Volumetric Behavior of the Methane–Hydrogen Sulfide System at Low Temperatures and High Pressures

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Hydrogen sulfide is extensively found as a component of natural gas and various refinery gases. In natural gas wells, its concentration runs occasionally as high as 30% (*1*). Because even small amounts of hydrogen sulfide in natural gases are objectionable because of odor, toxicity, and corrosiveness, it is desirable to study the phase and volumetric properties of hydrogen sulfide–hydrocarbon systems. The most obvious starting point is the extension of present phase and volumetric data of the methane–hydrogen sulfide system down to the temperature range at which solid phases form.

The present paper deals with the volumetric behavior of mixtures of methane and hydrogen sulfide at temperatures from −118° to 220°F. The data are part of a study including both the volumetric and phase behavior of the methane–hydrogen sulfide system.

PREVIOUS EXPERIMENTAL WORK

The volumetric behavior of methane has been studied by a number of investigators (*2, 5–7*), where the molal volume of methane as a function of temperature and pressure is presented with a probable error of less than 0.15%. The volumetric properties of hydrogen sulfide have been reported by several investigators (*8, 12*). Reamer, Sage, and Lacey (*8*) present data above 40°F., while West (*12*) presents data down to the atmospheric boiling point of hydrogen sulfide. These data are believed to be adequate for an accurate evaluation of the properties of the pure components.

Reamer, Sage, and Lacey (*9*) have studied the methane–hydrogen sulfide system employing a modified mercury displacement dew-point bubble-point apparatus. The composition of the dew point gas was determined by direct analytical methods. They studied the phase and volumetric behavior of five mixtures of these two components at temperatures ranging from 40° to 340°F. and pressures from 200 to 10,000 p.s.i.a. Their data were used as a check on the results of this study in the temperature and pressure ranges common to both investigations.

APPARATUS AND PROCEDURE

The equipment and methods used have been described in detail (*4*).

Briefly, the procedure involves the introduction of known increments of homogeneous gas mixture into a glass equilibrium cell maintained at a fixed temperature. As the pressure is raised, the mixture successively passes through the dew point and the bubble point. All phase changes are visually observed. The attainment of equilibrium is facilitated by agitating the mixture with a magnetically actuated steel ball.

The pressure was established by using a 16-inch dial Heise Bourdon tube gage having a range of 0 to 2000 p.s.i. and graduated at intervals of 5 p.s.i. The pressure gage was calibrated against a dead weight gage tester several times during the investigation. It is believed that the pressure measurements are accurate within ±2 p.s.i. over the entire pressure range.

Temperatures were determined using a platinum resistance thermometer which was calibrated against a National Bureau of Standards platinum resistance thermometer. The calibration of the thermometer was accurate within 0.04°F. relative to the international platinum scale. The temperature of the equilibrium cell was controlled within ±0.1°F.

The gas mixtures were analyzed by vapor density measurements. The molecular weights of carefully prepared known mixtures of methane and hydrogen sulfide were determined and used to prepare a calibration curve of composition vs. molecular weight. The maximum uncertainty of the composition of the five mixtures is believed to be less than ±0.005 mole fraction.

The gas mixtures were injected into the glass equilibrium cell by means of a 100-ml. stainless steel positive displacement pump graduated in 0.01-ml. increments. The temperature of the pump was controlled within ±1°F.

MATERIALS

The hydrogen sulfide used in this study was obtained in 9-pound net cylinders from the Matheson Co., Joliet, Ill., and was stated to be 99.9% pure. The vapor from the cylinder was passed under pressure through a drying tube containing activated alumina and then through a tube containing activated charcoal. Several isotherms were determined on this gas, and the vapor pressures were determined up to the critical point. Examination of the isotherms indicated that a pressure change of 4 p.s.i. changed the quality of the gas from 0.10 to 0.90. The vapor pressures agreed with the data given in the International Critical Tables within 4 p.s.i.a.

The "pure grade" methane was donated by the Phillips Petroleum Co. It was stated to have 99% minimum purity, the impurities being ethane, nitrogen, and carbon dioxide. The methane from the cylinder was passed under high pressure through a drying tube containing activated alumina and then through a stainless steel bomb containing activated charcoal. The bomb was maintained at −40°F. in a bath of dry ice and acetone. The molecular weight of this gas by gas density measurement was 16.13. An isotherm determined on the gas at −183.82°F. indicated that the quality of the vapor was increased from 0.10 to 0.90 by a pressure increase of 5 p.s.i.a. The vapor pressure data agreed with that of the International Critical Tables within 4 p.s.i.

EXPERIMENTAL RESULTS

The experimental volumetric data for the five mixtures of methane and hydrogen sulfide are presented in Figures 1 to 5. The data are presented as compressibility factors. The compressibility factors generally scatter more at the low pressures, where the percentage error in the pressure reading and the incremental volume delivered to the cell was greater. These errors were minimized by extrapolating the accurate portion of the compressibility curve to $Z = 1$ at zero pressure. The accuracy of the volumetric data at temperatures above the cricondentherm temperatures of the mixtures is better than ±0.4%. The accuracy is good in this region because the volumetric data were obtained by iso-

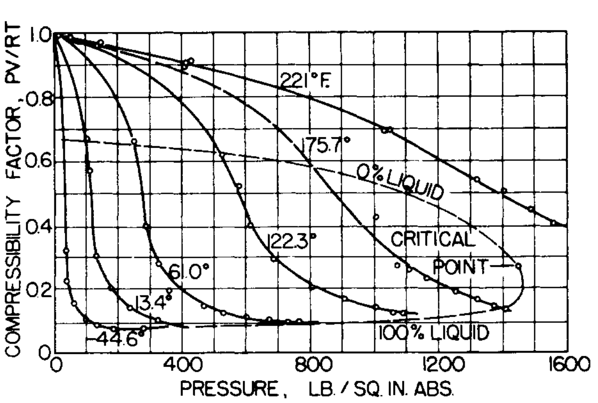

Figure 1. Volumetric behavior of 93.3 mole % hydrogen sulfide

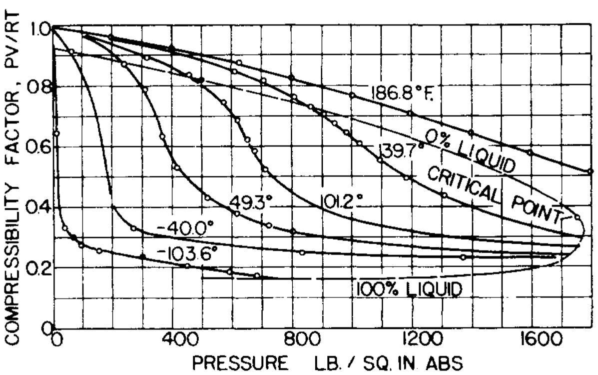

Figure 2. Volumetric behavior of 77.1 mole % hydrogen sulfide

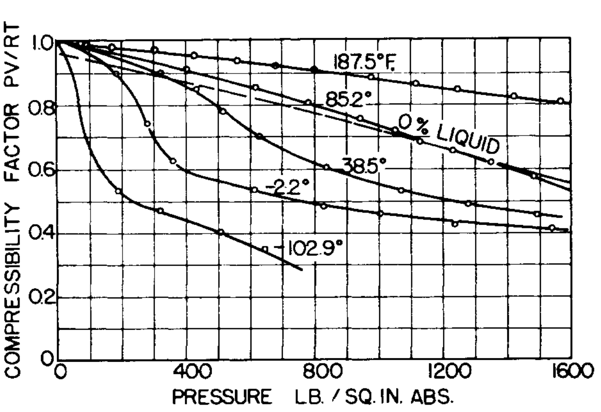

Figure 3. Volumetric behavior of 45.8 mole % hydrogen sulfide

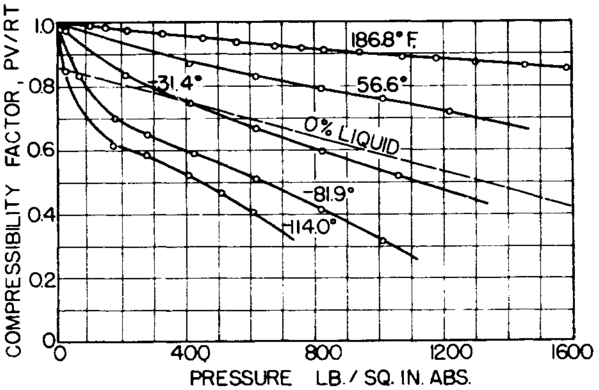

Figure 4. Volumetric behavior of 24.8 mole % hydrogen sulfide

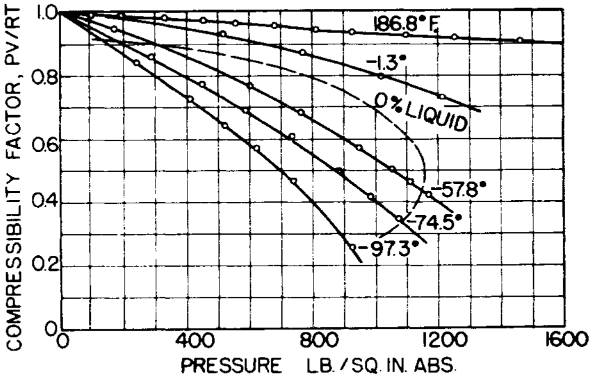

Figure 5. Volumetric behavior of 11.01 mole % hydrogen sulfide

thermal compression of the mixtures in the displacement pump without use of the equilibrium cells. At the lower temperatures where the mixtures were in the heterogeneous state, it was necessary to use the equilibrium cell. In this case additional errors were introduced because of the small incremental quantities of gas metered to the cell. The capacity of the cell was definitely limited by the pressure requirement. The lack of precise knowledge of the temperature of the neck of the equilibrium cell and of the steel tubing connecting the equilibrium cell with the displacement pump contributed to the loss in accuracy. The volumes in the neck of the equilibrium cell and in the interconnecting tubing were made as small as possible, but a residual effect on the accuracy remained. The average accuracy of the volumetric data in the two-phase region is believed to be better than ±3%.

The mean compressibility factors for the five mixtures studied were compared with the generalized compressibility factor chart. At a pseudo-reduced temperature of 1.2 or greater, the mean compressibility factors agreed with those of the generalized chart within 5% up to a pseudo-reduced pressure of 1.7. At a pseudo-reduced temperature of 1.1 the data agree within 5% with the data of Standing and Katz (*11*) when pseudo-reduced pressures are less than 1.2. At lower values of pseudo-reduced temperatures, the deviation of the mean compressibility factor from the generalized chart is somewhat greater. Therefore, for values of pseudo-reduced temperature of 1.1 or less, the compressibility factor charts for the individual mixtures presented in Figures 1 to 5 are recommended.

The molal volumes of the superheated mixtures are compared with those of Reamer, Sage, and Lacey (9) in Figure 6. The molal volume is plotted against mole per cent methane at lines of constant temperature and pressure. The average deviation of values of this study from those of Reamer, Sage, and Lacey is less than ±0.5% at 200 p.s.i.a. The average deviations are larger at the higher pressures; however, the average deviation of all the points compared is only slightly larger than ±1.0%.

Tables I and II record the values of the densities of the saturated vapor and the saturated liquid, respectively. At the lower temperatures the precision of the vapor density calculation is poor, because of the high percentage error in the pressure measurement. The dew point pressures were determined visually as the pressure at which the first minute droplets of liquid appeared on the cell wall. This method requires very careful observation. There is frequently a very large difference in the true bubble point pressure and the pressure at which measurable amounts of liquid form. In many cases the visual dew points were checked by the discontinuities in the isothermal volume-pressure derivatives. This was most easily accomplished by plotting the mass of material in the cell versus the pressure. Where differences between the visually observed dew point and the graphical dew point occurred, the graphical dew point was used as the best approximation of the true dew point.

Figure 7 presents the vapor densities as a function of temperature of three of the mixtures studied. The other two mixtures, representing vapor rich in hydrogen sulfide, are not shown on the diagram because this requires a concentration of data in a narrow region between the lines representing densities of pure hydrogen sulfide and 45.8 mole % of hydrogen sulfide.

Figure 8 presents graphically the liquid densities of mixtures in the composition range where saturated liquid existed. At temperatures below −100°F. the phase density behavior in the region where two liquid phases exist is indicated. The lines on the chart marked 50, 70, and 90 mole % of hydrogen sulfide were obtained by interpolation of the data of this study and the saturated liquid densities of Reamer, Sage, and Lacey (*8*). It is believed that the accuracy of the liquid density read from this chart is within 7%.

Figure 9 is a plot of the critical density as a function of the composition. The data points of Reamer, Sage, and Lacey shown on the chart were obtained by extensive interpolation and extrapolation of dew-point bubble-point data. The data points of this study were directly measured. No bubble points were found for the three mixtures representing 45.8, 24.8, and 11.01 mole % of hydrogen sulfide. Further, a bubble point was found for 5.25 mole % of hydrogen sulfide.

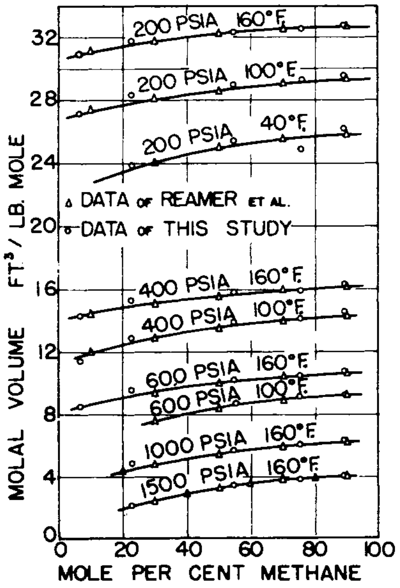

Figure 6. Molal volumes

Table I. Density of Saturated Vapor

Pressure, P.S.I.A.	Temp., °F.	Vapor Density, Lb./Cu. Foot
	93.3 Mole % H_2S	
31	−44.6	0.341
110	13.4	1.067
247	61.0	2.183
535	122.3	4.504
920	175.7	7.77
	77.1 Mole % H_2S	
7	−103.6	0.0591
49	−40.0	0.354
240	49.3	1.52
500	101.2	2.98
612	115.4	3.91
900	139.7	5.82
	45.8 Mole % H_2S	
17	−102.9	0.114
79	−44.1	0.454
191	−2.16	1.04
437	38.5	2.32
732	66.6	3.905
1089	85.2	6.51
	24.8 Mole % H_2S	
25	−114.0	0.165
65	−81.9	0.394
137	−50.2	0.780
240	−30.4	1.320
	11.01 Mole % H_2S	
98	−97.3	0.493
182	−74.5	0.873
377	−57.8	1.74
411	−46.8	1.90
519	−41.2	2.46

Table II. Density of Saturated Liquid

Pressure, P.S.I.A.	Temp., °F.	Liquid Density, Lb./Cu. Foot
	93.3 Mole % H_2S	
520	−44.6	52.90
660	13.4	49.10
764	61.0	47.10
1092	122.3	40.98
1420	175.7	38.05
	77.1 Mole % H_2S	
1542	−40.0	40.25
1640	49.3	37.47
1780	115.4	32.00
1770	139.7	24.24

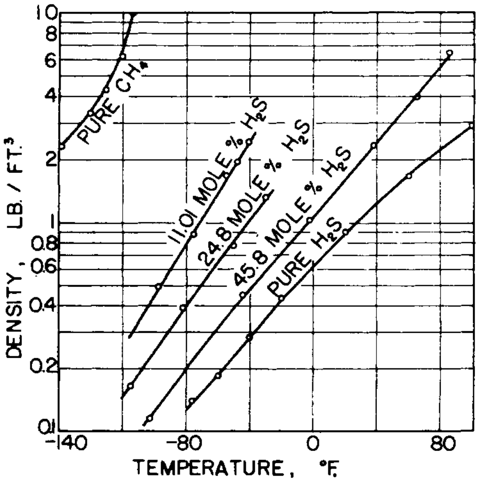

Figure 7. Density of saturated vapor

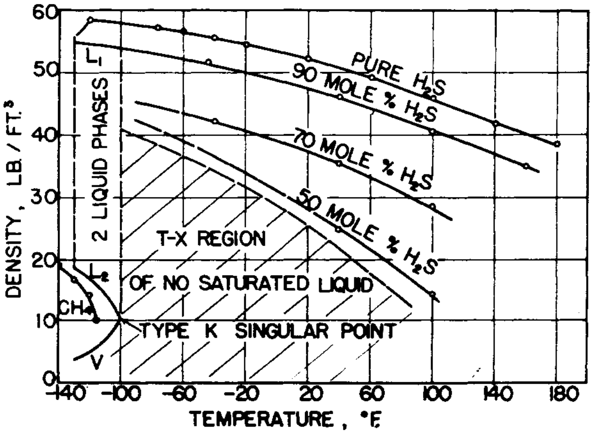

Figure 8. Density of saturated liquid

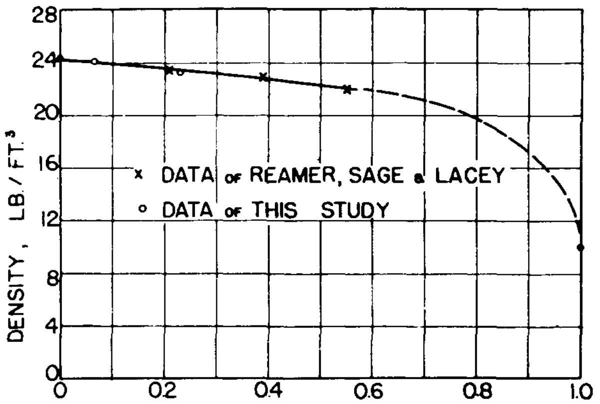

Figure 9. Critical density

It is necessary in order to explain this puzzling phenomenon to introduce the results of the rather extensive phase study made concurrently with the volumetric study on this system. It was discovered during this study that the methane–hydrogen sulfide system existed in two distinct liquid phases under certain pressure and temperature conditions. Kohn and Kurata (*3*) describe the phase behavior of this system. Ricci (*10*) also gives a discussion of the type of system involved here.

The bubble points observed by Reamer, Sage, and Lacey (*9*) at 30 and 40 mole % of hydrogen sulfide might be explained as a consequence of the manner in which they were determined. These investigators did not visually observe the bubble points. They were graphically calculated from the discontinuities in the isothermal volume-pressure derivatives. There are measurable discontinuities in the isothermal volume-pressure derivatives at the upper dew point line also.

In Figure 8, whereas the phase densities are indicated along the three-phase (L_1-L_2-V) line these densities leave something to be desired in the way of accuracy. The densities were calculated from isothermal compression lines and the small volumetric capacity of the equilibrium cell made the measurement of the incremental quantities of gas injected into the cell very difficult. The maximum error in the three-phase line densities is estimated at ±3% for the L_1 phase and ±10% for the L_2 and V phases.

CONCLUSION AND RECOMMENDATIONS

The volumetric data of this study are of sufficient accuracy for the design of equipment for the low temperature separation of hydrogen sulfide from methane. Because only two mixtures were studied which had bubble point curves, the bubble point density data are extremely meager. It would be desirable to supplement these data by additional low temperature data, especially on a mixture composed of approximately 50 mole % of hydrogen sulfide. It would be interesting, though of doubtful practical value, to obtain density data on the two-liquid phase region and along the critical solution line.

ACKNOWLEDGMENT

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NOMENCLATURE

P_c = critical pressure
P_c' = pseudo-critical pressure, $\left(\sum_{i=1}^{n} N_i Pc_i\right)$
Pr = pseudo-reduced pressure, P/P_c'
T_c = critical temperature
T_c' = pseudo-critical temperature, $\left(\sum_{i=1}^{n} N_i Tc_i\right)$
Tr = pseudo-reduced temperature, T/T_c'
Z = compressibility factor, PV/RT
K = type K singular point involving the critical identity of phases L_2 and V in presence of phase L_1
L_1 = liquid phase having properties similar to pure liquid hydrogen sulfide at same temperature
L_2 = liquid phase having properties similar to pure liquid methane at same temperature
V = vapor phase

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Thermal Conductivity of Fluids. Nitric Oxide

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Experimental determination of the thermal conductivity of nitric oxide in the gas phase is limited to measurements at atmospheric pressure. Johnston and Grilly (*7*) established the value of the thermal conductivity of nitric oxide at atmospheric pressure from –230° to 216° F. and Eucken (*2*) recorded values at –100° and 32° F. These data were obtained by use of hot wire cells of the potential lead type. Todd (*11*) measured the thermal conductivity of nitric oxide in equipment of parallel plate design. His reported experimental difficulties in the case of nitric oxide make the results uncertain. Winkelmann (*12*) was the first to measure the conductivity of nitric oxide, but because of the methods he employed the experimental results are primarily of historical interest.

Yost and Russell (*14*) summarized the properties of nitric oxide at atmospheric pressure; and the pressure-volume-