PETE 310

Lectures # 6 & # 7

Two Component Mixtures

Three & Multicomponent Mixtures

(and review Lecture#5)
Learning Objectives

After completing this chapter you will be able to:

- Understand pure component phase behavior as a function of pressure, temperature, and molecular size.
- Understand the behavior of binary and multicomponent mixtures.
- Behavior understood through proper interpretation of phase diagrams.
Pressure vs Specific Volume Pure Substance

Pressure (psia)

Specific Volume (ft³/lbm)

2-phase

CP

Tc

T

V

L

V
A Problem

Specific Volume (ft³ / lbm)

Pressure (psia)

2-phase

$V_L$, $V_V$
# Pure Component Properties

![Tabulated critical properties](McCain)

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Boiling point, °F</th>
<th>Vapor pressure, psia</th>
<th>Freezing point, °F</th>
<th>Pressure, psia</th>
<th>Temperature, °F</th>
<th>Volume, ft³/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane</td>
<td>CH₄</td>
<td>16.043</td>
<td>-258.74(28)</td>
<td>5000.1</td>
<td>-296.45 d</td>
<td>667.8</td>
<td>-116.68</td>
<td>0.0088</td>
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<tr>
<td>2</td>
<td>Ethane</td>
<td>C₂H₆</td>
<td>30.070</td>
<td>-127.44</td>
<td>800.0</td>
<td>-297.04 d</td>
<td>707.8</td>
<td>90.10</td>
<td>0.0788</td>
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<tr>
<td>3</td>
<td>Propane</td>
<td>C₃H₈</td>
<td>44.097</td>
<td>-43.73</td>
<td>188.0</td>
<td>-305.82 d</td>
<td>616.3</td>
<td>206.01</td>
<td>0.0737</td>
</tr>
<tr>
<td>4</td>
<td>n-Butane</td>
<td>C₄H₁₀</td>
<td>58.124</td>
<td>31.12</td>
<td>51.54</td>
<td>-217.05</td>
<td>550.7</td>
<td>306.62</td>
<td>0.0703</td>
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<tr>
<td>5</td>
<td>Isobutane</td>
<td>C₄H₁₀</td>
<td>58.124</td>
<td>10.74</td>
<td>72.39</td>
<td>-255.28</td>
<td>529.1</td>
<td>274.96</td>
<td>0.0724</td>
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<tr>
<td>6</td>
<td>n-Pentane</td>
<td>C₅H₁₂</td>
<td>72.151</td>
<td>96.91</td>
<td>15.57</td>
<td>-201.51</td>
<td>488.6</td>
<td>365.6</td>
<td>0.0674</td>
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<tr>
<td>7</td>
<td>Isopentane</td>
<td>C₅H₁₂</td>
<td>72.151</td>
<td>82.11</td>
<td>20.444</td>
<td>-255.82</td>
<td>490.4</td>
<td>369.03</td>
<td>0.0679</td>
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<tr>
<td>8</td>
<td>Neopentane</td>
<td>C₅H₁₂</td>
<td>72.151</td>
<td>49.10</td>
<td>36.66</td>
<td>2.21</td>
<td>464.0</td>
<td>321.08</td>
<td>0.0673</td>
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<tr>
<td>9</td>
<td>n-Hexane</td>
<td>C₆H₁₄</td>
<td>86.178</td>
<td>155.73</td>
<td>4.960</td>
<td>-139.58</td>
<td>436.9</td>
<td>453.6</td>
<td>0.0687</td>
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<td>10</td>
<td>2-Methylpentane</td>
<td>C₆H₁₄</td>
<td>86.178</td>
<td>140.47</td>
<td>6.79</td>
<td>-244.59</td>
<td>436.6</td>
<td>435.74</td>
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<td>11</td>
<td>3-Methylpentane</td>
<td>C₆H₁₄</td>
<td>86.178</td>
<td>145.89</td>
<td>6.103</td>
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<td>448.2</td>
<td>448.2</td>
<td>0.0682</td>
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<tr>
<td>12</td>
<td>Neohexane</td>
<td>C₆H₁₄</td>
<td>86.178</td>
<td>121.51</td>
<td>9.859</td>
<td>-147.77</td>
<td>446.9</td>
<td>420.04</td>
<td>0.0668</td>
</tr>
<tr>
<td>13</td>
<td>2,3-Dimethylbutane</td>
<td>C₆H₁₄</td>
<td>86.178</td>
<td>136.36</td>
<td>7.406</td>
<td>-199.37</td>
<td>453.5</td>
<td>440.20</td>
<td>0.0666</td>
</tr>
</tbody>
</table>
Pure Component Data in Excel

Should link to a downloadable Excel file...
Heat Effects Accompanying Phase Changes of Pure Substances

Clapeyron equation

\[ L_v = T \Delta V \frac{dP_v}{dT} \quad \text{Btu/lb-mol} \]

With

\[ \Delta V = V_{Mg} - V_{Ml} \]
Heat Effects Accompanying Phase Changes of Pure Substances

\[ L_v = T \Delta V \frac{dP^v}{dT} \]

Approximate relation (Clausius - Clapeyron Equation)

\[ \frac{dP^v}{dT} = \frac{L_v}{RT^2} P^v \]
Example of Heat Effects Accompanying Phase Changes
Example of Heat Effects
Accompanying Phase Changes

Steam flooding Problem:

Calculate how many BTU/day (just from the latent heat of steam) are provided to a reservoir by injecting 6000 bbl/day of steam at 80% quality and at a T=462 °F
COX - Vapor Pressure Charts
(normal paraffins)

Pressure vs. Temperature chart with log scale and non-linear scale.
Determination of Fluid Properties

Ps = saturation pressure

Temperature of Test Constant
Vapor Pressure Determination

Pressure

Volume

\[ P_S \]

\[ V_L \]

\[ T_1 \]

\[ T_2 \]
Binary Mixtures

- Relationships to analyze: $P$, $T$, molar or specific volume or (molar or mass density) - as for a pure component –

- COMPOSITION – Molar Composition
Hydrocarbon Composition

The hydrocarbon composition may be expressed on a weight basis or on a molar basis (most common)

Recall

\[ n_i = \frac{M_i}{M_{w_i}} = \frac{\text{mass of } ''i''}{\text{molecular weight of } ''i''} \]
Our Systems of Concern

Gas system

Oil system

open
Hydrocarbon Composition

By convention liquid compositions (mole fractions) are indicated with an $x$ and gas compositions with a $y$.

$$x_1 = \left( \frac{n_1}{n_1 + n_2} \right)_{\text{liquid}}$$

$$y_1 = \left( \frac{n_1}{n_1 + n_2} \right)_{\text{gas}}$$
A separator

\[ z_i(T_1, P_1) \quad \rightarrow \quad T_1, P_2 \quad \rightarrow \quad y_i(T_1, P_2) \]

\[ P_1 > P_2 \]

\[ x_i(T_1, P_2) \]
Mathematical Relationships

\[ z_1 = x_1 f_l + y_1 f_v \]
\[ z_1 = x_1 (1 - f_v) + y_1 f_v \]

with

\[ f_v = \frac{z_1 - x_1}{y_1 - x_1} \]

In general

\[ f_v = \frac{z_i - x_i}{y_i - x_i} \]
**Key Concepts**

- **Fraction of vapor (fv)**
- **Mole fractions in vapor (or gas) phase → yi**
- **Mole fractions in liquid (or oil) phase → xi**
- **Overall mole fractions (zi) → combining gas & liquid**
Phase Diagrams for Binary Mixtures

Types of phase diagrams for a two-component mixture

Most common

- \((PT)_{zi}\) at a fixed composition
- \((Pzi)_{T}\) at a fixed \(T\)
- \((Tzi)_{P}\) at a fixed \(P\)
- \((PV)_{zi}\) or \((Pr)_{zi}\)
Pressure vs Temperature Diagram (PT)_{zi}

- **Zi = fixed**
- **Bubble Curve**
- **Liquid**
- **Gas**
- **Dew Curve**

2 Phases
Pressure Composition Diagrams - Binary Systems

Pressure Composition Diagrams show the relationship between temperature and pressure for a binary system. The diagram includes two graphs:

1. **Pressure vs. Temperature**
   - The graph on the left shows the pressure (P) as a function of temperature (T) for two components, CP₁ and CP₂. The curves indicate the phase behavior, with different regions for liquid and vapor phases.

2. **Temperature vs. Composition**
   - The graph on the right shows the temperature (T) as a function of composition (x₁, y₁) for two phases: liquid and vapor. The curves include the bubble curve and dew curve, which define the boundaries of two-phase regions.

Key Points:
- **CP₁** and **CP₂** are critical points indicating phase changes.
- **P₁** and **P₂** represent vapor pressures for the two components.
- The **bubble curve** and **dew curve** delineate the two-phase regions.
- **Liquid** and **Vapor** regions are clearly marked.
Temperature vs. Composition Diagrams – Binary Systems

Diagram showing the relationship between temperature, composition, and pressure in a binary system. The diagram includes points CP₁ and CP₂, indicating phase transitions, and lines for the dew curve and bubble curve. The axes are labeled as T₁s, T₂s for temperature, P for pressure, and x₁, y₁ for composition.
3-D Phase Diagram

(P,x)_T

(T,x)_P
Gas-Liquid Relations

\[ z_1 = \text{fixed} \]

\[ P_B \quad \text{Pressure} \]

\[ P_D \]

\[ T_a \quad \text{Temperature} \]

\[ T = T_a \]

Point A

Point B

Point C

\[ z_1 = \text{overall mole fraction of [1]}, \quad y_1 = \text{vapor mole fraction of [1]}, \quad x_1 = \text{liquid mole fraction of [1]} \]
Supercritical Conditions Binary Mixture

Temperature $x_1, y_1$

$P_1$

$P_2^y$
Quantitative Phase Equilibrium Exercise

P-xy Diagram

Composition (%C1)

Pressure (psia)

T=160F
Quantitative Phase Equilibrium

Exercise

P-xy Diagram

- Composition (%C1)
- Pressure (psia)

Lines for different temperatures:
- T=100°F
- T=160°F
- T=220°F
Quantitative Phase Equilibrium Exercise

P-xy Diagram

Composition (%C1) vs. Pressure (psia) for T=160°F
Typical Black-Oil System

Phase Equilibria Methane/n-Decane

Pressure (psia)

BP (200)
DP (200)

Gas cap composition

Black Oil Composition

$x_1, y_1, z_1, (1 = \text{Methane})$
Ternary Diagrams: Review
Ternary Diagrams: Review

Pressure Effect

![Ternary Diagrams](image)

- **Gas**
  - $p = 14.7$ psia

- **2-phase**
  - $p = 380$ psia

- **Liquid**
  - $p = 500$ psia

- **2-phase**
  - $p = 1500$ psia

- **Liquid**
  - $p = 2000$ psia

- **Liquid**
  - $p = 2350$ psia
Ternary Diagrams: Review

Dilution Lines

C<sub>10</sub>  1
0  0.1  0.2  0.3  0.4  0.5  0.6  0.7  0.8  0.9

C<sub>1</sub>  1
0.1  0.2  0.3  0.4  0.5  0.6  0.7  0.8  0.9

n-C<sub>4</sub>  1
0  0.1  0.2  0.3  0.4  0.5  0.6  0.7  0.8  0.9
Ternary Diagrams: Review

Quantitative Representation of Phase Equilibria - Tie (or equilibrium) lines

- Tie lines join equilibrium conditions of the gas and liquid at a given pressure and temperature.
  - Dew point curve gives the gas composition.
  - Bubble point curve gives the liquid composition.
Ternary Diagrams: Review

Quantitative Representation of Phase Equilibria - Tie (or equilibrium) lines

- All mixtures whose overall composition \( z_i \) is along a tie line have the SAME equilibrium gas \( y_i \) and liquid composition \( x_i \), but the relative amounts on a molar basis of gas and liquid \( f_v \) and \( f_l \) change linearly (0 – vapor at B.P., 1 – liquid at B.P.).
Illustration of Phase Envelope and Tie Lines
Uses of Ternary Diagrams

Representation of Multi-Component Phase Behavior with a Pseudoternary Diagram

- Ternary diagrams may approximate phase behavior of multi-component mixtures by grouping them into 3 pseudocomponents

- heavy ($\text{C}_7^+$)
- intermediate ($\text{C}_2$-$\text{C}_6$)
- light ($\text{C}_1$, $\text{CO}_2$, $\text{N}_2$ - $\text{C}_1$, $\text{CO}_2$-$\text{C}_2$, ...)
Uses of Ternary Diagrams

Miscible Recovery Processes

Solvent 1

Solvent 2

Oil
Exercise

Find overall composition of mixture made with 100 moles oil "O" + 10 moles of mixture "A".
Practice Ternary Diagrams

Pressure Effect

T=180°F
P=14.7 psia

T=180°F
P=200 psia

T=180°F
P=400 psia

T=180°F
P=600 psia
Practice Ternary Diagrams

Pressure Effect

T=180°F
P=1000 psia

Pressure Effect

T=180°F
P=1500 psia

Pressure Effect

T=180°F
P=2000 psia

Pressure Effect

T=180°F
P=3000 psia

Pressure Effect

T=180°F
P=4000 psia
Practice Ternary Diagrams

**Temperature Effect**

- T=100°F, P=2000 psia
- T=150°F, P=2000 psia
- T=200°F, P=2000 psia
- T=300°F, P=2000 psia
Practice Ternary Diagrams

Temperature Effect

T = 350°F, P = 2000 psia

T = 400°F, P = 2000 psia

T = 450°F, P = 2000 psia
Pressure-Temperature Diagram for Multicomponent Systems

- Reservoir Pressure
- Reservoir Temperature

1-Phase
- Bubble-Curve
- 60%
- 20%
- Dew-Curve
- CP
- 0%

2-Phase
Changes During Production and Injection

![Diagram showing changes during production and injection with temperature and pressure axes, labeled with t1, t2, and t3. Sections for production, injection, and gas injection are illustrated.]
Homework

🌟 See Syllabus please
Phase Diagrams

Types of phase diagrams for a single component (pure substance)

- (PT)
- (PV) or (Pp)
- (TV) or (Tp)