Table II. Density and Viscosity Data for Binary Mixtures 45 °C

X_1	density, g/cm^3	viscosity × 10^{-1}, kg/(m/s)	X_1	density, g/cm^3	viscosity × 10^{-1}, kg/(m/s)
I. Bromoform (1)–Carbon Tetrachloride (2)					
0.0	1.561 31	0.744 85	0.6651	2.356 15	1.164 0
0.1597	1.745 45	0.821 50	0.8607	2.611 38	1.328 5
0.3179	1.932 34	0.913 11	1.0	2.782 32	1.476 40
0.5191	2.175 23	1.055 8			
II. Bromoform (1)–Dimethyl Sulfoxide (2)					
0.0	1.086 93	1.365 80	0.5441	2.108 15	1.982 00
0.1216	1.338 58	1.568 00	0.5955	2.190 30	1.982 50
0.2541	1.595 75	1.787 40	0.8193	2.533 66	1.716 10
0.4430	1.935 79	1.978 40	1.0	2.782 32	1.476 40
III. Bromoform (1)–Cyclohexane (2)					
0.0	0.762 49	0.633 77	0.6911	2.073 39	1.112 70
0.1748	1.061 27	0.723 62	0.8747	2.486 39	1.309 00
0.3427	1.368 45	0.820 05	1.0	2.782 32	1.476 40
0.5476	1.770 66	0.976 94			
IV. Bromoform (1)–Bromobenzene (2)					
0.0	1.476 39	0.853 55	0.6863	2.328 70	1.271 70
0.1693	1.671 23	0.950 44	0.8710	2.591 82	1.395 80
0.3354	1.870 48	1.051 10	1.0	2.782 32	1.476 40
0.5411	2.131 48	1.176 80			
V. Bromoform (1)–Dimethylformamide (2)					
0.0	0.934 68	0.634 84	0.6142	2.133 94	1.471 10
0.1317	1.211 87	0.819 00	0.7204	2.322 70	1.518 00
0.2705	1.490 88	1.046 40	0.8296	2.505 72	1.518 60
0.4636	1.861 02	1.313 20	1.0	2.782 32	1.476 40
VI. Bromoform (1)–Methyl Ethyl Ketone (2)					
0.0	0.787 81	0.341 67	0.6499	2.095 85	1.037 80
0.1474	1.086 13	0.467 77	0.8502	2.493 09	1.298 40
0.3005	1.396 04	0.622 83	1.0	2.782 32	1.476 40
0.5019	1.800 69	0.852 26			
VII. Bromoform (1)–Ethyl Acetate (2)					
0.0	0.879 11	0.382 92	0.7671	2.312 83	1.179 30
0.2695	1.361 01	0.600 53	1.0	2.782 32	1.476 40
0.5228	1.835 83	0.877 89			
VIII. Bromoform (1)–Methanol (2)					
0.0	0.775 90	0.434 53	0.7234	2.501 71	1.260 50
0.1630	1.390 94	0.693 47	0.8987	2.696 97	1.383 30
0.3122	1.795 70	0.884 43	1.0	2.782 32	1.476 40
0.4563	2.095 90	1.043 40			

Solvent mixtures were prepared by weighing a calculated volume of each solvent in the mixture; special airtight glass-stoppered bottles were used for this purpose. Densities (ρ) and viscosities (η) at 45 °C were measured by the procedure described earlier (*3*). Triplicate measurements of each composition of the mixture showed a reproducibility range for density of ±0.000 06 g/cm^3 and for viscosity of ±0.000 04 kg/(m/s). However, only the average data are presented in Table II. The mole fractions (X_1) were calculated from the measured volumes and densities of individual components (*3*).

Results and Discussion

Experimental data of ρ and η are listed in Table II as a function of mole fraction (X_1) of the first component in the mixture (i.e., bromoform). To the best of our knowledge no data were available for the systems investigated here and hence no comparison with the published results was possible.

The binary kinematic viscosity (η/ρ) data have been correlated by using the cubic equation of McAllister (*5*) as well as the Heric (*6*) and Auslander (*7*) relations. Statistical analysis of the back-calculated values of viscosities in comparison to the measured values indicated an average percent deviation from 1.0 to 1.5 for McAllister equation; for the Auslander or Heric relations, this was found to be between 2.0 and 3.0.

Registry No. Bromoform, 75-25-2; carbon tetrachloride, 56-23-5; dimethyl sulfoxide, 67-68-5; cyclohexane, 110-82-7; bromobenzene, 108-86-1; dimethylformamide, 68-12-2; ethyl acetate, 141-78-6; ethyl methyl ketone, 78-93-3; methanol, 67-56-1.

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Experimental Densities and Derived Thermodynamic Properties for Carbon Dioxide–Water Mixtures

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Vapor-phase densities have been measured for mixtures of 2, 5, 10, 25, and 50 mol % water in carbon dioxide by using a Burnett–isochoric apparatus. These experimental densities, which cover a temperature range from 323.15 to 498.15 K and a pressure range from 27 kPa to 10.34 MPa, are considered accurate to ±0.05%. Thermodynamic properties, derived from the experimental data for all five mixtures, have also been reported along with the corresponding pressure–enthalpy diagrams.

Introduction

Few high-accuracy density measurements are available for nonpolar/polar vapor mixtures over extended ranges of pressure, temperature, and composition. Such data are extremely important in developing reliable equations of state and in calculating thermodynamic properties.

Carbon dioxide–water mixtures have long been important in combustion studies and in the manufacture of carbonated beverages. Besides these well-known uses, they are de-

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Table I. Molar Densities and Dimensionless Thermodynamic Properties for the 98% CO_2–2% H_2O Gaseous Mixture[a]

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
T = 498.15 K							
0.000	0.000	1.000 00	1.1860	2.1860	−∞	−∞	∞
0.137 97	33.349	0.998 94	1.1823	2.1812	3.2350	4.2339	−2.0527
0.203 36	49.179	0.998 44	1.1805	2.1789	3.6229	4.6214	−2.4424
0.299 66	72.523	0.997 70	1.1778	2.1755	4.0106	5.0083	−2.8328
0.441 42	106.947	0.996 62	1.1740	2.1706	4.3979	5.3946	−3.2240
0.649 91	157.709	0.995 03	1.1683	2.1633	4.7848	5.7798	−3.6165
0.956 14	232.563	0.992 71	1.1599	2.1526	5.1708	6.1635	−4.0109
1.405 15	342.941	0.989 34	1.1476	2.1369	5.5558	6.5451	−4.4082
2.061 79	505.698	0.984 45	1.1296	2.1141	5.9391	6.9236	−4.8095
3.018 62	745.679	0.977 46	1.1034	2.0809	6.3202	7.2976	−5.2167
4.406 11	1099.515	0.967 60	1.0655	2.0331	6.6979	7.6655	−5.6324
6.405 66	1621.196	0.954 05	1.0111	1.9652	7.0711	8.0252	−6.0600
9.267 86	2390.295	0.936 20	0.9343	1.8705	7.4382	8.3744	−6.5040
T = 473.15 K							
0.000 00	0.000	1.000 00	1.0237	2.0237	−∞	−∞	∞
0.131 02	33.349	0.998 74	1.0196	2.0184	3.2917	4.2904	−2.2720
0.193 10	49.179	0.998 14	1.0177	2.0159	3.6795	4.6777	−2.6618
0.284 50	72.523	0.997 27	1.0149	2.0122	4.0671	5.0643	−3.0522
0.419 00	106.947	0.995 98	1.0107	2.0067	4.4542	5.4502	−3.4435
0.616 71	157.709	0.994 09	1.0046	1.9987	4.8407	5.8348	−3.8361
0.906 89	232.563	0.991 33	0.9956	1.9869	5.2263	6.2177	−4.2307
1.331 88	342.941	0.987 30	0.9823	1.9696	5.6106	6.5979	−4.6283
1.952 39	505.698	0.981 48	0.9629	1.9444	5.9930	6.9745	−5.0301
2.854 42	745.679	0.973 13	0.9345	1.9077	6.3727	7.3458	−5.4381
4.157 85	1099.515	0.961 33	0.8932	1.8545	6.7484	7.7097	−5.8552
6.026 81	1621.196	0.945 05	0.8334	1.7784	7.1187	8.0637	−6.2853
8.683 22	2390.295	0.923 49	0.7477	1.6712	7.4816	8.4051	−6.7339
T = 448.15 K							
0.000 00	0.00	1.000 00	0.8484	1.8484	−∞	−∞	∞
0.124 07	33.349	0.998 51	0.8440	1.8425	3.3423	4.3408	−2.4983
0.182 83	49.179	0.997 81	0.8419	1.8397	3.7300	4.7278	−2.8881
0.269 33	72.523	0.996 77	0.8389	1.8356	4.1174	5.1142	−3.2785
0.396 57	106.947	0.995 25	0.8344	1.8296	4.5043	5.4996	−3.6700
0.583 49	157.709	0.993 01	0.8277	1.8207	4.8905	5.8835	−4.0628
0.857 60	232.563	0.989 74	0.8179	1.8076	5.2756	6.2653	−4.4577
1.258 54	342.941	0.984 98	0.8035	1.7884	5.6591	6.6441	−4.8557
1.842 80	505.698	0.978 06	0.7823	1.7603	6.0404	7.0185	−5.2581
2.689 72	745.679	0.968 13	0.7511	1.7193	6.4184	7.3866	−5.6673
3.908 35	1099.515	0.954 05	0.7056	1.6596	6.7918	7.7459	−6.0862
5.644 68	1621.196	0.934 51	0.6391	1.5736	7.1587	8.0932	−6.5196
8.089 58	2390.295	0.908 35	0.5426	1.4509	7.5166	8.4250	−6.9741
T = 423.15 K							
0.000 00	0.000	1.000 00	0.6582	1.6582	−∞	−∞	∞
0.117 12	33.349	0.998 25	0.6534	1.6516	3.3853	4.3835	−2.7319
0.172 56	49.179	0.997 42	0.6511	1.6485	3.7729	4.7703	−3.1218
0.254 16	72.523	0.996 20	0.6477	1.6439	4.1601	5.1563	−3.5124
0.374 13	106.947	0.994 40	0.6427	1.6372	4.5467	5.5411	−3.9040
0.550 25	157.709	0.991 77	0.6354	1.6272	4.9325	5.9243	−4.2971
0.808 26	232.563	0.987 91	0.6246	1.6125	5.3170	6.3049	−4.6924
1.185 07	342.941	0.982 28	0.6087	1.5910	5.6997	6.6820	−5.0910
1.732 93	505.698	0.974 09	0.5853	1.5594	6.0797	7.0538	−5.4944
2.524 36	745.679	0.962 29	0.5507	1.5130	6.4558	7.4181	−5.9051
3.657 18	1099.515	0.945 48	0.4998	1.4453	6.8264	7.7719	−6.3266
5.258 26	1621.196	0.921 97	0.4250	1.3469	7.1892	8.1112	−6.7643
7.484 45	2390.295	0.890 06	0.3148	1.2049	7.5413	8.4314	−7.2265
T = 398.15 K							
0.000 00	0.000	1.000 00	0.4505	1.4505	−∞	−∞	∞
0.110 16	33.349	0.997 94	0.4452	1.4431	3.4188	4.4167	−2.9736
0.162 30	49.179	0.996 96	0.4426	1.4396	3.8062	4.8032	−3.3636
0.238 99	72.523	0.995 52	0.4389	1.4344	4.1932	5.1887	−3.7544
0.351 67	106.947	0.993 41	0.4333	1.4267	4.5795	5.5729	−4.1462
0.516 97	157.709	0.990 30	0.4251	1.4154	4.9648	5.9551	−4.5397
0.758 84	232.563	0.985 75	0.4131	1.3988	5.3486	6.3344	−4.9356
1.111 44	342.941	0.979 09	0.3952	1.3743	5.7303	6.7094	−5.3350
1.622 68	505.698	0.969 39	0.3689	1.3383	6.1088	7.0782	−5.7399
2.358 07	745.679	0.955 35	0.3300	1.2853	6.4827	7.4380	−6.1527
3.403 76	1099.515	0.935 22	0.2723	1.2075	6.8500	7.7852	−6.5777
T = 373.15 K							
0.000 00	0.000	1.000 00	0.2222	1.2222	−∞	−∞	∞
0.103 21	33.349	0.997 57	0.2162	1.2137	3.4403	4.4378	−3.2241
0.152 02	49.179	0.996 42	0.2133	1.2097	3.8275	4.8239	−3.6143
0.223 80	72.523	0.994 72	0.2090	1.2037	4.2143	5.2090	−4.0053

Table I (Continued)

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
0.329 20	106.947	0.992 22	0.2027	1.1949	4.6002	5.5924	−4.3975
0.483 65	157.709	0.988 55	0.1934	1.1820	4.9849	5.9735	−4.7915
0.709 32	232.563	0.983 15	0.1797	1.1628	5.3679	6.3511	−5.1882
1.037 57	342.941	0.975 25	0.1594	1.1346	5.7483	6.7236	−5.5889
1.511 87	505.698	0.963 70	0.1293	1.0930	6.1250	7.0887	−5.9957
			T = 348.15 K				
0.000 00	0.000	1.000 00	−0.0307	0.9693	−∞	−∞	∞
0.096 25	33.349	0.997 11	−0.0378	0.9594	3.4465	4.4436	−3.4842
0.141 74	49.179	0.995 74	−0.0411	0.9546	3.8336	4.8293	−3.8747
0.208 60	72.523	0.993 73	−0.0460	0.9477	4.2200	5.2137	−4.2660
0.306 69	106.947	0.990 76	−0.0533	0.9374	4.6054	5.5962	−4.6588
0.450 26	157.709	0.986 39	−0.0641	0.9222	4.9895	5.9758	−5.0536
0.659 65	232.563	0.979 96	−0.0801	0.8998	5.3714	6.3514	−5.4515
			T = 323.15 K				
0.000 00	0.000	1.000 00	−0.3136	0.6864	−∞	−∞	∞
0.089 29	33.349	0.996 54	−0.3220	0.6745	3.4332	4.4297	−3.7552
0.131 45	49.179	0.994 90	−0.3260	0.6689	3.8200	4.8149	−4.1459
0.193 37	72.523	0.992 48	−0.3319	0.6606	4.2060	5.1985	−4.5378

[a] Reference state: H_{ref} = 0.0 and S_{ref} = 0.0 at P_{ref} = 1.0 kPa, T_{ref} = 273.16 K.

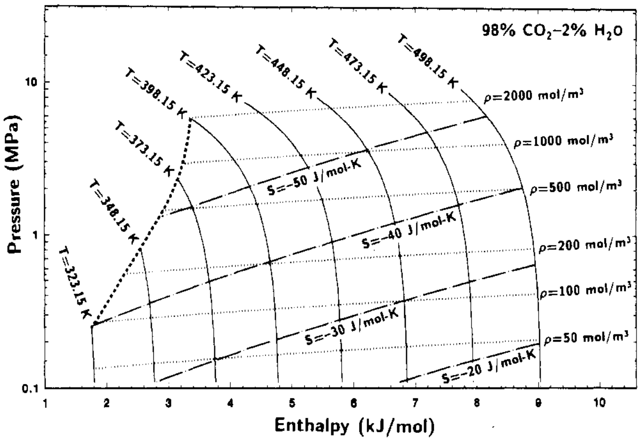

Figure 1. Pressure–enthalpy diagram for the 98% CO_2–2% H_2O mixture. Reference state is perfect gas at 273.16 K and 1.0 kPa. The densities and entropies are per mole of the gaseous mixture.

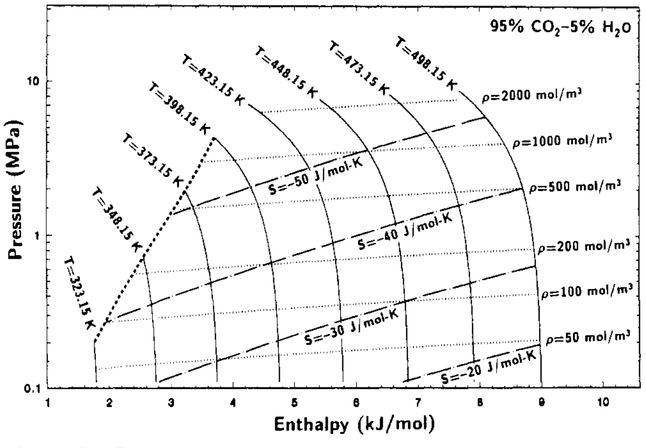

Figure 2. Pressure–enthalpy diagram for the 95% CO_2–5% H_2O mixture. Reference state is perfect gas at 273.16 K and 1.0 kPa. The densities and entropies are per mole of the gaseous mixture.

manding new interest in the area of tertiary recovery of crude oil. Data are needed for the saturated vapor over several compositions to determine the amount of dehydration required for the wet CO_2 gas from the source fields to prevent condensation and subsequent corrosion in the pipelines. Also, since CO_2–H_2O is a constitutive pair, such binary data are a prior necessity to understanding the complex phase equilibria and thermodynamic properties of the separate phases found in petroleum reservoirs undergoing tertiary CO_2 flooding.

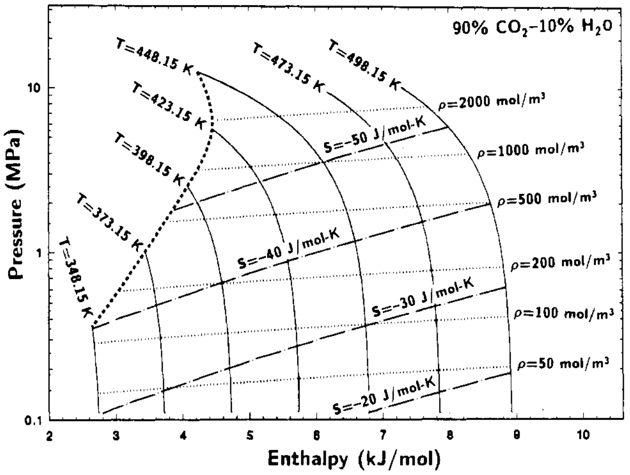

Figure 3. Pressure–enthalpy diagram for the 90% CO_2–10% H_2O mixture. Reference state is perfect gas at 273.16 K and 1.0 kPa. The densities and entropies are per mole of the gaseous mixture.

Carbon dioxide–water mixtures have been studied predominantly for liquid-phase properties. Numerous measurements for the solubility of CO_2 in liquid H_2O and of H_2O in compressed CO_2 include those by Weibe and Gaddy (*1–3*), Houghton et al. (*4*), Coan and King (*5*), and Zawisza and Malesińska (*6*). Further, Hicks and Young (*7*) have compiled data on the vapor–liquid critical locus (which exhibits a gas–gas equilibrium of the second type), and Vanderzee and Haas (*8*) have evaluated interaction second virial coefficients using measurements reported by Maass and Mennie (*9*) and Greenwood (*10*, *11*). Finally, excess enthalpy measurements (using a flow calorimeter) have been undertaken by Wormald's group (*12–14*). However, no comprehensive data on the density and enthalpy of saturated (dew point) and unsaturated mixtures are available over several compositions.

We present in this paper, experimental densities and derived thermodynamic properties (in dimensionless form) for mixtures of 2%, 5%, 10%, 25%, and 50% H_2O in CO_2 along with pressure–enthalpy diagrams for each.

Experimental Section

Materials. Ultra Pure Grade CO_2 was obtained from Scientific Gas Products Inc. The gas was certified to be 99.995%

Table II. Molar Densities and Dimensionless Thermodynamic Properties for the 95% CO_2–5% H_2O Gaseous Mixture[a]

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
			T = 498.15 K				
0.000 00	0.000	1.000 00	1.1762	2.1762	$-\infty$	$-\infty$	∞
0.132 17	31.947	0.998 97	1.1725	2.1714	3.1946	4.1935	−2.0221
0.194 82	47.112	0.998 48	1.1707	2.1692	3.5825	4.5810	−2.4118
0.287 09	69.476	0.997 76	1.1680	2.1658	3.9703	4.9680	−2.8022
0.422 92	102.455	0.996 71	1.1642	2.1609	4.3577	5.3544	−3.1935
0.622 71	151.089	0.995 17	1.1584	2.1536	4.7445	5.7397	−3.5861
0.916 20	222.805	0.992 91	1.1500	2.1429	5.1307	6.1236	−3.9807
1.346 59	328.558	0.989 62	1.1376	2.1272	5.5157	6.5054	−4.3781
1.976 14	484.496	0.984 85	1.1194	2.1042	5.8992	6.8841	−4.7799
2.893 78	714.425	0.978 03	1.0926	2.0706	6.2805	7.2585	−5.1879
4.224 93	1053.442	0.968 39	1.0534	2.0218	6.6585	7.6269	−5.6052
6.144 16	1553.277	0.955 12	0.9961	1.9512	7.0321	7.9872	−6.0360
8.892 50	2290.176	0.937 56	0.9128	1.8503	7.3997	8.3372	−6.4869
			T = 473.15 K				
0.000 00	0.000	1.000 00	1.0150	2.0150	$-\infty$	$-\infty$	∞
0.125 51	31.947	0.998 77	1.0110	2.0098	3.2508	4.2496	−2.2398
0.184 99	47.112	0.998 19	1.0091	2.0073	3.6387	4.6368	−2.6295
0.272 56	69.476	0.997 33	1.0063	2.0037	4.0263	5.0236	−3.0199
0.401 44	102.455	0.996 07	1.0022	1.9983	4.4134	5.4095	−3.4112
0.590 90	151.089	0.994 22	0.9961	1.9903	4.8000	5.7942	−3.8039
0.869 01	222.805	0.991 52	0.9872	1.9787	5.1857	6.1772	−4.1985
1.276 38	328.558	0.987 58	0.9740	1.9616	5.5701	6.5577	−4.5961
1.871 26	484.496	0.981 86	0.9547	1.9366	5.9526	6.9345	−4.9979
2.736 22	714.425	0.973 64	0.9264	1.9000	6.3325	7.3061	−5.4061
3.986 34	1053.442	0.961 98	0.8850	1.8470	6.7084	7.6704	−5.8234
5.778 85	1553.277	0.945 79	0.8248	1.7705	7.0790	8.0248	−6.2542
8.324 97	2290.176	0.924 10	0.7376	1.6617	7.4422	8.3663	−6.7046
			T = 448.15 K				
0.000 00	0.000	1.000 00	0.8409	1.8409	$-\infty$	$-\infty$	∞
0.118 85	31.947	0.998 54	0.8366	1.8351	3.3010	4.2995	−2.4644
0.175 15	47.112	0.997 85	0.8345	1.8324	3.6887	4.6866	−2.8542
0.258 04	69.476	0.996 84	0.8315	1.8284	4.0762	5.0730	−3.2446
0.379 95	102.455	0.995 35	0.8271	1.8224	4.4631	5.4585	−3.6360
0.559 08	151.089	0.993 16	0.8205	1.8137	4.8493	5.8425	−4.0288
0.821 79	222.805	0.989 96	0.8109	1.8009	5.2345	6.2245	−4.4236
1.206 12	328.558	0.985 28	0.7967	1.7820	5.6182	6.6035	−4.8215
1.766 30	484.496	0.978 49	0.7759	1.7544	5.9996	6.9781	−5.2238
2.578 50	714.425	0.968 70	0.7453	1.7140	6.3779	7.3466	−5.6325
3.747 42	1053.442	0.954 78	0.7006	1.6554	6.7515	7.7063	−6.0509
5.412 93	1553.277	0.935 33	0.6355	1.5708	7.1187	8.0540	−6.4832
7.756 37	2290.176	0.909 01	0.5411	1.4501	7.4770	8.3860	−6.9359
			T = 423.15 K				
0.000 00	0.000	1.000 00	0.6518	1.6518	$-\infty$	$-\infty$	∞
0.112 19	31.947	0.998 29	0.6471	1.6454	3.3436	4.3418	−2.6965
0.165 32	47.112	0.997 47	0.6449	1.6423	3.7312	4.7287	−3.0863
0.243 50	69.476	0.996 28	0.6416	1.6378	4.1185	5.1147	−3.4769
0.358 46	102.455	0.994 52	0.6367	1.6312	4.5051	5.4997	−3.8685
0.527 24	151.089	0.991 94	0.6295	1.6214	4.8910	5.8829	−4.2615
0.774 54	222.805	0.988 16	0.6189	1.6071	5.2756	6.2638	−4.6567
1.135 78	328.558	0.982 63	0.6033	1.5859	5.6584	6.6410	−5.0551
1.661 14	484.496	0.974 60	0.5803	1.5549	6.0386	7.0132	−5.4583
2.420 30	714.425	0.962 99	0.5465	1.5095	6.4150	7.3780	−5.8685
3.507 37	1053.442	0.946 41	0.4968	1.4432	6.7859	7.7323	−6.2891
5.044 25	1553.277	0.923 12	0.4239	1.3470	7.1491	8.0723	−6.7253
7.180 81	2290.176	0.891 28	0.3170	1.2083	7.5017	8.3930	−7.1847
			T = 398.15 K				
0.000 00	0.000	1.000 00	0.4453	1.4453	$-\infty$	$-\infty$	∞
0.105 53	31.947	0.997 98	0.4400	1.4380	3.3767	4.3747	−2.9367
0.155 48	47.112	0.997 02	0.4375	1.4345	3.7642	4.7612	−3.3267
0.228 97	69.476	0.995 62	0.4338	1.4294	4.1512	5.1469	−3.7174
0.336 95	102.455	0.993 54	0.4283	1.4219	4.5376	5.5312	−4.1093
0.495 37	151.089	0.990 50	0.4203	1.4108	4.9230	5.9135	−4.5027
0.727 21	222.805	0.986 03	0.4084	1.3944	5.3069	6.2930	−4.8986
1.065 27	328.558	0.979 50	0.3907	1.3702	5.6887	6.6682	−5.2980
1.555 58	484.496	0.969 97	0.3647	1.3347	6.0674	7.0374	−5.7027
2.261 16	714.425	0.956 16	0.3261	1.2823	6.4416	7.3978	−6.1155
3.264 98	1053.442	0.936 32	0.2689	1.2052	6.8093	7.7456	−6.5404
			T = 373.15 K				
0.000 00	0.000	1.000 00	0.2182	1.2182	$-\infty$	$-\infty$	∞
0.098 87	31.947	0.997 61	0.2121	1.2097	3.3979	4.3955	−3.1858
0.145 64	47.112	0.996 48	0.2092	1.2057	3.7852	4.7817	−3.5760
0.214 42	69.476	0.994 81	0.2050	1.1998	4.1720	5.1668	−3.9670

Table II (Continued)

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
0.315 42	102.455	0.992 36	0.1987	1.1910	4.5580	5.5504	-4.3593
0.463 45	151.089	0.988 75	0.1894	1.1781	4.9428	5.9316	-4.7535
0.679 76	222.805	0.983 45	0.1755	1.1590	5.3259	6.3094	-5.1504
0.994 47	328.558	0.975 66	0.1551	1.1307	5.7065	6.6821	-5.5514
1.449 34	484.496	0.964 27	0.1245	1.0888	6.0833	7.0476	-5.9588
			T = 348.15 K				
0.000 00	0.000	1.000 00	-0.0336	0.9664	$-\infty$	$-\infty$	∞
0.092 20	31.947	0.997 15	-0.0408	0.9563	3.4039	4.4010	-3.4447
0.135 79	47.112	0.995 80	-0.0442	0.9516	3.7910	4.7868	-3.8352
0.199 85	69.476	0.993 81	-0.0493	0.9445	4.1775	5.1713	-4.2267
0.293 85	102.455	0.990 88	-0.0568	0.9341	4.5630	5.5538	-4.6198
0.431 44	151.089	0.986 55	-0.0679	0.9187	4.9741	5.9336	-5.0150
0.632 11	222.805	0.980 18	-0.0844	0.8958	5.3291	6.3093	-5.4136
			T = 323.15 K				
0.000 00	0.000	1.000 00	-0.3155	0.6845	$-\infty$	$-\infty$	∞
0.085 53	31.947	0.996 56	-0.3243	0.6723	3.3904	4.3869	-3.7146
0.125 93	47.112	0.994 93	-0.3285	0.6665	3.7772	4.7721	-4.1056
0.185 26	69.476	0.992 51	-0.3347	0.6578	4.1632	5.1557	-4.4979

[a] Reference state: H_{ref} = 0.0 and S_{ref} = 0.0 at P_{ref} = 1.0 kPa, T_{ref} = 273.16 K.

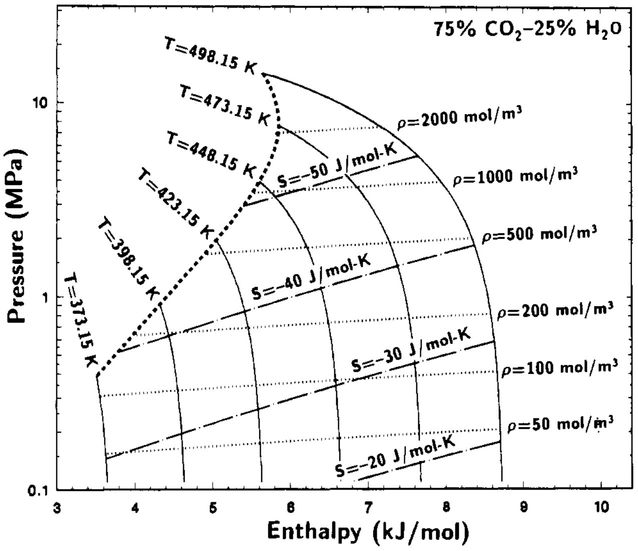

Figure 4. Pressure-enthalpy diagram for the 75% CO_2-25% H_2O mixture. Reference state is perfect gas at 273.16 K and 1.0 kPa. The densities and entropies are per mole of the gaseous mixture.

pure, with less than 10 ppm N_2, 5 ppm O_2, 10 ppm CO, 5 ppm H_2, and 5 ppm H_2O. The ultrapure water was prepared by several distillations of common distilled water in a Barnstead redistiller.

Apparatus and Procedure. The basic experimental measurements were made on a high-temperature Burnett-isochoric (B-I) apparatus described previously by Mansoorian et al. (*15*) and Eubank et al. (*16*). A more recent description of the apparatus and a detailed account of the operational procedure is contained in the Ph.D. dissertation of Patel (*17*). Briefly, however, the B-I experiment consists of filling a primary cell volume with the sample and noting its temperature and pressure, making an isochoric run (pressure measurements at fixed temperature increments), returning the cell to the original condition, and performing an expansion of the sample into a previously evacuated secondary cell volume. A series of such isochoric runs coupled with isothermal expansions, typically at the highest temperature, constitute a B-I surface run. An important feature of the B-I method is that it generates an entire P-ρ-T surface with one filling of the sample; hence, for mixtures there is no need to duplicate a composition.

Being the only two observables in the B-I experiment, the pressure and temperature are measured with extreme accuracy and precision. Pressure measurements are accurate to 0.01% and precise to 0.001%, whereas the temperatures are accurate to 10 mK with a precision of 5 mK or better. In determining mixture compositions, the largest error is in the amount of water charged. However, because of the difference-in-mass approach used in the charging procedure, the precision, rather than the actual accuracy, of the balance is taken into account. With these considerations, the uncertainties in the compositions decrease from 0.0023% for the 2% H_2O to 0.0002% for the 50% H_2O mixture.

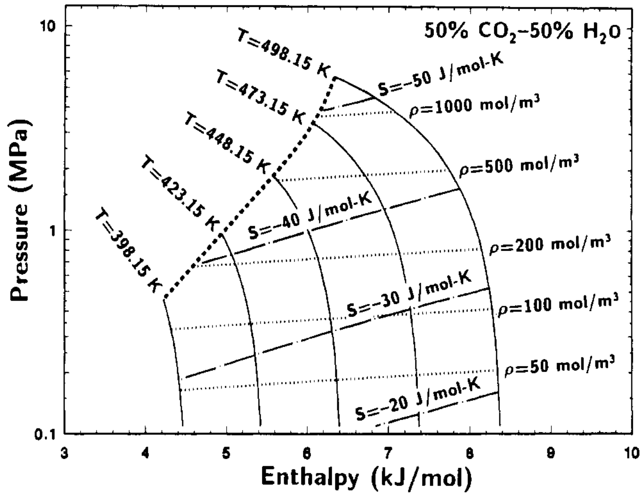

Figure 5. Pressure-enthalpy diagram for the 50% CO_2-50% H_2O mixture. Reference state is perfect gas at 273.16 K and 1.0 kPa. The densities and entropies are per mole of the gaseous mixture.

Data Reduction

Densities. Analysis of the measured pressures and temperatures for a B-I surface run provides the densities and compressibilities. Conventional Burnett and Burnett-isochoric analyses have been described by Holste et al. (*18*). However, for systems for which adsorption is diagnosed (see Hall and Eubank (*19*) for procedure), corrections for adsorption contributions have to be made independently. Such was the case for the present CO_2-H_2O mixtures. The adsorption correction procedure is described in detail by Patel (*17*) and will be published in the future. Furthermore, the virial coefficients resulting from the above analysis and experimental dew points have been published previously by Patel et al. (*20*).

Table III. Molar Densities and Dimensionless Thermodynamic Properties for the 90% CO_2–10% H_2O Gaseous Mixture[a]

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
T = 498.15 K							
0.00000	0.000	1.00000	1.1599	2.1599	$-\infty$	$-\infty$	∞
0.15477	37.420	0.99869	1.1553	2.1539	3.3566	4.3553	−2.2014
0.22812	55.188	0.99807	1.1530	2.1511	3.7445	4.7426	−2.5915
0.33612	81.391	0.99716	1.1498	2.1469	4.1321	5.1293	−2.9824
0.49504	120.035	0.99582	1.1450	2.1408	4.5193	5.5151	−3.3743
0.72863	177.022	0.99386	1.1379	2.1318	4.9058	5.8997	−3.7679
1.07144	261.060	0.99099	1.1275	2.1185	5.2914	6.2824	−4.1639
1.57338	384.984	0.98681	1.1122	2.0990	5.6756	6.6624	−4.5634
2.30597	567.715	0.98077	1.0897	2.0705	6.0578	7.0385	−4.9680
3.37037	837.150	0.97212	1.0568	2.0289	6.4371	7.4092	−5.3803
4.90738	1234.407	0.95992	1.0087	1.9686	6.8124	7.7723	−5.8037
7.10940	1820.098	0.94315	0.9387	1.8818	7.1820	8.1252	−6.2434
10.23673	2683.553	0.92107	0.8375	1.7586	7.5441	8.4652	−6.7066
T = 473.15 K							
0.00000	0.000	1.00000	1.0006	2.0006	$-\infty$	$-\infty$	∞
0.14697	37.420	0.99844	0.9957	1.9941	3.4120	4.4105	−2.4163
0.21659	55.188	0.99771	0.9934	1.9911	3.7998	4.7975	−2.8065
0.31908	81.391	0.99663	0.9899	1.9866	4.1873	5.1839	−3.1973
0.46983	120.035	0.99503	0.9849	1.9799	4.5742	5.5692	−3.5893
0.69126	177.022	0.99270	0.9774	1.9701	4.6903	5.9530	−3.9829
1.01592	261.060	0.98928	0.9665	1.9558	5.3453	6.3346	−4.3788
1.49063	384.984	0.98431	0.9504	1.9347	5.7287	6.7130	−4.7783
2.18205	567.715	0.99710	0.9268	1.9039	6.1097	7.0868	−5.1829
3.18357	837.150	0.96675	0.8922	1.8590	6.4873	7.4541	−5.5951
4.62318	1234.407	0.95211	0.8418	1.7939	6.8601	7.8122	−6.0182
6.67171	1820.098	0.93185	0.7687	1.7006	7.2260	8.1579	−6.4573
9.55205	2683.553	0.90488	0.6636	1.5685	7.5828	8.4877	−6.9192
T = 448.15 K							
0.00000	0.000	1.00000	0.8284	1.8284	$-\infty$	$-\infty$	∞
0.13916	37.420	0.99817	0.8231	1.8213	3.4614	4.4596	−2.6383
0.20506	55.188	0.99730	0.8206	1.8179	3.8491	4.8464	−3.0285
0.30204	81.391	0.99603	0.8169	1.8129	4.2363	5.2323	−3.4194
0.44461	120.035	0.99415	0.8114	1.8056	4.6229	5.6171	−3.8115
0.65388	177.022	0.99140	0.8034	1.7948	5.0087	6.0001	−4.2053
0.96038	261.060	0.98737	0.7915	1.7789	5.3931	6.3804	−4.6015
1.40783	384.984	0.98149	0.7741	1.7556	5.7755	6.7570	−5.0014
2.05803	567.715	0.97297	0.7485	1.7215	6.1552	7.1282	−5.4067
2.99652	837.150	0.96071	0.7109	1.6716	6.5309	7.4916	−5.8199
4.33840	1234.407	0.94330	0.6559	1.5992	6.9008	7.8441	−6.2449
6.23260	1820.098	0.91908	0.5755	1.4946	7.2626	8.1817	−6.6871
8.86381	2683.553	0.88652	0.4588	1.3453	7.6134	8.4999	−7.1546
T = 423.15 K							
0.00000	0.000	1.00000	0.6413	1.6413	$-\infty$	$-\infty$	∞
0.13136	37.420	0.99785	0.6354	1.6332	3.5033	4.5011	−2.8679
0.19353	55.188	0.99683	0.6326	1.6294	3.8908	4.8876	−3.2582
0.24899	81.391	0.99533	0.6284	1.6238	4.2778	5.2732	−3.6494
0.41937	120.035	0.99312	0.6224	1.6155	4.6641	5.6572	−4.0418
0.61646	177.022	0.98989	0.6134	1.6033	5.0494	6.0392	−4.4360
0.90475	261.060	0.98514	0.6001	1.5853	5.4330	6.4182	−4.8329
1.32485	384.984	0.97821	0.5806	1.5588	5.8145	6.7927	−5.2339
1.93355	567.715	0.96813	0.5517	1.5198	6.1926	7.1607	−5.6409
2.80836	837.150	0.95358	0.5089	1.4625	6.5659	7.1595	−6.0570
4.05082	1234.407	0.93281	0.4455	1.3783	6.9324	7.8653	−6.4869
T = 398.15 K							
0.00000	0.000	1.00000	0.4367	1.4367	$-\infty$	$-\infty$	∞
0.12355	37.420	0.99746	0.4299	1.4274	3.5358	4.5332	−3.1059
0.18200	55.188	0.99626	0.4267	1.4229	3.9231	4.9194	−3.4964
0.26793	81.391	0.99449	0.4219	1.4164	4.3098	5.3043	−3.8879
0.39410	120.035	0.99189	0.4149	1.4067	4.6957	5.6876	−4.2809
0.57897	177.022	0.98806	0.4044	1.3925	5.0804	6.0684	−4.6760
0.84896	261.060	0.98243	0.3890	1.3714	5.4632	6.4456	−5.0742
1.24146	384.984	0.97420	0.3660	1.3402	5.8433	6.8175	−5.4773
1.80812	567.715	0.96217	0.3318	1.2940	6.2195	7.1817	−5.8877
T = 373.15 K							
0.00000	0.000	1.00000	0.2115	1.2115	$-\infty$	$-\infty$	∞
0.11574	37.420	0.99698	0.2033	1.2003	3.5563	4.5533	−3.3530
0.17045	55.188	0.99555	0.1994	1.1950	3.9434	4.9390	−3.7440
0.25084	81.391	0.99344	0.1937	1.1871	4.3298	5.3233	−4.1362
0.36878	120.035	0.99032	0.1852	1.1755	4.7152	5.7056	−4.5301
0.54134	177.022	0.98574	0.1725	1.1582	5.0992	6.0849	−4.9266
0.79286	261.060	0.97898	0.1536	1.1326	5.4809	6.4598	−5.3272

Table III (Continued)

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
			T = 348.15 K				
0.000 00	0.000	1.000 00	−0.0385	0.9615	−∞	−∞	∞
0.107 91	37.420	0.996 35	−0.0487	0.9476	3.5618	4.5581	−3.6105
0.158 88	55.188	0.994 61	−0.0536	0.9410	3.9486	4.9432	−4.0022
0.233 71	81.391	0.992 04	−0.0609	0.9312	4.3345	5.3266	−4.3954

[a] Reference state: H_{ref} = 0.0 and S_{ref} = 0.0 at P_{ref} = 1.0 kPa, T_{ref} = 273.16 K.

Table IV. Molar Densities and Dimensionless Thermodynamic Properties for the 75% CO_2–25% H_2O Gaseous Mixture[a]

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
			T = 498.15 K				
0.000 00	0.000	1.000 00	1.1109	2.1109	−∞	−∞	∞
0.157 32	38.053	0.998 27	1.1052	2.1035	3.3856	4.3839	−2.2804
0.231 91	56.140	0.997 46	1.1024	2.0999	3.7736	4.7711	−2.6712
0.341 71	82.820	0.996 25	1.0984	2.0947	4.1613	5.1575	−3.0628
0.503 19	122.174	0.994 48	1.0925	2.0870	4.5483	5.5427	−3.4558
0.740 30	180.216	0.991 88	1.0837	2.0756	4.9343	5.9262	−3.8506
1.087 73	265.814	0.988 06	1.0708	2.0589	5.3191	6.3072	−4.2483
1.595 22	392.043	0.982 49	1.0518	2.0343	5.7201	6.6846	−4.6502
2.333 17	578.175	0.974 38	1.0239	1.9983	6.0823	7.0567	−5.0584
3.399 33	852.623	0.962 67	0.9829	1.9456	6.4586	7.4213	−5.4757
4.925 46	1257.273	0.945 93	0.9229	1.8688	6.8295	7.7754	−5.9066
7.081 96	1853.868	0.922 40	0.8352	1.7576	7.1925	8.1149	−6.3573
10.077 26	2733.414	0.890 18	0.7076	1.5978	7.5447	8.4349	−6.8371
			T = 473.15 K				
0.000 00	0.000	1.000 00	0.9573	1.9573	−∞	−∞	∞
0.149 38	38.053	0.997 97	0.9511	1.9491	3.4385	4.4365	−2.4874
0.220 17	56.140	0.997 01	0.9482	1.9452	3.8265	4.8235	−2.8783
0.324 35	82.820	0.995 59	0.9439	1.9395	4.2139	5.2094	−3.2700
0.477 46	122.174	0.993 50	0.9375	1.9310	4.6005	5.5940	−3.6630
0.702 12	180.216	0.990 43	0.9281	1.9185	4.9862	5.9766	−4.0581
1.030 90	265.814	0.985 92	0.9142	1.9001	5.3703	6.3562	−4.4561
1.510 29	392.043	0.979 33	0.8936	1.8729	5.7522	6.7315	−4.8586
2.205 48	578.175	0.969 73	0.8632	1.8329	6.1309	7.1006	−5.2677
3.205 66	852.623	0.955 79	0.8182	1.7740	6.5050	7.4608	−5.6869
4.628 03	1257.273	0.935 77	0.7153	1.6871	6.8726	7.8084	−6.1213
6.617 05	1853.868	0.907 38	0.6516	1.5590	7.2308	8.1382	−6.5792
			T = 448.15 K				
0.000 00	0.000	1.000 00	0.7908	1.7908	−∞	−∞	∞
0.141 44	38.053	0.997 62	0.7840	1.7816	3.4857	4.4833	−2.7017
0.208 43	56.140	0.996 49	0.7807	1.7772	3.8734	4.8699	−3.0927
0.306 97	82.820	0.994 82	0.7759	1.7707	4.2606	5.2554	−3.4846
0.451 72	122.174	0.992 36	0.7688	1.7612	4.6469	5.6392	−3.8781
0.663 90	180.216	0.988 75	0.7583	1.7470	5.0320	6.0207	−4.2737
0.973 98	265.814	0.983 44	0.7427	1.7261	5.4153	6.3987	−4.6726
1.425 11	392.043	0.975 65	0.7194	1.6951	5.7960	6.7716	−5.0766
2.077 16	578.175	0.964 25	0.6848	1.6490	6.1730	7.1372	−5.4882
3.010 34	852.623	0.947 63	0.6327	1.5803	6.5445	7.4921	−5.9118
			T = 423.15 K				
0.000 00	0.000	1.000 00	0.6095	1.6095	−∞	−∞	∞
0.133 49	38.053	0.997 19	0.6016	1.5988	3.5255	4.5227	−2.9239
0.196 68	56.140	0.995 86	0.5978	1.5936	3.9130	4.9089	−3.3152
0.289 58	82.820	0.993 89	0.5921	1.5860	4.2999	5.2937	−3.7077
0.425 93	122.174	0.990 99	0.5837	1.5747	4.6857	5.6767	−4.1020
0.625 56	180.216	0.986 70	0.5712	1.5579	5.0702	6.0569	−4.4990
0.916 77	265.814	0.980 37	0.5523	1.5326	5.4525	6.4329	−4.9002
1.339 24	392.043	0.971 03	0.5236	1.4946	5.8317	6.8028	−5.3082
			T = 398.15 K				
0.000 00	0.000	1.000 00	0.4107	1.4107	−∞	−∞	∞
0.125 54	38.053	0.996 66	0.4010	1.3977	3.5560	4.5527	−3.1550
0.184 91	56.140	0.995 06	0.3963	1.3914	3.9433	4.9384	−3.5470
0.272 14	82.820	0.992 69	0.3892	1.3819	4.3298	5.3225	−3.9405
0.400 03	122.174	0.989 18	0.3785	1.3677	4.7151	5.7043	−4.3365
0.586 97	180.216	0.983 96	0.3622	1.3461	5.0986	6.0826	−4.7365
			T = 373.15 K				
0.000 00	0.000	1.000 00	0.1913	1.1913	−∞	−∞	∞
0.117 57	38.053	0.995 92	0.1787	1.1746	3.5749	4.5708	−3.3962
0.173 11	56.140	0.993 95	0.1725	1.1664	3.9618	4.9558	−3.7893
0.254 62	82.820	0.991 01	0.1629	1.1539	4.3477	5.3388	−4.1848

[a] Reference State: H_{ref} = 0.0 and S_{ref} = 0.0 at P_{ref} = 1.0 kPa, T_{ref} = 273.16 K.

Table V. Molar Densities and Dimensionless Thermodynamic Properties for the 50% CO_2–50% H_2O Gaseous Mixture[a]

P, MPa	ρ, mol/m^3	Z	U/RT	H/RT	A/RT	G/RT	S/R
T = 498.15 K							
0.00000	0.000	1.00000	1.0293	2.0293	$-\infty$	$-\infty$	∞
0.12069	29.204	0.99782	1.0223	2.0201	3.1415	4.1393	-2.1192
0.17800	43.119	0.99678	1.0190	2.0158	3.5301	4.5269	-2.5111
0.26237	63.654	0.99525	1.0141	2.0093	3.9181	4.9133	-2.9040
0.38636	93.950	0.99299	1.0068	1.9998	4.3051	5.2981	-3.2983
0.56824	138.640	0.98966	0.9960	1.9857	4.6909	5.6806	-3.6949
0.83424	204.554	0.98476	0.9801	1.9649	5.0749	6.0597	-4.0948
1.22166	301.758	0.97754	0.9565	1.9341	5.4565	6.4340	-4.5000
1.78241	445.099	0.96693	0.9216	1.8885	5.8345	6.8014	-4.9130
2.58648	656.464	0.95135	0.8695	1.8209	6.2074	7.1588	-5.3379
3.72293	968.122	0.92853	0.7917	1.7202	6.5728	7.5014	-5.7812
T = 473.15 K							
0.00000	0.000	1.00000	0.8851	1.8851	$-\infty$	$-\infty$	∞
0.11459	29.204	0.99744	0.8774	1.8749	3.1904	4.1879	-2.3130
0.16898	43.119	0.99622	0.8738	1.8700	3.5789	4.5751	-2.7051
0.24899	63.654	0.99442	0.8684	1.8628	3.9666	4.9610	-3.0982
0.36652	93.950	0.99177	0.8603	1.8521	4.3532	5.3450	-3.4929
0.53873	138.640	0.98785	0.8484	1.8363	4.7384	5.7263	-3.8900
0.79021	204.554	0.98206	0.8307	1.8128	5.1216	6.1036	-4.2908
1.15559	301.758	0.97353	0.8044	1.7779	5.5019	6.4754	-4.6975
1.68244	445.099	0.96092	0.7648	1.7258	5.8780	6.8389	-5.1131
2.43328	656.464	0.94229	0.7051	1.6474	6.2479	7.1902	-5.5429
T = 448.15 K							
0.00000	0.000	1.00000	0.7282	1.7282	$-\infty$	$-\infty$	∞
0.10848	29.204	0.99700	0.7195	1.7165	3.2338	4.2308	-2.5143
0.15994	43.119	0.99556	0.7153	1.7108	3.6220	4.6176	-2.9068
0.23561	63.654	0.99344	0.7090	1.7024	4.0094	5.0028	-3.3004
0.34665	93.950	0.99031	0.6997	1.6900	4.3956	5.3859	-3.6959
0.50915	138.640	0.98568	0.6857	1.6714	4.7801	5.7658	-4.0943
0.74598	204.554	0.97882	0.6648	1.6436	5.1622	6.1410	-4.4975
1.08902	301.758	0.96863	0.6329	1.6015	5.5409	6.5096	-4.9081
1.58119	445.099	0.95347	0.5838	1.5372	5.9147	6.8681	-5.3309
T = 423.15 K							
0.00000	0.000	1.00000	0.5566	1.5566	$-\infty$	$-\infty$	∞
0.10237	29.204	0.99644	0.5459	1.5424	3.2702	4.2666	-2.7242
0.15089	43.119	0.99473	0.5408	1.5355	3.6581	4.6528	-3.1174
0.22218	63.654	0.99220	0.5330	1.5252	4.0451	5.0373	-3.5121
0.32669	93.950	0.98844	0.5212	1.5097	4.4307	5.4191	-3.9094
0.47936	138.640	0.98283	0.5033	1.4861	4.8143	5.7971	-4.3109
0.70121	204.554	0.97443	0.4755	1.4500	5.1950	6.1694	-4.7195
T = 398.15 K							
0.00000	0.000	1.00000	0.3675	1.3675	$-\infty$	$-\infty$	∞
0.09625	29.204	0.99569	0.3537	1.3494	3.2976	4.2933	-2.9439
0.14182	43.119	0.99361	0.3470	1.3406	3.6852	4.6788	-3.3382
0.20870	63.654	0.99050	0.3369	1.3274	4.0716	5.0621	-3.7347
0.30658	93.950	0.98585	0.3216	1.3075	4.4564	5.4422	-4.1348

[a] Reference state: $H_{\mathrm{ref}} = 0.0$ and $S_{\mathrm{ref}} = 0.0$ at $P_{\mathrm{ref}} = 1.0$ kPa, $T_{\mathrm{ref}} = 273.16$ K.

Thermodynamic Properties. Once these corrections have been made and the densities and compressibilities determined, calculation of the thermodynamic properties is achieved through the use of residual properties. A residual property is defined as the difference between the real fluid property value and the perfect gas state property value. Of the various forms of such property changes discussed by Hall et al. (*21*), the one used here is the real fluid property at the temperature and density of the fluid less the perfect gas property at a reference temperature, T_{ref}, and reference pressure, P_{ref}. Thus, for a property M, the residual property is defined as

$$M - M^*_{\mathrm{ref}} \equiv M(T,\rho) - M^*(T_{\mathrm{ref}},P_{\mathrm{ref}}/RT_{\mathrm{ref}}) \qquad (1)$$

where the * indicates the hypothetical perfect gas state. The path chosen for integration is

$$M(T,\rho) \rightarrow M^*(T,0) \rightarrow M^*(T_{\mathrm{ref}},0) \rightarrow M^*(T_{\mathrm{ref}},P_{\mathrm{ref}}/RT_{\mathrm{ref}})$$

With this formulation, it is most convenient to establish $(U - U^*_{\mathrm{ref}})$ and $(S - S^*_{\mathrm{ref}})$, and then to calculate the other properties from these two. The starting equations are

$$\mathrm{d}U = C_v\,\mathrm{d}T + R\left(\frac{\partial Z}{\partial 1/T}\right)_\rho \frac{\mathrm{d}\rho}{\rho} \qquad (2)$$

$$\mathrm{d}S = C_v\frac{\mathrm{d}T}{T} + R\left[\frac{1}{T}\left(\frac{\partial Z}{\partial 1/T}\right)_\rho - Z\right]\frac{\mathrm{d}\rho}{\rho} \qquad (3)$$

The residual internal energy then is determined by using

$$\frac{U - U^*_{\mathrm{ref}}}{RT} = \frac{1}{T}\int_0^\rho \left(\frac{\partial Z}{\partial 1/T}\right)_\rho \frac{\mathrm{d}\rho}{\rho} + \frac{1}{T}\int_{T_{\mathrm{ref}}}^{T} \frac{C^*_v}{R}\,\mathrm{d}T \qquad (4)$$

and the residual entropy by using

$$\frac{S - S^*_{\mathrm{ref}}}{R} = \int_0^{\rho} \left[1 - Z + \frac{1}{T}\left(\frac{\partial Z}{\partial 1/T}\right)_{\rho} \right] \frac{d\rho}{\rho} + \int_{T_{\mathrm{ref}}}^{T} \frac{C^*_v}{R}\frac{dT}{T} - \ln \frac{\rho R T_{\mathrm{ref}}}{P_{\mathrm{ref}}} \qquad (5)$$

Finally, the remaining residual properties are calculated from

$$\frac{H - H^*_{\mathrm{ref}}}{RT} = \frac{U - U^*_{\mathrm{ref}}}{RT} + Z - \frac{T_{\mathrm{ref}}}{T} \qquad (6)$$

$$\frac{A - A^*_{\mathrm{ref}}}{RT} = \frac{U - U^*_{\mathrm{ref}}}{RT} - \frac{S - S^*_{\mathrm{ref}}}{R} - \frac{S^*_{\mathrm{ref}}}{R}\left(1 - \frac{T_{\mathrm{ref}}}{T}\right) \qquad (7)$$

$$\frac{G - G^*_{\mathrm{ref}}}{RT} = \frac{H - H^*_{\mathrm{ref}}}{RT} - \frac{S - S^*_{\mathrm{ref}}}{R} - \frac{S^*_{\mathrm{ref}}}{R}\left(1 - \frac{T_{\mathrm{ref}}}{T}\right) \qquad (8)$$

Any reference state may be specified, but for a reference state for which H^*_{ref} and S^*_{ref} are chosen to equal zero, as is the case here, $G^*_{\mathrm{ref}} = 0$, $U^*_{\mathrm{ref}} = -RT_{\mathrm{ref}}$, and $A^*_{\mathrm{ref}} = -RT_{\mathrm{ref}}$.

Note that the only integrals required to calculate all the above residual properties are

$$\frac{1}{T}\int_0^{\rho}\left(\frac{\partial Z}{\partial 1/T}\right)_{\rho}\frac{d\rho}{\rho}$$

$$\int_0^{\rho}(Z - 1)\frac{d\rho}{\rho}$$

$$\frac{1}{T}\int_{T_{\mathrm{ref}}}^{T}\frac{C^*_v}{R}\,dT$$

$$\int_{T_{\mathrm{ref}}}^{T}\frac{C^*_v}{R}\frac{dT}{T}$$

The first two require simple applications of the equation of state, while the latter two involve only perfect-gas specific heats. Eubank et al. (*22*) show that density data obtained by the B–I method yield the above thermodynamic properties more accurately than do data from either straight Burnett or straight isochoric measurements.

Results

Tables I–V present the experimental densities and the derived energy properties for the five mixtures. The properties are based upon a reference state for which H_{ref} and S_{ref} are set to zero for P_{ref} = 1 kPa and T_{ref} = 273.16 K. The perfect-gas specific heats for pure CO_2 were taken from Angus et al. (*23*) and those for pure H_2O were taken from Haar et al. (*24*). The properties listed have the following estimated accuracies: densities and compressibility factors, 0.05%; internal energies and enthalpies, 0.15%; Helmholtz and Gibbs free energies, 0.20%; and entropies, 0.17%. Finally, Figures 1–5 depict the more practically used pressure–enthalpy (P–H) diagrams developed from the experimental data for each mixture.

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Glossary

A	Helmholtz free energy
C_v	specific heat capacity at constant volume
G	Gibbs free energy
H	enthalpy
M	general variable for U, H, A, G, or S
P	pressure
R	universal gas constant (8.31448 J/(mol·K))
S	entropy
T	absolute temperature
U	internal energy
Z	compressibility factor ($P/\rho RT$)

Greek Letters

ρ	density

Superscripts

*	perfect gas state

Subscripts

ref	reference state value

Registry No. CO_2, 124-38-9.

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