



**Volumetric properties for
 $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1 - x_1 - x_2)\text{N}_2\}$ at the pressures
(19.94, 39.94, 59.93, and 99.93) MPa and
temperatures (323.15, 373.15, 473.15, and
573.15) K**

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The densities for $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1 - x_1 - x_2)\text{N}_2\}$ were measured at the pressures (19.94, 39.94, 59.93, 99.93) MPa and temperatures (323.15, 373.15, 473.15, 573.15) K using a custom-designed, high-pressure, high-temperature vibrating-tube densimeter. Excess molar volumes V_m^E were calculated from the experimental results. Although V_m^E is generally positive, negative deviations are observed in ternary mixtures with compositions close to those of binary mixtures that exhibit negative deviations. V_m^E generally decreases as pressure increases from 20 MPa to 100 MPa. V_m^E is typically less than ± 4 per cent of the total volume of the mixture. V_m^E increases substantially as (p, T) conditions approach the critical point of CO_2 . Predictions of V_m^E for ternary mixtures may be made from experimental results for the binary subsystems. Comparisons with experimental results indicate that these methods are reasonably accurate for estimating the volumetric properties of ternary gas mixtures. © 1996 Academic Press Limited

1. Introduction

In the last 50 years, much progress has been made in developing a thermodynamic database for (carbon dioxide + methane + nitrogen). Most of the effort has

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been concentrated on the properties of the pure gas species. Recently, however, investigators have obtained experimental results for $\{(1-x)\text{CO}_2+x\text{CH}_4\}$,⁽¹⁻⁷⁾ $\{(1-x)\text{CO}_2+x\text{N}_2\}$,^(4,5,8-14) and $\{(1-x)\text{CH}_4+x\text{N}_2\}$.⁽¹⁵⁻²⁰⁾ These studies form a foundation for investigations of $\{x_1\text{CO}_2+x_2\text{CH}_4+(1-x_1-x_2)\text{N}_2\}$. The present study was undertaken to measure the volumetric properties of ternary mixtures in (carbon dioxide+methane+nitrogen) at the pressures (19.94, 39.94, 59.93, 99.93) MPa and temperatures (323.15, 373.15, 473.15, 573.15) K. We are unaware of any previous studies of $\{x_1\text{CO}_2+x_2\text{CH}_4+(1-x_1-x_2)\text{N}_2\}$ over a broad range of (p, T, x) conditions.

2. Experimental

A custom-designed vibrating-tube densimeter was used to measure the densities of the pure fluids and fluid mixtures at $10 \leq (p/\text{MPa}) \leq 100$ and $323 \leq (T/\text{K}) \leq 573$. The experimental apparatus and techniques are described elsewhere.^(7,21) Measurements on pure fluids were obtained under isobaric, isothermal no-flow conditions. For fluid mixtures, an isobaric, isothermal flow-through method was employed to obtain a statistically significant number of measurements ($n=100$ to $n=400$) for the period of vibration τ at each (p, T, x) condition. This procedure eliminated the effects of random noise caused by slight compositional heterogeneity ($x \ll 0.5 \cdot 10^{-2}$) in the mixtures as they flowed through the vibrating tube. High-accuracy (± 0.05 per cent) positive-displacement pumps were used to meter the gases to the vibrating tube. Gas mixtures were formed by flowing pure gases into T-junctions on the upstream side of the vibrating tube.

During each experimental session, three well-characterized standard gases (He, N₂, and Ar) were used to calibrate the response of the vibrating tube. The densities of He and N₂ were calculated from the equation of state of Friend;⁽²²⁾ the density of Ar was obtained from the equation of state developed by Stewart and Jacobsen.⁽²³⁾ Pressure was measured using Precise Sensors™ model 9522 pressure transducers (0 to 103.4 MPa full range). Periodically, the transducers were calibrated with a dead-weight tester. Experimental temperature was monitored with a stainless-steel-sheathed platinum RTD of resistance 100 Ω (Yellow Springs Instruments). Precisions achieved in experimentation were: ± 0.01 MPa and ± 0.01 K. Conservative estimates of accuracy are: ± 0.02 MPa and ± 0.05 K. Minimum purities for Ar, He, N₂, CO₂, and CH₄ were mass fractions 0.999998, 0.999998, 0.99999, 0.99993, and 0.9999, respectively. Estimated uncertainties for reported densities (tables 1 to 4) are generally less than $\pm 10^{-3}$ g·cm⁻³.

3. Results

Densities ρ and excess molar volumes V_m^E for 18 different mixtures in (carbon dioxide+methane+nitrogen) at the temperatures (323.15, 373.15, 473.15, and 573.15) K are presented in tables 1 to 4. These results supplement the volumetric

TABLE 1. Experimental densities ρ and excess molar volumes V_m^E for $\{x_1\text{CO}_2+x_2\text{CH}_4+(1-x_1-x_2)\text{N}_2\}$ at $T=323.15$ K

x_1	x_2	$p=19.94$ MPa		$p=39.94$ MPa		$p=59.93$ MPa		$p=99.93$ MPa	
		$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$
0.20	0.40	0.21491	7.08	0.36116	1.947	0.44841	0.597	0.54231	0.595
0.40	0.30	0.27950	9.31	0.46252	1.307	0.55640	0.575	0.65901	0.494
0.60	0.20	0.37683	7.41	0.58894	0.357	0.68439	0.153	0.78674	0.346
0.60	0.30			0.57856	0.709	0.66648	0.470	0.76174	0.502
0.60	0.10			0.59958	-0.055	0.70383	-0.298	0.81510	-0.001
0.80	0.10	0.53798	2.51	0.74596	-0.447	0.83160	-0.156	0.92738	0.154
0.10	0.80	0.17102	3.19	0.28429	1.034	0.34465	0.604	0.41089	0.609
0.20	0.60	0.20618	6.03	0.34256	1.626	0.41588	0.911	0.49657	0.779
0.10	0.60	0.18114	4.51	0.30546	1.291	0.37547	0.747	0.45510	0.616
0.30	0.60			0.38517	1.638	0.45952	1.026	0.54137	0.786
0.30	0.40	0.24246	8.50	0.40640	1.357	0.49137	0.822	0.58773	0.609
0.40	0.20	0.28271	9.62	0.47627	0.549	0.57237	0.390	0.68278	0.361
0.10	0.10	0.20934	3.04	0.35725	0.660	0.45046	0.437	0.56669	0.181
0.20	0.20	0.22540	6.63	0.38439	1.059	0.47798	0.499	0.58779	0.381
0.10	0.30					0.42103	0.621	0.52049	0.548
0.30	0.10					0.53841	0.318	0.65791	0.206
0.30	0.30	0.24719	8.46	0.41670	1.177	0.50816	0.563	0.61116	0.481
0.40	0.40	0.27697	8.67	0.45351	1.340	0.54019	0.751	0.63627	0.542

TABLE 2. Experimental densities ρ and excess molar volumes V_m^E for $\{x_1\text{CO}_2+x_2\text{CH}_4+(1-x_1-x_2)\text{N}_2\}$ at $T=373.15$ K

x_1	x_2	$p=19.94$ MPa		$p=39.94$ MPa		$p=59.93$ MPa		$p=99.93$ MPa	
		$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$
0.20	0.40	0.17383	7.19	0.30527	2.891	0.39107	1.467	0.49461	0.808
0.40	0.30	0.21609	11.05	0.38261	3.255	0.48348	1.452	0.59910	0.794
0.60	0.20	0.27035	11.93	0.47912	2.575	0.59135	1.065	0.71400	0.638
0.60	0.30	0.26850	10.59	0.47143	2.513	0.57689	1.237	0.69152	0.802
0.60	0.10	0.27380	12.45	0.48763	2.469	0.60801	0.647	0.73717	0.421
0.80	0.10	0.34846	8.60	0.60203	1.241	0.71750	0.528	0.84118	0.373
0.10	0.80	0.13693	2.64	0.24024	1.022	0.30327	0.703	0.37707	0.556
0.20	0.60	0.16383	6.29	0.28878	2.100	0.36510	1.225	0.45455	0.831
0.10	0.60	0.14809	3.34	0.25968	1.441	0.33095	0.902	0.41719	0.603
0.30	0.60	0.18237	7.88	0.32089	2.583	0.40196	1.449	0.49431	0.944
0.30	0.40	0.19185	8.98	0.33923	2.766	0.42976	1.387	0.53610	0.785
0.40	0.20	0.22105	11.05	0.39282	2.930	0.49782	1.266	0.62119	0.601
0.10	0.10	0.17411	3.99	0.30673	1.313	0.39834	0.690	0.51800	0.239
0.20	0.20	0.18326	7.99	0.32532	2.359	0.41972	1.050	0.53682	0.485
0.10	0.30	0.16252	5.34	0.28759	1.710	0.37160	0.889	0.47754	0.455
0.30	0.10	0.20540	10.17	0.36569	2.774	0.47091	1.052	0.59837	0.474
0.30	0.30	0.19612	9.68	0.34811	2.819	0.44410	1.222	0.55763	0.623
0.40	0.40	0.21182	10.49	0.37501	2.973	0.47072	1.391	0.57912	0.793

TABLE 3. Experimental densities ρ and excess molar volumes V_m^E for $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1-x_1-x_2)\text{N}_2\}$ at $T=473.15$ K

x_1	x_2	$p=19.94$ MPa		$p=39.94$ MPa		$p=59.93$ MPa		$p=99.93$ MPa	
		$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$
0.20	0.40	0.12967	3.44	0.23516	2.68	0.31456	1.578	0.42007	1.010
0.40	0.30	0.15619	4.46	0.28594	3.38	0.38089	2.063	0.50455	1.107
0.60	0.20	0.18522	4.74	0.34375	3.31	0.45628	1.899	0.59758	0.870
0.60	0.30	0.18042	4.89	0.33515	3.52	0.44481	1.956	0.57938	1.002
0.60	0.10			0.35069	3.55	0.46827	1.722	0.61593	0.711
0.80	0.10	0.21725	4.41	0.41154	2.39	0.54306	1.232	0.69926	0.504
0.10	0.80			0.18341	0.93	0.24263	1.021	0.32204	0.577
0.20	0.60			0.21907	2.30	0.29066	1.764	0.38614	1.030
0.10	0.60			0.20027	1.40	0.26597	1.260	0.35565	0.736
0.30	0.60			0.23964	2.77	0.31783	1.894	0.41859	1.159
0.30	0.40	0.14013	4.25	0.25609	2.95	0.34099	1.923	0.45333	1.055
0.40	0.20	0.16004	5.46	0.29387	3.39	0.39228	2.007	0.52237	0.968
0.10	0.10	0.13423	1.55	0.24138	1.39	0.32252	1.242	0.43898	0.666
0.20	0.20	0.13896	3.58	0.25195	2.40	0.33609	1.805	0.45421	0.859
0.10	0.30	0.12472	1.96	0.22463	1.80	0.29982	1.443	0.40580	0.752
0.30	0.10	0.15387	4.53	0.27963	3.15	0.37415	1.964	0.50520	0.776
0.30	0.30	0.14457	4.65	0.26391	3.10	0.35214	1.962	0.47063	0.979
0.40	0.40	0.15125	4.72	0.27773	3.40	0.36912	2.158	0.48791	1.083

TABLE 4. Experimental densities ρ and excess molar volumes V_m^E for $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1-x_1-x_2)\text{N}_2\}$ at $T=573.15$ K

x_1	x_2	$p=19.94$ MPa		$p=39.94$ MPa		$p=59.93$ MPa		$p=99.93$ MPa	
		$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{V_m^E}{\text{cm}^3\cdot\text{mol}^{-1}}$
0.20	0.40	0.10511	2.22	0.19253	2.10	0.26241	1.62	0.36464	0.966
0.40	0.30			0.23010	2.68	0.31452	1.82	0.43451	1.123
0.60	0.20	0.14488	3.57	0.27100	2.57	0.37045	1.79	0.50954	0.999
0.60	0.30	0.14073	3.79	0.26374	2.60	0.36062	1.75	0.49409	1.079
0.60	0.10	0.14893	3.44	0.27795	2.62	0.38052	1.73	0.52542	0.847
0.80	0.10			0.31679	1.54	0.43274	1.17	0.59086	0.620
0.10	0.80			0.14838	1.44	0.20256	0.81	0.27926	0.597
0.20	0.60	0.09675	2.31	0.17764	2.12	0.24211	1.56	0.33474	0.970
0.10	0.60			0.16352	1.58	0.22294	1.125	0.30927	0.693
0.30	0.60	0.10475	1.81	0.19255	2.40	0.26251	1.74	0.36158	1.082
0.30	0.40	0.11304	1.93	0.20726	2.50	0.28285	1.80	0.39168	1.064
0.40	0.20	0.12865	2.97	0.23756	2.51	0.32470	1.74	0.45031	0.951
0.10	0.10	0.10938	2.74	0.20041	1.20	0.27450	0.57	0.38398	0.460
0.20	0.20	0.11345	1.72	0.20702	2.06	0.28327	1.278	0.39467	0.835
0.10	0.30			0.18587	1.41	0.25369	1.011	0.35387	0.675
0.30	0.10	0.12426	3.77	0.22930	2.17	0.31367	1.44	0.43659	0.905
0.30	0.30	0.11630	3.72	0.21458	2.47	0.29315	1.71	0.40692	0.985
0.40	0.40	0.11990	4.28	0.22302	2.56	0.30412	1.92	0.41949	1.151

measurements of Seitz *et al.*⁽⁷⁾ for pure CO_2 and CH_4 , and for $\{(1-x)\text{CO}_2 + x\text{CH}_4\}$, $\{(1-x)\text{CO}_2 + x\text{N}_2\}$, and $\{(1-x)\text{CH}_4 + x\text{N}_2\}$ which were made over the same range of pressure and temperature. The V_m^E s for the ternary mixtures could be calculated with a high degree of precision because the volumetric properties of the end members were measured during the same experimental runs.

In figures 1 to 4, V_m^E s for $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1 - x_1 - x_2)\text{N}_2\}$ are presented for three pseudobinary joins at (323.15, 373.15, 473.15, and 573.15) K. Note that V_m^E decreases with increasing pressure from 19.94 MPa to 99.93 MPa. Generally, the effect of temperature on V_m^E is small, except at (p, T) conditions near the critical region of CO_2 ($p_c = 7.38$ MPa, $T_c = 304.2$ K). This is exemplified in figure 1 ($T = 323.15$ K) where very large values of V_m^E are observed along the $p = 19.94$ MPa isobar. Both positive and negative V_m^E s are observed for ternary mixtures. Negative values of V_m^E , however, occur only in compositional regions adjacent to negative deviations in the binary subsystems.

4. Discussion

There is considerable interest in estimating the thermodynamic properties of ternary or higher-order systems from the properties of the bounding binary subsystems. The prediction of thermodynamic properties of ternary (fluid or solid) solution phases by analytic or geometric projection from the binary sidelines is common, especially in the metallurgical and ceramic sciences.⁽²⁴⁻³⁰⁾ A wide variety of empirical methods have been developed which employ a projection-vector methodology. If the analysis is performed analytically, the resulting formulation for the multicomponent mixtures is automatically consistent with the equations for the binary mixtures.

We have evaluated various symmetric and asymmetric projection methods^(24,26,27,31) for estimating the excess volumes of ternary mixtures from volumetric results for the binary subsystems.⁽⁷⁾ These methods yield similar results; however, we prefer the formulation of Muggianu *et al.*⁽²⁶⁾ because of its mathematical simplicity. The Muggianu method is represented analytically by the relation:

$$V_m^E(\text{ternary}) = \Sigma(x_1x_2/v_{12}v_{21}) \cdot V_m^E(\text{binary})(v_{12}, v_{21}), \quad (1)$$

where

$$v_{12} = (1 + x_1 - x_2)/2, \quad (2)$$

and

$$v_{21} = (1 + x_2 - x_1)/2. \quad (3)$$

Seitz *et al.*⁽⁷⁾ have shown that V_m^E s for $\{(1-x)\text{CO}_2 + x\text{CH}_4\}$, $\{(1-x)\text{CO}_2 + x\text{N}_2\}$, and $\{(1-x)\text{CH}_4 + x\text{N}_2\}$ can be represented accurately by two-parameter Margules equations, where $V_m^E(\text{binary})$ is calculated at the binary compositions represented by v_{12} or v_{21} , of the form:

$$V_m^E(\text{binary}) = W(V_1)x_1x_2^2 + W(V_2)x_1^2x_2. \quad (4)$$

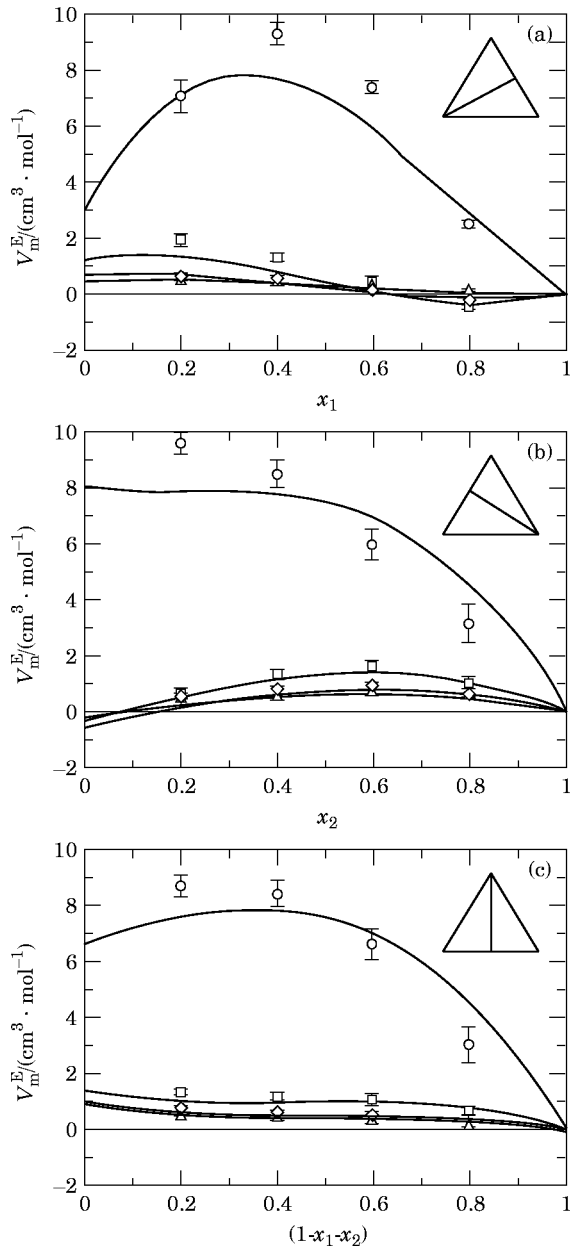


FIGURE 1. Excess molar volumes V_m^E for ternary mixtures along three pseudobinary joins: (a), $x_2 = (1 - x_1 - x_2)$; (b), $x_1 = (1 - x_1 - x_2)$; and (c), $x_1 = x_2$ at $T = 323.15$ K and at pressures: \circ , $p = 19.94$ MPa; \square , $p = 39.94$ MPa; \diamond , $p = 59.93$ MPa; and \triangle , $p = 99.93$ MPa. The symbols and curves represent experimental results and predictions, respectively, from the projection method of Muggianu *et al.*⁽²⁶⁾. The ternary diagrams illustrate schematically the position of each pseudobinary join.

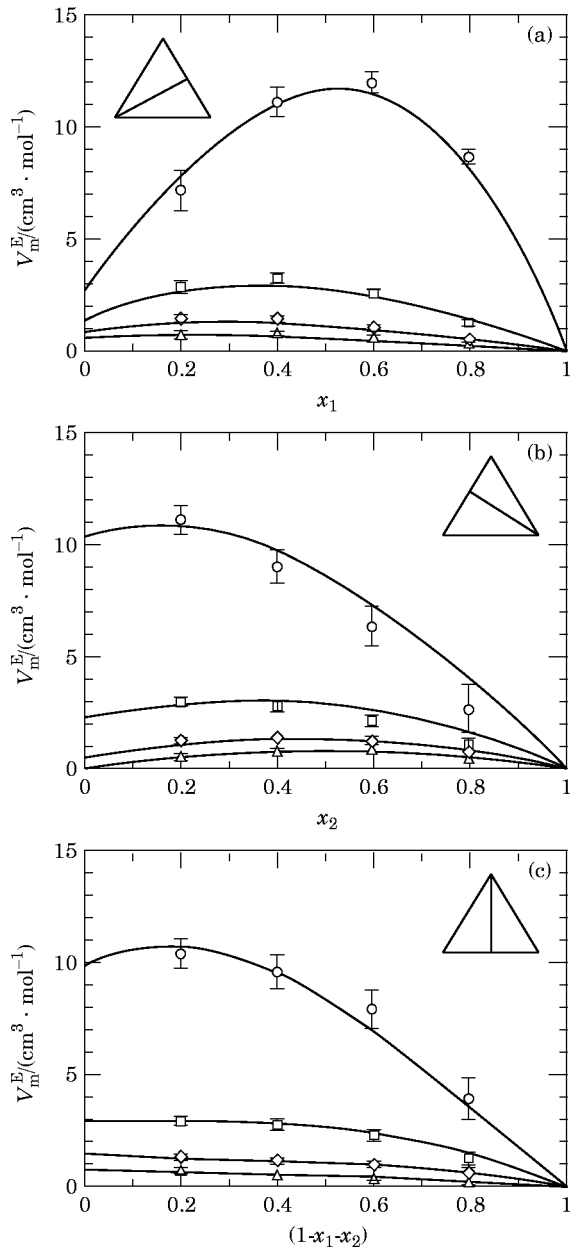


FIGURE 2. Excess molar volumes V_m^E for ternary mixtures along three pseudobinary joins: (a), $x_2 = (1 - x_1 - x_2)$; (b), $x_1 = (1 - x_1 - x_2)$; and (c), $x_1 = x_2$ at $T = 373.15$ K and at pressures: \circ , $p = 19.94$ MPa; \square , $p = 39.94$ MPa; \diamond , $p = 59.93$ MPa; and \triangle , $p = 99.93$ MPa. The symbols and curves represent experimental results and predictions, respectively, from the projection method of Muggianu *et al.*⁽²⁶⁾. The ternary diagrams illustrate schematically the position of each pseudobinary join.

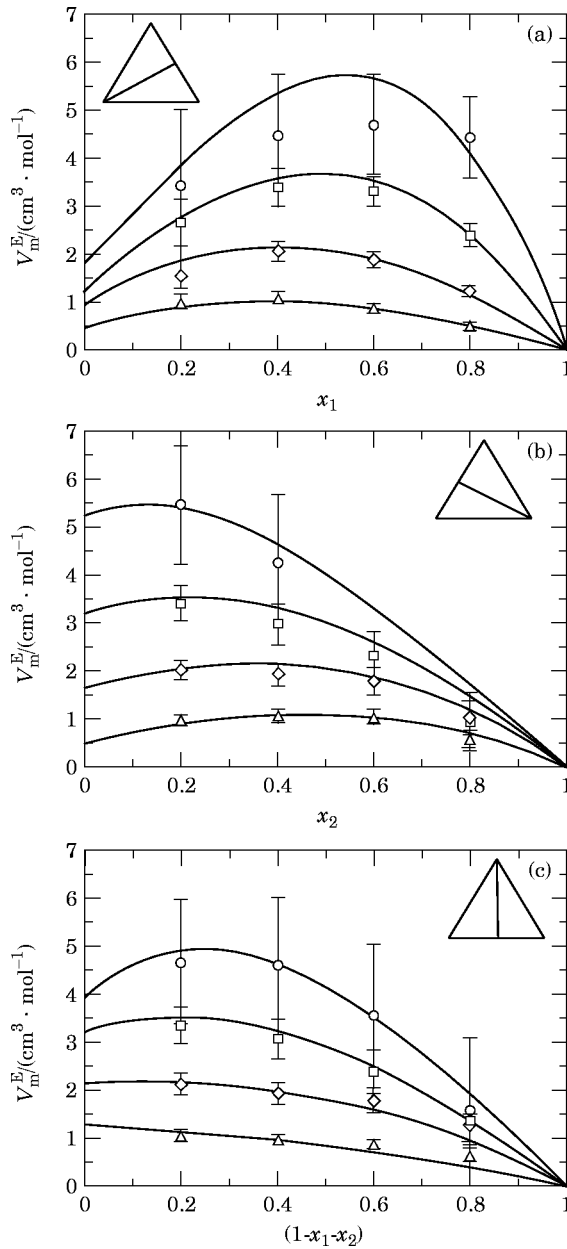


FIGURE 3. Excess molar volumes V_m^E for ternary mixtures along three pseudobinary joins: (a), $x_2 = (1-x_1-x_2)$; (b), $x_1 = (1-x_1-x_2)$; and (c), $x_1 = x_2$ at $T = 473.15$ K and the pressures: \circ , $p = 19.94$ MPa; \square , $p = 39.94$ MPa; \diamond , $p = 59.93$ MPa; and \triangle , $p = 99.93$ MPa. The symbols and curves represent experimental results and predictions, respectively, from the projection method of Muggianu *et al.*⁽²⁶⁾. The ternary diagrams illustrate schematically the position of each pseudobinary join.

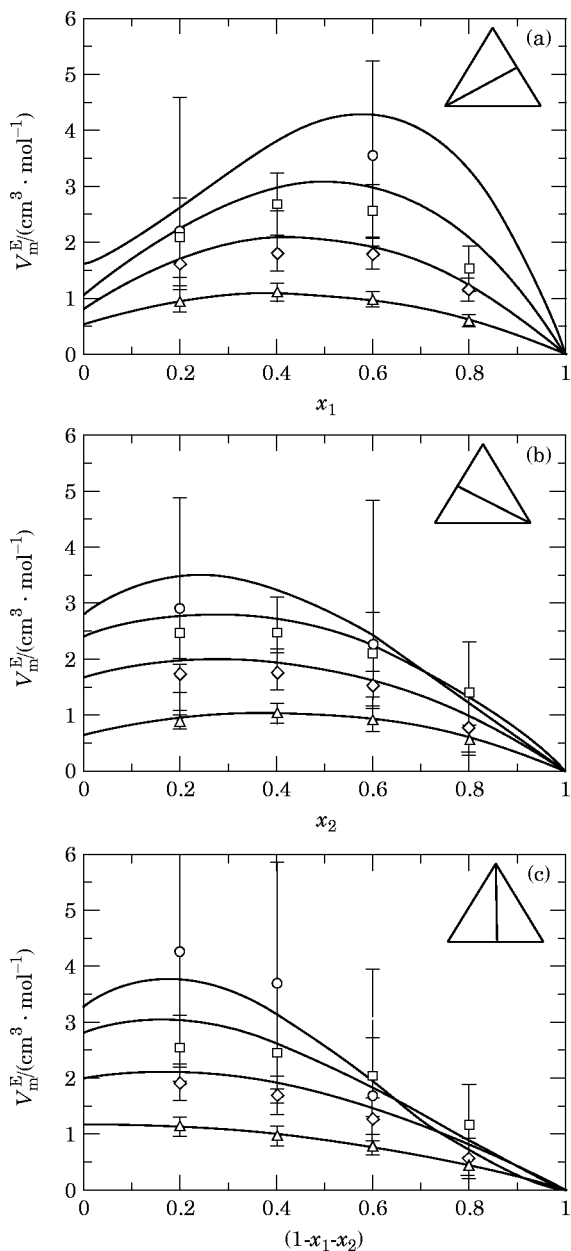


FIGURE 4. Excess molar volumes V_m^E for ternary mixtures along three pseudobinary joins: (a), $x_2=(1-x_1-x_2)$; (b), $x_1=(1-x_1-x_2)$; and (c), $x_1=x_2$ at $T=573.15\text{ K}$ and the pressures: \circ , $p=19.94\text{ MPa}$; \square , $p=39.94\text{ MPa}$; \diamond , $p=59.93\text{ MPa}$; and \triangle , $p=99.93\text{ MPa}$. The symbols and curves represent experimental results and predictions, respectively, from the projection method of Muggianu *et al.*⁽²⁶⁾. The ternary diagrams illustrate schematically the position of each pseudobinary join.

$W(V_1)$ and $W(V_2)$ were evaluated using V_m^E s for binary mixtures at each (p, T) condition.⁽⁷⁾ Figure 5 shows the predicted V_m^E surface for $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1-x_1-x_2)\text{N}_2\}$ at $p=99.84$ MPa and $T=323.15$ K.

Comparisons of experimentally determined and calculated⁽²⁶⁾ values of V_m^E are made in figures 1 to 4 for three different pseudobinaries at the temperatures (323.15, 373.15, 473.15, and 573.15) K. The experimental and computed values generally agree within experimental uncertainty. Notably, the experimental results for ternary mixtures at $p=19.94$ MPa and $T=323.15$ K show the largest degree of divergence from the model, which may be related to the close proximity of this (p, T) point to the critical region of CO_2 . Analysis of the entire experimental database indicates that the root mean square of the difference between experimental and calculated values is generally less than the mean experimental uncertainty at each (p, T) condition. Thus, we have demonstrated that, firstly, the method of Muggianu⁽²⁶⁾ accurately predicts ternary

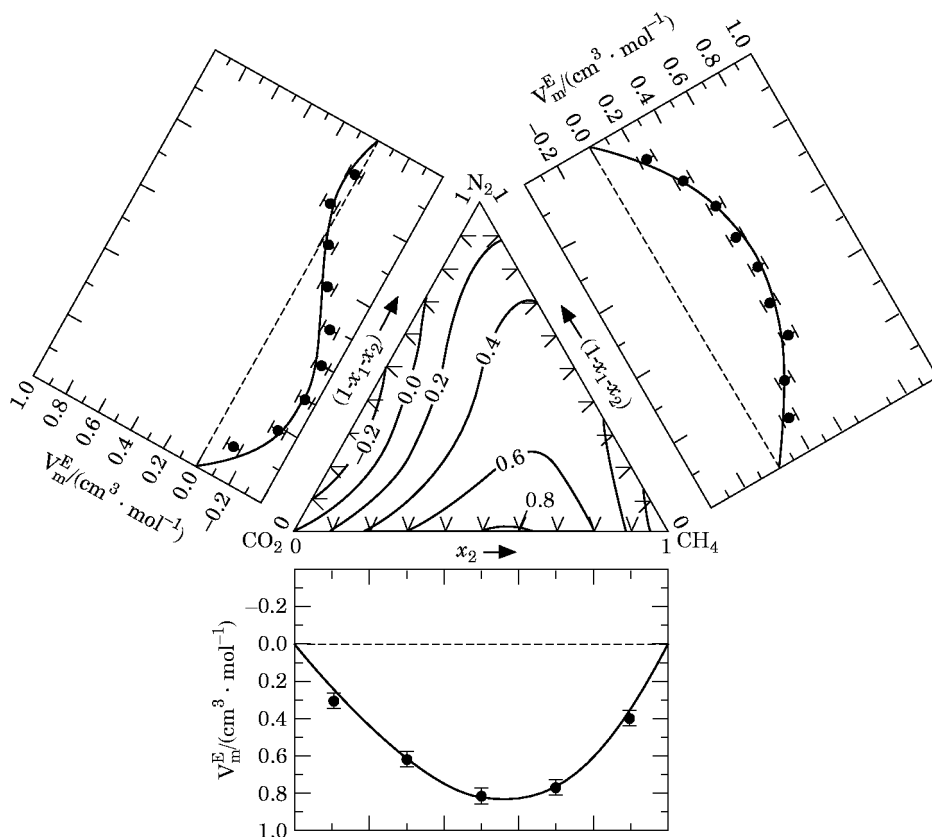


FIGURE 5. Ternary V_m^E surface for $\{x_1\text{CO}_2 + x_2\text{CH}_4 + (1-x_1-x_2)\text{N}_2\}$ at $p = 99.93$ MPa and $T = 323.15$ K predicted from the binary results of Seitz *et al.*⁽⁷⁾ and the method of Muggianu *et al.*⁽²⁶⁾ Ternary contours indicate mixtures of constant V_m^E . Plot symbols represent experimental results⁽⁷⁾ for binary subsystems, and the curves represent two-parameter Margules functions, equation (4), fitted to the results.

excess volumes for nonpolar fluid systems and, secondly, provided the (empirical) analytic expressions which describe the binary subsystems are accurate, that the Muggianu method⁽²⁶⁾ yields calculated values of V_m^E that are more accurate than those obtained from complex (empirical and semi-empirical) equations of state.^(32,33)

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REFERENCES

1. Reamer, H. H.; Olds, R. H.; Sage, B. H.; Lacey, W. N. *Indust. Eng. Chem.* **1944**, 36, 88–90.
2. Tong, J.; Liu, T. *Gongcheng Rewuli Xuebao* **1984**, 5, 119–124.
3. Magee, J. W.; Ely, J. F. *Int. J. Thermophys.* **1988**, 9, 547–557.
4. Brugge, H. B.; Hwang, C.-A.; Rogers, W. J.; Holste, J. C.; Hall, K. R.; Lemming, W.; Esper, G. J.; Marsh, K. N.; Gammon, B. E. *Physica A* **1989**, 156, 382–416.
5. Esper, G. J.; Bailey, D. M.; Holste, J. C.; Hall, K. R. *Fluid Phase Equilib.* **1989**, 49, 35–47.
6. McElroy, P. J.; Battino, R.; Dowd, M. K. *J. Chem. Thermodynamics* **1989**, 21, 1287–1300.
7. Seitz, J. C.; Blencoe, J. G.; Bodnar, R. J. *J. Chem. Thermodynamics* **1996**, 28, 521–538.
8. Kritschewsky, I. R.; Markov, V. P. *Acta Physicochim. U.R.S.S.* **1940**, 12, 59–66.
9. Haney, R. E. D.; Bliss, H. *Ind. Eng. Chem.* **1944**, 36, 985–989.
10. Kaminishi, G. *Kaotsu Gasu* **1978**, 15, 177–183.
11. Semenova, A. I.; Tsimmerman, S. S.; Tsiklis D. S. *Russ. J. Phys. Chem.* **1981**, 55, 1080–1081.
12. Altunin, V. V.; Filatov, N. Ya.; Likhatskii, M. A. *Experimental study of condensability, volume and baric effects of mixing gaseous solutions of nitrogen in trifluoromethane, carbon dioxide, and sulfur hexafluoride*. Mosk. Energ. Inst.: Moscow. Deposited document **1982**.
13. Hacura, A.; Yoon, J. H.; Baglin, F. G. *J. Chem. Eng. Data* **1988**, 33, 152–154.
14. Ely, J. F.; Haynes, W. M.; Bain, B. C. *J. Chem. Thermodynamics* **1989**, 21, 879–894.
15. Keyes, F. G.; Burks, H. G. *J. Am. Chem. Soc.* **1928**, 50, 1100–1106.
16. Kritschewsky, I. R.; Levchenko, G. T. *Acta Physicochim. U.R.S.S.* **1941**, 14, 271–278.
17. Blake, A. G.; Bretton, R. H.; Dodge, B. F. *AIChE Symp. Ser.* **1965**, 2, 105–114.
18. Semenova, A. I.; Emel'yanova, E. A.; Tsimmerman, S. S.; Tsiklis, D. S. *Russ. J. Phys. Chem.* **1979**, 53, 520–522.
19. Straty, G. C.; Diller, D. E. *J. Chem. Thermodynamics* **1980**, 12, 937–953.
20. Haynes, W. M.; McCarty, R. D. *J. Chem. Thermodynamics* **1983**, 15, 815–819.
21. Blencoe, J. G.; Drummond, S. E.; Seitz, J. C.; Nesbitt, B. E. *Int. J. Thermophys.* **1995**, in press.
22. Friend, D. G. *NIST Thermophysical Properties of Pure Fluids*, software. National Institute of Standards and Technology: Gaithersburg. **1992**.
23. Stewart, R. B.; Jacobsen, R. T. *J. Phys. Chem. Ref. Data* **1989**, 18, 639–798.
24. Kohler, F. *Monatsh. Chem.* **1960**, 91, 739–740.
25. Toop, G. W. *Trans. Metall. Soc. AIME* **1965**, 233, 850–855.
26. Muggianu, Y.-M.; Gambino, M.; Bros, J.-P. *J. Chim. Phys.* **1975**, 72, 83–88.
27. Hillert, M. *CALPHAD* **1980**, 4, 1–12.
28. Wohl, K. *Trans. AIChE* **1946**, 42, 215–249.
29. Wang, Z.-C.; Lück, R.; Predel, B. *CALPHAD* **1990**, 14, 217–234.
30. Wang, Z.-C.; Lück, R.; Predel, B. *CALPHAD* **1990**, 14, 235–256.

31. Colinet, C. D.E.S. Fac. Sci., Univ. Grenoble, France. **1967**.
32. Seitz, J. C.; Blencoe, J. G.; Joyce, D. B.; Bodnar, R. J. *Water-Rock Interaction 7*. Kharaka, Y. K.; Maest, A. S.: editors. Balkema: Rotterdam. **1992**, 1025–1028.
33. Seitz, J. C.; Blencoe, J. G.; Bodnar, R. J. *Geochim. Cosmochim. Acta* **1994**, 58, 1065–1071.

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