Reduced State Correlation for the Enskog Modulus of Normal Hydrogen

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PVT data available in the literature for normal hydrogen were used to produce a reduced density correlation which served as a basis to establish the Enskog modulus, $b\rho\chi$, for reduced temperatures up to $T_R = 40$ and reduced pressures to $P_R = 100$ for both the gaseous and liquid states. This modulus can be used to account for the effect of pressure on the transport properties of this substance. The value of this modulus at the critical point has been established from the PVT data to be $(b\rho\chi)_c = 0.57$. A method is outlined that permits the establishment of reliable $b\rho\chi$ values in the less dense gaseous region and also enables the calculation of the second virial coefficient, b, at zero density and σ, the collision diameter of hydrogen. The resulting reduced state correlation is expressed in terms of $1 + b\rho\chi$.

ONE OF the recent advances in the space program has resulted from the introduction of hydrogen as a booster propellant. Consequently, technical information must be made available on the thermodynamic and transport properties of this substance. The theoretical developments of Enskog (*1*) published in 1922 present the first attempt to account for the effect of pressure on the transport properties of dense gases and liquids. The model considered by Enskog involved collision between spherical molecules. For this idealized system, the effect of pressure on viscosity, thermal conductivity, and self-diffusivity was found to be:

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

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

$$\frac{(\rho D)}{(\rho D)^*} = \frac{b\rho}{b\rho\chi} \tag{3}$$

where $b = 2\pi N\sigma^3/3$ 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:

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

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

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

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

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

Following a statistical mechanical approach, Rice, Kirkwood, Ross, and Zwanzig (*5*) and Snider and Curtiss (*7*) developed equations for the transport properties comparable to those developed by Enskog. The Enskog modulus, $b\rho\chi$, should prove useful in checking the adequacy of these theories to account for the effect of pressure on the transport properties.

To generate values of the quantity $1 + b\rho\chi$, the reduced density correlation of Schaefer and Thodos (*6*) for normal hydrogen was used. From this correlation, constant density relationships of P_R *vs.* T_R were first established. Because of the wide range of reduced pressure, it became necessary to treat different regions separately. The isochoric relationships of P_R *vs.* T_R are presented in Figure 1 for reduced densities, $\rho_R \leqq 1.00$. These gaseous isochors possess a slight curvature and terminate on the vapor pressure curve. The isochor $\rho_R = 1.00$ is an extension of the vapor pressure curve beyond the critical point. Figure 2 presents the P_R *vs.* T_R relationships for reduced densities in the range $2.70 \leqq \rho_R \leqq$

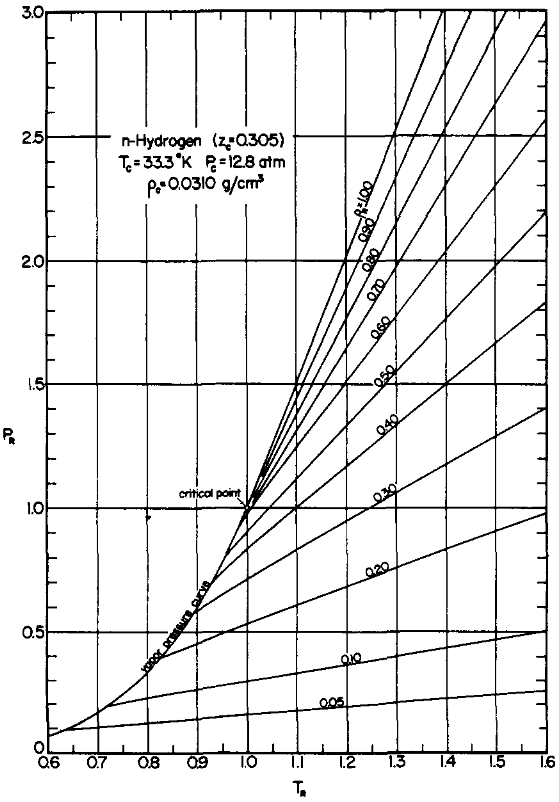

Figure 1. Isochoric relationships between P_R and T_R for normal hydrogen at reduced densities $\rho_R \leqq 1.00$

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1.00. These relationships also exhibit curvature, and terminate at either the vapor pressure curve or the solid-liquid line.

The isochors from large plots of Figures 1 and 2 were differentiated graphically to obtain values of the slope, $(\partial P_R/\partial T_R)_{\rho_R}$, for a complete range of temperatures and pressures. These values, along with $z_c = 0.305$ and corresponding reduced densities, enabled the establishment of the Enskog modulus according to Equation 6. Values of $1 + b\rho\chi$ obtained in this manner for each isochor were plotted against P_R to produce relationships which terminated on the saturated envelope. This approach included all the isochors from $\rho_R = 0.05$ up to $\rho_R = 2.70$. By using Figures 1 and 2, convenient reduced isotherms were introduced to produce the final correlation presented in Figure 3. In this figure the reduced density lines have been eliminated for the sake of clarity and the quantity $1 + b\rho\chi$ is related to P_R for constant reduced temperature lines. The quantity $1 + b\rho\chi$ was used as the correlating variable, since for the gaseous state it becomes unity at low pressures and approaches the value expected from ideal gas behavior. At the critical point, the Enskog modulus has been found to be $(b\rho\chi)_c = 0.57$.

Since the compilation of Schaefer and Thodos (*6*) appeared in the literature, additional *PVT* data on normal hydrogen were published by Michels *et al.* (*4*). The only values presented by Michels *et al.* not covered by the several other investigators lie between $T_R = 3.0$ and $T_R = 6.0$ and above $P_R = 15$. The 46 experimental values of Michels *et al.* in this region were compared with values obtained from the density isotherms generated by Schaefer and Thodos (*6*) and produced an average deviation of 1.2%. In view of this good agreement, it can be concluded that the experimental data of Michels *et al.* will reproduce the $b\rho\chi$ values presented in Figure 3.

Dependable values of $b\rho\chi$ can be obtained from Figure 3 for the dense gaseous and liquid regions. However, because of the converging nature of the isotherms in the moderate pressure region, the resulting $b\rho\chi$ values do not possess the desired accuracy. To obtain reliable values in the moderate

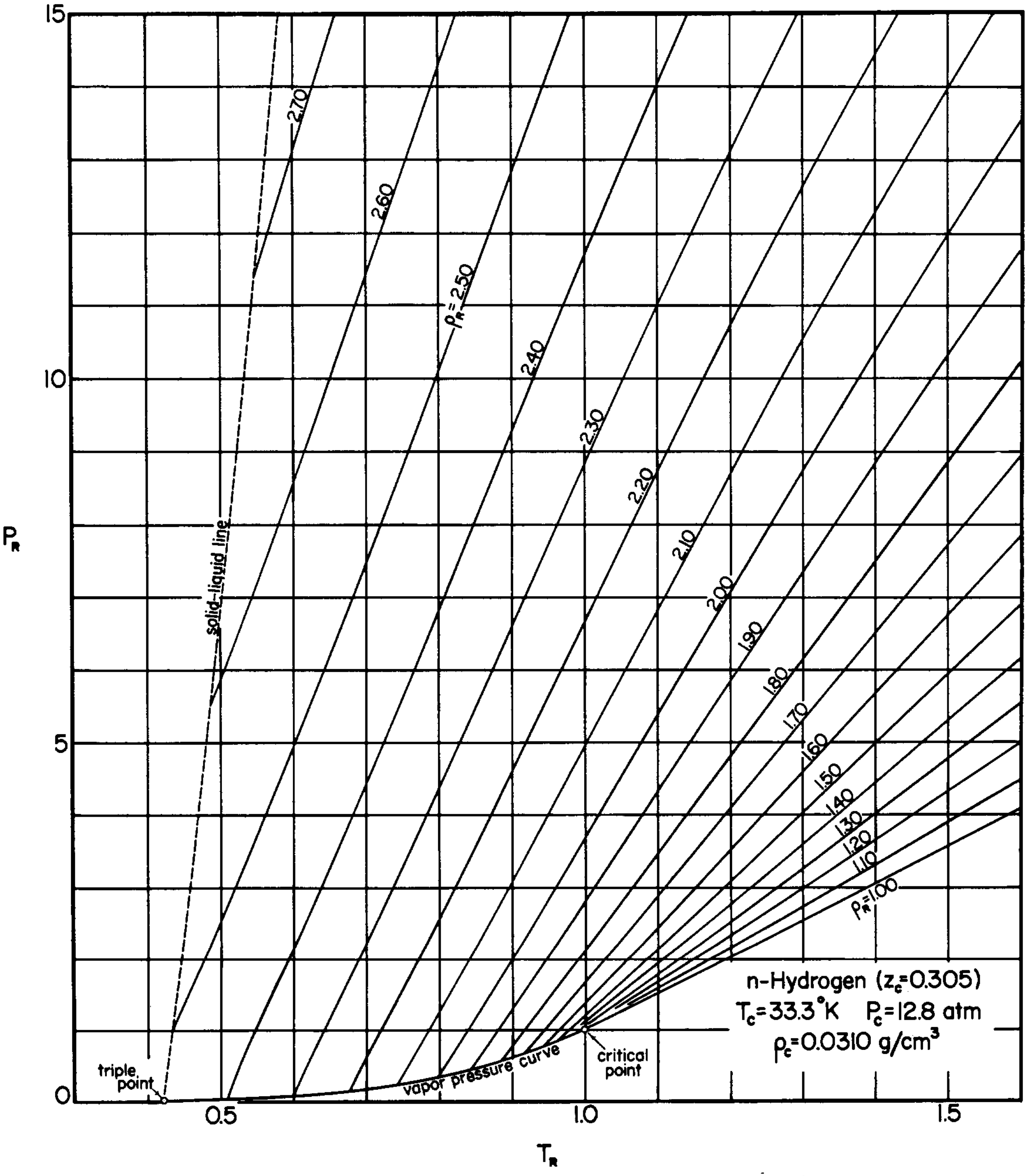

Figure 2. Isochoric relationships between P_R and T_R for normal hydrogen at reduced densities

$\rho_R \geqq 1.00$

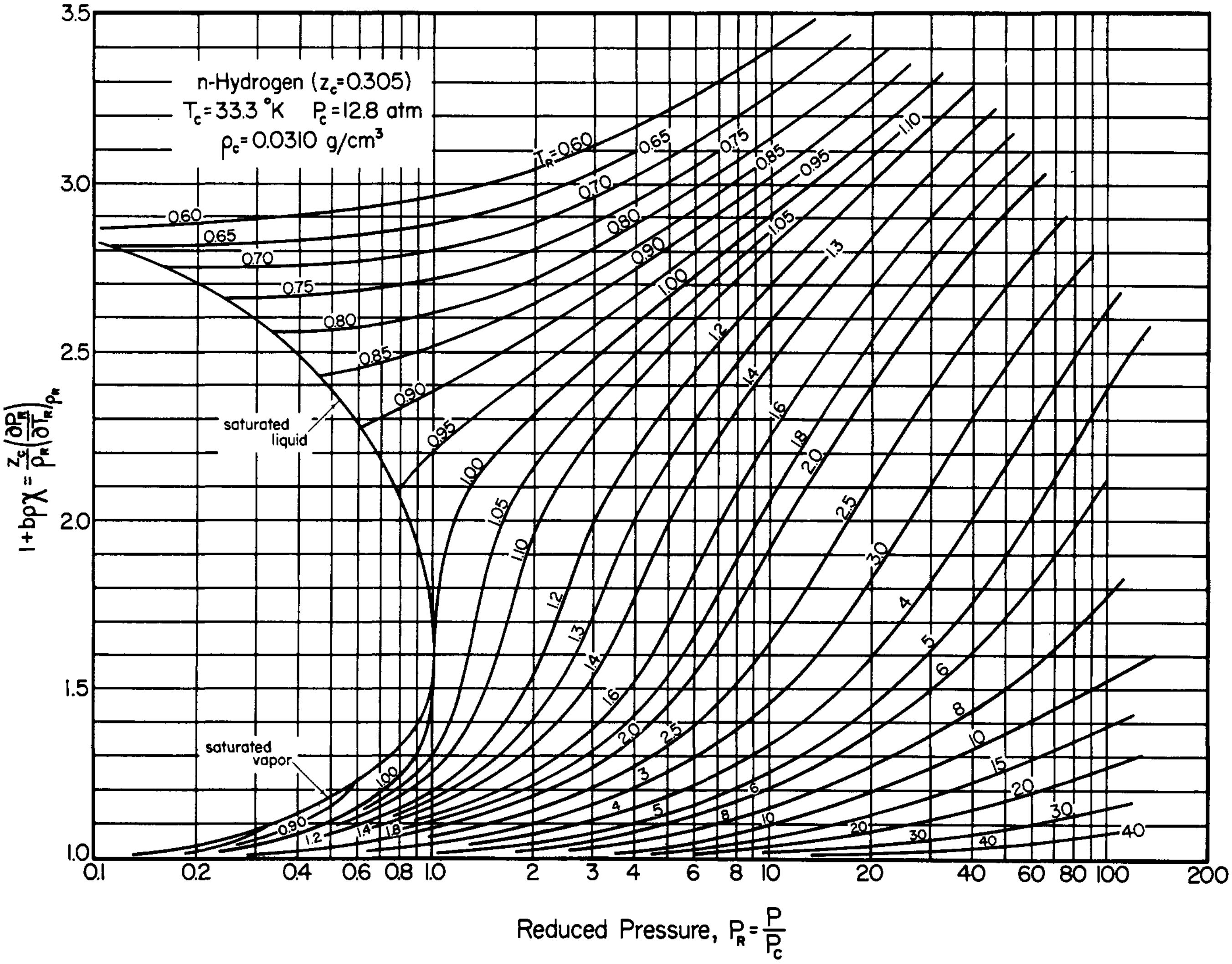

Figure 3. Reduced state correlation of the Enskog modulus, $b\rho\chi$, for normal hydrogen

pressure vicinity, the following approach is recommended. Values of $b\rho\chi$ at isothermal conditions are obtained over a wide range of pressures which extend into the dense gaseous region. A plot of these $b\rho\chi$ values in the dense gaseous region as the ratio $b\rho\chi/\rho_R$ *vs.* ρ_R produces straight-line relationships for each temperature which allow extrapolation to $\rho_R = 0$. This approach has been applied by Hamrin (*2*) to obtain reliable $b\rho\chi$ values at moderate pressures in an experimental thermal conductivity study carried out at 1.6°, 25.0°, 50.2°, and 74.6° C. (Figure 4). The four isothermal relationships of Figure 4 are linear in the dense gaseous region, where $b\rho\chi$ values are of adequate accuracy and allow extrapolation to $\rho_R = 0$. At $\rho_R = 0$, the ratio $b\rho\chi/\rho_R$ becomes $b\rho_c$, and therefore permits the direct establishment of b, the second virial coefficient, at each temperature. For these temperatures, the intercepts yield the following values of b, from which the associated collision diameters for hydrogen result:

t, ° C.	b, Cc./G.-Mole	σ, Cm.
1.6	29.1	2.85 × 10^{-8}
25.0	28.0	2.81
50.2	26.4	2.76
74.6	26.2	2.75
	27.4	2.79

The average values are in good agreement with those presented by Hirschfelder, Curtiss, and Bird (*3*), who report b = 29.76 cc./gram-mole and σ = 2.87 × 10^{-8} cm.

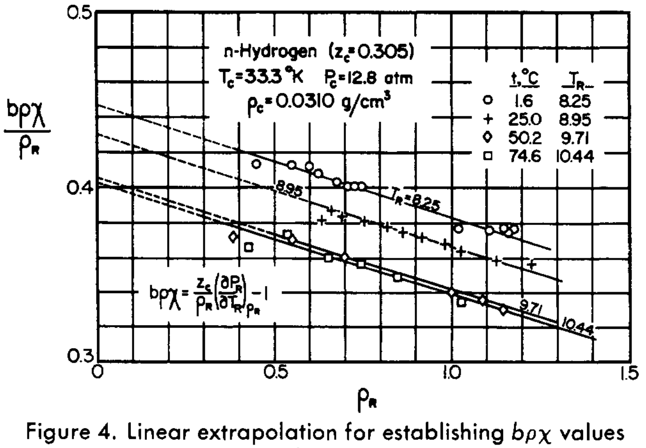

Figure 4. Linear extrapolation for establishing $b\rho\chi$ values at very low pressures

NOMENCLATURE

a, b = constants for Enskog equation of state
$b\rho\chi$ = Enskog modulus
k = thermal conductivity, cal./sec. cm. ° K.
k^* = thermal conductivity at 1 atm., cal./sec. cm. ° K.
M = molecular weight
N = Avogadro number, 6.02 × 10^{23} molecules/gram-mole
P = pressure, atm.
P_c = critical pressure atm.
P_R = reduced pressure, P/P_c
R = gas constant
t = temperature, ° C.
T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c

v = molar volume, cc./gram-mole
v_c = critical volume, cc./gram-mole
z_c = critical compressibility factor, $P_c v_c / RT_c$

Greek

D = self-diffusivity, sq. cm./sec.
μ = viscosity, g./cm. sec.
μ^* = viscosity at atmospheric pressure, g./cm. sec.
π = constant, 3.14159
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
σ = collision diameter, cm.
χ = probability of nearness

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Thermodynamic Properties of Uranium Carbides via the U-C-O System

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Equilibrium data of Piazza and Sinnott in the systems UO_2-"UC_2"-C-CO and UO_2-"UC_2"-UC-CO have been recalculated using both second and third law treatments. Internal consistency is excellent for the first system and acceptable for the second. Third law treatments predict the heats of formation, ΔH°_{298}, "UC_2" and UC to be −20.5 and −23.2 kcal. per mole, respectively, in excellent agreement with combustion measurements. The "best" value of $\Delta H^\circ_{f,298}$ "UC_2" is −20.8° 0.7 kcal. per mole.

THE influence of oxygen on uranium dicarbide could be important in reactor technology. A panel assembled in Vienna in 1962 by the International Atomic Energy Agency (*7*) assumed the existence of an "oxygen-stabilized uranium dicarbide," UC_xO_y. It has been estimated that the free energy of formation of oxygen-saturated "UC_2" is about 5 kcal. more negative than that of the pure dicarbide (*7, 15*), from which arises the term "oxygen-stabilized."

Piazza and Sinnott studied equilibria in the system UO_2-"UC_2"-C-CO by measuring CO partial pressures (*14*). For their stated reaction

$$UO_2 + 4C = UC_2 + 2CO \qquad (1)$$

Piazza and Sinnott reported

$$\Delta F^\circ_T = 164{,}500 - 74.23\ T \pm 1200 \text{ cal. per gram-mole} \qquad (2)$$

over the range 1714° to 1922° K. The Vienna Panel stated that "the derived heats and entropies are rather unreasonable." This note points out that auxiliary thermal data are now available to treat these measurements of Piazza and Sinnott in the usual fashion; that the internal consistency of these data is excellent; that reasonable heats and entropies are obtained; and that the data, combined with other information, predict that any stabilization by oxygen must be less than a few hundred calories. We also treat data on the UO_2-"UC_2"-UC-CO system by the same authors (*14*).

Two methods are customarily used to treat data of the type obtained by Piazza and Sinnott: the second law slope-intercept treatment and the third law method which involves the use of free energy functions (*9*). We have used these standard methods and the CO partial pressures of Piazza and Sinnott to treat the reaction

$$UO_2 + 3.86C = UC_{1.86} + 2CO \qquad (3)$$

Following Piazza and Sinnott, we estimated the activity of $UC_{1.86}$ to be 0.95 in all experiments they performed and a_{UO_2} and a_C to be unity. Auxiliary data have been obtained as follows. Uranium oxide thermal functions were calculated from the data of Conway and Hein (*1*) combined with the data of Moore and Kelly (*13*). The heat of formation of UO_2, $\Delta H^\circ_{f,298}$, was taken to be −259.0 kcal. per mole from the compilation of Rand and Kubaschewski (*16*). All data on CO were taken from the JANAF tables (*2*). Data for C (graphite) were taken from the compilation of Stull and Sinke (*17*). Thermal functions for $UC_{1.86}$ were calculated from the data of Levinson (*12*). The low-temperature C_p data of Jones, Gordon, and Long (*8*) were used for UO_2. The data of Westrum *et al.* (*3, 18*) were used for $UC_{1.86}$ with a small (and insignificant) correction for composition plus a configuration entropy term.

For the second law treatment of Reaction 3 an average ΔC_p of 1.0 cal. °K.$^{-1}$ was computed over the temperature range 1700° to 2000° K. The resulting equation calculated was

$$\Delta F^\circ = 182{,}300 - 1.0\ T \ln T - 77.1\ T \text{ cal.} \qquad (4)$$

an equation which is cast in the form

$$\Delta F^\circ = \Delta H^\circ_{1800} - 1800(\overline{\Delta C}_p) - \overline{\Delta C}_p\ T \ln T + IT \qquad (5)$$

where I is the computed intercept (*9*). We suggest that Piazza and Sinnott made a numerical error in computing the least squares slope and intercept; our calculated line fits their data better. The internal consistency of the data for Reaction 3 is excellent, much better than might be expected considering the narrow temperature range and small number of measurements, as demonstrated by the following: