

Vapor-Liquid Equilibrium of the CH₄-CO₂ System at Low Temperatures

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This paper reports the bubble-point compositions in the low-temperature region of the methane-carbon dioxide phase diagram. Liquid compositions in equilibrium with vapor were measured as a function of pressure on isotherms at -65.00, -81.40, -94.00, -112.00, -130.00, -148.00, and -184.00 °F (-53.89, -63.00, -70.00, -80.00, -90.00, -100.00, and -120.00 °C). The smoothed results were combined with previous dew-point data to provide tables and plots of isobaric and isothermal *K* values. The experimental method used was the vapor-recycle method in a temperature-controlled equilibrium cell with chromatographic analysis of the phases.

Introduction

Pikaar (7) reported the compositions of the liquid phase in equilibrium with solid CO₂ and of the vapor phase in equilibrium with solid CO₂ in the solid-liquid and solid-vapor regions, respectively, of the phase diagram for the system methane-carbon dioxide. Hwang et al. (4) reported the compositions of the vapor phase in equilibrium with liquid in the liquid-vapor region of the diagram. In order to complete the phase diagram of this important system, the present work was undertaken to determine the liquid compositions in the same liquid-vapor region as that studied by Hwang et al. For a typical example of the isothermal phase diagrams of the CH₄-CO₂ system at low temperatures, see Figure 1, which shows those portions of the diagram which have been determined by the various investigators. Hwang et al. chose to work on isotherms such that many of their temperatures would correspond to those reported in the earlier work of Pikaar. The same strategy has been followed in the present work, in that all of the isotherms reported here (except for that at -65.00 °F, which is above the triple point of CO₂) correspond exactly to temperatures studied by both Pikaar and Hwang et al.

A literature review of the previous investigations on this system has been given by Hwang et al. (4).

Calibration of the Chromatographic System

The method of calibration of the chromatographic system has been described in detail (6). Briefly it consists of preparing a calibration curve of thermal conductivity detector response vs. known compositions of CH₄-CO₂ gas mixtures. Individual streams of CH₄ and CO₂ of known molar flow rates are pumped by two precision positive displacement pumps into a mixing valve. In this manner gas streams ranging in composition from 0.02 to 0.997 mol fraction CH₄ are prepared and passed into the chromatographic system for analysis. The resulting calibration curve is then used to determine the compositions of mixtures withdrawn from the equilibrium cell during the low-temperature measurements.

Experimental Apparatus and Procedure

For the present measurements, a new vapor-liquid equilibrium cryostat was constructed in the Chemical Engineering Machine Shop at Rice University. This apparatus is essentially an improved version of similar cryostats described previously (7). CO₂ and CH₄ are introduced into a stainless steel equilibrium cell held

at low temperatures in a bath of isohexane, which is then further cooled to the desired temperature. The bath is under a cooling load produced by liquid nitrogen circulating through copper coils; in order to maintain the temperature constant at the desired value, the cooling is balanced by heat supplied by a Thermotrol (10) temperature controller, which maintains the temperature constant to generally better than ±0.02 °F (±0.01 °C). The temperature is determined with a Leeds and Northrup platinum thermometer, mounted in the wall of the equilibrium cell, whose resistance is measured on a Leeds and Northrup Mueller bridge. The galvanometer signal from the bridge is fed to a null detector, whose output in turn is fed to a strip chart recorder. In this way, deviations from the set temperature can be monitored continuously.

The vapor in the cell is recycled through the liquid by means of a magnetic pump (8) until equilibrium is achieved. Pressure in the cell is measured by means of precision Heise gauges. The equilibrium cell is equipped with glass windows, and the bath Dewar is windowed, so the phases can be visually observed in the cell.

After equilibrium is reached, the sample line to the chromatograph is evacuated, and a valve mounted on the cell is opened to withdraw sample into the line. There are valves located at the top, middle, and bottom of the cell, so that either a liquid or a vapor sample can be taken. The parts of the sample lines which pass through the bath fluid are heated to ensure immediate vaporization of the sample. Before entering the chromatographic oven, the sample streams enter a stainless steel mixing vessel, consisting of a Teflon-coated stirring bar which, when magnetically driven, agitates a number of glass beads against the walls and lid of the vessel. The emerging gas stream is thus ensured of complete homogeneity. This stream is then taken into the chromatographic unit and analyzed, using the calibration curve to determine the composition of the unknown sample from its detector response.

A twin 250-cm³ capacity positive displacement pump is connected to the equilibrium cell to provide a means of adjusting the pressure in the cell. When very low temperatures are desired, the equilibrium cell is cooled with only pure CH₄ present in order to prevent the formation of solid CO₂ upon cooling. With the valve to the cell closed, a mixture is prepared in the 500-cm³ pump at room temperature at approximately the right composition to give only liquid and vapor phases at the low temperature of the cell. To ensure homogeneity, this mixture is cycled back and forth between the twin 250-cm³ cylinders of the 500-cm³ pump. When the mixture is let into the cell, a liquid phase invariably condenses without the danger of solid CO₂ formation.

Materials

The methane used in this research was Matheson purity CH₄ (minimum purity 99.99%), and the carbon dioxide used was Coleman Instrument Grade CO₂ (minimum purity 99.99%), both from Matheson Gas Products. All materials were used as received without further purification.

Experimental Results

To check the performance of the new apparatus against previous, well-established equipment, vapor compositions were

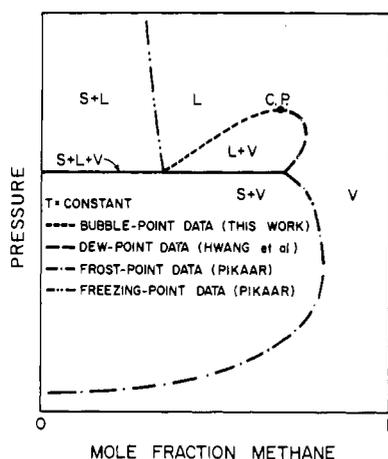


Figure 1. Schematic phase diagram for the methane-carbon dioxide system at low temperature.

Table I. Comparison of Present Data with Previous Work^a

$t, ^\circ\text{F}$	P, psia	Mole fraction CO_2 in vapor phase				% difference
		Hwang et al.	This work	Difference		
-65.0	700	0.205	0.1922	0.0128	6.2	
	800	0.2003	0.1885	0.0118	5.9	
	900	0.211	0.1973	0.0137	6.5	
-81.4	800	0.148	0.1412	0.0068	4.6	
	-94.0	750	0.1054	0.1025	0.0029	2.8
-112.0	770	0.110	0.1064	0.0036	3.3	
	625	0.0512	0.0510	0.0002	0.4	
	640	0.0446	0.0457	-0.0011	-2.5	
	650	0.0409	0.0418	-0.0009	-2.2	
	670	0.0323	0.0331	-0.0008	-2.5	

^a Reference 4.

measured at several temperatures and compared to those measured by the elution method of Hwang et al. (4). When plotted vs. pressure at a given temperature, the present data at the higher temperatures fell on a curve parallel to the previous work but displaced in composition. Typical data are shown in Table I.

It was originally thought that each apparatus had an approximate error of about 1% in the ability to determine the mole fraction of carbon dioxide in a given mixture. Several factors that might have been able to produce the larger discrepancies of Table I were carefully investigated, but no satisfactory answer was discovered. It seems probable, therefore, that the original estimates of a 1% accuracy in calibration combined with low-temperature sampling may have been too optimistic for both methods, and perhaps a $\pm 2\%$ total error would be more realistic for each method.

It should be pointed out, however, that the difference between the present work and that of Hwang et al. is still not a tremendous amount, and the difference gradually decreases with decreasing CO_2 concentration until, at -112°F , there is no real discrepancy, even on a percentage basis, outside of experimental error. No comparisons between the two apparatus were made at temperatures lower than -112°F . However, as can be seen from Figure 3, the excellent extrapolation of the liquid-phase data to the accurately known vapor pressure of pure CH_4 would seem to preclude any chance of a serious error at the temperatures -130°F and -148°F .

All the experimental data are shown in Table II and Figures 2 and 3, which are largely self-explanatory. Note that there is an inflection point in each of the liquidus curves for temperatures above the critical point of methane. It should also be pointed out that the data at -184°F were taken under rather severe conditions. Since the calibration curve for sample analysis only

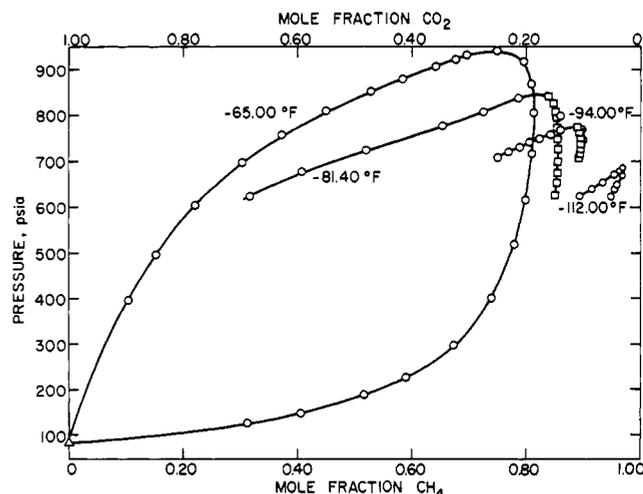


Figure 2. Pressure-composition diagram for the methane-carbon dioxide system for temperatures above critical temperature of methane: O, this work; □, Hwang et al. (4); Δ, vapor pressure of CO_2 from ref 9.

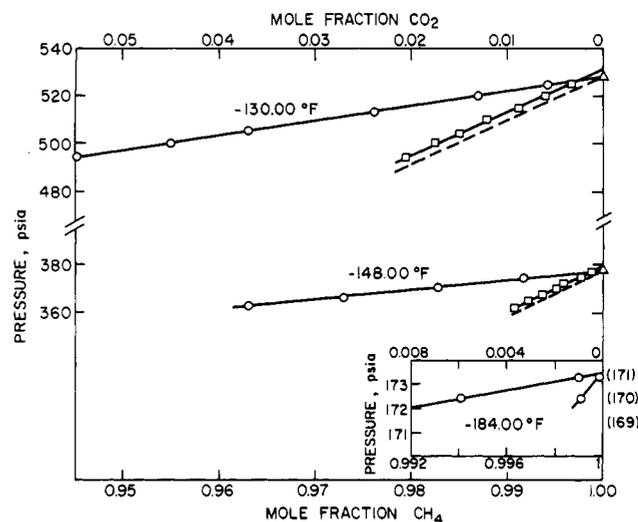


Figure 3. Pressure-composition diagram for the methane-carbon dioxide system for temperatures below critical temperature of methane: O, this work; □, Hwang et al. (4); Δ, vapor pressure of methane from ref 11 and 12. The dotted lines at -130°C and -148°C represent the vapor lines "normalized" for slight Heise gauge discrepancies. The pressures in parentheses at -184°F represent pressures when the lines are "normalized" to the known vapor pressure of methane, 171.0 psia, from ref 11 and 12.

extended to 0.997 mol fraction methane (0.003 CO_2), three of the compositions reported at -184°F are beyond the range of calibration, and the fourth is on the very end of it.

To arrive at these approximate values for composition, the calibration data were extrapolated. Therefore, the points at -184°F must carry more than the usual uncertainty in composition. Furthermore, it will be seen that all the pressures reported at -184°F are actually above the accepted vapor pressure of pure CH_4 (171.0 psia) (11, 12). This is especially surprising since the results at -130°F and -148°F extrapolate perfectly to the correct vapor pressure of CH_4 (Figure 3). The discrepancy in pressure at -184°F can only be attributed to the 1000 psia Heise gauge used in the present work, whose stated accuracy is ± 1 psia, but which, it must be assumed, could have been off in this case by about 2.5 psia. Despite all these complications, it still appears that the data at -184°F are of some value, since the pressures can be corrected to the true pressures, and all four compositions at this temperature were taken from the extrapolated calibration curve described above. Therefore there should be a good measure of relative consistency among them,

Table II. Experimental Vapor-Liquid Equilibrium Data for the Methane-Carbon Dioxide System

Pressure, psia	Mole Fraction of CO ₂	Pressure, psia	Mole Fraction of CO ₂
<i>t</i> = -65.00 °F = -53.89 °C			
Liquid		Liquid	
84.4 ^a	1.0000	625.0	0.6825
396.0	0.8965	675.0	0.5944
495.1	0.8493	725.0	0.4795
601.7	0.7811	776.4	0.3478
698.0	0.6972	809.7	0.2761
757.0	0.6265	839.4	0.2152
807.9	0.5512		
852.2	0.4735	Vapor	
880.7	0.4175	799.0	0.1412
909.2	0.3606	Critical	
925.1	0.3242	845.5	
932.8	0.3061	<i>t</i> = -94.00 °F = -70.00 °C	
935.9	0.2969		
Vapor		Liquid	
84.4 ^a	1.0000	710.1	0.2509
125.6	0.6889	720.0	0.2317
147.9	0.5951	730.0	0.2121
186.1	0.4859	740.0	0.1949
225.2	0.4131	750.0	0.1771
297.9	0.3280	760.3	0.1593
399.8	0.2620	770.3	0.1407
515.7	0.2222	Vapor	
615.7	0.2021	750.0	0.1025
717.8	0.1911	770.2	0.1064
805.8	0.1884	Critical	
870.9	0.1925	775.2	0.1216
919.9	0.2046	<i>t</i> = -148.00 °F = -100.00 °C	
Critical		Liquid	
940.8	0.2517	362.3	0.0370
<i>t</i> = -112.00 °F = -80.00 °C			
Liquid		Liquid	
625.0	0.1083	366.4	0.0270
640.0	0.0864	370.4	0.0172
655.0	0.0672	374.0	0.0083
670.0	0.0491	377.8 ^b	0.0000
680.0	0.0378	<i>t</i> = -184.00 °F = -120.00 °C ^c	
685.0	0.0326	Liquid	
Vapor		172.4	0.0059
625.0	0.0510	173.3	0.00105
639.9	0.0457	Vapor	
650.0	0.0418	172.4	0.00099
670.0	0.0331	173.3	0.00016
Critical			
687.5			
<i>t</i> = -130.00 °F = -90.00 °C			
Liquid			
494.2	0.0547		
500.0	0.0451		
504.9	0.0370		
513.0	0.0238		
520.0	0.0130		
524.9	0.0058		
528 ^b	0.0000		

^a Vapor pressure of pure CO₂ from ref 9. ^b Vapor pressure of pure CH₄ from ref 11, 12. ^c For explanation of how this isotherm was treated, see text.

and the *K* values taken from them should be of value.

Smoothed Data and *K* Values

The data of Table II were combined with those reported for the dew-point compositions by Hwang et al. (4) to provide smoothed values for the vapor-liquid equilibria of the meth-

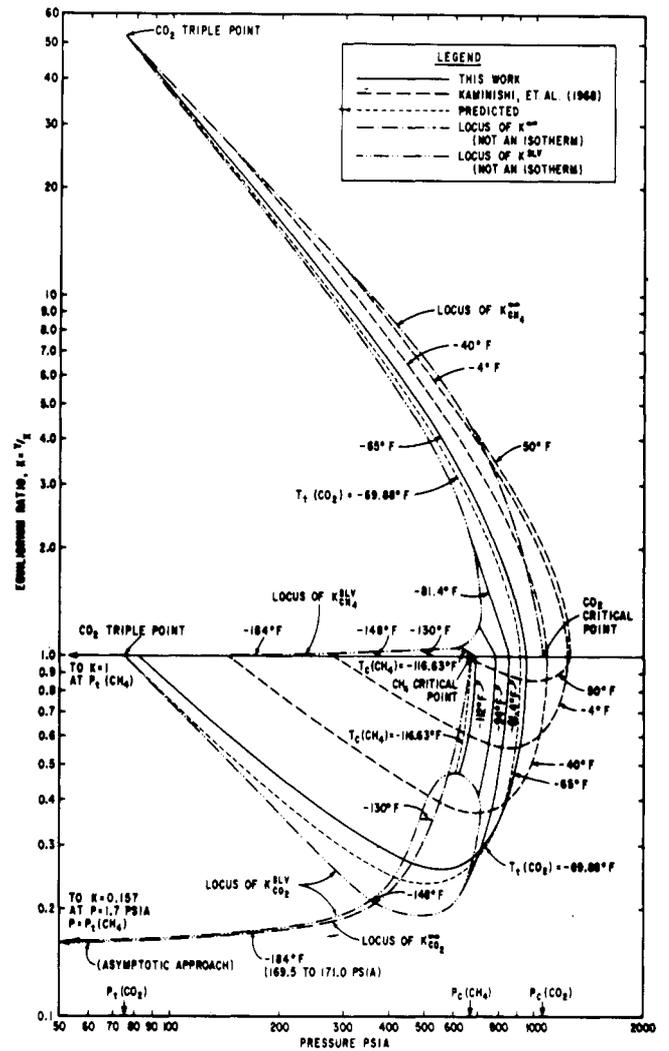


Figure 4. Isothermal *K* values for the methane-carbon dioxide system.

ane-carbon dioxide system. Because of the slight discrepancies between the two sets of data, certain judgments were made in order to treat the data such that the two sets would be "normalized" against each other. In this fashion each set was recognized to have high internal precision and was therefore adjusted slightly at each temperature in order to match the other at some common point. Thus the *K* values would be expected to be much better than those that could be calculated from the two separate sets of raw data.

At -65 °F, the experimental data from this work were smoothed to give liquid and vapor compositions at even pressures. At -81.4 and -94.0 °F, the shapes of the dew-point curves from the previous study (4) were used but were displaced by a small amount to land on the one or two dew-point data from this work. At -112.0 °F, since the discrepancies between the two sets of data (see Table I) are within the experimental error, the dew-point data from previous work (4) were combined with the bubble-point data to provide the *K* values.

For the three lowest temperatures (-130.0, -148.0, and -184.0 °F), the experimental results indicate that the pressure-composition curves, i.e., isothermal *P*-*x* and *P*-*y* curves, are linear. In this case, the *K* values can be calculated from the vapor pressure of methane and the slopes of both *P*-*x* and *P*-*y* curves (see Appendix).

The smoothed vapor-liquid equilibrium data are shown in Table III. Note the constancy of the *K* values for carbon dioxide for each of the three lowest temperatures.

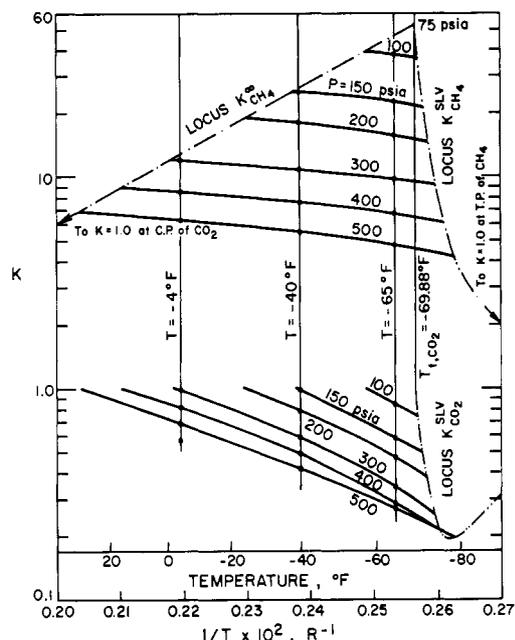
Figure 4 presents the data in the form of *K* values vs. pressure. Figure 5 and Table IV show the smoothed (from *K*-*P*

Table III. Smoothed Vapor-Liquid Equilibrium Data of Methane-Carbon Dioxide System

P , psia	P , atm	x_{CH_4}	y_{CH_4}	K_{CH_4}	K_{CO_2}
$t = -65.00^\circ F = -53.89^\circ C$					
84.4 ^a	5.74	0.0	0.0	46.40 ^b	1.00
100	6.80	0.0049	0.1860	37.96	0.8180
200	13.61	0.0355	0.5461	15.38	0.4706
300	20.41	0.0681	0.6745	9.905	0.3493
400	27.22	0.1054	0.7384	7.006	0.2924
500	34.02	0.1535	0.7740	5.042	0.2670
600	40.83	0.2180	0.7960	3.651	0.2609
700	47.63	0.3056	0.8078	2.643	0.2768
800	54.44	0.4368	0.8115	1.858	0.3347
900	61.24	0.6204	0.8027	1.294	0.5198
920	62.60	0.6620	0.7948	1.201	0.6071
939 ^c	63.83	0.7483	0.7483	1.000	1.0000
$t = -81.40^\circ F = -63.00^\circ C$					
612 ^d	41.64	0.3062	0.8482	2.770 ^e	0.2188 ^f
625	42.53	0.3175	0.8568	2.699	0.2098
650	44.23	0.3604	0.8587	2.383	0.2209
675	45.93	0.4056	0.8596	2.119	0.2362
700	47.63	0.4555	0.8602	1.888	0.2567
725	49.33	0.5205	0.8609	1.654	0.2901
750	51.03	0.5881	0.8610	1.464	0.3375
775	52.74	0.6486	0.8608	1.327	0.3961
800	54.44	0.7018	0.8587	1.224	0.4738
825	56.14	0.7544	0.8539	1.132	0.5949
845 ^c	57.50	0.8370	0.8370	1.000	1.0000
$t = -94.00^\circ F = -70.00^\circ C$					
700 ^d	47.63	0.7307	0.8914	1.220 ^e	0.4033 ^f
710	48.31	0.7491	0.8952	1.195	0.4177
720	48.99	0.7683	0.8962	1.166	0.4480
730	49.67	0.7879	0.8973	1.139	0.4842
740	50.35	0.8051	0.8976	1.115	0.5254
750	51.03	0.8229	0.8978	1.091	0.5771
760	51.71	0.8388	0.8967	1.069	0.6408
770	52.40	0.8568	0.8933	1.043	0.7451
774 ^c	52.67	0.8784	0.8784	1.000	1.0000
$t = -112.00^\circ F = -80.00^\circ C$					
622 ^d	42.32	0.8853	0.9473	1.0700 ^e	0.4595 ^f
630	42.87	0.8992	0.9507	1.0573	0.4891
640	43.55	0.9136	0.9554	1.0457	0.5162
650	44.23	0.9272	0.9591	1.0344	0.5618
660	44.91	0.9385	0.9635	1.0266	0.5935
670	45.59	0.9517	0.9677	1.0168	0.6687
680	46.27	0.9622	0.9718	1.0100	0.7460
687 ^c	46.75	0.9736	0.9736	1.0000	1.0000
$t = -130.00^\circ F = -90.00^\circ C$					
487.3 ^d	33.16	0.9350	0.9770	1.0449 ^e	0.3540 ^f
490.0	33.34	0.9393	0.9785	1.0418	0.3540
500.0	34.02	0.9553	0.9842	1.0303	0.3540
510.0	34.70	0.9712	0.9898	1.0191	0.3540
520.0	35.38	0.9872	0.99547	1.0084	0.3540
528.0 ^h	35.93	1.000	1.000	1.0000	0.3540 ⁱ
$t = -148.00^\circ F = -100.00^\circ C$					
357.7 ^d	24.34	0.9507	0.9896	1.0409 ^e	0.2112 ^f
360	24.50	0.9563	0.99078	1.0360	0.2112
365	24.84	0.9686	0.99337	1.0256	0.2112
370	25.18	0.9809	0.99596	1.0154	0.2112
377.8 ^h	25.71	1.0000	1.0000	1.0000	0.2112 ⁱ
$t = -184.00^\circ F = -120.00^\circ C$					
169.5 ^d	11.53	0.99192	0.99859	1.0067 ^e	0.1751 ^f
170.0	11.57	0.99461	0.999057	1.0045	0.1751
170.5	11.60	0.99730	0.999528	1.0022	0.1751
171.0 ^h	11.64	1.0000	1.0000	1.0000	0.1751 ⁱ

^a Vapor pressure of carbon dioxide from ref 9. ^b $K_{CH_4}^\infty$.
^c Critical point of mixture. ^d Triple-point pressure mixture from ref 2 and 3. ^e $K_{CH_4}^{SLV}$. ^f $K_{CO_2}^{SLV}$. ^g See Appendix for explanation of how these isotherms were treated. ^h Vapor pressure of methane from ref 11 and 12. ⁱ $K_{CO_2}^\infty$.

plot) isobaric K values in the high-temperature region.

Figure 5. Isobaric K values for the methane-carbon dioxide system.Table IV. Smoothed Isobaric K Values for Methane-Carbon Dioxide System

P , psia	t , $^\circ F$	K_{CO_2}	K_{CH_4}
150	-38.6 ^a	1.0	25.5 ^b
	-40.0	0.974	25.3
	-65.0	0.587	22.6
	-69.88 ^c	0.515	21.8
	-71.5 ^d	0.500 ^e	21.4 ^f
200	-23.6 ^a	1.0	18.9 ^b
	-40.0	0.782	18.0
	-65.0	0.464	15.8
	-69.88 ^c	0.409	14.9
	-72.5 ^d	0.370 ^e	14.6 ^f
300	-0.9 ^a	1.0	12.1 ^b
	-4.0	0.960	12.0
	-40.0	0.583	10.8
	-65.0	0.343	9.60
	-69.88 ^c	0.295	9.40
400	-74.5 ^d	0.248 ^e	9.10 ^f
	16.5 ^a	1.0	8.80 ^b
	-4.0	0.800	8.39
	-40.0	0.480	7.50
	-65.0	0.289	6.57
500	-69.88 ^c	0.251	6.34
	-76.5 ^d	0.200 ^e	6.00 ^f
	31.4 ^a	1.0	6.80 ^b
	-4.0	0.702	6.27
	-40.0	0.418	5.50
	-65.0	0.263	4.77
	-69.88 ^c	0.239	4.56
	-79.0 ^d	0.197 ^e	4.11 ^f

^a Saturation temperature of carbon dioxide from ref 9.
^b $K_{CH_4}^\infty$. ^c Triple-point temperature of carbon dioxide from ref 9. ^d Triple-point temperature of mixture from ref 2 and 3.
^e $K_{CO_2}^{SLV}$. ^f $K_{CH_4}^{SLV}$.

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Appendix. *K* Values for the Methane–Carbon Dioxide System at Low Temperatures

The linear relationships between the system pressure and compositions can be expressed as

$$P = m^L x_{\text{CO}_2} + b^L \quad (1)$$

and

$$P = m^V y_{\text{CO}_2} + b^V \quad (2)$$

where P = system pressure, x_{CO_2} = mole fraction of CO_2 in the liquid phase, y_{CO_2} = mole fraction of CO_2 in the vapor phase, m^L, m^V = slopes of the P - x_{CO_2} and P - y_{CO_2} curves, respectively, and b^L, b^V = intercepts of eq 1 and 2 at $x_{\text{CO}_2} = y_{\text{CO}_2} = 0$.

When $x_{\text{CO}_2} = y_{\text{CO}_2} = 0$, the system pressure will be equal to the vapor pressure of pure methane ($P^*_{\text{CH}_4}$) at system temperature. Thus

$$b^L = b^V = P^*_{\text{CH}_4}$$

Therefore, eq 1 and 2 become

$$P = m^L x_{\text{CO}_2} + P^*_{\text{CH}_4} \quad (3)$$

$$P = m^V y_{\text{CO}_2} + P^*_{\text{CH}_4} \quad (4)$$

then

$$\begin{aligned} K_{\text{CO}_2} &\equiv y_{\text{CO}_2}/x_{\text{CO}_2} \\ &= \frac{(P - P^*_{\text{CH}_4})/m^V}{(P - P^*_{\text{CH}_4})/m^L} \\ &= \frac{m^L}{m^V} \\ &= \frac{\text{slope of } P\text{-}x_{\text{CO}_2} \text{ curve}}{\text{slope of } P\text{-}y_{\text{CO}_2} \text{ curve}} \end{aligned}$$

= function of system temperature only

and

$$\begin{aligned} K_{\text{CH}_4} &\equiv y_{\text{CH}_4}/x_{\text{CH}_4} \\ &= (1 - y_{\text{CO}_2})/(1 - x_{\text{CO}_2}) \\ &= \frac{m^L(m^V - P + P^*_{\text{CH}_4})}{m^V(m^L - P + P^*_{\text{CH}_4})} \end{aligned}$$

= function of system temperature and pressure

A least-squares linear regression method was used to fit the experimental P - x_{CO_2} and P - y_{CO_2} data and obtain the slopes for each isotherm. Results are as follows:

$T, ^\circ\text{F}$	$10^{-3} m^L$	$10^{-4} m^V$	$K_{\text{CO}_2} = m^L/m^V$
-130.00	-0.625 71	-0.176 77	0.3540
-148.00	-0.407 69	-0.193 02	0.2112
-184.00	-0.185 57	-0.106 00	0.1751

The smoothed vapor–liquid equilibrium data can be calculated from the following equations at different system pressures:

$$x_{\text{CO}_2} = (P - P^*_{\text{CH}_4})/m^L \quad (5)$$

$$y_{\text{CO}_2} = (P - P^*_{\text{CH}_4})/m^V \quad (6)$$

and

$$K_{\text{CH}_4} = (1 - y_{\text{CO}_2})/(1 - x_{\text{CO}_2}) \quad (7)$$

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On the Solubility of Benzoic Acid in Aqueous Carboxymethylcellulose Solutions

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Solubility of benzoic acid in distilled and demineralized water and aqueous CMC solutions containing 0.5, 1.0, 1.5, and 2.0% polymer by weight has been determined in the temperature range of 15–45 °C. At any given temperature, the solubility in the polymer solution increases with polymer concentration and seems to approach a constant value at higher concentrations.

Introduction

Dissolution rate studies of low-solubility organic compounds such as benzoic acid, 2-naphthol, etc., have been frequently used as a technique in mass transfer investigations with Newtonian fluids. Such solutes have many inherent advantages. They can be easily molded and pelletized into various shapes. Their solubilities are of moderate range and the analytical procedures are simple. Above all, the dissolution of these