

***Applied
Hydrocarbon
Thermodynamics***

by

WAYNE C. EDMISTER

Professor Emeritus

Oklahoma State University

Consulting Chemical Engineer

San Rafael, California

VOLUME II

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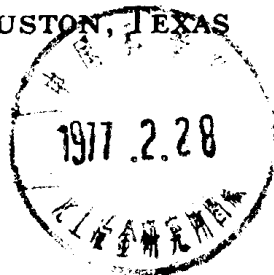
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VOLUME II



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To my colleagues and students in past studies
and applications of thermodynamics.

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The author is indebted to the following, who helped derive equations, make calculations and prepare charts, while graduate students at Oklahoma State University, Stillwater: Lyman Yarborough, R. L. Robinson, Jr., P. C. Tully, Moo Sup Han, A. N. Stuckey, Jr., B. I. Lee and others.

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APPLIED HYDROCARBON THERMODYNAMICS

Volume II

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Applied Hydrocarbon Thermodynamics

Preface

Although there are many books available on theoretical thermodynamics, there has been a shortage of material dealing with the practical application of these theoretical principles. There has been an even greater lack of converting the theoretical equations into working equations so the working process engineer can use them. Thus, there has developed over the years an ever increasing need for a single volume or two which would put this practical information into the hands of the working engineer—a volume which would be understandable yet one which would be consistent with theoretical meaning.

These two volumes of *Applied Hydrocarbon Thermodynamics* by Professor Wayne C. Edmister have at last filled this great void in our technical knowledge. As an example of how well this has been done, note the expertness with which the author has related fugacity and activity coefficients into the language of equilibrium ratio constants. He then presents these constants in terms of simplified equations and working nomographs for accurate and rapid usage by young and veteran engineers throughout the process design world.

It was no coincidence that Wayne C. Edmister was picked to prepare these books—for who else has a better background to prepare such a wealth of material for the design engineer? Professor Edmister was a natural choice because of his tremendous background in developing engineering design methods, data correlations, and other translations of theoretical literature into working information. As a reader, you will recognize immediately that the author draws heavily on his talents in the fields of engineering design, research and teaching in presenting his compilations with crystal clarity.

This volume includes working information on: (1) effects of pressure on entropy and enthalpy, (2) heat capacity difference and pressure effect on heat capacity, (3) isentropic and isenthalpic exponents for temperature changes and work calculation for gas compression and expansion, (4) ideal gas state enthalpies, entropies and heat capacities, (5) fugacities, imperfection pressure corrections and vapor/liquid *K*-ratios, (6) thermodynamic consistency tests, (7) heats of vaporization for mixtures, (8) enthalpy-composition diagrams, (9) heats of chemical reactions, and (10) chemical reaction equilibrium.

Individuals and organizations alike will for many years be grateful to Professor Edmister for making available *Applied Hydrocarbon Thermodynamics*.

JOHN J. MCKETTA
Chairman, Editorial Committee
Hydrocarbon Processing

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Derivative Compressibility Factors

Derivative compressibility factors have been defined, computed and illustrated by Reid and Valbert.⁹ These properties are so useful that plots have been made from the tabulations presented in this previous work. In addition the development and application of the Bridgeman¹ relationships are reviewed, using these derivative factors and the compressibility factors from which they were derived.

Compressibility Factor Equations. The generalized correlation of compressibility factor, $Z = PV/RT$, in terms of three parameters, developed by Pitzer et al.^{6,7} and presented in charts,⁴ has the form

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

where: $Z^{(0)}$ and $Z^{(1)}$ are functions of P_r and T_r (see Figures 4.1 to 4.4 of reference 4)

ω = acentric factor (defined by Equation 4.1 of reference 4)

This generalized correlation can be used in computing the effects of volume or pressure on thermodynamic properties, as well as in calculating fluid densities.

Thermodynamic properties computations involve evaluating and using the two first derivatives $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$. These can be found from compressibility factors by differentiating $V = ZRT/P$ and obtaining

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \left[Z + T \left(\frac{\partial Z}{\partial T}\right)_P \right] \quad (26.2)$$

and

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} \left[Z - P \left(\frac{\partial Z}{\partial P}\right)_T \right] \quad (26.3)$$

The two right hand side terms in brackets are defined as derivative compressibility factors and give the symbols Z_T and Z_P , as follows

$$Z_T = Z + T \left(\frac{\partial Z}{\partial T}\right)_P = Z + T_r \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \quad (26.4)$$

$$Z_P = Z - P \left(\frac{\partial Z}{\partial P}\right)_T = Z - P_r \left(\frac{\partial Z}{\partial P_r}\right)_{T_r} \quad (26.5)$$

In terms of these new factors, the derivatives in Equations 26.2 and 26.3 may be written

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} Z_T \quad (26.6)$$

and

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} Z_P \quad (26.7)$$

In terms of the acentric factor, ω , these derivative compressibility factors are

$$Z_T = Z_T^{(0)} + \omega Z_T^{(1)} \quad (26.8)$$

where

$$Z_T^{(0)} = Z_P^{(0)} + T_r \left(\frac{\partial Z^{(0)}}{\partial T_r}\right)_{P_r} \quad (26.9)$$

$$Z_T^{(1)} = Z^{(1)} + T_r \left(\frac{\partial Z^{(1)}}{\partial T_r}\right)_{P_r} \quad (26.10)$$

and

$$Z_P = Z_P^{(0)} + \omega Z_P^{(1)} \quad (26.11)$$

where

$$Z_P^{(0)} = Z^{(0)} - P_r \left(\frac{\partial Z^{(0)}}{\partial P_r}\right)_{T_r} \quad (26.12)$$

$$Z_P^{(1)} = Z^{(1)} - P_r \left(\frac{\partial Z^{(1)}}{\partial P_r}\right)_{T_r} \quad (26.13)$$

The four derivative compressibility factor terms, $Z_T^{(0)}$, $Z_T^{(1)}$, $Z_P^{(0)}$ and $Z_P^{(1)}$, are function of T_r and P_r only, as were the original compressibility factors, $Z^{(0)}$ and $Z^{(1)}$.

Compressibility Factor Plots. Tables of the $Z^{(0)}$ and $Z^{(1)}$ factors were published several years ago by Pitzer et al.^{6,7} Plots of $Z^{(0)}$ and $Z^{(1)}$ are functions of P_r and T_r were prepared from these tabulations in their article and are given as Figures 4.1 through 4.4 in Chapter 4, Vol. 1.

These same $Z^{(0)}$ and $Z^{(1)}$ tabulations were used by Reid and Valbert⁹ in deriving values of $Z_T^{(0)}$, $Z_T^{(1)}$, $Z_P^{(0)}$ and $Z_P^{(1)}$ as functions of P_r and T_r . These authors found that they could evaluate the $Z_P^{(0)}$ and $Z_P^{(1)}$ terms by numerical calculations on a digital computer, working with five evenly spaced, with P_r , values of $Z^{(0)}$ and $Z^{(1)}$ for each isotherm. Graphical methods were required in evaluating $Z_T^{(0)}$ and $Z_T^{(1)}$, however, because it was not possible to obtain accurate enough analytical expressions for the $Z^{(0)}$ vs T_r and $Z^{(1)}$ vs T_r isobars. Smooth curves were constructed and derivatives obtained as tangents to these curves.

From the temperature and pressure derivatives, thus obtained, the values of $Z_T^{(0)}$, $Z_T^{(1)}$, $Z_P^{(0)}$ and $Z_P^{(1)}$ were calculated by Equations 26.9, 26.10, 26.12 and 26.13. These results were presented in tabular form⁹ similar to the original Pitzer et al.^{6,7} tables of $Z^{(0)}$ and $Z^{(1)}$.

Plots have been prepared and are presented here as Figures 26.1 through 26.4. The simple fluid terms, i.e. $Z_T^{(0)}$ and $Z_P^{(0)}$ are plotted against P_r for lines of constant T_r on semi-log graph paper. The correction terms $Z_T^{(1)}$ and $Z_P^{(1)}$ are plotted against T_r with lines of constant T_r . As can be seen, the curves in Figures 26.1 and 26.3 are smooth and regular while those in Figures 26.2 and 26.4 are not. This is not too surprising when one recalls that the isobars on the $Z^{(1)}$ vs T_r plot, i.e. Figure 4.4, made from the Pitzer et al.^{6,7} values were also rather unusual. In constructing Figure 4.4, the tabulated values of $Z^{(1)}$ were smoothed while plotting and crossplotting. If the values of $Z_T^{(1)}$ and $Z_P^{(1)}$ had been derived from values of $Z^{(1)}$ that had first been smoothed in both T_r and P_r dimensions, the isobars on Figure 26.2 and 26.4 would probably have been more smooth and regular.

The $Z_T^{(0)}$ plot, i.e. Figure 26.1 is very similar to a plot developed previously^{2,3,5} representing the RZ_T function as a function of P_r and T_r . This product of the gas constant and the derivative compressibility factor was proposed previously for use in evaluating the exponent for computing temperature changes with changes in pressure for isentropic paths. Comparison of Figures 26.1 and 7.5 shows this similarity. The ordinates differ by a factor of R is a minor difference. Also Figure 7.5 gives RZ_T as a function of P_r and T_r while Figures 26.1 and 26.2 give Z_T as a function of P_r , T_r and ω .

Applications of these derivative compressibility factors will be discussed later, after developing some of the Bridgeman formulas in terms of Z , Z_T and Z_P .

Bridgeman Formulas. A "Condensed Collection of Thermodynamic Formulas" were first developed by Bridgeman¹ in 1926. Years later Ragatz⁸ reviewed these derivatives in "Systematic Derivations of Thermodynamic Relations" and Sage and Lacey included them in their

book.¹⁰ More recently, Reid and Valbert⁹ presented these Bridgeman formulas in terms of Z_T and Z_P . The derivation of these formulas is illustrated next for the extensive properties V , S , and H and the intensive properties T and P .

Define H as function of T and P , for which we can write

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (26.14)$$

Dividing by dT and keeping S constant gives

$$\left(\frac{\partial H}{\partial T}\right)_S = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S \quad (26.15)$$

Combine with the transformation

$$\left(\frac{\partial P}{\partial T}\right)_S = -\frac{(\partial S/\partial T)_P}{(\partial S/\partial P)_T} \quad (26.16)$$

Obtaining

$$\left(\frac{\partial H}{\partial T}\right)_S = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial H}{\partial P}\right)_T \frac{(\partial S/\partial T)_P}{(\partial S/\partial P)_T} \quad (26.17)$$

In a like manner, by defining V as a function of T and P , then introducing S and transforming results in the following analogous expression:

$$\left(\frac{\partial V}{\partial T}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial P}\right)_T \frac{(\partial S/\partial T)_P}{(\partial S/\partial P)_T} \quad (26.18)$$

It will be noted that Equation 26.18 differs from Equation 26.17 in that it contains the extensive property V where in the same places that Equation 26.17 contains the extensive property H .

Dividing Equation 26.17 by 26.18 gives

$$\left(\frac{\partial H}{\partial V}\right)_S = \frac{\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial H}{\partial P}\right)_T \frac{(\partial S/\partial T)_P}{(\partial S/\partial P)_T}}{\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial P}\right)_T \frac{(\partial S/\partial T)_P}{(\partial S/\partial P)_T}} \quad (26.19)$$

Multiply numerator and denominator of the right hand side by $(\partial S/\partial P)_T$ and separate the numerator and denominator of the left hand side, obtaining

$$\frac{(\partial H)_S}{(\partial V)_S} = \frac{(\partial H/\partial T)_P (\partial S/\partial P)_T - (\partial H/\partial P)_T (\partial S/\partial T)_P}{(\partial V/\partial T)_P (\partial S/\partial P)_T - (\partial V/\partial P)_T (\partial S/\partial T)_P} \quad (26.20)$$

Note that the numerator and denominator of Equation 26.20 are the same except that one contains V where the other contains H . Equation 26.20 may be regarded as the ratio of two equations. Other forms may be written by inspection, such as

$$(\partial H)_V = (\partial H/\partial T)_P (\partial V/\partial P)_T - (\partial H/\partial P)_T (\partial V/\partial T)_P \quad (26.21)$$

and

$$(\partial S)_V = (\partial S/\partial T)_P (\partial V/\partial P)_T - (\partial S/\partial P)_T (\partial V/\partial T)_P \quad (26.22)$$

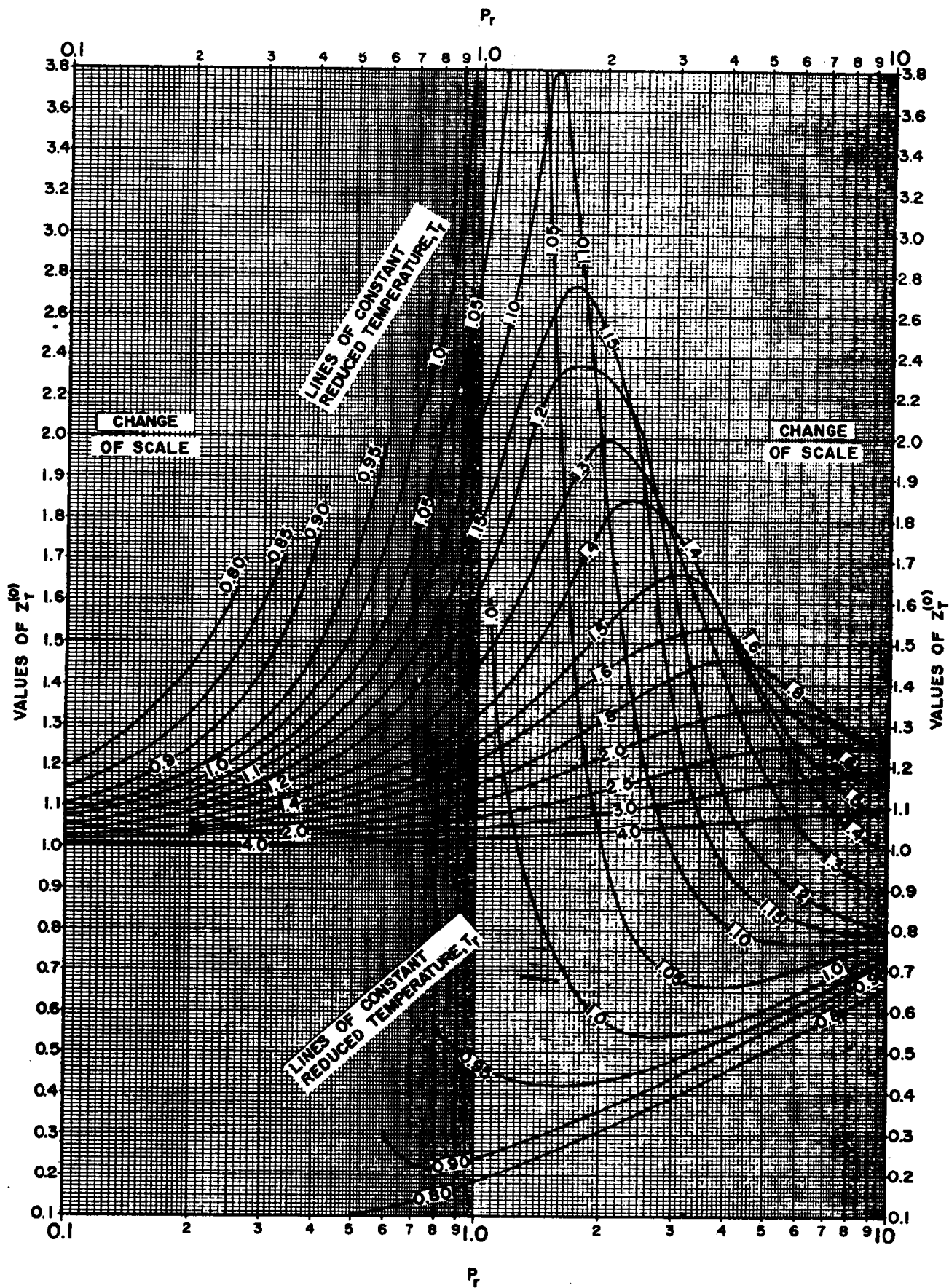


FIGURE 26.1—Values of $Z_T^{(0)}$.

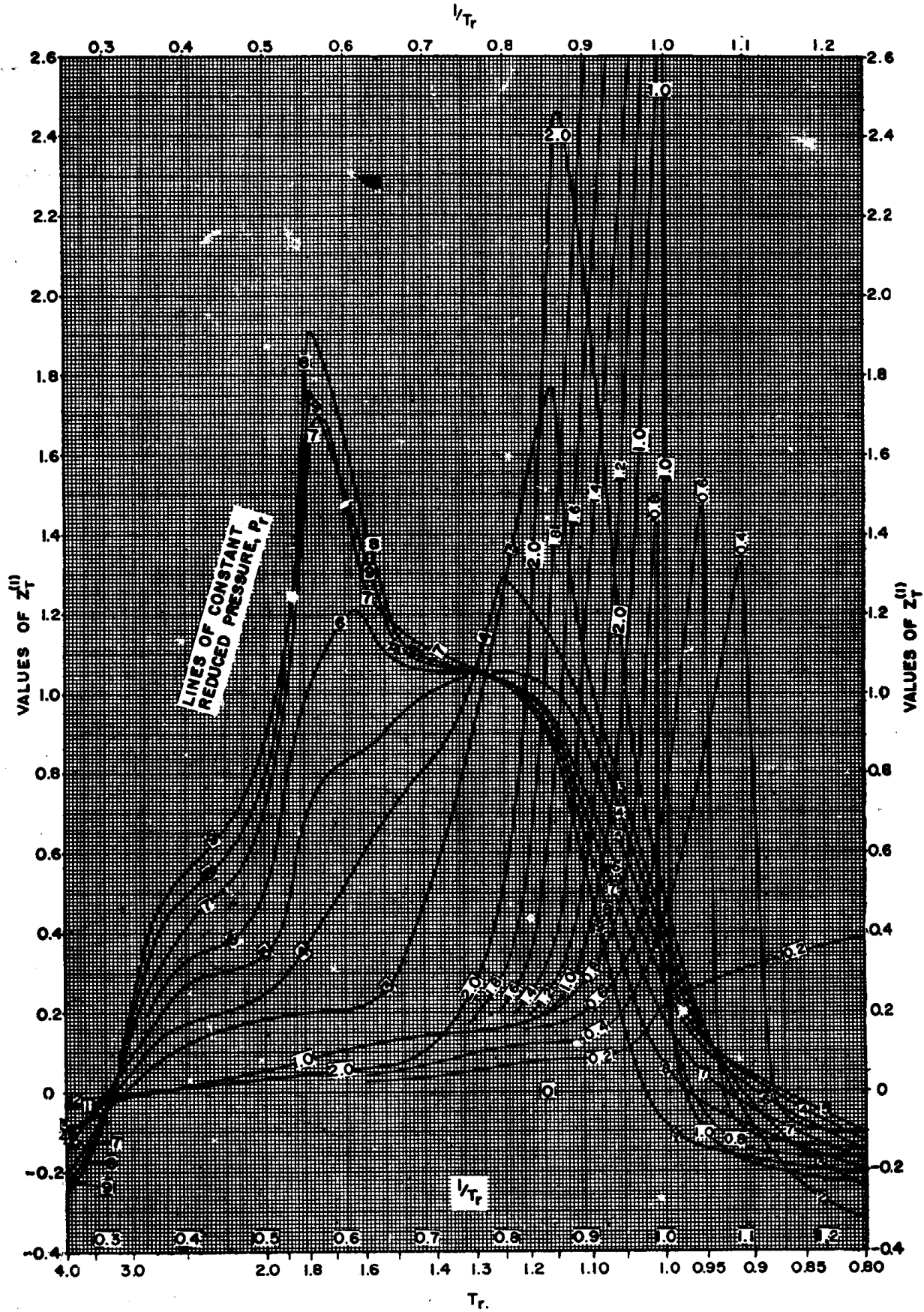


FIGURE 26.2—Values of $Z_T^{(1)}$.

These equations are combined with the heat capacity definitions, i.e. $C_P = (\partial H/\partial T)_P = T(\partial S/\partial T)_P$; $C_V = (\partial E/\partial T)_V = T(\partial S/\partial T)_V$, and with the Maxwell relations, i.e. $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$, $(\partial T/\partial P)_S = (\partial V/\partial S)_P$; $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, and $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, to obtain the Bridgeman formulas.

Such substitutions into Equation 26.22 gives

$$(\partial S)_V = \frac{C_P}{T} \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_P^2 \quad (26.23)$$

This expression for $(\partial S)_V$ is converted to a form using Z_T and Z_P by combining Equation 26.23 with Equations 26.6 and 26.7 and obtaining the following

$$(\partial S)_V = \frac{R}{P^2} (-C_P Z_P + R Z_T^2) \quad (26.24)$$

A similar manipulation, starting with another form of Equation 26.22, shows that $(\partial V)_S$ is equal to $-(\partial S)_V$.

The above procedure leads to the 28 Bridgeman formulas that Reid and Valbert⁹ present in terms of Z_T and Z_P . A few of these formulas are given here in Table 26.1 for convenient reference in applying the method to illustrating examples.

Applications. An expression for the isothermal effect of pressure on the enthalpy may be found from the formulas in Table 26.1, as follows:

$$\left(\frac{\partial H}{\partial P} \right)_T = \left(\frac{\partial H}{\partial P} \right)_T = \frac{R_T}{P} (Z - Z_T) \quad (26.25)$$

TABLE 26.1—Bridgeman (Abridged) Formulas in Terms of Z_T and Z_P . Source: Reid and Valbert⁹

$$\begin{aligned} (\partial T)_P &= -(\partial P)_T = 1 \\ (\partial V)_P &= -(\partial P)_V = \frac{RZ_T}{P} \\ (\partial S)_P &= -(\partial P)_S = C_P/T \\ (\partial H)_P &= -(\partial P)_H = C_P \\ (\partial V)_T &= -(\partial T)_V = \frac{Z_P RT}{P^2} \\ (\partial S)_T &= -(\partial T)_S = \frac{RZ_T}{P} \\ (\partial E)_T &= -(\partial T)_E = \frac{RT}{P} (Z_T - Z_P) \\ (\partial H)_T &= -(\partial T)_H = \frac{RT}{P} (Z_T - Z) \\ (\partial S)_V &= -(\partial V)_S = \frac{R}{P^2} (-C_P Z_P + RZ_T^2) \\ (\partial E)_V &= -(\partial V)_E = \frac{RT}{P^2} (-C_P Z_P + RZ_T^2) \\ (\partial H)_V &= -(\partial V)_H = \frac{RT}{P^2} (-C_P Z_P + RZ_T^2 - RZZ_T) \\ (\partial H)_S &= -(\partial S)_H = -\frac{ZRC_P}{P} \end{aligned}$$

An expression for the isothermal effect of pressure on the entropy is found in like manner

$$\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial S}{\partial P} \right)_T = -\frac{RZ_T}{P} \quad (26.26)$$

Likewise for the Joule-Thomson coefficient

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \left(\frac{\partial T}{\partial P} \right)_H = \frac{RT}{P} \left(\frac{Z_T - Z}{C_P} \right) \quad (26.27)$$

The Bridgeman formulas are not used in the derivations of the expressions for isothermal changes in the heat capacity and for the heat capacity difference. For these it is necessary to go back to earlier equations, as follows:

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P = -\frac{RT}{P} \left(\frac{\partial Z_T}{\partial T} \right)_P \quad (26.28)$$

and

$$C_P - C_V = -T \frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} = R \frac{Z_T^2}{Z_P} \quad (26.29)$$

Equations 26.25, 26.26, and 26.28 require an integration in their evaluations. These integrations may be performed graphically or numerically for each isotherm of interest, calculating the integrand from the above expressions and the values of Z , Z_T and Z_P found from Figures 4.3 and 4.4, 26.1 and 26.2, and 26.3 and 26.4.

The compilations of derivative compressibility factors and Bridgeman formulas only help solve the first two steps, i.e. formulation and differentiation. They do not contribute to the integration step. Because of this their utility is somewhat limited. In later chapters, more convenient correlations will be presented for evaluating the isothermal effects of pressure on these properties.

Other Derivative Factors. It is of interest to look at two other derivative compressibility factors that have more limited utility than the Z_T and Z_P factors. The latter involved temperature and pressure parameters. Two others, involving temperature and volume parameters, will be examined briefly.

The first derivatives of pressure, $(\partial P/\partial T)$ and $(\partial P/\partial V)_T$, are used in formulating some thermodynamic functions. These derivatives can also be found from compressibility factors by differentiating $P = ZRT/V$ and obtaining

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_V \right] \quad (26.30)$$

and

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{V^2} \left[Z - V \left(\frac{\partial Z}{\partial V} \right)_T \right] \quad (26.31)$$

The right hand side terms in brackets are defined as derivative compressibility factors and given the symbols Z_{TV} and Z_V , as follows:

$$Z_{TV} = Z + T \left(\frac{\partial Z}{\partial T} \right)_V = Z + T \left(\frac{\partial Z}{\partial T} \right)_{TV} \quad (26.32)$$

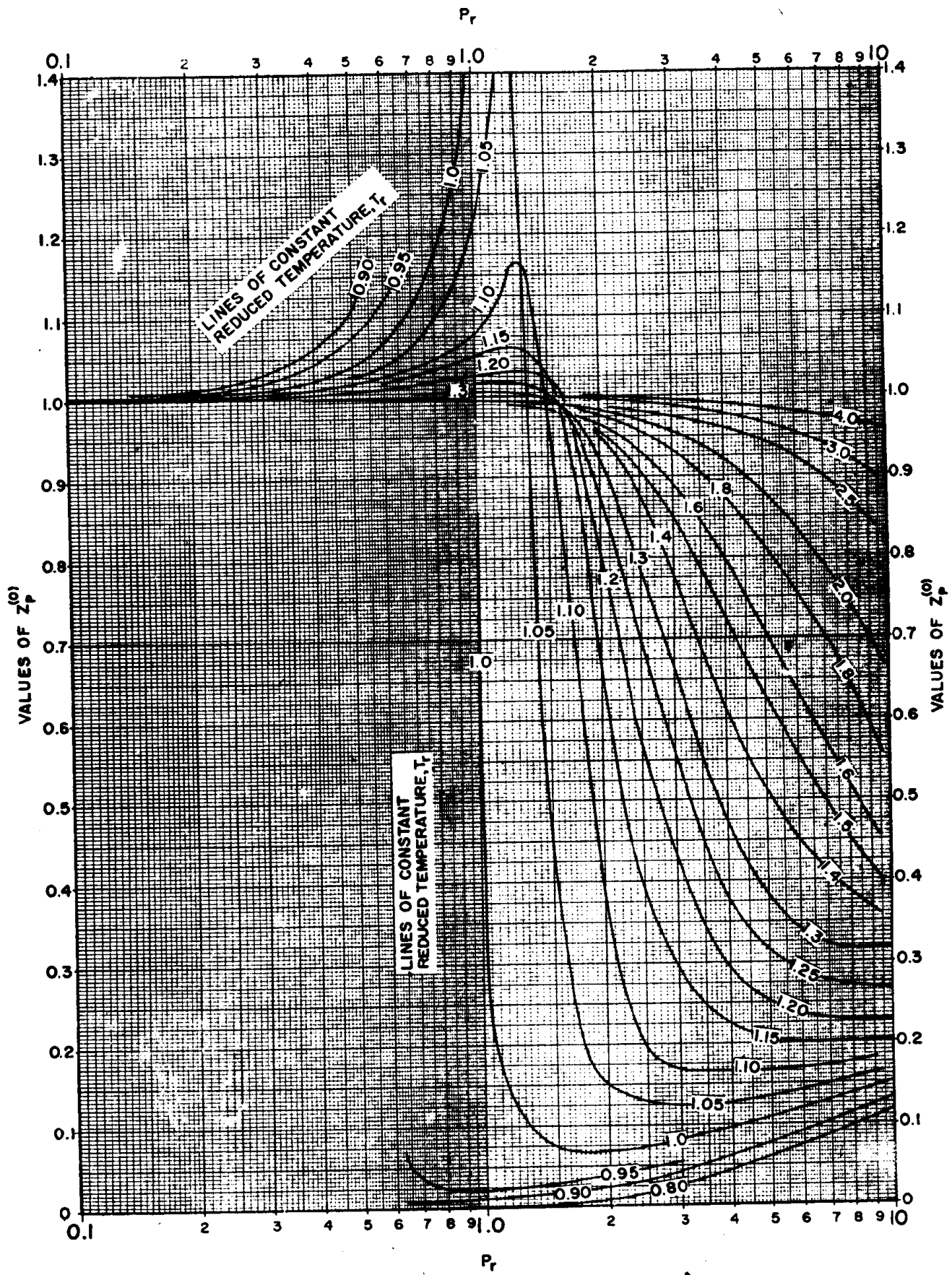


FIGURE 26.3—Values of $Z_p^{(0)}$.

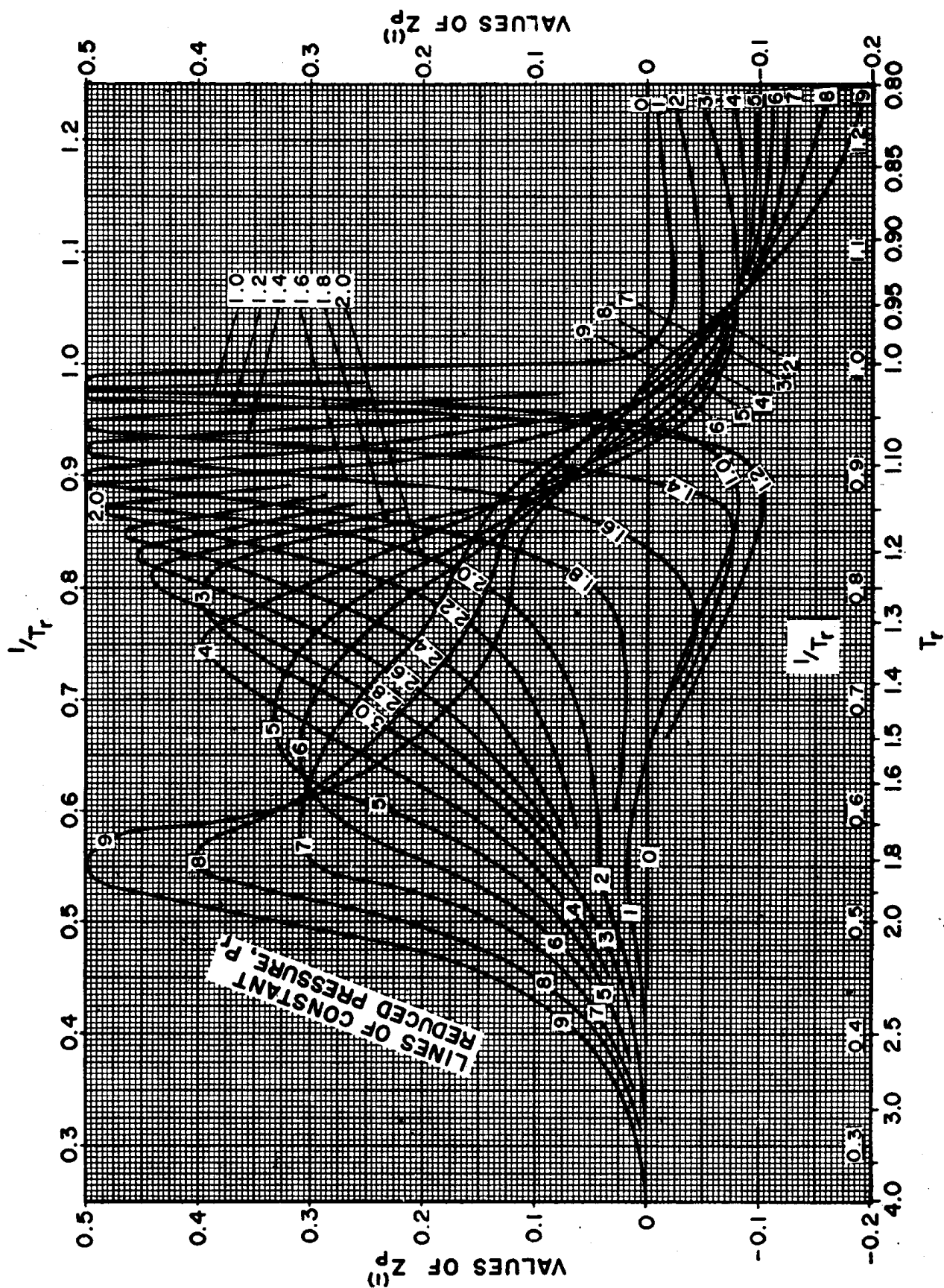


FIGURE 26.4—Values of $Z_p^{(1)}$.

and

$$Z_V = Z - V \left(\frac{\partial Z}{\partial V} \right)_T = Z - V_{rt} \left(\frac{\partial Z}{\partial V_{rt}} \right)_{T_r} \quad (26.33)$$

where: $V_{rt} = VP_c/RT_c =$ ideal reduced volume.

$$\text{(also } V_{rt} = ZT_r/P_r)$$

In terms of these new factors, the derivatives of Equations 26.30 and 26.31 may be written

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V} Z_{TV} \quad (26.34)$$

and

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{V^2} Z_V \quad (26.35)$$

In terms of the acentric factor, ω , these derivative factors are

$$Z_{TV} = Z_{TV}^{(0)} + \omega Z_{TV}^{(1)} \quad (26.36)$$

where

$$Z_{TV}^{(0)} = Z^{(0)} + T_r \left(\frac{\partial Z^{(0)}}{\partial T_r} \right)_{V_{rt}} \quad (26.37)$$

$$Z_{TV}^{(1)} = Z^{(1)} + T_r \left(\frac{\partial Z^{(1)}}{\partial T_r} \right)_{V_{rt}} \quad (26.38)$$

and

$$Z_V = Z_V^{(0)} + \omega Z_V^{(1)} \quad (26.39)$$

where

$$Z_V^{(0)} = Z^{(0)} - V_{rt}^{(0)} \left(\frac{\partial Z^{(0)}}{\partial V_{rt}} \right)_{T_r} \quad (26.40)$$

$$Z_V^{(1)} = Z^{(1)} - V_{rt}^{(1)} \left(\frac{\partial Z^{(1)}}{\partial V_{rt}} \right)_{T_r} \quad (26.41)$$

The four derivative compressibility factor terms, i.e. $Z_{TV}^{(0)}$, $Z_{TV}^{(1)}$, $Z_V^{(0)}$ and $Z_V^{(1)}$ are functions of the original compressibility factors $Z^{(0)}$ and $Z^{(1)}$, but with different parameters. The T_r and P_r parameters, used in the previous derivations, are not convenient for the evaluation of these two new factors. By manipulating the variables, in the following manner, these derivations can be made however. It will be noted that

$$V_{rt} = V_{rt}^{(0)} + \omega V_{rt}^{(1)} \quad (26.42)$$

$$\text{where: } V_{rt}^{(0)} = \frac{Z^{(0)} T_r}{P_r} \quad (26.43)$$

$$V_{rt}^{(1)} = \frac{Z^{(1)} T_r}{P_r} \quad (26.44)$$

By using Equations 26.43 and 26.44 and the Pitzer et al.⁷ tabulations, it is possible to convert the $Z^0(P_r, T_r)$ and $Z^1(P_r, T_r)$ correlations into $Z^0(T_r, V_{rt})$ and $Z^1(T_r, V_{rt})$ forms and evaluate the derivative factors in Equations 26.36 to 26.41. Values of $Z_{TV}^{(0)}$, $Z_{TV}^{(1)}$, $Z_V^{(0)}$ and $Z_V^{(1)}$, thus evaluated, can then be plotted against P_r and T_r to give correlations similar to Figures 26.1 through 26.4.

An applications of the Z_{TV} derivative compressibility factor is the isothermal effect of volume on the internal energy, which is

$$\left(\frac{\partial E}{\partial V} \right)_T = \frac{RT}{V} (Z_{TV} - Z) \quad (26.45)$$

The similarity between Equations 26.25 and 26.45 should be noted.

Another application is in the calculation of the heat capacity difference, i.e.

$$C_P - C_V = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V = R \frac{Z_T Z_{TV}}{Z} \quad (26.46)$$

and

$$C_P - C_V = -T \frac{(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T} = R \frac{Z_{TV}^2}{Z_V} \quad (26.47)$$

Comparisons between Equations 26.29, 26.46 and 26.47 show the following interrelationships

$$\frac{Z_T^2}{Z_P} = \frac{Z_T Z_{TV}}{Z} = \frac{Z_{TV}^2}{Z_V} \quad (26.48)$$

Another application of these two volume derivative factors, i.e. Z_{TV} and Z_V , is in the computation of the isothermal effects of volume on the heat capacity C_V . This computation will be discussed later in this series.

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Chapter 27

Isothermal Pressure Corrections to the Enthalpy and Entropy

Enthalpy and entropy are frequently used thermodynamic properties of all fluids. The predictions of changes in enthalpy and entropy with changes in temperature and pressure are among the most important applications of thermodynamics. Heat capacities at constant pressure, usually one atmosphere or the ideal gas state of the pressure, are used in calculating the effects of temperature on the enthalpy and entropy. Heat capacities cannot be generalized so specific component values are required in computing changes in enthalpy and entropy with changes in temperature. Reduced conditions are not involved in calculating the effects of temperature.

Isothermal changes of enthalpy and entropy with pressure on the other hand, can be generalized and correlations have been developed in terms of reduced properties. Such reduced properties correlations are presented and illustrated in this article for the prediction of the effects of pressure on the enthalpy and entropy.

Previous Work. During the 1940-1960 period, two parameter (P_r and T_r) generalized enthalpy pressure correction charts were widely used throughout the hydrocarbon processing industry. Typical of these were two charts that were based on generalized volume residuals.¹ In these terms the isothermal pressure correction to the enthalpy was evaluated by the relationship

$$\frac{H - H^0}{RT_c} = \frac{P_c \alpha_c}{RT_c} = \int_0^{P_r} \left[T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r} - \alpha_r \right] dP_r \quad (27.1)$$

where: $H - H^0$ = isothermal pressure effect on entropy

$$\alpha = \frac{RT}{P} - V = \text{residual volume}$$

$$\frac{P_c \alpha_c}{RT_c} = 0.724 \text{ (average value)}$$

During the development work on this correlation, it was hoped that α_c would be an effective third parameter, i.e. in addition to P_r and T_r . Effects of α_c were not clearly enough defined, however, so a two parameter correlation was developed. The ratio $\Delta H/RT_c$ is dimensionless.

The isothermal pressure correction to the entropy was evaluated by the following expression:

$$\left(\frac{S - S^0}{R} + \ln P \right) = \frac{\Delta S'}{R} = \frac{P_c \alpha_c}{RT_c} \int_0^{P_r} \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r} dP_r \quad (27.2)$$

where: $\Delta S'$ = residual entropy

The ratio $\Delta S'/R$ is dimensionless. In these previous correlations, $\Delta H/RT_c$ and $\Delta S'$ were given as functions of P_r and T_r . The dimensionless terms $\Delta H/RT_c$ and $\Delta S'/R$ could have been used with slight changes in the ordinates.

An evaluation study showed that the ΔH correlation was superior to any other two parameter generalized correlation available at that time for predicting the isothermal effect of pressure. Between 1955 and 1960, two three parameter generalized correlations were proposed^{2, 3, 4} for predicting the effects of pressure on the entropy and enthalpy.

Lydersen-Greenhorn-Hougen Correlation. A compressibility factor correlation, involving the three parameters T_r , P_r and Z_c , served as the basis for the computation of the effects of pressure on entropy and enthalpy in some very important work that appeared in 1955.² Tables and plots giving compressibility factors and other thermodynamic properties were given as functions of P_r ,

