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Compressibility Factors, Densities, and Residual Thermodynamic Properties for Methane–Water Mixtures

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Smoothed compressibility factors and residual thermodynamic properties for mixtures of 50, 25, and 10 mol % water vapor in methane are presented along with experimental densities. Pressure–enthalpy diagrams for the three mixtures are also provided. The measured densities cover a temperature range of 498.15–398.15 K and a pressure range of 72 kPa to 12 MPa. These densities were measured by use of a Burnett–isochoric (B–I) apparatus and are accurate to ±0.08%. The adsorption phenomenon normally present in vapor measurements of polar components was taken into account during the B–I data analysis. Thus the densities, and therefore the residual properties, presented here are free of the errors caused by the adsorption process.

Introduction

The CH_4–H_2O mixture is important in the study and processing of wet natural gases. Natural gas (i.e., mostly methane) is often saturated with water upon production from the earth. Knowledge of the properties of water–methane mixtures is useful not only in design and operation of separation facilities but also in studies of more complex phase behavior involving the water–methane binary pair. An example of such complex phase behavior is found in the mixtures resulting from secondary and tertiary oil and gas recovery.

Precise experimental compressibility measurements of the CH_4–H_2O vapor mixture are not only important because they contribute to an understanding of wet natural gas behavior but also because they contribute to an understanding of polar–nonpolar molecular interactions. Such high-precision data are thus valuable for developing reliable equations of state and in calculating residual thermodynamic properties. B–I density measurements allow calculation of the residual properties with a greater accuracy than do either purely Burnett or purely isochoric measurements.

In this paper, we present smoothed compressibility factors, densities, and residual thermodynamic properties for the CH_4–H_2O mixture at 50, 25, and 10 mol % water. This paper is analogous to a recent publication in this Journal (*1*) for CO_2–H_2O mixtures at 50, 25, 10, 5, and 2 mol % water.

Previous Water/Methane Measurements

Rigby and Prausnitz (*2*) used solubility measurements of water in compressed methane to extract interaction second virial coefficients at 298, 323, 348, and 373 K. O'Sullivan and Smith (*3*) and Sultanov et al. (*4*) published solubility measurements of methane in water. In addition, Rettich et al. (*5*) published Henry's constants for methane in water from solubility measurements.

Experimental measurements involving hydrate in equilibrium with methane have been made by Marshall et al. (*6*) and Aoyagi et al. (*7*). Aoyagi et al. (*7*) used a regression technique to extract interaction second and third virials at 240, 250, 260, and 270 K.

Most recently, Smith et al. (*8*) have measured excess enthalpies of water–methane vapor. They published results at water mole fractions of 0.35–0.67 and six temperatures ranging from 373.2 to 423.2 K. Using these excess enthalpies and assuming a second virial coefficient gas, they also extracted interaction second virial coefficients.

Other notable experimental measurements on water–methane mixtures are the dew-point pressure and equilibrium mole fraction measurements of Gillespie and Wilson (*9*) and Olds et al. (*10*). Also, Scheloske et al. (*11*) have measured dew-point pressures of water–sweet gas mixtures using a dry gas with 90% methane.

Experimental Section

***Apparatus and Procedure*.** The apparatus used for these measurements was first described by Anderson et al. (*12*) and most recently by Patel (*13*). The apparatus is capable of measuring pressures as high as 16.5 MPa to within 0.01% above 0.7 MPa and ±0.07 kPa below 0.7 MPa. The temperature can be measured between 50 and 225 °C to ±10 mK.

The experimental procedure is the Burnett–isochoric (B–I) method proposed by Burnett (*14*) and discussed in detail by Pope et al. (*15*) and Hall and Eubank (*16*). The B–I method yields data over the entire P–ρ–T surface with a single sample. This feature is very useful with mixtures since once a given sample has been prepared no duplication of it is required in order to complete the experimental measurements. In order to prepare the mixtures used in this study, a known mass of distilled water was charged into the secondary cell as a liquid. Methane, charged into the primary cell to a predetermined pressure, was then mixed with the water in the secondary cell. This mixing procedure is described in detail by Patel (*13*).

***Materials*.** The methane gas used in sample preparation was supplied by Scientific Gas Products and certified as having a 99.995 mol % purity (with less than 30 ppm N_2, 5 ppm C_3H_8, 5 ppm C_2H_4, 10 ppm O_2, 10 ppm CO_2, 5 ppm C_2H_2, and 5 ppm H_2O). The water used in sample preparation was distilled repeatedly in a Barnstead Redistiller.

Data Analysis

***Densities*.** Burnett (*17*) first proposed the original experimental technique and graphical analysis and much later (*14*) modified these procedures to a B–I-type analysis. Hall and Canfield (*18*) demonstrated a least-squares approach to the analysis of Burnett data. More recently, Holste et al. (*19*) have discussed both the Burnett and the Burnett–isochoric analyses. Both the Burnett and the Burnett–isochoric analyses work well for gases at temperatures well above the critical temperature where physical adsorption of the gas molecules onto the apparatus surface is not important. However, this phenomenon, which occurs at reduced temperatures near unity or less, causes the measured pressures to be lower than if there were no adsorption. These adsorption effects were taken into account during the analysis of the measured data. The analysis to account for these adsorption effects has been discussed in detail by Joffrion and Eubank (*20*). Additionally, it should be noted that the virial coefficients, dew-point measurements, and the densities of the 498.15 K isotherm have been published previously (*20*).

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Table I. Smoothed Compressibility Factors, Densities, and Properties for the 50% CH_4–50% H_2O Mixture[a]

P, MPa	ρ, mol/m^3	Z	$U - U^*_{ref}$, kJ/mol	$H - H^*_{ref}$, kJ/mol	$A - A^*_{ref}$, kJ/mol	$G - G^*_{ref}$, kJ/mol	$S - S^*_{ref}$, kJ/(mol·K)
T = 498.15 K							
0.090 76	21.94	0.9989	4.204	8.341	11.87	16.01	−0.0154
0.133 83	32.36	0.9984	4.198	8.333	13.48	17.61	−0.0186
0.197 30	47.75	0.9977	4.189	8.321	15.08	19.22	−0.0219
0.290 75	70.45	0.9965	4.175	8.303	16.69	20.82	−0.0251
0.428 24	103.93	0.9949	4.156	8.276	18.29	22.42	−0.0284
0.630 22	153.33	0.9924	4.126	8.237	19.90	24.01	−0.0317
0.926 32	226.20	0.9888	4.083	8.179	21.49	25.59	−0.0349
1.359 09	333.68	0.9835	4.020	8.093	23.08	27.15	−0.0383
1.988 61	492.21	0.9755	3.926	7.967	24.66	28.70	−0.0416
2.897 73	726.03	0.9637	3.789	7.780	26.22	30.21	−0.0450
4.195 48	1070.86	0.9460	3.587	7.505	27.76	31.67	−0.0485
T = 485.65 K							
0.088 48	21.94	0.9988	3.799	7.832	11.67	15.70	−0.0162
0.130 46	32.36	0.9983	3.792	7.823	13.24	17.27	−0.0195
0.192 31	47.75	0.9975	3.782	7.810	14.81	18.83	−0.0227
0.283 38	70.45	0.9963	3.767	7.790	16.37	20.39	−0.0260
0.417 32	103.93	0.9945	3.745	7.760	17.93	21.95	−0.0292
0.614 03	153.33	0.9918	3.711	7.716	19.49	23.50	−0.0325
0.902 26	226.20	0.9879	3.662	7.651	21.05	25.04	−0.0358
1.323 20	333.68	0.9822	3.588	7.554	22.60	26.56	−0.0391
1.934 78	492.21	0.9736	3.477	7.409	24.13	28.06	−0.0425
2.816 33	726.03	0.9607	3.310	7.189	25.65	29.53	−0.0460
T = 473.15 K							
0.086 19	21.94	0.9987	3.400	7.329	11.46	15.39	−0.0170
0.127 08	32.36	0.9981	3.392	7.319	12.99	16.92	−0.0203
0.187 32	47.75	0.9972	3.381	7.304	14.52	18.44	−0.0235
0.276 00	70.45	0.9959	3.364	7.282	16.04	19.96	−0.0268
0.406 38	103.93	0.9940	3.339	7.249	17.56	21.47	−0.0301
0.597 79	153.33	0.9911	3.301	7.200	19.08	22.98	−0.0334
0.878 08	226.20	0.9869	3.245	7.127	20.60	24.48	−0.0367
1.287 01	333.68	0.9805	3.160	7.018	22.10	25.96	−0.0400
1.880 20	492.21	0.9711	3.032	6.852	23.59	27.41	−0.0435
2.733 02	726.03	0.9570	2.833	6.598	25.07	28.83	−0.0470
T = 460.65 K							
0.083 90	21.94	0.9986	3.006	6.831	11.25	15.07	−0.0179
0.123 70	32.36	0.9980	2.997	6.820	12.73	16.55	−0.0211
0.182 33	47.75	0.9970	2.985	6.803	14.22	18.04	−0.0244
0.268 60	70.45	0.9956	2.966	6.779	15.70	19.51	−0.0276
0.395 42	103.93	0.9934	2.938	6.743	17.18	20.99	−0.0309
0.581 49	153.33	0.9903	2.896	6.689	18.66	22.45	−0.0342
0.853 76	226.20	0.9856	2.833	6.607	20.13	23.91	−0.0376
1.250 49	333.68	0.9786	2.737	6.485	21.59	25.34	−0.0409
1.824 82	492.21	0.9681	2.589	6.296	23.04	26.75	−0.0444
T = 448.15 K							
0.081 62	21.94	0.9985	2.617	6.338	11.02	14.74	−0.0187
0.120 32	32.36	0.9978	2.608	6.326	12.46	16.18	−0.0220
0.177 32	47.75	0.9967	2.594	6.308	13.91	17.62	−0.0252
0.261 19	70.45	0.9951	2.573	6.281	15.35	19.06	−0.0285
0.384 43	103.93	0.9927	2.542	6.241	16.79	20.49	−0.0318
0.565 13	153.33	0.9893	2.495	6.181	18.23	21.91	−0.0351
0.829 30	226.20	0.9840	2.425	6.091	19.66	23.32	−0.0385
1.213 63	333.68	0.9762	2.316	5.954	21.08	24.71	−0.0419
T = 423.15 K							
0.077 04	21.94	0.9981	1.856	5.368	10.53	14.04	−0.0205
0.113 55	32.36	0.9972	1.845	5.353	11.89	15.40	−0.0237
0.167 30	47.75	0.9959	1.828	5.332	13.25	16.76	−0.0270
0.246 34	70.45	0.9940	1.802	5.299	14.62	18.11	−0.0303
0.362 36	103.93	0.9910	1.765	5.251	15.97	19.46	−0.0336
0.532 21	153.33	0.9867	1.708	5.179	17.33	20.80	−0.0369
0.779 90	226.20	0.9801	1.621	5.069	18.67	22.12	−0.0403
T = 398.15 K							
0.072 45	21.94	0.9977	1.115	4.417	9.99	13.29	−0.0223
0.106 77	32.36	0.9966	1.101	4.400	11.28	14.57	−0.0256
0.157 26	47.75	0.9949	1.081	4.375	12.56	15.85	−0.0288
0.231 43	70.45	0.9924	1.051	4.336	13.84	17.12	−0.0321
0.340 15	103.93	0.9887	1.006	4.279	15.11	18.38	−0.0354

[a] Reference state: H^*_{ref} = 0.0 and S^*_{ref} = 0.0 at P_{ref} = 1.0 kPa and T_{ref} = 273.16 K.

Table II. Smoothed Compressibility Factors, Densities, and Residual Properties for the 75% CH_4–25% H_2O Mixture[a]

P, MPa	ρ, mol/m^3	Z	$U - U^*_{\text{ref}}$, kJ/mol	$H - H^*_{\text{ref}}$, kJ/mol	$A - A^*_{\text{ref}}$, kJ/mol	$G - G^*_{\text{ref}}$, kJ/mol	$S - S^*_{\text{ref}}$, kJ/(mol·K)
T = 498.15 K							
0.182 87	44.18	0.9994	4.559	8.698	14.69	18.83	−0.0203
0.269 65	65.17	0.9990	4.553	8.690	16.30	20.44	−0.0236
0.397 55	96.13	0.9986	4.543	8.679	17.91	22.05	−0.0268
0.586 00	141.79	0.9979	4.529	8.662	19.52	23.65	−0.0301
0.863 50	209.14	0.9970	4.507	8.637	21.12	25.25	−0.0334
1.271 83	308.47	0.9955	4.476	8.600	22.73	26.85	−0.0366
1.872 00	455.97	0.9935	4.430	8.545	24.33	28.44	−0.0399
2.752 80	671.04	0.9905	4.363	8.465	25.92	30.03	−0.0433
4.042 77	989.68	0.9863	4.263	8.348	27.51	31.60	−0.0467
5.926 91	1459.60	0.9805	4.115	8.176	29.10	33.16	−0.0501
8.670 11	2152.48	0.9726	3.897	7.925	30.67	34.70	−0.0537
T = 485.65 K							
0.178 26	44.18	0.9993	4.118	8.153	14.43	18.47	−0.0212
0.262 85	65.17	0.9989	4.111	8.145	16.00	20.03	−0.0245
0.387 50	96.13	0.9984	4.101	8.132	17.57	21.60	−0.0277
0.571 13	141.79	0.9976	4.085	8.114	19.13	23.16	−0.0310
0.841 48	209.14	0.9965	4.063	8.087	20.70	24.72	−0.0343
1.239 14	308.47	0.9949	4.029	8.047	22.26	26.28	−0.0375
1.823 32	455.97	0.9926	3.979	7.987	23.82	27.83	−0.0409
2.680 00	671.04	0.9892	3.905	7.899	25.38	29.37	−0.0442
3.933 16	989.68	0.9843	3.794	7.769	26.92	30.90	−0.0476
5.760 20	1459.60	0.9774	3.628	7.575	28.46	32.41	−0.0511
8.412 70	2152.48	0.9680	3.375	7.283	29.99	33.90	−0.0548
T = 473.15 K							
0.173 66	44.18	0.9992	3.685	7.615	14.16	18.09	−0.0221
0.256 04	65.17	0.9988	3.677	7.606	15.69	19.62	−0.0254
0.377 44	96.13	0.9982	3.666	7.593	17.22	21.14	−0.0286
0.556 25	141.79	0.9973	3.650	7.573	18.74	22.67	−0.0319
0.819 42	209.14	0.9961	3.625	7.544	20.27	24.18	−0.0352
1.206 38	308.47	0.9942	3.589	7.500	21.79	25.70	−0.0385
1.774 50	455.97	0.9915	3.535	7.436	23.31	27.21	−0.0418
2.606 83	671.04	0.9876	3.455	7.340	24.82	28.70	−0.0452
3.822 60	989.68	0.9819	3.332	7.195	26.32	30.19	−0.0486
5.590 98	1459.60	0.9738	3.146	6.976	27.82	31.65	−0.0521
T = 460.65 K							
0.169 05	44.18	0.9991	3.259	7.085	13.88	17.71	−0.0231
0.249 24	65.17	0.9986	3.251	7.075	15.37	19.19	−0.0263
0.367 38	96.13	0.9979	3.239	7.061	16.85	20.67	−0.0296
0.541 36	141.79	0.9970	3.221	7.040	18.34	22.16	−0.0328
0.797 34	209.14	0.9955	3.195	7.008	19.82	23.63	−0.0361
1.173 55	308.47	0.9934	3.157	6.961	21.30	25.11	−0.0394
1.725 51	455.97	0.9903	3.099	6.891	22.78	26.57	−0.0427
2.533 26	671.04	0.9857	3.011	6.786	24.25	28.02	−0.0461
3.711 01	989.68	0.9791	2.876	6.626	25.71	29.46	−0.0496
T = 448.15 K							
0.164 44	44.18	0.9989	2.840	6.563	13.59	17.31	−0.0240
0.242 43	65.17	0.9984	2.832	6.552	15.03	18.75	−0.0272
0.357 31	96.13	0.9977	2.819	6.537	16.48	20.19	−0.0305
0.526 45	141.79	0.9965	2.801	6.514	17.92	21.63	−0.0337
0.775 23	209.14	0.9949	2.773	6.480	19.36	23.07	−0.0370
1.140 66	308.47	0.9925	2.731	6.429	20.80	24.50	−0.0403
1.676 34	455.97	0.9889	2.669	6.353	22.24	25.92	−0.0437
2.459 25	671.04	0.9836	2.573	6.238	23.67	27.33	−0.0471
T = 423.15 K							
0.155 22	44.18	0.9986	2.026	5.540	12.96	16.48	−0.0258
0.228 80	65.17	0.9980	2.017	5.528	14.33	17.84	−0.0291
0.337 16	96.13	0.9970	2.002	5.510	15.69	19.20	−0.0324
0.496 59	141.79	0.9956	1.981	5.484	17.05	20.56	−0.0356
0.730 90	209.14	0.9934	1.949	5.444	18.41	21.91	−0.0389
1.074 61	308.47	0.9903	1.901	5.385	19.77	23.25	−0.0422
1.577 41	455.97	0.9855	1.829	5.296	21.12	24.59	−0.0456
T = 398.15 K							
0.145 99	44.18	0.9982	1.241	4.545	12.29	15.60	−0.0278
0.215 16	65.17	0.9974	1.230	4.532	13.58	16.88	−0.0310
0.316 97	96.13	0.9962	1.214	4.511	14.86	18.16	−0.0343
0.466 66	141.79	0.9943	1.190	4.481	16.14	19.43	−0.0375
0.686 40	209.14	0.9915	1.153	4.436	17.42	20.70	−0.0408

[a] Reference state: $H^*_{\text{ref}} = 0.0$ and $S^*_{\text{ref}} = 0.0$ at $P_{\text{ref}} = 1.0$ kPa and $T_{\text{ref}} = 273.16$ K.

Table III. Smoothed Compressibility Factors, Densities, and Residual Properties for the 90% CH_4–10% H_2O Mixture[a]

P, MPa	ρ, mol/m^3	Z	$U - U^*_{\text{ref}}$, kJ/mol	$H - H^*_{\text{ref}}$, kJ/mol	$A - A^*_{\text{ref}}$, kJ/mol	$G - G^*_{\text{ref}}$, kJ/mol	$S - S^*_{\text{ref}}$, kJ/(mol·K)
T = 498.15 K							
0.247 21	59.71	0.9997	4.730	8.871	15.90	20.05	−0.0224
0.364 55	88.05	0.9996	4.723	8.864	17.51	21.65	−0.0257
0.537 57	129.87	0.9995	4.714	8.853	19.12	23.26	−0.0289
0.792 65	191.54	0.9992	4.699	8.838	20.73	24.87	−0.0322
1.168 64	282.49	0.9989	4.678	8.815	22.34	26.48	−0.0355
1.722 77	416.63	0.9985	4.647	8.782	23.95	28.08	−0.0387
2.539 35	614.44	0.9979	4.601	8.734	25.55	29.68	−0.0421
3.742 69	906.17	0.9973	4.533	8.664	27.16	31.29	−0.0454
5.517 01	1336.37	0.9968	4.434	8.562	28.76	32.89	−0.0488
8.138 51	1970.75	0.9971	4.287	8.417	30.36	34.49	−0.0523
12.032 63	2906.13	0.9997	4.071	8.211	31.97	36.11	−0.0560
T = 473.15 K							
0.234 76	59.71	0.9996	3.822	7.754	15.32	19.25	−0.0243
0.346 16	88.05	0.9994	3.815	7.747	16.85	20.78	−0.0275
0.510 39	129.87	0.9991	3.805	7.735	18.38	22.31	−0.0308
0.752 42	191.54	0.9986	3.789	7.718	19.90	23.83	−0.0341
1.109 03	282.49	0.9980	3.767	7.693	21.43	25.35	−0.0373
1.634 22	416.63	0.9972	3.734	7.656	22.95	26.88	−0.0406
2.407 36	614.44	0.9960	3.685	7.603	24.48	28.39	−0.0439
3.544 95	906.17	0.9945	3.612	7.524	26.00	29.91	−0.0473
5.218 60	1336.37	0.9927	3.505	7.411	27.52	31.42	−0.0507
7.683 23	1970.75	0.9911	3.347	7.246	29.03	32.93	−0.0543
11.326 88	2906.13	0.9908	3.114	7.011	30.55	34.44	−0.0580
T = 448.15 K							
0.222 31	59.71	0.9993	2.949	6.672	14.69	18.41	−0.0262
0.327 77	88.05	0.9990	2.941	6.664	16.14	19.86	−0.0294
0.483 19	129.87	0.9986	2.930	6.651	17.58	21.30	−0.0327
0.712 17	191.54	0.9979	2.914	6.632	19.03	22.75	−0.0360
1.049 35	282.49	0.9970	2.890	6.605	20.47	24.19	−0.0392
1.545 52	416.63	0.9957	2.854	6.564	21.91	25.62	−0.0425
2.275 03	614.44	0.9938	2.802	6.504	23.35	27.06	−0.0459
3.346 47	906.17	0.9912	2.724	6.417	24.79	28.48	−0.0492
4.918 49	1336.37	0.9878	2.609	6.290	26.22	29.90	−0.0527
7.224 05	1970.75	0.9839	2.439	6.104	27.65	31.32	−0.0563
T = 423.15 K							
0.209 85	59.71	0.9991	2.109	5.624	14.01	17.53	−0.0281
0.309 37	88.05	0.9987	2.101	5.615	15.38	18.89	−0.0314
0.455 98	129.87	0.9980	2.089	5.601	16.74	20.25	−0.0346
0.671 88	191.54	0.9971	2.072	5.580	18.10	21.61	−0.0379
0.989 59	282.49	0.9958	2.046	5.549	19.47	22.97	−0.0412
1.456 64	416.63	0.9938	2.008	5.504	20.83	24.32	−0.0445
2.142 31	614.44	0.9911	1.952	5.438	22.18	25.67	−0.0478
3.147 11	906.17	0.9872	1.868	5.341	23.54	27.01	−0.0512
4.616 39	1336.37	0.9819	1.744	5.199	24.88	28.34	−0.0547
T = 398.15 K							
0.197 39	59.71	0.9988	1.303	4.609	13.28	16.59	−0.0301
0.290 95	88.05	0.9982	1.294	4.599	14.57	17.87	−0.0333
0.428 75	129.87	0.9973	1.282	4.583	15.85	19.15	−0.0366
0.631 55	191.54	0.9961	1.263	4.560	17.13	20.43	−0.0399
0.929 73	282.49	0.9943	1.235	4.526	18.41	21.70	−0.0431
1.367 55	416.63	0.9916	1.194	4.477	19.69	22.97	−0.0465
2.009 12	614.44	0.9878	1.133	4.403	20.96	24.23	−0.0498

[a] Reference state: $H^*_{\text{ref}} = 0.0$ and $S^*_{\text{ref}} = 0.0$ at $P_{\text{ref}} = 1.0$ kPa and $T_{\text{ref}} = 273.16$ K.

Residual Properties. The thermodynamic properties of internal energy (U), enthalpy (H), Helmholtz free energy (A), Gibbs free energy (G), and entropy (S) may be conveniently calculated with the compressibilities and densities of the above analysis using the concept of residual properties. A residual property is defined as the property value of the real fluid less that property value in the perfect gas state. Various forms of such residual properties are discussed by Hall et al. (*21*). The form of residual property described below 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, if M denotes the properties U, H, A, G, and S, then the residual property is defined as

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

where the asterisk indicates the hypothetical perfect gas state. The integration path is

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

Using this approach, it is convenient to derive $(U - U^*_{\text{ref}})$ and $(S - S^*_{\text{ref}})$ and then to calculate the remaining residual properties from these two. The starting equations are

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

and

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

Then, the residual internal energy is

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

and the residual entropy is

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

The remaining residual properties may be calculated from the following:

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

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

and

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

Any reference state may be specified, but a recommended reference state is one for which $H^*_{\rm ref}$ and $S^*_{\rm ref}$ are set equal to zero. In this case, $G^*_{\rm ref} = 0$, $U^*_{\rm ref} = -RT_{\rm ref}$, and $A^*_{\rm ref} = -RT_{\rm ref}$.

The only integrals required to calculate all the above residual properties are

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

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

$$\frac{1}{T}\int_{T_{\rm ref}}^T \frac{C_v^*}{R}\,dT$$

and

$$\int_{T_{\rm ref}}^T \frac{C_v^*}{R}\frac{dT}{T}$$

The first two require simple applications of the virial equation of state. The other two integrals involve only perfect gas specific heats. If the Leiden virial equation is used, the required derivatives may be obtained from

$$\left(\frac{\partial Z}{\partial(1/T)}\right)_\rho = -T^2\left[\left(\frac{dB}{dT}\right)\rho + \left(\frac{dC}{dT}\right)\rho^2 + \ldots\right] \qquad (9)$$

where $B(T)$ and $C(T)$ may be fit to an inverse temperature series.

Results

Tables I–III present the smoothed compressibility factors, densities, and residual thermodynamic properties for the three mixtures. The reference state for the residual properties is one for which $H^*_{\rm ref}$ are set equal to zero at $P_{\rm ref}$ = 1.0 kPa and $T_{\rm ref}$ = 273.16 K. The perfect gas specific heat capabilities used for this calculation were obtained from a four-constant polynomial regression of the data of Woolley (*22*) for water and of Angus et al. (*23*) for methane. The properties listed in the tables have the following estimated accuracies: densities, 0.08%; compressibilities, 0.09%; internal energy, 0.20%; entropies and enthalpies, 0.15%; Helmholtz and Gibbs free energies, 0.17%. Finally, Figures 1–3 show pressure–enthalpy

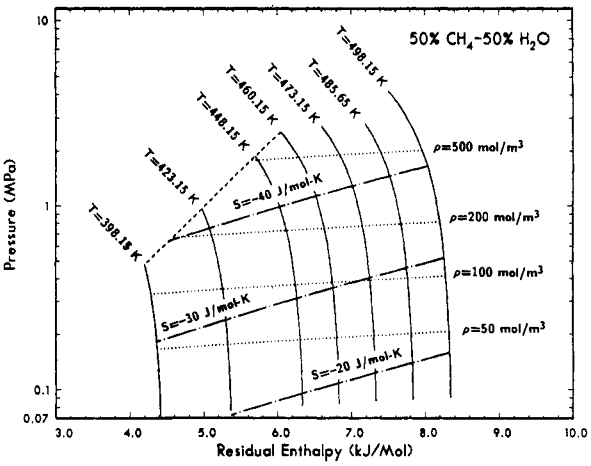

Figure 1. Pressure–enthalpy diagram for 50% CH$_4$–50% H$_2$O mixture. The reference state is $H_{\rm ref}$ = 0.0 and $S_{\rm ref}$ = 0.0 at $P_{\rm ref}$ = 1.0 kPa and $T_{\rm ref}$ = 273.16 K.

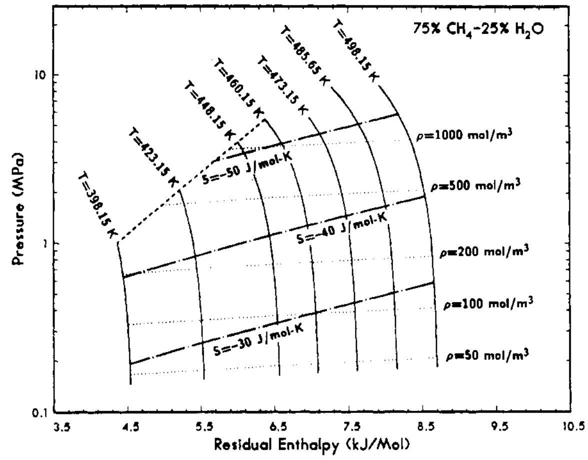

Figure 2. Pressure–enthalpy diagram for 75% CH$_4$–25% H$_2$O mixture. The reference state is $H_{\rm ref}$ = 0.0 and $S_{\rm ref}$ = 0.0 at $P_{\rm ref}$ = 1.0 kPa and $T_{\rm ref}$ = 273.16 K.

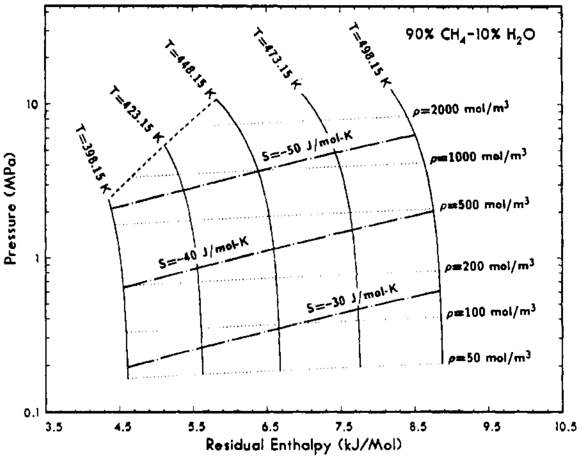

Figure 3. Pressure–enthalpy diagram for 90% CH$_4$–10% H$_2$O mixture. The reference state is $H_{\rm ref}$ = 0.0 and $S_{\rm ref}$ = 0.0 at $P_{\rm ref}$ = 1.0 kPa and $T_{\rm ref}$ = 273.16 K.

diagrams developed from the experimental data for each mixture.

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Glossary

A	Helmholtz free energy
B	second virial coefficient
C	third virial coefficient
C_v	specific heat capacity at constant volume
G	Gibbs free energy
H	enthalpy
P	pressure
R	universal gas constant
S	entropy
T	absolute temperature
U	internal energy
Z	compressibility factor

Greek Letters

ρ	density

Superscripts

*	perfect gas value

Subscripts

ref	reference-state value

Literature Cited

(1) Patel, M. R.; Eubank, P. T. *J. Chem. Eng. Data* **1988**, *33*, 185.
(2) Rigby, M.; Prausnitz, J. M. *J. Phys. Chem.* **1968**, *72*, 330.
(3) O'Sullivan, T. D.; Smith, N. O. *J. Phys. Chem.* **1970**, *74*, 1460.
(4) Sultanov, R. G.; Skripka, V. G.; Namiot, A. Y. *Gazov. Prom.* **1972**, *16*, 6.
(5) Rettich, T. R.; Handa, Y. P.; Battino, R.; Wilhelm, E. *J. Phys. Chem.* **1981**, *85*, 3230.
(6) Marshall, D. R.; Saito, S.; Kobayashi, R. *AIChE J.* **1964**, *10*, 202.
(7) Aoyagi, K.; Song, K. Y.; Sloan, D.; Dharmawardhana, P. B.; Kobayashi, R. *Proceedings of the 58th Annual Convention*; Gas Processors Association: Tulsa, OK, 1979.
(8) Smith, G.; Sellars, A.; Yerlett, T. K.; Wormald, C. J. *J. Chem. Thermodyn.* **1983**, *15*, 29.
(9) Gillespie, P. C.; Wilson, G. M. *Research Report RR-48*; Gas Processors Association: Tulsa, OK, 1982.
(10) Olds, R. H.; Sage, B. H.; Lacey, W. N. *Ind. Eng. Chem.* **1942**, *29*, 107.
(11) Scheloske, J. J.; Hall, K. R.; Holste, J. C.; Eubank, P. T. *Energy Prog.* **1983**, *15*, 29.
(12) Anderson, L. N. M.S. Thesis, Texas A&M University, College Station, TX, 1965.
(13) Patel, M. R. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1986.
(14) Burnett, E. S. *U.S. Bureau of Mines Rep. Inv.* **1963**, 6267.
(15) Pope, G. P.; Chappelear, P.; Kobayashi, R. *Physica* **1972**, *57*, 127.
(16) Hall, K. R.; Eubank, P. T. *Physica* **1972**, *61*, 346.
(17) Burnett, E. S. *Appl. Mech.* **1936**, *3*, A136.
(18) Hall, K. R.; Canfield, F. B. *Physica* **1970**, *47*, 99.
(19) Holste, J. C.; Watson, M. Q.; Bellomy, M. T.; Eubank, P. T.; Hall, K. R. *AIChE J.* **1980**, *26*, 954.
(20) Joffrion, L. L.; Eubank, P. T. *Fluid Phase Equilib.* **1988**, *43*, 263.
(21) Hall, K. R.; Eubank, P. T.; Holste, J. C. *Chem. Eng. Educ.* **1983**, Summer, 124.
(22) Wooley, H. W. *J. Res. Natl. Bur. Stand.* **1987**, *92*, 35.
(23) Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State—5, Methane*; Pergamon Press: Oxford, 1978.

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Phase Diagrams of Binary Solid Azole Systems

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Phase diagrams of the binary solid azoles pyrazole, imidazole, triazole, and tetrazole were measured. It was found that all binary mixtures formed simple eutectic systems except the imidazole–tetrazole system, which was found to form a 1:1 solid addition compound. Enthalpies of fusion for the pure solids were measured and used to calculate ideal phase diagrams. With the exception of tetrazole-rich mixtures, the simple eutectic systems approached ideality.

Introduction

Mixtures of imidazole ($C_3H_4N_2$), pyrazole ($C_3H_4N_2$), triazole ($C_2H_3N_3$), and tetrazole (CH_2N_4) have been shown to possess remarkable conducting properties at relatively low temperatures (*1*). Various binary and ternary mixtures of these azoles were shown to have specific conductivities in the range of 10^{-2}–10^{-3} Ω^{-1} cm^{-1} at 298 K. These mixtures also showed good solvent properties, dissolving many organic solvents and water. We measured the binary phase diagrams of these four solid azoles along with the enthalpies of fusion of the pure solids. All binary pairs except imidazole–tetrazole were found to form simple eutectic systems with several mixtures showing near-ideal behavior.

Experimental Section

Materials. Imidazole (99%), pyrazole (98%), 1,2,4-triazole (98%), and 1*H*-tetrazole (99%) from Aldrich Chemical Co. were twice sublimed, giving melting points of 363.7, 343.2, 393.5, and 430.7 K, respectively. All compounds completely melted within a range of 1 K.

Melting Points. Phase transitions were determined by a sealed-tube method (*2*). Ampules were made from 7-mm glass tubing. The tube was purged with nitrogen, a small Teflon-coated stirring bar was inserted, and appropriate amounts of pure compounds were weighed into the tube. The tube was again purged with nitrogen, and a thermocouple well made of 4-mm glass tubing was inserted and the tube sealed closed. Temperatures were measured using a copper–constantan thermocouple attached to appropriate computer interfacing and the data read directly into a microcomputer. The thermocouples were calibrated against an NBS Certified thermometer while in the measuring cell. The transition points were measured in an oil bath whose temperature was carefully controlled to ±0.1 °C; a bright backlight was used to observe the pres-

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