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PVT Measurements of Hydrogen/Methane Mixtures at High Pressures

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The *PVTx* properties of hydrogen/methane mixtures have been studied at 130, 140, and 159.2 K and at pressures to 111 MPa. The experimental results are compared to the predictions of the Redlich–Kwong and Deiters equations of state.

Introduction

Hydrogen/methane is a common mixture in oil and LNG processes; existing sources of *PVT* properties of this mixture are few (*1*, *2*). At low temperatures, no measurements have been made above 9.2 MPa. In this work (*3*) we have measured the *PVTx* properties of hydrogen, methane, and their mixtures at 130, 140, and 159.2 K, at pressures to 111 MPa, and at several compositions; this covers a wide range of liquid and supercritical mixture state conditions as shown in Figure 1. This work complements earlier studies of fluid-phase equilibria in hydrogen/methane mixtures carried out in this laboratory (*4*).

Experimental Method

The measurements reported here were obtained through the use of a gas-expansion *PVT* apparatus that was first used by Streett and Staveley (*5*), and later modified as described by Calado et al. (*6*). To facilitate the study of mixtures, the high-pressure cell was fitted with an iron stirring rod, activated by an external electromagnet, to ensure complete mixing of the liquid mixtures prior to expansion.

The mixtures used were prepared in this laboratory from hydrogen and methane of purity 0.9999 or better (Matheson Co.), and the compositions were measured by a thermal conductivity detector, calibrated from samples prepared by partial pressure addition. The compositions shown in Table I are estimated to be accurate to within ±0.003 in mole fraction. Temperatures were controlled to within ±0.03 K and measured by an NBS-calibrated platinum resistance thermometer. Pressures were measured by a Ruska Model 2450 dead-weight gauge, with an accuracy of ±0.1% or better, and a precision of about 0.01%. The overall accuracy of the reported specific volumes is estimated to be ±0.2% and the precision is estimated to be ±0.02%.

Experimental Results

The experimental *PVT* measurements are recorded in Table I. As mentioned earlier, published data on this system are scarce; Solbrig (*1*) measured nine isotherms at one composition (0.9097 mole fraction of hydrogen from 138.71 to 305.37 K). Within our temperature range, only low-pressure measurements were done (below 9.2 MPa); we did not measure enough points at low pressure to make a meaningful comparison.

Mueller (*2*) obtained data for methane and four different mixtures at six temperatures (from 144.26 to 283.15 K); these results are for the vapor phase and do not overlap our measurements.

Figure 2 shows volume–pressure graphs of the experimental results for pure hydrogen and methane and for two mixtures at 140 K. The results for 130 and 159.2 K are qualitatively similar. At these temperatures, methane is a liquid and hydrogen a highly supercritical gas, yet they are miscible in all proportions at pressures above the mixture critical point at each temperature. (The approximate mixture critical pressures are (*4*) at 130 K, 36.5 MPa; at 140 K, 28.7 MPa; at 159.2 K, 18.1 MPa.)

Figure 3 shows the results plotted as isobars on a volume–composition diagram for 140 K. The dashed lines represent ideal mixing; hence the differences in volume between these dashed lines and the corresponding curves are the excess volumes of the mixtures. The excess volumes are everywhere negative, except for hydrogen-rich mixtures at low pressures. In general, the excess volumes decrease in magnitude and become more symmetric with composition as pressure increases. Similar trends with pressure have been reported for other mixtures of simple liquids (*7–9*). At the lowest pressure shown in Figure 3 (300 bar), the isobar is nearly linear in the range between about 0.5 and 0.7 mole fraction hydrogen, and similar behavior is present in the low-pressure data at 130 and 159.2 K. At first we thought this might be a spurious effect due to errors in the measurements; however, a study of earlier measurements for neon/nitrogen (*9*) and neon/argon (*10*) mixtures, under comparable conditions, showed similar effects. The quasi-linear behavior of the isobars manifests itself as the mixture critical pressure is approached from above. In each case, the composition of the mixture critical point lies approximately at the center of the linear portion of the isobar.

Comparison with Equations of State

Some earlier publications (*4*, *11*) describe correlations of p–x phase diagrams of the H_2/CH_4 system with equations of state. Now the volumetric data for the H_2/CH_4 system offer an opportunity to check the density predictions of these equations of state too. For the calculations of the molar volumes we have used the Redlich–Kwong equation (*12*)

$$p = \frac{RT}{V_m - b} - \frac{8RT^{\circ 1.5}b}{T^{0.5}V_m(V_m + b)} \tag{1}$$

and the Deiters equation (*11*) including quantum corrections

$$p = \frac{RT}{V_m}\left[1 + cc_0\frac{4\zeta - 2\zeta^2}{(1-\zeta)^3}\right][1 - \textstyle\sum i r_i y^i] - \frac{RT^\circ b}{V_m^{\,2}}\frac{\tilde{T}}{Y}\left[\exp\left(\frac{Y}{\tilde{T}}\right) - 1\right]I_1 \tag{2}$$

with

$$\tilde{T} = cT/T^\circ; \quad \zeta = \pi(2^{1/2}b)/6V_m$$

The Redlich–Kwong equation contains two substance-specific parameters: the characteristic temperature, T°, and the co-

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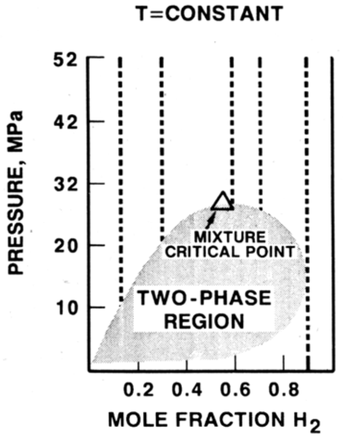

Figure 1. Schematic pressure composition diagram showing the region in which density measurements were made at each of three temperatures. The closed loop is the region of separation into two phase (vapor–liquid equilibrium), bounded at high pressures by the mixture critical point. Outside the loop, hydrogen and methane are miscible in all proportions. In this work, densities have been measured for mixtures of fixed composition (the dashed lines) starting at a pressure of about 100 MPa, and extending down to a pressure just above the region of phase separation, or to lower pressures at high hydrogen compositions.

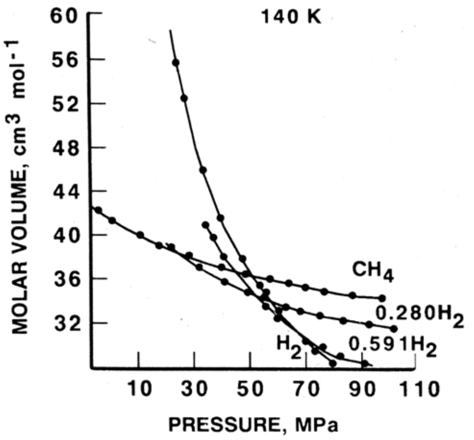

Figure 2. Experimental pressure volume results for pure hydrogen and methane and for two mixtures at 140 K. The behavior is liquidlike at high methane compositions and gaslike at high hydrogen compositions.

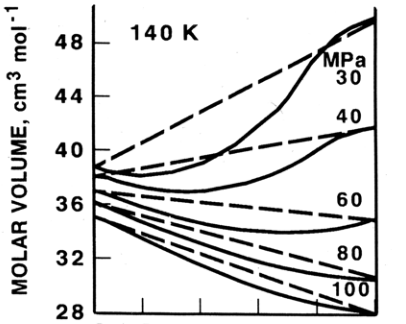

Figure 3. Experimental results for 140 K plotted as isobars on a volume composition diagram. Similar behavior was observed in measurements for neon/nitrogen mixtures (*9*).

volume, b. Equation 2 contains four substance-specific parameters, namely the characteristic temperature, T°, the covolume, b, the anisotropy factor, c, and the molar mass on which the reduced wavelength, y, depends. In the case of hydrogen and methane, the anisotropy is neglected ($c = 1$), so that eq 2 has two adjustable parameters only. The other variables in (2) are constants or functions of density, the meaning of which has been explained elsewhere (*11*, *13*).

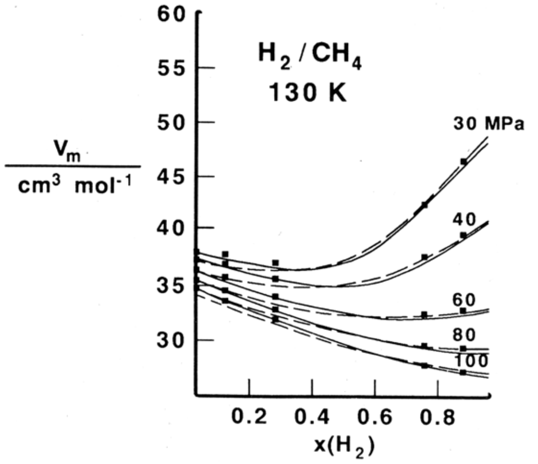

Figure 4. Molar volumes of hydrogen/methane mixtures at 130 K: ■, this work; —, calculated with eq 2; – – –, calculated with eq 1.

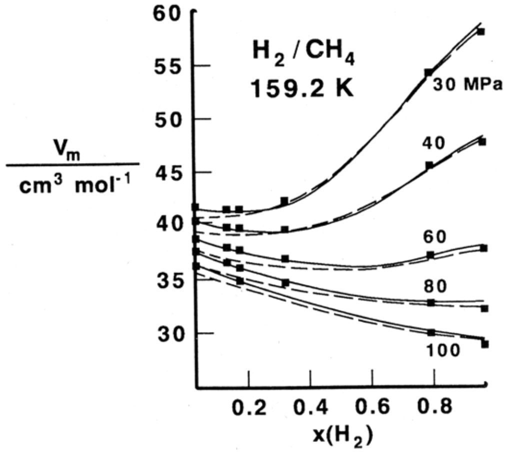

Figure 5. Molar volumes of hydrogen/methane mixtures at 159.2 K: ■, this work; —, calculated with eq 2; – – –, calculated with eq 1.

In order to make the comparison of the two equations of state more discriminating, we did not fit the equations to the experimental isopleths individually, but followed a procedure which we also would use for the calculation of phase equilibria:

1. The parameters of pure H_2 were computed from experimental *PVT* data of Table I.
2. The parameters of pure CH_4 were obtained from vapor pressure data in the range 130–160 K, as this usually gives best results with phase equilibrium calculations.
3. The unlike interaction parameter, T°_{12}, was calculated from phase equilibrium data at 130 K, 28–34 MPa (from ref *4*).
4. The molar volumes were then calculated from eq 1 and 2, with the following mixing rules:

$$b = b_{11}x_1 + b_{22}x_2 \qquad (1 = H_2,\ 2 = CH_4) \tag{3}$$

for RK:
$$T^\circ = T^\circ_{11}x_1^2 + 2T^\circ_{12}x_1x_2 + T^\circ_{22}x_2^2 \tag{4}$$

for D:
$$T^\circ = T^\circ_{11}x_1 + T^\circ_{22}x_2 + \frac{2x_1s_{11}q_2\Delta T^\circ}{1 + \left[1 + 4q_1q_2\left(\exp\left(\frac{\Delta T^\circ}{T}\right) - 1\right)\right]^{1/2}} \tag{5}$$

with

$$q_i = \frac{x_is_{ii}}{x_1s_{11} + x_2s_{22}}; \qquad \Delta T^\circ = \frac{2T^\circ_{12}}{s_{12}} - \frac{T^\circ_{11}}{s_{11}} - \frac{T^\circ_{22}}{s_{22}}$$

The s_{ij} are size parameters, which depend on the covolume ratio as described in ref 11. Table II contains the parameters

Table I. Experimental Values of the Molar Volume, V, at Pressure, P, of Liquid Methane, Hydrogen, and Liquid Mixtures

P/MPa	V/cm^3 mol^{-1}	P/MPa	V/cm^3 mol^{-1}	P/MPa	V/cm^3 mol^{-1}	P/MPa	V/cm^3 mol^{-1}
T = 159.20 K							
CH_4							
1.587	47.387	8.902	44.780	25.157	41.514	63.062	38.271
1.781	47.263	10.197	44.441	27.856	41.175	69.930	37.843
2.248	47.042	11.575	44.092	30.873	40.819	77.666	37.392
2.975	46.745	12.987	43.742	34.565	40.441	83.364	37.079
3.726	46.449	14.701	43.349	38.863	40.045	89.509	36.765
4.587	46.132	16.437	42.986	42.582	39.733	92.706	36.608
5.562	45.810	18.448	42.588	46.867	39.400	96.192	36.456
6.630	45.466	20.494	42.223	51.675	39.048	99.802	36.305
7.752	45.119	22.925	41.839	56.951	38.675		
0.100 H_2 + 0.900 CH_4							
9.041	45.711	21.418	42.127	37.170	39.783	66.502	37.313
9.984	45.323	23.463	41.723	40.174	39.469	72.826	36.895
11.121	44.902	25.378	41.386	43.342	39.141	80.061	36.460
12.498	44.439	27.568	41.035	46.965	38.801	85.269	36.162
13.931	43.991	30.089	40.668	51.140	38.459	90.877	35.861
15.639	43.498	32.197	40.381	55.673	38.095	93.950	35.688
17.457	43.022	34.594	40.089	60.784	37.714	97.230	35.540
19.289	42.596						
0.148 H_2 + 0.852 CH_4							
10.177	46.419	21.045	42.539	39.222	39.291	71.744	36.349
11.726	45.993	22.747	42.109	41.964	38.961	75.939	36.070
12.691	45.509	24.648	41.667	44.967	38.623	80.390	35.785
13.662	45.060	26.370	41.299	48.356	38.275	85.171	35.491
14.599	44.657	28.353	40.922	52.090	37.912	90.407	35.197
15.680	44.245	30.571	40.534	56.292	37.543	95.946	34.905
16.864	43.805	33.064	40.131	60.907	37.156	101.899	34.617
18.256	43.349	36.646	39.762	66.046	36.761	105.014	34.474
19.571	42.949						
0.303 H_2 + 0.697 CH_4							
15.627	49.850	23.380	43.851	39.084	39.248	66.845	35.577
15.893	49.439	24.578	43.327	41.619	38.784	71.185	35.184
16.265	48.815	25.922	42.798	44.374	38.312	75.925	34.784
16.699	48.197	27.375	42.265	46.110	37.768	81.202	34.379
17.457	47.502	29.035	41.723	50.023	37.471	85.005	34.107
18.331	46.805	30.867	41.165	52.847	37.102	89.056	33.835
19.330	46.103	32.947	40.615	55.892	36.728	93.369	33.562
20.287	45.489	34.820	40.164	59.205	36.350	95.670	33.425
21.348	44.876	36.852	39.710	62.836	35.965	98.054	33.290
22.319	44.369						
0.600 H_2 + 0.400 CH_4							
65.632	35.178	80.195	32.530	86.644	31.726	90.295	31.326
69.462	34.153	83.309	32.128	89.055	31.459	91.535	31.192
72.810	33.610						
0.813 H_2 + 0.187 CH_4							
14.819	90.542	36.522	46.756	61.286	36.069	86.273	31.436
17.050	80.225	40.373	44.194	66.019	34.948	90.490	30.885
20.467	69.172	44.567	41.951	71.351	33.844	94.858	30.367
24.778	59.979	48.604	40.155	76.614	32.898	98.330	29.982
28.573	54.382	52.572	38.667	81.685	32.097	100.769	29.727
32.424	50.168	56.650	37.356				
H_2							
8.756	156.641	33.440	52.312	62.535	35.975	88.322	30.335
15.858	92.770	38.748	47.566	67.017	34.696	91.080	29.913
17.788	84.700	43.264	44.480	71.774	33.491	94.113	29.499
19.995	76.933	48.332	41.653	77.704	32.198	96.320	29.226
22.063	71.145	53.434	39.209	81.530	31.471	98.595	28.954
25.993	62.681	57.744	37.567	84.874	30.900	100.870	28.683
29.716	56.837						
T = 140.00 K							
CH_4							
1.806	42.264	13.442	40.487	33.052	38.441	71.148	36.295
2.272	42.192	15.949	40.125	39.087	38.042	79.967	35.874
5.039	41.754	18.863	39.759	45.286	37.680	86.609	35.590
7.784	41.342	21.384	39.469	50.481	37.378	93.650	35.311
9.571	41.062	24.373	39.161	56.432	37.044	97.440	35.179
11.403	40.783	28.231	38.820	63.322	36.687	101.505	35.056
0.076 H_2 + 0.924 CH_4							
6.300	43.291	7.039	41.745	12.604	40.546	21.246	39.160
6.486	42.808	9.916	41.050	16.418	39.873	26.233	38.572

Table I (Continued)

P/MPa	V/cm^3 mol^{-1}	P/MPa	V/cm^3 mol^{-1}	P/MPa	V/cm^3 mol^{-1}	P/MPa	V/cm^3 mol^{-1}
31.185	38.067	47.766	36.815	73.793	35.319	94.532	34.351
36.035	37.646	54.407	36.401	82.033	34.911	101.642	34.074
43.033	37.128	60.097	36.065	88.027	34.630	105.294	33.941
$0.280\ H_2 + 0.720\ CH_4$							
20.936	39.886	28.864	38.123	54.599	35.020	85.133	32.914
21.494	39.756	33.534	37.363	61.323	34.470	94.944	32.410
21.811	39.652	40.670	36.418	69.397	33.894	103.074	32.030
24.035	39.097	47.772	35.646	76.603	33.413	106.120	31.907
25.998	38.687						
$0.591\ H_2 + 0.409\ CH_4$							
26.671	43.995	35.194	39.159	61.515	33.273	91.236	30.235
28.023	42.868	41.414	37.311	68.832	32.352	99.401	29.649
29.242	41.913	48.833	35.413	76.486	31.528	104.941	29.302
32.101	40.444	55.432	34.195	84.084	30.807	106.817	29.187
$0.714\ H_2 + 0.286\ CH_4$							
25.373	47.092	38.886	39.218	60.260	33.206	88.115	29.363
26.200	46.288	43.988	37.402	66.879	32.048	94.872	28.732
30.337	43.335	49.297	35.768	74.118	31.024	102.732	28.110
34.612	40.974	54.813	34.319	81.082	30.132	104.731	27.988
$0.900\ H_2 + 0.100\ CH_4$							
3.447	344.998	26.890	52.839	55.985	35.152	81.634	30.010
10.342	115.274	31.233	47.807	62.397	33.513	93.906	28.509
16.272	76.716	38.473	42.391	68.465	32.196	98.664	28.015
20.960	63.146	44.885	39.060	74.877	31.029	105.421	27.407
25.028	55.362	51.504	36.569				
H_2							
20.408	63.348	46.264	38.615	69.430	32.641	90.321	29.032
27.648	51.921	52.607	36.200	76.118	31.302	96.388	28.263
34.198	45.761	63.018	34.198	83.082	30.082	104.042	27.525
39.852	41.916						
T = 130.00 K							
CH_4							
0.854	40.594	11.376	39.385	35.476	37.334	73.764	35.489
1.148	40.549	14.868	38.981	40.946	37.042	83.313	35.085
1.954	40.465	19.290	38.505	47.641	36.708	94.172	34.673
3.682	40.265	24.752	38.033	55.660	36.320	106.629	34.304
6.961	39.893	30.034	37.671	65.497	35.869	111.149	34.202
$0.091\ H_2 + 0.909\ CH_4$							
5.338	42.842	9.660	41.495	17.756	39.493	26.005	38.226
7.580	42.091	13.394	40.527	20.626	38.987	29.318	37.827
$0.100\ H_2 + 0.900\ CH_4$							
9.377	41.675	12.410	39.377	42.334	36.362	76.118	34.445
9.515	41.218	15.168	38.953	48.884	35.943	85.081	34.014
9.722	40.812	19.167	38.433	54.468	35.602	91.907	33.719
10.342	40.399	28.131	37.492	60.812	35.239	99.698	33.421
11.445	39.786	35.784	36.841	68.396	34.859	104.318	33.275
$0.288\ H_2 + 0.712\ CH_4$							
23.028	37.710	37.025	35.564	63.018	33.362	90.114	31.792
24.132	37.400	44.057	34.859	70.947	32.858	96.251	31.526
28.889	36.559	50.332	34.310	76.463	32.453	103.214	31.265
30.888	36.270	56.261	33.847	84.530	32.061		
$0.770\ H_2 + 0.230\ CH_4$							
28.820	42.942	37.576	37.970	57.640	32.608	83.840	29.038
30.475	41.777	41.713	36.357	63.776	31.535	90.390	28.504
32.130	40.681	46.471	35.090	70.326	30.583	97.768	27.857
33.715	39.747	51.780	33.797	77.152	29.751	104.248	27.385
$0.910\ H_2 + 0.090\ CH_4$							
1.724	638.267	19.305	61.797	43.782	37.322	76.532	29.745
5.516	193.624	23.925	52.739	49.504	35.318	83.702	28.795
8.963	119.584	26.958	48.835	56.813	33.522	90.942	27.973
12.410	89.039	32.405	43.600	63.156	32.037	98.181	27.304
14.755	76.792	37.645	40.270	69.775	30.826	104.938	26.702
H_2							
1.172	447.460	23.511	55.298	50.194	35.674	80.324	28.924
3.516	199.597	27.303	50.159	54.813	34.122	87.288	27.958
7.653	128.324	30.957	47.048	62.260	32.253	93.079	27.258
11.100	96.378	35.232	42.969	68.603	31.006	98.457	26.685
14.203	79.447	40.610	39.826	74.325	29.891	105.490	26.008
18.064	66.251	45.712	37.405				

Table II. Parameters for the Redlich-Kwong and Deiters Equations of State

parameter	RK	D
$T^{\circ}_{11}/\mathrm{K}$	29.17581	33.35546
$T^{\circ}_{12}/\mathrm{K}$	66.32667	73.03337
$T^{\circ}_{22}/\mathrm{K}$	136.93072	132.65855
$b_{11}/\mathrm{dm^3\ mol^{-1}}$	0.0171576	0.0108770
$b_{22}/\mathrm{dm^3\ mol^{-1}}$	0.0290569	0.0218388
s_{11}		1.0
s_{22}		1.591521
s_{12}		1.244681

used in the calculations. The results for the molar volumes are shown in Figure 4. With respect to the expanded scale in Figure 5, both equations of state represent the experimental data quite well. In agreement with experiment, both equations predict an inflection point in the $V_m - x$ lines at lower pressure and high hydrogen concentration. The RK equation shows considerable deviations at high methane concentration, however, because it cannot fit *PVT* data and vapor pressure data well at the same time.

Registry No. H_2, 1333-74-0; CH_4, 74-82-8.

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Density Values of Carbon Dioxide and Nitrogen Mixtures from 500 to 2500 bar at 323 and 348 K

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The density of binary mixtures of carbon dioxide–nitrogen with mole fractions of 0.25, 0.5, and 0.74 were measured at 323 and 348 K and in a pressure range between 500 and 2500 bar. These results have been used for numerical calculations of the second and third virial coefficients of these mixtures.

Introduction

Experimental data for the densities of gas mixtures at high pressures and different temperatures are very useful to broaden our understanding of intermolecular forces. In particular, they allow the separation of density and temperature effects for spectroscopic studies. The paucity of these data in the literature (*1–4*), or rather their absence for the high-pressure range (>500 bar) for mixtures of carbon dioxide and nitrogen, initiated these measurements. The purpose of this paper is to present *unsmoothed* P vs ρ experimental data which have a very small interval between points. This will allow one to rather accurately calculate intermediate densities by interpolation.

Experimental Method

Materials. The nitrogen gas was obtained from Alphagaz Corp. and has minimum purity of 99.998%. The carbon dioxide "Precision Aquarator" grade used in this work was supplied by Linde-Union Carbide with reported minimum purity of 99.99% with $O_2 < 7$ ppm, $CO < 7$ ppm, and total hydrocarbons less then 7 ppm. These gases (with certified analyses) were used without further purifications. The composition analysis of mixtures were made by gas chromatography by direct comparison of the peak area ratio of the carbon dioxide signal to the nitrogen signal, with the maximum error limit being ±0.5%.

Apparatus. A schematic diagram of the $P-V-T$ apparatus is shown in Figure 1. It was a small high-pressure system using an Omega Model 158 temperature controller which allows this system to achieve an accuracy of ±0.5 K. The main part of the system was a calibrated high-pressure hand pump with a screw-type positive displacement, nonrotating piston and CO_2 resistant seal produced by Nova-Swiss AG. No leaking was detected during the measurement. Using the calibrated vernier scale on the pump, we can control injection flow (e.g., changes of the initial volume of system) very accurately (±0.03 cm^3). The total volume of the high-pressure system was 31.9 cm^3. This value was chosen to obtain a reasonable change of pressure of our mixtures using the hand pump. The particular volumes of hand pump, connections, and gauge were 5.6, 12.3, and 14.0 ± 0.1 cm^3, respectively. The pressure measurements were made with a Heise 0–4000 bar gauge which has a precision of ±2.5 bar. The Heise gauge was calibrated at elevated temperature for "zero position" and the upper pressure limit variation is 1%/38 °C.

The density measuring principle simply used the experimental pressure–volume dependence along with a known constant mass of gas mixture inside the system at constant temperature. This mass was evaluated by using a medium pressure autoclave vessel (45.47 cm^3) and an electronic balance (Arbor Model 2007) with 0.001-g resolution and 2500-g capacity for

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