

# Liquid-Vapor Equilibria at 250.00K for Systems Containing Methane, Ethane, and Carbon Dioxide

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Liquid-vapor equilibria for the binary systems methane-ethane, methane-carbon dioxide, and ethane-carbon dioxide and for the ternary system of methane-ethane-carbon dioxide were measured at 250.00K and at pressures of 13-80 atm. Additional liquid-vapor measurements are reported for methane-carbon dioxide at 230.00 and 270.00K.

The increased emphasis of recent years in the low-temperature processing of natural gas has resulted in the need for the phase equilibrium properties of light hydrocarbon-carbon dioxide systems. Some experimental data are available for the binary systems composed of methane, ethane, and carbon dioxide, but no measurements have been made on the ternary system. Thus, the work reported here will be of considerable value to both the thermodynamicist and the process design engineer.

## Previous Experimental Work

Experimental phase equilibrium measurements for the binary systems methane-ethane, methane-carbon dioxide, and ethane-carbon dioxide prior to 1973 have been listed in a recent review paper (9). Table I summarizes all the recent work not reported in ref. 9. There are no experimental data available for the ternary system.

## Experimental Equipment and Procedure

The basic equipment and procedures have been discussed in some detail previously (2); thus, only a brief description of two recent modifications will be presented here. The first modification was the conversion of the single-pass equilibrium system into a closed-loop, vapor-recirculation system by the addition of a diaphragm metering pump and a gas sample loop. This change was made to allow a more rapid attainment of equilibrium. The second modification was the replacement of the copper cell and its equilibrium trays with an empty stainless-steel cell of approximately the same volume. The modified system was very similar in principle to that used by Miller et al. (11).

The system pressures were measured with two Heise Bourdon-tube gauges having ranges of 0-34 and 0-100 atm. The 0-100 atm gauge had been calibrated earlier with a dead-weight gauge. The temperature was measured on IPTS-68 with a calibrated platinum resistance thermometer. The liquid and vapor samples were analyzed on a gas chromatograph equipped with a thermal conductivity detector.

Vapor-pressure measurements were made on the ethane and the carbon dioxide used in the program, and the values obtained are compared with the best available literature values in Table II.

The values of Meyers and Van Dusen (10) were adjusted to IPTS-68; no adjustments were necessary for the ethane values from Goodwin (5). The discrepancy observed at

270.00K is believed due to some slight impurity present during that particular measurement or to operator reading error, since all other values are in excellent agreement. The data of Table II verify the accuracy of the temperature and pressure measurements and the purity of the ethane and carbon dioxide. The methane was Matheson ultrahigh purity grade with a maximum impurity of 0.03%.

Based on observations and calibrations, it is believed that the temperature measurements are accurate to  $\pm 0.01$ K, the pressure measurements accurate to  $\pm 0.03$  atm (34 atm or less) and  $\pm 0.05$  atm (34-100 atm), and the compositions accurate to  $\pm 1.5\%$  of the reported values.

## Results

The results of the experimental program are presented in Table III and IV and in Figures 1-6.

The binary data were tested for consistency in two ways. First, three graphical methods were employed to evaluate the reliability of the low-pressure results for both the liquid and vapor phases, and second, the numerical method of orthogonal collocation was used for the high-pressure data.

The graphical methods were: a plot of the enhancement factor (defined as  $y_1P/p_1^\circ$ ) vs.  $P$ ; a plot of  $K_1P$  vs.  $P$ ; and a graph of  $x_2$  against  $(P - p_1^\circ)$ . The enhancement factor provides an excellent check on the reliability of the low-pressure vapor-phase measurements, since the data must be on a smooth curve extrapolating to a value of one at the ordinate. The plot of  $K_1P$  against  $P$  provides a check of both the liquid and vapor-phase measurements at low pressures, since the data must be on a smooth curve extrapolating to a value of  $p_1^\circ$ . Finally, the reliability of the liquid-phase measurements may be judged by plotting liquid composition vs. pressure dif-

Table I. Summary of Recent Phase Equilibrium Measurements for Binary Systems

System	Temp range, K	Press range, atm	Lit
CH <sub>4</sub> -C <sub>2</sub> H <sub>6</sub>	130	1-3	(14)
CH <sub>4</sub> -CO <sub>2</sub>	253, 273, 288	26-84	(1)
CO <sub>2</sub> -C <sub>2</sub> H <sub>6</sub>	223-293	5-56	(4)
	242-283	10-49	(6)
	222-289	7-56	(7)
	283-293	30-62	(8)
	253	14-23	(12)
	289	35-56	(13)

Table II. Comparison of Vapor-Pressure Measurements on Ethane and Carbon Dioxide with Literature Values

Component	Temp, K	Vapor press, atm		
		This investigation	Meyers and Van Dusen (10)	Goodwin (5)
CO <sub>2</sub>	230.00	8.80	8.818	...
	250.00	17.62	17.620	...
	270.00	31.53	31.611	...
C <sub>2</sub> H <sub>6</sub>	250.00	12.85	...	12.85

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Table III. Vapor-Liquid Equilibria for Binary Systems

System press, atm	$Y_{CH_4}$	$X_{CH_4}$	$Y_{C_2H_6}$	$X_{C_2H_6}$	$K_{CH_4}$	$K_{C_2H_6}$
CH <sub>4</sub> -C <sub>2</sub> H <sub>6</sub> , 250.00K						
12.85	0.00	0.00	1.00	1.00	...	1.00
15.10	0.134	0.024	0.866	0.976	5.702	0.887
22.00	0.365	0.089	0.635	0.911	4.101	0.697
22.50	0.383	0.097	0.617	0.903	3.948	0.683
32.50	0.540	0.196	0.460	0.804	2.755	0.572
34.00	0.554	...	0.446	...	...	...
45.00	0.643	0.320	0.357	0.680	2.009	0.525
55.20	0.673	0.426	0.327	0.574	1.580	0.570
65.70	0.673	0.546	0.327	0.454	1.233	0.720
67.50	Single-phase region					
System press, atm	$Y_{CH_4}$	$X_{CH_4}$	$Y_{CO_2}$	$X_{CO_2}$	$K_{CH_4}$	$K_{CO_2}$
CH <sub>4</sub> -CO <sub>2</sub> , 230.00K						
8.80	0.00	0.00	1.00	1.00	...	1.00
15.00	0.399	0.027	0.601	0.973	14.67	0.618
20.00	0.525	0.050	0.475	0.950	10.50	0.500
32.00	0.683	0.115	0.317	0.885	5.94	0.398
40.00	0.728	0.170	0.277	0.830	4.28	0.328
48.00	0.751	0.235	0.249	0.765	3.20	0.325
55.00	0.764	0.318	0.236	0.686	2.43	0.344
61.10	0.752	0.397	0.248	0.603	1.89	0.411
62.00	0.762	0.394	0.238	0.606	1.93	0.393
65.00	0.757	0.472	0.243	0.528	1.60	0.461
68.00	0.751	0.534	0.249	0.466	1.41	0.534
68.44	0.732	0.526	0.268	0.474	1.39	0.565
69.08	0.730	0.543	0.270	0.457	1.34	0.591
69.81	0.725	0.561	0.275	0.439	1.29	0.626
70.47	0.716	0.584	0.284	0.416	1.23	0.683
70.81	Single-phase region					
CH <sub>4</sub> -CO <sub>2</sub> , 250.00K						
17.62	0.00	0.00	1.00	1.00	...	1.00
20.00	0.104	0.010	0.896	0.990	10.40	0.905
23.32	0.223	0.023	0.777	0.977	9.70	0.795
24.68	0.254	...	0.746	...	...	...
30.00	0.361	0.053	0.639	0.947	6.81	0.675
40.00	0.491	0.105	0.509	0.895	4.68	0.569
50.00	0.575	0.166	0.425	0.834	3.46	0.510

System press, atm	$Y_{CH_4}$	$X_{CH_4}$	$Y_{CO_2}$	$X_{CO_2}$	$K_{CH_4}$	$K_{CO_2}$
CH <sub>4</sub> -CO <sub>2</sub> , 250.00K						
60.00	0.605	0.237	0.395	0.763	2.55	0.518
70.00	0.615	0.326	0.385	0.674	1.89	0.571
77.00	0.605	0.400	0.395	0.600	1.51	0.658
78.50	0.564	0.405	0.436	0.595	1.39	0.733
79.88	0.558	0.446	0.442	0.554	1.25	0.798
80.70	Single-phase region					
CH <sub>4</sub> -CO <sub>2</sub> , 270.00K						
31.53	0.00	0.00	1.00	1.00	...	1.00
35.09	0.083	0.014	0.917	0.986	6.09	0.930
36.53	0.108	0.018	0.892	0.982	5.95	0.908
39.75	0.162	0.032	0.838	0.968	5.09	0.866
41.59	0.190	0.040	0.810	0.960	4.78	0.844
49.97	0.282	0.077	0.718	0.923	3.68	0.778
57.81	0.353	0.113	0.647	0.887	3.13	0.730
69.29	0.405	0.166	0.595	0.834	2.43	0.714
79.58	0.411	0.260	0.589	0.740	1.58	0.795
84.08	0.375	0.319	0.625	0.681	1.17	0.919
84.81	Single-phase region					

System press, atm	$Y_{C_2H_6}$	$X_{C_2H_6}$	$Y_{CO_2}$	$X_{CO_2}$	$K_{C_2H_6}$	$K_{CO_2}$
C <sub>2</sub> H <sub>6</sub> -CO <sub>2</sub> , 250.00K						
12.85	1.00	1.00	0.00	0.00	1.00	...
14.23	0.8885	0.9556	0.1115	0.0444	0.9298	2.511
15.68	0.7774	0.8965	0.2226	0.1035	0.8672	2.151
16.93	0.6991	0.8320	0.3009	0.1680	0.8403	1.791
18.04	0.6303	0.7755	0.3697	0.2245	0.8128	1.647
19.23	0.5526	0.6917	0.4447	0.3083	0.7989	1.451
20.03	0.4964	0.6020	0.5056	0.3980	0.8213	1.270
20.56	0.4478	0.5308	0.5522	0.4692	0.8436	1.177
20.99	0.3735	0.4010	0.6265	0.5990	0.9314	1.046
21.07	0.3198	0.3100	0.6802	0.6900	1.032	0.9858
20.80	0.2533	0.2092	0.7467	0.7908	1.211	0.9442
19.99	0.1783	0.1171	0.8217	0.8829	1.523	0.9307
19.40	0.1304	0.0740	0.8696	0.9260	1.762	0.9391
18.51	0.0622	0.0299	0.9378	0.9701	2.080	0.9667
17.62	0.00	0.00	1.00	1.00	...	1.000

Table IV. Vapor-Liquid Equilibria for Ternary System CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub>-CO<sub>2</sub> at 250.00K

System press, atm	$Y_{CH_4}$	$Y_{C_2H_6}$	$Y_{CO_2}$	$X_{CH_4}$	$X_{C_2H_6}$	$X_{CO_2}$	$K_{CH_4}$	$K_{C_2H_6}$	$K_{CO_2}$	
21.00	0.0265	0.4432	0.5303	0.0033	0.4512	0.5455	8.030	0.9823	0.9721	
	0.1728	0.5700	0.2572	...	...	...	...	...	...	
	0.1602	0.5615	0.2783	...	...	...	...	...	...	
	0.2500	0.6200	0.1300	0.0352	0.7898	0.1750	7.102	0.7850	0.7429	
	0.0288	0.2007	0.7715	...	...	...	...	...	...	
	0.0374	0.1700	0.7926	0.0020	0.1198	0.8782	18.70	1.419	0.9025	
	0.0400	0.1600	0.8000	0.0022	0.0986	0.8992	18.18	1.623	0.8897	
	0.0235	0.2154	0.7611	...	...	...	...	...	...	
	25.00	0.3521	0.5377	0.1102	0.0999	0.8189	0.0812	3.525	0.6566	1.357
		0.3264	0.5264	0.1472	0.0950	0.8097	0.0953	3.436	0.6501	1.545
0.1901		0.4148	0.3951	0.0508	0.5792	0.3700	3.742	0.7162	1.068	
0.1323		0.2937	0.5740	0.0298	0.3157	0.6545	4.439	0.9303	0.8770	
0.1387		0.2601	0.6012	0.0282	0.2662	0.7056	4.918	0.9771	0.8520	
0.1701		0.1623	0.6676	0.0247	0.1392	0.8361	6.887	1.1660	0.7985	
0.2464		0.4730	0.2806	...	...	...	...	...	...	
30.00	0.4021	0.4531	0.1448	0.1351	0.7350	0.1300	2.976	0.6165	1.1138	
	0.2605	0.2845	0.4550	0.0705	0.3741	0.5554	3.695	0.7605	0.8192	
	0.2580	0.2420	0.5000	0.0685	0.3250	0.6064	3.766	0.7446	0.8245	
	0.3025	0.0935	0.6040	...	...	...	...	...	...	
	0.2630	0.2270	0.5100	0.0520	0.2495	0.7085	5.058	0.9098	0.7198	
	0.3448	0.4182	0.2370	0.1203	0.6652	0.2145	2.966	0.6287	1.1050	

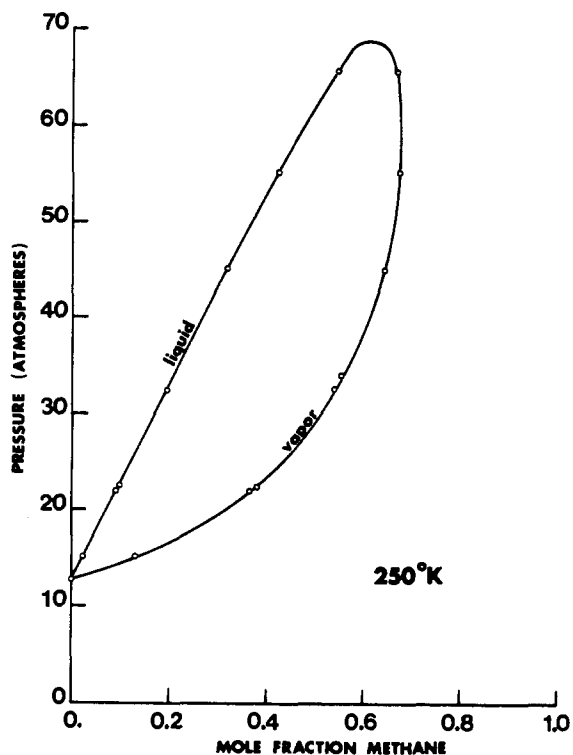


Figure 1. Liquid-vapor equilibria in methane-ethane system

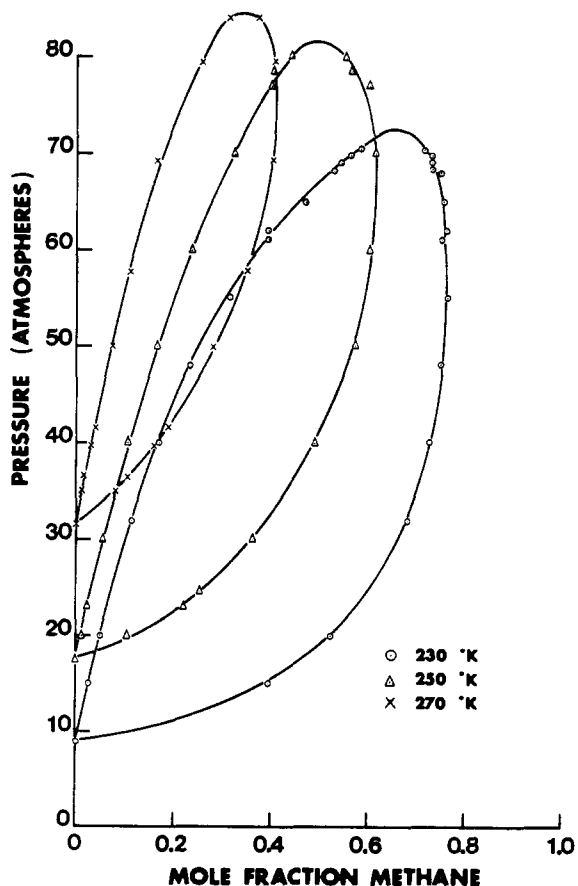


Figure 2. Liquid-vapor equilibria in methane-carbon dioxide system

ference and determining if the data lie on a smooth curve (or a straight line at very low concentrations) through the origin. The results of these graphical tests applied to the data of Table III confirm the internal and thermodynamic consistency of the low-pressure measurements.

A good indication of the reliability of the high-pressure data may be obtained by application of the numerical method of orthogonal collocation, as suggested by Christiansen and Frendsiund (3). This method tests the reliability of high-pressure vapor-liquid data by using the measured values of  $T$ ,  $P$ , and  $x$  to calculate  $y$ , and then comparing the calculated and experimental  $y$  values. The application of their method to the  $\text{CH}_4$ - $\text{C}_2\text{H}_6$  and the  $\text{C}_2\text{H}_6$ - $\text{CO}_2$  data of Table III results in average differences between the calculated and experimental  $y$  values for the two systems of 0.85 and 0.37%, respectively, again confirming the consistency of the data.

The isotherms of methane-ethane and methane-carbon dioxide are typical for systems having one component above its critical point. The estimated critical pressures for these isotherms are: methane-ethane, 67.4 atm at 250.00K; methane-carbon dioxide, 70.7, 80.6, and 84.7 atm at 230.00, 250.00, and 270.00K, respectively. These values are in good agreement with critical locus values reported by previous investigators (9).

The ethane-carbon dioxide system exhibits atypical behav-

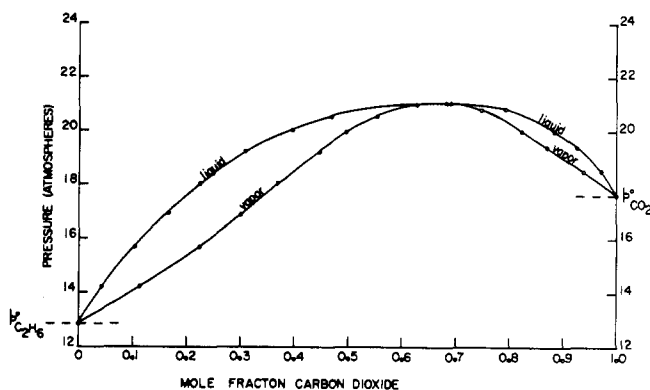


Figure 3. Liquid-vapor equilibria in carbon dioxide-ethane system at 250.00K

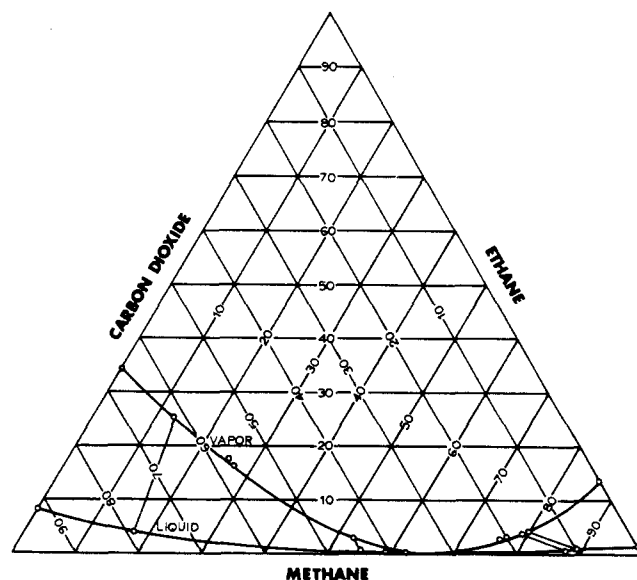


Figure 4. Ternary system at 21.0 atm and 250.00K

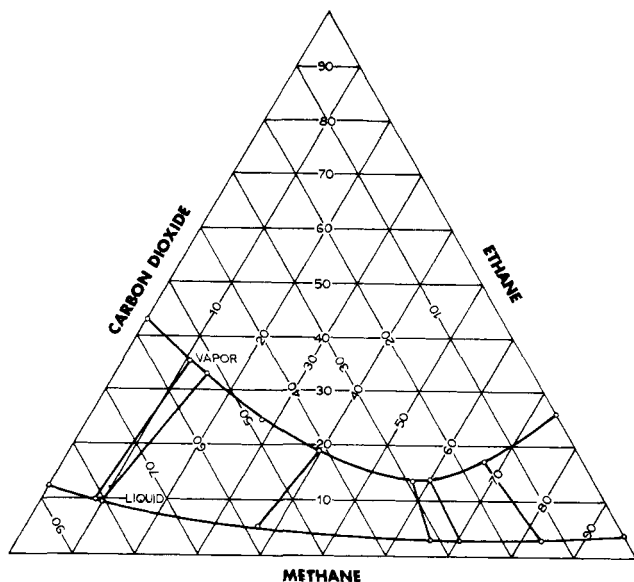


Figure 5. Ternary system at 25.0 atm and 250.00K

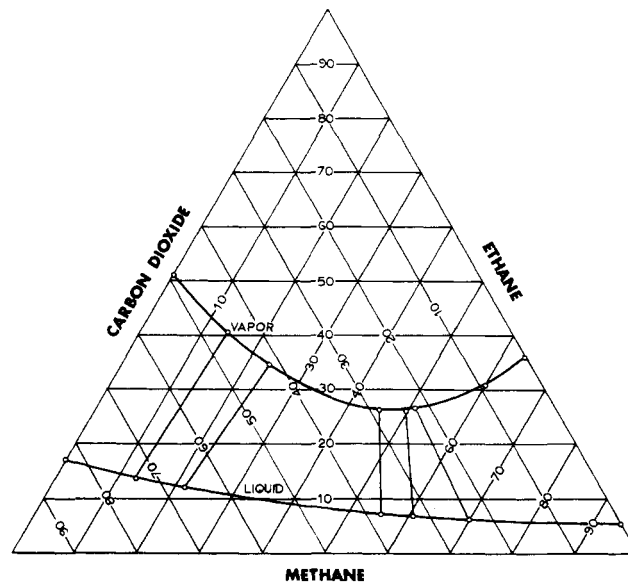


Figure 6. Ternary system at 30.0 atm and 250.00K

ior in the form of an azeotrope at 21.0 atm and a carbon dioxide mole fraction of 0.67, values that are in excellent agreement with Fredenslund and Mollerup (4).

An interesting feature of the ternary system is the behavior of the minimum in the vapor curve of Figures 4-6. A graph of pressure vs. percent ethane at the minimum in the vapor curve is a straight line beginning at the  $C_2H_6-CO_2$  azeotrope at 21.00 atm.

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#### Nomenclature

$$K = y/x$$

$$P = \text{total system pressure}$$

$$p^\circ = \text{vapor pressure}$$

$$T = \text{temperature}$$

$$x = \text{liquid-phase mole fraction}$$

$$y = \text{vapor-phase mole fraction}$$

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