$$y_i^{\text{sample}} = (A_i^{\text{sample}}/A_i^{\text{standard}})y_i^{\text{standard}}/\{(A_i^{\text{sample}}/A_i^{\text{standard}})y_i^{\text{standard}} + (A_j^{\text{sample}}/A_j^{\text{standard}})y_j^{\text{standard}}\}$$

Results and Discussion

The experimentally determined dew points for the nitrogen-propane mixtures, the nitrogen-*n*-butane mixtures, and the nitrogen-isobutane mixtures are presented in Tables I-XI. The results are presented graphically in Figures 4-6. The maximum uncertainty in pressure measurements was estimated to be ±0.015 MPa and the maximum uncertainty in temperature measurements was estimated to be ±0.05 K.

Figure 7 shows a comparison between the isothermal pressure-composition measurements by Grauso et al. (*4*) for the nitrogen-propane system and the measurements made in this study. Figure 8 shows a similar comparison between the nitrogen-isobutane data of Kalra et al. (*9*) and the data obtained in this study. Although the agreement is good, the range of overlapping data is small and the dew point temperatures from this work used in the comparison do not correspond exactly to the temperatures of the other studies.

Registry No. Nitrogen, 7727-37-9; propane, 74-98-6; butane, 106-97-8; isobutane, 75-28-5.

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Dew and Bubble Point Measurements for a Methane-Ethane-Propane Mixture

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Dew and bubble point measurements were made for a ternary mixture of methane, ethane, and propane (z_{CH_4} = 0.8511; $z_{C_2H_6}$ = 0.1007). The temperature range of measurements was 144-245 K and the pressure range was 0.689-7.235 MPa. A complete phase boundary curve was developed. The mixture critical point was determined to be 224.21 K and 6.850 MPa.

Introduction

The purpose of this paper is to present experimentally determined dew and bubble points for a mixture of methane, ethane, and propane which establishes a complete phase boundary for the mixture. These data can be used in the development and testing of correlations for prediction of properties under conditions of vapor-liquid equilibrium.

Some vapor-liquid equilibrium data for the methane-ethane-propane system are presented by Price and Kobayashi (*1*). They employed a vapor circulation method and determined vapor- and liquid-phase compositions by infrared spectroscopy and gas-liquid partition chromatography. Vairogs et al. (*2*) presented the results of a phase equilibria study for a multicomponent mixture containing methane, ethane, and propane.

Dew and bubble point measurements for simulated natural gas mixtures were presented by Gonzalez and Lee (*3*). Techniques for the determination of dew points were presented by Van Poolen (*4*) and Bloomer et al. (*5*).

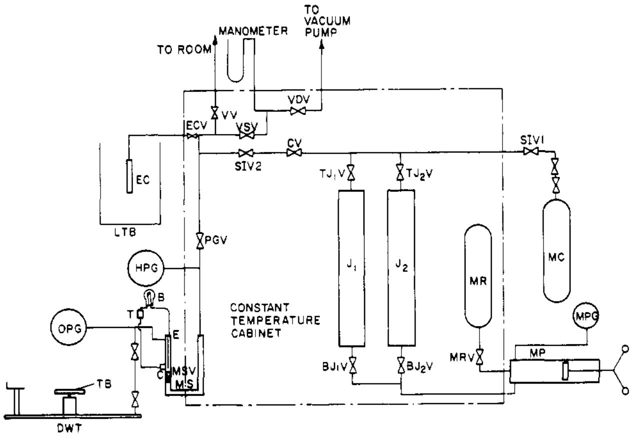

Figure 1. Schematic diagram of apparatus.

Experimental Section

Equipment. A schematic diagram of the dew and bubble equipment is presented in Figure 1. The equipment is a modified version of the phase equilibrium apparatus employed by Bloomer and Parent (*6*).

Dew and bubble points were determined with visual aid in Pyrex glass equilibrium cells (Figure 1, EC). The glass equilibrium cell used to determine the dew points is similar in design to that used by Van Poolen (*4*). The approximate volume of

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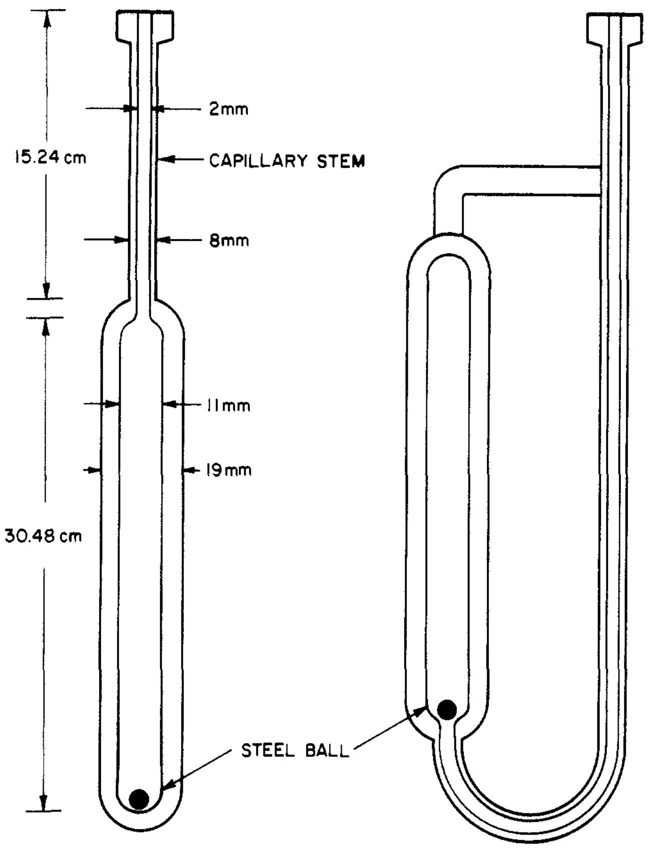

a. DEW POINT CELL b. BUBBLE POINT CELL

Figure 2. Dew and bubble point cells.

the glass cell is 28 cm^3. The cell has a bore of 11 mm and an o.d. of 19 mm. It is connected to a glass-to-metal connector by a section of capillary tubing with a 2-mm bore and 8-mm o.d. The glass cell used to determine bubble points is similar in design to those reported before (*4*). The cell used for determination of the bubble points is constructed of heavy-wall tubing with a bore of 9 mm and an o.d. of 19 mm. Each type of cell contains a steel ball which provides agitation of the fluid in the cell when raised and lowered by manual movement of a U magnet. The cells were pressure tested and proved to be reliable up to pressures of approximately 8.27 MPa. Schematic diagrams of the dew and bubble point cells are presented in Figure 2.

The glass-to-metal connector used in this work was constructed of nickel. The seal was effected by compression of a Teflon O ring, confined in a groove in the nickel fitting against the flat end of the glass capillary. The glass tubing is connected to the connector by a metal coupling, threaded over a steel ring, mounted on the capillary tube. A rubber O ring prevents the steel ring from direct contact with the glass at the top.

The seal (the connector with the glass cell) was tested approximately at 8.27-MPa pressure for more than 12 h without bursting or leaking. It was used in all the runs up to a maximum pressure of approximately 7.58 MPa. The seal was effective at the low temperatures encountered in this work.

Thermostatic conditions for the observations were achieved by placing the equilibrium cell inside a Dewar flask containing isopentane as a bath fluid. The Dewar flask was provided with windows to permit visual observation of the glass cell and its contents. A rubber pad at the top of the Dewar prevented it from direct contact with the surface of the equipment and also served as a seal.

The temperature of the bath was maintained constant partially by regulating the flow of the liquid nitrogen through copper coils in the bath and partially by operating a heating element as needed. The flow of the liquid nitrogen was regulated by manually controlling the valve. The copper tube heater was regulated by a temperature control unit through a probe mounted in the bath. The temperature control unit is a Bayley temperature controller which is capable of controlling the temperature in the range 73–373 K within ±0.01 K.

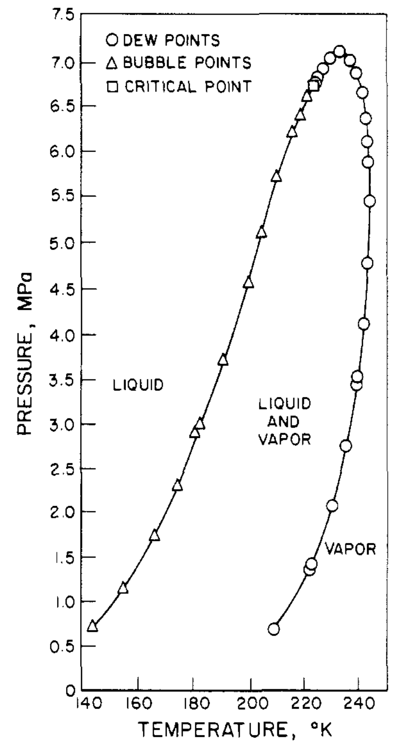

Figure 3. Dew and bubble point diagram for methane–ethane–propane mixture (z_{CH_4} = 0.8511; $z_{C_2H_6}$ = 0.1007).

The temperature of the cell contents at equilibrium was assumed to be that of the fluid in the bath. The temperature was measured by a calibrated copper–constantan thermocouple mounted in the bath. The emf produced by the thermocouple was balanced with a Leeds and Northrup K-4 potentiometer with a reference cold junction maintained at 273.15 K.

The pressure inside the equilibrium cell was measured with a 2000 psia (13.79 MPa) capacity dead-weight tester supplied by Chandler Engineering Co. A 2000 psia (13.79 MPa) Heise pressure gauge was used to obtain an approximate value of pressure within ±2 psia (±0.0138 MPa). The dead-weight tester was employed to determine more accurate values of the pressure. Pressure measurements in the range of experimentation were made with the dead-weight tester with an uncertainty of ±0.001 P.

Procedure. The mixture cylinder (MC) was charged with the mixture. The equilibrium cell, the Jerguson sight gauges (J_1 and J_2), the lines connecting them, and the line extending to the pressure measuring device all were evacuated by operating the vacuum pump and opening the top Jerguson valves (TJ_1V and TJ_2V), the connecting valve (CV), the sample inlet valve (SIV2), the pressure gauge valve (PGV), the equilibrium cell valve (ECV), the vacuum to system valve (VSV), and the vacuum direct valve (VDV). The mercury separator valve (MSV), the vent valve (VV), and the SIV1 were kept closed. The above evacuation procedure was carried out for the first run. For successive runs, it was not necessary to evacuate the Jerguson gauges. The vacuum of the system was measured by the mercury manometer. The valves VDV and VSV were closed once complete evacuation was achieved. Then valve SIV1 or SIV2 was opened as required.

The Jerguson gauge was used for storage of the mixture as well as a pressure booster for the mixture.

Table I. Dew and Bubble Points for Methane-Ethane-Propane Mixture with $z_{CH_4} = 0.8511$ and $z_{C_2H_6} = 0.1007$

P, MPa	T, K	P, MPa	T, K
	Dew Points		
0.6893	210.15	6.760	241.87
1.379	223.26	6.978	239.82
1.440	223.71	7.134	237.59
2.068	231.04	7.235	234.15
2.757	236.21	7.154	230.37
3.446	239.87	7.037	227.59
4.136	242.59	6.914	225.37
4.825	244.26	6.896	225.04
5.514	244.43	6.863	224.54
5.967	244.26	6.850	224.21
6.465	243.15		
	Bubble Points		
0.7155	144.15	5.162	205.37
1.145	155.26	5.789	210.93
1.747	166.48	6.304	216.37
2.302	174.82	6.494	219.28
2.899	181.48	6.716	221.98
3.000	183.15	6.833	223.87
3.730	191.48	6.850[a]	224.21[a]
4.599	200.93		

[a] Critical point.

The pressure of the system could be increased in either of two ways. It could be increased by transferring more material to the system from the mixture cylinder provided the pressure in the mixture cylinder is higher than that in the system. The pressure of the system could also be increased by pushing the mercury into the Jerguson gauge from the mercury pump (MP). The bottom Jerguson valve (BJ_1V or BJ_2V) was opened for the latter purpose. The pressure of the system could be decreased by transferring the mercury from the system to the mercury pump. A mercury reservoir (MR) was used to effect large changes in the pressure of the system through use of the mercury pump.

Mixture Analysis. The methane, ethane, and propane used in this work were respectively stated to be 99.99, 99.90, and 99.99 mol % pure. The overall mixture composition was determined by mass spectrometer analysis and the component mole fractions were found to be as follows: $z_{CH_4} = 0.8511 \pm 0.0032$, $z_{C_2H_6} = 0.1007 \pm 0.0023$, $z_{C_3H_8} = 0.0480 \pm 0.0005$.

Visual Observation Technique

Dew and bubble points and the critical point of the mixture were determined by visual observation. A graphical technique for determination of dew points (*5*, *6*) was tested, but we found the visual observation technique to be more accurate. In the visual observation technique, the glass cell was continually and carefully observed for occurrence of a phase change. A cathetometer was used to obtain a magnified view of the glass cell. A tube light aided the vision by reflecting the light from the cell.

The visual observation technique to determine the dew points has been employed by many investigators (*3*-*6*). Following is a description of the method as employed in this study. The mixture in the cell was cooled at an assigned constant pressure to determine the dew point temperature at that pressure. The rate of cooling was rapid at first and considerably slower as the temperature approached the dew point temperature. In the neighborhood of the dew point, the cell temperature was decreased in approximately 1 K intervals. As the temperature more closely approached the dew point temperature, the cell temperature was decreased by smaller increments, of the order of 0.1-0.05 K until the dew point was reached. After each incremental decrease in temperature, the cell contents were vigorously agitated by means of the magnet and steel ball. The cell was constantly observed through the cathetometer during this process until the beginning of condensation in the cell was observed. The temperature of the cell at which condensation began (the inner surface of the cell became hazy) was identified as the dew point temperature for the given pressure. The dew point temperatures determined by this technique were reproducible to ±0.05 K.

Bubble point determination by visual observation turned out to be simple, quick, and reliable as reported by others (*3*-*6*). All bubble points for this mixture were determined by constant-temperature operation. In constant-temperature operation, the bubble point is determined by increasing the pressure of the cell at constant temperature. The mixture in the cell was first brought to the desired temperature. After the desired temperature was reached, and the cell contents were in the two-phase region, the bubble point was approached by introducing additional mixture to the cell (and agitating the contents of the cell), thereby increasing the pressure and increasing the fraction of liquid in the cell. The process was continued until a point was reached when a very small bubble of gas was observed at the top of the soil. The contents of the cell were vigorously agitated at this point. If the bubble did not disappear by agitation, a very small amount of the mixture was introduced to the cell and the cell contents were agitated again. The pressure at which this bubble just disappeared was identified as the bubble point pressure at the given temperature.

The critical point was determined by visual observation of the state in which the meniscus between the gas and liquid phases just disappeared and agitation of the fluid in the cell effected the appearance of fumes. This point was identified as the critical point of the mixture.

Results and Discussion

Experimentally determined dew and bubble points for the mixture of methane, ethane, and propane are presented in Table I and shown in the form of a complete phase boundary in Figure 3.

As mentioned earlier, all bubble point measurements were made by the constant-temperature procedure. The uncertainty in reported bubble point temperature is ±0.005 K, which corresponds to the precision of the temperature measuring device. The uncertainty in reported dew point pressures was estimated to be ±0.001 P. Almost all of the dew point measurements were made by the constant-pressure procedure. In the constant-pressure method, the uncertainty in the dew point temperature was estimated to be ±0.05 K.

The critical temperature and pressure of the mixture were determined to be 224.2 K and 6.850 MPa, respectively.

Registry No. Methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6.

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