

## 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.

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

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

# 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.

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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
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			0.923

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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:

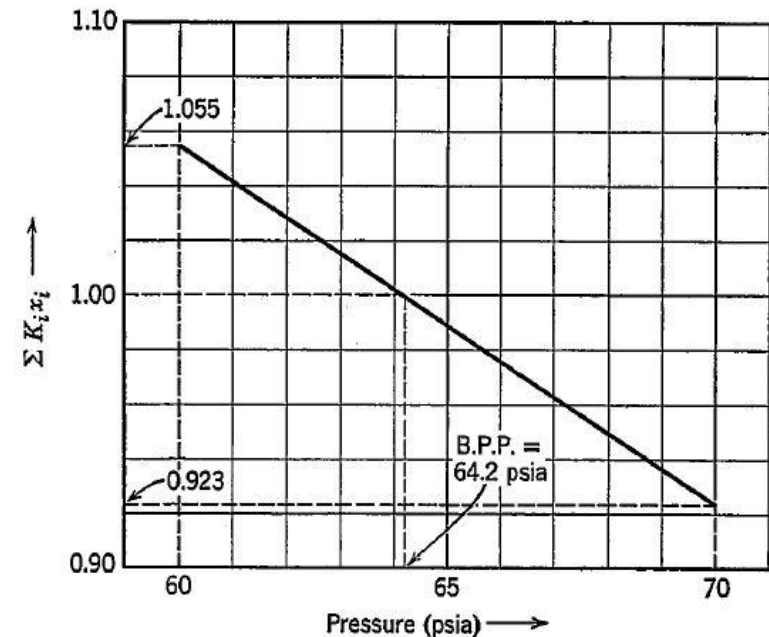
Since the summation is greater than 1 then the bubble point pressure will be between 60-70 psia  
The exact value can be obtained either mathematically (interpolation) or graphically.

## 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
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			0.984



# Non-Ideal Solutions

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## Solution:

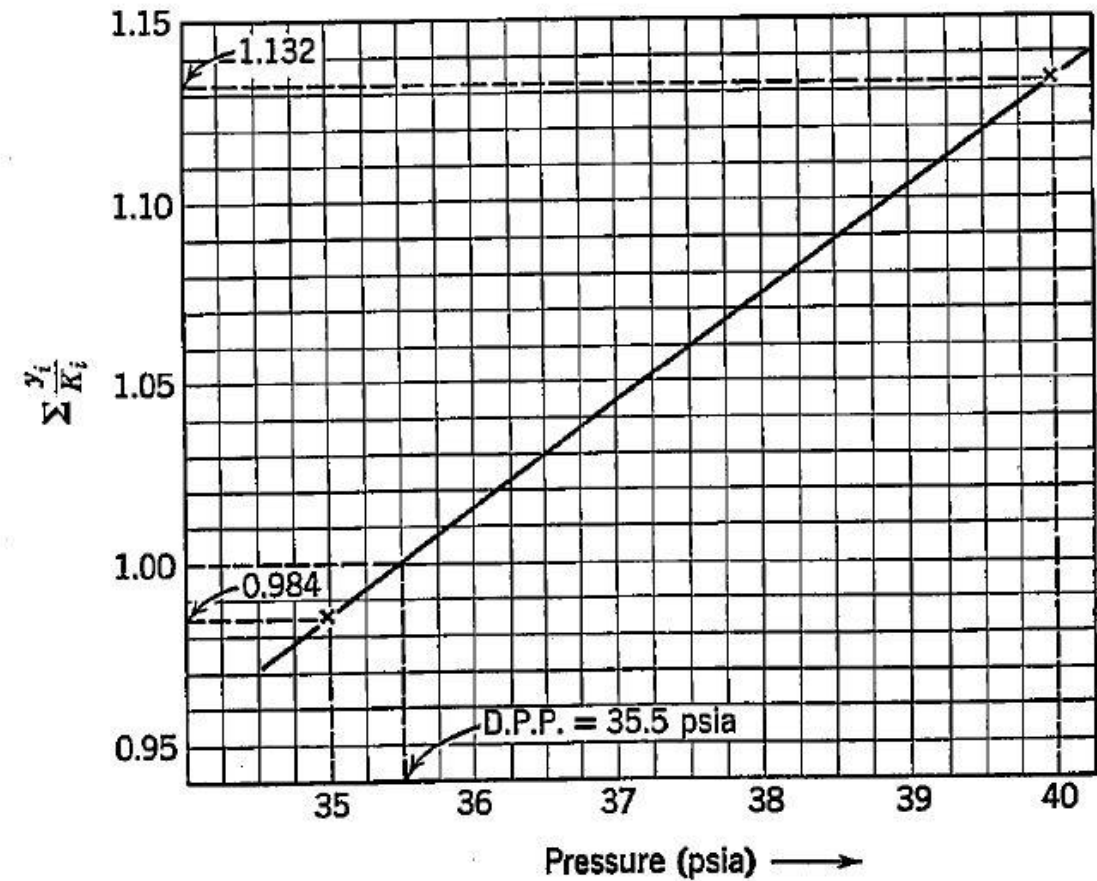
Since the required summation is low the calculation will be repeated at 40 psia

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
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			0.998

# Non-Ideal Solutions

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## Henry's Law:

- Henry's law expresses the effect of pressure on the solubility of a gas in a liquid.
- The weight of gas dissolved in a given quantity of liquid and at a given temperature is directly proportional to the pressure of the gas.
- Henry's Law and Raoult's Law are related in the following manner.
- The total pressure equation  $P_T = \sum x_i P_i^\circ$  is applicable to any component in an ideal solution.
- However, if the component in question is a gas dissolved in a liquid it is unlikely that the solution will exhibit ideal behavior.

# 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.