Experimental Liquid Mixture Densities for Testing and Improving Correlations for Liquefied Natural Gas

Liquid molar volumes and excess volumes have been experimentally determined for some methane-rich binary and ternary mixtures containing ethane, propane, isobutane, and nitrogen between 91 and 115 K. A gas expansion type system calibrated against pure methane densities was used to make the necessary pure fluid and mixture measurements.

The best of the available density correlations predicts the experimental methane-ethane molar volumes within ±0.2%, while larger systematic deviations are found for the methane-propane and methane-isobutane systems. Molar volumes for methane-nitrogen and ternary mixtures containing nitrogen diverge strongly from the correlation predictions at 108 K and higher temperatures. An empirical scheme is proposed for predicting molar volumes of methane-rich liquefied natural gases using reported methane-ethane and methane-nitrogen excess volumes. This method predicts all binary and ternary molar volumes from this investigation within ±0.1%.

JAMES B. RODOSEVICH
and REID C. MILLER

Department of Chemical Engineering
University of Wyoming
Laramie, Wyoming 82070

SCOPE

Long distance transportation of liquefied natural gas (LNG) is increasing rapidly throughout the world. With domestic gas supplies projected to lag behind demands in many countries, the LNG industry should continue to gain importance in the future energy picture. Large scale custody transfer of LNG is posing new technical problems in the gas industry. Accurate liquid mixture densities are required to convert volumetric meter readings into market values, which are based on total heating values. A systematic error in estimated density of as little as 1% may amount to very serious monetary discrepancies ($15,000/ocean tanker load by current standards).

There are only a few published high-accuracy densities for liquid hydrocarbon mixtures containing more than 70 mole % methane (Klosek and McKinley, 1968; Shana'a and Canfield, 1968). This data has been used in conjunction with mixture data outside this composition range and pure fluid data to develop an empirical density correlation (Klosek and McKinley, 1968; Boyle and Reece, 1971).

To date, this LNG density correlation has not been satisfactorily tested. Correlation accuracy is probably a strong function of gas composition and temperature; however, this has never been established by independent experimentation. Two inherent problems need clarification.

First, the accuracy of the experimental LNG densities needs to be checked by independent investigation. Additional data for typical compositions should be produced in this effort. Second, the present correlation simply applies a volume reduction correction to the ideal mixture molar volume. This correction is taken to be a function of average molecular weight of the mixture and temperature only, pressure and actual composition being ignored. Such a correlation may be too simple to achieve an accuracy approaching ±0.1% in the density, even for normal LNG variations in composition. A set of experiments designed to test the limits of such a correlation has been badly needed. With the above problems in mind, an experimental program was undertaken to provide accurate density data for testing and improving correlations for LNG.

CONCLUSIONS AND SIGNIFICANCE

A gas expansion experiment suitable for measuring molar volumes of liquids at low temperatures has been calibrated with pure liquid methane. Liquid molar volumes have been measured between 91 and 115 K for pure ethane, propane, isobutane, and nitrogen; methane-rich binary mixtures containing 0 to 31 mole % ethane, 0 to 10 mole % propane, 0 to 8.5 mole % isobutane, and 0 to 15 mole % nitrogen; and three methane-rich ternary mixtures of selected compositions. These results agree within ±0.15% of the previous measurements by Shana'a and Canfield (1968) and Klosek and McKinley (1968) where overlapping of data occurs. Excess volumes have been calculated from the pure fluid and mixture molar volumes.

The LNG density correlation of Klosek and McKinley (1968) predicts experimental methane-ethane molar volumes within ±0.2% up to fairly high ethane concentrations (probably to the equimolar mixture). Predictions are within the same accuracy for methane-propane only to 10 or 15 mole % propane and for methane-isobutane only to about 3 mole % isobutane. Densities for methane-nitrogen and nitrogen-containing ternary mixtures are predicted quite well at low temperatures but diverge significantly from the correlation at temperatures of 108

Correspondence concerning this paper should be addressed to R. C. Miller.

K and higher, even for concentrations as low as 5 mole % nitrogen.

Experimental molar volumes for methane-propane, methane-isobutane, and methane-nitrogen are found to be more poorly correlated than methane-ethane mixtures of the same average molecular weight. This indicates that the principle on which the correlation is based is not rigorous. Caution should be used in trying to predict densities for LNG mixtures containing large amounts of components other than methane and ethane.

A simple empirical scheme has been developed which correlates all of the present experimental molar volumes for methane-rich LNG mixtures within ±0.1%. The only data required are pure fluid molar volumes (for evaluation of the ideal solution contribution), excess volumes for methane-ethane, and excess volumes for binary mixtures of methane with each nonhydrocarbon material present. All excess volume contributions from methane-hydrocarbon interactions can be taken from the methane-ethane data by use of an equivalent ethane concentration.

EXPERIMENTAL METHOD

The equipment and procedure used to measure liquid molar volumes have been described in detail by Liu and Miller (1972), Massengill and Miller (1973), and Miller (1972). This system is similar to an earlier apparatus employed by Streett and Staveley (1968) and is based on the gas expansion method. The basic experiment consists of condensation of either a pure fluid or mixture into a volumetric cell, measurement of cell temperature and pressure, expansion into gas reservoirs thermostated near room temperature, and determination of pressure in these reservoirs. Pressure developed in the reservoirs (always less than 150 kN m^{-2})* is used to calculate the amount of liquid expanded from the cell. The virial equation of state, truncated after the second virial coefficient term, adequately describes the *P-V-T* behavior of this expansion reservoir gas.

Cell temperatures are measured with a platinum resistance thermometer calibrated by the National Bureau of Standards on the IPTS-68. The measured temperatures are accurate within ±0.02 K. Pressures above the volumetric cell are read from one of two calibrated Bourdon-tube gauges (0 to 340 kN m^{-2} and 340 to 3 450 kN m^{-2}). Each gauge is accurate to within 0.1% of the full scale reading. Expansion reservoir pressures are determined by mercury manometry with a precision always better than 1 part in 10,000.

The volumetric cell is held at low temperature by being immersed in a boiling liquid nitrogen bath. Temperature control is maintained by fixing the pressure above this bath with a cartesian manostat. The expansion reservoirs are located in a stirred water bath at 25°C, in which temperature fluctuations do not exceed ±0.03°C.

The pure gases are used as obtained from a commercial supplier. Stated minimum purity (on a mole basis) was 99.97% for methane, 99.98% for ethane, 99.99% for propane, 99.96% for isobutane, and 99.997% for nitrogen. The methane impurities have been determined to have negligible effect on molar volume by limited experimental comparison with a 99.997% minimum purity methane sample (Miller, 1972). Mixtures are prepared by weight from the pure gases. The mole fraction compositions should be accurate to four decimal places as reported.

CALIBRATION

Fundamental volumetric measurements are not made with the experimental system described above. Rather, the experiment is calibrated by use of a pure fluid for which saturated liquid densities are known. For measurement on methane-rich liquid mixtures, pure methane has been used as the calibration fluid. A survey of saturated liquid methane densities indicated that the equation listed by Goodwin and Prydz (1972) as closely fitting their experimental results should serve as a suitable basis. A preponderance of recent experimental evidence confirms these methane densities to within ±0.15% for the temperature range 91 to 130 K (Miller, 1972).

Calibration was accomplished by performing a series of runs for pure methane and determining the necessary equipment constants by a least squares fit of the reference molar volume data. The results of these calibration runs are presented in Table 1. Cell pressures employed in the calibration runs, as in most experiments reported here, were less than 30 kN m^{-2} above the saturation pressures. These methane molar volumes were assumed to be those for the saturated liquid, since the largest compressibility correction was estimated to be only 0.002 cm^3 mol^{-1}.

A very close fit was obtained between the experimental molar volumes and those of Goodwin and Prydz, the average absolute deviation being less than 0.01%. This must be considered to represent the highest attainable precision level for the experiment and not the absolute accuracy. Uncertainties in the methane reference densities, plus possible systematic experimental errors, will increase the absolute uncertainty in reported molar volumes to about 0.1%.

EXPERIMENTAL RESULTS

Molar volumes are reported in Table 2 for pure methane, ethane, propane, and nitrogen at temperatures near 91, 100, 108, and 115 K. Each measurement was performed at a pressure slightly above saturation. Also shown in Table 2 are the vapor pressures and molar volumes corrected to these pressures. Methane and nitrogen isothermal compressibilities were taken from Rowlinson (1969) and those for ethane and propane estimated from Renon, Eckert, and Prausnitz (1967). Mixture isothermal compressibilities were assumed to be equal to mole fraction averages of the pure fluid values. Compressibility corrections were very small for all pure fluid and mixture experi-

TABLE 1. PURE METHANE CALIBRATION EXPERIMENTAL RESULTS USING THE MOLAR VOLUME DATA OF GOODWIN AND PRYDZ (1972) FOR REFERENCE

T/K	$P/\text{kN m}^{-2}$	Experimental v/cm^3 mol^{-1}	Goodwin-Prydz v/cm^3 mol^{-1}	Δv
91.09	42	35.570	35.570	0.000
95.02	45	35.988	35.988	0.000
95.09	46	35.995	35.995	0.000
98.62	48	36.388	36.385	0.003
105.06	83	37.133	37.136	−0.003
109.96	117	37.749	37.745	0.004
115.05	151	38.416	38.418	−0.002

---

* 101.325 kN m^{-2} = 1 atmosphere.

ments reported here. The maximum adjustment in molar volume was 0.1% for the pure nitrogen point at 115 K.

Shana'a and Canfield (1968) reported methane, ethane, and propane densities at 108.15 K, while Chui and Canfield (1971) reported a more recent ethane measurement at 115.77 K. Their results are compared with interpolated values from the present work in Table 3. The agreement between the two investigations is excellent, the maximum discrepancy being 0.05% for the propane point.

Isobutane has a triple point of about 113.5 K, which defines the lower temperature limit for studying its pure liquid equilibrium properties. Thus, molar volume measurements were made at temperatures from 114 to 120 K, and these results were extrapolated to lower temperatures for use in calculating excess volumes. The experimental molar volumes and some extrapolated values are given in Table 4. These molar volumes may be taken as those for the saturated liquid, as compressibility effects were negligible.

Table 2. Experimental Molar Volumes for Pure Fluids at the Experimental Pressures and also Corrected to the Mixture Saturation Pressures

Species	T/K	P/kN m^{-2}	Experimental v/cm^3 mol^{-1}	Saturation P/kN m^{-2}	Saturation v/cm^3 mol^{-1}
CH_4	91.00	52	35.563	13	35.565
	100.15	56	36.556	35	36.557
	108.05	95	37.503	74	37.504
	114.94	155	38.401	133	38.403
C_2H_6	91.01	21	46.212	0	46.212
	100.02	21	46.920	0	46.920
	108.11	21	47.563	0	47.564
	115.05	20	48.143	0	48.144
C_3H_8	91.01	13	60.660	0	60.660
	100.01	13	61.382	0	61.382
	108.15	20	62.094	0	62.094
	115.00	16	62.709	0	62.709
N_2	91.01	395	37.871	392	37.872
	100.00	790	40.624	778	40.628
	108.00	1,324	43.983	1,304	43.998
	115.00	1,971	48.288	1,939	48.342

Table 3. Comparison of Pure Fluid Molar Volumes from the Present Work with Previous Results of Canfield and Co-workers

Species	T/K	Literature v/cm^3 mol^{-1}	This work v/cm^3 mol^{-1}
CH_4	108.15	37.52[a]	37.52
C_2H_6	108.15	47.56[a]	47.57
	115.77	48.20[b]	48.20
C_3H_8	108.15	62.12[a]	62.09

[a] Shana'a and Canfield (1968).

[b] Chui and Canfield (1971).

Table 4. Molar Volumes for Pure Isobutane and Comparison with Values Tabulated by Klosek and McKinley (1968)

T/K	P/kN m^{-2}	Experimental v/cm^3 mol^{-1}	Klosek-McKinley v/cm^3 mol^{-1}
95.00	—	76.65[a]	75.25
100.00	—	77.11[a]	75.76
108.00	—	77.85[a]	76.60
114.00	13	78.41	77.21
115.00	13	78.49	77.31
120.00	14	78.96	77.84

[a] Extrapolated values.

Table 5. Experimental Molar Volumes and Excess Volumes for Binary Mixtures of Methane(1)-Ethane(2)

x_1	T/K	P/kN m^{-2}	Experimental v/cm^3 mol^{-1}	Saturation v/cm^3 mol^{-1}	v^E/cm^3 mol^{-1}
0.9478	91.09	34	36.012	36.013	−0.11
	100.01	52	36.951	36.952	−0.13
	108.08	92	37.873	37.875	−0.16
	115.60	149	38.822	38.824	−0.18
0.8516	91.01	37	36.899	36.900	−0.24
	100.00	47	37.776	37.777	−0.30
	108.02	89	38.630	38.631	−0.36
	115.13	142	39.427	39.429	−0.44
0.7528	91.13	26	37.860	37.860	−0.35
	100.01	54	38.699	38.700	−0.41
	108.01	88	39.488	39.489	−0.50
0.7026	91.00	26	38.366	38.366	−0.36
	108.00	63	39.976	39.977	−0.51
	115.00	113	40.697	40.698	−0.61
0.6909	91.00	23	38.461	38.462	−0.39
	100.00	40	39.297	39.298	−0.45
	108.00	67	40.083	40.084	−0.52
	115.00	112	40.798	40.799	−0.62
	115.00	106	40.795	40.796	−0.63

Also shown in Table 4 are molar volumes interpolated from the listing of Klosek and McKinley (1968). These authors estimated the iC_4H_{10} molar volumes by use of an equation developed by Francis (1957) from density data near room temperature. Extrapolation to temperatures near 100 K yields molar volumes about 1.5% smaller than the present experimental results.

Molar volumes have been determined for binary methane solutions containing 0 to 31 mole % ethane, 0 to 10 mole % propane, 0 to 8.5 mole % isobutane, and 0 to 15 mole % nitrogen, again at temperatures between 91 and 115 K. These results are listed in Tables 5 to 8 along with the molar volumes corrected to the mixture saturation pressures (bubble point pressures) and the excess volumes at the saturation pressures. Saturation pressures were so low for the hydrocarbon systems that Raoult's law was considered adequate for their estimation. Values for CH_4-N_2 were estimated from the vapor-liquid equilibrium data of Sprow and Prausnitz (1966), Cines et al. (1953), and Miller et al. (1973).

Excess volumes were calculated from

$$v^E(T, P^s) = v(T, P^s) - \Sigma x_i v_i(T, P^s), \qquad (1)$$

where the mixture molar volumes and pure fluid molar volumes (Table 2 and 4 values adjusted to the appropriate temperature) were all corrected to the mixture saturation pressure. The excess volumes are all small negative numbers at 91 K and become more negative with increase of temperature.

Methane-ethane liquid mixture densities were reported by Shana'a and Canfield (1968) and Klosek and McKinley (1968). Each source listed results for one mixture containing in excess of 70 mole % methane. These results are compared in Table 9 with values linearly interpolated from the present work. Agreement is quite good, being within

TABLE 6. EXPERIMENTAL MOLAR VOLUMES AND EXCESS VOLUMES FOR BINARY MIXTURES OF METHANE(1)-PROPANE(3)

x_1	T/K	$P/\mathrm{kN\ m^{-2}}$	Experimental $v/\mathrm{cm^3\ mol^{-1}}$	Saturation $v/\mathrm{cm^3\ mol^{-1}}$	$v^E/\mathrm{cm^3\ mol^{-1}}$
0.9737	90.99	35	36.117	36.118	−0.10
	100.03	56	37.075	37.077	−0.12
	107.87	95	37.970	37.972	−0.16
	114.99	127	38.866	38.866	−0.18
0.9262	91.01	28	37.157	37.158	−0.25
	100.06	48	38.070	38.071	−0.31
	108.01	88	38.937	38.938	−0.37
	114.97	144	39.751	39.753	−0.45
0.8997	91.02	34	37.766	37.768	−0.31
	100.05	50	38.655	38.656	−0.38
	108.01	90	39.499	39.500	−0.46
	114.98	140	40.287	40.289	−0.56

TABLE 7. EXPERIMENTAL MOLAR VOLUMES AND EXCESS VOLUMES FOR BINARY MIXTURES OF METHANE(1)-ISOBUTANE(4)

x_1	T/K	$P/\mathrm{kN\ m^{-2}}$	Experimental $v/\mathrm{cm^3\ mol^{-1}}$	Saturation $v/\mathrm{cm^3\ mol^{-1}}$	$v^E/\mathrm{cm^3\ mol^{-1}}$
0.9462	100.00	49	38.459	38.460	−0.27
	108.00	87	39.333	39.334	−0.34
	115.00	140	40.185	40.186	−0.38
0.9152	95.00	39	39.072	39.073	−0.36
	100.00	47	39.579	39.580	−0.40
	108.00	87	40.439	40.441	−0.48
	115.00	137	41.247	41.248	−0.56

TABLE 8. EXPERIMENTAL MOLAR VOLUMES AND EXCESS VOLUMES FOR BINARY MIXTURES OF METHANE(1)-NITROGEN(N)

x_1	T/K	$P/\mathrm{kN\ m^{-2}}$	Experimental $v/\mathrm{cm^3\ mol^{-1}}$	Saturation $v/\mathrm{cm^3\ mol^{-1}}$	$v^E/\mathrm{cm^3\ mol^{-1}}$
0.9488	91.00	43	35.625	35.625	−0.06
	99.99	97	36.644	36.644	−0.12
	108.01	168	37.634	37.634	−0.24
	114.98	242	38.572	38.568	−0.48
0.8449	91.05	112	35.757	35.757	−0.17
	100.35	166	36.909	36.904	−0.35
	108.13	288	37.978	37.967	−0.66
	115.05	454	39.009	38.991	−1.32

TABLE 9. COMPARISON OF EXPERIMENTAL METHANE(1)-ETHANE(2) MOLAR VOLUMES WITH PREVIOUS WORK

x_1	T/K	Literature $v/\mathrm{cm^3\ mol^{-1}}$	This work $v/\mathrm{cm^3\ mol^{-1}}$
0.8668	108.15	38.51[a]	38.52
0.8082	100.43	38.20[b]	38.23
	102.65	38.43	38.46
	105.15	38.72	38.72
	107.93	39.06	39.00

[a] Shana'a and Canfield (1968).
[b] Klosek and McKinley (1968).

0.15% for all points. Thus, all three investigations are in good agreement, at least for the methane-ethane system.

Methane-propane excess volumes have been reported at 90.68 K by Stoeckli and Staveley (1970) and at 108.15 K by Shana'a and Canfield (1968). Neither previous study involved propane concentrations as low as those of the present study. Stoeckli and Staveley measured molar volumes and calculated excess volumes for methane mole fractions x_1 between 0.27 and 0.78. The equation which fits their data predicts a v^E of -0.26 cm^3 mol^{-1} at x_1 of 0.9, compared to the present v^E result of -0.31 cm^3 mol^{-1} from Table 6. Shana'a and Canfield determined molar volumes and excess volumes at 108.15 K for x_1 between 0.25 and 0.85. Extrapolating their data to x_1 of 0.9 yields -0.46 cm^3 mol^{-1} for v^E, in perfect agreement with the present result.

Fuks and Bellemans (1967) estimated excess volumes for methane-nitrogen at 91 K from mixture molar volume data. The excess volume equation they reported yields -0.10 cm^3 mol^{-1} at x_1 of 0.845, compared with -0.17 cm^3 mol^{-1} from Table 8. The results of Fuks and Bellemans involved some rather severe temperature extrapolations and are not considered to be highly accurate. The data of Liu and Miller (1972), taken in the present equipment, indicates a v^E value of -0.35 cm^3 mol^{-1} for equimolar methane-nitrogen at 91 K, while the Fuks and Bellemans equation gives -0.21 cm^3 mol^{-1}. Thus, results from the present equipment uniformly indicate larger deviations from ideal solution behavior than reported by Fuks and Bellemans.

Some molar volume data and excess volumes have also been determined for ternary mixtures of CH_4—C_2H_6—C_3H_8, CH_4—C_2H_6—N_2 and CH_4—C_3H_8—N_2. These results are reported in Table 10. No previous results appear to be available for mixtures near to these compositions and temperatures.

COMPARISON WITH CORRELATION

The previous LNG density correlation that has been tested was originally developed by Klosek and McKinley (1968) and later reintroduced by Boyle and Reece (1971) in a modified form. The following equation is used to calculate mixture molar volumes at saturation pressures:

$$v = \Sigma x_i v_i - x_1 C \qquad (2)$$

The first term is the ideal solution (Amagat's law) contribution and the second term is the negative of the more usual excess volume:

$$v^E = -x_1 C \qquad (3)$$

Both papers tabulate pure component molar volumes for evaluation of the ideal solution term. For the species and temperatures of the present study the two listings are almost identical.

The molar volume reduction factor C is assumed to be a unique function of temperature and mixture average molecular weight. Klosek and McKinley presented a graphical relationship which covered the temperature range 88.71 to 133.15 K and molecular weights from 16 to 33. Boyle and Reece gave a tabular relationship covering the ranges 98.15 to 133.15 K and 16 to 25 in molecular weight. Using linear interpolation, there are no ambiguities in the results obtained from this tabular correlation. Thus, all results which are here reported from the Klosek-McKinley correlation were calculated from the more easily utilized Boyle and Reece form.

Pure methane molar volumes listed in both papers are about 0.1% larger than the Goodwin and Prydz (1972)

Table 10. Experimental Molar Volumes and Excess Volumes for Three Ternary Mixtures Composed of Methane(1), Ethane(2), Propane(3), and Nitrogen(N)

Mixture	x_1	x_2	x_3	x_N
1	0.8466	0.1025	0.0509	
2	0.8409	0.1086		0.0505
3	0.9055		0.0497	0.0447

Mixture	T/K	P/kN m^{-2}	Experimental v/cm³ mol^{-1}	Saturation v/cm³ mol^{-1}	v^E/cm³ mol^{-1}
1	100.01	49	38.487	38.488	−0.39
	108.01	81	39.320	39.322	−0.46
	108.02	84	39.326	39.327	−0.46
	115.00	128	40.095	40.096	−0.55
2	91.00	68	36.563	36.564	−0.27
	100.00	110	37.499	37.500	−0.39
	108.00	181	38.398	38.400	−0.56
	115.01	275	39.257	39.261	−0.85
3	91.00	70	36.665	36.667	−0.25
	108.00	185	38.547	38.549	−0.50

values which served as a basis for the present work. Pure ethane and propane molar volumes are generally within 0.1% of the present results as well. Tabulated isobutane molar volumes are about 1.5% low, as discussed in the section on Experimental Results (compare Table 4). The nitrogen molar volumes are in good agreement with experiment at 100 and 108 K, but quite low at 115 K. Since the values listed by Boyle and Reece near this temperature agree with the Klosek-McKinley listing, they are pseudo molar volumes of some kind. As will be discussed below, use of these pseudo molar volumes for nitrogen does not give mixture molar volumes for CH_4—N_2 in good agreement with experiment at 115 K, even for nitrogen contents as low as 5 mole %.

Figures 1 to 3 were prepared to illustrate the agreement between the Klosek-McKinley correlation and experiment. Percent deviation between correlation and experiment is plotted versus composition for each binary system at 100, 108, and 115 K. Both the results of the present work and the data of Shana'a and Canfield (1968) near 108 K are presented in Figure 2. The curves in all figures are drawn through the present results to intersect unit methane mole fraction at a deviation appropriate to the pure methane discrepancy (about +0.1%).

For binary mixtures of CH_4—C_2H_6, CH_4—C_3H_8, CH_4—iC_4H_{10}, and CH_4—N_2 the following generalizations can be made:

1. The Klosek-McKinley correlation predicts CH_4—C_2H_6 molar volumes within ±0.2% of experimental results for temperatures from 100 to 115 K and for ethane mole fractions from 0 to greater than 0.31.

2. For CH_4—C_3H_8 the correlation predicts molar volumes within ±0.2% of the experimental results only up to about 10 to 15 mole % propane at temperatures of 100 to 115 K.

3. In evaluating the correlation for CH_4—iC_4H_{10}, the pure iC_4H_{10} molar volumes from this work were used in place of those listed by Klosek and McKinley. This substitution improves the correlation predictions. However, the predictions are found to be within 0.2% of the experimental CH_4—iC_4H_{10} results only up to about 3 mole % iC_4H_{10}.

4. There are systematic trends for the deviations between correlation and experiment for these hydrocarbon systems. With increasing C_3H_8 or iC_4H_{10} concentration there is a systematic trend to correlation predictions that are too low. These trends may be reversed at higher concentrations. In particular, correlation predictions for CH_4—C_3H_8 appear to be once again within 0.2% of the Shana'a and Canfield results at compositions near the equimolar mixture. There is some improvement in the correlation molar volume predictions as the temperature increases.

5. For CH_4—N_2 mixtures the ability of the correlation to predict molar volumes is a strong function of temperature. At 100 K the predictions are within ±0.1% for nitrogen concentrations up to 15 mole %. However, at 115 K prediction and experiment deviate by more than 0.6% for 5 mole % nitrogen. Based on the current experiments, the Klosek-McKinley correlation should not be expected to yield highly accurate results for mixtures containing significant nitrogen (greater than about 2%) if the temperature is higher than 108 K.

NEW EXCESS VOLUME CORRELATION

An inspection of the excess volume data for CH_4—C_2H_6 and CH_4—C_3H_8 leads to the conclusion that nearly equal excess volumes are found for these two binary systems if the mole fraction C_2H_6 is two times the mole fraction C_3H_8. The excess volumes are nearly equal for the CH_4—C_2H_6 and CH_4—iC_4H_{10} systems when the mole fraction C_2H_6 is 2.4 times the mole fraction iC_4H_{10}. A simple correlation can be developed by use of the equation

$$v = \Sigma x_i v_i + v^E{}_{1-2} + v^E{}_{1-N} \qquad (4)$$

The $v^E{}_{1-2}$ term represents the excess volume contribution due to unlike hydrocarbon interactions. It is evaluated as the CH_4—C_2H_6 excess volume at an equivalent ethane

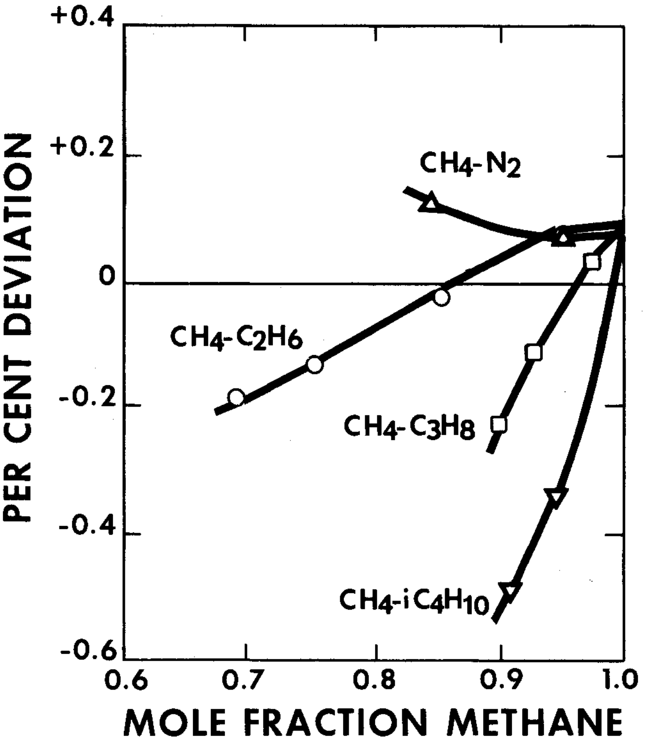

Fig. 1. Percent deviation of Klosek-McKinley correlation from experimental molar volumes for methane-rich binary mixtures at 100 K. (△, ○, □, and ▽—this work).

mole fraction calculated as $x_2 + 2x_3 + 2.4x_4$. The v^E_{1-N} term accounts for nonideal behavior due to nitrogen-hydrocarbon interactions. As a first approximation it may be taken equal to the CH_4—N_2 excess volume at the same nitrogen mole fraction as in the actual mixture. As an aid in applying these notions Figures 4 and 5 were prepared. These graphs present smoothed values of excess volume as a function of temperature and composition for CH_4—C_2H_6 and CH_4—N_2.

The predictions of the Klosek-McKinley correlation and predictions of Equation 4 are compared with the ternary mixture data in Table 11. The Klosek-McKinley correlation predictions are within ±0.2% of experiment, except for the mixtures containing nitrogen at the higher temperatures (108 and 115 K). Predictions from Equation 4 are within ±0.1% of all binary and ternary results reported here. The accuracy of these ternary predictions confirms that excess volumes for methane-rich multicomponent LNG mixtures can be closely estimated by summing the binary excess volumes for each minor component in methane.

For this correlation to be highly useful it should work at temperatures somewhat higher than those of the present study, and mixtures containing other higher hydrocarbons (in particular *n*-butane) must be incorporated by modification of the definition for the equivalent ethane mole fraction. Data is not now available for binary mixtures at higher temperatures or containing low concentrations of other hydrocarbons with methane. By its very nature the correlation must fail when the concentrations of minor

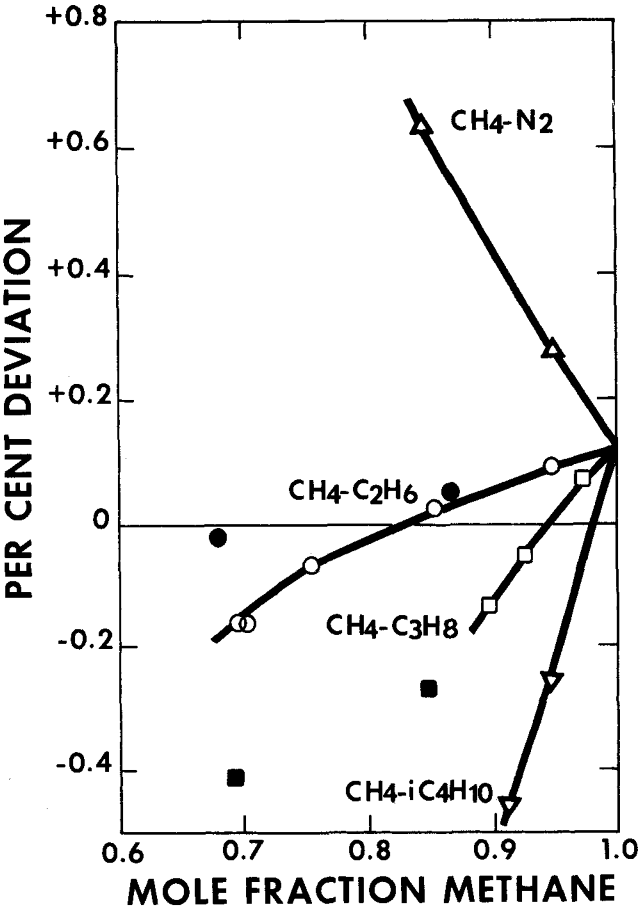

Fig. 3. Percent deviation of Klosek-McKinley correlation from experimental molar volumes for methane-rich binary mixtures at 115 K. (△, ○, □ and ▽—this work).

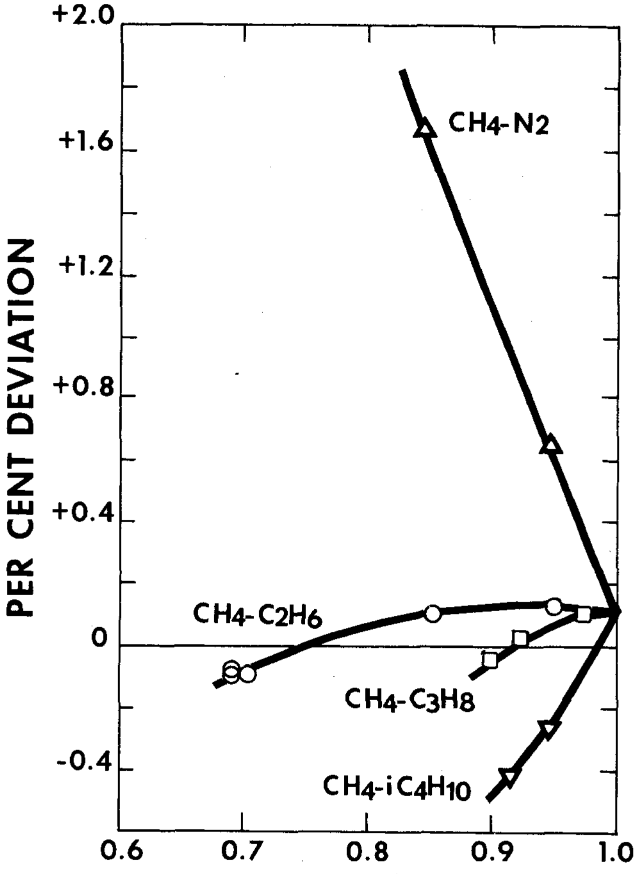

Fig. 2. Percent deviation of Klosek-McKinley correlation from experimental molar volumes for methane-rich binary mixtures at 108 K. [△, ○, □ and ▽—this work; ● and ■—Shana'a and Canfield (1968)]

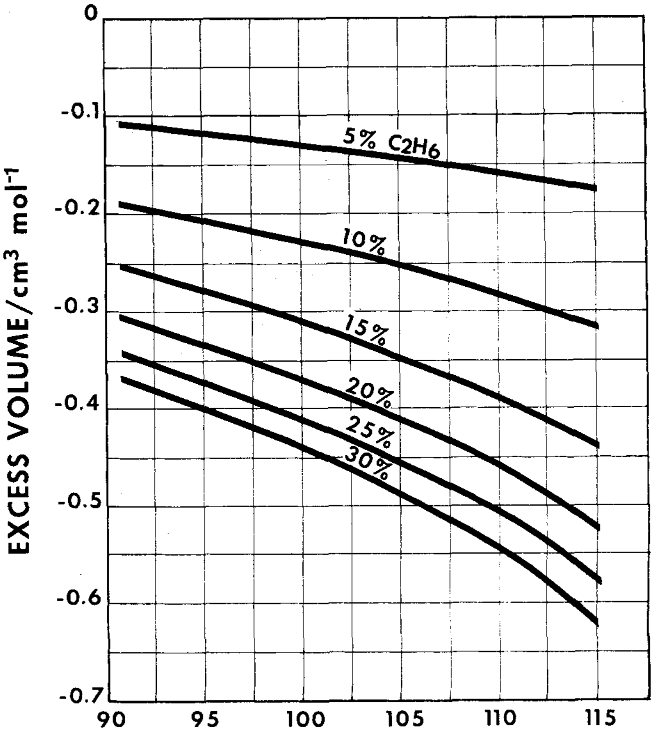

Fig. 4. Smoothed curves of excess volume as a function of temperature and composition for methane-rich CH_4—C_2H_6 mixtures.

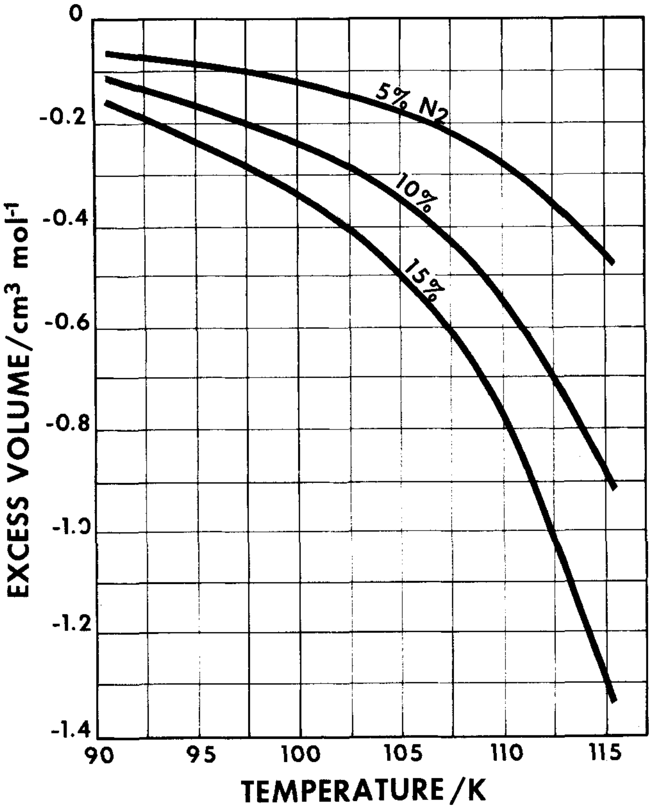

Fig. 5. Smoothed curves of excess volume as a function of temperature and composition for methane-rich CH_4—N_2 mixtures.

TABLE 11. COMPARISON OF THE EXPERIMENTAL MOLAR VOLUMES FOR THE TERNARY SYSTEMS WITH THOSE FROM THE KLOSEK-MCKINLEY CORRELATION AND THOSE CALCULATED BY EQUATION (4)

Mixture	x_1	x_2	x_3	x_N
1	0.8466	0.1025	0.0509	
2	0.8409	0.1086		0.0505
3	0.9055		0.0497	0.0447

Mixture	T/K	Experimental v/cm^3 mol^{-1}	Klosek-McKinley v/cm^3 mol^{-1}	Equation 4 v/cm^3 mol^{-1}
1	100.01	38.49	38.43	38.50
	108.01	39.32	39.29	39.34
	108.02	39.33	39.29	39.34
	115.00	40.10	40.09	40.09
2	91.00	36.56	—	36.58
	100.00	37.50	37.56	37.52
	108.00	38.40	38.56	38.43
	115.01	39.26	39.57	39.29
3	91.00	36.67	—	36.69
	108.00	38.55	38.66	38.54

components become large enough that interactions between them make large contributions to the excess volume. As a rough guide, the equivalent ethane concentration plus the nitrogen concentration should not exceed about 30 mole %.

ACKNOWLEDGMENT

Financial support for this investigation was provided by The American Gas Association, Incorporated, Arlington, Virginia.

NOTATION

C = molar volume reduction factor defined by Equation (2)
P = pressure
P^s = saturation pressure of the mixture
T = temperature
v = molar volume
v_i = molar volume of pure component i
v^E = molar excess volume at the mixture saturation pressure
$v^E{}_{1-N}$ = methane-nitrogen excess volume
$v^E{}_{1-2}$ = methane-ethane excess volume
x_i = mole fraction of component i
x_N = mole fraction of nitrogen
x_1 = mole fraction of methane
x_2 = mole fraction of ethane
x_3 = mole fraction of propane
x_4 = mole fraction of isobutane

LITERATURE CITED

Boyle, G. J., and D. Reece, "How to Calculate Density of LNG at Cryogenic Temperatures," *Oil Gas J.*, **69** (3), 56 (1971).

Chui, C. -H., and F. B. Canfield, "Liquid Density and Excess Properties of Argon + Krypton and Krypton + Xenon Binary Liquid Mixtures and Liquid Density of Ethane," *Trans. Faraday Soc.*, **67**, 2933 (1971).

Cines, M. R., J. T. Roach, R. J. Hogan, and C. H. Rowland, "Nitrogen-Methane Vapor-Liquid Equilibria," *Chem. Eng. Progr. Symp. Ser. No. 49*, 1 (1953).

Francis, A. W., "Pressure-Temperature-Liquid Density Relations of Pure Hydrocarbons," *Ind. Eng. Chem.*, **49**, 1779 (1957).

Fuks, S., and A. Bellemans, "Excess Free Energies and Volumes of Two Simple Binary Liquid Mixtures—Methane-Krypton and Nitrogen-Methane," *Bull. Soc. Chim. Belg.*, **76**, 290 (1967).

Goodwin, R. D., and R. Prydz, "Densities of Compressed Liquid Methane and the Equation of State," *J. Res. Nat. Bur. Stand.* (U.S.), **76A** (Phys. and Chem.) 81 (1972).

Klosek, J., and C. McKinley, "Densities of Liquefied Natural Gas and of Low Molecular Weight Hydrocarbons," *Proc. First Intern. Conf. on LNG*, Chicago (1968).

Liu, Y.-P., and R. C. Miller, "Temperature Dependence of Excess Volumes for Simple Liquid Mixtures: Ar + CH_4, N_2 + CH_4," *J. Chem. Thermodynam.*, **4**, 85 (1972).

Massengill, D. R., and R. C. Miller, "Temperature Dependence of Excess Volumes for Simple Liquid Mixtures: N_2 + Ar, N_2 + Ar + CH_4," *ibid.*, **5**, 207 (1973).

Miller, R. C., "Experimental Liquid Mixture Densities for Testing and Improving Correlations for LNG," Ann. Report to Am. Gas Assoc. Inc., Arlington, Va., A.G.A. Project BR-76-1 (1972).

Miller, R. C., A. J. Kidnay, and M. J. Hiza, "Liquid-Vapor Equilibria at 112.00 K for Systems Containing Nitrogen, Argon, and Methane," *AIChE J.*, **19**, 145 (1973).

Renon, H., C. A. Eckert, and J. M. Prausnitz, "Molecular Thermodynamics of Simple Liquids," *Ind. Eng. Chem. Fundamentals*, **6**, 52 (1967).

Rowlinson, J. S., *Liquids and Liquid Mixtures*, 2nd Edit., Plenum Press, New York (1969).

Shana'a, M. Y., and F. B. Canfield, "Liquid Density and Excess Volume of Light Hydrocarbon Mixtures at −165°C," *Trans. Faraday Soc.*, **64**, 2281 (1968).

Sprow, F. B., and J. M. Prausnitz, "Vapor-Liquid Equilibria for Five Cyrogenic Mixtures," *AIChE J.*, **12**, 780 (1966).

Stoeckli, H. F., and L. A. K. Staveley, "The Excess Gibbs Function and the Volumes of Mixing for the System Methane + Propane at 90.68 K," *Helv. Chim. Acta*, **53**, 1961 (1970).

Street, W. B., and L. A. K. Staveley, "The *P-V-T* Behavior of Liquid Nitrogen at Temperatures from 77° to 120°K and Pressure to 680 Atmospheres," *Adv. Cryo. Engr.*, **13**, 363 (1968).

Manuscript received October 10, 1972; revision received and accepted January 30, 1973.