



## Properties of Reservoir Fluids (PGE 362)

# Quantitative Phase Behavior

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# Non-Ideal Solutions

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Calculation of bubble-point pressure and dew-point pressure using equilibrium constants:

Since the total pressure  $P_T$  no longer appears implicitly in equations 14 to 19 but is contained in the  $K$  values, it is no longer possible to solve directly for the bubble-point and dew-point pressure as was done in the case of ideal solutions.

(Properties of petroleum reservoir fluids: Burcik – Pages 92 & 93)

$$\sum y_i = \sum \frac{z_i n}{n_v + \frac{n_l}{K_i}} = 1 = \sum \frac{z_i n}{0 + \frac{n_l}{K_i}} = \sum K_i z_i \qquad \sum K_i x_i = 1$$

$$\sum x_i = \sum \frac{z_i n}{n_l + K_i n_v} = 1 = \sum \frac{z_i n}{0 + K_i n_v} = \sum \frac{z_i}{K_i} \qquad \sum \frac{y_i}{K_i} = 1$$

# Non-Ideal Solutions

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EXAMPLE. A system has the following overall composition

| Component                   | Mole Fraction |
|-----------------------------|---------------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403         |
| $n\text{-C}_5\text{H}_{12}$ | 0.325         |
| $n\text{-C}_6\text{H}_{14}$ | 0.272         |

At 160° F calculate the bubble-point pressure, the composition of the vapor at the bubble point, the dew-point pressure, and the composition of the liquid at the dew point.

# Non-Ideal Solutions

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## Solution:

Raoult's Law will be used to guess the first value bubble point pressure  $BPP = \sum x_i P_i^\circ$

$$BPP = 0.403 \times 123 + 0.325 \times 43.0 + 0.272 \times 15.8 = 67.85 \text{ psia}, \quad BPP = 70 \text{ psia (first trial)}$$

| Component                   | $x_i$ | $K_i$ (70 psia and 160° F) | $K_i x_i$ |
|-----------------------------|-------|----------------------------|-----------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403 | 1.63                       | 0.657     |
| $n\text{-C}_5\text{H}_{12}$ | 0.325 | 0.61                       | 0.198     |
| $n\text{-C}_6\text{H}_{14}$ | 0.272 | 0.25                       | 0.068     |
|                             |       |                            | <hr/>     |
|                             |       |                            | 0.923     |

# Non-Ideal Solutions

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## Solution:

Since the summation is less than 1 then a lower value of pressure will be chosen,  $BPP = 60$  psia

| Component                   | $x_i$ | $K_i$ (60 psia and 160° F) | $K_i x_i$   |
|-----------------------------|-------|----------------------------|-------------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403 | 1.86                       | 0.750       |
| $n\text{-C}_5\text{H}_{12}$ | 0.325 | 0.70                       | 0.228       |
| $n\text{-C}_6\text{H}_{14}$ | 0.272 | 0.285                      | 0.077       |
|                             |       |                            | <hr/> 1.055 |

# Non-Ideal Solutions

## Solution:

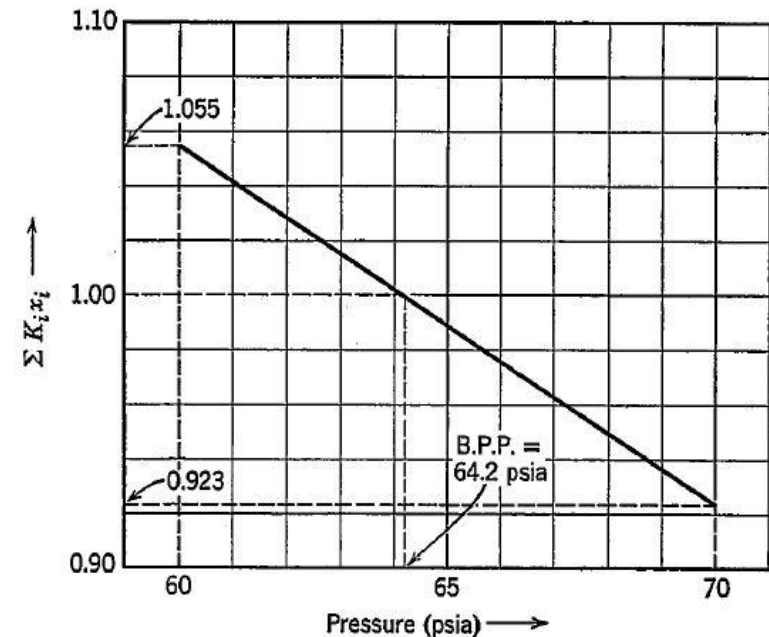
Since the summation is greater than 1 then the bubble point pressure will be between 60-70 psia  
The exact value can be obtained either mathematically (interpolation) or graphically.

## Interpolation:

$$\frac{70 - 60}{70 - BPP} = \frac{0.923 - 1.055}{0.923 - 1.000}$$

$$BPP = 64.2 \text{ psia}$$

## Graphically:



# Non-Ideal Solutions

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## Solution:

To calculate the composition of the vapor at the BPP the  $K$  values at 160 °F and 64.2 psia are obtained by interpolation from the appropriate charts and  $K_i x_i$  computed.

| Component                   | $x_i$ | $K_i$ (64.2 psia and 160° F) | $y_i = K_i x_i$ |
|-----------------------------|-------|------------------------------|-----------------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403 | 1.76                         | 0.709           |
| $n\text{-C}_5\text{H}_{12}$ | 0.325 | 0.66                         | 0.214           |
| $n\text{-C}_6\text{H}_{14}$ | 0.272 | 0.27                         | 0.073           |
|                             |       |                              | <hr/> 0.996     |

# Non-Ideal Solutions

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## Solution:

To calculate the dew point pressure choose a pressure of 35 psia as point of departure and calculate  $\sum \frac{y_i}{K_i}$

| Component                   | $y_i$ | $K_i$ (35 psia and 160° F) | $y_i/K_i$ |
|-----------------------------|-------|----------------------------|-----------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403 | 3.17                       | 0.127     |
| $n\text{-C}_5\text{H}_{12}$ | 0.325 | 1.17                       | 0.278     |
| $n\text{-C}_6\text{H}_{14}$ | 0.272 | 0.47                       | 0.579     |
|                             |       |                            | <hr/>     |
|                             |       |                            | 0.984     |



# Non-Ideal Solutions

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## Solution:

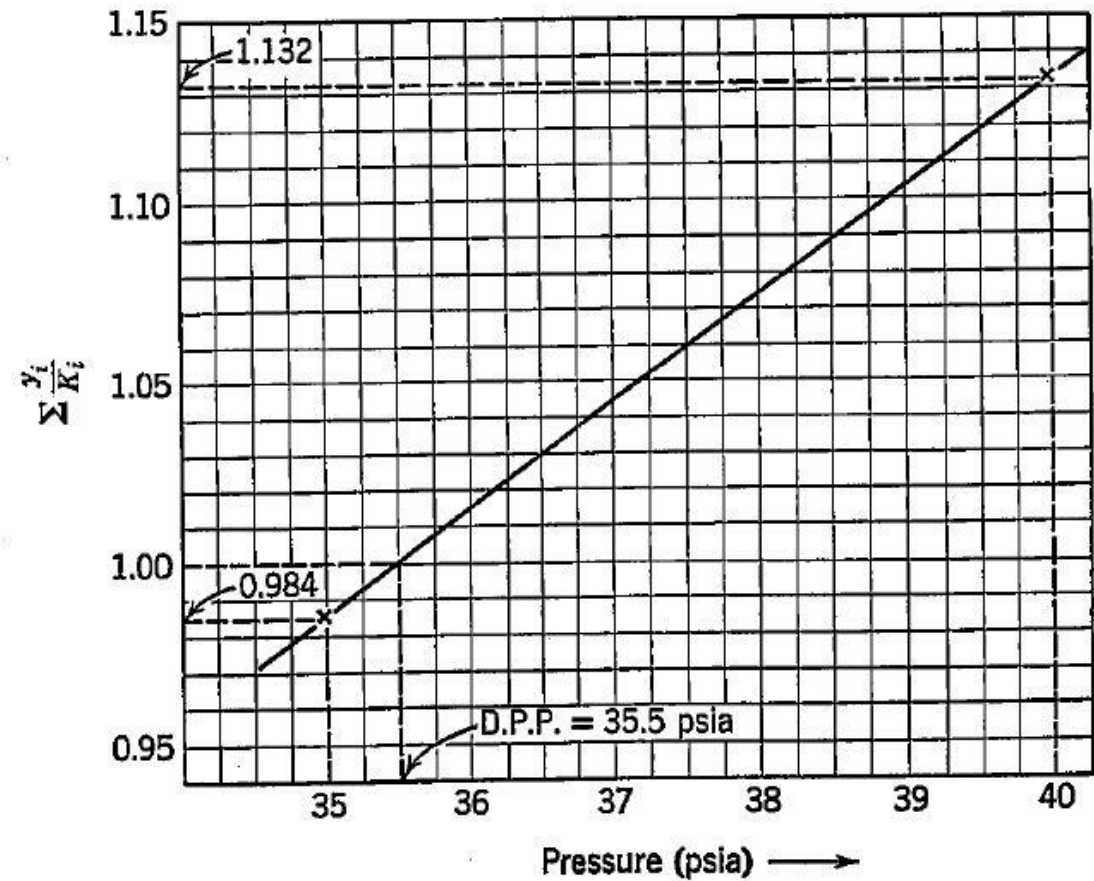
Since the required summation is low the calculation will be repeated at 40 psia

| Component                   | $y_i$ | $K_i$ (40 psia and 160° F) | $y_i/K_i$   |
|-----------------------------|-------|----------------------------|-------------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403 | 2.75                       | 0.147       |
| $n\text{-C}_5\text{H}_{12}$ | 0.325 | 1.01                       | 0.322       |
| $n\text{-C}_6\text{H}_{14}$ | 0.272 | 0.41                       | 0.663       |
|                             |       |                            | <hr/> 1.132 |

# Non-Ideal Solutions

## Solution:

The dew point pressure can be estimated graphically  $DPP = 35.5$  psia



# Non-Ideal Solutions

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## Solution:

The composition of the dew-point liquid is computed as follows;

| Component                   | $y_i$ | $K_i$ (35.5 psia and 160° F) | $x_i = \frac{y_i}{K_i}$ |
|-----------------------------|-------|------------------------------|-------------------------|
| $n\text{-C}_4\text{H}_{10}$ | 0.403 | 3.13                         | 0.129                   |
| $n\text{-C}_5\text{H}_{12}$ | 0.325 | 1.15                         | 0.283                   |
| $n\text{-C}_6\text{H}_{14}$ | 0.272 | 0.464                        | 0.586                   |
|                             |       |                              | <hr/>                   |
|                             |       |                              | 0.998                   |

# Non-Ideal Solutions

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## Henry's Law:

- Henry's law is one of the gas laws formulated by William Henry in 1803
- At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid
- An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid

$$C = kP_{gas}$$

$C$  : is the solubility of a gas at a fixed temperature in a particular solvent (mole/L)

$k$  : is Henry's law constant (often in units of L. atm/mole)

$P_{gas}$  : is the partial pressure of the gas (often in units of atm)

# Non-Ideal Solutions

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## Henry's Law:

- Equation becomes  $P_i = Cx_i$   
C: the proportional constant, experimentally determined  
(not the vapor pressure of the pure component)
- If the liquid is relatively non-volatile  $P_i$  is essentially equal to  $P_T$
- If the gas is not too soluble,  $x_i$  is proportional to the weight of gas dissolved ( $W$ ).
- $P_T = C'W$   
C': the new proportionality constant
- Henry's Law is not exact law
  - At high pressure and in cases where the gas is very soluble in the liquid marked deviation occur.
  - Solution of natural gases in crude oil do not follow Henry's Law at very low pressures.