these four generalized functions ($Z_T^{(0)}$, $Z_T^{(1)}$, $Z_P^{(0)}$ and $Z_P^{(1)}$) we are able to calculate the derivative compressibility factors Z_T and Z_P by means of equations (53) and (54). Through these functions required useful equilibrium properties for pure compounds can be obtained easily. For example, the fugacity coefficients, enthalpy and entropy departures can be evaluated by equations (13) to (19) and furthermore, they can be obtained by means of the Bridgman table established from the Z_P and Z_T values proposed by Reid and Valbert {142} (1962) and by Reid and Sherwood {143} (1966) through thermodynamic relationships.

It is suggested that other important thermodynamic properties be evaluated from the derivative compressibility factor functions such as the isochoric heat capacity calculated from the difference

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T\left(\frac{\partial P}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)\right]^2_P = \frac{RZ_T{}^2}{Z_P} \qquad (59)$$

and the Joule-Thomson coefficient calculated by

$$\mu_{J.T.} \equiv \left(\frac{\partial T}{\partial P}\right)_H = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]/C_p = \frac{RT}{PC_p}(Z_T - Z) \qquad (60)$$

The plots of $(C_p.\mu_{J.T.})$ and $(C_p - C_v)$ as functions of T_r and P_r were shown by Edmister {49}{50}{51} (1948, 1949, 1957) without introducing a third parameter. Those plots were derived from hydrocarbon P-V-T data, whereas the Z_T, Z_P values recommended here are obtained from the three-parameter generalized correlations and as such should be applicable to most types of materials, not limited to only hydrocarbons. Furthermore, as pointed out by Reid and Sherwood {143} (1966), a further illustration of the use of the derivative compressibility factors was demonstrated by Sherwood {156} (1962) in obtaining the generalized sonic velocity correlation for compressed gases.

The Binary Interaction Parameters

Due to the lack of accurate information concerning the behaviour and properties of mixtures for which the binary interaction parameter is a key factor, the study of the k_{ij} values is of primary importance. However, most of the equations of state proposed are of empirical nature and since the constants which appear in such empirical equation of state have at best only approximate physical significance, it is very difficult to justify mixing rules for expressing the constants without introducing further arbitrary assumptions. Therefore, it is highly recommended that the binary interaction coefficients be evaluated using the virial equation of state which has a sound theoretical foundation and is free of arbitrary assumptions. As to the ways of approach, it is suggested that attention be focused on the relations between virial coefficients and the various intermolecular potential functions, as summarized by Hirschfelder et al. {70} (1954) as well as by Prausnitz {134} (1969).

From statistical mechanics, for a gas composed of simple, spherically symmetric molecules such as argon or methane, the second virial coefficient is given as a function of temperature and is determined by W(r), the potential energy between two molecules, by the relation

$$B = 2\pi N \int_0^\infty (1 - \exp(-W(r)/kT))r^2 dr \qquad (61)$$

where N is Avogadro's number, r is the distance between molecular centers and k is Boltzmann's constant. Moreover, when we extend equation (61) to mixtures, the extension requires no arbitrary assumptions, as the most important advantage of the virial equation of state for application to phase equilibria problems lies in its direct extension to mixtures. Hence, in a binary mixture containing species i and j, if i and j are spherically symmetric molecules, the second virial coefficient corresponding to the i-j interaction B_{ij}, as determined by the system temperature and the potential energy between molecules i and j, W_{ij}, is given by the same expression as that given in equation (61):

$$B_{ij} = 2\pi N \int_0^\infty (1 - \exp(-W_{ij}(r)/kT))r^2 dr \qquad (62)$$

From equation (62) it is clearly shown that the potential function $W_{ij}(r)$ must be interpreted in terms of r, the binary molecular distance; and that B_{ij} is a function of temperature only, not a function of pressure (or density) and what is more important, not a function of the binary compositions. The study of the potential function is emphasized here for the reason that whenever the right hand side of equation (62) contains temperature or energy parameters, it can establish a certain relationship between the B_{ij} values and the temperature (as is pertinently reasoned that the cross second virial coefficient is a function of temperature only) hence provides a way to calculate the binary interaction coefficients from second virial coefficients data. Although engineering applications of potential functions are at present limited because of low accuracy, there can be no doubt that future developments in phase-equilibrium thermodynamics will increasingly utilize these functions for solving practical problems and hence they will offer ample opportunities for further study.

Among the potential function models, the simplest (and trivial) case is for ideal gas, which assumes $W(r) = 0$ for all values of r so as to make the second, third and higher virial coefficients zero for all temperatures and hence the virial equation reduces to the ideal-gas law. This case is called "potential function with zero adjustable parameter". Others which have drawn special attention for suggestions here are the hard-sphere model (potential function with one adjustable parameter); the Lennard-Jones model (two-parameter) and the square-well model (with three adjustable parameters).

For the hard-sphere model, there is no force between the molecules when their centers are separated by a distance larger than σ, the hard-sphere diameter; but the force of repulsion becomes infinitely large when they touch, at a separation equal to σ. The potential function is given by

$$\left.\begin{aligned} W(r) &= 0 \quad \text{for} \quad r > \sigma \\ W(r) &= \infty \quad \text{for} \quad r \leqq \sigma \end{aligned}\right\} \tag{63}$$

Substituting into equation (62) we obtain

$$B_{ij} = \frac{2}{3}\pi N\left(\frac{\sigma_i + \sigma_j}{2}\right)^3 \tag{64}$$

This model gives a highly oversimplified picture of real molecules since, for a given gas, it predicts second virial coefficients which are independent of temperature. However, Bienkowski et al. {10} (1973) augmented a generalized hard-sphere virial equation of state employing the correlations of Pitzer and Curl {129} (1957) which can be served as an approach to calculate the k_{ij} values from B_{ij} values. Also possible modifications can be made on the original proposal.

The most useful and best known two-parameter potential model is the Lennard-Jones potential function with the form

$$W(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{65}$$

where ε is the depth of the energy well (minimum potential energy) and σ is the collision diameter, i.e., the separation where $W = 0$. Lennard-Jones {97}{99} (1924, 1937) deduced from equation (61) and (65) the formulae for the second virial coefficient, and the integration required is not simple. However, numerical results were obtained by Hirschfelder et al.{70} (1954) and that gives the reduced virial coefficient as a function of reduced temperature. The reducing parameter for the virial coefficient itself is proportional to the collision diameter σ raised to the third power and that for the temperature is proportional to the characteristic energy ε. These were both for pure components. Furthermore, Lennard-Jones and Cook {98} (1927) found from experimental data on mixtures that it is a good approximation to average collision radii when the relative kinetic energy is zero and for mixing properties both Fowler and Guggenheim {55} (1939) and Hirschfelder and Roseveare {69} (1939) used relations of arithmetic mean for the collision radii and geometric mean for the energy parameter for the treatment of mixtures. Here we can introduce the binary interaction parameters as denoting the deviation from the geometric mean of the energy parameter and calculated these parameters from the Lennard-Jones second virial coefficient equations as presented by Beattie and Stockmayer {5}{6} (1942).

Since the Lennard-Jones potential is not a simple, although derivable, mathematical function and in order to simplify the calculations, another model is proposed having the general shape of the Lennard-Jones function. The square-well potential model has been regarded as being particularly useful for the description of the behaviour of gases consisting of complex molecules and was applied by Chang and Lu {19} (1972) for pure components. Further this model may be considered as the simplest, most useful and flexible model, and the flexibility arises from the fact that it contains three adjustable parameters: the collision diameter, σ, the well depth (minimum potential energy), ε, and the reduced well width, R'. Mathematically, the square-well potential is given by

$$\left.\begin{array}{lll} W = \infty & \text{for } r \leqq \sigma \\ W = -\varepsilon & \text{for } \sigma < r \leqq R'\sigma \\ W = 0 & \text{for } r > R'\sigma \end{array}\right\} \qquad (66)$$

By using this model, the cross second-virial coefficient equation (62) may be integrated to give

$$B_{ij} = \frac{2}{3}\pi N\sigma_{ij}^{3}\left[1 - (R_{ij}'^{3} - 1)(\exp(\varepsilon_{ij}/kT) - 1)\right] \qquad (67)$$

where

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \qquad (68)$$

$$R_{ij}' = (R_i' + R_j')/2 \qquad (69)$$

$$\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{\frac{1}{2}}(1 - k_{ij}) \qquad (70)$$

here the k_{ij} values are the binary interaction parameters. Equation (67) can be expressed in the reduced form as

$$\frac{B_{ij}P_c}{RT_c} = \frac{u_{ij}P_c}{RT_c}\left[R'^3_{ij} - (R'^3_{ij} - 1)\exp(\varepsilon_{ij}/kT_cT_r)\right] \qquad (71)$$

where

$$u_{ij} = \frac{2}{3}\pi N\sigma^3_{ij} \qquad (72)$$

Now from either equation (67) or equation (71), together with equations (68) to (70), whenever we have a value of B_{ij}, the cross second-virial coefficient at one temperature for a binary system, with σ_{ij} and R'_{ij} calculated from those of the constituents, we can obtain ε_{ij}, hence k_{ij} value at the system temperature. Moreover, here the k_{ij} is defined by equation (70) due to the fact that the critical temperature is usually viewed as the parameter which characterizes the intermolecular interaction energy (Pitzer et al.{128} (1955)).

CHAPTER IX

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CHAPTER X

APPENDIX

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A. Sources of the Physical Properties Used in This Work

The physical properties needed in this investigation are the molecular weight, the critical constants and the acentric factor for all the pure compounds.

For the molecular weight and critical properties of all hydrocarbons, data were taken from the API Technical Data Book {1} (1971), with the exception of T_c and P_c for methane, which were taken from the values reported by Prydz and Goodwin {135} (1972). For argon, the critical data given by Michels et al.{118} (1958) were employed, while for nitrogen, the critical data were taken from Din{42} (1961). For hydrogen sulfide, methyl chloride and ammonia, the critical values reported by Canjar and Manning {15} (1967) were used; for difluoromethane, critical constants were taken from the original paper (Malbrunot et al.{105} (1968)). And for compounds of oxygen, carbon dioxide, carbon monoxide, perfluoromethane, chlorodifluoromethane, chlorotrifluoromethane, dichlorodifluoromethane, dichloromethane, trichloromethane and perchloromethane, the critical properties and molecular weights given by Kudchadker et al.{93} (1968) were employed. For all the other compounds used in this work, the molecular weights and critical constants were taken from Reid and Sherwood {143} (1966).

As to the acentric factor ω, the revised values of ω for hydrocarbons reported by Passut and Danner {125} (1973) were used with the exceptions of 1-Pentene and acetylene, which were calculated from the generalized equation of Lee and Kesler {96} (1975). The acentric factors of nitrogen, hydrogen sulfide, carbon dioxide, carbon monoxide, perfluoromethane and ammonia were taken from the work of Prausnitz {134} (1969). For difluoromethane, the ω value was calculated from the original work (Malbrunot et al.{105} (1968)) by the definition of the acentric factor. For all the other compounds used in this study, the ω values were taken from Reid and Sherwood {143} (1966).

B. Properties of Normal Fluid

From the series of papers by Pitzer and co-workers {127} {128}{129}{34}{101} (1955, 1957, 1958, 1972), the properties of "simple" and "normal" fluids have been discussed, both microscopically and macroscopically. These properties are outlined in the following paragraphs. Generally speaking, the category of simple fluids consists of heavier inert gases, namely argon, krypton and xenon with simple spherical molecules; while that of normal fluids consists of non-polar or slightly polar fluids with varied shapes of molecules.

The understanding of the forces operating between molecules developed ever since the emergence of a satisfactory quantum theory in 1926. Particularly important was the work of London on the attractive forces between molecules. Also it became clear that certain anomalous properties of hydrogen and helium arose from quantum effects in the translational motion of those molecules. However, the understanding of intermolecular forces also indicated a bewildering complexity of effects which probably tended to discourage attempts at systemization, such as the quantum and highly polar effects. Former attempts for establishing a third parameter included the proposal of critical compressibility factor by Meissner and Seferian {108} (1951), but their attempt to include highly polar substances such as water necessarily impaired the accuracy of the results. Riedel {144}{145}{146} (1954) discussed vapor pressures on a basis very similar to the acentric factor. He excluded highly polar or associated liquids and the quantum liquids (H_2 and He), and showed that the remaining normal liquids had reduced vapor pressure curves falling accurately into a single family.

For the classification of substances, the simplest class following corresponding states behaviour comprises the heavier rare gases (Ar, Kr and Xe). The principal characteristics are spherical shape (for which shape methane also gains somewhat by rapid and relatively free rotation) and an inverse sixth power attractive potential. London's theory yields this force law and applies to cases where the valence shells of all atoms are filled. The term "simple fluid" is adopted for this class of substances. However, for the repulsive potential, little was known other than that this repulsion is a manifestation of the Pauli exclusion principle. For this purpose, the model of Lennard-Jones or 6-12 potential was chosen as expressed by equation (65):

$$W(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{65}$$

$$= \varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right] \tag{73}$$

where

$$r_0 = \sigma(2^{\frac{1}{6}}) \tag{74}$$

The r_0 value is the intermolecular distance at the minimum potential. Hence the simple fluid was assumed to be one having an intermolecular potential essentially like equation (73). Each substance has its own value of ε and r_0. But the shape of the intermolecular potential curve is the same for all simple fluids.

Furthermore, to develop the properties of normal fluids, different shapes of molecules were considered. For the globular molecules, the core model of Kihara {90} (1953) was adopted. He assumed a core inside each molecule and then took the Lennard-Jones potential for the shortest distance between molecular cores. The potential is thus

$$W = \varepsilon\left[\left(\frac{\rho_0'}{\rho'}\right)^{12} - 2\left(\frac{\rho_0'}{\rho'}\right)^{6}\right] \tag{75}$$

where ρ' is the shortest distance between the cores, and ρ_0' is this distance at the potential minimum. It was further shown that for the case of spherical cores, $\rho' = r - 2a$, and a is the radius of the spherical core. Then the derivation of the theory of corresponding states for simple fluids was easily extended to substances with globular molecules as in the realm of normal fluids, through the above core model. The essential requirement was that the shape of the intermolecular potential curve be the same for all substances in the class which was to conform to the theory. Thus on any one of the core models, if the ratio of the core radius to the intermolecular distance at the potential minimum (a/r_0) was the same for a group of substances, then that group would follow corresponding states behaviour. The behaviour of this group would differ, however, from that of simple fluids where the core radius was zero. Therefore the volumetric behaviour of a fluid with globular molecules was a function of three variables: (1) the depth of the potential minimum ε , (2) the intermolecular distance at the minimum r_0, and (3) the relative core size a/r_0. Moreover, after testing and comparison with the second virial coefficients data, Pitzer {127} (1955) verified that the behaviour of a substance with non-polar molecules of non-spherical shape such as a thin rod would conform closely to that of globular molecules with some value of the (a/r_0) parameter, and this was also the case for molecules with modest dipoles which are slightly polar. Thereat by these properties of the normal fluids, the acentric factor was defined.

In conclusion, statistical theory shows that a group of substances will conform to the principle of corresponding states only if their intermolecular potentials are identical except for distance and energy-scale factors characteristic of each substance. Also, their intermolecular motion and influence must be classical, i.e., quantum and highly polar effects must be negligible. The only group of substances which may be expected to conform to these criteria are the heavier rare gases, Ar, Kr and Xe, which do conform accurately to corresponding-states behaviour. These are called "simple fluids". Various types of molecular shapes and molecular dipole moments might be expected to cause different deviations from the macroscopic properties of simple fluids. It is found, however, that the reduced theoretical second virial coefficients for a wide variety of these molecular types fall into a single family of curves which may be characterized by a single parameter, namely the acentric factor. The molecules falling into this single family are just those commonly called "normal fluids or liquids".

It should be mentioned that within the series of papers, Curl and Pitzer {34} (1958) demonstrated the surface tension as a criterion of a normal liquid, hence provided an operational test to the properties of the normal fluids.

C. Computer Program for the Correlational Work

D. Computer Program for the Evaluation of the Binary Interaction Constant

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C
C
C     ************************************************************
C                                  APPENDIX  C
C             COMPUTER PROGRAM FOR THE CORRELATIONAL WORK
C     ************************************************************
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(40,40),B(40,40),X(100),Y(100,1),C(40,40),YC(100),
     1DY(100),YCAL(100),YORIG(100,1),DYO(100), XX(100) ,TITLE(20)
      DIMENSION EDY(100)
        DIMENSION WW(100)
    1 READ (5, 101, END=3) W, XK
          L = 1
      M=1
       WRITE (6, 307) W
  307 FORMAT (1H0, '  W=', D16.10)
      READ(5, 102) (TITLE(I), I = 1, 19)
  102 FORMAT(19A4)
      WRITE(6, 306) (TITLE(I), I = 1, 19)
  306 FORMAT(1H0, 19A4)
       IF (XK .LT. .0) READ(5, 101) TC
       I = 1
  101 FORMAT(4D10.5)
   20  READ (5, 101) X(I), (Y(I,J), J = 1, L)
        IF ( XK .LT. .0) X(I) = X(I)/TC
      IF (X(I).LT. -10.) GO TO 21
      WW(I) = 1.
       WRITE (6, 300) X(I), (Y(I,J), J = 1, L)    ,WW(I)
  300 FORMAT (1H0, 3D20.14)
        I = I + 1
         GO TO 20
   21 N = I - 1
      DO 30 I = 1, N
   30 C(I, 1) = 1.0
      MP1 = M+1
      DO 35 J =2, MP1
      DO 35 I = 1, N
   35 C(I,J) = C(I, J-1)*X(I)
      DO 40 I = 1, MP1
      DO 40 J = 1, MP1
      A(I,J) =0.
      DO 40 K =1, N
   40 A(I,J) = A(I,J) + C(K,I)*C(K,J) *WW(K)
      DO 45 J = 1, L
      DO 45 I =1, MP1
      B(I,J) = 0.
       DO 45 K = 1, N
   45 B(I,J) = B(I,J) + C(K,I)*Y(K,J) *WW(K)
```

```
      CALL CHAP8(A, MP1, B, L, DET)
      WRITE(6, 111)
  111 FORMAT (1H0, '-------------------------------------------------')
      WRITE (6, 301) N
  301 FORMAT(1H ,' THE NUMBER OF GIVEN DATA POINTS=', I3)
       WRITE (6, 302) M
  302 FORMAT(1H , ' THE DEGREE OF POLYNOMIAL=',I3)
      DO 50 J = 1, L
      DO 50 I = 1, MP1
      II = I - 1
   50 WRITE (6, 303) II, B(I,J)
  303 FORMAT(1H0, I3,'    DEGREE COEFFICIENT= ', D20.14)
 1919 FORMAT (4D20.8)
      SEDY = 0.
       SDY = 0.0
         XMEDY = 0.
       DO 70 J = 1, N
       YC(J) = 0.
      DO 60 IL = 1, L
      DO 60 I = 1, MP1
      II = I - 1
       IF (X(J) .EQ. 0.0) GO TO 80
      YC(J) = YC(J) + B(I, IL)*X(J)**II
   60 CONTINUE
   90 DY(J) = YC(J) - Y(J,IL)
       EDY(J) = (DY(J)/Y(J,IL))*100.
         IF ( XMEDY .LT. DABS(EDY(J))) XMEDY = DABS(EDY(J))
      SEDY = SEDY + DABS(EDY(J))
      SDY = SDY + DABS(DY(J))
   70 WRITE (6, 304) J, YC(J),J,DY(J) ,J, EDY(J)
  304 FORMAT(1H0,'  YC(',I2,')=',D20.14,'  DY(',I2,')=',D20.14,
     1'  EDY(',I2,')=',D20.14,'%')
      EDYAV =  SEDY/N
          SDYAV = SDY/N
      WRITE (6,305) SDY, EDYAV,SDYAV
  305 FORMAT(1H0,' SUM OF DY=',D20.14,'  AVE. D.Y.=',D20.14,'%.  AVE. D.
     1Y.=',D20.14)
         WRITE ( 6, 308) XMEDY
  308    FORMAT (1H0,' MAX. DEVIATION = ', D20.14)
         GO TO 1
   80 YC(J) = B(I, IL)
       GO TO 90
    3 RETURN
      END
```

```
      SUBROUTINE CHAP8 (A,N,B,M,DET)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(40,40),B(40,40),IPVOT(40),INDEX(40,2),PIVOT(40)
      COMMON IPVOT, INDEX, PIVOT
      EQUIVALENCE (IROW, JROW), (ICOL, JCOL)
   57 DET = 1.
      DO 17 J = 1, N
   17 IPVOT(J) = 0
      DO 135 I = 1, N
      T = 0.
      DO 9 J = 1, N
      IF (IPVOT(J) - 1) 13, 9, 13
   13 DO 23 K = 1, N
        IF  (IPVOT(K) -1) 43, 23, 81
   43 IF(DABS(T) - DABS(A(J,K))) 83, 23, 23
   83 IROW = J
      ICOL = K
      T = A(J, K)
   23 CONTINUE
    9 CONTINUE
      IPVOT(ICOL) = IPVOT(ICOL) + 1
      IF (IROW - ICOL) 73, 109, 73
   73 DET = - DET
      DO 12 L = 1, N
      T = A(IROW, L)
      A(IROW, L) = A(ICOL, L)
   12 A(ICOL, L) = T
      IF(M) 109, 109, 33
   33 DO 2 L = 1, M
      B(IROW, L) = B(ICOL, L)
      T = B(IROW, L)
    2 B(ICOL, L) = T
  109 INDEX(I,1) = IROW
      INDEX(I,2) = ICOL
      PIVOT(I) = A(ICOL, ICOL)
      DET = DET*PIVOT(I)
      A(ICOL, ICOL) = 1.
      DO 205 L = 1, N
  205 A(ICOL, L) = A(ICOL, L)/PIVOT(I)
        IF (M) 347, 347, 66
   66 DO 52 L = 1, M
   52 B(ICOL, L) = B(ICOL, L)/PIVOT(I)
  347 DO 135 LI = 1, N
      IF(LI - ICOL) 21, 135, 21
   21 T = A(LI, ICOL)
      A(LI, ICOL) = 0.
      DO 89 L = 1, N
   89 A(LI, L) = A(LI, L) - A(ICOL, L) *T
```

```
      IF (M) 135, 135, 18
   18 DO 66 L = 1, M
   68 B(LI, L) = B(LI, L) - B(ICOL, L) *T
  135 CONTINUE
  222 DO 3 I = 1, N
      L = N - I + 1
      IF (INDEX(L, 1) - INDEX(L, 2)) 19, 3, 19
   19 JROW = INDEX(L, 1)
      JCOL = INDEX(L,2)
      DO 549 K = 1, N
      T = A(K, JROW)
      A(K, JROW) = A(K, JCOL)
      A(K, JCOL) = T
  549 CONTINUE
    3 CONTINUE
   81 RETURN
    . END
```

```
 W=0.0
TR = 1.4    PR = 1.0
0.20000000000000D-020.88830000000000D 000.10000000000000D 01
0.20000000000000D-020.88450000000000D 000.10000000000000D 01
-.20000000000000D-020.88250000000000D 000.10000000000000D 01
-.20000000000000D-020.87870000000000D 000.10000000000000D 01
-.20000000000000D-020.87940000000000D 000.10000000000000D 01
0.72000000000000D-020.88400000000000D 000.10000000000000D 01
0.21000000000000D-010.88680000000000D 000.10000000000000D 01
0.40000000000000D-010.88460000000000D 000.10000000000000D 01
0.49000000000000D-010.88460000000000D 000.10000000000000D 01
0.90800000000000D-010.88540000000000D 000.10000000000000D 01
0.85600000000000D-010.88390000000000D 000.10000000000000D 01
0.14770000000000D 000.88680000000000D 000.10000000000000D 01
0.14540000000000D 000.88550000000000D 000.10000000000000D 01
0.17400000000000D 000.88620000000000D 000.10000000000000D 01
0.20200000000000D 000.88770000000000D 000.10000000000000D 01
0.21300000000000D 000.88760000000000D 000.10000000000000D 01
0.22500000000000D 000.88780000000000D 000.10000000000000D 01
0.22500000000000D 000.88640000000000D 000.10000000000000D 01
0.60000000000000D 000.89410000000000D 000.10000000000000D 01
-----------------------------------------
 THE NUMBER OF GIVEN DATA POINTS= 19
 THE DEGREE OF POLYNOMIAL=  1

  0   DEGREE COEFFICIENT= 0.88340069733582D 00

  1   DEGREE COEFFICIENT= 0.18072019885481D-01
```

```
YC( 1)=0.883436841375590 00  DY( 1)=-.48631586244053D-02  EDY( 1)=-.54746804282397D 00%
YC( 2)=0.88343684137559D 00  DY( 2)=-.10631586244053D-02  EDY( 2)=-.12019882695368D 00%
YC( 3)=0.88336455329605D 00  DY( 3)=0.86455329605278D-03  EDY( 3)=0.97966379156123D-01%
YC( 4)=0.88336455329605C 00  DY( 4)=0.46645532960528D-02  EDY( 4)=0.53084708046578D 00%
YC( 5)=0.88336455329605D 00  DY( 5)=0.39645532960528D-02  EDY( 5)=0.45082480055183D 00%
YC( 6)=0.88353081587900D 00  DY( 6)=-.46918412100079D-03  EDY( 6)=-.53075126810044D-01%
YC( 7)=0.88378020975342D 00  DY( 7)=-.30197902465811D-02  EDY( 7)=-.34052664034519D 00%
YC( 8)=0.88412357813124D 00  DY( 8)=-.47642186875700D-03  EDY( 8)=-.53857321812910D-01%
YC( 9)=0.88428622631021D 00  DY( 9)=-.31377368978767D-03  EDY( 9)=-.35470686161844D-01%
YC(10)=0.88504163674143D 00  DY(10)=-.35836325857454D-03  EDY(10)=-.40474729904511D-01%
YC(11)=0.88494766223802D 00  DY(11)=0.10476622380210D-02  EDY(11)=0.11852723588878D 00%
YC(12)=0.88606993467291D 00  DY(12)=-.73006532709065D-03  EDY(12)=-.82325814962861D-01%
YC(13)=0.88602836902717D 00  DY(13)=0.52836902717274D-03  EDY(13)=0.59669003633285D-01%
YC(14)=0.88654522879590D 00  DY(14)=0.34522879589752D-03  EDY(14)=0.38956081685570D-01%
YC(15)=0.88705124535269D 00  DY(15)=-.64875464730901D-03  EDY(15)=-.73082645861103D-01%
YC(16)=0.88725003757143D 00  DY(16)=-.34996242856870D-03  EDY(16)=-.39427943732391D-01%
YC(17)=0.88746690181006D 00  DY(17)=-.33309818994294D-03  EDY(17)=-.37519507765594D-01%
YC(18)=0.88746690181006D 00  DY(18)=0.10669018100571D-02  EDY(18)=0.12030347135120D 00%
YC(19)=0.89424390926711D 00  DY(19)=0.14390926711259D-03  EDY(19)=0.16095433073772D-01%
SUM OF DY=0.25251462052842D-01  AVE. D.Y.=0.15035140910213D 00%.  AVE. D.Y.=0.13290243185706D-02
MAX. DEVIATION = 0.54746804282397D 00
```

```
 W=0.0
TR = 1.4    PP = 1.0
0.20000000000000D-020.88830000000000D 000.10000000000000D 01
0.20000000000000D-020.88450000000000D 000.10000000000000D 01
-.20000000000000D-020.88250000000000D 000.10000000000000D 01
-.20000000000000D-020.87870000000000D 000.10000000000000D 01
-.20000000000000D-020.87940000000000D 000.10000000000000D 01
0.72000000000000D-020.88400000000000D 000.10000000000000D 01
0.21000000000000D-010.88680000000000D 000.10000000000000D 01
0.40000000000000D-010.88460000000000D 000.10000000000000D 01
0.49000000000000D-010.88460000000000D 000.10000000000000D 01
0.90800000000000D-010.88540000000000D 000.10000000000000D 01
0.85600000000000D-010.88390000000000D 000.10000000000000D 01
0.14770000000000D 000.88680000000000D 000.10000000000000D 01
0.14540000000000D 000.88550000000000D 000.10000000000000D 01
0.17400000000000D 000.88620000000000D 000.10000000000000D 01
0.20200000000000D 000.88770000000000D 000.10000000000000D 01
0.21300000000000D 000.88760000000000D 000.10000000000000D 01
0.22500000000000D 000.88780000000000D 000.10000000000000D 01
0.22500000000000D 000.88640000000000D 000.10000000000000D 01
0.60000000000000D 000.89410000000000D 000.10000000000000D 01
0.0                 0.84960000000000D 000.10000000000000D 01
0.0                 0.84000000000000D 000.10000000000000D 01
0.25000000000000D 000.87200000000000D 000.10000000000000D 01
0.34800000000000D 000.87110000000000D 000.10000000000000D 01
-------------------------------------------
 THE NUMBER OF GIVEN DATA POINTS= 23
 THE DEGREE OF POLYNOMIAL=  1
```

```
 0   DEGREE COEFFICIENT= 0.87770838242113D 00
 1   DEGREE COEFFICIENT= 0.24881172454204D-01
 YC( 1)=0.87775814476604D 00  DY( 1)=-.10541855233963D-01  EDY( 1)=-.11867449323385D 01%
 YC( 2)=0.87775814476604D 00  DY( 2)=-.67418552339626D-02  EDY( 2)=-.76222218586349D 00%
 YC( 3)=0.87765862007622D 00  DY( 3)=-.48413799237794D-02  EDY( 3)=-.54859829164639D 00%
 YC( 4)=0.87765862007622D 00  DY( 4)=-.10413799237794D-02  EDY( 4)=-.11851370476607D 00%
 YC( 5)=0.87765862007622D 00  DY( 5)=-.17413799237794D-02  EDY( 5)=-.19801909526716D 00%
 YC( 6)=0.87788752686280D 00  DY( 6)=-.61124731372007D-02  EDY( 6)=-.69145623723990D 00%
 YC( 7)=0.87823088704267D 00  DY( 7)=-.85691129573327D-02  EDY( 7)=-.96629600330771D 00%
 YC( 8)=0.87870362931930D 00  DY( 8)=-.58963706807029D-02  EDY( 8)=-.66655784317238D 00%
 YC( 9)=0.87892755987139D 00  DY( 9)=-.56724401286150D-02  EDY( 9)=-.64124351442630D 00%
 YC(10)=0.87996759287997D 00  DY(10)=-.54324071200293D-02  EDY(10)=-.61355400045509D 00%
 YC(11)=0.87983821078321D 00  DY(11)=-.40617892167912D-02  EDY(11)=-.45953040126612D 00%
 YC(12)=0.88138333159261D 00  DY(12)=-.54166684073852D-02  EDY(12)=-.61081060074257D 00%
 YC(13)=0.88132610489597D 00  DY(13)=-.41738951040298D-02  EDY(13)=-.47136026019535D 00%
 YC(14)=0.88204770642815D 00  DY(14)=-.41622935718396D-02  EDY(14)=-.46967880521774D 00%
 YC(15)=0.88273437925668D 00  DY(15)=-.49656207431219D-02  EDY(15)=-.55938050502669D 00%
 YC(16)=0.88300807215387D 00  DY(16)=-.45919278461257D-02  EDY(16)=-.51734202863065D 00%
 YC(17)=0.88330664622332D 00  DY(17)=-.44933537766752D-02  EDY(17)=-.50612229969309D 00%
 YC(18)=0.88330664622332D 00  DY(18)=-.30933537766752D-02  EDY(18)=-.34897944231444D 00%
 YC(19)=0.89263708589365D 00  DY(19)=-.14629141063489D-02  EDY(19)=-.16361862278815D 00%
 YC(20)=0.87770838242113D 00  DY(20)=0.28108382421129D-01  EDY(20)=0.33084254262157D 01%
 YC(21)=0.87770838242113D 00  DY(21)=0.37708382421129D-01  EDY(21)=0.44890931453725D 01%
 YC(22)=0.88392867553468D 00  DY(22)=0.11928675534680D-01  EDY(22)=0.13679673778303D 01%
 YC(23)=0.88636703043519D 00  DY(23)=0.15267030435192D-01  EDY(23)=0.17526151343350D 01%
SUM OF DY=0.18602494162427D 00  AVE. D.Y.=0.93122303730918D 00%,  AVF. D.Y.=0.80880409401855D-02
MAX. DEVIATION = 0.44890931453725D 01
```

```
C
C
C     *************************************************************
C                                 APPENDIX  D
C         COMPUTER PROGRAM FOR THE EVALUATION OF THE BINARY
C                        INTERACTION CONSTANT
C     *************************************************************
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TITLE(20)
      TOL=0.000000000001
    1 READ (5,500) (TITLE(I),I=1,20)
  500 FORMAT(20A4)
      WRITE (6,605) (TITLE(I),I=1,20)
  605 FORMAT(1H1,20A4)
      READ (5,501) VC1,VC2,W1,W2,TC1,TC2
  501 FORMAT(6F10.5)
      IF (VC1 .LE. 0.0) GO TO 6
      W12=0.5*(W1+W2)
      VC12=(0.5*(VC1**(1./3.)+VC2**(1./3.)))**3.
    4 READ (5,502) B12,T
  502 FORMAT(2F10.5)
      IF (B12 .GE. 90.) GO TO 1
      A8=B12*(0.291-0.08*W12)/VC12-(0.1445+0.073*W12)
      A7=-(0.46*W12-0.33)
      A6=0.1385+0.5*W12
      A5=0.0121+0.097*W12
      A4=0.
      A3=0.
      A2=0.
      A1=0.
      A0=0.0073*W12
      B8=8.
      B7=7.
      B6=6.
      B5=5.
      B4=4.
      B3=3.
      B2=2.
      B1=1.
      B0=0.
      A=0.
      N=1
      DO 7 J=1,8
      TR=T/DSQRT(TC1*TC2)
      WRITE (6,603) TR
  603 FORMAT(1H0,'TR=',F16.4)
      I=J-1
```

```
      C7=A8*A+A7
      C6=C7*A+A6
      C5=C6*A+A5
      C4=C5*A+A4
      C3=C4*A+A3
      C2=C3*A+A2
      C1=C2*A+A1
      C0=C1*A+A0
    2 F= A8*TR**(B8-I)+C7*TR**(B7-I)+C6*TR**(B6-I)+C5*TR**(B5-I)+C4*TR
     &**(B4-I)+C3*TR**(B3-I)+C2*TR**(B2-I)+C1*TR**(B1-I)+C0*TR**(B0-I)
      DF= A8*(B8-I)*TR**(B8-I-1)+C7*(B7-I)*TR**(B7-I-1)+C6*(B6-I)*TR**
     &(B6-I-1)+C5*(B5-I)*TR**(B5-I-1)+C4*(B4-I)*TR**(B4-I-1)+C3*(B3-I)
     &*TR**(B3-I-1)+C2*(B2-I)*TR**(B2-I-1)+C1*(B1-I)*TR**(B1-I-1)+C0*
     &(B0-I)*TR**(B0-I-1)
      IF (DABS(F) .LE. TOL) GO TO 3
      IF (DABS(DF) .LE. TOL) GO TO 5
      TRN=TR-F/DF
      IF (DABS(TR-TRN)/TRN .LE. TOL) GC TO 3
      TR=TRN
      N=N+1
      IF (N .LE. 100) GO TO 2
      WRITE (6,600)
  600 FORMAT(1H0,'INITIAL GUESS SHCULD BE CHANGED')
    3 TC12=T/TR
      XK12=1-TC12/DSQRT(TC1*TC2)
      WRITE (6,601) B12,T,TC12,XK12,TR
  601 FORMAT(1H0,'B12=',F16.4,'T=',F16.4,'TC12=',F16.4,'K12=',F16.4,
     &'TR=',F16.4)
      A=TRN
      WRITE (6,604) A8,C7,C6,C5,C4,C3,C2,C1,C0
  604 FORMAT(1H0,5F16.4/5F16.4)
    7 CONTINUE
      GO TO 4
    5 WRITE (6,602)
  602 FORMAT(1H0,'DF EQUALS TO ZERO')
    6 RETURN
      END
```

```
METHANE-ETHANE
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          242.6827K12=          -0.0060TR=          1.2279
         -0.3077              0.3075              0.1630            0.0169           0.0
         0.0                  0.0                 0.0               0.0004
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=         1914.4911K12=          -6.9363TR=          0.1557
         -0.3677             -0.1440             -0.0138           -0.0001          -0.0002
        -0.0002             -0.0002             -0.0003             0.0000
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          242.9033K12=          -0.0069TR=          1.2268
         -0.3677              0.5162             -0.1300            0.0907          -0.0515
         0.0292              -0.0166              0.0094           -0.0050
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          572.6481K12=          -1.3739TR=          0.5204
         -0.3677             -0.1436             -0.0132            0.0007           0.0009
         0.0011               0.0013              0.0016            0.0023
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          242.9033K12=          -0.0069TR=          1.2268
         -0.3677              0.1161              0.2234            0.1331           0.0693
         0.0361               0.0188              0.0098            0.0054
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          572.6481K12=          -1.3739TR=          0.5204
         -0.3677             -0.1436             -0.0132            0.0007           0.0009
         0.0011               0.0013              0.0016            0.0023
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          242.9033K12=          -0.0069TR=          1.2268
         -0.3677              0.1161              0.2234            0.1331           0.0693
         0.0361               0.0188              0.0098            0.0054
TR=          1.2353
B12=           -93.0000T=          298.0000TC12=          241.2295K12=           0.0    TR=          1.2353
         -0.3677             -0.1436             -0.0132            0.0007           0.0009
         0.0011               0.0013              0.0016            0.0023
TR=          1.3390
B12=           -79.0000T=          323.0000TC12=          245.1198K12=          -0.0161TR=          1.3177
         -0.3346              0.3075              0.1630            0.0169           0.0
         0.0                  0.0                 0.0               0.0004
TR=          1.3390
B12=           -79.0000T=          323.0000TC12=         1369.6911K12=          -4.6780TR=          0.2358
         -0.3346             -0.1335             -0.0129           -0.0001          -0.0001
        -0.0002             -0.0002             -0.0003             0.0000
TR=          1.3390
B12=           -79.0000T=          323.0000TC12=          245.1195K12=          -0.0161TR=          1.3177
         -0.3346              0.3131              0.1577            0.0142          -0.0002
         0.0000              -0.0000              0.0000            0.0004
TR=          1.3390
B12=           -79.0000T=          323.0000TC12=         1053.0353K12=          -3.3653TR=          0.3067
         -0.3346             -0.1335             -0.0129           -0.0001          -0.0001
        -0.0002             -0.0002             -0.0003            -0.0000
```

```
TR=        1.3390
B12=         -79.0000T=        323.0000TC12=        245.1154K12=        -0.0161TR=        1.3177
       -0.3346      0.3968           0.0570           0.0016      -0.0004
       0.0001      -0.0000           0.0000           0.0004
TR=        1.3390
B12=         -79.0000T=        323.0000TC12=        733.0312K12=        -2.0387TR=        0.4406
       -0.3346     -0.1335          -0.0129          -0.0001      -0.0001
      -0.0002      -0.0002          -0.0003          -0.0001
TR=        1.3390
B12=         -79.0000T=        323.0000TC12=        245.1197K12=        -0.0161TR=        1.3177
       -0.3346      0.3101           0.1606           0.0156      -0.0001
       0.0000      -0.0000           0.0000           0.0004
TR=        1.3390
B12=         -79.0000T=        323.0000TC12=        241.2295K12=         0.0    TR=        1.3390
       -0.3346     -0.1335          -0.0129          -0.0001      -0.0001
      -0.0002      -0.0002          -0.0003          -0.0000
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        248.3801K12=        -0.0296TR=        1.4011
       -0.3086      0.3075           0.1630           0.0169       0.0
       0.0          0.0              0.0              0.0004
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=       2363.1376K12=        -8.7962TR=        0.1473
       -0.3086     -0.1250          -0.0121          -0.0001      -0.0001
      -0.0001      -0.0002          -0.0003           0.0000
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        249.1634K12=        -0.0329TR=        1.3967
       -0.3086      0.5314          -0.2226           0.1784      -0.1295
       0.0940      -0.0682           0.0495          -0.0355
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        481.3283K12=        -0.9953TR=        0.7230
       -0.3086     -0.1236          -0.0096           0.0034       0.0048
       0.0066       0.0093           0.0130           0.0185
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        249.1634K12=        -0.0329TR=        1.3967
       -0.3086      0.0843           0.2240           0.1788       0.1293
       0.0935       0.0676           0.0489           0.0357
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        481.3283K12=        -0.9953TR=        0.7230
       -0.3086     -0.1236          -0.0096           0.0034       0.0048
       0.0066       0.0093           0.0130           0.0185
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        249.1634K12=        -0.0329TR=        1.3967
       -0.3086      0.0843           0.2240           0.1788       0.1293
       0.0935       0.0676           0.0489           0.0357
TR=        1.4426
B12=         -68.0000T=        348.0000TC12=        241.2295K12=         0.0    TR=        1.4426
       -0.3086     -0.1236          -0.0096           0.0034       0.0048
       0.0066       0.0093           0.0130           0.0185
TR=        1.5462
B12=         -56.0000T=        373.0000TC12=        247.2158K12=        -0.0248TR=        1.5088
       -0.2803      0.3075           0.1630           0.0169       0.0
       0.0          0.0              0.0              0.0004
```

```
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=        1678.3989K12=         -5.9577TR=          0.2222
         -0.2803         -0.1155          -0.0112         -0.0000         -0.0001
        -0.0001         -0.0002          -0.0002          0.0000
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=         247.2153K12=         -0.0248TR=          1.5088
         -0.2803          0.3340           0.1314          0.0044         -0.0004
         0.0000         -0.0000           0.0000          0.0004
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=        1167.8176K12=         -3.8411TR=          0.3194
         -0.2803         -0.1155          -0.0112         -0.0000         -0.0001
        -0.0001         -0.0002          -0.0003         -0.0000
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=         247.2140K12=         -0.0248TR=          1.5088
         -0.2803          0.4024           0.0267          0.0078         -0.0026
         0.0009         -0.0003           0.0001          0.0003
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=         855.3541K12=         -2.5458TR=          0.4361
         -0.2803         -0.1155          -0.0112         -0.0001         -0.0001
        -0.0001         -0.0002          -0.0003         -0.0001
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=         247.2154K12=         -0.0248TR=          1.5088
         -0.2803          0.3296           0.1370          0.0060         -0.0005
         0.0000         -0.0000           0.0000          0.0004
TR=          1.5462
B12=        -56.0000T=        373.0000TC12=         241.2295K12=          0.0    TR=         1.5462
         -0.2803         -0.1155          -0.0112         -0.0000         -0.0001
        -0.0001         -0.0002          -0.0002         -0.0000
```

```
METHANE-PROPANE
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          268.7031K12=          -0.0123TR=          1.1090
         -0.4241            0.2949            0.1766          0.0195          0.0
          0.0              0.0               0.0             0.0006
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=         1778.9578K12=          -5.7018TR=          0.1675
         -0.4241           -0.1754           -0.0179         -0.0003          -0.0004
        -0.0004           -0.0005           -0.0005          0.0000
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          268.8060K12=          -0.0127TR=          1.1086
         -0.4241            0.5057           -0.0748          0.0567          -0.0282
          0.0140           -0.0070            0.0035         -0.0012
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          769.3398K12=          -1.8983TR=          0.3873
         -0.4241           -0.1752           -0.0176         -0.0000          -0.0000
        -0.0000           -0.0000           -0.0000          0.0005
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          268.8060K12=          -0.0127TR=          1.1086
         -0.4241            0.1306            0.2273          0.1075           0.0416
          0.0161            0.0062            0.0024          0.0015
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          769.3398K12=          -1.8983TR=          0.3873
         -0.4241           -0.1752           -0.0176         -0.0000          -0.0000
        -0.0000           -0.0000           -0.0000          0.0005
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          268.8060K12=          -0.0127TR=          1.1086
         -0.4241            0.1306            0.2273          0.1075           0.0416
          0.0161            0.0062            0.0024          0.0015
TR=        1.1226
B12=     -139.0000T=            298.0000TC12=          265.4464K12=           0.0    TR=          1.1226
         -0.4241           -0.1752           -0.0176         -0.0000          -0.0000
        -0.0000           -0.0000           -0.0000          0.0005
TR=        1.2168
B12=     -116.0000T=            323.0000TC12=          268.6006K12=          -0.0119TR=          1.2025
         -0.3787            0.2949            0.1766          0.0195           0.0
          0.0              0.0               0.0             0.0006
TR=        1.2168
B12=     -116.0000T=            323.0000TC12=         1285.9919K12=          -3.8446TR=          0.2512
         -0.3787           -0.1605           -0.0164         -0.0002          -0.0003
        -0.0003           -0.0004           -0.0005          0.0000
TR=        1.2168
B12=     -116.0000T=            323.0000TC12=          268.6001K12=          -0.0119TR=          1.2025
         -0.3787            0.2981            0.1742          0.0180          -0.0002
          0.0000           -0.0000            0.0000          0.0006
TR=        1.2168
B12=     -116.0000T=            323.0000TC12=          970.3976K12=          -2.6557TR=          0.3329
         -0.3787           -0.1605           -0.0164         -0.0002          -0.0003
        -0.0003           -0.0004           -0.0005         -0.0000
```

```
TR=        1.2168
B12=      -116.0000T=         323.0000TC12=          268.5950K12=          -0.0119TR=          1.2026
         -0.3787           0.3338         0.1424          0.0049           -0.0005
         0.0001           -0.0000         0.0000          0.0006
TR=        1.2168
B12=      -116.0000T=         323.0000TC12=          763.3910K12=          -1.8759TP=          0.4231
         -0.3787          -0.1605        -0.0164         -0.0002           -0.0003
        -0.0003           -0.0004        -0.0005         -0.0000
TR=        1.2168
B12=      -116.0000T=         323.0000TC12=          268.5839K12=          -0.0118TR=          1.2026
         -0.3787           0.4349         0.0160          0.0136           -0.0050
         0.0019           -0.0007         0.0003          0.0005
TR=        1.2168
B12=      -116.0000T=         323.0000TC12=          265.4464K12=           0.0    TR=          1.2168
         -0.3787          -0.1606        -0.0164         -0.0003           -0.0003
        -0.0004           -0.0005        -0.0006         -0.0001
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          263.6730K12=           0.0067TR=          1.3198
         -0.3334           0.2949         0.1766          0.0195            0.0
         0.0               0.0            0.0             0.0006
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=         2215.3950K12=          -7.3459TR=          0.1571
         -0.3334          -0.1451        -0.0149         -0.0001           -0.0002
        -0.0002           -0.0003        -0.0004          0.0000
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          264.3679K12=           0.0041TR=          1.3163
         -0.3334           0.5227        -0.1805          0.1428           -0.0976
         0.0667           -0.0456         0.0311         -0.0207
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          528.2010K12=          -0.9899TR=          0.6588
         -0.3334          -0.1440        -0.0129          0.0026            0.0034
         0.0045            0.0059         0.0077          0.0108
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          264.3679K12=           0.0041TP=          1.3163
         -0.3334           0.0752         0.2262          0.1685            0.1110
         0.0732            0.0482         0.0318          0.0215
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          528.2010K12=          -0.9899TR=          0.6588
         -0.3334          -0.1440        -0.0129          0.0026            0.0034
         0.0045            0.0059         0.0077          0.0108
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          264.3679K12=           0.0041TP=          1.3163
         -0.3334           0.0752         0.2262          0.1685            0.1110
         0.0732            0.0482         0.0318          0.0215
TR=        1.3110
B12=       -93.0000T=         348.0000TC12=          265.4464K12=           0.0    TP=          1.3110
         -0.3334          -0.1440        -0.0129          0.0026            0.0034
         0.0045            0.0059         0.0077          0.0108
TR=        1.4052
B12=       -75.0000T=         373.0000TC12=          259.9249K12=           0.0208TR=          1.4350
         -0.2979           0.2949         0.1766          0.0195            0.0
         0.0               0.0            0.0             0.0006
```

```
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=         1580.6030K12=          -4.9545TR=          0.2360
         -0.2979          -0.1326          -0.0137          -0.0001          -0.0001
        -0.0002          -0.0003          -0.0004          -0.0000
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=          259.9236K12=           0.0208TR=          1.4350
         -0.2979           0.3231           0.1460           0.0057          -0.0005
         0.0001          -0.0000           0.0000           0.0006
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=         1065.0592K12=          -3.0123TR=          0.3502
         -0.2979          -0.1326          -0.0137          -0.0001          -0.0001
        -0.0002          -0.0003          -0.0004          -0.0000
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=          259.9237K12=           0.0208TR=          1.4350
         -0.2979           0.3219           0.1475           0.0061          -0.0006
         0.0001          -0.0000           0.0000           0.0006
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=          890.1318K12=          -2.3533TR=          0.4190
         -0.2979          -0.1326          -0.0137          -0.0001          -0.0001
        -0.0002          -0.0003          -0.0004          -0.0000
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=          259.9213K12=           0.0208TR=          1.4350
         -0.2979           0.4175           0.0048           0.0175          -0.0072
         0.0030          -0.0012           0.0005           0.0003
TR=        1.4052
B12=        -75.0000T=          373.0000TC12=          265.4464K12=           0.0    TR=          1.4052
         -0.2979          -0.1326          -0.0137          -0.0001          -0.0002
        -0.0002          -0.0003          -0.0005          -0.0001
```

```
ETHANE-PRCPANE
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           335.4080K12=          0.0020TR=         0.8885
         -0.5963          0.2757           0.1975             0.0236          0.0
          0.0            0.0              0.0                0.0009
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=          1397.2893K12=         -3.1576TR=         0.2133
         -0.5963         -0.2342          -0.0285            -0.0016         -0.0014
        -0.0012         -0.0011          -0.0010            -0.0000
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           335.2306K12=          0.0025TR=         0.8889
         -0.5963          0.3934           0.1198            -0.0001          0.0000
        -0.0000          0.0000          -0.0000             0.0009
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           798.5097K12=         -1.3759TR=         0.3732
         -0.5963         -0.2544          -0.0286            -0.0019         -0.0017
        -0.0015         -0.0013          -0.0012            -0.0002
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           335.1249K12=          0.0028TR=         0.8892
         -0.5963          0.4735           0.0404             0.0101         -0.0034
          0.0011        -0.0004           0.0001             0.0008
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           613.3838K12=         -0.8251TR=         0.4858
         -0.5963         -0.2546          -0.0289            -0.0021         -0.0019
        -0.0017         -0.0015          -0.0013            -0.0003
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           335.1722K12=          0.0027TR=         0.8891
         -0.5963          0.4329           0.0835             0.0016         -0.0004
          0.0001        -0.0000           0.0000             0.0009
TR=           0.8867
B12=        -274.0000T=            298.0000TC12=           336.0810K12=          0.0    TR=      0.8867
         -0.5963         -0.2545          -0.0288            -0.0020         -0.0018
        -0.0016         -0.0014          -0.0013            -0.0003
TR=           0.9611
B12=        -230.0000T=            323.0000TC12=           334.7149K12=          0.0041TR=         0.9650
         -0.5252          0.2757           0.1975             0.0236          0.0
          0.0            0.0              0.0                0.0009
TR=           0.9611
B12=        -230.0000T=            323.0000TC12=          3957.7698K12=        -10.7762TR=         0.0816
         -0.5252         -0.2311          -0.0255            -0.0010         -0.0010
        -0.0010         -0.0009          -0.0009            -0.0000
TR=           0.9611
B12=        -230.0000T=            323.0000TC12=           355.8678K12=         -0.0589TR=         0.9076
         -0.5252          0.6920          -0.3511             0.3019         -0.2394
          0.1898        -0.1505           0.1193            -0.0937
TR=           0.9611
B12=        -230.0000T=            323.0000TC12=           334.6393K12=          0.0043TR=         0.9652
         -0.5252          0.3555           0.1435             0.0017         -0.0003
          0.0000        -0.0000           0.0000             0.0009
```

```
TR=           0.9611
B12=        -230.0000T=          323.0000TC12=          781.8102K12=           -1.3263TR=          0.4131
          -0.5252          -0.2312          -0.0256          -0.0012           -0.0011
         -0.0011          -0.0011          -0.0010          -0.0001
TR=           0.9611
B12=        -230.0000T=          323.0000TC12=          334.5942K12=            0.0044TR=          0.9653
          -0.5252           0.4032           0.0996          -0.0006            0.0002
         -0.0000           0.0000          -0.0000           0.0009
TR=           0.9611
INITIAL GUESS SHOULD BE CHANGED
B12=        -230.0000T=          323.0000TC12=          234.5785K12=            0.3020TR=          1.3769
          -0.5252          -0.2313          -0.0257          -0.0013           -0.0012
         -0.0012          -0.0012          -0.0011          -0.0002
TR=           0.9611
INITIAL GUESS SHOULD BE CHANGED
B12=        -230.0000T=          323.0000TC12=          278.4606K12=            0.1714TR=          1.1599
          -0.5252          -0.4475          -0.4186          -0.5528           -0.7612
         -1.0481          -1.4431          -1.9871          -2.7352
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=          332.7096K12=            0.0100TR=          1.0460
          -0.4653           0.2757           0.1975           0.0236            0.0
          0.0              0.0              0.0              0.0009
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=         1712.6887K12=           -4.0961TR=          0.2032
          -0.4653          -0.2110          -0.0232          -0.0007           -0.0007
         -0.0008          -0.0008          -0.0008           0.0000
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=          332.6260K12=            0.0103TR=          1.0462
          -0.4653           0.4174           0.0704           0.0021           -0.0006
          0.0002          -0.0001           0.0000           0.0009
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=          939.7670K12=           -1.7963TR=          0.3703
          -0.4653          -0.2112          -0.0234          -0.0009           -0.0009
         -0.0010          -0.0010          -0.0011          -0.0002
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=          130.8537K12=            0.6106TR=          2.6595
          -0.4653           1.4410          -3.4112           8.5664          -21.4533
         53.7266        -134.5501         336.9604        -843.8656
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=           61.8786K12=            0.8159TR=          5.6239
          -0.4653           2.6841         -13.6951          70.9081         -367.0123
       1899.6145       -9832.1921       50890.3249     -263402.6207
TR=           1.0355
B12=        -193.0000T=          348.0000TC12=           15.9343K12=            0.9526TR=         21.8396
          -0.4653           8.9785        -167.7247        3136.9453       -58669.6520
    1097286.6085   -20522329.0195   383824959.7914-7178600421.9643
TR=           1.0355
INITIAL GUESS SHOULD BE CHANGED
B12=        -193.0000T=          348.0000TC12=           21.6235K12=            0.9357TR=         16.0936
          -0.4653           6.6942         -92.1415        1271.0096       -17532.1078
     241835.1599    -3335836.4753    46014008.0230 -634710049.4997
TR=           1.1099
B12=        -165.0000T=          373.0000TC12=          332.6501K12=            0.0102TR=          1.1213
          -0.4200           0.2757           0.1975           0.0236            0.0
          0.0              0.0              0.0              0.0009
```

```
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=        15784.7970K12=             -45.9672TR=             0.0236
         -0.4200          -0.1953             -0.0214              -0.0005           -0.0005
          -0.0006        -0.0007             -0.0008              -0.0000
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=          316.8180K12=               0.0573TR=             1.1773
         -0.4200           0.7268             -0.5830               0.6497           -0.6977
          0.7493         -0.8048              0.8643              -0.9274
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=          333.2651K12=               0.0084TR=             1.1192
         -0.4200           0.5226             -0.1097               0.0880           -0.0517
          0.0304         -0.0179              0.0105              -0.0053
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=          722.2298K12=              -1.1490TR=             0.5165
         -0.4200          -0.1944             -0.0201               0.0011            0.0012
          0.0014          0.0015              0.0017               0.0028
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=          333.2651K12=               0.0084TR=             1.1192
         -0.4200           0.0587              0.2279               0.1413            0.0730
          0.0377          0.0195              0.0100               0.0061
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=          722.2298K12=              -1.1490TR=             0.5165
         -0.4200          -0.1944             -0.0201               0.0011            0.0012
          0.0014          0.0015              0.0017               0.0028
TR=         1.1099
B12=       -165.0000T=            373.0000TC12=          333.2651K12=               0.0084TR=             1.1192
         -0.4200           0.0587              0.2279               0.1413            0.0730
          0.0377          0.0195              0.0100               0.0061
```

```
C
C
C     ************************************************************
C                                APPENDIX  D
C         COMPUTER PROGRAM FOR THE EVALUATION OF THE BINARY
C                         INTERACTION CONSTANT
C     ************************************************************
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TITLE(20)
      TOL=0.0000000000001
    1 READ (5,500) (TITLE(I),I=1,20)
  500 FORMAT(20A4)
      WRITE (6,605) (TITLE(I),I=1,20)
  605 FORMAT(1H1,20A4)
      READ (5,501) VC1,VC2,W1,W2,TC1,TC2
  501 FORMAT(6F10.5)
      IF (VC1 .LE. 0.0) GO TO 6
      W12=0.5*(W1+W2)
      VC12=(0.5*(VC1**(1./3.)+VC2**(1./3.)))**3.
    4 READ (5,502) B12,T
  502 FORMAT(2F10.5)
      IF (B12 .GE. 20.) GO TO 1
      A8=B12*(0.291-0.08*W12)/VC12-(0.1445+0.073*W12)
      A7=-(0.46*W12-0.33)
      A6=0.1385+0.5*W12
      A5=0.0121+0.097*W12
      A4=0.
      A3=0.
      A2=0.
      A1=0.
      A0=0.0073*W12
      B8=8.
      B7=7.
      B6=6.
      B5=5.
      B4=4.
      B3=3.
      B2=2.
      B1=1.
      B0=0.
      A=0.
      N=1
      DO 7 J=1,8
      TR=T/DSQRT(TC1*TC2)
      TR=1.5
      WRITE (6,603) TR
  603 FORMAT(1H0,'TR=',F16.4)
      I=J-1
```

```
      C7=A8*A+A7
      C6=C7*A+A6
      C5=C6*A+A5
      C4=C5*A+A4
      C3=C4*A+A3
      C2=C3*A+A2
      C1=C2*A+A1
      C0=C1*A+A0
    2 F= A8*TR**(B8-I)+C7*TR**(B7-I)+C6*TR**(B6-I)+C5*TR**(B5-I)+C4*TR
     &**(B4-I)+C3*TR**(B3-I)+C2*TR**(B2-I)+C1*TR**(B1-I)+C0*TR**(B0-I)
      DF= A8*(B8-I)*TR**(B8-I-1)+C7*(B7-I)*TR**(B7-I-1)+C6*(B6-I)*TR**
     &(B6-I-1)+C5*(B5-I)*TR**(B5-I-1)+C4*(B4-I)*TR**(B4-I-1)+C3*(B3-I)
     &*TR**(B3-I-1)+C2*(B2-I)*TR**(B2-I-1)+C1*(B1-I)*TR**(B1-I-1)+C0*
     &(B0-I)*TR**(B0-I-1)
      IF (DABS(F) .LE. TOL) GO TO 3
      IF (DABS(DF) .LE. TOL) GO TO 5
      TRN=TR-F/DF
      IF (DABS(TR-TRN)/TRN .LE. TOL) GO TO 3
      TR=TRN
      N=N+1
      IF (N .LE. 100) GO TO 2
      WRITE (6,600)
  600 FORMAT(1H0,'INITIAL GUESS SHOULD BE CHANGED')
    3 TC12=T/TR
      XK12=1-TC12/DSQRT(TC1*TC2)
      WRITE (6,601) B12,T,TC12,XK12,TR
  601 FORMAT(1H0,'B12=',F16.4,'T=',F16.4,'TC12=',F16.4,'K12=',F16.4,
     &'TR=',F16.4)
      A=TRN
      WRITE (6,604) A8,C7,C6,C5,C4,C3,C2,C1,C0
  604 FORMAT(1H0,5F16.4/5F16.4)
    7 CONTINUE
      GO TO 4
    5 WRITE (6,602)
  602 FORMAT(1H0,'DF EQUALS TO ZERO')
    6 RETURN
      END
```

```
METHANE-ETHANE
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          242.6827K12=          -0.0060TP=          1.2279
          -0.3677               0.3075              0.1630              0.0169            0.0
            0.0               0.0                 0.0                 0.0004
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=         1527.3625K12=          -5.3316TR=          0.1951
          -0.3677              -0.1440             -0.0138             -0.0001          -0.0002
         -0.0002              -0.0002             -0.0003              0.0000
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          242.6759K12=          -0.0060TP=          1.2280
          -0.3677               0.3979              0.0651              0.0008          -0.0002
          0.0001              -0.0000              0.0000              0.0004
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          871.0557K12=          -2.6109TR=          0.3421
          -0.3677              -0.1440             -0.0138             -0.0002          -0.0002
         -0.0002              -0.0003             -0.0003             -0.0001
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          242.6764K12=          -0.0060TR=          1.2280
          -0.3677               0.3911              0.0740              0.0000          -0.0000
          0.0000              -0.0000              0.0000              0.0004
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          704.1392K12=          -1.9190TR=          0.4232
          -0.3677              -0.1440             -0.0138             -0.0002          -0.0002
         -0.0002              -0.0003             -0.0003             -0.0001
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          242.6785K12=          -0.0060TP=          1.2280
          -0.3677               0.3631              0.1081              0.0005          -0.0001
          0.0000              -0.0000              0.0000              0.0004
TR=          1.5000
B12=          -93.0000T=              298.0000TC12=          198.6667K12=           0.1764TR=          1.5000
          -0.3677              -0.1440             -0.0138             -0.0001          -0.0002
         -0.0002              -0.0003             -0.0003             -0.0000
TR=          1.5000
B12=          -79.0000T=              323.0000TC12=          245.1198K12=          -0.0161TR=          1.3177
          -0.3346               0.3075              0.1630              0.0169            0.0
          0.0                 0.0                 0.0                 0.0004
TR=          1.5000
B12=          -79.0000T=              323.0000TC12=         1659.4068K12=          -5.8790TR=          0.1946
          -0.3346              -0.1335             -0.0129             -0.0001          -0.0001
         -0.0002              -0.0002             -0.0003              0.0000
TR=          1.5000
B12=          -79.0000T=              323.0000TC12=          245.1155K12=          -0.0161TR=          1.3177
          -0.3346               0.3957              0.0587              0.0014          -0.0004
          0.0001              -0.0000              0.0000              0.0004
TR=          1.5000
B12=          -79.0000T=              323.0000TC12=          962.1050K12=          -2.9883TR=          0.3357
          -0.3346              -0.1335             -0.0129             -0.0001          -0.0001
         -0.0002              -0.0002             -0.0003             -0.0001
```

```
TR=         1.5000
B12=        -79.0000T=       323.0000TC12=         245.4040K12=        -0.0173TR=       1.3162
         -0.3346        0.5144          -0.1552          0.1128         -0.0698
         0.0432        -0.0267          0.0165          -0.0099
TR=         1.5000
B12=        -79.0000T=       323.0000TC12=         554.1002K12=        -1.2970TR=       0.5829
         -0.3346       -0.1329          -0.0120          0.0011          0.0014
         0.0019         0.0025          0.0032           0.0046
TR=         1.5000
B12=        -79.0000T=       323.0000TC12=         245.4040K12=        -0.0173TR=       1.3162
         -0.3346        0.1124           0.2285          0.1501          0.0875
         0.0510         0.0297          0.0173           0.0105
TR=         1.5000
B12=        -79.0000T=       323.0000TC12=         215.3333K12=         0.1074TR=       1.5000
         -0.3346       -0.1329          -0.0120          0.0011          0.0014
         0.0019         0.0025          0.0032           0.0046
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=         248.3801K12=        -0.0296TR=       1.4011
         -0.3086        0.3075           0.1630          0.0169          0.0
         0.0            0.0              0.0             0.0004
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=        1791.8069K12=        -6.4278TR=       0.1942
         -0.3086       -0.1250          -0.0121         -0.0001         -0.0001
        -0.0001        -0.0002         -0.0003          -0.0000
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=         248.3771K12=        -0.0296TR=       1.4011
         -0.3086        0.3936           0.0532          0.0020         -0.0006
         0.0002        -0.0000           0.0000          0.0004
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=        1028.8738K12=        -3.2651TR=       0.3382
         -0.3086       -0.1250          -0.0121         -0.0001         -0.0001
        -0.0002        -0.0002         -0.0003          -0.0001
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=         248.4286K12=        -0.0298TR=       1.4008
         -0.3086        0.4759          -0.0967          0.0696         -0.0380
         0.0207        -0.0113           0.0062         -0.0030
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=         734.6141K12=        -2.0453TR=       0.4737
         -0.3086       -0.1249          -0.0119          0.0002          0.0002
         0.0003         0.0004           0.0006          0.0012
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=         248.4286K12=        -0.0298TR=       1.4008
         -0.3086        0.1613           0.2394          0.1303          0.0617
         0.0292         0.0138           0.0066          0.0035
TR=         1.5000
B12=        -68.0000T=       348.0000TC12=         232.0000K12=         0.0383TR=       1.5000
         -0.3086       -0.1249          -0.0119          0.0002          0.0002
         0.0003         0.0004           0.0006          0.0012
TR=         1.5000
B12=        -56.0000T=     37000.0000TC12=       24522.7496K12=      -100.6573TR=       1.5088
         -0.2803        0.3075           0.1630          0.0169          0.0
         0.0            0.0              0.0             0.0004
```

```
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=    191047.5574K12=     -790.9743TR=          0.1937
       -0.2803      -0.1155       -0.0112       -0.0000          -0.0001
      -0.0001      -0.0002       -0.0002        0.0000
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=     24522.5749K12=     -100.6566TR=          1.5088
       -0.2803       0.3910        0.0465        0.0030          -0.0009
       0.0003      -0.0001        0.0000        0.0004
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=    108000.9005K12=     -446.7102TR=          0.3426
       -0.2803      -0.1155       -0.0112       -0.0001          -0.0001
      -0.0001      -0.0002       -0.0003       -0.0001
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=     24522.6161K12=     -100.6568TR=          1.5088
       -0.2803       0.4170        0.0001        0.0168          -0.0066
       0.0026      -0.0010        0.0004        0.0002
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=     87753.1794K12=     -362.7747TR=          0.4216
       -0.2803      -0.1155       -0.0112       -0.0001          -0.0001
      -0.0001      -0.0002       -0.0003       -0.0001
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=     24522.6592K12=     -100.6570TR=          1.5088
       -0.2803       0.3498        0.1101        0.0002          -0.0000
       0.0000      -0.0000        0.0000        0.0004
TR=        1.5000
B12=      -56.0000T=    37000.0000TC12=     24666.6667K12=     -101.2539TR=          1.5000
       -0.2803      -0.1155       -0.0112       -0.0001          -0.0001
      -0.0001      -0.0002       -0.0003       -0.0000
```

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METHANE-PROPANE
TR=          1.5000
B12=      -139.0000T=          298.0000TC12=          268.7031K12=          -0.0123TR=          1.1090
        -0.4241            0.2949            0.1766            0.0195          0.0
        0.0                0.0               0.0               0.0006
TR=          1.5000
B12=      -139.0000T=          298.0000TC12=         2525.0943K12=          -8.5126TR=          0.1180
        -0.4241           -0.1754           -0.0179           -0.0003         -0.0004
       -0.0004           -0.0005           -0.0005            0.0000
TR=          1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=      -139.0000T=          298.0000TC12=          299.6377K12=          -0.1288TR=          0.9945
        -0.4241            0.6323           -0.3264            0.2792         -0.2222
        0.1768            -0.1406            0.1119           -0.0885
TR=          1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=      -139.0000T=          298.0000TC12=          242.9789K12=           0.0846TR=          1.2264
        -0.4241           -0.1269            0.0505            0.0697          0.0693
        0.0690             0.0686            0.0682            0.0684
TR=          1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=      -139.0000T=          298.0000TC12=          303.6370K12=          -0.1439TR=          0.9814
        -0.4241           -0.2252           -0.0995           -0.1026         -0.1258
       -0.1543            -0.1892           -0.2321           -0.2841
TR=          1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=      -139.0000T=          298.0000TC12=          276.3526K12=          -0.0411TR=          1.0783
        -0.4241           -0.1213            0.0576            0.0760          0.0746
        0.0732             0.0719            0.0705            0.0698
TR=          1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=      -139.0000T=          298.0000TC12=          404.7111K12=          -0.5246TR=          0.7363
        -0.4241           -0.1624            0.0015            0.0212          0.0228
        0.0246             0.0265            0.0286            0.0314
TR=          1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=      -139.0000T=          298.0000TC12=          324.3658K12=          -0.2220TR=          0.9187
        -0.4241           -0.0174            0.1639            0.1402          0.1032
        0.0760             0.0560            0.0412            0.0309
TR=          1.5000
B12=      -116.0000T=          323.0000TC12=          268.6006K12=          -0.0119TR=          1.2025
        -0.3787            0.2949            0.1766            0.0195          0.0
        0.0                0.0               0.0               0.0006
TR=          1.5000
B12=      -116.0000T=          323.0000TC12=         2783.1328K12=          -9.4847TR=          0.1161
        -0.3787           -0.1605           -0.0164           -0.0002         -0.0003
       -0.0003            -0.0004           -0.0005           -0.0000
TR=          1.5000
B12=      -116.0000T=          323.0000TC12=          299.4723K12=          -0.1282TR=          1.0786
        -0.3787            0.6298           -0.3803            0.3558         -0.3147
        0.2783            -0.2461            0.2176           -0.1919
TR=          1.5000
B12=      -116.0000T=          323.0000TC12=           74.6559K12=           0.7188TR=          4.3265
        -0.3787            1.9151           -8.0159           34.3110       -146.7794
      627.9088         -2686.1366        11491.0484       -49157.6604
```

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TR=             1.5000
B12=          -116.0000T=           323.0000TC12=           72.0470K12=          0.7286TR=            4.4832
           -0.3787            1.8718            -7.6165            31.7308         -132.1114
         550.0473        -2290.1276          9534.9706        -39698.9509
TR=             1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=          -116.0000T=           323.0000TC12=          254.2122K12=          0.0423TR=            1.2706
           -0.3787            0.7122            -0.6081             0.6895          -0.7597
            0.8371           -0.9224             1.0163            -1.1193
TR=             1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=          -116.0000T=           323.0000TC12=         1988.0327K12=         -6.4894TR=            0.1625
           -0.3787           -0.1863            -0.0601            -0.0568          -0.0722
           -0.0918           -0.1166            -0.1481            -0.1877
TR=             1.5000
INITIAL GUESS SHOULD BE CHANGED
B12=          -116.0000T=           323.0000TC12=          273.9729K12=         -0.0321TR=            1.1789
           -0.3787            0.2334             0.2146             0.0544           0.0088
            0.0014            0.0002             0.0000             0.0006
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=          263.6730K12=          0.0067TR=            1.3198
           -0.3334            0.2949             0.1766             0.0195           0.0
            0.0               0.0                0.0                0.0006
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=         3059.8997K12=        -10.5274TR=            0.1137
           -0.3334           -0.1451            -0.0149            -0.0001          -0.0002
           -0.0002           -0.0003            -0.0004             0.0000
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=          288.2119K12=         -0.0858TR=            1.2074
           -0.3334            0.6269            -0.4475             0.4651          -0.4631
            0.4611           -0.4592             0.4572            -0.4547
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=          263.6645K12=          0.0067TR=            1.3199
           -0.3334            0.4164             0.0249             0.0104          -0.0038
            0.0014           -0.0005             0.0002             0.0005
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=          837.9752K12=         -2.1569TR=            0.4153
           -0.3334           -0.1451            -0.0149            -0.0002          -0.0002
           -0.0003           -0.0004            -0.0005            -0.0001
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=          263.6703K12=          0.0067TR=            1.3198
           -0.3334            0.3289             0.1431             0.0049          -0.0005
            0.0001           -0.0000             0.0000             0.0006
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=          763.2807K12=         -1.8755TR=            0.4559
           -0.3334           -0.1451            -0.0149            -0.0001          -0.0002
           -0.0003           -0.0003            -0.0005            -0.0000
TR=             1.5000
B12=           -93.0000T=           348.0000TC12=           64.1129K12=          0.7585TR=            5.4279
           -0.3334            1.7300            -7.2697            31.3111         -134.7746
         580.1194        -2497.0470         10748.2086        -46264.2418
TR=             1.5000
B12=           -75.0000T=           373.0000TC12=          259.9249K12=          0.0208TR=            1.4350
           -0.2979            0.2949             0.1766             0.0195           0.0
            0.0               0.0                0.0                0.0006
```

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TR=          1.5000
B12=           -75.0000T=          373.0000TC12=       3342.5796K12=         -11.5923TR=          0.1116
           -0.2979        -0.1326          -0.0137          -0.0001         -0.0001
          -0.0002        -0.0003          -0.0004           0.0000
TR=          1.5000
B12=           -75.0000T=          373.0000TC12=        279.2744K12=          -0.0521 TR=          1.3356
           -0.2979         0.6242          -0.5132           0.5867         -0.6484
           0.7166        -0.7920           0.8753          -0.9669
TR=          1.5000
B12=           -75.0000T=          373.0000TC12=        259.9246K12=           0.0208TR=          1.4350
           -0.2979         0.3021           0.1694           0.0154         -0.0004
           0.0000        -0.0000           0.0000           0.0006
TR=          1.5000
B12=           -75.0000T=          373.0000TC12=       1025.3146K12=          -2.8626TR=          0.3638
           -0.2979        -0.1326          -0.0137          -0.0001         -0.0001
          -0.0002        -0.0003          -0.0004          -0.0000
TR=          1.5000
B12=           -75.0000T=          373.0000TC12=        259.9204K12=           0.0208TR=          1.4351
           -0.2979         0.4067           0.0241           0.0105         -0.0039
           0.0015        -0.0006           0.0002           0.0005
TR=          1.5000
B12=           -75.0000T=          373.0000TC12=        737.0904K12=          -1.7768TR=          0.5060
           -0.2979        -0.1326          -0.0137          -0.0001         -0.0002
          -0.0002        -0.0003          -0.0005          -0.0001
TR=          1.5000
B12=           -75.0000T=          373.0000TC12=        260.5696K12=           0.0184TR=          1.4315
           -0.2979         0.5129          -0.1986           0.1648         -0.1206
           0.0882        -0.0646           0.0472          -0.0340
```

```
ETHANE-PROPANE
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          335.4080K12=          0.0020TR=          0.8885
         -0.5963             0.2757          0.1975            0.0236           0.0
          0.0                0.0             0.0               0.0009
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=         1174.4649K12=         -2.4946TR=          0.2537
         -0.5963            -0.2542         -0.0283           -0.0016          -0.0014
         -0.0012            -0.0011         -0.0010            0.0000
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          335.3868K12=          0.0021TR=          0.8885
         -0.5963             0.2897          0.1908            0.0191          -0.0004
          0.0000            -0.0000          0.0000            0.0009
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          824.6233K12=         -1.4536TR=          0.7614
         -0.5963            -0.2542         -0.0283           -0.0016          -0.0014
         -0.0013            -0.0011         -0.0010           -0.0000
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          335.3817K12=          0.0021TR=          0.8885
         -0.5963             0.2931          0.1890            0.0180          -0.0005
          0.0000            -0.0000          0.0000            0.0009
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          683.7683K12=         -1.0345TR=          0.4358
         -0.5963            -0.2542         -0.0283           -0.0016          -0.0014
         -0.0013            -0.0011         -0.0010           -0.0000
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          335.5744K12=          0.0015TR=          0.8880
         -0.5963             0.5553         -0.0628            0.0530          -0.0248
          0.0116            -0.0055          0.0026           -0.0003
TR=         1.5000
B12=       -274.0000T=          298.0000TC12=          198.6667K12=          0.4089TR=          1.5000
         -0.5963            -0.2539         -0.0279           -0.0012          -0.0011
         -0.0010            -0.0009         -0.0008            0.0002
TR=         1.5000
B12=       -230.0000T=          323.0000TC12=          334.7149K12=          0.0041TR=          0.9650
         -0.5252             0.2757          0.1975            0.0236           0.0
          0.0                0.0             0.0               0.0009
TR=         1.5000
B12=       -230.0000T=          323.0000TC12=         1273.0261K12=         -2.7879TR=          0.2537
         -0.5252            -0.2311         -0.0255           -0.0010          -0.0010
         -0.0010            -0.0009         -0.0009           -0.0000
TR=         1.5000
B12=       -230.0000T=          323.0000TC12=          334.6980K12=          0.0041TR=          0.9650
         -0.5252             0.2935          0.1876            0.0172          -0.0006
          0.0000            -0.0000          0.0000            0.0009
TR=         1.5000
B12=       -230.0000T=          323.0000TC12=          924.1552K12=         -1.7498TR=          0.3495
         -0.5252            -0.2311         -0.0255           -0.0011          -0.0010
         -0.0010            -0.0010         -0.0009           -0.0000
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TR=          1.5000
B12=       -230.0000T=        323.0000TC12=         334.5863K12=          0.0044TR=         0.9654
         -0.5252         0.4117          0.0910            0.0000          -0.0000
          0.0000        -0.0000          0.0000            0.0009
TR=          1.5000
B12=       -230.0000T=        323.0000TC12=         645.7687K12=         -0.9215TR=         0.5002
         -0.5252        -0.2313         -0.0258           -0.0013          -0.0013
        -0.0012         -0.0012         -0.0011           -0.0002
TR=          1.5000
B12=       -230.0000T=        323.0000TC12=         334.7094K12=          0.0041TR=         0.9650
         -0.5252         0.2815          0.1944            0.0214          -0.0002
          0.0000        -0.0000          0.0000            0.0009
TR=          1.5000
B12=       -230.0000T=        323.0000TC12=         215.3333K12=          0.3593TR=         1.5000
         -0.5252        -0.2311         -0.0255           -0.0010          -0.0010
        -0.0010         -0.0009         -0.0009           -0.0000
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=         332.7096K12=          0.0100TR=         1.0460
         -0.4653         0.2757          0.1975            0.0236           0.0
          0.0            0.0             0.0               0.0009
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=        1372.4891K12=         -3.0838TR=         0.2536
         -0.4653        -0.2110         -0.0232           -0.0007          -0.0007
        -0.0008         -0.0008         -0.0008            0.0000
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=         332.6974K12=          0.0101TR=         1.0460
         -0.4653         0.2963          0.1844            0.0154          -0.0007
          0.0000        -0.0000          0.0000            0.0009
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=        1041.7435K12=         -2.0997TR=         0.3341
         -0.4653        -0.2110         -0.0232           -0.0007          -0.0008
        -0.0008         -0.0008         -0.0009           -0.0000
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=         150.1063K12=          0.5534TR=         2.3184
         -0.4653         1.2623         -2.4787            5.2791         -11.1929
        23.7315        -50.3164        106.6827         -226.1916
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=         332.8971K12=          0.0095TR=         1.0454
         -0.4653         0.5138         -0.0653            0.0570          -0.0291
          0.0149        -0.0076          0.0039           -0.0011
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=         950.3547K12=         -1.8278TR=         0.3662
         -0.4653        -0.2108         -0.0228           -0.0002          -0.0003
        -0.0003         -0.0003         -0.0003            0.0006
TR=          1.5000
B12=       -193.0000T=        348.0000TC12=         332.8971K12=          0.0095TR=         1.0454
         -0.4653         0.1053          0.2361            0.1100           0.0403
          0.0148         0.0054          0.0020            0.0016
TR=          1.5000
B12=       -165.0000T=        373.0000TC12=         332.6501K12=          0.0102TR=         1.1213
         -0.4200         0.2757          0.1975            0.0236           0.0
          0.0            0.0             0.0               0.0009
```

```
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=          1472.6232K12=          -3.3818TR=          0.2533
        -0.4200        -0.1953              -0.0214           -0.0005     -0.0005
       -0.0006        -0.0007              -0.0008           -0.0000
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=           332.6412K12=           0.0102TR=          1.1213
        -0.4200         0.2980               0.1817            0.0139     -0.0007
        0.0000        -0.0000               0.0000            0.0009
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=          1020.1952K12=          -2.0356TR=          0.3656
        -0.4200        -0.1953              -0.0215           -0.0005     -0.0006
       -0.0006        -0.0007              -0.0008           -0.0000
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=           332.6401K12=           0.0102TR=          1.1213
        -0.4200         0.3006               0.1797            0.0129     -0.0008
        0.0000        -0.0000               0.0000            0.0009
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=           809.2619K12=          -1.4079TR=          0.4609
        -0.4200        -0.1953              -0.0215           -0.0005     -0.0006
       -0.0006        -0.0007              -0.0008           -0.0000
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=           332.6348K12=           0.0103TR=          1.1214
        -0.4200         0.3142               0.1688            0.0081     -0.0007
        0.0001        -0.0000               0.0000            0.0009
TR=          1.5000
B12=      -165.0000T=        373.0000TC12=           248.6667K12=           0.2601TR=          1.5000
        -0.4200        -0.1953              -0.0215           -0.0005     -0.0006
       -0.0007        -0.0007              -0.0008           -0.0001
```