

Part I

The Liquid Phase Volumetric Behavior of The Helium-Methane System

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Experimental liquid phase volumetric data for the helium-methane system are presented. The density of pure liquid methane was determined at various temperatures and pressures. Good agreement is noted between the results of this study and previously published data for the density of the saturated liquid. Experimental values in the compressed liquid region agree well with predictions from the principle of corresponding states. The partial molal volumes of helium and methane were obtained from density measurements of liquid helium-methane mixtures. Smoothed values of solution molal volume are presented for each temperature at intervals of 200 p.s.i. and 0.01 mole ratio. The accuracy of the data is estimated to be $\pm 1\%$. At high temperatures, the partial molal volume of helium is a function of temperature, pressure, and concentration. Experimental partial molal volumes were compared to values calculated from the phase data by the Krichevsky-Kasarnovsky equation. The calculated values showed only qualitative agreement with experimental values.

VOLUMETRIC DATA for liquid solutions are necessary for calculating thermodynamic and transport properties of the solutions from phase equilibria data. The helium-methane system is of current interest, but volumetric data for this system have not been reported in the literature.

The liquid phase partial molal volumes of helium and methane were obtained from density measurements of pure methane and methane-helium mixtures. The experimental method used consists essentially of metering a known quantity of gas into a cell of known volume under constant temperature conditions and observing the resultant pressure in the cell.

Figure 1 illustrates the various steps involved. The solubility of helium in liquid methane as a function of temperature and pressure has been determined previously (?) and is plotted on a P - X chart (A). First, a desired liquid concentration is selected, such as (n). The cell, in the low temperature bath, is brought to the highest temperature to be investigated (T_3). Since the cell volume and the density of pure methane are known, the approximate quantity of helium required is calculated. This amount is metered into the cell. The cell is then closed off, the metering system evacuated and filled with methane at the highest pressure to be reached (p).

Methane is metered into the cell in steps, and the cell contents are agitated between the addition of each increment. The cell pressure is plotted as a function of the volume of methane injected (B). As the cell fills with liquid, the pressure increases slowly (line hj). At point j , the cell is just filled with liquid at its bubble-point pressure. Thereafter, (line jk), the cell liquid is compressed.

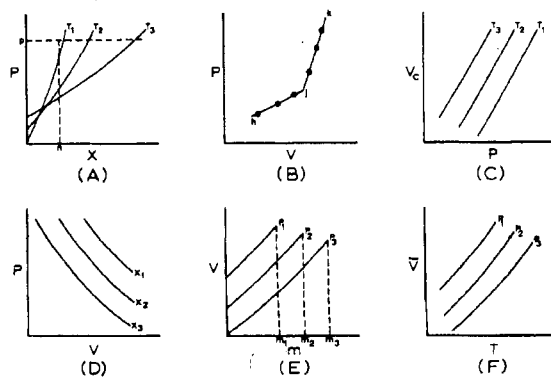


Figure 1. Experimental method

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In (B) the volume plotted is that volume of gas metered which is actually inside the cell. It is necessary to calibrate out the amount of material passing through the metering valve which does not reach the cell—i.e., the amount contained in the line from the metering valve to the cell inlet. The calibration is accomplished in the form of a volume correction, which is subtracted from the injection pump reading, as a function of the cell temperature and pressure (C). The volumes plotted in (B) are, therefore, the actual volume injected by the pump minus the correction volume determined from (C).

Eventually a series of graphs (B) are obtained at a number of concentrations for each isotherm. By using the data along line *jk* in (B), the helium concentration, moles of helium per cc., and the solution molal volume, cc. of solution per mole of methane, can be computed from the quantities of gas metered into the cell and the cell volume. The results for a given isotherm will be a series of lines showing the relationship between pressure and molal volume at fixed helium concentrations (D).

By using the smoothed data in (D) to interpolate for even values of pressure and to compute the mole ratio (m = moles of helium per mole of methane), a plot of solution molal specific volume vs. mole ratio may be obtained (E). The partial molal volume of helium in liquid methane is obtained from this plot as the slope of the line at the point of interest. This follows from the definition of the partial molal volumes:

$$\bar{V} = \left(\frac{\partial V}{\partial n_1} \right)_{T,P,n_2} \quad (1)$$

The partial molal volume of methane can be determined by a completely analogous procedure. Where it is impossible to ascertain the bubble point owing to lack of a definite break in the P - V curve (B), the volume curves (E) are simply extrapolated to the values (m_1, m_2, m_3) determined from the previously measured equilibrium phase concentrations.

The slopes of the lines at their end points represent the partial molal volume of helium in a liquid methane-helium mixture that is in equilibrium with its own vapor. These values can be summarized in a single graph (F) as functions of both temperature and pressure. In this diagram, concentration is implicit, being that of the bubble point mixture at a given temperature and pressure.

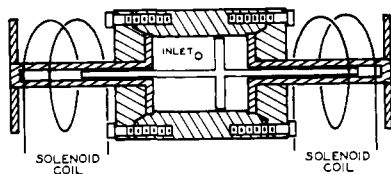


Figure 2. Density cell

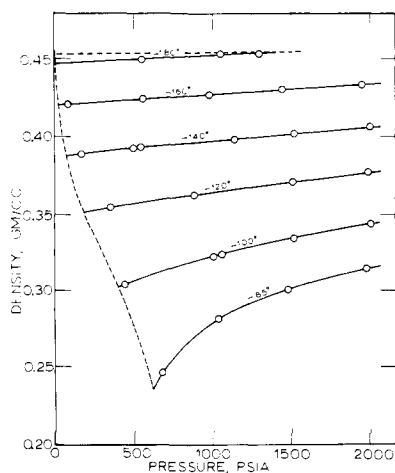


Figure 3. Density of liquid methane

EXPERIMENTAL

The experimental cell used for liquid density measurements is shown in Figure 2. This cell was designed to give efficient mixing of the liquid, either with or without a small amount of gas present. The inlet is in the side of the cell as shown. This allows the helium-rich gas phase to be trapped at the top of the cell as pure methane is metered in and fills the cell. As the plunger moves rapidly back and forth under the influence of the solenoid coils, the entire quantity of liquid is forced at high velocity through the small clearance between the plunger and cell wall.

The internal volume of the cell (approximately 15 cc.) was determined at room temperature and then corrected for the thermal contraction at experimental temperatures.

A positive displacement piston pump, calibrated in increments of 0.01 cc., was used for metering gas into the cell. Pressures were measured with bourdon tube gages which were calibrated against a dead-weight tester and are accurate to ± 1.5 p.s.i. Temperatures were measured to within $\pm 0.02^\circ$ C. with a platinum resistance thermometer.

The heat transfer medium in the low temperature bath containing the experimental cell was air, circulated at high velocity. Complete details of the equipment and operating procedures are available elsewhere (6).

A special, analyzed helium stock, containing less than 12 p.p.m. of impurities, was furnished by the Bureau of Mines. The methane was "pure grade," 99 mole % minimum purity, furnished by Phillips Petroleum Company. The actual analyses of these gases is given in Table I.

In calculating the mass of material metered into the cell, the compressibility factors for helium and methane were obtained from Stroud, Miller, and Brandt (8) and API 44 (1), respectively.

EXPERIMENTAL RESULTS

The density of pure methane was measured initially. In Figure 3, the original data points are plotted, showing the density of liquid methane as a function of pressure along each of the isotherms studied. The dashed line defining the low pressure limit represents the measured methane vapor pressure curve. Methane does not exist as a liquid to the left of this line. The dashed line defining the limit at high densities represents

Table I. Purity of Materials

Helium Analysis	
Contaminant	Concn., P.P.M.
Water	0.4
Neon	8.2
Nitrogen	2.8
Oxygen	0.5
Carbon dioxide	0.1
	12.0
Methane Analysis	
Component	Concn., Mole %
Methane	99.13
Nitrogen	0.56
Carbon dioxide	0.16
Ethane	0.12
Propane	0.02
Helium	0.01
	100.00

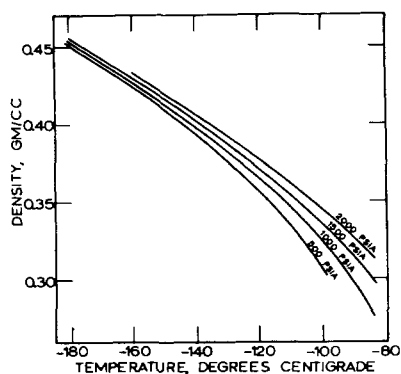


Figure 4. Density of liquid methane

the methane freezing point curve as reported by Clusius and Weigand (2). At -180°C . the reported freezing pressure is 1414 p.s.i.a. Although it was not possible to observe a distinct freezing point with the techniques used in this work, the presence of solid methane was indicated by an anomalously large quantity of methane required to bring the cell pressure up to 2000 p.s.i.a.

Figure 4, describing the isobaric change of density with temperature, was obtained by interpolating the data in Figure 3 at even pressures.

Methane density data have been reported in the literature for the saturated liquid, but not in the compressed liquid region. Thodos and Matscke (9) utilized the available data for both gaseous and liquid states to obtain a reduced density correlation as a function of reduced temperature and pressure. In the compressed liquid region, a corresponding-states approach was used to calculate the density of methane from data for the density of compressed liquid nitrogen. Their results, for the region covered in this study, are reproduced in Figure 5. The solid line represents the saturated liquid locus, based on experimental values reported in the literature. In the compressed liquid region, the lines are broken to indicate that they were obtained by calculation from liquid nitrogen data. The experimental points shown were obtained from Figure 3 by interpolation at the required pressures.

Very good agreement is evident between the results of this study and the values predicted by Thodos and Matscke. The average deviation of the points from the lines in Figure 5 is on the order of 0.5%. This is comparable with the lowest average deviation reported by the authors for any one set of the experimental data used to form the correlation.

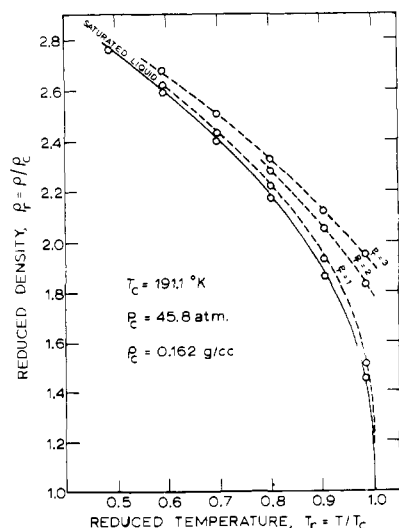


Figure 5. Reduced density correlation

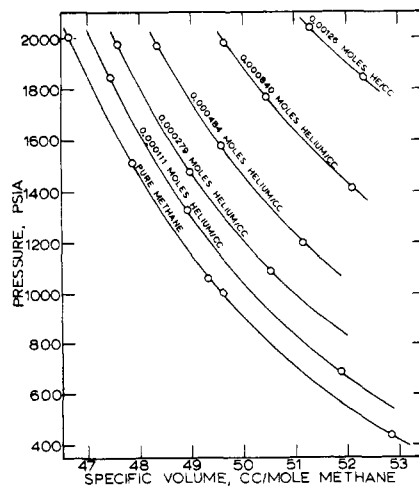


Figure 6. Specific volume at -100°C .

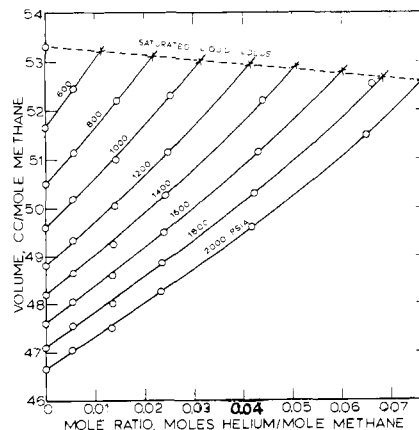


Figure 7. Solution volume at -100°C .

After the density of pure methane was determined, runs were made with a number of mixtures of different helium concentrations. For purposes of illustration, the original data points at -100°C . have been plotted in Figure 6, which corresponds to step (D) in Figure 1. Interpolating the data of Figure 6 and converting the concentration units yields Figure 7, corresponding to step (E) in Figure 1. Again, in Figure 7 the data points are shown to illustrate the amount of scatter present and the degree of extrapolation necessary to obtain the bubble point volumes. The X marks indicate the end points of the volume lines as calculated from the vapor-liquid concentration data (cf. points at m_1, m_2, m_3 , Figure 1).

Only the smoothed lines are presented for the other temperatures in Figures 8, 9, 10, and 11. Numerical values for the smoothed data are listed in Table II.

The slopes of the lines in Figures 7 through 11 represent the partial molal volume of helium in liquid methane at constant temperature and pressure. At -85°C . and -100°C ., the partial volume is a function of the concentration of helium in the liquid. At the lower temperatures, where the maximum concentration of helium is very small, the partial volume, within the precision of the experimental data, is independent of concentration. Figure 12 summarizes the bubble-point partial volumes, corresponding to step (F) in Figure 1. At low temperatures, the partial volume converges toward the molal volume of pure liquid helium. As the temperature increases toward the critical temperature of the mixture, the partial volume approaches the molal volume of pure helium gas at the same temperature and pressure. Numerical data are given in Table III, along with the corresponding values for the partial molal volume of methane. Because of the very small range of helium concentration found in the system, the partial molal volume of methane is at all times equal to the molal volume of pure methane within the experimental error.

ACCURACY OF DATA

Volumetric density measurements are subject to several sources of error. Data which must be known are: volume of the cell, temperature and pressure in the cell, temperature, pressure, volume, and compressibility of helium and methane injected, and the quantity of methane remaining in the line (line correction). An error analysis of the above factors yielded a probable upper limit of 1% error in the raw density values. An additional factor, which is not easily evaluated, is the necessity of performing a smoothing and interpolating operation upon the raw data before obtaining values of density as a function of composition. However, the above estimate of maximum error appears

Table II. Smoothed Volumetric Data

Pressure, P.S.I.A.	Mole Ratio He/CH ₄	Volume, Cc./Mole CH ₄	Mole Ratio, He/CH ₄	Volume, Cc./Mole CH ₄	Pressure, P.S.I.A.	Mole Ratio He/CH ₄	Volume, Cc./Mole CH ₄	Mole Ratio, He/CH ₄	Volume, Cc./Mole CH ₄
Temperature = -85°C.					Temperature = -120°C.				
620	0	70.0			800	0	44.33	0.01	44.95
800	0	61.3	0.01	65.0		0.0163	45.33		
	0.02	68.7	0.0230	69.8	1000	0	44.00	0.01	44.56
1000	0	57.5	0.01	59.8		0.02	45.13	0.0216	45.22
	0.02	62.4	0.03	65.0	1200	0	43.69	0.01	44.24
	0.04	67.7	0.0475	69.7		0.02	44.77	0.0262	45.11
1200	0	55.4	0.01	57.2	1400	0	43.38	0.01	43.91
	0.02	59.2	0.03	61.3		0.02	44.44	0.03	44.96
	0.04	63.4	0.05	65.6		0.0308	45.01		
	0.06	67.6	0.0690	69.6	1600	0	43.09	0.01	43.61
1400	0	53.8	0.01	55.2		0.02	44.14	0.03	44.66
	0.02	56.7	0.03	58.4		0.0349	44.92		
	0.04	60.2	0.05	62.0	1800	0	42.82	0.01	43.34
	0.06	63.8	0.07	65.5		0.02	43.86	0.03	44.38
	0.08	67.3	0.0920	69.6		0.0385	44.83		
1600	0	52.6	0.01	53.7	2000	0	42.55	0.01	43.04
	0.02	54.9	0.03	56.2		0.02	43.55	0.03	44.06
	0.04	57.6	0.05	59.2		0.04	44.56	0.0430	44.72
	0.06	60.8	0.07	62.6	Temperature = -140° C.				
	0.08	64.2	0.09	66.0	66	0	41.33		
	0.10	67.6	0.1110	69.5	200	0	41.17	0.0018	41.25
1800	0	51.6	0.01	52.5	400	0	40.95	0.0044	41.14
	0.02	53.5	0.03	54.6	600	0	40.75	0.0068	41.02
	0.04	55.9	0.05	57.3	800	0	40.56	0.0093	40.92
	0.06	58.8	0.07	60.3	1000	0	40.38	0.0100	40.76
	0.08	61.9	0.09	63.4		0.0116	40.82		
	0.10	65.0	0.11	66.6	1200	0	40.20	0.0100	40.57
	0.12	68.2	0.129	69.4		0.0139	40.71		
2000	0	50.8	0.01	51.6	1400	0	40.03	0.0100	40.40
	0.02	52.6	0.03	53.6		0.0161	40.62		
	0.04	54.7	0.05	55.9	1600	0	39.86	0.0100	40.21
	0.06	57.1	0.07	58.4		0.0186	40.50		
	0.08	59.8	0.09	61.2	1800	0	39.69	0.0100	40.05
	0.10	62.6	0.11	64.0		0.0200	40.42	0.0202	40.43
	0.12	65.5	0.13	66.9	2000	0	39.52	0.0100	39.89
	0.14	68.3	0.1490	69.4		0.0200	40.25	0.0224	40.33
Temperature = -100°C.					Temperature = -160° C.				
385	0	53.30			Pressure, P.S.I.A.	Mole Ratio, He/CH ₄	Volume, Cc./Mole CH ₄		
600	0	51.65	0.01	53.00	Temperature = -180° C.				
	0.0115	53.20			3	0	35.82		
800	0	50.50	0.01	51.65	200	0	35.74		
	0.02	52.85	0.0220	53.10	400	0	35.67		
1000	0	49.60	0.01	50.60	600	0	35.59		
	0.02	51.70	0.03	52.80	800	0	35.51		
	0.0315	53.00			1000	0	35.43		
1200	0	48.80	0.01	49.70	1200	0	35.36		
	0.02	50.70	0.03	51.70	1400	0	35.28		
	0.04	52.75	0.0415	52.90					
1400	0	48.20	0.01	49.00					
	0.02	49.85	0.03	50.80					
	0.04	51.75	0.05	52.80					
	0.0505	52.85							
1600	0	47.60	0.01	48.35					
	0.02	49.15	0.03	50.00					
	0.04	50.85	0.05	51.75					
	0.0600	52.75							
1800	0	47.10	0.01	47.80					
	0.02	48.55	0.03	49.30					
	0.04	50.10	0.05	50.95					
	0.06	51.80	0.0685	52.65					
2000	0	46.65	0.01	47.30					
	0.02	48.00	0.03	48.75					
	0.04	49.45	0.05	50.20					
	0.06	51.05	0.07	51.95					
	0.0765	52.60							
Temperature = -120° C.									
180	0	45.70							
400	0	45.08	0.0060	45.55					
600	0	44.68	0.01	45.37					
	0.0111	45.45							

reasonable in view of the deviations noted in Figure 5 for the density of pure methane.

Porter (5) obtained a few points for the density of saturated liquid methane-helium mixtures. Saturated liquid densities were determined for a number of temperatures at approximately 1000 p.s.i.a. Porter's data points deviate from the smoothed values of this study by less than 1%.

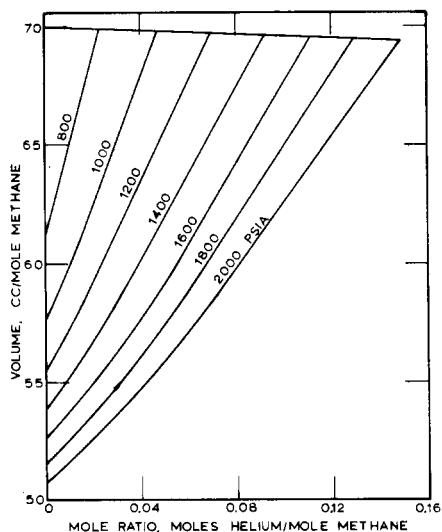


Figure 8. Solution volume at -85°C .

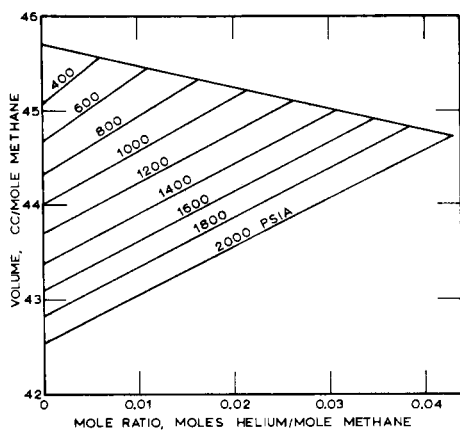


Figure 9. Solution volume at -120°C .

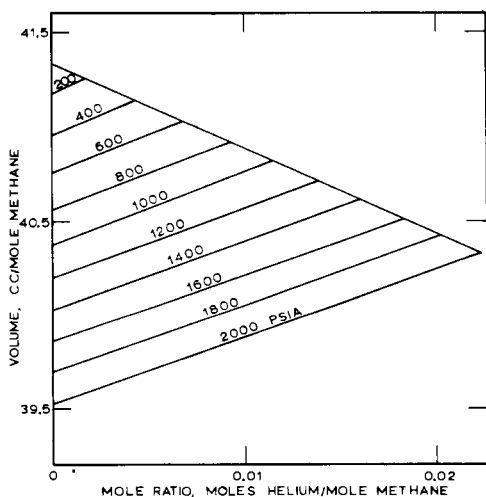


Figure 10. Solution volume at -140°C .

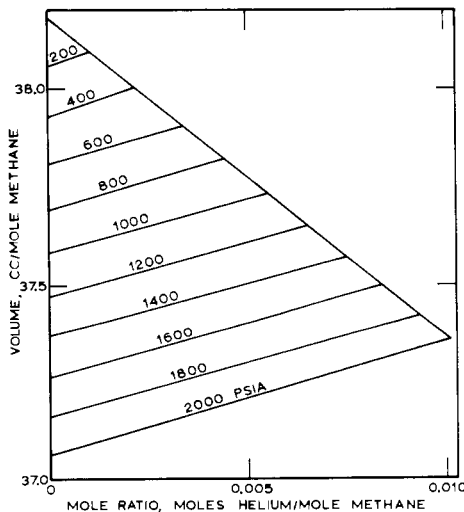


Figure 11. Solution volume at -160°C .

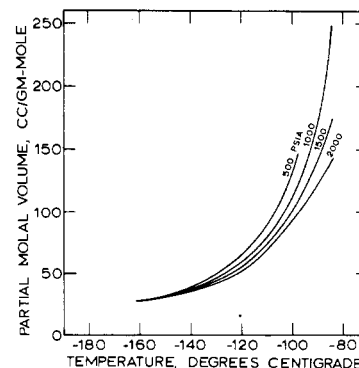


Figure 12. Partial molal volume of helium in liquid methane

Table III. Bubble-Point Partial Molal Volumes of Helium and Methane

Temp. $^{\circ}\text{C}$.	Pressure, P.S.I.A.	Helium Partial Volume, Cc./Gram-Mole	Methane Partial Volume, Cc./Gram-Mole
-160	500	28	37.9
	1000	28	37.6
	1500	28	37.3
	2000	28	37.1
-140	500	40	40.8
	1000	38	40.4
	1500	37	39.9
	2000	36	39.6
-120	500	65	44.9
	1000	56	44.0
	1500	52	43.2
	2000	50	42.6
-100	500	134	52.5
	1000	113	49.5
	1500	102	47.8
	2000	94	47.0
-85	1000	240	57.5
	1500	168	52.6
	2000	140	49.8

Table IV. Scatter of Volumetric Data

Temperature, $^{\circ}\text{C}$.	-85	-100	-120	-140	-160
Figure number	8	7	9	10	11
Standard deviation, Cc./mole	0.27	0.060	0.074	0.061	0.055
Standard deviation % of mean value	0.45	0.12	0.17	0.15	0.15
Standard deviation, % of isobaric range	1.4	1.0	3.4	9.1	18.3
90% confidence interval for partial molal volume, \pm Cc./mole	5.1	1.8	3.2	5.3	10.2

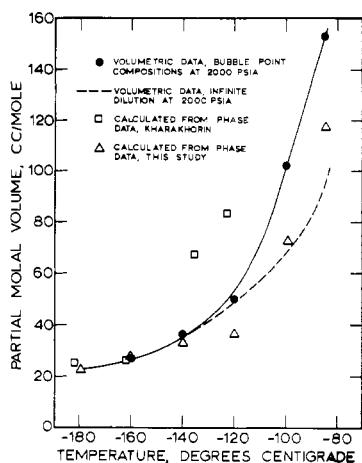


Figure 13. Partial molal volume of helium in liquid methane

scatter at one temperature relative to that at another temperature. The molar volume (density) data at the four lower temperatures would all be considered equally reliable.

The situation differs, however, in regard to the partial molal volume. Because of the lower solubility of helium at lower temperatures, the volumetric data extend over a much shorter range of concentration. The partial molal volume depends upon the slope of the volume *vs.* concentration relationship. Obviously, the accuracy with which the slope of a line can be determined decreases with closer spacing of the points along the abscissa, even though the relative scatter in the ordinate values remains the same. An intuitive approach to allow for this fact is to express the scatter (standard deviation) as a per cent of the total change in volume occurring along an isobaric line. The result, listed in Table IV, indicates a strong decrease in reliability for the partial molal volume of helium as temperature decreases.

Another approach is possible through statistical methods. Table IV shows the results of calculating 90% confidence intervals for the slopes of straight lines through data exhibiting the given standard deviations about the lines. Again, a great decrease in reliability of the partial volume with decreasing temperature is indicated.

COMPARISON OF EXPERIMENTAL WITH CALCULATED PARTIAL MOLAL VOLUME

Kharakhorin (3) reported calculated values of the partial molal volume of helium in liquid methane which were obtained by means of the Krichevsky-Kazarnovsky equation (4):

$$\text{Log } (f/x)_1 = \text{Log } K + \bar{V}_1(P - P_2^0)/(2.3RT) \quad (2)$$

The latest vapor-liquid equilibrium data for the helium-methane system were also correlated by means of Equation 2. Calculated partial volumes from these two sources (3, 7) are compared with the experimental values in Figure 13. The solid line, based on the circled data points, represents the experi-

mental partial molal volumes at the bubble-point compositions. The dotted line represents the partial molal volumes at the same temperatures and pressures, but at infinite dilution of helium. Only qualitative agreement is evident, as the deviations increase with temperature.

NOMENCLATURE

- f = fugacity
- K = Henry's law constant
- n = moles
- P = pressure
- R = perfect gas law constant
- T = temperature
- V = volume
- \bar{V} = partial molal volume
- x = mole fraction

Subscripts

- 1 = component 1, lighter component
- 2 = component 2, heavier component

Superscripts

- 0 = pure component value

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