Molar Heat Capacity at Constant Volume for $[xCO_2 + (1 - x)C_2H_6]$ from 220 to 340 K at Pressures to 35 MPa

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Measurements of the molar heat capacity at constant volume (C_v) for $[xCO_2 + (1 - x)C_2H_6]$, x = 0.25, 0.49, 0.74, were conducted. Temperatures ranged from about 220 to 340 K, and pressures were as high as 35 MPa. Measurements were conducted on samples in compressed gas and liquid states. The primary sources of uncertainty are the estimated temperature rise and the estimated quantity of substance in the calorimeter. Overall, the uncertainty ($\pm 2\sigma$) of the C_v values is estimated to be less than ±2.0% for vapor and ±0.5% for liquid.

Introduction

One of the long-range objectives of thermophysical property research at the National Institute of Standards and Technology (NIST) is the development of accurate predictive methods for calculating the properties of gaseous and liquid mixtures. These models play a key role in process equipment design, in metering applications, and in design and operation of transportation systems such as pipelines. The ongoing development and testing of these models relies heavily on benchmark experimental measurements. These measurements are conducted on selected pure components and their mixtures to provide a data base that is representative of broad classes of fluid types.

The substances CO_2 and C_2H_6 are key components of natural gas. Knowledge of the thermophysical properties for the pure components and their mixtures is vital to the development of predictive models for natural gas mixtures. In addition, the $(CO_2 + C_2H_6)$ binary system is of fundamental interest to chemical engineers due to its azeotropic behavior. Furthermore, both substances have critical temperatures near ambient; thus, experiments on its mixtures will demonstrate near-critical behavior at temperatures only slightly above room temperature. Earlier experiments with the same gas samples have characterized the density (*1, 2*) and viscosity (*3, 4*) behavior of $(CO_2 + C_2H_6)$ mixtures. Together with the density data, the heat capacity measurements will provide a data base for developing a new equation of state and testing predictive models for $(CO_2 + C_2H_6)$ mixtures.

Apparatus and Procedures

The heat capacity measurements in this study were performed in the calorimeter described by Goodwin (*5*) and Magee (*6*). Briefly, in this method, a sample of well-established mass (or number N of moles) is confined to a bomb of approximately 73 cm³ volume; the exact volume varies with temperature and pressure. When a precisely measured amount of electrical energy (Q) is applied, the resulting temperature rise ($\Delta T = T_2 - T_1$) is measured. When the energy (Q_0) required to heat the empty bomb is subtracted from the total, the heat capacity is

$$C_v = (Q - Q_0)N^{-1}\Delta T^{-1} \quad (1)$$

For this study, a sample was charged to the bomb, and then the charge valve was sealed. To ensure that the sample's composition remained uniform, both the supply cylinder and the gas compressor were heated to a temperature in the supercritical region for the mixture. The bomb and its contents were then cooled to a temperature just above the saturation temperature. Then, measurements were begun and continued in the single-phase region until either the upper temperature (about 345 K) or pressure (35 MPa) was obtained. At the completion of a run, some of the sample was discharged to obtain the next filling density. A series of such runs at different densities (ϱ) completes the $C_v(\varrho,T)$ surface for the substance under study.

The mixture samples used in the experimental measurements of heat capacity were gravimetrically prepared in thoroughly cleaned aluminum cylinders from research grade gases. The purity of the component gases has been verified by chemical analysis. Three cylinders of $(CO_2 + C_2H_6)$ were prepared with mole fractions of carbon dioxide: 0.25166, 0.49245, 0.73978. The combined mole fraction uncertainty, at the $\pm 2\sigma$ level, due to low levels of impurities and to weighing uncertainties is ±0.00001.

Results and Discussion

Presentation of Results and Assessment of Uncertainties. Significant adjustments must be applied to the raw data for the energy required to heat the empty calorimeter from initial (T_1) to final temperature (T_2). This is accomplished using the results of previous experiments done with a thoroughly evacuated bomb. These results were fitted to a 12-parameter polynomial $Q_0(T)$ given previously (*6*). Additionally, an adjustment for PV work done by the fluid on the thin-walled bomb as the pressure rises from P_1 to P_2 is applied for each point. Corrections for PV work on the bomb were calculated by an equation discussed in a previous publication (*7*) from this laboratory

$$C_{PV} = k[T_2(\partial P/\partial T)_{\varrho_2} - \Delta P/2]\Delta V_m/\Delta T \quad (2)$$

where k = 1000 J·MPa^{-1}·dm^{-3}, the pressure rise is $\Delta P = P_2 - P_1$, and the volume change per mole is $\Delta V_m = \varrho_2^{-1} -$

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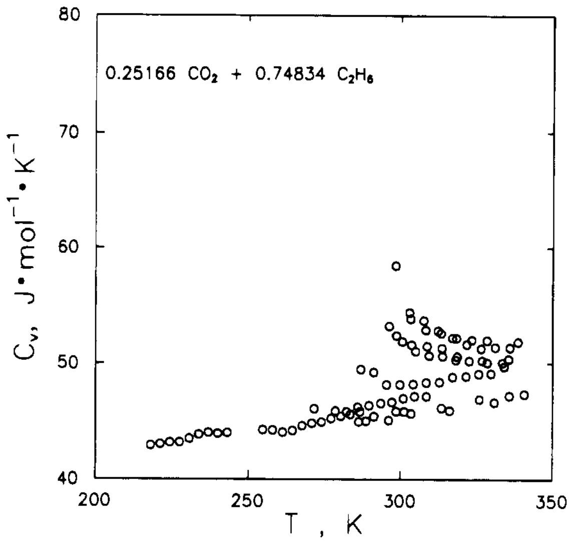

Figure 1. Heat capacity of gaseous and liquid $(0.25166)CO_2$ + $(0.74834)C_2H_6$ as a function of temperature.

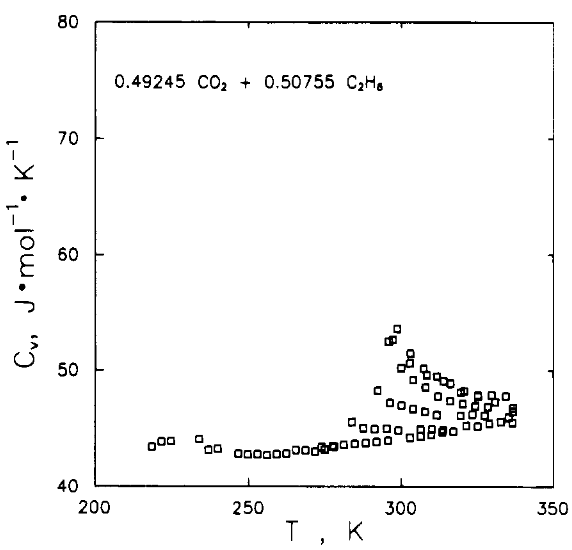

Figure 2. Heat capacity of gaseous and liquid $(0.49245)CO_2$ + $(0.50755)C_2H_6$ as a function of temperature.

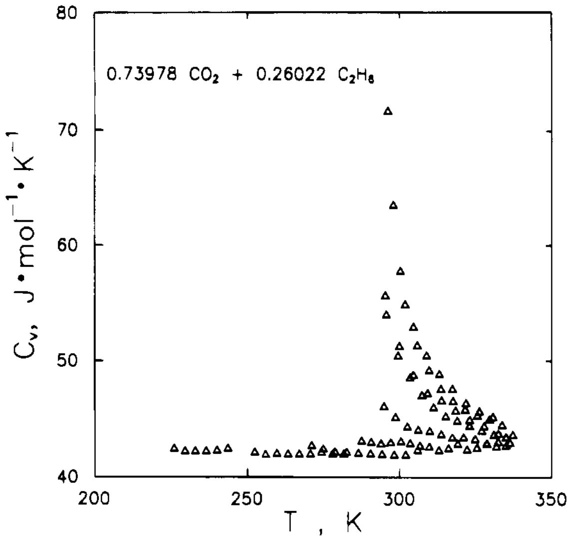

Figure 3. Heat capacity of gaseous and liquid $(0.73978)CO_2$ + $(0.26022)C_2H_6$ as a function of temperature.

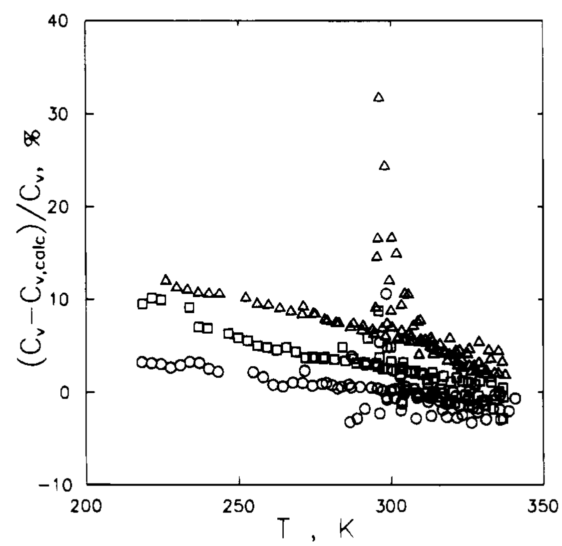

Figure 4. Comparison of heat capacity measurements on gaseous and liquid $[xCO_2 + (1-x)C_2H_6]$ mixtures (○, $x = 0.25166$; □, $x = 0.49245$; △, $x = 0.73978$) with the calculations of an extended corresponding states model (*8*).

ϱ_1^{-1}. The derivative has been calculated with an extended corresponding states model, DDMIX (*8*), which was optimized for CO_2-containing mixtures.

Table 1 gives the carbon dioxide composition, temperature, pressure, and density for each value of the single-phase vapor or liquid heat capacity. The composition, temperature, and pressure are experimental values. The uncertainty of temperature does not exceed ±0.03 K, while the uncertainty of the pressure is $\pm(0.0007 + 0.0001p)$ MPa. The density value has been calculated with the DDMIX model with an estimated uncertainty of ±0.15%. The moles of substance used in eq 1 is the product $V_{\text{bomb}}\varrho$, where V_{bomb} has been determined previously as a function of pressure and temperature (*6*). Data for a total of 260 state conditions are given. A correction for *PV* work on the bomb, given by eq 2, has been applied. The magnitude of this adjustment ranges from 0.4 to 6% of the final heat capacity values. A detailed analysis of the uncertainties (*6*) concludes that the uncertainty of the heat capacity values is ±2.0% for the vapor and ±0.5% for the liquid. An exception to this general level of uncertainty occurs close to the critical points. For the purposes of this discussion, this region includes all C_v values that are at least 10 $J\cdot mol^{-1}\cdot K^{-1}$ greater than the background heat capacity. For these points, it is estimated that the uncertainty expands to ±10%. Primarily, this is attributed to larger than normal uncertainties of the density and the temperature rise. The final experimental C_v values are plotted in Figures 1−3. These figures illustrate that the temperature dependence is practically the same exhibited by CO_2 (*9*) and by C_2H_6 (*10*), when they were studied previously using the same calorimeter. This result is not surprising, considering the proximity of the mixture's critical temperature locus to the critical temperatures of both CO_2 and C_2H_6.

Comparison with an Extended Corresponding States Model. Often, when thermophysical property models are used for predicting heat capacities of liquid mixtures, they give predictions that are not closer than about 20−50% from experimental values. Since DDMIX is one of the most accurate models available, it was decided to test it with the measured values of this study. The calculated C_v values in Table 1 were derived from this corresponding

Table 1. Molar Heat Capacities for [xCO_2 + (1 − x)C_2H_6]: T, Temperature (ITS-90); ρ, Density; p, Pressure

T/K	ρ^a/mol·dm^{-3}	p/MPa	C_v/ (J·mol^{-1}·K^{-1})	$C_{v,calcd}$^{a}/ (J·mol^{-1}·K^{-1})	diff.^{b}	T/K	ρ^a/mol·dm^{-3}	p/MPa	C_v/ (J·mol^{-1}·K^{-1})	$C_{v,calcd}$^{a}/ (J·mol^{-1}·K^{-1})	diff.^{b}
					(0.25166)CO_2 + (0.74834)C_2H_6						
218.15	18.38	10.102	42.91	41.53	3.22	304.88	10.23	7.153	51.04	50.76	0.54
221.32	18.36	13.118	43.03	41.69	3.10	309.23	10.19	7.960	50.65	50.81	−0.31
224.49	18.35	16.104	43.16	41.87	3.00	313.59	10.17	8.780	50.61	50.85	−0.48
227.64	18.34	19.066	43.18	42.05	2.63	317.97	10.16	9.611	50.28	50.90	−1.24
230.78	18.33	21.998	43.49	42.24	2.88	322.35	10.14	10.449	50.21	50.97	−1.51
233.89	18.32	24.906	43.85	42.43	3.24	326.75	10.13	11.293	50.23	51.06	−1.66
237.00	18.31	27.743	44.01	42.63	3.14	335.56	10.11	12.998	50.37	51.31	−1.87
240.09	18.30	30.568	43.93	42.83	2.50	298.43	9.39	5.694	58.44	52.25	10.59
243.17	18.29	33.339	44.01	43.05	2.18	302.90	8.46	6.179	54.39	53.47	1.69
254.71	16.18	8.198	44.26	43.31	2.15	307.52	8.18	6.732	53.70	53.51	0.34
257.96	16.17	10.224	44.23	43.51	1.63	312.20	8.07	7.306	52.81	53.36	−1.04
261.20	16.16	12.250	44.06	43.72	0.79	316.89	8.02	7.889	52.20	53.20	−1.90
264.43	16.15	14.264	44.21	43.93	0.62	321.62	7.98	8.480	51.64	53.06	−2.75
267.65	16.14	16.265	44.61	44.15	1.03	326.36	7.96	9.074	51.27	52.96	−3.29
270.87	16.13	18.256	44.82	44.38	0.99	331.11	7.94	9.672	51.39	52.90	−2.94
274.07	16.12	20.235	44.93	44.61	0.70	335.87	7.93	10.272	51.36	52.87	−2.95
277.27	16.11	22.200	45.25	44.85	0.89	303.21	6.49	5.918	53.85	54.92	−1.98
280.46	16.10	24.155	45.43	45.09	0.76	308.17	6.28	6.355	52.88	54.39	−2.84
283.64	16.09	26.096	45.60	45.34	0.58	313.19	6.18	6.794	52.59	53.94	−2.56
286.82	16.08	28.024	45.82	45.59	0.50	318.24	6.12	7.234	52.17	53.58	−2.70
271.57	14.30	4.584	46.09	45.03	2.29	323.31	6.09	7.675	52.02	53.30	−2.46
278.62	14.26	7.516	45.88	45.42	0.98	328.39	6.06	8.115	51.98	53.10	−2.16
282.36	14.24	9.110	45.82	45.64	0.40	338.59	6.03	8.995	51.85	52.91	−2.06
286.07	14.23	10.702	46.23	45.86	0.81	298.60	4.13	5.078	52.39	52.80	−0.79
289.80	14.22	12.296	46.34	46.08	0.56	303.53	4.10	5.351	51.59	52.24	−1.24
293.52	14.21	13.890	46.55	46.32	0.49	308.49	4.08	5.619	51.47	51.79	−0.62
297.22	14.20	15.482	46.64	46.56	0.17	313.44	4.07	5.881	51.32	51.44	−0.23
300.93	14.19	17.069	46.96	46.81	0.31	318.42	4.05	6.140	50.58	51.19	−1.20
304.63	14.18	18.653	47.15	47.07	0.17	328.42	4.03	6.659	50.07	50.95	−1.75
308.33	14.18	20.233	47.16	47.34	−0.39	333.43	4.03	6.917	50.04	50.93	−1.78
287.02	12.30	4.926	49.46	47.57	3.83	286.43	2.03	3.318	44.96	46.42	−3.24
291.26	12.24	6.066	49.22	47.76	2.95	291.35	2.03	3.431	45.42	46.23	−1.79
295.53	12.21	7.234	48.14	47.94	0.40	296.28	2.03	3.543	45.09	46.13	−2.31
299.80	12.19	8.430	48.17	48.11	0.12	301.20	2.03	3.654	45.82	46.11	−0.63
304.08	12.18	9.638	48.20	48.29	−0.19	315.96	2.02	3.980	45.92	46.38	−1.00
308.36	12.17	10.855	48.34	48.48	−0.28	325.82	2.02	4.194	46.89	46.80	0.20
312.64	12.16	12.079	48.38	48.67	−0.60	330.76	2.02	4.301	46.64	47.06	−0.91
316.92	12.15	13.306	48.82	48.89	−0.14	335.71	2.02	4.407	47.20	47.35	−0.32
321.21	12.14	14.539	48.89	49.11	−0.46	340.68	2.01	4.513	47.35	47.67	−0.68
325.49	12.13	15.772	49.07	49.35	−0.58	288.82	2.03	3.371	45.03	46.31	−2.85
329.78	12.12	17.008	49.10	49.60	−1.02	298.60	2.03	3.596	45.85	46.11	−0.57
334.06	12.11	18.243	49.72	49.87	−0.30	303.48	2.03	3.707	45.67	46.12	−0.98
296.25	10.49	5.626	53.22	50.37	5.35	313.28	2.02	3.926	46.14	46.31	−0.35
300.55	10.30	6.368	51.88	50.67	2.34						
					(0.49245)CO_2 + (0.50755)C_2H_6						
218.47	20.19	11.604	43.42	39.29	9.49	283.94	14.16	6.914	45.55	43.34	4.84
221.55	20.18	14.923	43.87	39.42	10.13	287.66	14.15	8.252	45.05	43.43	3.58
224.61	20.13	17.375	43.90	39.54	9.93	291.40	14.14	9.608	44.96	43.53	3.19
233.74	20.23	29.785	44.06	40.04	9.12	295.14	14.13	10.968	45.01	43.63	3.07
236.77	20.12	30.584	43.16	40.14	7.01	298.89	14.12	12.345	44.85	43.73	2.50
239.78	20.10	33.614	43.26	40.29	6.86	306.39	14.11	15.103	44.94	43.97	2.16
243.43	18.28	7.203	44.35	40.00	9.81	310.15	14.10	16.488	44.96	44.10	1.92
246.58	18.26	9.493	42.84	40.14	6.31	313.91	14.09	17.872	44.90	44.24	1.47
249.76	18.25	11.893	42.78	40.28	5.84	321.46	14.08	20.652	45.25	44.55	1.55
252.93	18.24	14.288	42.80	40.43	5.53	325.23	14.07	22.046	45.20	44.72	1.06
256.10	18.23	16.674	42.72	40.59	4.99	329.03	14.06	23.439	45.43	44.90	1.18
259.26	18.22	19.044	42.80	40.75	4.80	332.83	14.06	24.834	45.58	45.09	1.08
262.41	18.21	21.401	42.86	40.91	4.54	336.63	14.05	26.231	45.50	45.28	0.47
265.56	18.20	23.739	43.16	41.08	4.81	292.29	12.26	6.707	48.26	45.47	5.79
268.70	18.19	26.065	43.13	41.26	4.34	296.14	12.25	7.675	47.23	45.48	3.72
271.83	18.18	28.377	43.03	41.44	3.70	300.01	12.25	8.667	47.01	45.48	3.27
274.97	18.17	30.669	43.21	41.62	3.69	303.91	12.24	9.669	46.69	45.48	2.60
278.09	18.16	32.944	43.43	41.81	3.73	307.81	12.24	10.685	46.45	45.49	2.07
274.01	16.13	10.021	43.42	41.78	3.77	311.73	12.23	11.711	46.15	45.51	1.37
277.62	16.12	11.894	43.49	41.93	3.60	319.58	12.23	13.778	46.11	45.60	1.11
281.22	16.11	13.769	43.61	42.08	3.50	323.51	12.22	14.820	46.22	45.67	1.21
284.83	16.10	15.641	43.71	42.24	3.37	327.47	12.22	15.867	46.12	45.75	0.82
288.42	16.09	17.511	43.77	42.41	3.11	335.41	12.20	17.976	45.97	45.95	0.04
292.02	16.08	19.376	43.86	42.58	2.92	295.95	10.51	6.622	52.49	47.91	8.73
295.63	16.07	21.243	43.97	42.76	2.74	299.92	10.49	7.345	50.22	47.78	4.85
302.81	16.05	24.943	44.23	43.14	2.47	303.93	10.48	8.089	49.19	47.62	3.18
306.40	16.04	26.788	44.34	43.34	2.26	307.97	10.48	8.853	48.56	47.47	2.25
309.99	16.03	28.627	44.45	43.55	2.03	312.07	10.49	9.635	47.77	47.33	0.93
313.59	16.02	30.453	44.70	43.76	2.11	316.18	10.49	10.425	47.38	47.22	0.34
317.19	16.01	32.269	44.75	43.98	1.73	320.28	10.49	11.216	47.14	47.13	0.02

Table 1. (Continued)

T/K	ϱ^a/mol·dm^{-3}	p/MPa	C_v/(J·mol^{-1}·K^{-1})	$C_{v,calcd}{}^a$/(J·mol^{-1}·K^{-1})	diff.[b]	T/K	ϱ^a/mol·dm^{-3}	p/MPa	C_v/(J·mol^{-1}·K^{-1})	$C_{v,calcd}{}^a$/(J·mol^{-1}·K^{-1})	diff.[b]
					(0.49245)CO_2 + (0.50755)C_2H_6						
324.40	10.49	12.014	46.93	47.07	−0.30	329.84	7.33	9.973	47.89	48.35	−0.96
328.53	10.48	12.815	46.86	47.04	−0.38	334.40	7.32	10.475	47.80	48.19	−0.82
336.84	10.47	14.432	46.78	47.04	−0.55	297.26	6.69	6.228	52.65	51.34	2.49
298.67	7.67	6.522	53.59	51.01	4.81	302.79	6.48	6.738	50.61	50.41	0.40
303.01	7.51	7.003	51.46	50.48	1.89	308.38	6.40	7.252	49.61	49.66	−0.11
307.41	7.44	7.491	50.17	49.98	0.39	314.00	6.35	7.764	49.08	49.06	0.03
311.84	7.40	7.982	49.50	49.53	−0.07	319.65	6.32	8.276	48.12	48.59	−0.99
316.30	7.37	8.477	48.89	49.15	−0.53	325.30	6.30	8.786	47.79	48.23	−0.92
320.79	7.35	8.975	48.25	48.83	−1.20	330.99	6.29	9.296	47.29	47.97	−1.44
325.31	7.34	9.473	47.88	48.57	−1.44	336.72	6.28	9.808	46.46	47.78	−2.85
					(0.73978)CO_2 + (0.26022)C_2H_6						
226.13	22.32	12.168	42.51	37.35	12.14	317.42	14.02	15.069	43.48	41.54	4.47
229.64	22.31	16.201	42.29	37.46	11.42	321.20	14.02	16.291	43.48	41.51	4.54
233.15	22.30	20.251	42.31	37.58	11.18	324.99	14.02	17.510	43.34	41.50	4.25
236.66	22.29	24.238	42.28	37.70	10.85	328.79	14.02	18.735	42.90	41.49	3.29
240.16	22.27	28.166	42.38	37.82	10.75	332.60	14.02	19.964	43.09	41.51	3.68
243.65	22.26	32.075	42.52	37.95	10.76	336.44	14.02	21.200	43.00	41.53	3.41
252.32	20.15	9.649	42.21	37.86	10.31	295.69	11.49	6.961	54.07	45.04	16.69
256.02	20.13	12.691	42.02	37.96	9.65	299.52	11.81	7.834	50.52	44.36	12.19
259.73	20.12	15.740	42.09	38.08	9.53	303.39	11.93	8.723	48.62	43.99	9.52
263.43	20.11	18.759	42.06	38.19	9.19	307.30	12.03	9.645	47.10	43.68	7.26
267.12	20.10	21.777	42.03	38.32	8.83	311.23	12.08	10.573	46.07	43.43	5.73
270.81	20.08	24.769	42.03	38.44	8.52	315.18	12.11	11.514	45.31	43.22	4.62
274.49	20.07	27.738	42.20	38.58	8.59	319.15	12.14	12.462	44.90	43.03	4.15
278.15	20.06	30.675	42.07	38.72	7.97	323.13	12.15	13.419	44.47	42.88	3.58
281.82	20.05	33.615	42.06	38.86	7.60	327.13	12.17	14.383	44.07	42.74	3.00
271.19	18.13	8.367	42.79	38.79	9.37	331.15	12.17	15.351	43.70	42.63	2.45
275.04	18.12	10.675	42.50	38.86	8.55	335.18	12.18	16.334	43.48	42.54	2.15
278.89	18.11	12.993	42.25	38.94	7.82	297.93	9.12	7.048	63.55	47.98	24.49
282.75	18.10	15.313	42.22	39.03	7.56	301.78	9.84	7.747	54.94	46.67	15.06
286.61	18.09	17.632	42.13	39.12	7.14	305.69	10.08	8.451	51.41	45.93	10.64
290.46	18.08	19.947	42.07	39.22	6.78	309.64	10.21	9.166	49.28	45.40	7.87
294.31	18.07	22.255	42.01	39.33	6.40	313.62	10.29	9.890	47.65	44.96	5.63
298.16	18.06	24.556	42.01	39.44	6.12	317.62	10.34	10.622	46.59	44.60	4.28
302.01	18.05	26.846	42.00	39.56	5.82	321.65	10.37	11.355	45.85	44.29	3.41
305.85	18.04	29.124	42.39	39.68	6.40	325.70	10.40	12.102	45.35	44.01	2.95
287.63	16.32	9.695	43.19	39.94	7.52	329.78	10.41	12.849	45.02	43.78	2.76
290.79	16.32	11.123	43.08	39.97	7.24	333.87	10.42	13.603	44.54	43.57	2.18
293.95	16.31	12.558	42.94	39.99	6.87	296.10	7.13	6.619	71.69	48.84	31.87
297.12	16.31	13.995	43.04	40.03	6.99	300.23	7.78	7.183	57.84	48.14	16.77
300.28	16.30	15.435	43.12	40.06	7.08	304.47	7.98	7.741	53.03	47.34	10.74
303.44	16.30	16.879	42.99	40.10	6.72	308.77	8.06	8.301	50.53	46.64	7.71
306.60	16.30	18.324	42.78	40.15	6.15	313.12	8.10	8.863	48.95	46.02	5.97
309.77	16.29	19.767	42.68	40.20	5.81	317.50	8.13	9.427	47.67	45.49	4.56
312.92	16.28	21.213	42.39	40.26	5.03	321.92	8.14	9.994	46.43	45.03	3.03
316.09	16.28	22.655	42.56	40.32	5.26	326.36	8.16	10.562	45.71	44.62	2.38
319.26	16.27	24.087	42.93	40.39	5.92	330.83	8.16	11.132	45.22	44.28	2.08
322.43	16.26	25.538	42.43	40.47	4.62	295.42	5.85	6.357	55.74	47.54	14.71
325.60	16.26	26.987	42.59	40.55	4.79	299.95	5.96	6.781	51.33	46.78	8.88
328.81	16.25	28.433	43.01	40.64	5.52	304.54	5.99	7.195	48.83	46.00	5.79
332.02	16.24	29.887	42.70	40.73	4.62	309.16	6.00	7.604	47.27	45.30	4.17
335.24	16.24	31.345	42.78	40.83	4.57	313.81	6.00	8.009	46.66	44.69	4.22
294.94	13.97	7.993	46.15	41.88	9.24	318.49	6.00	8.412	45.77	44.17	3.49
298.66	13.98	9.127	45.22	41.83	7.50	323.20	6.01	8.814	44.98	43.73	2.78
302.40	14.00	10.309	44.41	41.75	5.99	327.92	6.01	9.214	44.43	43.36	2.41
306.13	14.01	11.478	44.14	41.68	5.57	332.67	6.01	9.614	43.80	43.06	1.67
309.89	14.02	12.670	44.04	41.62	5.49	337.44	6.01	10.014	43.69	42.82	1.99
313.65	14.02	13.871	43.72	41.57	4.90						

[a] Extended corresponding states model DDMIX (*8*). [b] Diff = $100(C_v - C_{v,calcd})/C_v$.

states model using the relation

$$C_v(T,\varrho) = C_v^0(T) - T\int_0^{\varrho}(\partial^2 P/\partial T^2)_{\varrho}\, d\varrho/\varrho^2 \qquad (3)$$

where C_v^0 is the heat capacity for the ideal gas. The deviations of the calculated values from the experimental ones are plotted in Figure 4. This figure shows that the predicted values are generally within ±10% of the measurements, except for those in the extended critical region, with the larger differences found at the highest densities. In the extended critical region, the calculated values are as much as 30% from the measurements. Each of the calculated heat capacities is smaller in magnitude than its experimental counterpart. Overall, the root-mean-square deviation of calculated from experimental values of C_v is 5.6%. This is good agreement for the DDMIX model considering that it was not optimized with the data from this study.

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