Critical Loci of Binary Mixtures of Propane with Methane, Carbon Dioxide, and Nitrogen

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The minimum pressure of miscibility was determined by observations in a windowed cell for systems of propane with methane, carbon dioxide, and nitrogen, as functions of composition and temperature.

OBSERVATIONS in a windowed cell were used to determine the minimum pressure of miscibility as functions of composition and temperature (approximately 90° to 190° F.) for systems of propane with methane, carbon dioxide, and nitrogen. Where comparison is possible, the authors' values for the critical pressure of these mixtures at a given temperature are consistently less than the published values.

EXPERIMENTAL

Visual observations on the gas-liquid phase behavior of these fluids were made in the authors' cell with internal window. Although the present cell is modified somewhat in design and instrumentation, it is roughly equivalent to one described earlier (7).

Known volumes of the two fluids were metered separately into the evacuated cell to give the desired composition. Densities of the constituent fluids were obtained from published data (5, 6). Any consistent or systematic error in establishing the composition would not affect the determination of the maximum pressure on a curve such as Figure 1 or the critical locus on a plot of pressure *vs.* temperature, as in Figure 2. The critical compositions included in Table I may be subject to significant uncertainty. While the temperature was held constant, the pressure on the mixture was changed in small steps. After each pressure change the sample was agitated, and observations were made on the nature and location of the interface between the liquid phase and the gas phase. The relative sizes of the two phases were observed qualitatively over successive pressure changes until one phase vanished at a bubble point or a dew point. Except very near the critical point, a bubble could be followed down to pinpoint size and could be made to disappear and to reappear at very small pressure changes—often at the limit of sensitivity of the authors' pressure measurement, ±0.5 p.s.i. Observations of a dew point were generally less precise, and when the composition fell very near that of the critical point, opalescence occurred. However, even here small pressure changes caused changes in fogging and cloudiness that permitted selecting a pressure which, when later plotted with observed bubble point and dew point pressures at the same temperature, gave a smooth curve, such as that in Figure 1.

Temperatures were measured on a thermocouple which had been calibrated against a platinum resistance thermometer certified by the National Bureau of Standards.

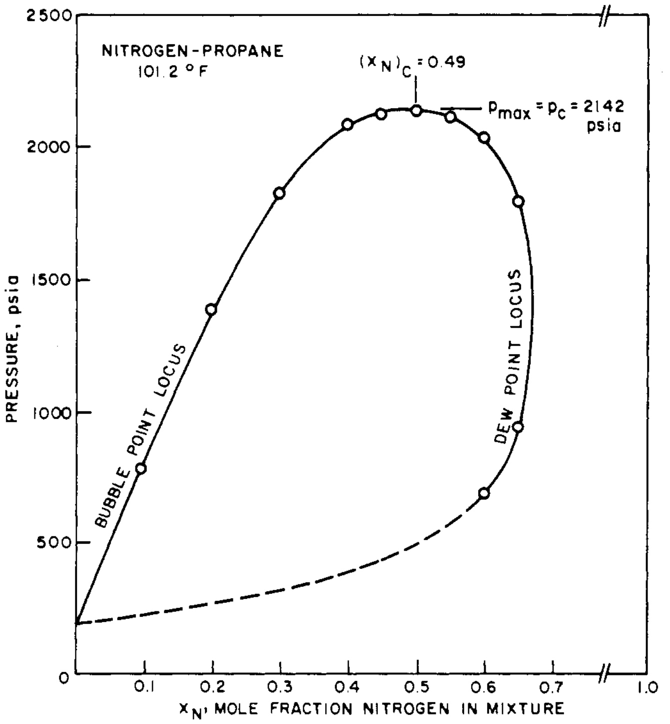

Figure 1. Typical two-phase envelope

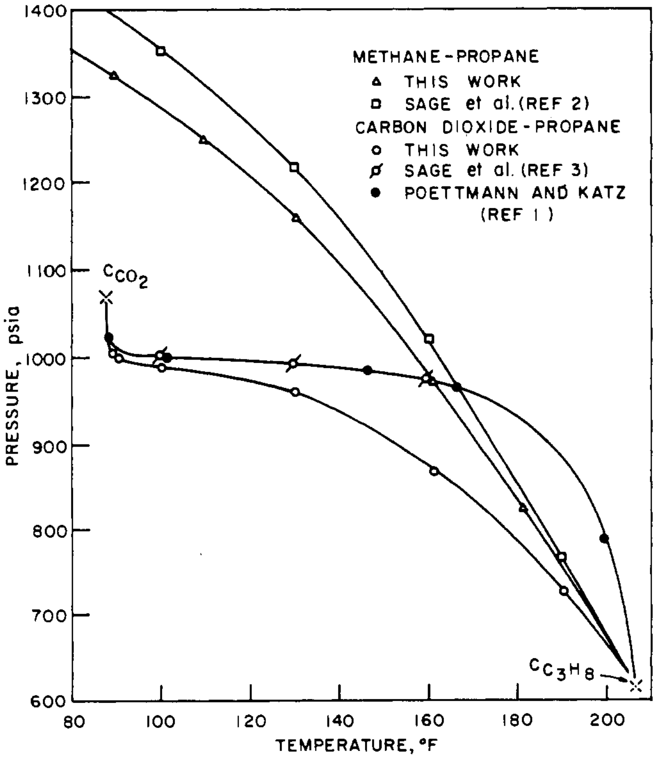

Figure 2. Comparisons with published values

Table I. Experimental Data on Critical Loci

Temperature, °F.	Pressure, P.S.I.A.	Composition, Mole Fraction Propane
	Propane-Methane	
89.3	1323	0.43
109.5	1250	0.51
130.7	1158	0.58
161.0	971	0.72
181.4	823	0.83
	Propane-Carbon Dioxide	
89.3	1005	0.08
90.9	1000	0.11
95.1	989	0.17
130.3	960	0.45
161.6	867	0.65
190.6	728	0.87
	Propane-Nitrogen	
101.2	2142	0.49
129.1	1776	0.60
160.0	1313	[a]
197.7	749	0.94

[a] Absolute value not obtained.

Pressures were measured on a fluid-pressure balance which was sensitive to 1 p.s.i. and which had been calibrated against an American Instrument Co. dead-weight gage.

The materials used were carbon dioxide (Matheson, bone dry, 99.8 mole % minimum), methane (Phillips, pure grade, 99 mole % minimum), nitrogen (Matheson, prepurified, 99.996 mole % minimum), and propane (Matheson, extra pure, 99.9 mole % minimum).

Since our critical loci for the methane-propane and the carbon dioxide-propane systems differed considerably from published values, checks were made on the purity of the propane and the methane stock. Within the limitations of a gas chromatographic technique, analyses were reported as follows: methane—0.1% ethane, 0.2% nitrogen, no detectable oxygen; propane—trace of methane, no detectable air.

RESULTS

The type of data obtained is illustrated by Figure 1. As more was learned about a particular system, the observations could be restricted to a smaller range in composition. Often only four to seven closely spaced compositions were needed to locate the maximum pressure. This maximum of an isothermal plot of pressure *vs.* composition in a two-component system is necessarily a critical point; this point gives both the critical pressure and the critical composition of the system at this temperature. Experimental data are given in Table I.

The authors' results on the methane-propane and carbon dioxide-propane systems are shown in Figure 2 to be in considerable disagreement with published data (*1-3, 5, 6*), on the critical loci of these systems. Roberts *et al.* (*4*) have reported serious disagreement with a portion of Sage's critical locus in the methane-butane system (*5*).

The precision and accuracy of the observations were such that any error of ±5 p.s.i. in pressure is unlikely. The authors' measurements on the vapor pressure of propane (at bubble point) at 109.3° and 159.7° F. agreed within 1 p.s.i. with the values interpolated (on a plot of log p *vs.* $1/T$) from published data (*5*). Although one may question the critical properties of mixtures as reported by Sage and coworkers, their vapor pressure measurements on one-component systems appear to be reliable, especially at temperatures well below the critical temperature.

Use of a blind cell (*2, 3*) could well have led to errors in determining the two-phase boundary. Discontinuities in the isothermal pressure-volume relationship were used to establish both the bubble point and the dew point pressures. Discontinuities at the latter are generally poorly defined at high pressures, and both become nebulous near the critical point of a mixture.

Direct visual observation is desirable in phase studies, but even here the results may not be too meaningful in the absence of proper instrumentation and if there is a paucity of data. Poettmann and Katz (*1*) used a Jerguson gage for a cell; any blind space at the end of the gage would hamper precise observations. Their pressure-composition plots are inconsistent in shape for the different isotherms and are always shown with a sharp cusp at the apex. Apparently only six compositions were used to cover the full range of isotherms. The authors' closer spacing showed each two-phase loop to be well rounded at the top. Reamer, Sage, and Lacey (*3*) showed a more rounded apex to an isotherm than did Poettmann and Katz, but their supporting data comprise only four widely separated compositions.

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