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Reduced State Correlation for the Enskog Modulus Developed from *PVT* Data for Ethane

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PVT data available in the literature for ethane have been utilized to establish the Enskog modulus, $b\rho\chi$, for reduced temperatures up to T_R = 2.0 and reduced pressures up to P_R = 15 for both the gaseous and liquid states. This modulus can be applied to account for the effect of pressure on viscosity, thermal conductivity, and self-diffusivity. The value of this modulus at the critical point has been established from the PVT data to be $(b\rho\chi)_c$ = 0.784 and is identical to the value resulting from the relationship $(b\rho\chi)_c = \alpha_c z_c - 1$. The resulting reduced state correlation should be applicable to substances having critical compressibility factors similar to ethane (z_c = 0.285).

PRESENT interest in the calculation of the transport properties of substances in their dense gaseous and liquid states has been expressed along the lines proposed by Enskog (*6*). The model considered by Enskog involved collisions between rigid spherical molecules. For this idealized system, the effect of pressure on viscosity, thermal conductivity, and self-diffusivity was:

$$\frac{\mu}{\mu^*} = b\rho\left[\frac{1}{b\rho\chi} + \frac{4}{5} + 0.7614\, b\rho\chi\right] \tag{1}$$

$$\frac{k}{k^*} = b\rho\left[\frac{1}{b\rho\chi} + \frac{6}{5} + 0.7574\, b\rho\chi\right] \tag{2}$$

$$\frac{(\rho\Delta)}{(\rho\Delta)} = \frac{b\rho}{b\rho\chi} \tag{3}$$

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where $b = (2\pi\sigma^3/3m)$ for rigid spherical molecules and χ is a correction factor accounting for the probability of collisions. These relationships require that $b\rho\chi$, the Enskog modulus, be known at the conditions of temperature and pressure for which the transport properties of the substance are desired. The Enskog modulus is defined by the equation of state:

$$P + a\rho^2 = \frac{RT}{M}\left[1 + b\rho\chi\right] \tag{4}$$

from which the following relationship results with the assumption that a and b are constant:

$$b\rho\chi = \frac{M\rho}{R}\left(\frac{\partial P}{\partial T}\right)_\rho - 1 \tag{5}$$

Equation 5 can be expressed in terms of reduced variables to give:

$$b\rho\chi = \frac{z_c}{\rho_R}\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} - 1 \tag{6}$$

Therefore, to obtain values of $b\rho\chi$, one must have complete PVT data of the substance corresponding to the pressure and temperature conditions. Since Equation 6 defines the quantity, $b\rho\chi$, in terms of reduced variables, a correlation of this type should be applicable to substances having similar PVT behavior. Lydersen, Greenkorn, and Hougen (*10*) utilized the critical compressibility factor, z_c, as a criterion of similarity for the PVT behavior of substances. Hamrin and Thodos (*8*) have verified this conclusion for the monatomic gases, argon, krypton, and xenon, and Byrne and Thodos (*4*) have extended this concept to include the diatomic gases, nitrogen, oxygen, and carbon monoxide. For these monatomic and diatomic gases, z_c ranges from 0.294 for carbon monoxide to 0.290 for xenon.

Using PVT data available for argon in the gaseous and liquid states, Damasius and Thodos (*5*) developed a correlation of the Enskog modulus, $b\rho\chi$, in terms of reduced temperature and pressure. The resulting correlation for argon is representative of the class of substances having values of $z_c \approx 0.291$. An extension of this study to substances of lower z_c values should be of value in further applications of the Enskog approach to the transport properties of substances. In this regard, it appears appropriate to consider a typical hydrocarbon for which sufficient experimental PVT data are available. The PVT behavior of ethane has been extensively studied by Phillips and Thodos (*13*), who utilized the available experimental data of 10 references (*1-3, 9, 11, 12, 14, 15, 17, 19*) to compile reduced density correlations in rectilinear and logarithmic coordinates.

DEVELOPMENT OF REDUCED STATE CORRELATION

The rectilinear reduced state correlation for ethane provided exacting reduced values in the dense gaseous and liquid phases, whereas the log-log plot proved useful in the lower density region. Using both of these correlations, isochors were plotted as reduced pressure *vs.* reduced temperature relationships. These relationships are nearly linear, and all terminate at the reduced vapor pressure curve. However, the critical isochor becomes an extension of the vapor pressure function beyond the critical point. Figure 1 presents the isochors of ethane for reduced densities ranging from $\rho_R = 0.10$ for the gaseous state up to $\rho_R = 2.5$ for the liquid state. The range of reduced temperature covered extends up to $T_R = 2.0$ and of reduced pressure, up to $P_R = 15$.

The isochors of Figure 1 were graphically differentiated to obtain values of the slope, $(\partial P_R/\partial T_R)_{\rho_R}$, for a complete range of temperatures and pressures. These values, with $z_c = 0.285$ and the corresponding reduced densities, enabled the establishment of the Enskog modulus according to Equation 6. Values of the Enskog modulus obtained in this manner were plotted against reduced temperature for constant reduced pressures (Figure 2). In this figure, the reduced temperature extends up to $T_R = 2.0$ and the reduced pressure up to $P_R = 15$. This correlation is most useful for establishing the transport properties in the dense gaseous and liquid regions of ethane. Another representation of the Enskog modulus, $b\rho\chi$, is presented in the log-log plot of Figure 3. In this figure, $b\rho\chi$ is plotted against reduced pressure for parameters of constant reduced temperature. Figure 3 is most useful in the low density region for reduced pressures as low as $P_R = 0.3$ and reduced temperatures of $T_R = 0.80$. Used in combination, Figures 2 and 3 should give reliable $b\rho\chi$ values over the entire temperature and pressure range for which density data have been reported. To test the accuracy of values obtained from Figures 2 and 3, the PVT data of Michels, van Straaten, and Dawson (*12*) for ethane were numerically differentiated to obtain $b\rho\chi$ values. These values ranged in temperature from $T_R = 0.894$ to $T_R = 1.39$ and pressures up to $P_R = 4.5$. Corresponding values obtained from Figures 2 and 3 were in agreement within 5% for 56 points examined.

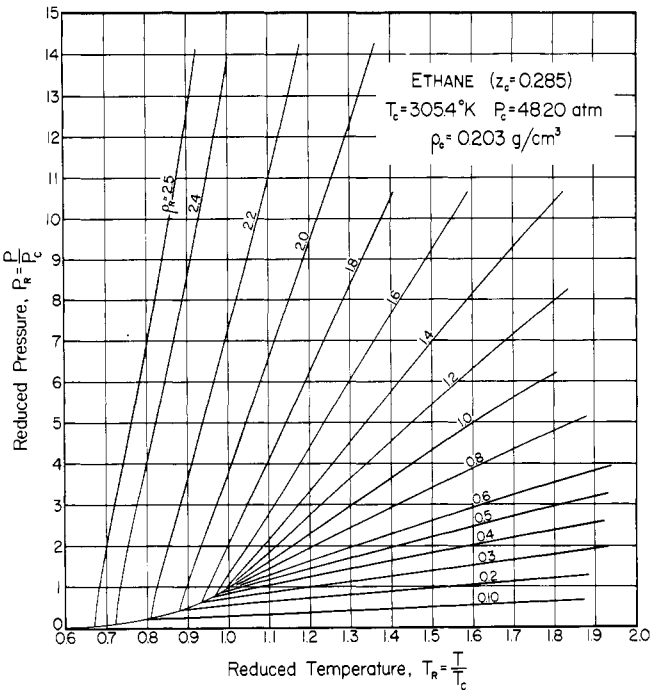

Figure 1. Isochoric relationships between reduced pressure and reduced temperature for ethane

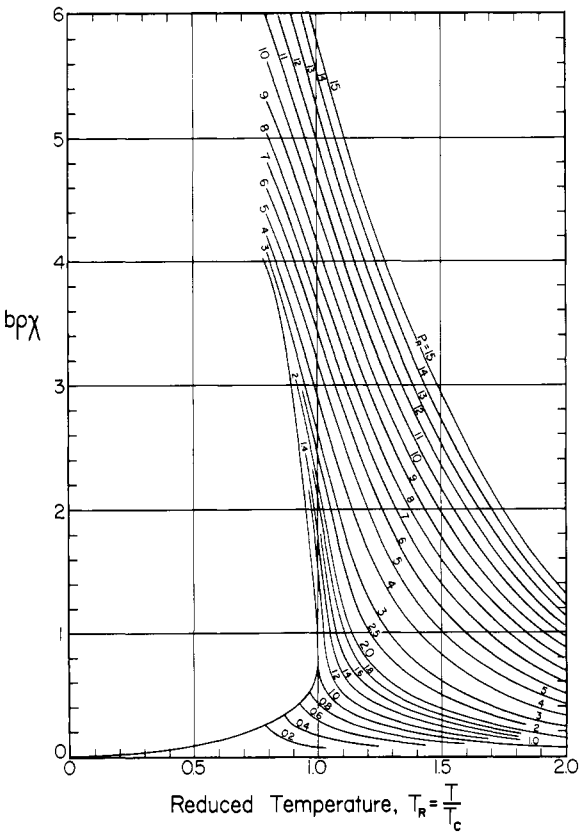

Figure 2. Relationships between the Enskog modulus, $b\rho\chi$, and reduced temperature for parameters of reduced pressure (z_c = 0.285)

ENSKOG MODULUS AT THE CRITICAL POINT

From the graphical procedure outlined for the development of this correlation, the Enskog modulus at the critical

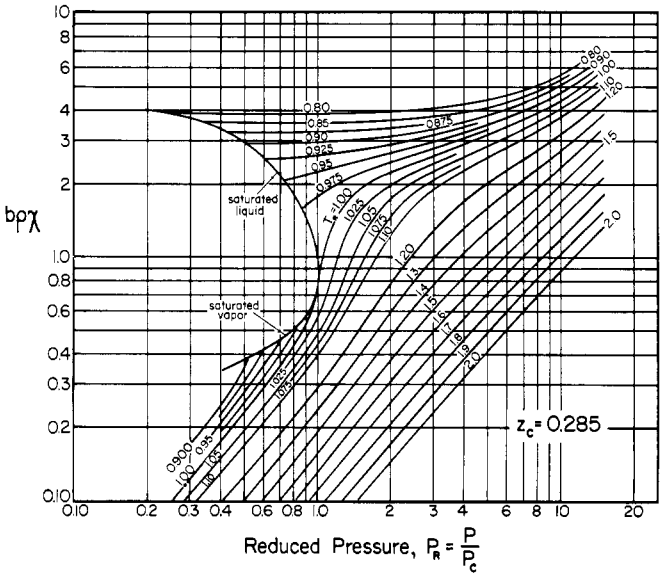

Figure 3. Correlation of the Enskog modulus, $b\rho\chi$, with reduced pressure and reduced temperature (developed from *PVT* data of ethane)

point was $(b\rho\chi)_c = 0.784$. Damasius and Thodos (*5*) have shown that the Enskog modulus at the critical point is

$$(b\rho\chi)_c = \alpha_c z_c - 1 \tag{7}$$

where $\alpha_c = (\partial P_R/\partial T_R)_{\rho\chi=1.00}$, the Riedel parameter at the critical point (*16*). The Riedel parameter, $\alpha = d \ln P/d \ln T$, defined along the vapor pressure curve, can be evaluated from the Frost-Kalkwarf vapor pressure equation (*7*):

$$\log P = A + (B/T) + C \log T + D\,(P/T^2) \tag{8}$$

Expressing Equation 8 in reduced form and differentiating the resulting vapor pressure equation, the Riedel parameter becomes:

$$\alpha = \frac{T_R}{P_R}\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_c} = \frac{\gamma - 2.303\beta - 0.8438 P_R/T_R^2}{1 - 0.4219\, P_R/T_R^2} \tag{9}$$

where $\beta = B/T_c$ and $\gamma = C$. Since at the critical point, $T_R = 1.0$ and $P_R = 1.0$, Equation 9 reduces to:

$$\alpha_c = \frac{\gamma - 2.303\beta - 0.8438}{0.5781} \tag{10}$$

For ethane, Sondak and Thodos (*18*) present the following values: $B = -1070.59$, $C = -3.60963$, and $T_c = 305.465°$ K. Therefore, $\beta = -1070.59/305.465 = -3.50479$, and $\gamma = -3.60963$. Substituting these values into Equation 10, the Riedel parameter at the critical point becomes $\alpha_c = 6.259$. Lydersen, Greenkorn, and Hougen (*10*) report for ethane a value of $\alpha_c = 6.28$. Substituting $\alpha_c = 6.259$ and $z_c = 0.285$ into Equation 7, the Enskog modulus at the critical point becomes

$$(b\rho\chi)_c = (6.259)(0.285) - 1 = 0.784$$

This calculated value of $(b\rho\chi)_c$ is identical to that derived from the graphical approach.

GENERAL REMARKS

Although Figures 2 and 3 have been developed from *PVT* data for ethane, their use need not be limited to this hydrocarbon. These figures should also be applicable to substances having critical compressibility factors, $z_c \approx$ 0.285. This study presents an extension for the evaluation of the Enskog modulus which has been based on the *PVT* behavior of a more complex molecule than argon.

NOMENCLATURE

a, b	=	constants for Enskog equation of state, Equation 4
A, B, C, D	=	constants for vapor pressure equation, Equation 8
k	=	thermal conductivity, cal./sec. cm. ° K.
k^*	=	thermal conductivity at normal pressures, cal./sec. cm. ° K.
m	=	mass per molecule, g.
M	=	molecular weight
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_c	=	critical molar volume, cc./g.-mole
z_c	=	critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α	=	Riedel parameter, $d \ln P/d \ln T$
α_c	=	Riedel parameter at critical point
β	=	constant for reduced vapor pressure equation, B/T_c
γ	=	constant for reduced vapor pressure equation, C
Δ	=	self-diffusivity, sq. cm./sec.
Δ^*	=	self-diffusivity at normal pressures. sq. cm./sec.
μ	=	viscosity, g./cm. sec.
μ^*	=	viscosity at normal pressures, g./cm. sec.
π	=	constant, 3.1416
ρ	=	density, g./cc.
ρ^*	=	density at normal pressures, g./cc.
ρ_c	=	critical density, g./cc.
ρ_R	=	reduced density, ρ/ρ_c
σ	=	collision diameter, cm.
χ	=	factor for probability of collisions

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