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Phase Equilibria in Hydrocarbon Systems

II. Methane-Propane System

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IN STUDIES of the equilibrium behavior of systems consisting of hydrocarbons, such as the mixtures of petroleum and natural gas found in nature, the investigator is faced with a problem of great complexity. It would seem desirable, therefore, to approach the problem by establishing first the behavior of some simpler hydrocarbon systems under similar conditions of temperature and pressure. By choosing a two-component system, a complete record of equilibrium data may be obtained for the desired range of conditions at the expense of a small fraction of the time required to reach even a partial solution of the very complex case.

The results of such a study of the methane-propane system are here reported. The pressures and temperatures were restricted to those generally found in petroleum formations—

The methane-propane system is studied throughout the temperature and pressure ranges commonly found in underground petroleum formations. This system may be considered as illustrating the behavior of a simplified case of natural gas in contact with very high-gravity volatile oil. Complete equilibrium data are accompanied by illustrative diagrams prepared therefrom.

were employed at each temperature. Dew points were obtained for both normal and retrograde condensation.

The total density and composition were determined by measuring the increase in equilibrium pressure due to the addition of successive known quantities of methane to an equilibrium cell containing a known amount of propane.

By a series of seven or eight sets of measurements of this nature at systematically chosen concentrations of propane (expressed as grams per liter of total space), the entire field of compositions could be mapped for the chosen temperature. For illustration, two such sets of measurements made at 21.1 C. (70° F.) are shown in Figure 1. In the case of the curve with the lower concentration of propane there was very little liquid phase in the equilibrium cell and this rapidly disappeared. In the other case the cell was over half full of liquid at the beginning of the addition of methane, and the volume of the liquid phase increased until the cell was completely full at the break in the curve. This point represents the pressure of saturated liquid of the composition corresponding to the total composition of the mixture at this point. The locus of these break points for different sets of measurements gave the relations of pressure, density, and composition for saturated liquid. The volume of the liquid phase was also measured after each addition of methane to furnish a check on the boundary measurements. These measurements were carried on at five temperatures evenly distributed

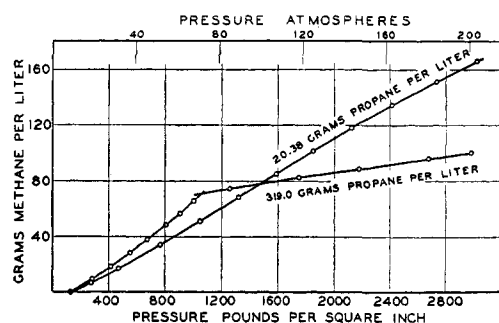


FIGURE 1. TYPICAL EXPERIMENTAL CURVES FROM EQUILIBRIUM CELL

i. e., 1 to 200 atmospheres and 20° to 90° C. The compositions were varied continuously from pure propane to pure methane. Measurements of density and composition were made in both the one- and two-phase regions, including a large region above the critical pressures of the system.

EXPERIMENTAL METHOD

A detailed description of the apparatus used and methods employed for a two-component system is given in Part I of this series (6). In brief the method consisted of the following steps: The pressure-composition relations of saturated gas¹ were determined by dew point measurements at a series of temperatures. Eight or ten different compositions

¹ The term "saturated gas" is used here to designate the gaseous phase in equilibrium with a corresponding liquid phase. The latter phase is referred to as the saturated liquid.

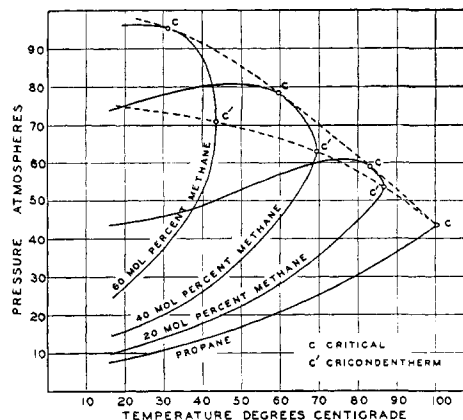


FIGURE 2. CONSTANT COMPOSITION CURVES ON PRESSURE VS. TEMPERATURE DIAGRAM

TABLE I. DENSITIES OF MIXTURES OF METHANE AND PROPANE

(Compositions expressed in mole per cent methane, densities in grams per liter)

| PRESSURE Atm. | 20.0 MOLE % | | 30.0 MOLE % | | 40.0 MOLE % | | 50.0 MOLE % | | 60.0 MOLE % | | 70.0 MOLE % | | 80.0 MOLE % | | 90.0 MOLE % | |
|---------------------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|
| | Density | State | Density | State | Density | State | Density | State | Density | State | Density | State | Density | State | Density | State |
| TEMPERATURE, 20° C. | | | | | | | | | | | | | | | | |
| 10.0 | 18.0 | G | 16.3 | G | 14.8 | G | 13.3 | G | 11.8 | G | 10.4 | G | 9.2 | G | 8.0 | G |
| 20.0 | 107.8 | L | 61.4 | L | 41.1 | L | 29.4 | L | 24.2 | L | 21.1 | L | 19.0 | L | 16.3 | L |
| 30.0 | 245.5 | L | 126.9 | L | 84.9 | L | 59.7 | L | 44.0 | L | 35.0 | L | 29.5 | L | 24.6 | L |
| 40.0 | 381.4 | L | 213.7 | L | 135.4 | L | 92.7 | L | 67.3 | L | 50.9 | L | 41.4 | L | 33.8 | L |
| 50.0 | ... | ... | 308.5 | L | 193.1 | L | 130.8 | L | 93.7 | L | 70.1 | L | 54.8 | L | 43.8 | L |
| 60.0 | ... | ... | 421.8 | L | 260.1 | L | 174.3 | L | 123.3 | L | 91.5 | L | 69.7 | L | 55.0 | L |
| 70.0 | ... | ... | ... | ... | 339.3 | L | 221.8 | L | 156.1 | L | 113.8 | L | 85.6 | L | 66.2 | L |
| 80.0 | ... | ... | ... | ... | 385.0 | L | 279.5 | L | 195.0 | L | 138.2 | L | 102.3 | L | 78.2 | L |
| 90.0 | ... | ... | ... | ... | 393.5 | L | 333.6 | L | 239.2 | L | 167.2 | L | 119.6 | L | 90.3 | L |
| 100.0 | ... | ... | ... | ... | 400.1 | L | 345.5 | L | 276.2 | L | 196.1 | L | 138.0 | L | 102.1 | L |
| 120.0 | ... | ... | ... | ... | 410.6 | L | 366.0 | L | 306.0 | L | 235.7 | L | 172.8 | L | 127.5 | L |
| 140.0 | ... | ... | ... | ... | 418.8 | L | 380.0 | L | 327.9 | L | 265.6 | L | 203.0 | L | 147.4 | L |
| 160.0 | ... | ... | ... | ... | 425.7 | L | 391.1 | L | 344.0 | L | 286.9 | L | 227.1 | L | 172.9 | L |
| 180.0 | ... | ... | ... | ... | 432.8 | L | 401.3 | L | 357.1 | L | 304.0 | L | 247.9 | L | 193.0 | L |
| 200.0 | ... | ... | ... | ... | 438.8 | L | 410.0 | L | 367.7 | L | 317.4 | L | 265.5 | L | 210.9 | L |
| TEMPERATURE, 40° C. | | | | | | | | | | | | | | | | |
| 10.0 | 16.8 | G | 15.2 | G | 13.9 | G | 12.6 | G | 11.3 | G | 10.0 | G | 8.6 | G | 7.6 | G |
| 20.0 | 47.1 | L | 34.2 | L | 31.7 | L | 26.0 | L | 23.2 | L | 20.0 | L | 17.7 | L | 15.1 | L |
| 30.0 | 152.1 | L | 83.9 | L | 58.6 | L | 44.0 | L | 37.6 | L | 31.2 | L | 26.3 | L | 22.8 | L |
| 40.0 | 270.8 | L | 146.9 | L | 97.9 | L | 70.1 | L | 55.0 | L | 44.8 | L | 37.1 | L | 31.1 | L |
| 50.0 | 417.9 | L | 224.6 | L | 141.5 | L | 99.3 | L | 75.4 | L | 58.7 | L | 48.4 | L | 40.0 | L |
| 60.0 | 422.1 | L | 316.6 | L | 193.0 | L | 133.1 | L | 98.7 | L | 74.8 | L | 60.6 | L | 49.6 | L |
| 70.0 | 427.2 | L | 384.2 | L | 255.1 | L | 170.1 | L | 123.1 | L | 93.3 | L | 73.6 | L | 59.4 | L |
| 80.0 | ... | ... | 393.1 | L | 328.6 | L | 211.0 | L | 156.0 | L | 112.7 | L | 87.0 | L | 69.0 | L |
| 90.0 | ... | ... | 400.2 | L | 347.2 | L | 264.2 | L | 180.1 | L | 132.3 | L | 101.9 | L | 78.8 | L |
| 100.0 | ... | ... | 406.1 | L | 358.8 | L | 289.5 | L | 209.7 | L | 151.6 | L | 115.9 | L | 89.1 | L |
| 120.0 | ... | ... | 416.7 | L | 376.1 | L | 317.8 | L | 249.6 | L | 188.5 | L | 144.5 | L | 110.2 | L |
| 140.0 | ... | ... | 425.2 | L | 388.6 | L | 337.1 | L | 278.2 | L | 220.1 | L | 169.8 | L | 129.5 | L |
| 160.0 | ... | ... | 433.3 | L | 399.4 | L | 352.5 | L | 299.2 | L | 245.0 | L | 192.8 | L | 149.8 | L |
| 180.0 | ... | ... | 440.0 | L | 407.3 | L | 365.1 | L | 316.4 | L | 263.8 | L | 213.1 | L | 167.7 | L |
| 200.0 | ... | ... | ... | ... | 415.1 | L | 375.4 | L | 331.0 | L | 279.8 | L | 229.2 | L | 183.7 | L |
| TEMPERATURE, 60° C. | | | | | | | | | | | | | | | | |
| 10.0 | 16.3 | G | 14.8 | G | 13.2 | G | 12.1 | G | 10.9 | G | 9.6 | G | 8.3 | G | 7.1 | G |
| 20.0 | 35.2 | L | 30.3 | L | 27.5 | L | 24.5 | L | 22.0 | L | 19.4 | L | 16.7 | L | 14.3 | L |
| 30.0 | 83.4 | L | 52.0 | L | 44.9 | L | 38.8 | L | 33.8 | L | 29.6 | L | 25.5 | L | 22.0 | L |
| 40.0 | 188.0 | L | 105.2 | L | 87.0 | L | 56.3 | L | 47.8 | L | 40.0 | L | 35.0 | L | 29.4 | L |
| 50.0 | 295.6 | L | 166.4 | L | 107.9 | L | 77.9 | L | 64.0 | L | 52.7 | L | 44.4 | L | 37.2 | L |
| 60.0 | 379.1 | L | 236.7 | L | 150.6 | L | 105.9 | L | 82.2 | L | 66.5 | L | 54.9 | L | 45.6 | L |
| 70.0 | 389.9 | L | 320.3 | L | 198.1 | L | 136.2 | L | 102.1 | L | 81.1 | L | 65.8 | L | 54.2 | L |
| 80.0 | 397.3 | L | 345.2 | L | 252.5 | L | 119.4 | L | 123.6 | L | 96.4 | L | 77.2 | L | 63.2 | L |
| 90.0 | 403.4 | L | 359.8 | L | 284.2 | L | 202.6 | L | 145.7 | L | 111.9 | L | 89.1 | L | 71.9 | L |
| 100.0 | 408.4 | L | 369.7 | L | 308.3 | L | 231.7 | L | 168.3 | L | 127.5 | L | 101.4 | L | 80.8 | L |
| 120.0 | ... | ... | 384.2 | L | 336.7 | L | 274.1 | L | 211.3 | L | 159.9 | L | 125.5 | L | 98.8 | L |
| 140.0 | ... | ... | 395.3 | L | 356.3 | L | 302.8 | L | 243.3 | L | 190.0 | L | 149.4 | L | 117.1 | L |
| 160.0 | ... | ... | 405.3 | L | 371.8 | L | 324.1 | L | 268.4 | L | 216.9 | L | 171.2 | L | 135.2 | L |
| 180.0 | ... | ... | 414.4 | L | 383.2 | L | 338.6 | L | 288.6 | L | 237.9 | L | 191.5 | L | 152.1 | L |
| 200.0 | ... | ... | ... | ... | 392.2 | L | 351.7 | L | 304.9 | L | 256.1 | L | 208.8 | L | 166.9 | L |
| TEMPERATURE, 70° C. | | | | | | | | | | | | | | | | |
| 10.0 | 15.5 | G | 14.1 | G | 12.8 | G | 11.5 | G | 10.3 | G | 9.1 | G | 7.9 | G | 6.8 | G |
| 20.0 | 33.5 | L | 29.1 | L | 26.5 | L | 23.8 | L | 21.1 | L | 18.8 | L | 16.4 | L | 13.7 | L |
| 30.0 | 57.9 | L | 46.8 | L | 42.0 | L | 36.5 | L | 32.3 | L | 27.7 | L | 24.9 | L | 20.4 | L |
| 40.0 | 113.1 | L | 71.5 | L | 59.2 | L | 51.0 | L | 44.8 | L | 38.0 | L | 33.4 | L | 28.0 | L |
| 50.0 | 201.6 | L | 113.6 | L | 82.0 | L | 67.8 | L | 57.5 | L | 48.9 | L | 42.0 | L | 35.2 | L |
| 60.0 | 308.5 | L | 173.7 | L | 113.2 | L | 87.3 | L | 71.2 | L | 60.3 | L | 50.9 | L | 42.7 | L |
| 70.0 | 339.8 | L | 239.5 | L | 153.9 | L | 109.9 | L | 87.5 | L | 72.2 | L | 60.8 | L | 50.8 | L |
| 80.0 | 353.9 | L | 283.8 | L | 196.4 | L | 136.7 | L | 104.4 | L | 85.1 | L | 70.9 | L | 58.8 | L |
| 90.0 | 362.4 | L | 310.3 | L | 232.1 | L | 165.9 | L | 122.9 | L | 98.2 | L | 81.0 | L | 67.1 | L |
| 100.0 | 368.8 | L | 327.0 | L | 260.6 | L | 193.8 | L | 143.2 | L | 112.9 | L | 92.2 | L | 75.0 | L |
| 120.0 | ... | ... | 348.3 | L | 297.9 | L | 236.9 | L | 180.9 | L | 140.7 | L | 113.5 | L | 91.3 | L |
| 140.0 | ... | ... | 364.3 | L | 324.1 | L | 269.4 | L | 215.3 | L | 168.9 | L | 135.4 | L | 107.9 | L |
| 160.0 | ... | ... | ... | ... | 342.9 | L | 294.8 | L | 240.9 | L | 195.6 | L | 156.4 | L | 125.1 | L |
| 180.0 | ... | ... | ... | ... | 357.6 | L | 310.9 | L | 262.5 | L | 216.4 | L | 175.9 | L | 140.9 | L |
| 200.0 | ... | ... | ... | ... | 368.6 | L | 326.8 | L | 279.6 | L | 234.9 | L | 191.0 | L | 155.1 | L |
| TEMPERATURE, 90° C. | | | | | | | | | | | | | | | | |
| 10.0 | 14.6 | G | 13.2 | G | 12.0 | G | 10.8 | G | 9.7 | G | 8.5 | G | 7.4 | G | 6.4 | G |
| 20.0 | 32.9 | L | 27.8 | L | 25.1 | L | 23.0 | L | 20.2 | L | 17.1 | L | 15.7 | L | 13.1 | L |
| 30.0 | 54.4 | L | 45.9 | L | 41.6 | L | 36.1 | L | 31.2 | L | 26.8 | L | 24.8 | L | 20.1 | L |
| 40.0 | 81.7 | L | 66.0 | L | 57.0 | L | 49.0 | L | 42.3 | L | 37.0 | L | 31.8 | L | 26.8 | L |
| 50.0 | 117.1 | L | 90.3 | L | 73.5 | L | 62.9 | L | 54.3 | L | 47.0 | L | 39.9 | L | 33.5 | L |
| 60.0 | 169.7 | L | 118.9 | L | 93.4 | L | 78.4 | L | 66.2 | L | 56.5 | L | 47.9 | L | 40.5 | L |
| 70.0 | 242.2 | L | 157.8 | L | 117.4 | L | 96.3 | L | 81.0 | L | 67.8 | L | 56.9 | L | 47.3 | L |
| 80.0 | 288.3 | L | 203.2 | L | 144.5 | L | 114.4 | L | 95.4 | L | 79.1 | L | 66.0 | L | 55.0 | L |
| 90.0 | 313.2 | L | 238.7 | L | 175.0 | L | 134.9 | L | 111.0 | L | 91.5 | L | 74.4 | L | 62.8 | L |
| 100.0 | 327.7 | L | 264.8 | L | 202.9 | L | 155.8 | L | 125.3 | L | 102.9 | L | 85.0 | L | 70.1 | L |
| 120.0 | ... | ... | 304.6 | L | 245.9 | L | 195.3 | L | 155.4 | L | 127.9 | L | 105.1 | L | 85.9 | L |
| 140.0 | ... | ... | 330.2 | L | 278.3 | L | 226.7 | L | 183.2 | L | 150.0 | L | 124.1 | L | 100.9 | L |
| 160.0 | ... | ... | ... | ... | 302.2 | L | 253.2 | L | 207.8 | L | 172.0 | L | 141.1 | L | 115.9 | L |
| 180.0 | ... | ... | ... | ... | 320.4 | L | 273.9 | L | 228.9 | L | 190.8 | L | 158.3 | L | 130.0 | L |
| 200.0 | ... | ... | ... | ... | 335.5 | L | 291.8 | L | 244.9 | L | 209.1 | L | 174.2 | L | 142.4 | L |

over the range from 20° to 90° C. As illustrated in the curves of Figure 1, the measurements were carried in each case far beyond the disappearance of the two-phase region.

PREPARATION OF MATERIALS

The methane used for this work was prepared from natural gas. The gas under 20 atmospheres pressure was passed through a trap, immersed in a mixture of solid carbon dioxide and methanol, to remove water and heavy hydrocarbons. The gas was then completely liquefied in a steel bomb immersed in liquid air. The partially filled bomb was pumped down to a pressure of 4 to 6 cm. of mercury for an extended

time to remove nitrogen and other noncondensable gases. The methane was then partially separated from the other hydrocarbons by a simple distillation into a cooled (10° C.) steel cell containing activated charcoal. This cell was operated at a pressure of about 34 atmospheres. The methane from the cell was stored in steel cylinders. A combustion and modified condensation analysis gave the following composition for the methane:

| | |
|----------------------|--------|
| Ethane (and heavier) | Mole % |
| Nitrogen | 0.03 |
| Methane | 99.47 |

TABLE II. COMPOSITIONS AND DENSITIES OF SATURATED LIQUID AND SATURATED GAS PHASES

(Compositions in mole per cent methane, densities in grams per liter)

| PRES- SURE Atm. | At 20° C. | | | | At 40° C. | | | | At 55° C. | | | |
|-----------------------|-------------|--------|---------|--------|-------------|--------|---------|--------|-------------|--------|---------|--------|
| | COMPOSITION | | DENSITY | | COMPOSITION | | DENSITY | | COMPOSITION | | DENSITY | |
| | Gas | Liquid | Gas | Liquid | Gas | Liquid | Gas | Liquid | Gas | Liquid | Gas | Liquid |
| 10.0 | 13.2 | 0.8 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 15.0 | 38.6 | ... | ... | ... | 7.9 | 0.7 | ... | ... | ... | ... | ... | ... |
| 20.0 | 50.5 | 6.2 | 28.8 | 491.3 | 27.3 | 3.5 | 36.0 | 461.9 | 3.7 | 0.5 | 41.8 | 439.2 |
| 25.0 | 57.5 | ... | ... | ... | 37.9 | ... | ... | ... | 19.6 | ... | ... | ... |
| 30.0 | 61.9 | 11.6 | 40.8 | 479.1 | 45.1 | 9.2 | 49.1 | 448.6 | 29.2 | 5.5 | 55.0 | 425.8 |
| 35.0 | 65.4 | ... | ... | ... | 50.3 | ... | ... | ... | 35.5 | ... | ... | ... |
| 40.0 | 68.1 | 17.6 | 54.3 | 464.9 | 54.2 | 14.9 | 61.5 | 432.3 | 40.1 | 10.8 | 67.7 | 407.8 |
| 45.0 | 70.1 | ... | ... | ... | 57.1 | ... | ... | ... | 43.9 | ... | ... | ... |
| 50.0 | 71.4 | 23.6 | 68.5 | 447.1 | 59.2 | 20.8 | 75.8 | 413.9 | 47.0 | 16.7 | 82.9 | 387.6 |
| 55.0 | ... | ... | ... | ... | 60.6 | ... | ... | ... | ... | ... | ... | ... |
| 60.0 | 72.8 | 29.8 | 84.3 | 424.3 | 61.5 | 26.6 | 93.0 | 392.0 | 51.1 | 22.8 | 102.1 | 361.4 |
| 65.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 70.0 | 73.6 | 36.3 | 102.2 | 396.7 | 62.2 | 32.9 | 113.9 | 366.1 | 52.4 | 29.2 | 127.2 | 327.8 |
| 75.0 | ... | ... | ... | ... | ... | ... | ... | ... | 52.1 | 32.6 | ... | ... |
| 80.0 | 73.4 | 43.6 | 123.8 | 361.6 | 62.1 | 39.5 | 140.4 | 332.9 | 50.1 | 37.5 | 172.4 | 271.4 |
| 85.0 | ... | ... | ... | ... | 61.4 | 43.9 | ... | ... | ... | ... | ... | ... |
| 90.0 | 71.4 | 52.4 | 155.2 | 312.8 | 59.3 | 50.6 | 190.2 | 265.2 | ... | ... | ... | ... |
| 95.0 | 69.0 | 58.3 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

| PRES- SURE Atm. | At 70° C. | | | | At 80° C. | | | | At 90° C. | | | |
|-----------------------|-------------|--------|---------|--------|-------------|--------|---------|--------|-------------|--------|---------|--------|
| | COMPOSITION | | DENSITY | | COMPOSITION | | DENSITY | | COMPOSITION | | DENSITY | |
| | Gas | Liquid | Gas | Liquid | Gas | Liquid | Gas | Liquid | Gas | Liquid | Gas | Liquid |
| 10.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 15.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 20.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 25.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 30.0 | 10.3 | 2.1 | 64.7 | 401.4 | ... | ... | ... | ... | ... | ... | ... | ... |
| 35.0 | 18.9 | ... | ... | ... | 8.5 | 2.0 | ... | ... | ... | ... | ... | ... |
| 40.0 | 25.2 | 7.4 | 79.0 | 381.8 | 14.9 | 4.6 | 97.4 | 361.2 | 4.4 | 1.0 | 127.5 | 332.2 |
| 45.0 | 29.9 | ... | ... | ... | 20.2 | ... | ... | ... | 12.1 | 3.8 | ... | ... |
| 50.0 | 33.6 | 13.0 | 97.1 | 354.9 | 24.3 | 10.6 | 118.4 | 328.1 | 15.2 | 6.9 | 163.6 | 282.7 |
| 55.0 | ... | ... | ... | ... | 27.4 | 2.8 | ... | ... | ... | ... | ... | ... |
| 60.0 | 38.8 | 19.9 | 122.2 | 318.2 | 27.3 | 18.3 | 171.5 | 265.2 | ... | ... | ... | ... |
| 65.0 | 39.2 | 24.1 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 70.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 75.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 80.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 85.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 90.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 95.0 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

Owing to the method of analysis employed, the quantity of nitrogen reported is possibly somewhat larger than that actually present.

The propane used for this work was obtained from the Phillips Petroleum Corporation and was not further purified. The Phillips Petroleum Corporation upon careful analysis, found the sample to be pure propane, containing neither ethane nor isobutane in appreciable amounts.

The purity of the methane was further tested by comparison of its measured densities under various pressures with those

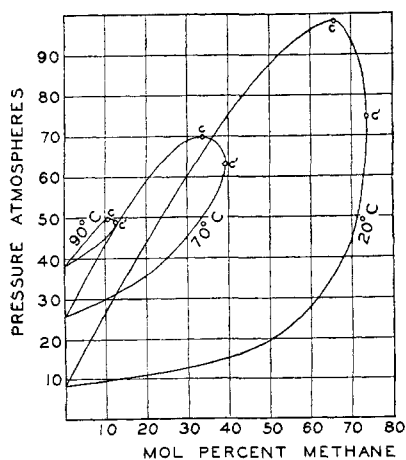


FIGURE 3. CONSTANT TEMPERATURE CURVES ON PRESSURE vs. COMPOSITION DIAGRAM

calculated from published compressibility factors (5). The deviation of the two values was in all cases less than one gram per liter over the entire pressure range (1 to 200 atmospheres). The vapor pressure, as well as the saturated vapor and saturated liquid densities of the propane, agreed within experimental accuracy with published values (3).

ACCURACY OF MEASUREMENTS

The absolute accuracy of the pressure measurements was 0.10 atmosphere.

The temperatures were measured to 0.01° C. and are accurate to at least 0.10° C. The methane and propane were measured to 1.0 ml. (standard conditions) with an estimated absolute accuracy of 0.1 per cent.

EXPERIMENTAL RESULTS

Since the direct experimental data, as typified by the points shown in Figure 1, present the results in a form difficult to tabulate or to use, they have been plotted on as large a scale as is consistent with their accuracy, and the corresponding curves drawn. From these curves points have been read at suitable regular intervals. The data so obtained are reported in the tables. The maximum temperature interpolation was 2.20° C. The absolute accuracy of the tabulated data is: temperature to 0.10° C., pressures to 0.10 atmosphere, compositions to 0.10 mole per cent, and densities to 0.50 gram per liter.

Table I shows the total densities for a series of temperatures, pressures, and total compositions. The state of the system under these specified conditions is also given. L represents

liquid only; G, gas phase only; and L + G, coexistence of liquid and gas phases. R denotes the occurrence of retrograde condensation. In Table II are given the densities and compositions of saturated liquid and of gas for a series of pressures and temperatures. More data are given for the saturated gas because a correspondingly greater number of measurements was made on the dew point than on the saturated liquid boundary. Table III gives critical and cricondentherm (2) pressures, temperatures, and densities for a series of compositions.

TABLE III. CRITICAL AND CRICONDENTHERM DATA

| COMPOSITION Mole % CH ₄ | CRITICAL | | | CRICONDENTHERM | | |
|--|-------------------|------------------|----------------------------|----------------|------------------|----------------------------|
| | Temp. ° C. | Pressure Atm. | Density Grams /liter | Temp. ° C. | Pressure Atm. | Density Grams /liter |
| 10.0 | 91.0 | 52.1 | 232 | 93.7 | 48.6 | 199 ^a |
| 20.0 | 81.2 | 60.6 | 232 | 86.5 | 53.8 | 171 |
| 30.0 | 70.9 | 69.3 | 232 | 78.5 | 58.8 | 149 |
| 40.0 | 59.3 | 78.8 | 231 | 69.2 | 63.4 | 133 |
| 50.0 | 46.3 | 87.9 | 231 | 57.9 | 67.2 | 121 |
| 60.0 | 31.1 | 95.7 | 229 | 43.5 | 70.8 | 115 |
| 70.0 | 10.4 ^a | 99.9 | 225 ^a | 26.8 | 73.8 | 113 |

^a Extrapolated.

DISCUSSION OF SYSTEM

In order to aid in visualizing the behavior of the system, a number of typical plots have been drawn from the tabulated data. Figure 2 shows the pressure-temperature relations for three mixtures. The upper part of each curve represents the vapor pressure of a liquid of that composition; the lower part represents the pressure for initial condensation of a gas of that composition. The higher dotted curve is the locus of the critical points, and the lower dotted curve is the locus of the cricondentherms for various compositions. These two curves come together at the critical point of propane, reach a maximum at somewhat lower temperatures than those shown on the plot, and again come together at the critical point of methane. For each composition the point of maxi-

imum pressure for the existence of two phases occurs at a lower temperature than the critical. This difference in pressure can be seen to increase from zero at the critical point of pure propane to a maximum in the neighborhood of 40 mole per cent methane and again to decrease at higher compositions. From thermodynamic considerations (4) this difference would be expected to increase from zero at the critical point of

pure propane, pass through a maximum, and again reach zero at the maximum critical pressure of the system. The large region of retrograde condensation of the first kind (normal) between C and C' is to be expected, owing to the large difference in critical temperatures of the components. The large increase in critical pressure with composition can be attributed to the same reason. Similar phenomena were observed in the case of mixtures of carbon dioxide and hydrogen by Verschaffelt (7).

In Figure 3 are shown isothermal plots of the relation of the composition of the saturated gas and liquid to pressure. Again the large region of retrograde condensation is shown, as well as the rapid increase in critical pressure with decreasing temperature. The relative quantity of each phase present for any condition of pressure and total composition can be obtained directly from such plots by consideration of the composition of each phase in relation to the total composition of the system.

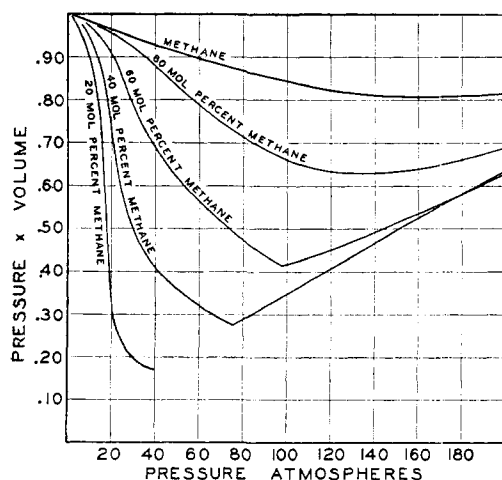


FIGURE 6. CONSTANT COMPOSITION CURVES AT 20° C. ON PERFECT GAS DEVIATION vs. PRESSURE DIAGRAM

Figure 4 is a plot at 20° C. of the relations of pressure and density for the entire pressure range studied. The upper part of the boundary curve shows the density-pressure relation for saturated liquid, while the part below C shows the same relation for the saturated gas. The total composition lines represent the change in density during the course of an

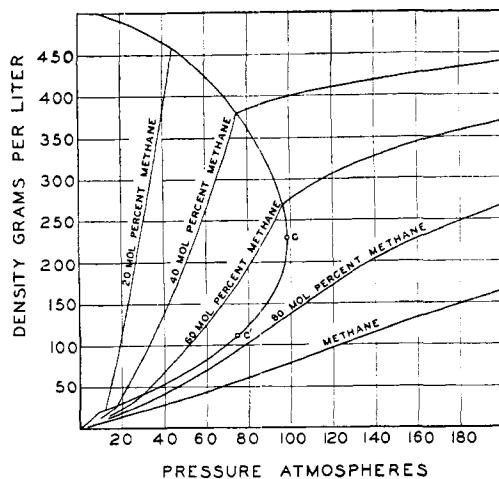


FIGURE 4. CONSTANT COMPOSITION CURVES AT 20° C. ON DENSITY vs. PRESSURE DIAGRAM, GIVING BOUNDARY OF TWO-PHASE REGION

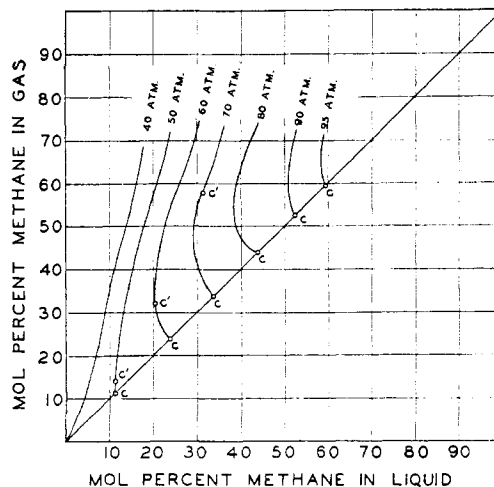


FIGURE 5. CONSTANT PRESSURE CURVES ON GAS COMPOSITION vs. LIQUID COMPOSITION DIAGRAM

isothermal compression. The curved line connecting the origin with the lower end of the saturated vapor curve represents the density of pure propane in the superheated region. As there were no satisfactory density data for pure propane above 30 atmospheres known to the authors, the lines in the upper part of the liquid region were omitted. The curve for methane was calculated from published compressibility factors (3) and agreed closely with that directly determined experimentally. The intersections of the constant-composition lines with the boundary curve give the density and pressure of the saturated liquid and gas of that composition.

In Figure 5 is presented the relation of the composition of liquid and vapor in equilibrium for a series of pressures. The inversion of slope at pressures exceeding 50 atmospheres is due to retrograde condensation. This inversion again disappears as the maximum pressure for the two-phase region is approached. The curves were not continued to higher concentrations of methane since this would necessitate data at temperatures lower than those studied.

From the data in Tables I to III and calculations of the perfect gas densities the compressibilities of given mixtures at various temperatures and pressures can be calculated. The results of such calculations for 20° C. are shown in Figure 6. Again the values for methane were interpolated from published data (5) and were plotted for the sake of comparison. The pressure-volume products for each mixture are compared to that of the same mixture at one atmosphere and 20° C. as unity. The breaks in some of the curves are due to the transition from the two-phase liquid-gas region to the one-phase liquid region.

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