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Volumetric properties for $\{(1-x)CO_2+xCH_4\}$, $\{(1-x)CO_2+xN_2\}$, and $\{(1-x)CH_4+xN_2\}$ at the pressures (9.94, 19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and temperatures (323.15, 373.15, 473.15, and 573.15) K

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Densities ρ of pure CO_2, CH_4, and $\{(1-x)CO_2+xCH_4\}$, $\{(1-x)CO_2+xN_2\}$, and $\{(1-x)CH_4+xN_2\}$ were measured at the pressures (9.94, 19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and temperatures (323.15, 373.15, 473.15, and 573.15) K. For each binary system, results were obtained at intervals of $0.1{\cdot}x$ from mole fraction $x=0$ to $x=1$. The results were obtained with a custom-designed, high-pressure, high-temperature vibrating-tube densimeter. Excess molar volumes V_m^E were calculated from the densities for the end members and mixtures. V_m^E is generally positive, although negative values of V_m^E were observed for some CO_2-bearing mixtures. V_m^E is typically less than ± 4 per cent of the total volume of the mixture. A dramatic increase in V_m^E is observed for CO_2-containing mixtures as (p, T) conditions approach those of the critical point for CO_2. The values of V_m^E are accurately represented by two-parameter Margules equations. Our results are in good agreement with those obtained by previous investigators.

1. Introduction

The gases CO_2, CH_4, and N_2 are key volatile constituents of the earth, and are either consumed or produced in a wide variety of commercial enterprises.

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Consequently, thermochemical data for these gases and their mixtures have numerous applications in geoscience research, fossil fuel industries, and supercritical fluid technologies. Thus, it is significant that volumetric information for (carbon dioxide + methane), (carbon dioxide + nitrogen), and (methane + nitrogen) is scarce, particularly at elevated pressures and temperatures. In this study, we present densities ρ for pure CO_2 and CH_4, and $\{(1-x)CO_2+xCH_4\}$, $\{(1-x)CO_2+xN_2\}$, and $\{(1-x)CH_4+xN_2\}$, and excess molar volumes V_m^E for the mixtures at the pressures $p=(9.94,\ 19.94,\ 29.94,\ 39.94,\ 59.93,\ 79.93,\ \text{and}\ 99.93)$ MPa and temperatures $T=(323.15,\ 373.15,\ 473.15,\ \text{and}\ 573.15)$ K.

2. Experimental

A custom-designed vibrating-tube densimeter was used to measure the densities of the pure fluids and fluid mixtures at $10 \leqslant (p/\text{MPa}) \leqslant 100$ and $323 \leqslant (T/\text{K}) \leqslant 573$. The experimental apparatus and techniques are described elsewhere.[1] 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 (from 100 to 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 ($x \ll 0.005$) in the mixtures as they flowed through the vibrating tube. High-accuracy (± 0.05 per cent) positive-displacement pumps[1] 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.

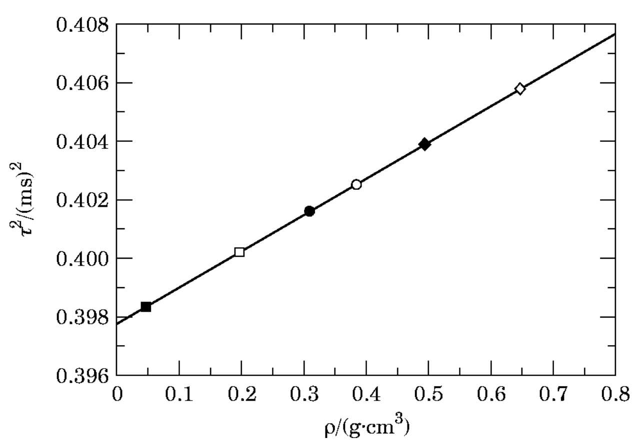

FIGURE 1. Square of the period of vibration τ^2 against density ρ for three reference fluids: ■, He; ●, N_2; ◆, Ar; and three analytes: □, CH_4; ○, $(0.50CO_2+0.50CH_4)$; ◇, CO_2 at $p=59.93$ MPa and $T=473.15$ K. The line represents a linear least-squares fit to the results for the reference fluids. The deviation $\delta\rho$ of the measured point from the regressed line is $\delta\rho=3\cdot10^{-5}$ g·cm^{-3} for He, $\delta\rho=-6\cdot10^{-5}$ g·cm^{-3} for N_2, and $\delta\rho=4\cdot10^{-5}$ g·cm^{-3} for Ar. The densities of the analytes are determined by referencing the measured period of vibration to the regression line.

TABLE 1. Experimentally determined densities ρ of pure CO_2 and CH_4 and differences between experimental and calculated [a] values ($\delta\rho = \rho_{exp} - \rho_{calc}$)

	CO_2		CH_4	
$\frac{p}{MPa}$	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{\delta\rho}{g \cdot cm^{-3}}$	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{\delta\rho}{g \cdot cm^{-3}}$
		$T = 323.15$ K		
9.94	0.38032	0.0022	0.06738	0.0012
19.94	0.78296	−0.0015	0.13652	0.0008
29.94	0.87041	<0.0001	0.19064	0.0013
39.94	0.92338	<0.0001	0.22798	0.0017
59.93	0.99395	<0.0001	0.27568	0.0020
99.93	1.0812	−0.0008	0.32945	0.0022
		$T = 373.15$ K		
9.94	0.18736	0.0004	0.05438	0.0004
19.94	0.47923	−0.0007	0.10914	0.0009
29.94	0.66084	−0.0014	0.15547	0.0009
39.94	0.75633	0.0003	0.19179	0.0011
59.93	0.86504	0.0007	0.24257	0.0016
79.93	0.93146	−0.0012	0.27629	0.0014
99.93	0.98338	< −0.0001	0.30197	0.0021
		$T = 473.15$ K		
9.94	0.12163	<0.0001	0.04110	0.0006
19.94	0.25818	−0.0003	0.08056	0.0011
29.94	0.38882	−0.0003	0.11580	0.0013
39.94	0.49679	< −0.0001	0.14687	0.0019
59.93	0.64586	< −0.0001	0.19515	0.0025
99.93	0.81153	−0.0020	0.25843	0.0033
		$T = 573.15$ K		
9.94	0.09452	<0.0001	0.03328	0.0004
19.94	0.19148	−0.0001	0.06515	0.0011
29.94	0.28409	< −0.0001	0.09387	0.0014
39.94	0.36791	0.0002	0.11969	0.0017
59.93	0.50312	−0.0006	0.16284	0.0022
99.93	0.67988	−0.0044	0.22442	0.0029

[a] Reference 2.

During each experimental session, three well-characterized standard gases (He, N_2, and Ar) were used to calibrate the response of the vibrating tube. Figure 1 illustrates the linear relationship between the square of the measured period of vibration τ^2 and density ρ for the three standard gases. The densities of He and N_2 were calculated from the equation of state of Friend;[(2)] the density of Ar was obtained from the equation of state developed by Stewart and Jacobsen.[(3)] Calibration of the instrument using three (rather than two) standard gases over a broad range of densities verified that the response of the vibrating tube was linear. Analysis of our results at all (p, T) conditions indicated that the root mean square of the deviation $\delta\rho$ between the calculated density for a standard fluid and the density determined by reference to the regressed line was $6 \cdot 10^{-5}$ g·cm^{-3} with $\delta\rho_{max} = 2 \cdot 10^{-4}$ g·cm^{-3} and

TABLE 2. Experimentally determined densities ρ and excess molar volumes V_m^E for $\{(1-x)CO_2+xCH_4\}$

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$T=323.15$ K, $p=9.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.23814	0.19500	0.16696	0.14379	0.12457	0.10791		
$V_m^E/(cm^3\cdot mol^{-1})$		21.12	30.23	32.92	31.91	29.44	25.04		
$T=323.15$ K, $p=19.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.54624	0.45320	0.38026	0.32023	0.27113		0.19469	
$V_m^E/(cm^3\cdot mol^{-1})$		1.880	4.027	5.627	6.956	7.50		5.96	
$T=323.15$ K, $p=29.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.76127		0.57792	0.50057	0.43195	0.37282	0.31974	0.27195	0.22926
$V_m^E/(cm^3\cdot mol^{-1})$	0.216		0.995	1.574	2.156	2.321	2.341	2.125	1.380
$T=323.15$ K, $p=39.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.72911	0.64389	0.56794	0.49684	0.43340	0.37571	0.32269	0.27407
$V_m^E/(cm^3\cdot mol^{-1})$		0.486	0.846	1.048	1.419	1.541	1.474	1.222	0.641
$T=323.15$ K, $p=59.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.89758	0.80775	0.72445	0.64738	0.57504	0.50771	0.44403	0.38505	0.32893
$V_m^E/(cm^3\cdot mol^{-1})$	0.246	0.499	0.716	0.857	0.980	1.005	1.006	0.781	0.473
$T=323.15$ K, $p=99.93$ MPa									
$\rho/(g\cdot cm^{-3})$			0.81481		0.65983		0.51922		0.39017
$V_m^E/(cm^3\cdot mol^{-1})$			0.613		0.806		0.759		0.389
$T=373.15$ K, $p=9.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.15127	0.13587	0.12197	0.10910	0.09700	0.08553	0.07491	
$V_m^E/(cm^3\cdot mol^{-1})$		7.04	9.23	10.17	10.26	9.75	8.69	5.83	
$T=373.15$ K, $p=19.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.40439	0.34915	0.30434	0.26467	0.23238	0.20275	0.17708	0.15291	0.13071
$V_m^E/(cm^3\cdot mol^{-1})$	4.56	7.16	8.66	10.12	9.80	9.37	7.53	5.54	2.66
$T=373.15$ K, $p=29.94$ MPa									
$\rho/(g\cdot cm^{-3})$			0.43686		0.33469	0.29196	0.25314	0.21881	
$V_m^E/(cm^3\cdot mol^{-1})$			3.961		4.820	4.713	4.308	3.011	
$T=373.15$ K, $p=39.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.66833	0.59079	0.52279	0.46161	0.40641	0.35577	0.31045	0.26830	0.22823
$V_m^E/(cm^3\cdot mol^{-1})$	0.931	1.745	2.307	2.733	2.963	3.073	2.691	2.086	1.444
$T=373.15$ K, $p=59.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.77786	0.69783	0.62821	0.56198	0.50061	0.44271	0.38871	0.33734	0.28827
$V_m^E/(cm^3\cdot mol^{-1})$	0.581	1.123	1.246	1.425	1.473	1.474	1.297	1.053	0.742
$T=373.15$ K, $p=79.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.84848	0.76846	0.69537	0.62492	0.55987	0.49702	0.43863	0.38202	0.32879
$V_m^E/(cm^3\cdot mol^{-1})$	0.243	0.580	0.731	0.949	0.974	1.047	0.883	0.734	0.316
$T=373.15$ K, $p=99.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.89979	0.81914	0.74423	0.67190	0.60315	0.53793	0.47569	0.41559	0.35781
$V_m^E/(cm^3\cdot mol^{-1})$	0.212	0.470	0.595	0.748	0.842	0.841	0.748	0.609	0.362

TABLE 2—*continued*

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$T = 473.15$ K, $p = 9.94$ MPa									
$\rho/(g \cdot cm^{-3})$		0.10327	0.09524	0.08723	0.07973	0.07170	0.06427	0.05684	
$V_m^E/(cm^3 \cdot mol^{-1})$		4.47	3.60	3.03	0.52	0.84	−1.64	−3.98	
$T = 473.15$ K, $p = 19.94$ MPa									
$\rho/(g \cdot cm^{-3})$		0.21364	0.19430		0.15903	0.14251	0.12644	0.11108	0.09591
$V_m^E/(cm^3 \cdot mol^{-1})$		3.62	4.26		4.01	3.40	2.70	1.38	0.16
$T = 473.15$ K, $p = 29.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.35065	0.31683	0.28679	0.25803	0.23147	0.20677	0.18266	0.15967	0.13773
$V_m^E/(cm^3 \cdot mol^{-1})$	1.81	2.99	3.40	3.88	3.86	3.29	2.83	2.04	0.78
$T = 473.15$ K, $p = 39.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.44752	0.40420	0.36461	0.32800	0.29369	0.26178	0.23147	0.20267	
$V_m^E/(cm^3 \cdot mol^{-1})$	1.440	2.326	2.912	3.22	3.33	3.04	2.52	1.65	
$T = 473.15$ K, $p = 59.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.58603	0.53084	0.48004	0.43277	0.38785	0.34591	0.30523	0.26802	
$V_m^E/(cm^3 \cdot mol^{-1})$	0.777	1.414	1.839	2.075	2.242	2.138	2.059	1.332	
$T = 473.15$ K, $p = 99.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.74269	0.67921	0.61824	0.56074	0.50531	0.45217	0.40118	0.35153	
$V_m^E/(cm^3 \cdot mol^{-1})$	0.477	0.760	1.030	1.166	1.267	1.281	1.179	1.040	
$T = 573.15$ K, $p = 9.94$ MPa									
$\rho/(g \cdot cm^{-3})$		0.08103	0.07514	0.06973	0.06334	0.05744	0.05161	0.04587	
$V_m^E/(cm^3 \cdot mol^{-1})$		5.21	3.51	2.29	0.17	−1.48	−3.76	−7.11	
$T = 573.15$ K, $p = 19.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.17636	0.16191	0.14917	0.13675	0.12440	0.11262		0.08871	
$V_m^E/(cm^3 \cdot mol^{-1})$	2.21	4.16	4.03	3.65	3.34	2.12		0.98	
$T = 573.15$ K, $p = 29.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.26179	0.23977	0.21935	0.19990	0.18131	0.16281	0.14510		0.11078
$V_m^E/(cm^3 \cdot mol^{-1})$	0.91	2.11	2.67	2.88	2.70	2.74	2.28		0.76
$T = 573.15$ K, $p = 39.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.33650	0.30826	0.28150	0.25613	0.23173	0.20807	0.18529	0.16300	0.14149
$V_m^E/(cm^3 \cdot mol^{-1})$	1.41	2.12	2.59	2.76	2.74	2.59	2.15	1.58	0.55
$T = 573.15$ K, $p = 59.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.46157	0.4223	0.38513	0.34962	0.31607	0.28373	0.25217	0.22166	0.19203
$V_m^E/(cm^3 \cdot mol^{-1})$	0.710	1.301	1.700	1.99	2.001	1.868	1.684	1.302	0.693
$T = 573.15$ K, $p = 99.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.62523	0.57464	0.52599	0.47846	0.43354	0.38949	0.34694	0.30510	0.26448
$V_m^E/(cm^3 \cdot mol^{-1})$	0.509	0.769	0.961	1.167	1.148	1.125	0.961	0.777	0.419

TABLE 3. Experimentally determined densities ρ and excess molar volumes V_m^E for $\{(1-x)CO_2+xN_2\}$

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$T=323.15$ K, $p=9.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.27440	0.21689	0.19160	0.17027	0.15446	0.13924	0.13023	0.11995	0.11150
$V_m^E/(cm^3\cdot mol^{-1})$	22.92	40.61	41.48	41.49	37.84	35.91	24.80	17.15	6.59
$T=323.15$ K, $p=19.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.53550	0.44246	0.37797	0.32888	0.29093	0.26087	0.23630	
$V_m^E/(cm^3\cdot mol^{-1})$		2.409	6.023	8.115	9.31	9.30	8.00	5.51	
$T=323.15$ K, $p=29.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.77096	0.67942	0.59557	0.52075	0.45860	0.40727	0.36491		
$V_m^E/(cm^3\cdot mol^{-1})$	−0.814	−1.019	−0.510	0.616	1.654	2.361	2.524		
$T=323.15$ K, $p=39.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.83963		0.68326		0.54897		0.44614		0.36721
$V_m^E/(cm^3\cdot mol^{-1})$	−0.769		−1.129		−0.155		0.556		0.415
$T=323.15$ K, $p=59.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.92334	0.85397	0.78658	0.72280	0.66239	0.60735	0.55591	0.50913	0.46711
$V_m^E/(cm^3\cdot mol^{-1})$	−0.469	−0.732	−0.794	−0.730	−0.521	−0.351	−0.107	0.052	0.020
$T=323.15$ K, $p=99.93$ MPa									
$\rho/(g\cdot cm^{-3})$	1.01860	0.95962	0.90048	0.84286	0.78726	0.73341	0.68226	0.63376	0.58902
$V_m^E/(cm^3\cdot mol^{-1})$	−0.128	−0.292	−0.332	−0.311	−0.249	−0.128	−0.013	0.086	0.054
$T=373.15$ K, $p=9.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.17135	0.15657	0.14364	0.13317	0.12386	0.11536	0.10771		
$V_m^E/(cm^3\cdot mol^{-1})$	3.88	8.29	11.89	12.60	12.17	10.98	8.57		
$T=373.15$ K, $p=19.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.35331	0.31415	0.28188	0.25615	0.23349	0.21393	0.19672	
$V_m^E/(cm^3\cdot mol^{-1})$		8.21	9.78	10.66	10.09	9.15	7.42	4.97	
$T=373.15$ K, $p=29.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.57798	0.50682	0.45032	0.40297	0.36397	0.33008	0.30163	0.27631	0.25400
$V_m^E/(cm^3\cdot mol^{-1})$	1.427	3.222	4.420	5.330	5.583	5.54	4.72	3.55	1.82
$T=373.15$ K, $p=39.94$ MPa									
$\rho/(g\cdot cm^{-3})$	0.67925	0.61121	0.55060	0.49791	0.45175	0.41185	0.37644	0.34521	
$V_m^E/(cm^3\cdot mol^{-1})$	0.424	0.933	1.553	2.053	2.406	2.420	2.208	1.634	
$T=373.15$ K, $p=59.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.79799	0.73643	0.67768	0.62305	0.57324	0.52752	0.48598	0.44780	
$V_m^E/(cm^3\cdot mol^{-1})$	−0.010	−0.020	0.043	0.369	0.543	0.674	0.679	0.583	
$T=373.15$ K, $p=99.93$ MPa									
$\rho/(g\cdot cm^{-3})$	0.92503	0.86933	0.81562	0.76312	0.71351	0.66584	0.62092	0.57848	0.53861
$V_m^E/(cm^3\cdot mol^{-1})$	−0.034	−0.065	−0.064	0.019	0.075	0.157	0.192	0.176	0.071
$T=473.15$ K, $p=9.94$ MPa									
$\rho/(g\cdot cm^{-3})$		0.10862	0.10287	0.09734	0.09209	0.08701	0.08200	0.07712	
$V_m^E/(cm^3\cdot mol^{-1})$		3.64	3.97	4.07	3.61	2.93	2.46	1.91	

TABLE 3—*continued*

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
					$T = 473.15$ K, $p = 19.94$ MPa				
$\rho/(g \cdot cm^{-3})$		0.22200	0.20733	0.19364	0.18108	0.16974	0.15899	0.14873	0.13905
$V_m^E/(cm^3 \cdot mol^{-1})$		4.17	4.86	5.36	5.36	4.66	3.71	2.59	1.08
					$T = 473.15$ K, $p = 29.94$ MPa				
$\rho/(g \cdot cm^{-3})$	0.35624	0.32868	0.30389	0.28205	0.26224	0.24421	0.22784	0.21236	0.19797
$V_m^E/(cm^3 \cdot mol^{-1})$	1.95	3.15	4.10	4.50	4.56	4.23	3.42	2.48	1.16
					$T = 473.15$ K, $p = 39.94$ MPa				
$\rho/(g \cdot cm^{-3})$	0.45614	0.41984	0.38815	0.35963	0.33389	0.31046	0.28889	0.26903	0.25027
$V_m^E/(cm^3 \cdot mol^{-1})$	1.175	2.189	2.79	3.14	3.19	2.96	2.49	1.71	0.80
					$T = 473.15$ K, $p = 59.93$ MPa				
$\rho/(g \cdot cm^{-3})$	0.59944	0.55619	0.51694	0.48040	0.44711	0.41579	0.38699	0.35986	0.33484
$V_m^E/(cm^3 \cdot mol^{-1})$	0.443	0.904	1.217	1.492	1.580	1.635	1.496	1.279	0.818
					$T = 473.15$ K, $p = 99.93$ MPa				
$\rho/(g \cdot cm^{-3})$	0.76419	0.71888	0.67613	0.63504	0.59608	0.55890	0.52367	0.48987	0.45804
$V_m^E/(cm^3 \cdot mol^{-1})$	0.135	0.277	0.368	0.471	0.527	0.552	0.509	0.435	0.239
					$T = 573.15$ K, $p = 9.94$ MPa				
$\rho/(g \cdot cm^{-3})$		0.08600	0.08207	0.07819	0.07431		0.06714	0.06386	
$V_m^E/(cm^3 \cdot mol^{-1})$		1.86	1.57	1.30	1.31		−1.64	−5.16	
					$T = 573.15$ K, $p = 19.94$ MPa				
$\rho/(g \cdot cm^{-3})$			0.16147	0.15298	0.14496	0.13717	0.12920	0.12170	
$V_m^E/(cm^3 \cdot mol^{-1})$			3.40	3.23	2.60	1.84	1.76	1.06	
					$T = 573.15$ K, $p = 29.94$ MPa				
$\rho/(g \cdot cm^{-3})$	0.26650	0.25081	0.23616	0.22249	0.20978	0.19737	0.18567	0.17470	0.16374
$V_m^E/(cm^3 \cdot mol^{-1})$	1.41	2.18	2.70	2.90	2.71	2.60	2.16	1.30	0.68
					$T = 573.15$ K, $p = 39.94$ MPa				
$\rho/(g \cdot cm^{-3})$	0.34480	0.32284		0.28510	0.26831	0.25212	0.23700	0.22236	0.20840
$V_m^E/(cm^3 \cdot mol^{-1})$	0.94	1.91		2.54	2.39	2.22	1.74	1.22	0.51
					$T = 573.15$ K, $p = 59.93$ MPa				
$\rho/(g \cdot cm^{-3})$	0.47115	0.44213	0.41558	0.39051	0.36665	0.34458	0.32346	0.30333	0.28410
$V_m^E/(cm^3 \cdot mol^{-1})$	0.745	1.240	1.491	1.656	1.767	1.618	1.40	1.06	0.60
					$T = 573.15$ K, $p = 99.93$ MPa				
$\rho/(g \cdot cm^{-3})$	0.64257	0.60721	0.57363	0.54157	0.51045	0.48114	0.45293	0.42570	0.39944
$V_m^E/(cm^3 \cdot mol^{-1})$	0.252	0.444	0.573	0.649	0.732	0.687	0.594	0.453	0.252

TABLE 4. Experimentally determined densities ρ and excess molar volumes V_m^E for $\{(1-x)CH_4+xN_2\}$

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
				$T=323.15$ K, $p=9.94$ MPa					
$\rho/(g\cdot cm^{-3})$		0.07460	0.07799	0.08159	0.08505	0.08853	0.09189	0.09519	
$V_m^E/(cm^3\cdot mol^{-1})$		1.67	2.61	2.48	2.48	2.14	1.90	1.59	
				$T=323.15$ K, $p=19.94$ MPa					
$\rho/(g\cdot cm^{-3})$	0.14261	0.14767	0.15345	0.15911	0.16488	0.17069	0.17616	0.18246	0.18811
$V_m^E/(cm^3\cdot mol^{-1})$	0.80	2.09	2.51	2.81	2.81	2.60	2.49	1.59	1.06
				$T=323.15$ K, $p=29.94$ MPa					
$\rho/(g\cdot cm^{-3})$	0.19668	0.20498	0.21269	0.22078	0.22859	0.23679	0.24610	0.25532	0.26280
$V_m^E/(cm^3\cdot mol^{-1})$	1.600	1.988	2.453	2.587	2.700	2.513	1.763	0.967	0.762
				$T=323.15$ K, $p=39.94$ MPa					
$\rho/(g\cdot cm^{-3})$	0.23877		0.26019	0.27089	0.28143	0.29183	0.30226		
$V_m^E/(cm^3\cdot mol^{-1})$	0.486		1.047	1.139	1.163	1.128	0.994		
				$T=323.15$ K, $p=59.93$ MPa					
$\rho/(g\cdot cm^{-3})$	0.29197	0.30706	0.32220	0.33735	0.35227	0.36724	0.38199	0.39679	0.41165
$V_m^E/(cm^3\cdot mol^{-1})$	0.123	0.389	0.552	0.633	0.687	0.666	0.627	0.530	0.376
				$T=323.15$ K, $p=99.93$ MPa					
$\rho/(g\cdot cm^{-3})$	0.35088	0.37265	0.39368	0.41549	0.43673	0.45833	0.47955	0.50129	0.52311
$V_m^E/(cm^3\cdot mol^{-1})$	0.179	0.262	0.403	0.407	0.451	0.428	0.423	0.345	0.243
				$T=373.15$ K, $p=9.94$ MPa					
$\rho/(g\cdot cm^{-3})$	0.05770	0.06085		0.06740	0.07057	0.07384	0.07705	0.08033	0.08351
$V_m^E/(cm^3\cdot mol^{-1})$	1.04	2.50		3.14	3.52	3.17	3.86	2.12	1.58
				$T=373.15$ K, $p=19.94$ MPa					
$\rho/(g\cdot cm^{-3})$			0.12623	0.13152	0.13696	0.14273	0.14824		
$V_m^E/(cm^3\cdot mol^{-1})$			1.90	2.52	2.76	2.43	2.24		
				$T=373.15$ K, $p=29.94$ MPa					
$\rho/(g\cdot cm^{-3})$	0.16334	0.17090	0.17858	0.18626	0.19396	0.20174	0.20928	0.21726	0.22497
$V_m^E/(cm^3\cdot mol^{-1})$	0.66	1.31	1.68	1.88	1.91	1.78	1.66	1.18	0.77
				$T=373.15$ K, $p=39.94$ MPa					
$\rho/(g\cdot cm^{-3})$	0.20190	0.21132	0.22158	0.23137	0.24106	0.25078	0.26051	0.27050	0.28032
$V_m^E/(cm^3\cdot mol^{-1})$	0.461	1.040	1.125	1.273	1.342	1.295	1.151	0.837	0.511
				$T=373.15$ K, $p=59.93$ MPa					
$\rho/(g\cdot cm^{-3})$	0.25689	0.27052	0.28417	0.29790	0.31145	0.32482	0.33844	0.35191	0.36562
$V_m^E/(cm^3\cdot mol^{-1})$	0.218	0.507	0.692	0.771	0.819	0.838	0.744	0.628	0.419
				$T=373.15$ K, $p=99.93$ MPa					
$\rho/(g\cdot cm^{-3})$	0.32134	0.34099	0.36073	0.38027	0.39985	0.41930	0.43901	0.45883	0.47873
$V_m^E/(cm^3\cdot mol^{-1})$	0.231	0.359	0.428	0.488	0.508	0.516	0.466	0.380	0.268
				$T=473.15$ K, $p=9.94$ MPa					
$\rho/(g\cdot cm^{-3})$		0.04631		0.05164	0.05437	0.05706	0.05965		
$V_m^E/(cm^3\cdot mol^{-1})$		3.26		3.94	3.46	3.04	3.15		

TABLE 4—*continued*

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$T = 473.15$ K, $p = 19.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.08569	0.09039	0.09521	0.10025	0.10503	0.11004		0.11966	0.12472
$V_m^E/(cm^3 \cdot mol^{-1})$	0.32	1.36	1.87	1.71	1.91	1.51		1.08	0.26
$T = 473.15$ K, $p = 29.94$ MPa									
$\rho/(g \cdot cm^{-3})$		0.12976	0.13637	0.14320	0.15000	0.15674	0.16357	0.17035	0.17723
$V_m^E/(cm^3 \cdot mol^{-1})$		0.79	1.30	1.41	1.41	1.36	1.12	0.82	0.36
$T = 473.15$ K, $p = 39.94$ MPa									
$\rho/(g \cdot cm^{-3})$		0.16396	0.17260	0.18103	0.18957	0.19810	0.20664	0.21517	0.22366
$V_m^E/(cm^3 \cdot mol^{-1})$		0.92	1.09	1.25	1.24	1.13	0.93	0.67	0.35
$T = 473.15$ K, $p = 59.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.20658	0.21837	0.22996	0.24182	0.25343	0.26519	0.27676	0.28847	0.30016
$V_m^E/(cm^3 \cdot mol^{-1})$	0.486	0.706	0.900	0.904	0.921	0.825	0.730	0.539	0.313
$T = 473.15$ K, $p = 99.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.27526	0.29185	0.30859	0.32541	0.34185	0.35859	0.37536	0.39234	0.40928
$V_m^E/(cm^3 \cdot mol^{-1})$	0.207	0.400	0.506	0.550	0.626	0.609	0.560	0.448	0.323
$T = 573.15$ K, $p = 9.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.03543		0.03992	0.04211	0.04440	0.04665	0.04901	0.05122	0.05358
$V_m^E/(cm^3 \cdot mol^{-1})$	2.54		4.00	5.04	4.58	4.43	2.96	3.03	1.43
$T = 573.15$ K, $p = 19.94$ MPa									
$\rho/(g \cdot cm^{-3})$			0.07768	0.08195	0.08618	0.09036	0.09470	0.09896	
$V_m^E/(cm^3 \cdot mol^{-1})$			1.86	1.74	1.61	1.48	0.78	0.21	
$T = 573.15$ K, $p = 29.94$ MPa									
$\rho/(g \cdot cm^{-3})$			0.11195	0.11787	0.12383	0.12976			
$V_m^E/(cm^3 \cdot mol^{-1})$			0.85	0.99	0.95	0.84			
$T = 573.15$ K, $p = 39.94$ MPa									
$\rho/(g \cdot cm^{-3})$	0.12707	0.13465	0.14205	0.14973	0.15730	0.16481	0.17244	0.17972	0.18719
$V_m^E/(cm^3 \cdot mol^{-1})$	0.63	0.88	1.18	1.07	0.98	0.87	0.57	0.49	0.20
$T = 573.15$ K, $p = 59.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.17318	0.18352	0.19372	0.20400	0.21424	0.22453	0.23492	0.24519	0.25531
$V_m^E/(cm^3 \cdot mol^{-1})$	0.34	0.56	0.76	0.83	0.85	0.77	0.60	0.44	0.29
$T = 573.15$ K, $p = 99.93$ MPa									
$\rho/(g \cdot cm^{-3})$	0.23899	0.25386	0.26890	0.28380	0.29872	0.31362	0.32855	0.34345	0.35893
$V_m^E/(cm^3 \cdot mol^{-1})$	0.306	0.455	0.504	0.545	0.545	0.519	0.454	0.374	0.150

$\delta\rho_{min} = -2 \cdot 10^{-4}$ g·cm^{-3}. This analysis indicates that the equations of state chosen for the standard fluids are extremely accurate, that the regressed calibration line is precisely determined, and that the response of the vibrating tube is linear over a wide range of densities (and viscosities) for these fluids.

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, N_2, CO_2, and CH_4 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 for pure CO_2 and CH_4 are listed in table 1. Agreement between our results for CO_2 and the equations of state[2,4] is excellent, except near the critical point

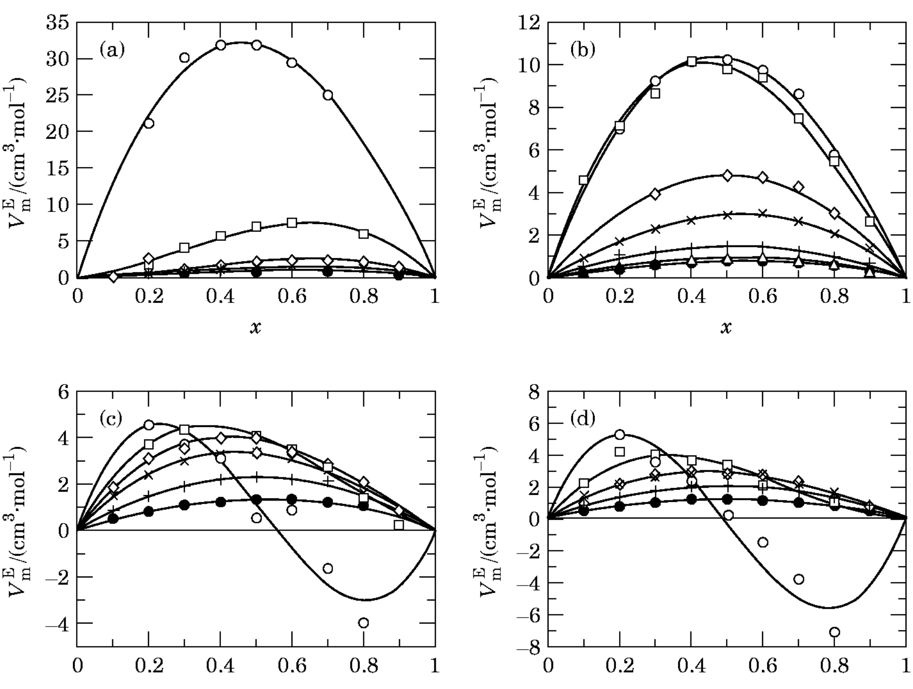

FIGURE 2. Excess molar volumes V_m^E for $\{(1-x)CO_2 + xCH_4\}$ at the temperatures: (a) $T = 323.15$ K, (b) $T = 373.15$ K, (c) $T = 473.15$ K, and (d) $T = 573.15$ K and pressures: ○, $p = 9.94$ MPa; □, $p = 19.94$ MPa; ◇, $p = 29.94$ MPa; ×, $p = 39.94$ MPa; +, $p = 59.93$ MPa; △, $p = 79.93$ MPa; and ●, $p = 99.93$ MPa. The curves represent two-parameter Margules equations fitted to the individual isobaric, isothermal data sets.

($p_c = 7.38$ MPa, $T_c = 304.2$ K). Deviations of our measured densities for CH_4 from values obtained from the equations of state[2,5] are generally greater than can be accounted for by the uncertainties in the experimental results and the equations of state. The cause of these discrepancies is unknown; however, prior to the present study, few results for CH_4 had been collected at elevated pressures and temperatures.

Densities and excess molar volumes for $\{(1-x)CO_2 + x(CH_4)\}$, $\{(1-x)CO_2 + x(N_2)\}$, and $\{(1-x)CH_4 + x(N_2)\}$ are given in tables 2, 3, and 4, respectively. Because the volumetric properties for the end members and mixtures were determined during the same experimental runs, V_m^E could be determined with a high degree of precision from a single, internally consistent set of results. It is often convenient to present volumetric results in terms of V_m^E in order to visualize the effects of pressure, temperature, and fluid composition on nonideal mixing of the species. Figures 2 to 4 show values for V_m^E plotted against x, and V_m^E curves calculated from two-parameter Margules equations[6] fit to the individual isobaric, isothermal data sets. Several features are evident from these figures. First, we observed both positive and negative V_m^Es. Secondly, V_m^E is accurately represented by two-parameter

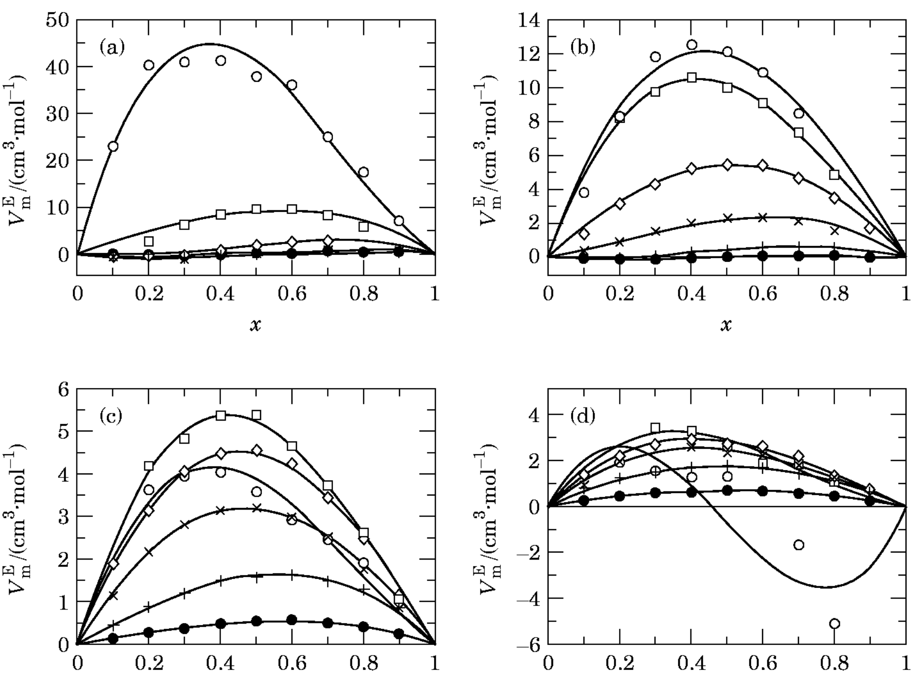

FIGURE 3. Excess molar volumes V_m^E for $\{(1-x)CO_2 + xN_2\}$ at the temperatures: (a) $T = 323.15$ K, (b) $T = 373.15$ K, (c) $T = 473.15$ K, and (d) $T = 573.15$ K and pressures: ○, $p = 9.94$ MPa; □, $p = 19.94$ MPa; ◇, $p = 29.94$ MPa; ×, $p = 39.94$ MPa; +, $p = 59.93$ MPa; and ●, $p = 99.93$ MPa. The curves represent two-parameter Margules equations fitted to the individual isobaric, isothermal data sets.

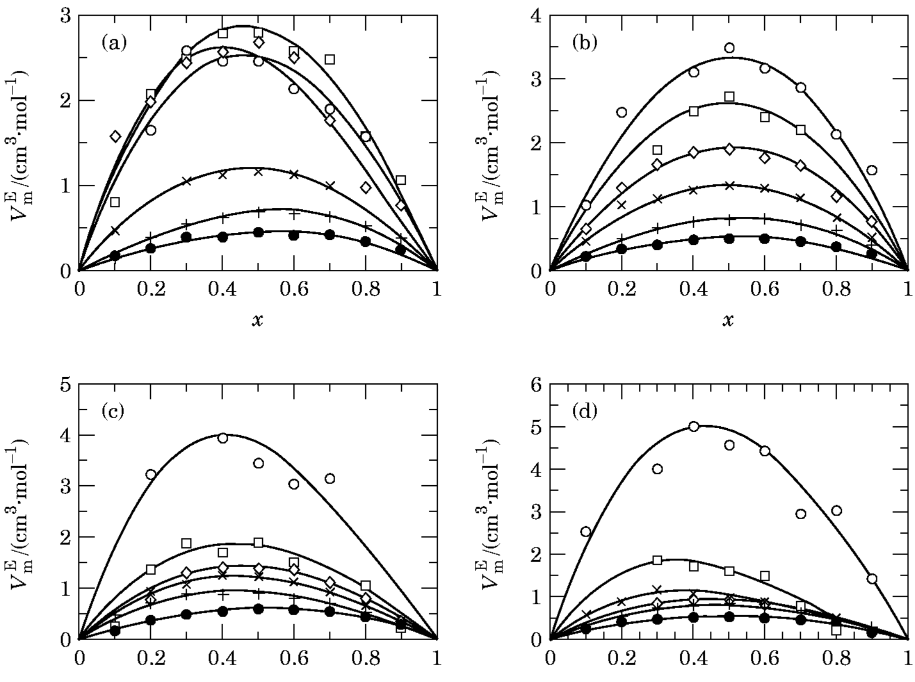

FIGURE 4. Excess molar volumes V_m^E for $\{(1-x)CH_4+xN_2\}$ at the temperatures: (a) $T=323.15$ K, (b) $T = 373.15$ K, (c) $T = 473.15$ K, and (d) $T = 573.15$ K and pressures: ○, $p = 9.94$ MPa; □, $p=19.94$ MPa; ◇, $p=29.94$ MPa; ×, $p=39.94$ MPa; +, $p=59.93$ MPa; and ●, $p=99.83$ MPa. The curves represent two-parameter Margules equations fitted to the individual isobaric, isothermal data sets.

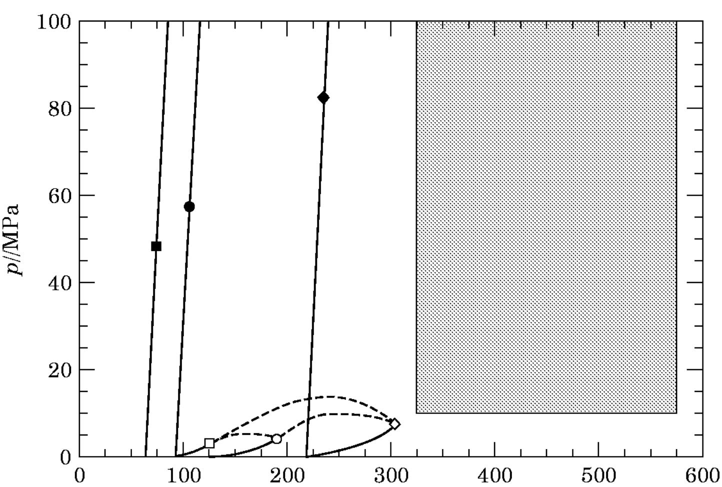

FIGURE 5. Plot of saturation curves terminated by critical points for: ◇, CO_2; ○, CH_4; and □, N_2 and melting curves for: ◆, CO_2; ●, CH_4; and ■, N_2. The dashed curves represent the approximate positions of the critical loci for the binary systems. The stippled region represents the (p, T) range of our experimental results.

TABLE 5. Volumetric results from the literature for $\{(1-x)CO_2+xCH_4\}$, $\{(1-x)CO_2+xN_2\}$, and $\{(1-x)CH_4+xN_2\}$ at (p,T) conditions which are near, or overlap, this study. The (p,T,x) ranges for each set are summarized, as well as the number n of data points reported

Reference	p/MPa	T/K	x	n	Comments
		$\{(1-x)CO_2+xCH_4\}$			
Reamer *et al.*[7]	0.7 to 68.9	311 to 511	0.08 to 0.67	560	Smoothed results
Tong and Liu[8]	7.1 to 12.9	381 to 452	0.49, 0.54	24	
Magee and Ely[9]	2.1 to 35.8	225 to 400	0.02	91	
Brugge *et al.*[10]	0.2 to 9.8	300, 320	0.10 to 0.90	155	Virial coefficients reported
Esper *et al.*[11]	0.1 to 48.3	205 to 320	0.524	119	Virial coefficients reported
McElroy *et al.*[12]	0.6 to 12.0	303 to 333	0.3 to 0.7	132	Mixtures contain small amounts of N_2; virial coefficients reported
		$\{(1-x)CO_2+xN_2\}$			
Kritschewsky and Markov[13]	5.1 to 50.7	273 to 473	(52.7, 75.8) [a]	54	Smoothed results
Haney and Bliss[14]	3.0 to 50.7	269 to 325	0.49, 0.75	150	Smoothed results
Kaminishi[15]	2.7 to 19.6	243 to 333	0.05 to 0.09	48	
Semenova *et al.*[16]	200 to 800	323 to 473	0.57	37	Smoothed results
Altunin *et al.*[17]	0.2 to 43.5	323, 373	0.24 to 0.75	75	
Hacura *et al.*[18]	49 to 274	323, 348	0.25 to 0.75	256	
Brugge *et al.*[10]	0.2 to 10.6	300, 320	0.09 to 0.89	196	Virial coefficients reported
Ely *et al.*[19]	2.2 to 33.0	250 to 330	0.02	79	
Esper *et al.*[11]	0.1 to 48.4	208 to 320	0.55	152	Virial coefficients reported
		$\{(1-x)CH_4+xN_2\}$			
Keyes and Burks[20]	2.9 to 33.2	273 to 473	0.20 to 0.57	110	
Kritschewsky and Levchenko[21]	10.1 to 70.9	273 to 473	(25.8 to 72.8) [a]	105	Smoothed results
Blake *et al.*[22]	30.4 to 506.7	299.5	0.02 to 0.50	98	Smoothed results
Semenova *et al.*[23]	200 to 900	323 to 473	0.25 to 0.75	135	Smoothed results
Straty and Diller[24]	0.9 to 35.6	82 to 320	0.28 to 0.74	479	
Haynes and McCarty[25]	1.0 to 16.4	140 to 320	0.27 to 0.68	85	

[a] Volume per cent N_2 reported in mixture.

Margules equations. Thirdly, V_m^E for CO_2-bearing mixtures increases sharply near the critical point of CO_2 ($p_c=7.36$ MPa, $T_c=304.25$ K). Fourthly, V_m^E increases sharply at very low density to a maximum value at a pressure below 20 MPa. Above this maximum, V_m^E decreases rapidly with increasing pressure. Lastly, the effect of temperature on V_m^E is generally small except for CO_2-bearing mixtures near the critical point of CO_2. A complete thermodynamic analysis of the results of this study, including a polybaric, polythermal two-parameter Margules equation of state, will be presented in a subsequent paper.

In figure 5, the (p,T) range of our experimental results for the pure gases and binary mixtures is illustrated. In addition, the saturation and melting curves for pure CO_2, CH_4, and N_2 and the critical loci for (carbon dioxide + methane), (carbon dioxide + nitrogen), and (methane + nitrogen) are plotted. This figure illustrates the relative positions of our experimental results to the two-phase (liquid + vapor) regions and critical loci and indicates that, in all cases, our results are for single-phase supercritical fluids.

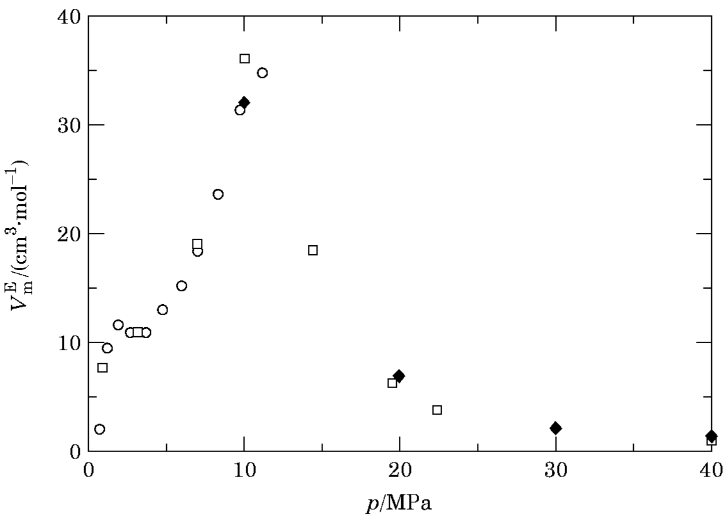

FIGURE 6. Comparisons of excess molar volumes V_m^E for: ○, ($\approx$0.54CO_2+0.46CH_4) at the temperature $\approx$323 K from McElroy *et al.*;[12] □, (0.48CO_2+0.52CH_4) at the temperature $\approx$320 K from Esper *et al.*;[11] and ◆, (0.50CO_2+0.50CH_4) at T=323.15 K from this study.

4. Comparison with other results

The volumetric properties of (carbon dioxide+methane),[7–12] (carbon dioxide+nitrogen),[10,11,13–19] and (methane+nitrogen)[20–25] have been measured previously (see table 5), but generally at lower pressures and temperatures than in the present study. Previous investigators have reported their experimental results in a wide variety of ways (as V_m, V_m^E, compressibility factors, and pseudoisochores). To facilitate direct comparison of the results from these various studies, we have used the original values from the earlier studies to calculate V_m^E. The equation of state of Friend[2] was used to calculate the ideal volume of mixtures if experimental results for the end members were not reported. Because our experiments do not duplicate the exact (p,T,x) conditions of those in any previous study, only semi-quantitative comparisons with the literature can be made.

In figure 6, V_m^E for (0.54CO_2+0.46CH_4) at $T\approx$323 K from McElroy *et al.*[12] and (0.48CO_2+0.52CH_4) at $T\approx$320 K from Esper *et al.*[11] are compared with our experimental results for (0.50CO_2+0.50CH_4) at T=323.15 K. Excess molar volumes derived from McElroy *et al.*[12] were calculated using the compressibility factors for pure CO_2, pure CH_4, and (carbon dioxide+methane) reported by those investigators. Excess molar volumes obtained from Esper *et al.*[11] were computed using the molar densities for binary mixtures reported by those investigators and ideal molar volumes obtained from the equation of state of Friend.[2] In figures 7(a) and 7(b), V_m^E curves derived from the smoothed compressibility factors for pure CO_2 and (carbon dioxide+methane) acquired by Reamer *et al.*[7] at T=377.5 K and T=477.5 K are compared with the experimental values that we obtained at

$T = 373.15$ K and $T = 473.15$ K. In order to calculate V_m^E, the molar volume for pure CH_4 was estimated by regression analysis of the isothermal, isobaric data sets for pure CO_2 and (carbon dioxide + methane). The mean deviation between V_m^Es volumes predicted by this method and from the equation of state of Friend[2] is -0.11 per cent. Figures 6 and 7 indicate that our results for $\{(1-x)CO_2 + xCH_4\}$ are in good agreement with the literature.

We have also compared our measured densities for $\{(1-x)CO_2 + xN_2\}$ with results reported by previous investigators. In figure 8, V_m^E derived from our experimentally determined densities for $(0.50CO_2 + 0.50N_2)$ at $T = 323.15$ K are compared with V_m^E for compositions near $(0.5CO_2 + 0.5CH_4)$ from Altunin *et al.*[17] and Esper *et al.*[11] The

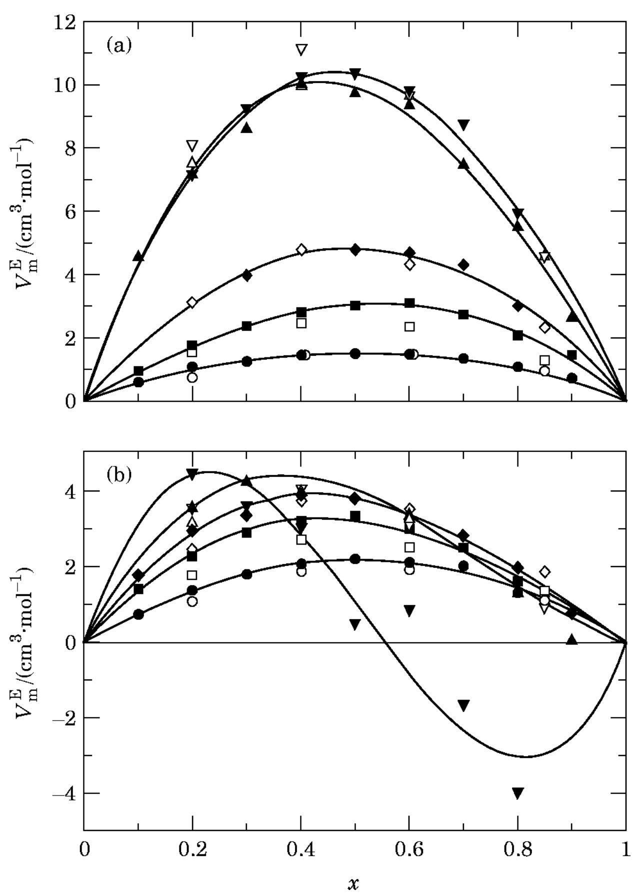

FIGURE 7(a) and (b). Comparison of V_m^E for $\{(1-x)CO_2 + xCH_4\}$. Open symbols represent results from Reamer *et al.*[7] at: (a) $T = 377.5$ K and (b) $T = 477.5$ K and the pressures: ▽, $p = 10.3$ MPa; △, $p = 20.7$ MPa; ◇, $p = 31.0$ MPa; □, $p = 41.3$ MPa; and ○, $p = 62.0$ MPa. Filled symbols represent results from this study at: (a) $T = 373.15$ K and (b) $T = 473.15$ K and the pressures: ▼, $p = 9.94$ MPa; ▲, $p = 19.94$ MPa; ◆, $p = 29.94$ MPa; ■, $p = 39.94$ MPa; ●, $p = 59.93$ MPa. The curves represent two-parameter Margules equations fitted to results obtained in this study (see text).

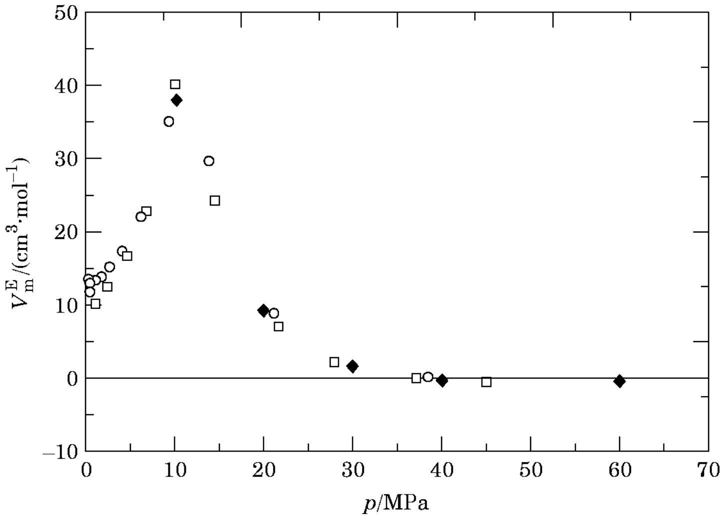

FIGURE 8. Comparisons of excess molar volumes V_m^E for: ○, $(0.51CO_2+0.49N_2)$ at $T = 323.15$ K from Altunin *et al.*;[17] □, $(0.45CO_2 + 0.55N_2)$ at the temperature ≈320 K from Esper *et al.*;[11] and ◆, $(0.50CO_2+0.50N_2)$ at $T = 323.15$ K from this study.

experimental results of Altunin *et al.*[17] are reported as V_m and V_m^E. Excess molar volumes were derived from molar densities for binary mixtures reported by Esper *et al.*[11] and volumetric predictions for the end members calculated from the equation of state of Friend.[2] It is evident from figure 8 that there is good agreement among the results obtained in these three investigations of $\{(1-x)CO_2+xN_2\}$.

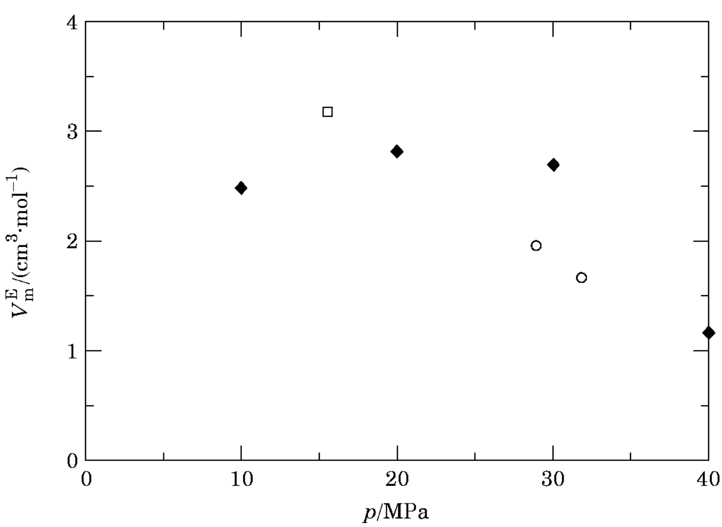

FIGURE 9. Comparisons of excess molar volumes V_m^E for $(0.50CO_2+0.50N_2)$: ○, at $T = 320$ K from Straty and Diller;[24] □, at $T = 320$ K from Haynes and McCarty;[25] and ◆, at $T = 323.15$ K from this study.

The experimental database for $\{(1-x)CH_4+xN_2\}$ is less extensive than for $\{(1-x)CO_2 + xCH_4\}$ or $\{(1-x)CO_2 + xN_2\}$. In figure 9 comparisons are made between our experimental results at $T = 323.15$ K and values of V_m^E derived from Straty and Diller[24] and Haynes and McCarty[25] at $T = 320$ K for $(0.50CH_4+0.50N_2)$. Excess molar volumes were calculated from molar densities for the binary mixtures and volumetric predictions for the end members were calculated from the equation of state of Friend.[2] The apparent discrepancies are larger than can be accounted for by experimental or calculational uncertainties, or both.

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