Heterogeneous Phase Equilibria of the Methane–hydrogen Sulfide System

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The experimental apparatus and procedures which were developed for the determination of the heterogeneous phase behavior of the methane-hydrogen sulfide system have been described in a previous paper (*2*). The apparatus and procedures were tested and employed at temperatures in the range of −300 to 300°F. and at pressures up to 2000 lb./sq. in. abs. The vapor-liquid, vapor-solid, liquid-solid, liquid-vapor-solid, liquid-liquid-vapor and liquid-liquid-solid phase border curves were determined for six mixtures of methane and hydrogen sulfide. The phase compositions were determined at selected points along the three-phase univariant equilibrium lines. An invariant point (quadruple point) was found which involves the equilibrium of two liquid phases, a vapor phase, and a solid phase. These data are presented on *P-T* and *T-X* diagrams.

The data contribute to the understanding of phase behavior of light hydrocarbons containing hydrogen sulfide.

The increased application of low temperatures for processing of petroleum hydrocarbons in connection with petrochemical and natural-gas industries has led to engineering operations which frequently require a knowledge of phase and volumetric behavior of hydrocarbon systems at low temperatures and high pressures. Although considerable data are available on hydrocarbon systems at room temperature and above, only a few experimental data on low temperature properties of hydrocarbons are available.

The acidic components such as carbon dioxide and hydrogen sulfide are frequently found in natural and refinery gases. Since these components are widely different from hydrocarbons, the study of mixtures of these acidic components and hydrocarbons should increase the understanding of the phase behavior of such mixtures. Although data have recently appeared giving the low-temperature behavior of carbon dioxide-methane system (*1*), no similar data are available for the hydrogen sulfide-methane system. Reamer, Sage, and Lacey (*4*) have studied the phase and volumetric behavior of hydrogen sulfide-methane system at temperatures ranging from 40 to 340°F., and under pressures from 200 to 10,000 lb./sq. in. abs. Their data were compared to the results of this study in the range of temperatures and pressures common to both investigations.

This investigation seemed appropriate in view of the dearth of low-temperature phase behavior data and in view of increasing interest in low-temperature processing.

EXPERIMENTAL APPARATUS AND PROCEDURE

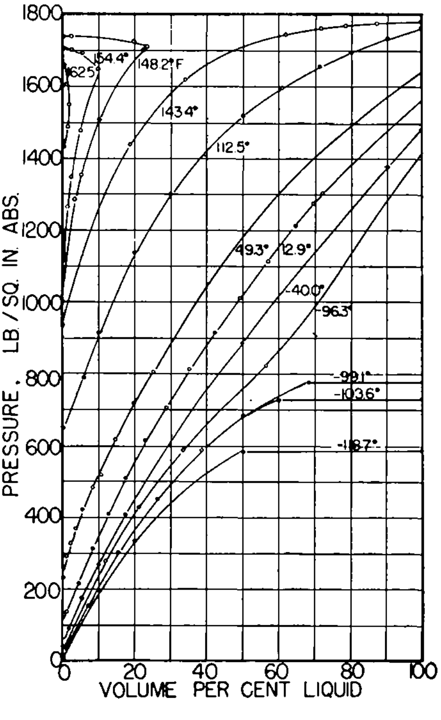

Fig. 1. Isotherms of 77.1% H_2S.

In the paper (*2*), previously referred to, the method used is a low-temperature modification of the dew-point bubble-point method where a known amount of a particular gas mixture is introduced into a glass equilibrium cell. As the pressure or the temperature or both are varied, the gas mixture undergoes various phase changes which may be visually observed. A special sampling adaptor was designed for the glass equilibrium cell which allowed sampling of the various phases in the cell.

Materials Used

The hydrogen sulfide used in this study was obtained in 9-lb. cylinders from the Matheson Company. It was stated to be 99.9% pure. This hydrogen sulfide was passed through activated alumina and then through activated charcoal. An isotherm determined at 98.0°F. for this gas showed that a pressure change of 4 lb./sq. in. changed the quality of the gas from 0.10 to 0.90. The vapor pressures determined for the gas agreed with the data given in the International Critical Tables (*6*) within 4 lb./sq. in. The experimental critical point was 213.3°F. and 1297 lb./sq. in. abs. International Critical Tables report a value of 212.7°F. and 1304 lb./sq. in. abs. The molecular weight of this gas by density measurements was 34.29. These data indicated that the impurities in the hydrogen sulfide were probably less than 0.001 mole fraction.

The "Pure Grade" methane was donated by the Phillips Petroleum Company. It was stated to be 99 mole % minimum purity with the impurities being mainly ethane, carbon dioxide, and nitrogen. This gas was passed through activated alumina and then through a tube containing activated charcoal maintained in a dry-ice and acetone bath. An isotherm determined at −183.8°F. for this gas showed that the quality of the gas was increased from 0.10 to 0.90 by a pressure change of 5 lb./sq. in. abs. The vapor pressures of this gas agreed with those of the International Critical Tables within 4 lb./sq. in. abs., and its molecular weight from density measurements was found to be 16.13. These data indicate that the methane contained less than 0.003 mole fraction impurities.

Preparation of Mixtures

The hydrogen sulfide vapor from a cylinder was purified as previously described and passed under its own vapor pressure to be condensed in a stainless-steel gas reservoir maintained in a dry ice-acetone bath. A weighed amount of hydrogen sulfide was allowed to condense in the reservoir. Then purified methane was passed into the gas reservoir at pressures up to 1400 lb./sq. in. abs. The uncertainty of the composition of a gas mixture made up in this manner was less than 10%. The exact composition was determined after the mixture has been heated and allowed to come to equilibrium. Standard deviations were calculated from 5 to 7 vapor density determinations made on each mixture. The deviations in every case were caused by weighing errors plus barometric and temperature errors. The maximum uncertainty of the compositions of the six mixtures is believed to be 0.005 mole fraction.

Gas Analysis

The mixtures and the phase samples in each case were analyzed by gas density

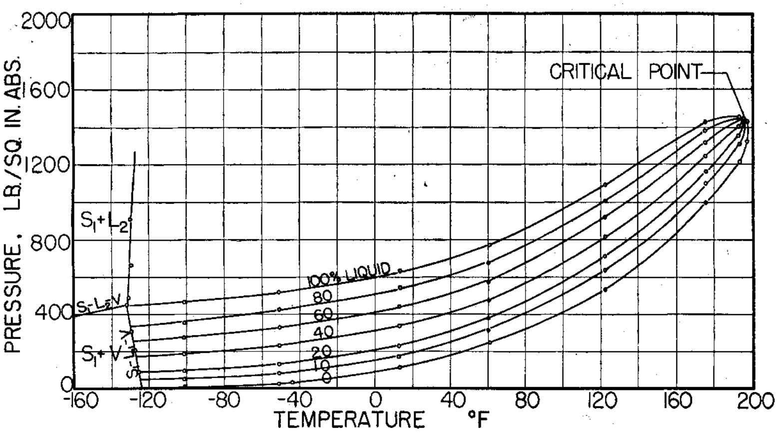

Fig. 2. *P-T* diagram for 93.3 mole % H_2S.

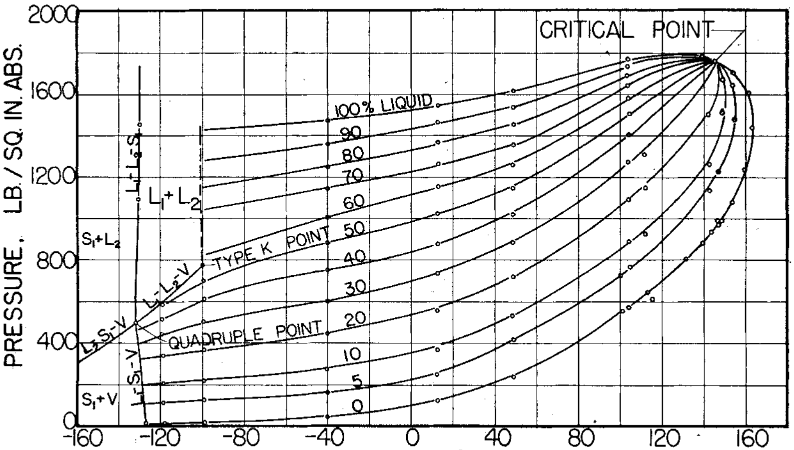

Fig. 3. *P-T* diagram for 77.1 mole % H_2S.

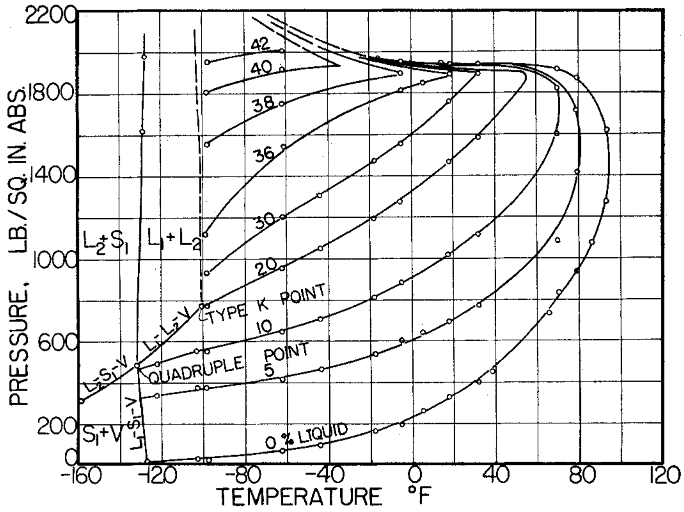

Fig. 4. *P-T* diagram for 45.8 mole % H_2S.

measurement. Mixtures of hydrogen sulfide and methane closely approximate ideal gas behavior at atmospheric pressure and room temperature (*4*). The vapor densities of mixtures of hydrogen sulfide and methane are nearly linear interpolations between the vapor density of the pure components. Three known mixtures were prepared and used to determine the calibration between the vapor densities of the mixtures and their corresponding composition.

EXPERIMENTAL RESULTS

Figure 1 presents the experimental isotherms for one of the six mixtures studied. Charts of pressure vs. temperature, with volume per cent liquid as parameter, are presented in Figures 2-7. These pressure-temperature diagrams were prepared from the experimental isotherms for the six mixtures by crossplotting at constant percentage liquid. The critical temperature and pressure were determined as the point at which all constant per cent liquid lines converge.

The pressure-temperature diagrams of Figures 2-7 represent three variables—temperature, pressure, and volume per cent liquid. Temperature is the most important variable to control, since a temperature change can affect both the pressure and the volume per cent liquid. In isothermal operation, pressure changes do not affect the temperature but only the volume per cent liquid. The precision of the temperature measurement was ±0.02°F.; the accuracy is within ±0.1°F. over the entire temperature range of the investigation. The pressure measurement was accurate to ±2 lb./sq. in. It is difficult to evaluate an over-all absolute error in measuring the volume percent liquid, because several sizes of equilibrium cells were used in the investigation. The accuracy of the equilibrium cells was always better than ±3% at 5-100% liquid. The absolute error at the dew point, determined by the detection of traces of moisture on the cell walls and agitator ball was considerably less than 0.2% liquid. The critical temperatures are believed to be accurate to ±1°F. and the critical pressures to ±10 lb./sq. in. abs.

With reference to Figure 1, the high-temperature isotherms are similar to those of many binary hydrocarbon systems. There is a large difference in pressure between the temperatures in the range of 49.3°F. to −96.3°F. The high bubble-point pressures indicate the low solubility of methane vapor in a hydrogen sulfide rich liquid even at low temperatures. The inflection in the −96.3°F. isotherm would not be expected in binary hydrocarbon systems. In this case, however, this behavior is the result of the temperature proximity of this isotherm to a critical point. A discontinuity occurs in the bubble-point pressure line at −99.1°F. and 775 lb./sq. in. abs., the point at which a second liquid

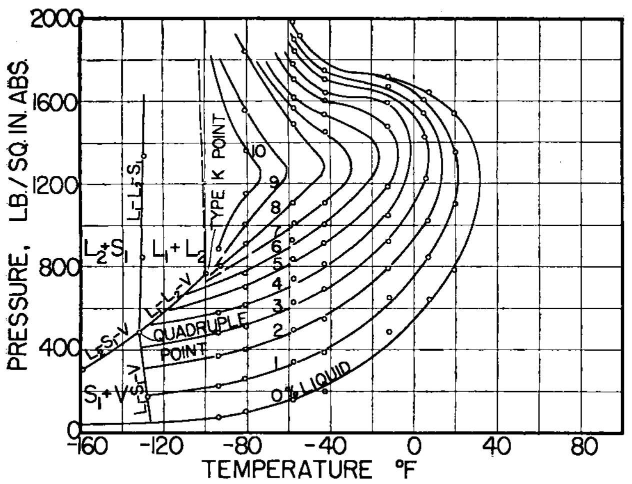

Fig. 5. *P-T* diagram for 24.8 mole % H_2S.

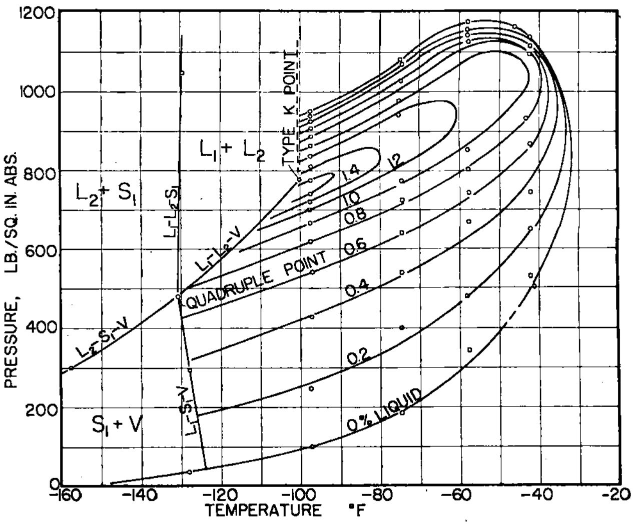

Fig. 6. *P-T* diagram for 11.01 mole % H_2S.

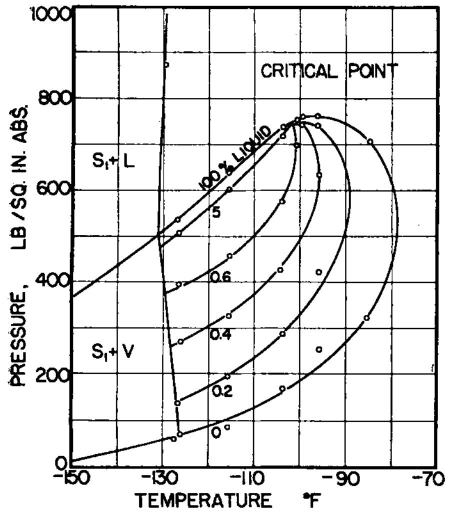

Fig. 7. *P-T* diagram for 5.25 mole % H_2S.

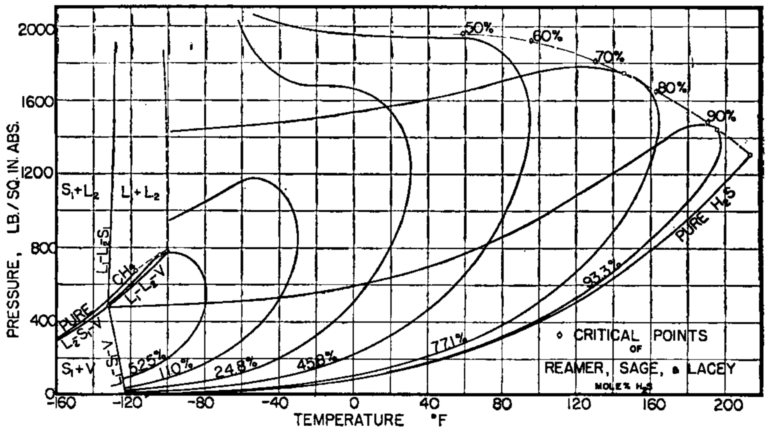

Fig. 8. Phase border curves of CH_4–H_2S system.

phase (methane rich) first appears. This liquid phase is in critical identity with the vapor because a slight rise in temperature causes the disappearance of this phase while a slight decrease in temperature causes its reappearance. The heavier phase is the hydrogen sulfide rich phase and it is in noncritical equilibrium with the two critical phases. A point such as this where two phases are in critical identity in the presence of a third phase has been termed a "type-K singular point" (*5*).

It is desirable to discuss Figure 3 (before Figure 2 is discussed), which was obtained by cross-plotting the data of Figure 1 at lines of constant volume per cent liquid. The additional phase boundary data not shown on Figure 1 are presented in Figure 3. The upper end of the vapor-liquid envelope appears conventional in most respects. The dew-point curve and the bubble-point curve are continuous; they meet at the critical point without a cusp. The critical point is 146.2°F. and 1742 lb./sq. in. abs. There are small regions of isothermal and isobaric retrograde condensation. The cricondenbar is at 120°F. and 1789 lb./sq. in. abs.

The type-K singular point referred to above is indicated at the upper end termination of the L_1-L_2-V line. This line represents a univariant equilibrium of a liquid rich in hydrogen sulfide (L_1), a liquid rich in methane (L_2) and a vapor which is rich in methane.

The L_1-L_2-V line is the binary system analog of the vapor-pressure curve for a pure component. Along this line there is only one degree of freedom. Fixing the temperature fixes the pressure and the composition of each of the three phases. Thus the phases may be sampled without disturbing the equilibrium as long as all three phases exist in the cell. The L_1-L_2-V line terminates on the low-temperature end at an invariant point found at −131.7°F. and 490 lb./sq. in. abs. This point is the quadruple point at which four phases (L_1-L_2-V-S_1) are in equilibrium. Four three-phase lines meet at this point. The essential transition at the quadruple point is the transition of L_1, (liquid rich in hydrogen sulfide) to S_1 (substantially pure solid hydrogen sulfide). The quadruple-point temperature is the lowest temperature at which a hydrogen sulfide rich liquid phase can exist in the methane-hydrogen sulfide system. Below this temperature only methane-rich liquid and vapor phases and substantially pure solid phases can exist.

Figure 2 is the pressure-temperature diagram for an over-all mixture composed of 93.3 mole % hydrogen sulfide and 6.7 mole % methane. The usual type of vapor-liquid critical point is indicated at 195.8°F. and 1448 lb./sq. in. abs. An L_2 liquid phase was not observed for this mixture; however, a small amount of L_2 is compositionally possible. This is assumed in marking the $S_1 + L_2$ liquid-solid region.

Figures 4 and 5 are unusual because of the extremely large regions of isothermal retrograde condensation which extend from the cricondentherm temperatures down to the temperature of the type-K singular point at −100°F. The upper dew-point lines rise with lowering temperatures. The pressure limitation of the glass equipment did not permit following the dew-point lines to higher pressures than shown on the diagram.

Figure 6 also shows a large isothermal retrograde condensation region. At this over-all composition the upper dew-point line is seen to have a positive slope in contrast to the upper dew-point lines of Figures 4 and 5 which have negative slopes.

Figure 7 shows that the mixture composed of 5.25 mole % hydrogen sulfide possesses a conventional type of vapor-liquid critical point. Two liquid phases were not found for this mixture.

Figure 8 presents the phase border curves for the six mixtures. The locus of vapor-liquid critical points of Reamer, Sage, and Lacey (*4*) is indicated by the dotted line. It may be observed that the critical points determined for mixtures composed of 93.3 mole % and 77.1 mole % hydrogen sulfide fall closely on this line, indicating good agreement with the data of Reamer, Sage, and Lacey in this range.

Figures 9 to 12 present temperature-composition diagrams for the hydrogen sulfide-methane system. These were obtained by cross-plotting the smoothed experimental data from large-scale isotherm-pressure charts, smoothing these data on large-scale pressure-temperature diagrams, and cross-plotting the resulting curves at even values of pressure on the pressure-composition diagrams.

With reference to Figure 9, it is observed that at 300 lb./sq. in. abs. the vapor-liquid envelope is intersected by a large area of the solid-vapor region. The horizontal line at −129°F. represents the three-phase equilibrium of L_1-S_1-V. L_1 is a liquid phase composed of 5.5 mole % methane in equilibrium with a vapor phase containing 97.5 mole % methane and a solid phase which is substantially pure hydrogen sulfide. It was impossible to determine the composition of the solid phase by the methods employed in this study. However, since a miscibility gap in the liquid state is never expected in a binary system with continuous solid solution (*7*), it can be assumed that the solid phases are substantially pure components.

The L_2-S_1-V transition temperature is indicated in Figure 9 by the horizontal line at −158°F. The liquid and the vapor phases were sampled at this point with the special sampling adaptor. L_2 was found to be composed of 96.3 mole % methane and the vapor phase was composed of 98.4 mole % methane. There is an extremely large area below −158°F., representing equilibrium between L_2 and S_1. The transition lines below −158°F. are dotted in this region to indicate that their positions are not exactly known. The transition temperature indicated at −298°F. represents the equilibrium between a liquid phase rich in methane, substantially pure solid hydrogen sulfide, and substantially pure solid methane (L_2-L_1-S_2). This temperature may be in error as much as 4°F., but when one considers solid-solubility relationships, this temperature is within 2°F. of the actual L_2-S_1-S_2 transition temperature.

The 500 lb./sq. in. abs. isobar presented in Figure 10 shows the presence of the miscibility gap extending through the vapor-liquid region. The L_1-L_2-V line is shown as the horizontal line at −130°F. This temperature is near the quadruple point temperature, but the pressure is slightly higher than the quadruple-point pressure. If the pressure were reduced to 490 lb./sq. in. abs., the L_1-L_2-V and the L_1-L_2-S_1 lines would converge to a single line at −130.9°F. The observed quadruple point is found at these particular conditions. Figure 10 also shows that temperatures below −132°F. do not permit the existence of a vapor phase There is a small L_2-V loop extending to the right-hand axis of the diagram. Thus it is possible to obtain substantially pure methane by distillation at this pressure.

Figure 11 represents the temperature-composition equilibria at 700 lb./sq. in. abs. Since this pressure is higher than the critical pressure of pure methane, it is not possible to obtain pure methane by distillation at this pressure. There is a vapor-liquid critical point, representing identity of the phases L_2 and V at −112°F. and at a composition of approximately 96.5 mole % methane. At pressures higher than 700 lb./sq. in. abs. the L_2-V loop becomes smaller. At 768 lb./sq. in. abs. and −100°F., the L_2-V loop has contracted to a single point. This is the type-K singular point.

The high-pressure isobars are presented in Figure 12. There is no unusual phenomenon shown by any of these isobars. The dew- and bubble-point curves were not extended into the low-temperature range because the dew- and bubble-point lines do not exist at these conditions.

TABLE 1

COMPARISON OF EQUILIBRIUM COMPOSITIONS WITH DATA OF REAMER, SAGE, AND LACEY (*4*)

Pressure lb./ sq. in. abs.	Vapor phase Mole fraction CH_4	Deviation from data of Reamer *et al.*	Liquid phase Mole fraction CH_4	Deviation from data of Reamer *et al.*
		40°F.		
200	0.140	0.003	0.005	−0.001
300	0.392	+0.002	0.021	0.000
400	0.513	0.000	0.035	0.000
500	0.580	−0.008	0.049	0.000
600	0.632	−0.007	0.062	−0.002
700	0.655	−0.020	0.071	−0.007
800	0.690	−0.009	0.090	−0.018
1000	0.720	−0.004	0.125	0.000
1200	0.727	−0.005	0.162	−0.002
1400	0.725	−0.001	0.205	−0.009
1600	0.705	−0.002	0.238	−0.052
1800	0.665	−0.004		
	Avg. deviation	0.005	Avg. deviation	0.008
		100°F.		
400	0.012	0.000	0.001	0.000
500	0.180	+0.016	0.013	0.000
600	0.280	+0.011	0.0255	0.000
700	0.342	0.000	0.038	−0.001
800	0.405	+0.007	0.051	−0.001
1000	0.485	+0.014	0.080	−0.001
1200	0.508	0.000	0.110	−0.008
1400	0.523	−0.001	0.157	−0.005
1600	0.520	0.000	0.200	−0.019
1800	0.475	−0.005		
	Avg. deviation	0.005	Avg. deviation	0.004
		160°F.		
800	0.020	0.000	0.003	0.000
1000	0.155	0.000	0.027	−0.004
1200	0.238	+0.001	0.052	−0.010
1400	0.255	−0.026	0.085	−0.017
1600	0.250	−0.008	0.155	0.000
	Avg. deviation	0.007	Avg. deviation	0.006

TABLE 2

VAPORIZATION EQUILIBRIUM CONSTANTS OF THE METHANE-HYDROGEN SULFIDE SYSTEM

Temperature °F.	Vapor phase Mole fraction CH_4	Liquid phase Mole fraction CH_4	Equilibrium constant CH_4	H_2S
		200 lb./sq. in. abs.		
40	0.140	0.005	28.0	0.864
0	0.522	0.009	58.0	0.482
− 40	0.754	0.0125	60.3	0.248
− 80	0.906	0.018	50.3	0.0957
−120	0.968	0.025	38.7	0.0328
		400 lb./sq. in. abs.		
80	0.251	0.016	15.7	0.761
40	0.513	0.035	14.7	0.504
0	0.720	0.045	16.0	0.292
− 40	0.862	0.054	16.0	0.145
− 80	0.935	0.062	15.1	0.0693
−120	0.969	0.066	14.7	0.0332
		600 lb./sq. in. abs.		
120	0.143	0.015	9.53	0.870
80	0.406	0.038	10.7	0.617
40	0.628	0.058	10.8	0.395
0	0.792	0.072	11.0	0.224
− 40	0.900	0.083	10.8	0.109
− 80	0.947	0.093	10.2	0.0584
−100	0.955	0.101	9.45	0.0500
		800 lb./sq. in. abs.		
150	0.104	0.010	10.4	0.905
120	0.290	0.035	8.29	0.736
100	0.405	0.051	7.94	0.627
80	0.501	0.068	7.37	0.535
60	0.596	0.086	6.93	0.442
40	0.690	0.090	7.67	0.341
		1200 lb./sq. in. abs.		
200	0.025	0.006	4.17	0.981
160	0.238	0.052	4.58	0.804
120	0.432	0.095	4.55	0.628
80	0.582	0.135	4.31	0.483
40	0.727	0.162	4.49	0.326
		1600 lb./sq. in. abs.		
160	0.250	0.155	1.61	0.888
120	0.441	0.184	2.40	0.685
100	0.520	0.200	2.60	0.600
80	0.586	0.213	2.75	0.526
40	0.705	0.238	2.96	0.387

Table 1 presents the comparison of the equilibrium compositions in the vapor-liquid region with the data of Reamer, Sage, and Lacey (*6*). The equilibrium compositions were taken from large-scale temperature-composition diagrams and are compared with those of Reamer, Sage, and Lacey at three temperatures. The agreement of the vapor compositions is excellent. In one case, the liquid composition differed from that of Reamer, Sage, and Lacey by 0.052 mole fraction. This is a rather large difference but the over-all comparison is considered good and stands as a check on the reliability of the vapor-liquid data obtained in this study.

The vaporization equilibrium constants for methane and hydrogen sulfide are presented in Table 2. These data were condensed from smoothed data taken from the original large-scale temperature-composition charts (*3*). Since the probable accuracy of the temperature-composition charts is approximately ±0.005 mole fraction, the *K* values for methane scatter at the higher temperatures where only a small quantity of methane can exist in the liquid phase. The over-all accuracy of the methane *K* values is considered to be better than ±4%. The *K* values for methane at every pressure pass through a maximum, but generally do not show a wide variation over large temperature ranges. On the other hand, the *K* values for hydrogen sulfide do not pass through a maximum, but constantly decrease with decreasing temperature.

Figure 13 is a pressure-composition projection showing the equilibrium compositions of phases along the L_1-L_2-V and L_2-S_1-V lines. The quadruple point is indicated by the dashed horizontal line at 490 lb./sq. in. abs. At this point, the vapor has a composition of 3.3 mole % hydrogen sulfide; L_1 has a composition of 89.6 mole % hydrogen sulfide; L_2 has a composition of 6.5 mole % hydrogen sulfide; and the solid is substantially pure hydrogen sulfide. The compositions of the phases at both the singular point and the quadruple point were obtained by short extrapolations. Sufficient samples were analyzed in each case to justify estimation of standard deviations. The compositions are believed to be accurate within 0.005 mole fraction, and the

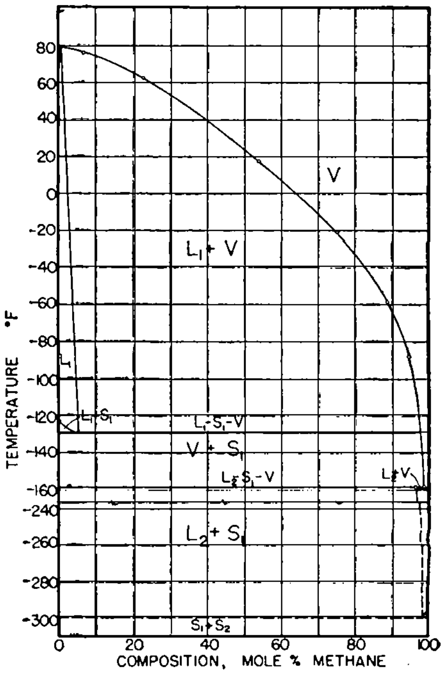

Fig. 9. Temperature-composition 300 lb./sq. in. abs.

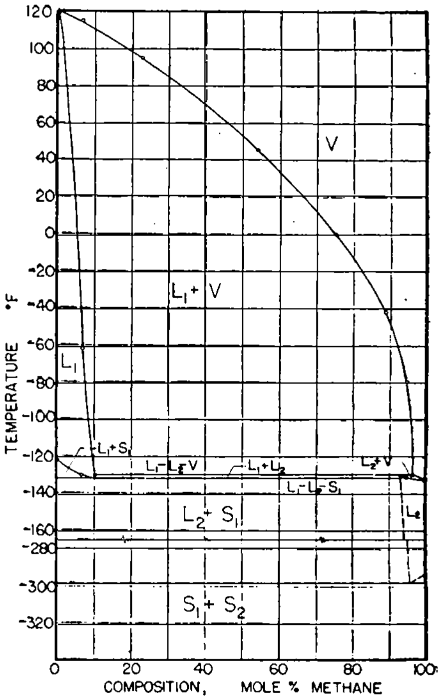

Fig. 10. Temperature-composition 500 lb./sq. in abs.

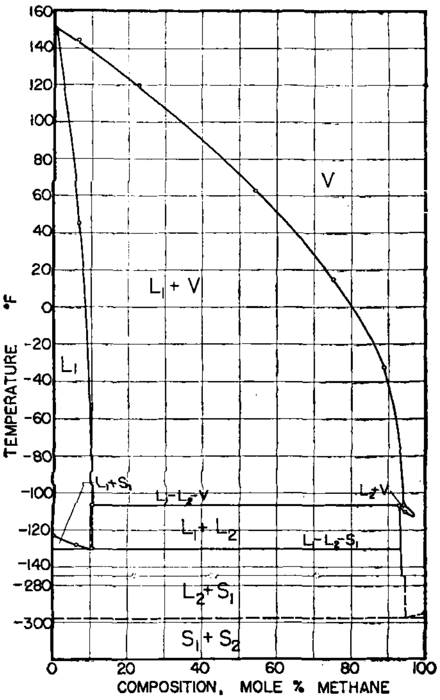

Fig. 11. Temperature-composition 700 lb./sq. in. abs.

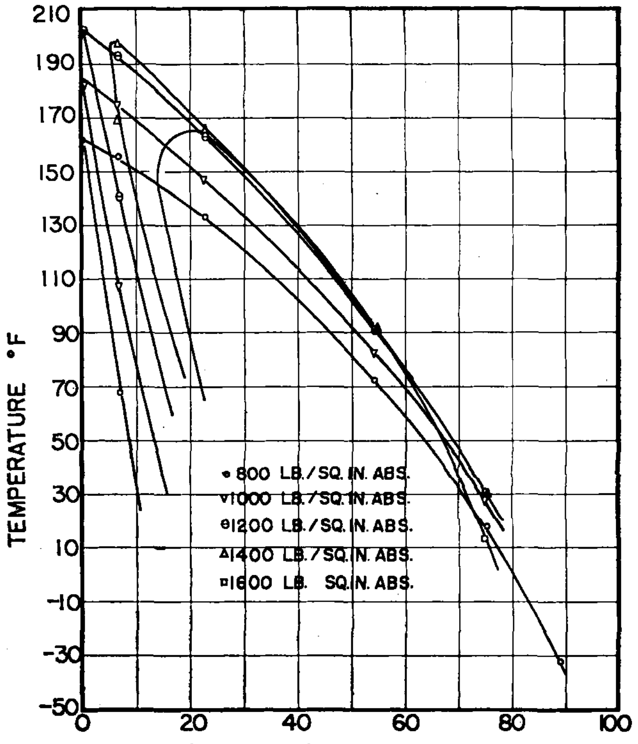

Fig. 12. High-pressure isobars.

deviations are attributed to weighing, barometric, temperature errors and to nonuniform samples.

The behavior along the L_2-S_1-V line is represented in Figure 13 by the lines below the quadruple point dashed line at 490 lb./sq. in. abs. It is interesting to note that the solubility of solid hydrogen sulfide in liquid and vapor state methane decreases rapidly with decreasing pressure. The solubility of hydrogen sulfide is less than 0.1 mole % in both liquid and vapor state methane at atmospheric pressure.

The quadruple point L_1-L_2-V-S_1 is not the only one possible in the methane-hydrogen sulfide system. The data show that the point S_1-S_2-L_1-L_2 is impossible, because L_1 cannot exist at temperatures below −130.9°F. and S_2 cannot exist at temperatures higher than −295°F. The quadruple point S_1-S_2-L_2-V is possible and does exist. If the three-phase equilibrium L_2-S_1-V is followed down to the low-temperature–low-pressure range, a point can be reached at which L_2 transforms to S_2. This point should be below −295°F. and at subatmospheric pressure.

Figure 14 is a qualitative representation of the critical and phase phenomena shown by the methane-hydrogen sulfide system. The composite diagram simulates orthographic projections of the three-dimensional space-phase model. The pressure-temperature (P-T), pressure-composition (P-X), and the temperature-composition (T-X) projections show the critical loci and critical points plus whatever phase lines are necessary for a proper understanding of the diagram.*

Since it was not possible with the equipment used in this study to investigate the two-phase equilibria of L_1-L_2, these equilibria are approximated by the dashed lines in the region labeled $L_1 + L_2$ on the pressure-temperature projection. In this region phase L_2 cannot be distinguished from vapor phase V and could probably be called V with little ambiguity. The L_1-L_2 phases must display critical solution phenomena. In view of the large composition differences between these two phases on the L_1-L_2-V three-phase line, the critical solution pressures would be expected to be high. Approximate extrapolations of the upper dew-point lines of mixtures 5 and 6 (see Figures 4 and 5) indicate that the critical solution pressures are of the order of 4000–6000 lb./sq. in. abs. The locus of critical solution points is indicated by the dashed line marked $L_1 = L_2 = V$ at the top of the P-T projection. This locus of critical solution points must be continuous with the locus of vapor-liquid critical points indicated by the dashed line marked $L_1 = V$. This must be true, because along the locus of critical points, L_2 and V are perfectly continuous and a single phase. The locus of critical solution points must obviously terminate on the low-temperature end of the L_1-L_2-S_1 line. Thus a second type-K singular point exists, involving the critical identity of L_1 and L_2 in the presence of the noncritical phase S_1. This singular point is designated by K_C'. The compositions of phases existing at K_C' are not exactly known. It seems highly probable that the solid phase S_1 is fairly pure hydrogen sulfide. The composition of the critical phase $L_1 = L_2$ is believed to be quite close to 45.8 mole % hydrogen sulfide.

This figure is reasonably accurate because this study showed no vapor-liquid critical point for a mixture containing 45.8 mole % hydrogen sulfide and Reamer, Sage, and Lacey (4) reported a vapor-liquid critical for 50 mole % hydrogen sulfide. It can be seen from the temperature-composition projection that some mixtures of methane and hydrogen sulfide are too lean in hydrogen sulfide to intersect the vapor-liquid critical locus $L_1 = V$. Since the 50 mole % hydrogen sulfide mixture intersects $L_1 = V$ while the 45.8 mole % hydrogen sulfide mixture does not, the maximum inaccuracy in the composition at K_C' is about 4.2 mole %. The composition of the critical phases at K_C' is indicated by the point C_2. Since the vapor-liquid critical point for the 50 mole % mixture is at approximately 60°F. and 1950 lb./sq. in. abs. it is highly likely that the critical composition at K_C' is nearer 45.8 mole % hydrogen sulfide than 50 mole % hydrogen sulfide. This lower composition appears more reasonable because K_C' is known to be at −125 ±3°F. and 4000–6000 lb./sq. in. abs.

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*The table of nomenclature at the end of the paper gives the definitions of the symbols used in Figure 14.

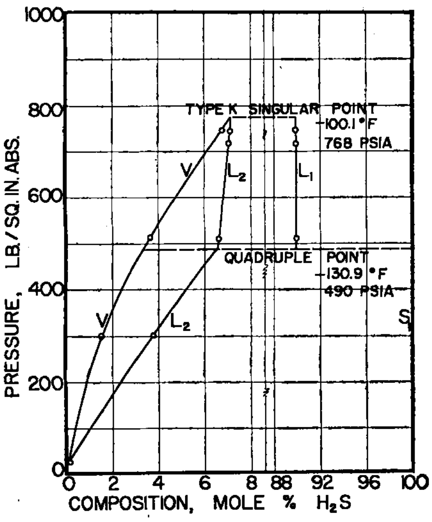

Fig. 13. Three-phase composition of CH_4-H_2S.

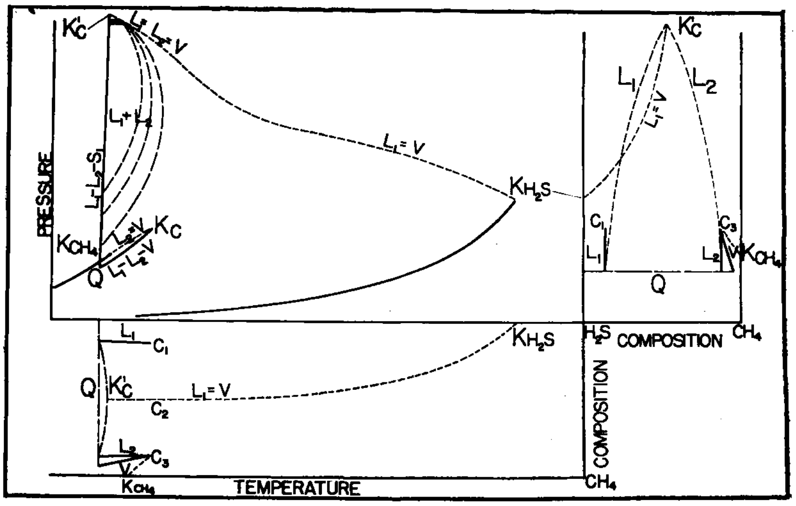

Fig. 14. Schematic diagram of critical phenomena.

On the temperature-composition section, the compositions of the phases existing at the type-K singular point K_C are indicated by the two points C_1 and C_3. At this point the phases L_2 and V are in critical identity. The compositional values of the phases existing at K_C are given in Figure 13, C_2 is about 6.5 mole % hydrogen sulfide and C_1 is about 90 mole % hydrogen sulfide.

If the three-phase system L_1-L_2-V is heated at constant volume, the pressure and temperature rise according to the curve QK_C, while the compositions of the phases vary as indicated in the P-X and T-X projections. If the over-all composition lies between point C_1 and C_3, then there occurs the special critical point $L_2 = V$ with L_1 present. If the composition lies between C_2 and C_3, the two phases left at K_C (L_1 and V) undergo no further critical phenomenon; the liquid simply evaporates to leave V. This behavior was shown by mixtures 5, 6, and 7. If the over-all composition lies between C_1 and C_2, the phases L_1 and V undergo a second critical phenomenon ($L_1 = V$) on the curve $C_2K_{H_2S}$, as shown by mixture 2a. If the over-all concentration of methane is greater than C_3, only the usual $L_2 = V$ critical phenomenon can occur on the curve $K_{CH_4}C_3$, as shown by mixture 8. If the over-all concentration of methane is less than C_1, the only possibility is the critical phenomenon $L_1 = V$ on the upper part of the curve $C_2K_{H_2S}$, as shown by mixture 1.

The peculiar properties of the methane-hydrogen sulfide systems are similar in some respects to those of the ether-water system (*8*). Phase behavior of this type has been discussed by Ricci (*7*).

The formation of two liquid phases of relatively large composition difference at low temperatures and moderate pressures in the methane-hydrogen sulfide system readily suggests simple decantation methods of separation. In the use of decantation under equilibrium conditions, Figure 13 is of utility in choosing a pressure level for the separation and furnishing the compositional values of the equilibrium phases. The temperature is fixed once the pressure is selected. The separation should always be conducted along the three phase L_1-L_2-V or L_2-S_1-V lines because at any fixed temperature or pressure along these lines the phases may be decanted without disturbing the equilibrium.

CONCLUSIONS

The phase behavior of the methane-hydrogen sulfide system offers data of sufficient accuracy and utility for the design of processes for the nonchemical removal of hydrogen sulfide from methane. The critical behavior of this system aids greatly in understanding the role of hydrogen sulfide as a component gas in natural-gas reservoirs and its effect on the critical properties of the natural gas.

ACKNOWLEDGMENT

The authors sincerely appreciate the financial aid given by the University of Kansas Fund for Research Project 17 and by the Dow Chemical Corporation. Appreciation is also felt for the donation of the pure-grade methane used in this study by the Phillips Petroleum Company.

NOTATION

C_1 = composition of phase L_1 at point K_C
C_2 = composition of phase L_1 at point K_C'
C_3 = composition of phase L_2 at point K_C
($C_2K_{H_2S}$, $K_{CH_4}C_3$, $L_1 = V$) = loci of vapor-liquid critical points
K_C = type-K singular point involving the critical identity of phases L_2 and V in the presence of phase L_1
K_C' = type-K singular point involving the critical identity of phases L_1 and L_2 in the presence of phase S_1
K_{CH_4} = critical point of pure methane
K_{H_2S} = critical point of pure hydrogen sulfide
L_1 = liquid phase having properties similar to pure liquid hydrogen sulfide at the same temperature
L_2 = liquid phase having properties similar to pure liquid methane at the same temperature
L_1-L_2-V, L_1-L_2-S_1, etc. = three-phase equilibria lines
Q = quadruple point = (L_1-L_2-S_1-V), invariant equilibrium of these four phases
S_1 = solid phase having all the properties of pure hydrogen sulfide
"Type K singular point" = a critical point involving the critical identity of two phases in a three-phase equilibrium
v = vapor phase

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Manuscript received Sept. 5, 1957; revision received Jan. 13, 1958; paper accepted Jan. 13, 1958.