Reprinted from JOURNAL OF CHEMICAL & ENGINEERING DATA, Vol. 11, No. 2, April 1966, Page 202
Copyright 1965 by the American Chemical Society and reprinted by permission of the copyright owner
1351

Coefficient of Thermal Expansion

Reduced State Correlation Developed form Ethane *PVT* Data

CHARLES E. HAMRIN, JR.[1], and GEORGE THODOS
Northwestern University, Evanston, Ill.

PVT data available in the literature for ethane in the gaseous and liquid states have been utilized to develop a reduced state correlation for the dimensionless modulus, βT_c in terms of T_R and P_R. The coefficient of thermal expansion is defined by the thermodynamic relationship, $\beta = (1/V)(\partial V/\partial T)_P$. At low pressures, the modulus βT_c approaches $1/T_R$, which represents ideal gas behavior. For the critical isotherm, this quantity increases rapidly with P_R, becoming infinite at the critical pressure, and steadily decreases for $P_R > 1.0$. The correlation developed in this study is applicable to nonpolar substances having critical compressibility factors comparable to that of ethane, $z_c = 0.285$.

THE coefficient of thermal expansion, β, is a thermodynamic property of gases and liquids, which finds direct application in natural convective heat transfer processes. Heat transfer studies of this type are identified by the dimensionless Grashof number, $Gr = \rho^2 g b^3 \beta \Delta T/\mu^2$. The physical properties ρ and μ included in this modulus have been studied extensively and have been presented in reduced state correlations (*4, 5, 7, 19*). The coefficient of thermal expansion has been presented recently as a reduced state correlation by Damasius and Thodos (*6*), who utilized *PVT* data for argon in the gaseous and liquid states. Their final correlations were presented in terms of the dimensionless quantities, βT_c, T_R, and P_R. In their work, argon was selected as representative of substances which have a simple molecular structure and which are characterized by a critical compressibility factor, $z_c \approx 0.291$. These substances include the monatomic gases argon, krypton, and xenon; the diatomic gases, nitrogen, oxygen, and carbon monoxide; and the hydrocarbon, methane. An extension of this work using ethane as a reference substance has been carried out in this study. Ethane was selected because its molecular structure is more complex than that of argon and also because it has a critical compressibility factor, $z_c = 0.285$.

REDUCED STATE CORRELATION FOR ETHANE

A comprehensive literature survey made by Phillips and Thodos (*11*) resulted in the development of a reduced density correlation for ethane applicable for the gaseous and liquid regions. Ten references supplied the pertinent *PVT* data for ethane (*1, 2, 3, 8, 9, 10, 15, 16, 18, 20*), which permitted the construction of a reduced density correlation for temperatures up to $T_R = 2.0$ and pressures up to $P_R = 14$. In the original, the correlation includes the basic density data utilized for its development. A reproduction of this ethane reduced density correlation is presented in Figure 1 with the experimental points deleted for the sake of clarity. For the regions of the compressed liquid phase and the dense gaseous phase for which no data are available, the isobars in Figure 1 are presented as dashed lines.

The coefficient of thermal expansion of a pure substance is defined as follows:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad (1)$$

To develop a generalized correlation for this property, Equation 1 can be expressed in terms of the dimensionless parameters of density and temperature as follows:

---

[1] Present address: Union Carbide Nuclear Division Y-12 Plant, Oak Ridge, Tenn.

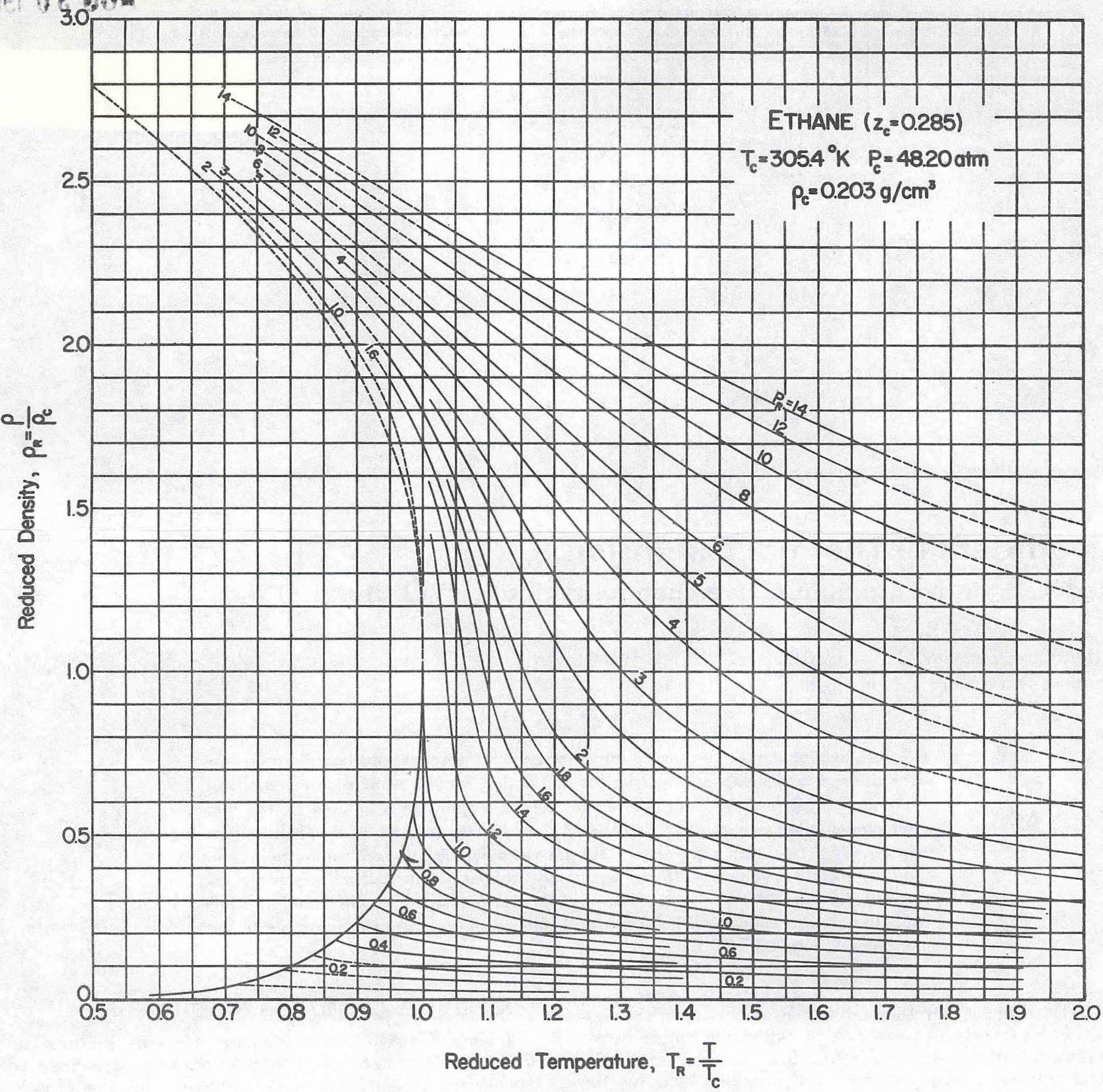

Figure 1. Reduced density behavior of ethane

$$\beta T_c = -\frac{1}{\rho_R}\left(\frac{\partial \rho_R}{\partial T_R}\right)_{P_R} \tag{2}$$

Equation 2 indicates that βT_c should depend on the independent variables reduced temperature and reduced pressure. Since ρ_R also depends on the third parameter, z_c, it follows that βT_c is also dependent on this parameter. Another correlating parameter, ω, the acentric factor, introduced by Pitzer (*12, 13*) has been employed to characterize the *PVT* behavior of a number of nonpolar substances. This parameter is defined as follows:

$$\omega + 1 = -\log P_R \tag{3}$$

where P_R represents the reduced vapor pressure of the substance at $T_R = 0.70$. Riedel (*14, 17*) has introduced still another characterizing parameter, similar to the acentric factor, defined as follows:

$$\alpha_c = \left(\frac{\mathrm{dln}\, P_R}{\mathrm{dln}\, T_R}\right)_{T_c} \tag{4}$$

In Equation 4, α_c represents the slope of the vapor pressure curve in reduced coordinates, $\ln P_R$ *vs.* $\ln T_R$ at the critical point. These three characterizing parameters, z_c, ω, and α_c, are related to each other and possess the ability to characterize nonpolar substances.

Values of the reduced density obtained from each isobar of an enlarged plot of Figure 1 were graphically differentiated with respect to the corresponding reduced temperature to produce the negative quantity $(\partial\rho_R/\partial T_R)_{P_R}$ for various reduced temperatures. Thus, the quantity, βT_c was calculated from Equation 2, for each reduced temperature and pressure for which this partial derivative was obtained, by dividing each derivative by the corresponding reduced density. In order to present the quantity βT_c on log-log coordinates, reduced pressure was chosen as the abscissa for parameters of constant reduced temperature, as shown in Figures 2 and 3. In these figures, the reduced pressure extends up to $P_R = 14$ and the reduced temperature up to $T_R = 2.0$. To avoid confusion in reading values of βT_c, two figures were necessary to express the dependence of this

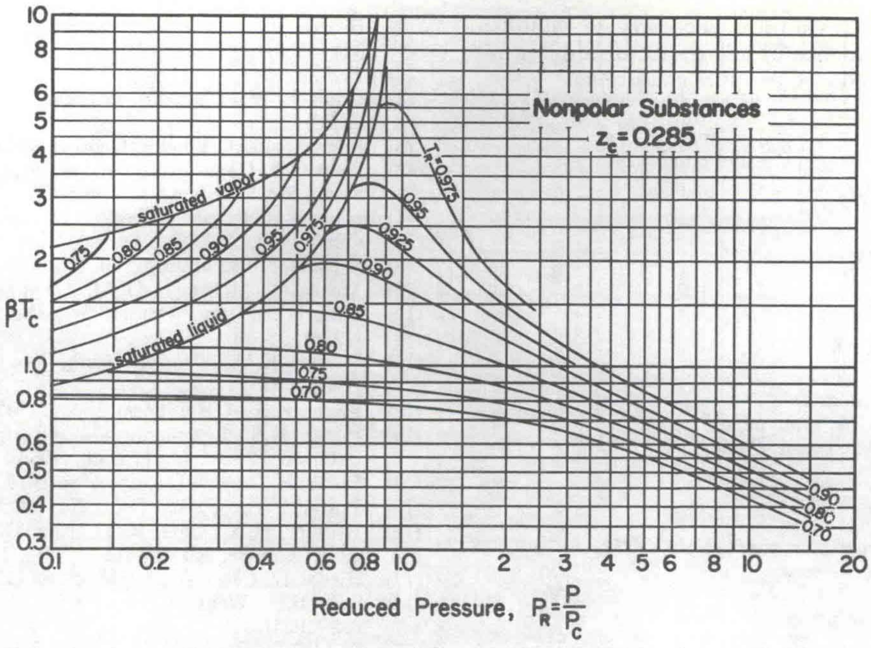

Figure 2. Reduced state correlation for the coefficient of thermal expansion of fluids ($0.7 \leqq T_R < 1.0$)

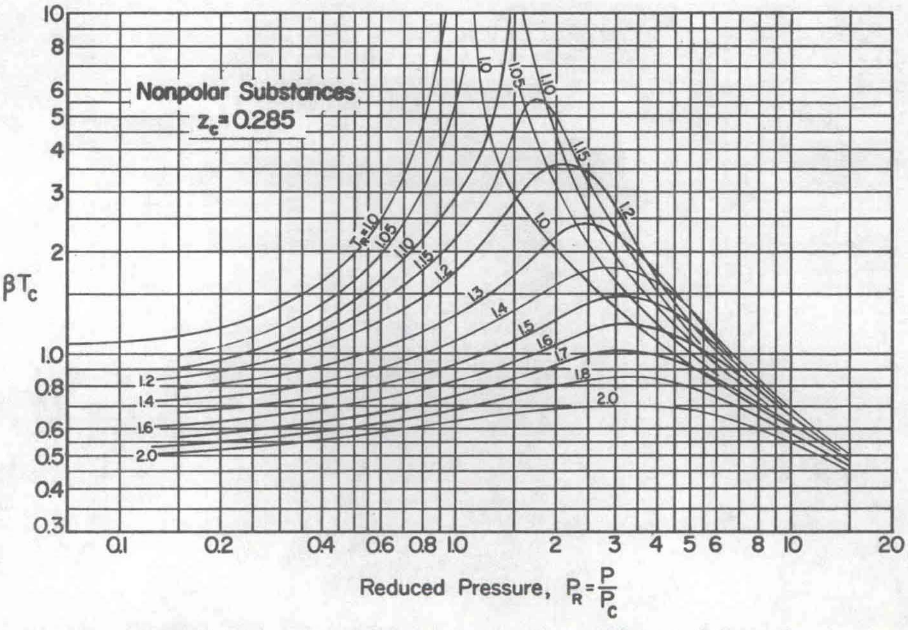

Figure 3. Reduced state correlation for the coefficient of thermal expansion of fluids ($1.0 \leqq T_R \leqq 2.0$)

quantity on reduced temperature and reduced pressure.

For reduced temperatures of $T_R < 1.00$, the isotherms for the gaseous and liquid states terminate at the saturation envelope, as shown in Figure 2. For the isotherms of the gaseous state, the limiting value at low reduced pressures becomes $\beta T_c = 1/T_R$. For the isotherms, $1.0 \leqq T_R \leqq 2.0$, the reduced state correlation of βT_c of the fluid state is expressed in Figure 3. This figure presents a series of isotherms, each exhibiting a maximum which decreases continuously as reduced temperature increases. For the critical isotherm, $T_R = 1.00$, the maximum becomes infinite; for $T_R = 2.00$, the entire isotherm becomes a curve of a slowly changing slope. As pointed out for Figure 2, at low reduced pressures βT_c again approaches the idealized value of $1/T_R$ for the isotherms $1.0 \leqq T_R \leqq 2.0$ of Figure 3. Thus, the use of Figures 2 and 3 permits the rapid determination of the quantity, βT_c, over a broad range of temperatures and pressures.

The information presented in these figures, although developed from ethane *PVT* data, should be applicable to other substances having the same critical compressibility factor of $z_c \approx 0.285$. The βT_c plots developed from ethane data and those developed from argon data (*6*) have been compared. In general, the variation of βT_c with reduced pressure is quite similar, although some differences between these two representative substances are noted, particularly for reduced temperatures of $T_R < 1.0$ This similarity is to be expected since the critical compressibility factors of argon and ethane are not appreciably different. For substances of z_c values in the range, $0.23 < z_c < 0.25$, it is expected that the deviation of their βT_c values to those corresponding to ethane will become more pronounced. Further work dealing with substances of lower z_c values is necessary to establish quantitatively the dependence of βT_c on z_c for similar reduced temperature and reduced pressure conditions.

NOMENCLATURE

b = characterizing dimension in Grashof number
g = acceleration of gravity
Gr = Grashof number, $\rho^2 g b^3 \beta \Delta t / \mu_2$
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant
T = temperature, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c
V = volume, cm.^{3} per gram mole
v_c = critical volume, cm.^{3} per gram mole
z_c = critical compressibility factor, $P_c v_c / R T_c$

GREEK

α_c = Riedel parameter
β = coefficient of thermal expansion, $(1/V)(\partial V/\partial T)_P$
μ = viscosity, grams per cm. sec.
ρ = density, grams per cc.
ρ_c = critical density, grams per cc.
ρ_R = reduced density, ρ/ρ_c
ω = acentric factor

LITERATURE CITED

(1) Beattie, J.A., Hadlock, Cawfield, Poffenberger, Noland, *J. Chem. Phys.* **3**, 93 (1935).
(2) Beattie, J.A., Su, G.J., Simard, G.L., *J. Am. Chem. Soc.* **61**, 924 (1939).
(3) *Ibid.*, p. 926.
(4) Brebach, W.J., Thodos, George, *Ind. Eng. Chem.* **50**, 1095 (1958).
(5) Byrne, Robert, Thodos, George, *A.I.Ch.E. J.* **7**, 185 (1961).
(6) Damasius, Gediminas, Thodos, George, *Chem. Eng. Progr., Symp. Ser.* **59**, No. 44, 42 (1963).
(7) Hamrin, C.E., Jr., Thodos, George, *A.I.Ch.E. J.* **4**, 480 (1958).
(8) Kuenen, J.P., *Phil. Mag.* **40**, 173 (1895).
(9) Maass, O., McIntosh, D., *J. Am. Chem. Soc.* **36**, 737 (1914).
(10) Michels, A., van Straaten, W., Dawson, J., *Physica* **20**, 17 (1954).
(11) Phillips, E.M., Thodos, George, *Soc. Petrol. Engrs. J.* **2**, 83 (1962).
(12) Pitzer, K.S., *J. Am. Chem. Soc.* **77**, 3427 (1955).
(13) Pitzer, K.S., Lippmann, D.Z., Curl, R.F., Huggins, C.M., Petersen, D.E., *Ibid.*, **77**, 3433 (1955).
(14) Plank, R., Riedel, L., *Ing.-Arch.* **16**, 255 (1948).
(15) Porter, Frank, *J. Am. Chem. Soc.* **48**, 2055 (1926).
(16) Reamer, H.H., Olds, R.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **36**, 956 (1944).
(17) Riedel, L., *Chem. Ingr. Tech.* **26**, 83 (1954).
(18) Sage, B.H., Webster, D.C., Lacey, W.N., *Ind. Eng. Chem.* **29**, 658 (1937).
(19) Shimotake, Hiroshi, Thodos, George, *A.I.Ch.E. J.* **4**, 257 (1958).
(20) Yee, Edward G., Ph.D. dissertation, University of Michigan, Ann Arbor, Mich., 1936.

Received for review June 21, 1965. Accepted January 24, 1966.