

Reservoir Fluids

PETE 310

Lab 4: Determination of Phase Boundaries (Bubblepoints and Dewpoints) and Retrograde Condensation

Learning Objectives

- Determine phase boundaries: bubblepoint pressures and dewpoint pressures for given temperatures.
- Determine effect of compositions upon the phase envelope of binary mixtures made with ethane and *n*-heptane.
- Determine and compare liquid and gas densities as a function of pressure and composition.
- Determine the amount of liquid, expressed as a liquid saturation (V_l/V_l+V_g), dropping in a reservoir at different pressures during depletion due to retrograde condensation.
- Compare your “virtual” measurements with the data provided in Fig. 2-37 of your textbook (unit conversions are required).

General Skills

- Use Excel spread sheets and graphs.
- Calculate relationships between moles, mass, and molecular weight.
- Convert mass percentage to mole percentage.
- Work with different systems of units and convert one set to another.

Background Requirements

The behavior of a mixture is not as simple as the behavior of a pure component. A distinct feature of the single-component system is that, at a fixed temperature, two phases can exist in equilibrium at only one pressure. For a binary system, two phases can coexist in equilibrium at various pressures at the same temperature. Thermodynamic and physical properties of a multicomponent system change with composition. This composition can be specified in terms of mole or weight fractions.

To study the phase behavior of a binary system, we must recall some important definitions. These are the bubblepoint line, dewpoint line, critical point, critical pressure, critical temperature, cricondentherm, and cricondenbar. The two-phase region is bounded by the

bubblepoint line and the dewpoint line. The two lines join at the critical point.

- **Critical Temperature:** The critical temperature of a pure component is defined as the highest temperature at which two phases could coexist. For binary and multicomponent systems, gas and liquid phases may exist at temperatures greater than the critical temperature of the individual components.
- **Critical Pressure:** The critical pressure of a pure component is the highest pressure at which two phases can coexist in equilibrium. For binary and multicomponent systems, gas and liquid phases may exist at pressures greater than the critical pressure of the individual components.
- **Locus of Critical Points:** Any combination of compositions in the mixture gives different phase envelopes, each with its corresponding critical point. The line that goes through all the critical points for the different compositions is called the *locus* of the critical points. Analyze in your text book the different phase diagrams for the binary systems composed of methane/ethane.
- **Cricondenbar:** The cricondenbar is the maximum pressure at which two phases can exist in equilibrium.
- **Cricodentherm:** The cricodentherm is the maximum temperature at which two phases can exist in equilibrium.
- **Retrograde Condensation:** This behavior is characterized by any isotherm between the critical point and the cricodentherm. In this region, a special thermodynamic behavior is observed. Describe what you observe in your experiments.

Experiment

Prepare the following mixtures of ethane and *n*-heptane.
Note that the percentage is expressed as weight %

wt % ethane

Mixture A	90.22
Mixture B	9.78
Mixture C	70.22

The phase envelopes you need to reproduce are highlighted in the following graph from your text book. Mixture C will be used to analyze the retrograde behavior.

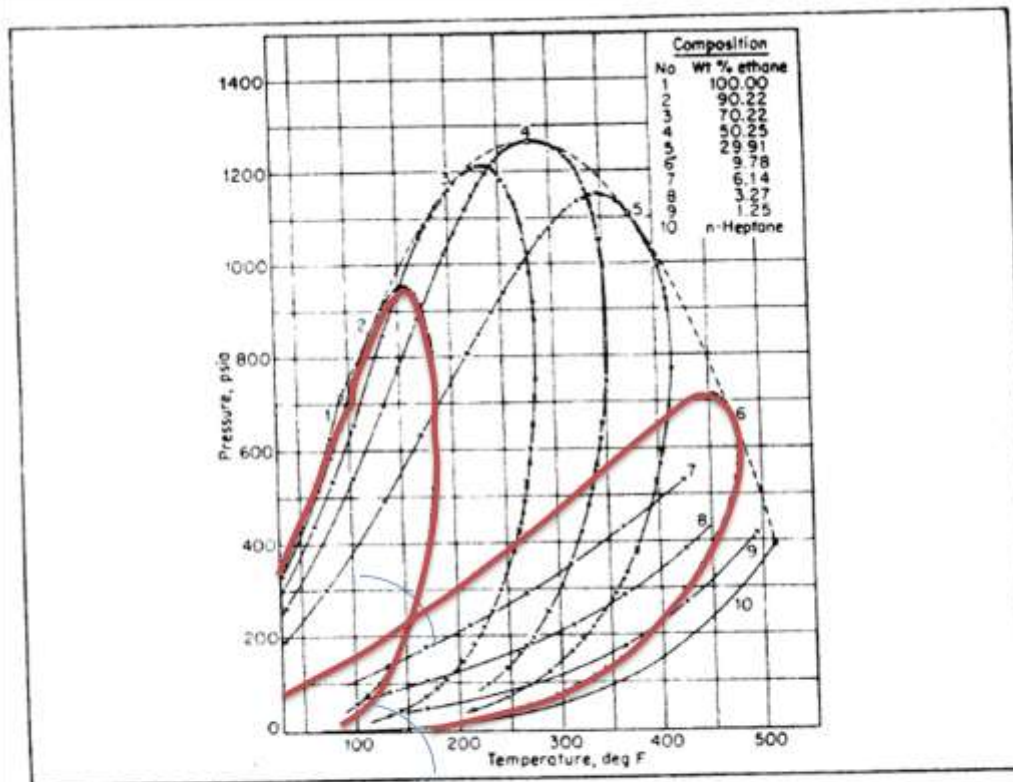


Fig. 2-37. Phase diagrams of mixtures of ethane and n-heptane. (Reprinted with permission from *Industrial and Engineering Chemistry* 30, 461. Copyright 1938 American Chemical Society.)

Indicate the number of moles used for each component.

Determining Bubblepoint

- Indicate the number of moles used for each mixture.
- Set the temperature of the experiment at 50°F; this will be the lowest temperature for all the mixtures.
- Charge the sample at a pressure such that the mixture is in the liquid phase; provide the amount of sample charged to the cell in mass and moles. For example, if you have 20 millimoles of ethane and 60 millimoles of n-heptane these correspond to $20 \times 10^{-3} \times M_{w_{C_2}}$ grams of ethane and to $60 \times 10^{-3} \times M_{w_{C_7}}$ grams of n-heptane. The weight fractions required must be converted into mole fractions. Remember they **are not the same**.
- Start reducing the pressure on the sample until the first bubble of gas appears. You should determine this pressure within ± 0.05 bar of uncertainty (0.75 psia).

- Increase the temperature to determine a new bubblepoint pressure for this new temperature. Use your judgment; you want to determine enough bubblepoints to define the phase envelope for every mixture you are evaluating. You need to estimate the cricondenbar pressure to have a good definition of the phase envelope.
- Adjust the pressure of the PVT cell to determine this new bubblepoint pressure. You may have to increase this or to decrease it. Explain your procedure.
- *At some temperature the state of your system when you pressurize it up to a single phase may indicate dense gas. Explain why this happens and at what temperature this occurred for each mixture.*
- Once you have determined the bubblepoint line for your mixture, begin determining the dewpoints.

Determining Dewpoint

Continue with the same mixture you used for the bubblepoint determinations and at the highest temperature you reached in the bubblepoint determinations.

- Estimate the temperature range over which it is likely that you might cross the phase envelope. This should be between the critical and the cricondenthem temperatures.
- Set your cell at a pressure and temperature such that your fluid exhibits a single phase; this is a dense-gas phase.
- Reduce the pressure about 6 to 7 bar (100 psia) such that you are in the two-phase region.
- At a fixed pressure, adjust the temperature of the cell such that the amount of liquid formed in the PVT cell is infinitesimal. Your dewpoint temperature at the specified pressure should have an accuracy of 0.05°C.
- Keep reducing the pressure using decrements of 7 to 14 bar (100 to 200 psia) and determine the dewpoint temperature as explained in the previous step.

At lower pressures you may need to work with a smaller sample size, since the expansions may exceed the size of the PVT cell. When this occurs, make sure that the components in the mixture preserve the same proportions, although the amounts charged are less.

Determination of Retrograde Condensation

Fig. 2-37 of your textbook shows the phase diagrams for the mixtures that you evaluated in this lab. Your “experimental results” should be close to the experimental results that were

published in 1938 (here samples 2 and 6 correspond to the mixtures you will be evaluating in this lab)

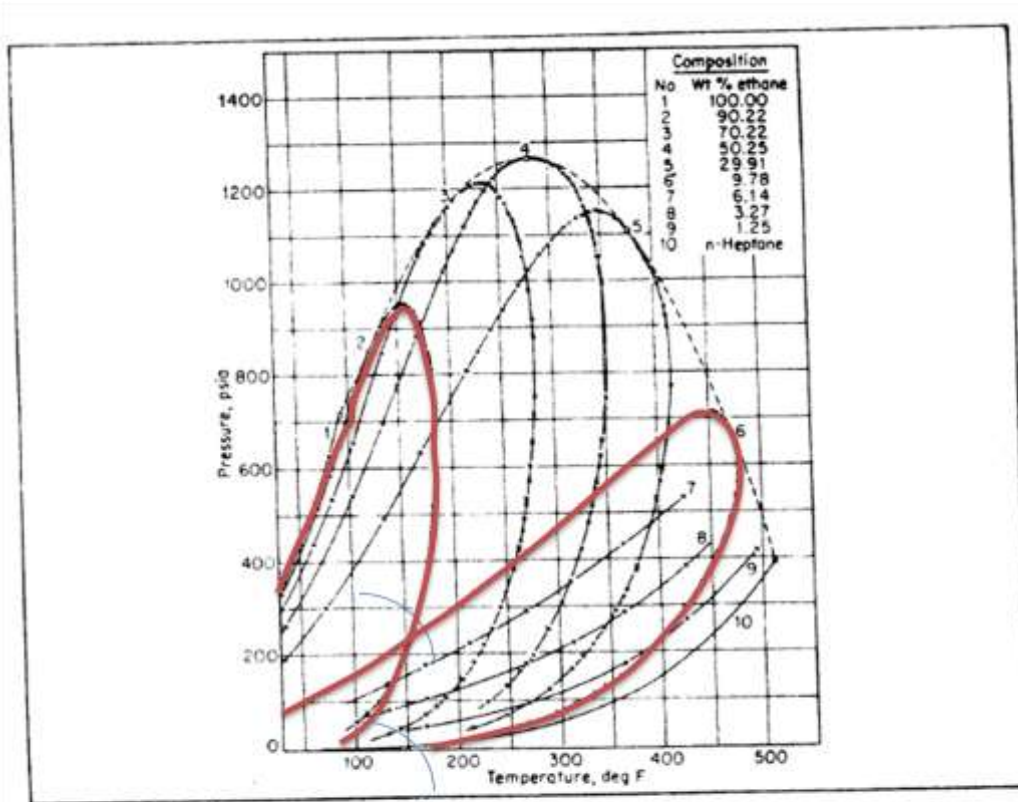


Fig. 2-37. Phase diagrams of mixtures of ethane and n-heptane. (Reprinted with permission from *Industrial and Engineering Chemistry* 30, 461. Copyright 1938 American Chemical Society.)

- Use a mixture with 70.22 wt % of ethane (Mixture C) and set the cell temperature between the critical temperature and the cricondentherm. Select this temperature as close to the critical point as possible (this corresponds to sample 3 in the graph)

The sample size should be selected such that you have enough cell volume to allow for the expansion that will occur from the upper dewpoint pressure to the lower dewpoint pressure; this may require some trial and error.

- Begin the experiment close to the upper dewpoint pressure.
- Reduce the pressure slightly using small increments (1 bar).
- Record these pressures and the proportion of liquid formed in the cell.
- Continue lowering the pressure until the lower dewpoint pressure is achieved.

Specific Requirements

- Plot the phase envelopes obtained (PT phase diagrams) for the two mixtures overlapped as in Fig. 2-37 of your textbook. **Include** the data points from Fig. 2-37 in this plot to compare your data with the published data in 1938. You do not need to have exactly the same temperatures or pressures, but you can certainly appreciate whether your data

follows the correct trend or not. Note: You will need to convert pressures and temperatures to the units used in Fig. 2-37.

- Indicate the approximate values for the mixture critical points, cricondenbars, and cricondentherms. Some graphical approximations will be necessary.
- Plot the percentage of liquid formed versus pressure for the retrograde condensation experiment with Mixture C.

Analysis

- What are the main differences among the mixtures analyzed?
- What does the shape of the phase envelope tell you?
- What is the effect of composition upon bubblepoint pressures for a fixed temperature?