Phase Equilibria for the Ternary System: CH_4–CO_2–H_2S at Low Temperatures

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The heterogeneous phase behavior of the methane–carbon dioxide–hydrogen sulfide system was studied between 300 and 700 p.s.i.a. at −34° and −51°C. Vapor-liquid equilibrium values were determined from analyses of vapor and liquid samples of mixtures rich, intermediate, and lean in hydrogen sulfide. Equilibrium ratios, calculated for the individual components, were found to be a function of concentration, temperature, and pressure. Calculated activity coefficients indicate the solutions to be nonideal under most of the conditions investigated.

A LITERATURE SURVEY revealed that the phase equilibria of the ternary system CH_4–CO_2–H_2S has only been determined at temperatures above 4° C. Robinson and Bailey studied this sytem at 38° C. (*15*), and later extended their work to 4° and 71° C. (*16*). Phase relationships of binary mixtures of the three gases of interest have been obtained both at high and low temperatures. The CO_2–H_2S binary system has been reported by many workers (*1, 8, 9, 17-19*). Donnelly and Katz (*2, 3*) studied the phase equilibria for the CH_4–CO_2 system, while Reamer and coworkers (*14*) and Kohn and Kurata (*11*) obtained data on the CH_4–H_2S system.

In this investigation the phase behavior of the CH_4–CO_2–H_2S system was determined at −34° and −51 °C. Vapor-liquid equilibrium data were obtained at several pressures and concentrations at each temperature.

THEORY

For real systems at equilibrium, the composition of a component in the vapor and liquid phase is related by the expression:

$$y_a f = \gamma x_a f_a^\circ \tag{1}$$

where y_a is the mole fraction of component (a) in the vapor phase, x_a is the mole fraction in the liquid phase, f is the fugacity of the pure component (a) in the vapor phase at the system temperature and pressure, f_a° is the fugacity of pure component (a) as a liquid at the temperature and corresponding vapor pressure of this component in the system, and γ is the activity coefficient. The fugacity terms account for the deviation of the gas from ideality while the activity coefficient is a measure of the nonideality of the liquid.

The fugacity ratio, f/f_a° is thermodynamically related to the system parameters by the equation (*10, 15*).

$$RT \ln \frac{f}{f_a^\circ} = \int_{P_a^\circ}^{P} \bar{v}_a dP \tag{2}$$

This equation permits calculation of the fugacity ratio for any component in a gas mixture provided its partial molal volume is known as a function of pressure. However, for the gas mixture of interest, as well as most gas mixtures, the partial molal volume-pressure relationships are not available. If it is assumed that the Lewis and Randall fugacity rule (*12*) is obeyed in the temperature and pressure range of this investigation, then molal volumes can be substituted for the partial molal volumes in Equation 2. Lewis and Randall have shown that the partial molal volume can be replaced by the molal volume in most cases without appreciable error (*12*); this is generally done because of the scarcity of partial and molal volume data for mixtures (*15, 16*). Thus, the value of the ratio f/f_a° can be obtained by graphical integration of Equation 2 using a molal volume-pressure curve for component (a) between the working pressure and the vapor pressure at a given temperature. When combined with the experimental x-y data, the fugacity ratio can be used to calculate activity coefficients by rearranging Equation 1 as follows:

$$\gamma_a = \frac{y_a f}{x_a f_a^\circ} \tag{3}$$

The phase behavior of the individual components of a ternary system can best be described by their vapor-liquid equilibrium ratio:

$$K_a = \frac{y_a}{x_a} \tag{4}$$

Where

- K_a is the equilibrium ratio for an individual component (a)
- y_a is the mole fraction of component (a) in the vapor phase
- x_a is the mole fraction of component (a) in the liquid phase

Equilibrium ratios are functions not only of temperature and pressure, but also of concentration. Therefore, a complete study of a ternary system requires data through the entire range of concentration.

EXPERIMENTAL

The method used for obtaining vapor-liquid equilibrium data consisted of the following steps. Hydrogen sulfide–carbon dioxide gas mixtures were made up in a mixing vessel at moderate pressures by successive additions of each component. Three mixtures were prepared, corresponding to lean, intermediate and rich in H_2S content. A suitable portion of a mixture was then condensed into the equilibrium cell using a liquid nitrogen bath. Following, the cell was adjusted to the desired temperature by circulating cooled acetone. Final pressure was adjusted by adding methane to the mixture. The mixture was rocked to hasten equilibrium; vapor and liquid samples were analyzed by gas chromatography until no further change in analyses was obtained. Hensel (*5*) gives complete details for procedure.

Materials. The compressed gases were obtained from the Matheson Co., Inc. Hydrogen sulfide and methane were of CP grade and carbon dioxide was Bone Dry grade.

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Minimum purities of the gases were given as: hydrogen sulfide, 99.5%; methane, 99.0%; and carbon dioxide, 99.95%. The gases were used directly from the cylinders without further purification

Apparatus. The basic components of the vapor-liquid equilibrium system consisted of a mixing cylinder, equilibrium cell, sample tap and flow meter. The mixing cylinder was a stainless steel cylinder of about 3-liter capacity. The equilibrium cell was specially fabricated of 316 stainless steel; overall dimensions were 2½ inches diameter by 2¼ inches high, and internal volume was approximately 100 cc. The cell was provided with two taps for taking gas and liquid samples, one at the top and the other located near the bottom of the cell. The entire apparatus was mounted on a rocking platform. Two ½ inch stainless steel balls inside the equilibrium cell, in conjunction with the rocking motion, helped speed up attainment of vapor-liquid equilibrium. Number 300 series stainless steel was used on all tubing, valves, connectors and the equilibrium cell due to the corrosive nature of hydrogen sulfide. Pressure was measured with a bourdon-type gauge, 0–1000 p.s.i., which was calibrated against a dead-weight tester. A rotameter permitted metering of the gas flow during sampling. The gas mixture was bubbled through caustic to remove the acidic components before venting to the atmosphere.

The cooling system, also mounted on the rocking platform, employed circulating acetone as a heat-transfer medium between the equilibrium cell bath (acetone) and a low temperature, dry ice–isopropanol bath. The temperature of the cell bath was held constant to within ±1° C. by means of a Wheelco controller, which regulated the on-off cycle of the circulating pump. Temperatures were measured with an alcohol thermometer, which checked against a copper-constantan thermocouple to within 0.2° C.

Analytical. Gas and liquid phase samples were analyzed by gas chromatography, using helium as carrier gas. The separation column was 16 feet of 316 stainless steel packed with 30 wt. % DC 550 on 30–60 mesh Chromasorb P. About one cc. samples of gas or vaporized liquid were obtained in a one cc. tuberculin syringe by injecting it into a rubber septum in the sample tap while purging a small amount of the gas or liquid. Gas chromatographic instrument response was calibrated by use of gases of known mixtures. The relative error in these analyses was 2%.

Procedure. Hydrogen sulfide and carbon dioxide, in the approximate proportions desired, were added successively to the mixing cylinder by pressure measurements. The gases were allowed to mix for at least a week. A portion of the gas mixture was then condensed into the reactor with liquid nitrogen, such that a pressure drop in the mixing cylinder of about 100 p.s.i. was obtained. The equilibrium cell was adjusted to the desired temperature and methane added. A pressure reducing valve on the methane cylinder maintained the pressure constant while adding the methane. The reactor was rocked to speed up attainment of equilibrium. The procedure followed did not permit determination of the overall ternary mixture compositions.

If the pressure remained constant after the methane supply was shut off, then samples of gas and liquid were taken for analysis. When four consecutive samples, at half-hour intervals, gave consistent results (±2% relative), equilibrium was assumed. The equilibrium values reported are an average of at least four consistent results.

After equilibrium data were obtained at one temperature and pressure, the pressure was reduced by releasing gas through the gas sample valve until the next lower desired pressure was obtained. Another experimental run was made on the remaining material using the same procedure as above.

In order to test the apparatus and experimental procedure, data were obtained on two binary mixtures and compared to literature values. As shown in Table I the experimental results are in good agreement with the literature values, indicating the method used to be satisfactory.

RESULTS

The experimental vapor-liquid equilibrium data obtained are presented in Table II. Data were obtained as a function of concentration, temperature and pressure. Initial charge runs are designated as *a* under the run number, and the consequent run on the same charge as *b*. Included in Table II are the literature values (interpolated) for CH_4–CO_2 and CH_4–H_2S binary mixtures for the comparable temperatures and pressures.

The phase behavior of ternary systems, in which vapor is in equilibrium with one liquid phase, is typically represented by a triangular diagram showing the concentration of coexisting vapor and liquid phases at constant pressure and temperature. Figures 1 to 3 represent the corresponding ternary isobaric diagrams of the experimental data. The results obtained indicate that at these temperatures and pressures, the two-phase (liquid-vapor) region extends from boundary to boundary, that is, from the methane—hydrogen sulfide axis to the methane–carbon dioxide axis.

Equilibrium ratios were calculated from the experimental x–y data and are included in Table II. The variations of equilibrium ratios with pressure (at constant temperature and concentration) show a systematic decrease with increasing pressure, except for H_2S at the highest pressure. On the other hand, increasing temperature (at constant pressure and concentration) causes an increase in the equilibrium ratios, except for CH_4, whose equilibrium ratio is essentially unchanged with temperature. Finally, with increasing H_2S concentration (at constant CO_2 concentration, pressure and temperature), the equilibrium ratios for CH_4 and CO_2 increase; however, the opposite obtains for H_2S, indicating that enrichment of H_2S in the condensed phase is greater than that in the gaseous state as overall H_2S concentration is increased.

Fugacity ratios were calculated according to Equation 2 for each component by graphical integration. A hypothetical vapor pressure for methane was estimated by extrapolating to operating temperature a log P *vs.* $1/T$ plot beyond the critical pressure. Vapor pressure and specific volume data for methane, carbon dioxide and hydrogen sulfide were taken from the literature (*7, 13, 20*). Specific volume data for methane vapor are empirical above the critical temperature. Hypothetical specific volumes of methane at higher temperatures were estimated from the law of rectilinear diameter.

Activity coefficients were calculated from the equilibrium fugacity ratios according to Equation 3, and are incorporated in the basic data, Table II. Activity coefficients are generally a function of pressure, concentration, and temperature. However, inspection of the calculated values presented in Table II shows carbon dioxide activity coefficients are independent of these variables within the range studied. Increasing the pressure, maintaining temperature and concentration constant, decreases the activity coefficient for methane and increases it for hydrogen sulfide. The effect of increasing hydrogen sulfide concentration, at constant pressure and at −34° C., is just the reverse; that is, the value for methane increases while that for hydrogen sulfide decreases. At −51° C., the activity coefficient for methane shows a maximum while that for hydrogen sulfide shows a minimum with increasing hydrogen sulfide concentration. Increasing the temperature at constant pressure and concentration decreases the activity coefficient of both methane and hydrogen sulfide. Since all the activity coefficient values are greater than

Table I. Experimental vs. Literature Vapor-Liquid Equilibrium Values

Temp., °F.	Pressure, P.S.I.A.	Equilibrium Values: Experimental Gas	Experimental Liq.	Literature Gas	Literature Liq.
				Ref. 14	
−40	200	75.5% CH_4 24.5% H_2S	2.0% CH_4 98.0% H_2S	75.4% CH_4 24.6% H_2S	1.3% CH_4 97.7% H_2S
				Ref. 2	
−25	350	39.7% CH_4 60.3% CO_2	5.1% CH_4 94.9% CO_2	40.4% CH_4 59.6% CO_2	4.1% CH_4 95.9% CO_2

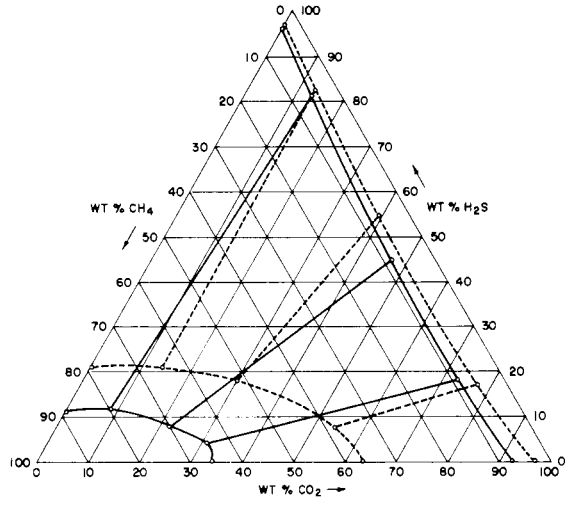

Figure 1. Phase diagram at 300 P.S.I.A. and −34.4° and −51° C.
----- −34.4° C.
—— −51° C.

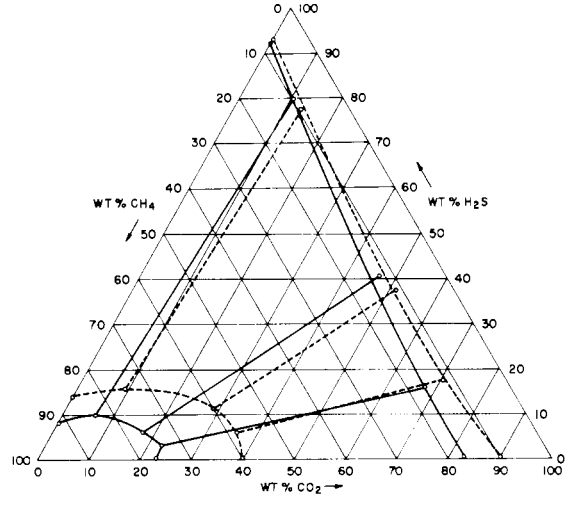

Figure 2. Phase diagram at 500 P.S.I.A. and −34.4° and −51° C.
----- −34.4° C.
—— −51° C.

1.0, the variables which decrease this value make that component in the liquid phase more ideal, whereas variables which increase coefficient values have the opposite effect.

DISCUSSION

The experimental data obtained are consistent with binary data from the literature since in all cases smooth ternary plots were obtained. The error in the analyses

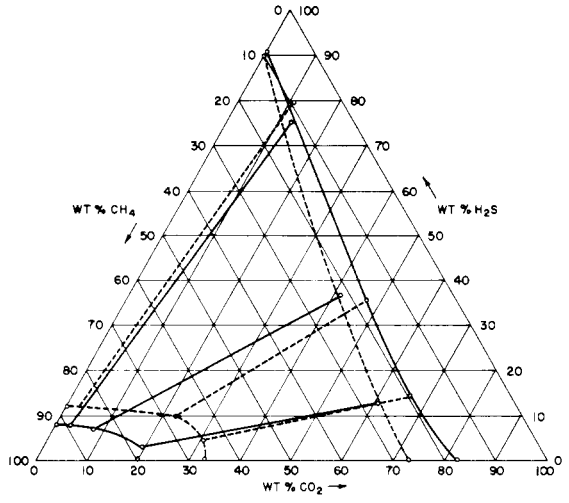

Figure 3. Phase diagram at 700 P.S.I.A. and −34.4° and −51° C.
----- −34.4° C.
—— −51° C.

was 2% relative, which is standard for this type of gas chromatographic analyses. Analysis of the data indicate the error in the carbon dioxide results to be greater than that of the other gases.

Fugacity ratios were calculated for each of the components in the vapor phase, assuming the Lewis and Randall fugacity rule holds. This is probably the most widely used method for calculating fugacities from vapor-liquid equilibrium data. The error incurred by use of this assumption is directly related to the error of assuming the partial molal volumes of a component is equal to the molal volume of the pure component for all pressures, up to the pressure of the solution, and over the temperature range of interest.

There are two general methods for evaluating fugacity values computed, assuming the Lewis and Randall rule to apply. Gilliland and Sullivan (*4*) state that the Lewis and Randall rule is not likely to be satisfactory at pressures greater than 0.6 times the critical pressure of the component in question. Hougan and Watson (*6*) state that this rule is satisfactory for pseudoreduced pressures of less than 0.8.

The above two methods were used to provide a criteria for evaluating the Lewis and Randall rule for the system investigated. These rules indicate the fugacities calculated at 300 and 500 p.s.i. may be reasonable values, whereas, those calculated for the data at 700 p.s.i.a. may be in considerable error.

In the system under investigation, two of the components do not exist as a liquid at the temperature and pressure of the investigation; thus, the specific volumes (used to calculate fugacity ratios) are imaginary. Methane is above

Table II. Equilibrium Data for CH_4–CO_2–H_2S System

Run No.	Ref. 11	Ref. 11	Ref. 11	1b	2a	2b	3a	4b	6b	7a	7b	Ref. 2	Ref. 2	Ref. 2
Temp., ° C.	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4	−34.4
H_2S/CO_2 ratio	∞	∞	∞	6.3	6.3	6.3	1.17	1.17	0.23	0.23	0.23	0	0	0
Press., P.S.I.A.	700	500	300	700	500	300	700	500	700	500	300	700	500	300
Vapor Phase Mole Fraction														
CH_4	88	86	79	86.0	75.0	65.2	67.7	60.0	65.1	57.9	38.2	67	60	36.5
CO_2	0	0	0	2.4	9.5	14.0	22.6	28.9	30.5	36.8	54.3	33	40	63.5
H_2S	12	14	21	11.6	15.5	20.9	9.7	11.1	4.3	5.3	7.8	0	0	0
Liquid Phase Mole Fraction														
CH_4	9.5	7	3	12.8	9.5	4.8	17.2	11.4	19.4	11.8	5.6	17.5	10	3
CO_2	0	0	0	11.4	13.4	12.7	47.1	51.1	66.2	70.9	77.6	82.5	90	97
H_2S	90.5	93	97	75.8	77.1	82.5	35.7	37.5	14.4	17.5	16.9	0	0	0
Activity Coefficient														
CH_4	9.26	12.3	26.3	6.72	7.89	13.6	3.49	5.26	3.36	4.91	6.82	3.83	6.0	12.2
CO_2	...	...	...	0.211	0.709	1.1	0.480	0.566	0.461	0.519	0.700	0.400	0.444	0.655
H_2S	0.133	0.151	0.216	0.153	0.201	0.253	0.272	0.296	0.299	0.303	0.462	...	...	...
Equilibrium Ratios														
CH_4	5.49	6.48	10.3	3.98	4.15	5.32	2.33	2.77	1.99	2.58	2.66	2.27	3.16	4.77
CO_2	...	...	...	0.666	1.99	2.42	1.66	1.59	1.54	1.46	1.58	1.32	1.25	1.44
H_2S	2.18	1.86	1.42	2.51	2.48	1.67	4.46	3.64	4.90	3.74	3.05	...	...	...

Run No.	Ref. 11	Ref. 11	Ref. 11	8a	1a	8b	9a	4a	9b	6a	10a	10b	Ref. 2	Ref. 2	Ref. 2
Temp., ° C.	−51	−51	−51	−51	−51	−51	−51	−51	−51	−51	−51	−51	−51	−51	−51
H_2S/CO_2 ratio	∞	∞	∞	6.3	6.3	6.3	1.02	1.17	1.02	0.23	0.23	0.23	0	0	0
Press., P.S.I.A.	700	500	300	700	500	300	700	500	300	700	500	300	700	500	300
Vapor Phase Mole Fraction															
CH_4	92	92	89	89.3	82.8	79.8	85.6	76.4	70.5	77.7	74.4	65.1	80	77	66
CO_2	0	0	0	2.6	6.3	8.5	8.5	17.7	21.9	19.5	23.0	30.9	20	23	34
H_2S	8	8	11	8.5	11.0	11.7	5.8	5.9	7.6	2.8	2.6	4.0	0	0	0
Liquid Phase Mole Fraction															
CH_4	10.3	8	4	12.6	9.6	5.8	21.8	12.8	8.2	26.9	16.3	9.0	27	17	7.5
CO_2	0	0	0	12.2	10.8	13.0	41.5	46.6	47.0	60.6	68.4	73.2	73	83	92.5
H_2S	89.7	92	96	75.1	79.6	81.2	36.6	40.6	44.7	12.5	15.3	17.8	0	0	0
Equilibrium Ratios															
CH_4	8.93	11.5	22.3	7.09	8.63	13.8	3.93	5.97	8.60	2.89	4.56	7.23	2.96	4.53	8.80
CO_2	...	...	...	0.213	0.583	0.654	0.205	0.380	0.466	0.322	0.336	0.422	0.274	0.277	3.68
H_2S	0.089	0.087	0.115	0.113	0.138	0.144	0.158	0.145	0.170	0.224	0.170	0.225	...	...	...
Activity Coefficient															
CH_4	8.64	11.0	19.7	6.85	8.24	12.8	3.80	5.71	7.97	2.79	4.35	6.70	2.87	4.32	8.16
CO_2	...	...	...	1.22	2.56	1.82	1.17	1.67	1.30	1.84	1.48	1.17	1.57	1.22	1.02
H_2S	3.56	2.54	1.72	4.52	4.03	2.16	6.31	4.24	2.55	8.95	4.97	3.38	...	...	...

its critical temperature, and carbon dioxide is in the vapor-solid region. Therefore, no attempt was made to correct the fugacity of the liquid for pressure.

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