Solid-Liquid-Vapor Phase Behavior of the Methane-Carbon Dioxide System

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The phase behavior of the methane-carbon dioxide system has been determined experimentally along the solid-liquid-vapor locus. Pressure-temperature measurements were made along this locus from the triple point of carbon dioxide to —284°F. Compositions of the vapor phase along the solid-liquid-vapor locus were determined with sampling techniques over a composition range of 0.1 to 12% carbon dioxide. Liquid-phase compositions were obtained from crystal-point determinations on eleven methane-carbon dioxide mixtures ranging from 0.16 to 20% carbon dioxide.

With the pressure-temperature for the solid-liquid-vapor locus as the termination locus of the dew and bubble data of Donnelly and Katz (2), consistent liquid- and vapor-phase compositions were obtained over the remaining concentration range.

Changes in the pressure-temperature relationship of the solid-liquid-vapor locus caused by using a methane stock containing 0.56 mole % nitrogen are also reported.

Interest in low-temperature processing of natural gas has increased in recent years. In many cases low-temperature processing may provide a more economical method of removing acid components of a gas than is now offered by more conventional methods. Clark and Kurata (*1*) have suggested such a method for the removal of carbon dioxide from natural gas. In addition to the fact that shipping and storage of natural gas as a liquid offer certain obvious advantages, recent government action in the helium conservation field has created added interest in low-temperature processing.

Since carbon dioxide is a common constituent in natural gases, detailed evaluation of any of the above processes requires a knowledge of the phase behavior of carbon dioxide systems. Of particular importance is a knowledge of those conditions which cause solid formation and subsequent fouling of heat exchangers or plugging of process lines.

Donnelly and Katz (2) have studied the phase behavior of the methane-carbon dioxide system from the critical locus to −110°F., including the upper portion of the solid-liquid-vapor locus. They also present extrapolated three-phase data at lower temperatures. Kohn and Kurata (*4*) investigated three points along the solid-liquid-vapor locus, and their work indicated a discrepancy in the three-phase data of Donnelly and Katz. Sterner (*6*) reported three-phase data taken in the vicinity of the critical temperature of methane (−116°F.). Pikaar (5) presents much of the solid-vapor and solid-liquid behavior in his thesis, but this work has not yet been published.

The experimental work described here was undertaken to determine the solid-liquid-vapor phase behavior of the methane-carbon dioxide binary at lower temperatures corresponding to carbon dioxide concentrations com-

TABLE 1. PRESSURE-TEMPERATURE RELATIONSHIP, SOLID-LIQUID-VAPOR LOCUS, METHANE-CARBON DIOXIDE SYSTEM

Temperature, °F.	Pressure, lb./sq. in. abs.	Temperature, °F.	Pressure, lb./sq. in. abs.
—78.6	470	—164.7	264
—85.1	655	—169.6	236
—90.3	706	—172.7	224
—97.4	699	—186.3	165
—104.1	669	—192.2	142
—108.6	630	—200.6	115
—111.1	627	—208.4	93
—120.5	562	—221.4	63
—127.9	506	—226.5	52
—135.1	454	—232.8	44
—138.8	425	—242.2	31
—140.9	413	—249.9	22.5
—148.0	365	—259.2	14.9
—152.3	338	—269.8	8.9
—154.1	324	—284.1	4.1
—160.3	290		

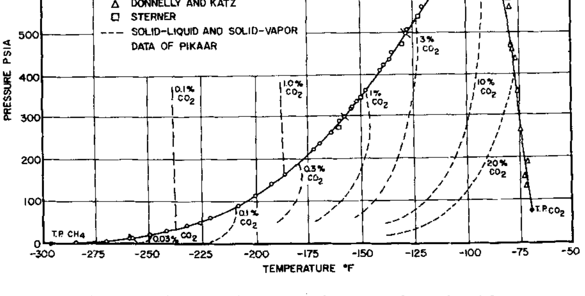

Fig. 1. Solid-liquid-vapor locus methane-carbon dioxide system.

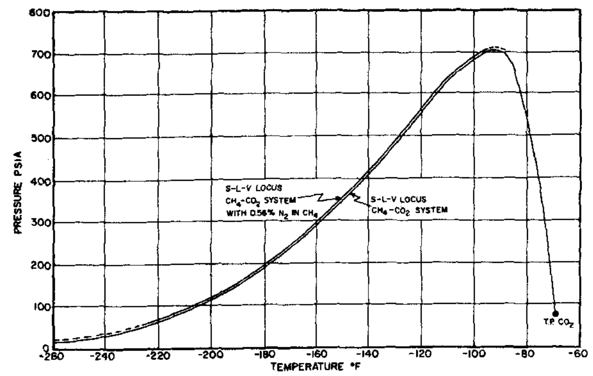

Fig. 2. Effect of nitrogen on solid-liquid-vapor locus methane-carbon dioxide system.

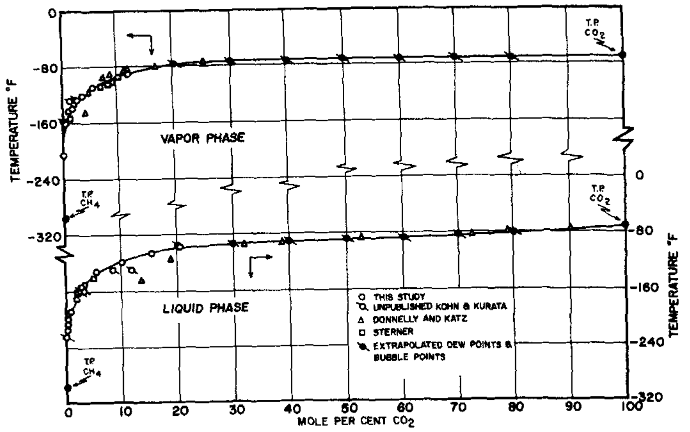

Fig. 3. Composition along solid-liquid-vapor locus methane-carbon dioxide system.

monly encountered in natural gases, and to resolve the discrepancies among published three-phase data at higher temperatures.

EXPERIMENTAL EQUIPMENT

A complete description of the equipment is given by Kohn and Kurata (3). Basically the equipment consisted of a heavy-walled glass equilibrium cell of 5- to 10-ml. volume maintained in a silvered Dewar constant temperature bath. Unsilvered strips on the Dewar allowed visual observation of the cell and its contents. The cell contents were agitated by a magnetically actuated steel ball in the cell.

The Dewar flask was filled with a suitble solvent depending upon the desired bath temperature. The bath was cooled with liquid nitrogen, and control was achieved by adding a small amount of electrical heat through a temperature controller. Bath temperature was controlled to within 0.02°C. of the desired level and was measured with a platinum resistance thermometer with a precision of 0.01°C. A Bourdon tube gauge indicated cell pressure to within 1 lb./sq. in.

Capillary tubes could be mounted inside the equilibrium cell to allow sampling of the various phases.

EXPERIMENTAL PROCEDURES

Solid-Liquid-Vapor Locus

To determine the pressure-temperature relationship of the solid-liquid-vapor locus the bath was first cooled to a few degrees above the triple point of carbon dioxide. The equilibrium cell was evacuated and flushed with carbon dioxide. Then enough carbon dioxide was added to the cell to fill it with 5 to 10% liquid. Methane was added to bring the cell pressure up to about 200 lb./sq. in. abs. The contents of the cell were well agitated and the bath temperature lowered until solid formed in the cell.

When solid forms in the cell there are three phases (solid, liquid, vapor) present in a binary system. Therefore the system is univariant. If the temperature is fixed, the system is completely defined. More methane can then be added to the contents of the equilibrium cell without changing the equilibrium pressure or the phase composition (as long as material balance requirements are met).

The bath temperature was set with three phases present and the contents of the cell agitated until a constant pressure was attained. The pressure and the temperature were noted, the bath temperature was lowered, and the process repeated. After a series of such readings a fraction of the contents of the cell was vented (to remove any nitrogen), and a second series of readings were taken with increasing temperature increments.

Vapor-Phase Composition Along the Solid-Liquid-Vapor Locus

To determine the composition of the vapor phase a capillary tube was inserted into the equilibrium cell as previously described, and samples were removed for analysis. Since the samples were withdrawn from a three-phase binary system with a fixed temperature, the composition of the vapor phase should not change during sampling. The contents of the cell were agitated, while the sample was slowly withdrawn.

Vapor samples containing more than 1% carbon dioxide were analyzed by gas-density measurements, two to four samples being taken at each temperature. Samples containing less than 1% carbon dioxide were analyzed by mass spectrometer.

Liquid-Phase Composition Along the Solid-Liquid-Vapor Locus

By reversing the procedure for determining the vapor composition the difficulties of sampling a liquid in the presence of a solid were eliminated. Thus the composition was fixed, and the bubble temperature experimentally determined where solid appeared and disappeared. Mixtures of methane and carbon dioxide were made up volumetrically and the compositions checked by gas density analysis for mixtures containing more than 1% carbon dioxide and by mass spectrometer for samples containing less than 1% carbon dioxide.

The bath was cooled to a temperature somewhat above the snow point of the mixture (to prevent solid from freezing in the neck of the cell), and the cell was filled to the bubble point. The bath temperature was then slowly lowered, and the mixture of known composition was added as necessary to maintain the liquid level. The temperature was noted when solid first formed in the cell. The bath temperature was then slowly increased until all but a few crystals of solid had melted, and the temperature was again noted. With these few crystals as seed crystals the bath temperature was again lowered until more solid formed. This process was repeated with constant agitation of the cell contents until the difference between the upper and lower temperatures agreed to within 0.1° to 0.3°C. (with the exception of mixtures containing less than 0.5% carbon dioxide, where the determination of the crystal point was somewhat more difficult and the temperature difference amounted to 0.4° to 0.8°C.). A certain amount of supercooling always resulted on initial cooling, usually of the order of 1°C.

TABLE 2. SOLID-LIQUID-VAPOR LOCI FOR METHANE-CARBON DIOXIDE SYSTEM COMPARED WITH METHANE-CARBON DIOXIDE SYSTEM WITH 0.56 MOLE % NITROGEN IN METHANE

Temperature, °F.	S-L-V pressure with nitrogen in methane lb./sq. in. abs.	S-L-V pressure for CH_4-CO_2 (smoothed) lb./sq. in. abs.
−95.0	709	705
−115.3	600	593
−130.9	485	476
−144.6	389	384
−158.3	305	298
−175.4	214	209
−203.7	109	105
−226.5	56	52

TABLE 3. COMPOSITION OF VAPOR PHASE ALONG SOLID-LIQUID-VAPOR LOCUS OF METHANE-CARBON DIOXIDE SYSTEM

Temperature, °F.	Mole % CO_2
−206.0	0.12
−161.6	0.63
−143.1	1.08
−140.0	1.72
−128.5	2.79
−120.0	3.67
−111.1	5.65
−89.4	11.73

RESULTS AND DISCUSSION

Solid-Liquid-Vapor Locus

The pressure-temperature relation for the solid-liquid-vapor locus was determined from the triple point of carbon dioxide to −284°F. The data are given in Table 1. As shown in Figure 1 there is disagreement below −90°F. between the data of this study and those of Donnelly and Katz (*2*). The data of this study and those of Sterner (*6*) agree except at Sterner's highest temperature point. As Sterner's data were presented only in graphical form, exact comparison cannot be made.

At a given temperature the corresponding pressure of this study should be accurate to ± 2 lb./sq. in. This is due to very small amounts of impurities in the system, that is nitrogen.

A mass spectrometer analysis of the methane indicated a purity of 99.72 mole % with 0.28% nitrogen. Analysis of the carbon dioxide indicated a purity of 99.9 + %. By taking a series of pressure-temperature measurements along the solid-liquid-vapor locus, distilling off 15 to 20% of the cell contents to remove as much of the nitrogen as possible, then repeating the measurements, the decrease in pressure for a given temperature was about 1 lb./sq. in. Further distillation had no effect on the pressure.

Donnelly and Katz postulate the existence of a eutectic in the system. Although experimental measurements were not made to the triple point of methane (−296.4°F.) but stopped at −284°F., two factors indicate that no significant eutectic exists. First, the pressure along the solid-liquid-vapor locus very closely approximates the vapor pressure of pure methane below −180°F.; second, the composition of the liquid phase decreases to less than 0.2% carbon dioxide at −225°F., some 70°F. above the triple point of methane.

Figure 2 gives the pressure-temperature relationship for the solid-liquid-vapor locus of the methane-carbon dioxide system plus the pressure-temperature relationship determined for the mixture in which methane containing 0.56 mole % nitrogen was used. Table 2 compares the pressures along the solid-liquid-vapor locus at a series of temperatures for the methane-carbon dioxide system and the methane-carbon dioxide system with nitrogen. At a given temperature the pressure of the system containing nitrogen was from 4 to 9 lb./sq. in. above that of the nonnitrogen system.

Solid-Vapor and Solid-Liquid Behavior

The dashed lines in Figure 1 are the pressure-temperature projections at constant composition for the solid-vapor and the solid-liquid regions. These data were taken from the data of Pikaar (*5*) and are reproduced with his permission. As Pikaar points out the system exhibits retrograde sublimation over part of the composition range; that is there is a maximum temperature for each composition in the vapor region. The solid-liquid behavior is normal.

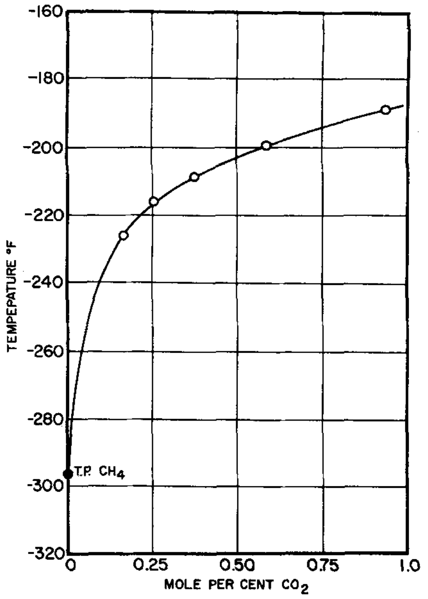

Fig. 4. Composition of liquid phase methane-carbon dioxide system.

Solid-Phase Composition Along the Solid-Liquid-Vapor Locus

Donnelly and Katz (*2*) indicate that the melting point of the solid found in equilibrium with the vapor and liquid had the same melting point as pure carbon dioxide. This indicates that the solid is essentially pure carbon dioxide.

Vapor-Phase Composition Along the Solid-Liquid-Vapor Locus

The vapor phase was sampled at eight temperatures ranging from −89.4° to −206.0°F. and a corresponding composition range of 11.73 to 0.12 mole % carbon dioxide (see Table 3). These data along with those of Sterner (*6*) and Donnelly and Katz (*2*) are presented in Figure 3. The agreement of this study with the data of Sterner is good.

TABLE 4. COMPOSITION OF LIQUID PHASE ALONG SOLID-LIQUID-VAPOR LOCUS OF METHANE-CARBON DIOXIDE SYSTEM

Temperature, °F.	Mole % CO_2
−226.3	0.16
−216.3	0.25
−208.7	0.37
−199.5	0.58
−189.0	0.93
−168.0	1.83
−153.9	2.94
−131.8	5.85
−119.0	10.08
−105.2	15.39
−97.4	20.50

Also plotted in Figure 3 is a series of points labled extrapolated dew points. These points were obtained in the following manner. The logs of the dew-point pressures were plotted vs. the reciprocals of the absolute temperatures for a series of constant compositions (original data of Donnelly and Katz). This plot gives a series of essentially straight lines. The solid-liquid-vapor locus determined in this study was also plotted, and the dew lines were extrapolated to this locus. The pressure-temperature-composition relations were taken from the intersections of the dew lines with the solid-liquid-vapor locus.

The extrapolated data points allow a smooth curve for the vapor composition to be drawn through the data of the vapor composition to be drawn through the data of this study. This study's data agree closely with the data of Donnelly and Katz above 35% carbon dioxide.

Liquid-Phase Composition Along the Solid-Liquid-Vapor Locus

The crystal points of eleven mixtures ranging from 20.5 to 0.16 mole % carbon dioxide were determined (Table 4) and are plotted along with the data of Sterner and of Donnelly and Katz in Figure 3. As was the case with the vapor composition, the agreement with the data of Sterner is fairly good.

Those points noted as extrapolated bubble points were determined by means of the previously described method with the bubble-point data of Donnelly and Katz and the solid-liquid-vapor data of this study.

Figure 4 presents data on the composition of the liquid phase in the region below 1% carbon dioxide.

ACKNOWLEDGMENT

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LITERATURE CITED

1. Clark, W. C., and Fred Kurata, *Petrol. Refiner*, 38, 249 (1959).
2. Donnelly, H. G., and D. L. Katz, *Ind. Eng. Chem.*, **46**, 511 (1954).
3. Kohn, J. P., and Fred Kurata, *A.I.Ch.E. Journal*, 4, 211 (1958).
4. ————, Unpublished data, University of Kansas, Lawrence, Kansas (1955).
5. Pikaar, M. J., Ph.D. thesis, Univ. London, London, England (October, 1959).
6. Sterner, C. J., Paper presented at Cryogenic Conference, Boulder, Colorado (August, 1960).

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