values of $\gamma^{\pm}$ at a particular molality being higher in a medium of higher dielectric constant, as expected from the Debye-Hückel equation, which essentially expresses the departure from the ideal behavior resulting from interionic electrostatic forces.

The occurrence of a minimum in the activity coefficients with increasing concentration is a general feature exhibited by electrolytes in any medium. Obviously, two opposing factors are operating, one tending to decrease and the other to increase the activity coefficient. The first factor is important at low concentrations, whereas the second one becomes predominant at higher concentrations. Apparently, a lower dielectric constant causes a relatively sharper minimum in the activity coefficient. But the dielectric constant of the medium is certainly not the determining factor. Figure 1 shows that in 90% glycol, the minimum is fairly well defined. At 25°C, this medium has nearly the same dielectric constant (43.7) as 40% dioxane. Results of the acivity coefficients of HCl in the dioxane-water mixture (*2*), however, show that even in 70% dioxane (D = 17.7), only a flat minimum is exhibited, which tends to become rather well defined (though less so than in 90% glycol) only when we go down to 82% dioxane (D = 9.5). For 0-70% glycol, the minimum occurs somewhere around 0.4*m* HCl, but at 90% glycol there appears to be a noticeable shift of the minimum toward a lower concentration. Recently (*5*), it has been seen that alkali-metal halides have minimum activity coefficients at relatively lower molalities in ethylene glycol than in water, and it has been suggested that solvation is stronger in ethylene glycol. Probably, this is also true for HCl in 90% glycol.

The activity coefficients of HCl at all concentrations decrease with increasing temperature in all the solvents. The case is similar when pure water is the solvent.

Acknowledgment

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Compressibility Factors of Nitrogen-Hydrogen Sulfide Mixtures

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Experimental compressibility factors were determined for two gas mixtures, one containing 8.6 mol % hydrogen sulfide and 91.4 mol % nitrogen and the other containing 22.2 mol % hydrogen sulfide, 76.5 mol % nitrogen, and 1.3 mol % carbon dioxide. Measurements were made at 20°, 40°, 60°, 80°, and 100°C at pressures to about 4500 psia. Second virial coefficients were calculated for both mixtures at each temperature. The experimental compressibility factors were compared with those calculated with the Benedict-Webb-Rubin equation of state. The root-mean-square difference was 0.81% for the 8.6 mol % mixture and 0.62% for the 22.2 mol % mixture.

The work reported in this paper represents part of a continuing study on the properties and phase behavior of binary systems containing hydrocarbons and related nonhydrocarbons. During the course of the study, it became increasingly evident that sets of independent experimental measurements on properties such as density, heat capacity, and equilibrium-phase compositions would be extremely helpful in equation-of-state development, parameter estimating, and related correlation efforts. Accordingly, a series of such measurements has been made on the equilibrium-phase properties of mixtures of nitrogen and hydrogen sulfide at five temperatures and up to 3000 psia, on the heat capacity of two mixtures of nitrogen and hydrogen sulfide at three temperatures and pressures to 2350 psia, and on the density of the same two mixtures at five temperatures and pressures to about 4500 psia. The density measurements are the subject of this paper.

Experimental Method

The experimental method used in this work was based on that proposed in 1936 by Burnett (*3*). Briefly, it consists of expanding the gas under investigation from a high-pressure chamber into an evacuated chamber at constant temperature and then successively continuing the expansions until a low enough pressure has been reached so that extrapolations can be made to zero pressure.

The experimental routine commences by filling chamber 1 to an initial pressure P_0. Chamber 2 is then evacuated, the temperature of the combined system is allowed to equilibrate, and the gas is expanded through a constant volume valve so that both chambers are filled. When the constant temperature has been restored, the pressure is measured, the constant volume valve is closed, and chamber 2 is again evacuated. This sequence is repeated so that a series of pressures, P_0, P_1, . . . P_{j-1}, P_j, is obtained for each experimental run at the chosen temperature.

The details of this procedure and the derivation of the equations necessary for determining the cell constant, the run constant, and the compressibility factor at each pressure have been presented by other workers (*3, 4, 6*).

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For convenience, some of the pertinent relationships are given here.

If V_1 and V_2 represent the volumes of chambers 1 and 2, the states of the gas prior to and at the jth expansion are given by:

$$P_{j-1}(V_1)_{j-1} = Z_{j-1}\cdot n_{j-1}\cdot RT_{j-1} \tag{1}$$

$$P_j(V_1 + V_2)_j = Z_j\cdot n_j\cdot RT_j \tag{2}$$

Since chamber 2 was evacuated prior to the jth expansion, $n_{j-1} = n_j$ and also $T_{j-1} = T_j$. Thus:

$$\frac{P_j(V_1 + V_2)_j}{P_{j-1}(V_1)_{j-1}} = \frac{Z_j}{Z_{j-1}} \tag{3}$$

By defining $V_1 + V_2/V_1$ as the cell constant N_j, the following is obtained:

$$\frac{P_j}{P_{j-1}} = \frac{1}{N_j}\frac{Z_j}{Z_{j-1}} \tag{4}$$

Assuming that Z_j and Z_{j-1} approach unity when P_j approaches zero, then:

$$\lim_{P_j \to 0} \frac{P_j}{P_{j-1}} = \frac{1}{N_0} \tag{5}$$

where N_0 is the cell constant at zero pressure. If the vessel deforms measurably under pressure, this value must be corrected for the pressure conditions at and before the jth expansion to obtain the cell constant at the jth expansion.

If the values of P_{j-1}/Z_{j-1} from Equation 4 for $j = 2$, 3, . . . are successively substituted into the equation for the first expansion where $j = 1$, the following is obtained:

$$\frac{P_0}{Z_0} = \frac{P_j N^j}{Z_j} \tag{6}$$

If $Z_j = 1$ when P_j approaches zero, the run constant P_0/Z_0 can be obtained from:

$$\lim_{P_j \to 0} P_j\cdot N_j = \frac{P_0}{Z_0} \tag{7}$$

Once the cell constant is obtained from Equation 5 and the run constant from Equation 7, the compressibility factor at any pressure P_j is obtained from Equation 6.

Experimental Apparatus

A schematic representation of the experimental equipment is given in Figure 1. The Burnett cell was a Model No. 2501-1 fabricated from a 400 series steel by the Ruska Instrument Corp. Pressures were measured using a Ruska Instrument Corp. dead weight gauge type 2400 HL equipped with piston assemblies for pressures of 5–2300 and 30–12,000 psi. All component parts of the cell including the charging, expansion, and exhaust valves and the differential pressure indicator were immersed in a constant-temperature oil bath. The temperature was controlled with a Hallikainen thermotrol unit with a nickel resistance thermometer in the sensing element. Both gain and reset settings were adjusted at each temperature as required to obtain optimum controlling action.

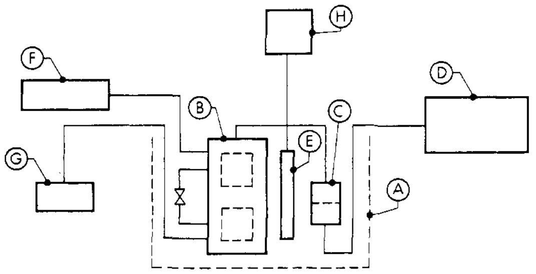

Figure 1. Schematic representation of experimental equipment

A. Oil bath
B. Burnett cell
C. D/P cell
D. Dead weight gauge
E. Pt. resistance thermometer
F. Gas supply
G. Vacuum pump
H. Mueller bridge

Temperatures were read by the resistance of a Leeds and Northrup platinum resistance thermometer immersed in the bath near the cell and calibrated regularly by the National Bureau of Standards. Resistance measurements equivalent to ±0.001K were made, but since the bath temperature could not be controlled this closely, temperatures are reported to the nearest 0.01K. The precision of temperature control for any run was better than ±0.02K.

The barometric pressure was read with a calibrated mercury barometer to within ±0.002 psia. The local gravitational acceleration is accurate to 0.007%. The relative error from all pressure correction sources was 0.027% at 50 psia.

The sources of error in the dead weight gauge piston and cylinder diameters and the weights calibration are estimated to be ±0.02% at the lowest pressures. Thus, the maximum error in pressure from all sources is ±0.047% at 50 psia. This decreases to ±0.021% at 2000 psia.

Experimental Procedures

The experimental methods used for obtaining the cell and run constants and for determining the compressibility factors of the nitrogen–hydrogen sulfide mixtures were the same. The procedure consisted of bringing the bath to the desired temperature, making the zero adjustment of the differential pressure cell, charging the gas to the Burnett cell at the required high pressure, attaining steady temperature conditions for the entire system, and carrying out the sequence of expansions to a final low pressure. Between expansions the second chamber in the Burnett cell was evacuated to about 5 μ. Periods in the order of an hour or more were required to attain thermal equilibrium between expansions.

In this study, helium was used for calibrating the equipment and determining the cell constant. Compressibility measurements were made on two mixtures having the following compositions:

	Mole fraction		
	N_2	H_2S	CO_2
Mixture 1	0.914	0.086	Trace
Mixture 2	0.765	0.222	0.013

These are the same mixtures for which experimental heat capacity measurements have been reported (*5*). Compressibility factors were determined for each of the mixtures, and the cell constant was obtained with helium at temperatures of 20°, 40°, 60°, 80°, and 100°C.

Experimental Results

As indicated earlier in Equation 5, the cell constant N_0 at zero pressure is given by the ratio of P_{j-1} to P_j as the pressure appoaches zero. Initially, the value of N_0 is obtained by a least-squares fit of the experimental values of P_{j-1}/P_j to a linear equation in pressure. This value of N_0 is used as a basis for determining a corrected value of N_0 by a procedure similar to that suggested by Canfield et al. (*4*).

The virial equation of state may be expressed in the following form:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots + \qquad (8)$$

where V is the molar volume, and B, C, D, . . . are the virial coefficients.

Algebraic rearrangement of Equation 8 gives:

$$(Z - 1)V = B + \frac{C}{V} + \frac{D}{V^2} + \ldots + \qquad (9)$$

At relatively low pressures, where V becomes large, terms involving the reciprocal of higher powers of V become progressively less important, and in this region $(Z - 1)V$ varies linearly with $1/V$. However, the function $(Z - 1)V$ becomes exceedingly sensitive to the slightest experimental error at low pressures, and consequently considerable systematic scatter of the data invariably results at densities less than about 1 g mol/l. However, Equation 9 requires that $(Z - 1)V$ vary linearly with density right down to zero density. To meet this criterion, the value of N_0 can be adjusted slightly by trial and error until the linearity condition is satisfied. The values of N_0 determined for each temperature were as follows:

Temp, °C	N_0
20	1.47577
40	1.47736
60	1.47895
80	1.47964
100	1.47834

When the best value of N_0 has been determined, the value of n_j at any pressure P_j is obtained by:

$$N_j = \frac{N_0(1 + aP_j)}{1 + aP_{j-1}}$$

where $a = 1.3 \times 10^{-7}$/psi. A similar relationship was used by Canfield et al. (*4*) and is based on Lamé's formula for calculating the elastic distortion of the cell as a function of pressure. After determining the corrected value of N_j, the value of P_0/Z_0 was determined by extrapolating the low-pressure values of $P_j \, \Pi_{i=1}^{j} N_i$ to zero pressure as indicated by Equation 6. The compressibility factors at the various experimental pressures were then determined using this equation.

Data Smoothing

The compressibility factors obtained by these procedures were used to make plots of $(Z - 1)V$ vs. $1/V$. In accordance with Equation 9, as explained earlier, these plots should be linear where the terms involving reciprocals in higher powers of V become relatively small. Plots of this type were prepared for all temperatures for both mixtures of nitrogen and hydrogen sulfide. A multiplying factor was then determined for each isotherm by trial and error so that when the experimentally observed compressibility factors were multiplied by the factor, the plots of $(Z - 1)V$ vs. $1/V$ satisfied the linearity criterion.

The multiplying factors ranged from 0.997 to 0.999. Figure 2 shows an example of these plots for the 8.6% hydrogen sulfide mixture at 40°C. Values of the compressibility factor were calculated in this way for each of the mixtures at each of the temperatures for each of the experimental pressures. Tables for these values are available. (Tabulations of the original experimental data are filed with the National Depository of Unpublished Data, National Science Library, National Research Council, Ottawa, Ont., K1A 0S2, Canada.) A graphical representa-

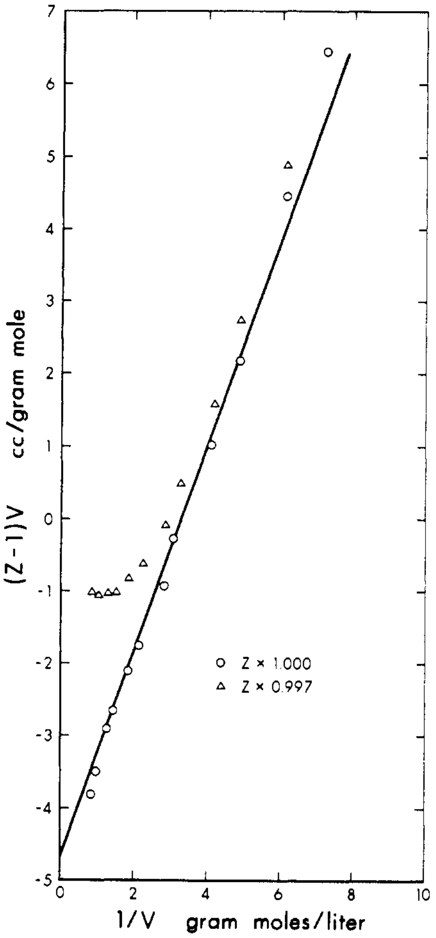

Figure 2. Typical representation of data smoothing for 8.6 mol % hydrogen sulfide mixture at 40°C

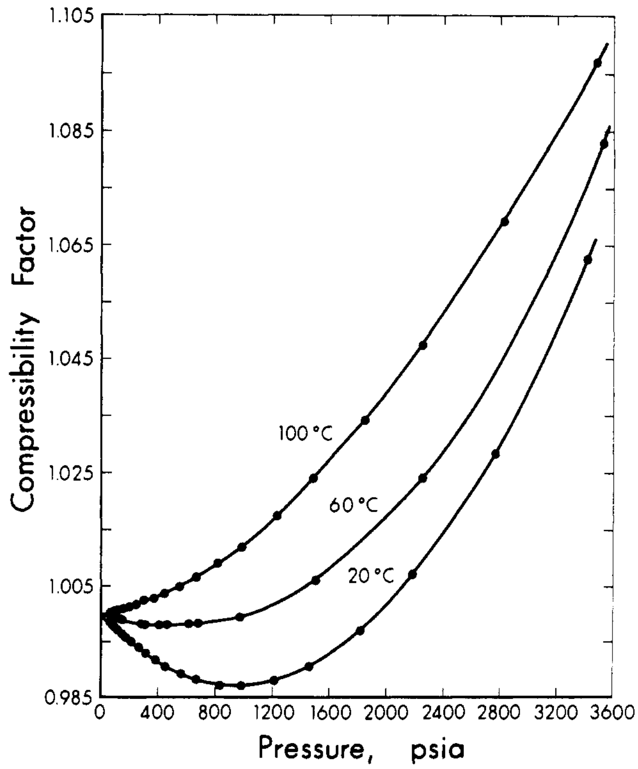

Figure 3. Representative compressibility factor curves for mixture containing 8.6 mol % hydrogen sulfide

Table I. Smoothed Compressibility Factors for Nitrogen-Hydrogen Sulfide Mixtures

Press, psia	Temp, °C 20	40	60	80	100
	Mixture containing 8.6% hydrogen sulfide				
0	1.0000	1.0000	1.0000	1.0000	1.0000
250	0.9940	0.9973	0.9984	1.0003	1.0015
500	0.9899	0.9958	0.9979	1.0019	1.0041
750	0.9876	0.9956	0.9983	1.0044	1.0077
1000	0.9870	0.9967	0.9996	1.0079	1.0123
1500	0.9908	1.0026	1.0054	1.0177	1.0240
2000	1.0010	1.0136	1.0159	1.0311	1.0389
2500	1.0174	1.0295	1.0316	1.0479	1.0564
3000	1.0395	1.0502	1.0532	1.0679	1.0761
3500	1.0671	1.0756	1.0813	1.0910	1.0976
	Mixture containing 22.2% hydrogen sulfide				
0	1.0000	1.0000	1.0000	1.0000	1.0000
250	0.9826	0.9863	0.9893	0.9921	0.9955
500	0.9667	0.9743	0.9802	0.9858	0.9923
750	0.9534	0.9643	0.9728	0.9811	0.9902
1000	0.9426	0.9563	0.9673	0.9781	0.9892
1500	0.9282	0.9462	0.9613	0.9767	0.9908
2000	0.9234	0.9439	0.9620	0.9810	0.9966
2500	0.9280	0.9492	0.9688	0.9908	1.0066
3000	0.9416	0.9619	0.9816	1.0056	1.0205
3500	0.9640	0.9818	0.9999	1.0250	1.0380

Table II. Second Virial Coefficient B_M for Nitrogen-Hydrogen Sulfide Mixtures

	B_M, cc/mol	
T, °C	Mixture I, 8.6 mol % H_2S	Mixture II, 22.2 mol % H_2S
19.6	−9.5	−26.41
44.1	−4.9	−21.54
59.9	−2.6	−18.00
79.7	−0.275	−13.3
98.9	−1.917	−8.84

Table III. Deviation Between Experimental and BWR Prediction Z Values

Mol % H_2S	Rms % deviation
8.6	0.71
22.2	0.81

tion of the experimental values is shown for three isotherms for the 8.6% hydrogen sulfide mixture in Figure 3.

Following this, each of the isotherms was fit to a low-order polynominal so that the fit was an order of magnitude better than the experimental uncertainty. These polynomials were then used to generate values of the compressibility factor at uniform pressure increments as shown in Table I.

Second Virial Coefficients

The experimental compressibility factors were used to evaluate the second virial coefficients for the mixtures investigated. Equation 9 yields:

$$B = \lim_{1/V \to 0} V(Z - 1) \qquad (10)$$

Equation 10 was used to get the second virial coefficients by a linear least-squares fit of the data for $V(Z - 1)$ vs. $1/V$. The values of the second virial coefficients for the mixtures, B_M, are listed in Table II and are shown as a function of temperature in Figure 4.

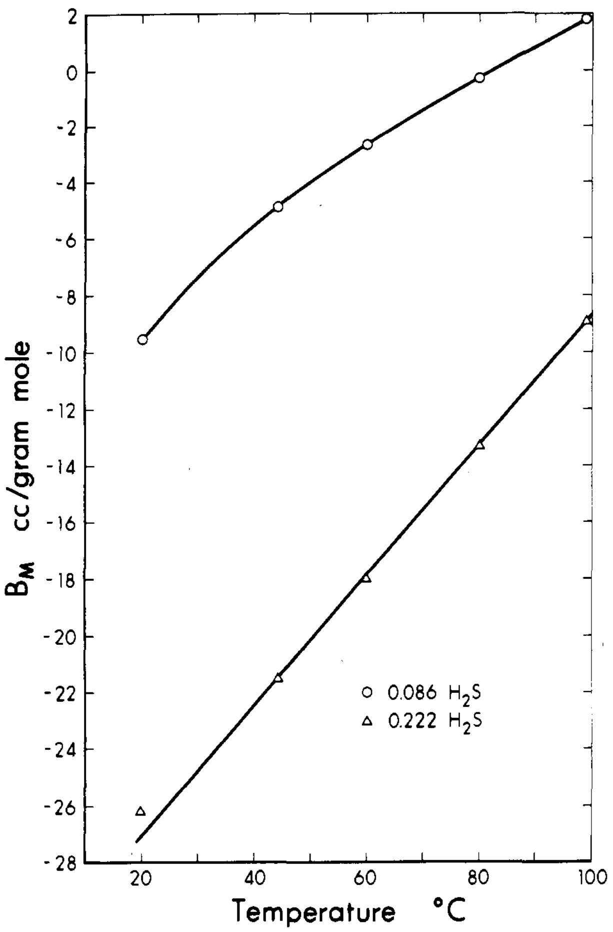

Figure 4. Variation of second virial coefficients for mixtures

Discussion of Results

The compressibility factors of the mixtures containing 8.6 mol % hydrogen sulfide and 22.2 mol % hydrogen sulfide, for all the temperatures and pressures studied, were predicted using the BWR equation of state and the mixing rules and coefficients proposed by Bishnoi and Robinson (*1*, *2*). The calculated compressibility factors are compared with experimental values as the root-mean-square % error for each mixture. These comparisons are shown in Table III where good agreement is obtained between the experimental and predicted compressibility values in both cases. This is further confirmation of the fact that when a binary interaction parameter is incorporated into the mixing rules for the BWR equation, it gives excellent property predictions. None of the results obtained in this work was used in calculating the coefficients used in the BWR equation.

Accuracy

Errors in temperatures, errors in N_0 at zero pressure, uncertainty in the intercept P_0/Z_0, and errors in pressure will give rise to errors in compressibility factors. The temperature measurement reported here is correct to ±0.01K, and this corresponds to a maximum relative error of 0.006% in compressibility factors.

The maximum error in pressure is 0.047%. Corresponding to this, the error in N_0 at zero pressure, ϵ, is 0.014%. This includes the standard error in the least-squares fit. The relative error in P_0/Z_0 from this source after an average of 12 expansions is 0.0024%. The relative error in the compressibility factors at intermediate pressures is then approximately $0.0024 - j\epsilon$ for the jth expansion, because this error in any individual Z value is caused only by the effect of the N_0 error on the subsequent expansions. Therefore, the error in compressibility factor from this source at initial pressure is 0.168%.

The maximum uncertainty in the extrapolation in the curve $P_j \Pi_{i=1}^{j} N_i$ vs. P_j to get the cell constant is 0.02%. When all these possible errors are considered, the Z values determined are probably accurate to ±0.19%.

Acknowledgment

The assistance of H. Kalra in processing some of the data is recognized.

Nomenclature

a = coefficient in equation for elastic distortion of steel
B, C, D = virial coefficients
n = number of moles
N = Burnett cell constant
P = absolute pressure
R = gas constant
T = absolute temperature
V = molal volume
Z = compressibility factor

Subscripts and Superscripts

0 = value as P approaches zero
1, 2 = number of expansion in Burnett experiment or designation of volume chambers in Burnett cell
i, j = any expansion in Burnett experiment
M = value for a mixture

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Equilibrium-Phase Properties of Nitrogen–Hydrogen Sulfide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the nitrogen–hydrogen sulfide system at 1.9°, 40.1°, 80.4°, 119.7°, and 160°F from the vapor pressure of hydrogen sulfide to a pressure of 3000 psia. The equilibrium ratios were calculated for each component at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index by use of the Lorentz-Lorenz molar refractivity relationship.

In recent years there has been an increasing interest in the volumetric and phase behavior of binary systems, particularly those containing one of the nonhydrocarbon components frequently found in petroleum or natural gas reservoirs. Information on binary systems is required for evaluating the parameters used in improved correlations for predicting the behavior of multicomponent systems and for evaluating the coefficients in equations of state. Although the behavior of many binary systems containing nitrogen or hydrogen sulfide as one of the components is reported in the literature, the authors were unable to find reference to any previous work on the phase behavior of the nitrogen–hydrogen sulfide system itself. The information presented in this paper is based on a recent study of the coexisting phase properties of the nitrogen–hydrogen sulfide system at temperatures between 0° and 160°F and at pressures up to 3000 psia. The work is part of an overall study of this system which has included heat capacity (*3*) and density (*8*) measurements.

Experimental Method

The experimental equipment and procedures have been described in detail in earlier papers by Besserer and Robinson (*1*, *2*). Experiments were carried out at each of five temperatures which were nominally 0°, 40°, 80°, 120°, and 160°F. At temperatures below ambient, the temperature of the cell contents was maintained by circulating a refrigerated fluid through the cooling coil in the aluminum shroud at each end of the cell. At each temperature, measurements of equilibrium-phase compositions and refractive indices were made at a series of pressures from the vapor pressure of hydrogen sulfide to pressures in the vicinity of the critical region or to 3000 psia, whichever was lower. The temperature was measured with a calibrated pair of iron constantan thermocouples with the reference junction in an ice bath and is believed known to ±0.1°F. The pressure was measured with a 3000-psia calibrated stainless-steel bourdon tube Heise gauge so that pressures are believed known to ±3 psi.

Materials and Analysis

The nitrogen used in this work was obtained from a local supplier and was stated to have a purity of 99.993 mol %. A sample of this material was analyzed on a silica gel column, and no impurity peaks were detected. The

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