

# *Phase Equilibria & Equations of State*

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COURSE: GEOSTATISTICS & RESERVOIR SIMULATION

BY: MOHAMMAD EBADI

*SPRING 2019*

# Outlines:

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Introduction

Equilibrium Ratios

Flash Calculations

Equations Of State (EOS)

EOS Applications

# Hydrocarbon Systems

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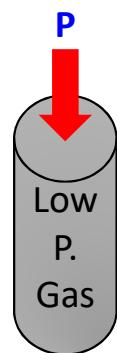
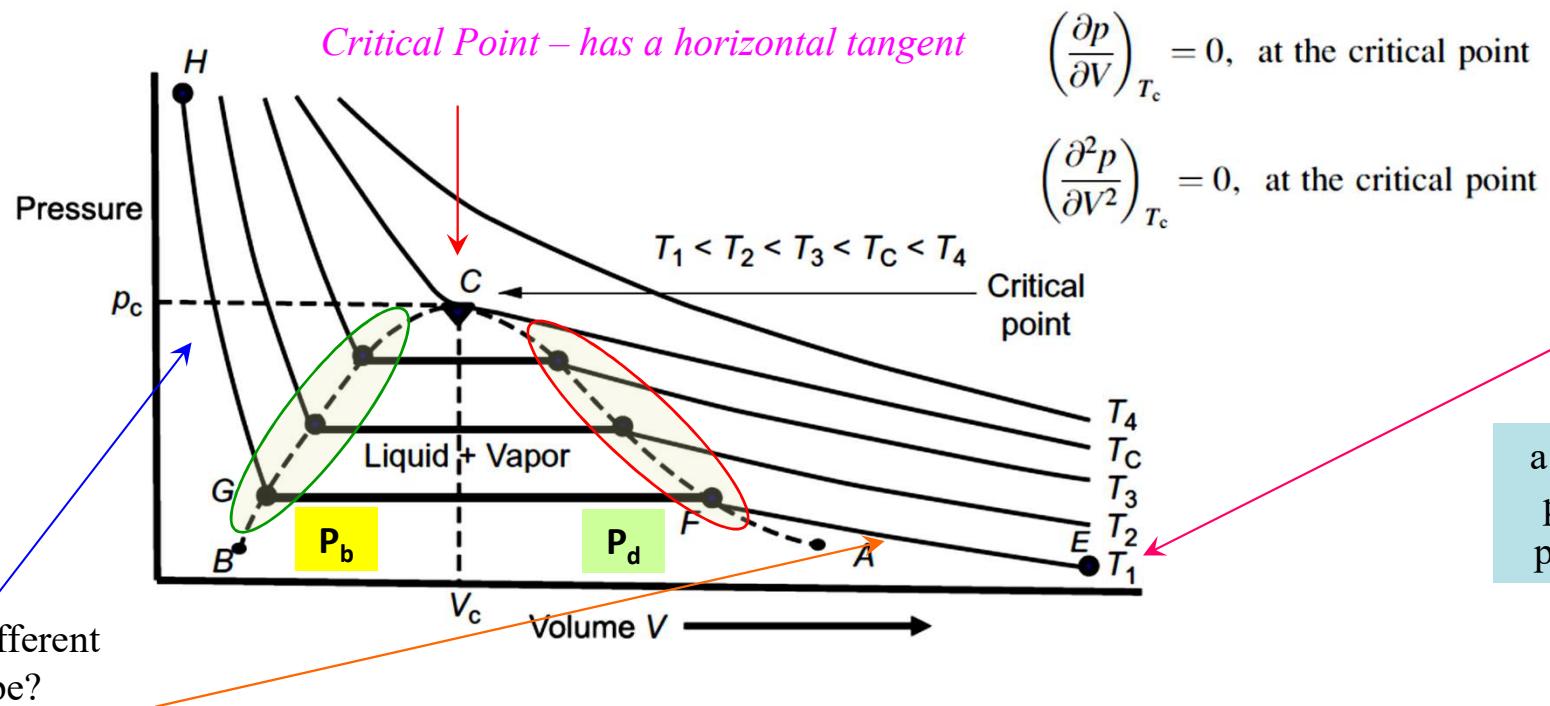
- ❖ Hydrocarbon systems found in **petroleum reservoirs** are known to display **multiphase behavior** over **wide ranges of pressures and temperatures**. The most important phases that occur in petroleum reservoirs are a liquid phase, such as crude oils or condensates, and a gas phase, such as natural gases.

# Single-Component system

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- ❖ The **simplest type of hydrocarbon system** to consider is that **containing one component** (the number of molecular or **atomic species present in the substance**).
- ❖ A **single-component system** is composed **entirely of one kind of atom** or molecule.
- ❖ The **qualitative** understanding of the **relationship** between temperature **T**, pressure **p**, and volume **V** of **pure components** can provide an excellent basis for **understanding** the phase behavior of **complex petroleum mixtures**.

# P-V diagram – Single Component



a fixed quantity of a pure component is placed in a cylinder

# Critical Point

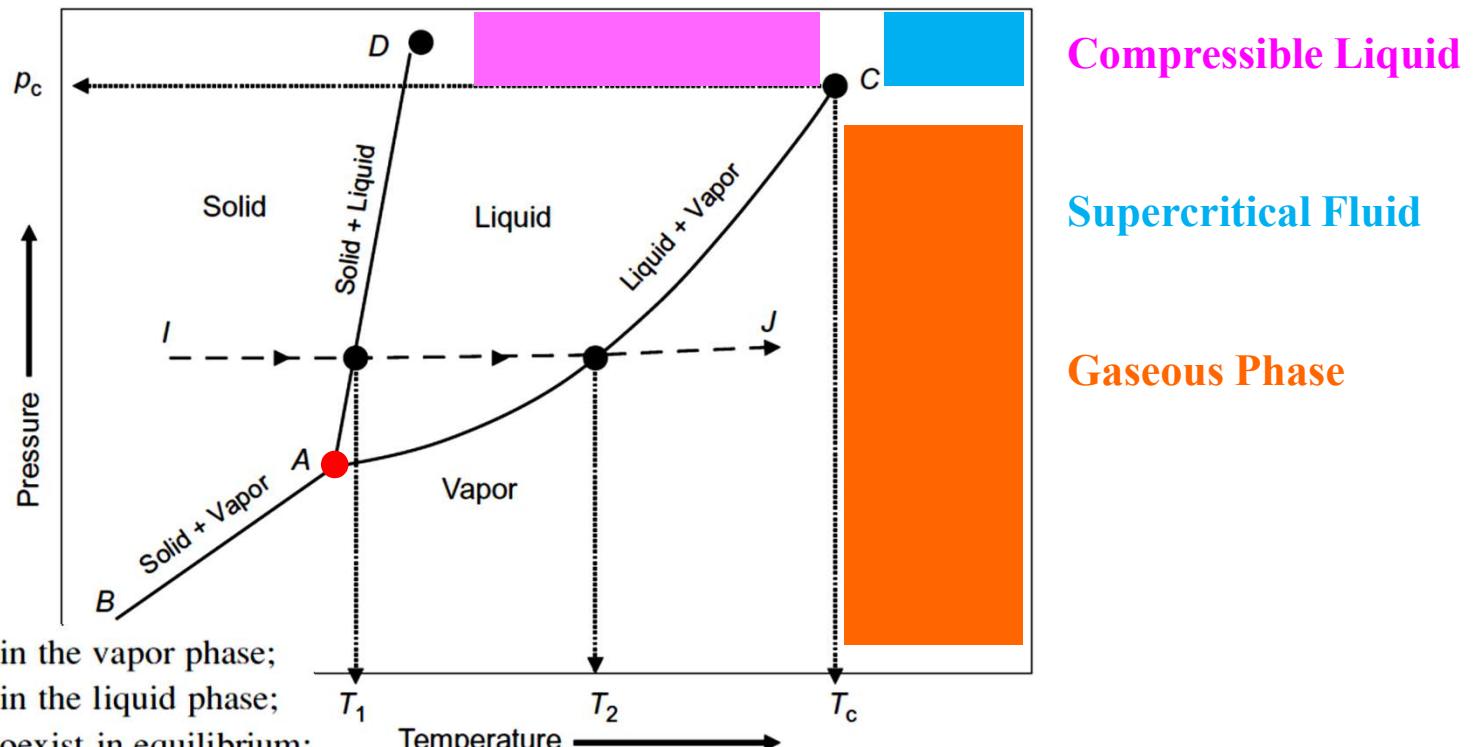
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- ❖ For a single-component system, the **critical point** is defined as the **highest value of pressure and temperature** at which **two phases can coexist**.
- ❖ The critical point is the point at which **all intensive properties of the gas and liquid phases are equal.** (*independent of the quantity of the system*)

# P-T diagram – Single Component

Triple point

**represents the pressure and temperature** at which solid, liquid, and vapor coexist under equilibrium conditions.



If  $p < p_v \rightarrow$  the system is entirely in the vapor phase;

If  $p > p_v \rightarrow$  the system is entirely in the liquid phase;

If  $p = p_v \rightarrow$  the vapor and liquid coexist in equilibrium;

# Example 1

Pure propane is held in a laboratory cell at **80°F** and **200 psia**. Determine the “existence state” (as a gas or liquid) of the substance.

1. Lee and Kesler (1975) :  $p_v = p_c \exp(A + \omega B)$

$$A = 5.92714 - \frac{6.09648}{T_r} - 1.2886 \ln(T_r) + 0.16934(T_r)^6$$

$$B = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.4357(T_r)^6$$

$$T_r = \frac{T}{T_c}$$

$T_r$ =reduced temperature

$T$ =substance temperature, °R

$T_c$ =critical temperature of the substance, °R

$p_c$ =critical pressure of the substance, psia

$\omega$ =acentric factor of the substance

The **acentric factor**  $\omega$  is a unique correlating parameter that is used as a **measure of the centricity** or the **deviation of the component molecular shape from that of a spherical**. The shape of the **Argon** molecule is considered **completely spherical** and is assigned an **acentric factor of zero**.

# Example 1 – Cont.

$$\omega = -\log \left( \frac{p_v}{p_c} \right)_{T=0.7T_c} - 1$$

The acentric factor frequently is used as a **third parameter** in **corresponding states** and **equation-of-state** correlations.  
(Physical Properties)

$p_c$ =critical pressure of the substance, psia

$p_v$ =vapor pressure of the substance at a temperature equal to 70% of the substance critical temperature (ie,  $T=0.7T_c$ ), psia

$$T_c = 666.01^\circ\text{R}$$

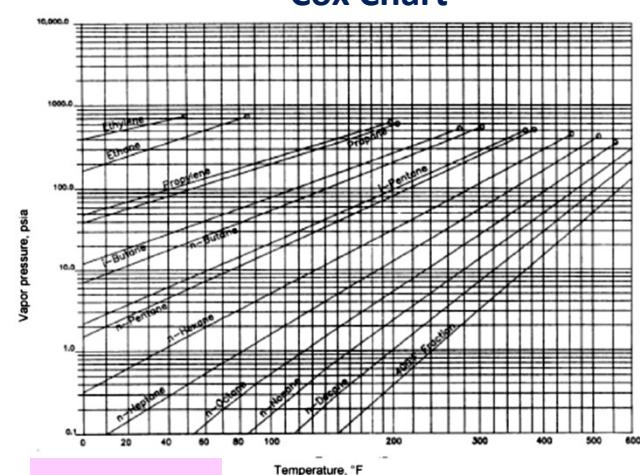
$$p_c = 616.3 \text{ psia} \quad \rightarrow \quad A = -1.273590$$

$$B = -1.147045$$

$$\omega = 0.1522$$

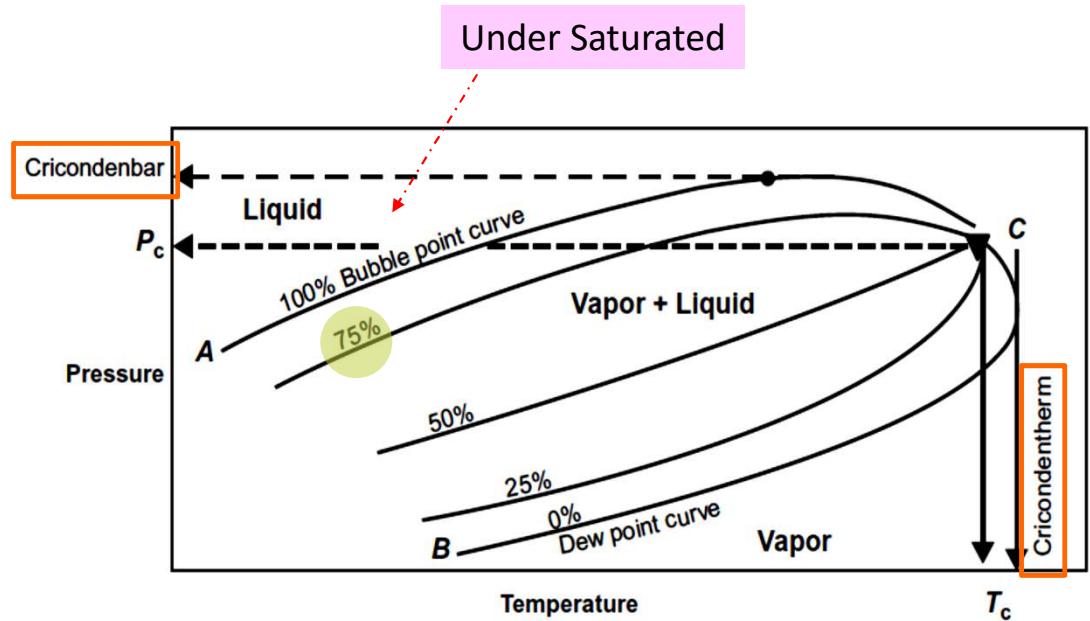
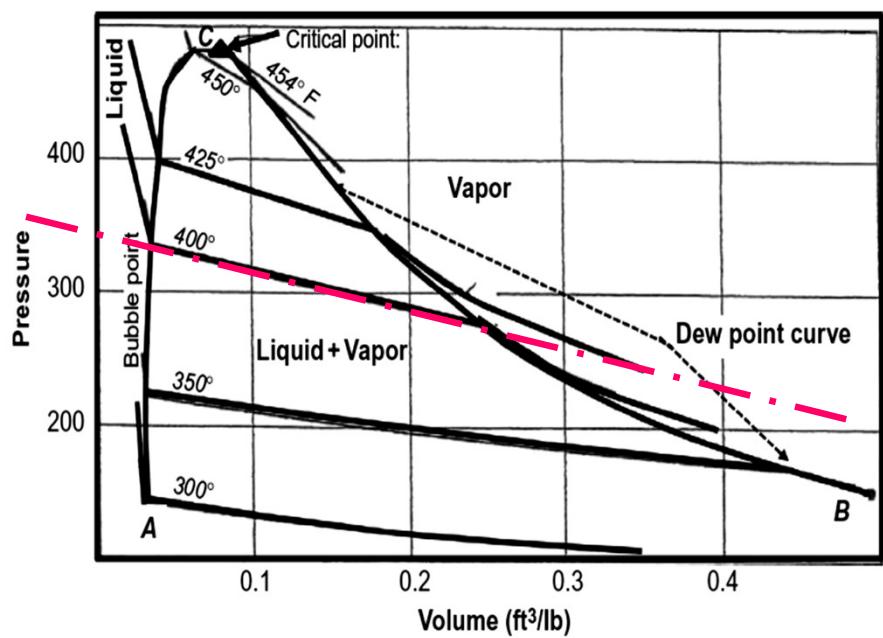
$$p_v = (616.3) \exp [-1.27359 + 0.1572(-1.147045)] = 145 \text{ psia}$$

$$p > p_v$$



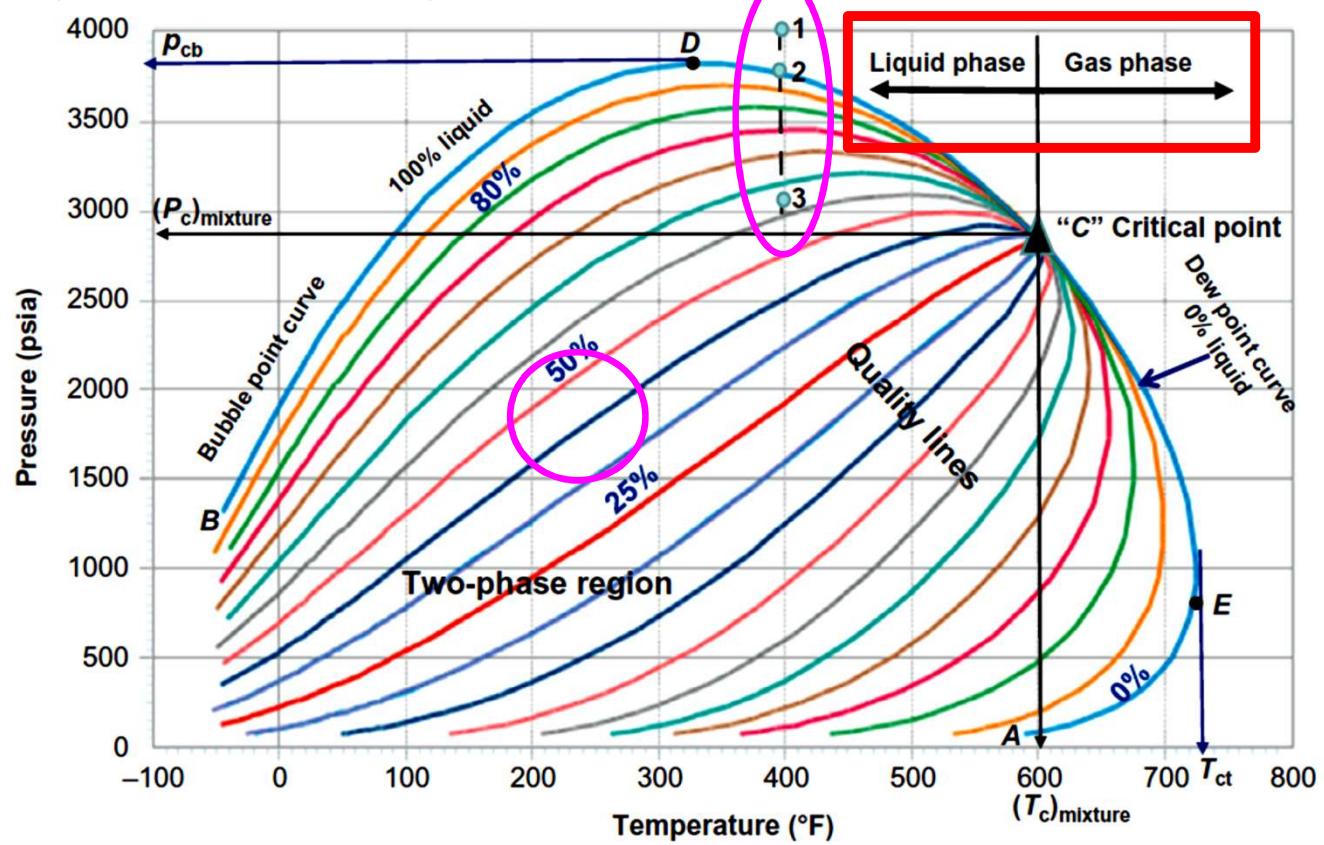
Liq. C<sub>3</sub>H<sub>8</sub>

# Two-Component Systems



# Multicomponent Systems

The impact of **fluid composition** on the **shape and size of the phase envelope** must technically be considered.



# Main Classification

Based on  $p_i$  vs.  $p_b$ , the oil reservoirs are:

1. Undersaturated
2. Saturated
3. Gas-Cap Reservoirs

Classification of reservoirs is defined by  $T$  &  $(T_c)_{\text{hydrocarbon}}$

% of  $C_1$  &  $C_{7+}$  in the system will impact  $(T_c)_{\text{mixture}}$

$(T_c)_{\text{mixture}} = f(\text{composition})$

Oil reservoirs  
 $T < (T_c)_{\text{mixture}}$

Gas reservoirs  
 $T > (T_c)_{\text{mixture}}$

Near critical reservoirs  
 $T \approx (T_c)_{\text{mixture}}$

Special case:  
Critical mixture separates the gas-cap from the oil rim

Critical mixture  
 $T = (T_c)_{\text{mixture}}$

# What is a Phase?

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- A phase is the part of a system that is uniform in physical and chemical properties, homogeneous in composition, and separated from other coexisting phases by definite boundary surfaces. The most important phases occurring in petroleum production are the hydrocarbon liquid phase and gas phase.
- These can **coexist in equilibrium** when the variables describing change in the entire system remain constant in time and position.
- The governing variables that *determine the state of equilibrium* are system temperature, system pressure, and composition.

# Applications & Calculations

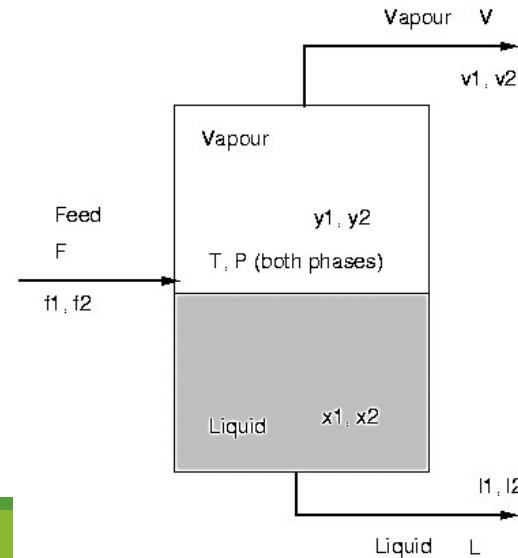
- Designing Surface Separation

## Facilities

- Developing Compositional Models

- Equilibrium Ratios

- Flash Calculations



# Equilibrium Ratios

In a multicomponent system, the **partitioning and the tendency** of components to **escape between the liquid and gas phase** are described by the equilibrium ratio “ $K_i$ ” of a given component.

$$K_i = \frac{y_i}{x_i}$$

The above expression indicates that when the  $K_i$ -value for a given component **is greater than 1**, it signifies that the component tends to concentrate in the gas phase.

**equilibrium ratio of component  $i$**

**mole fraction of component  $i$  in the gas phase**

**mole fraction of component  $i$  in the liquid phase**

# Raoult's and Dalton's laws

Applicable when  $P < 100 \text{ psi}$

For ideal solutions provide a simplified means of predicting equilibrium ratios

Raoult's law

$$p_i = x_i p_{vi}$$

Dalton's law

$$p_i = y_i p$$

$p_i$  = partial pressure of a component  $i$ , psia

$p_{vi}$  = vapor pressure of component  $i$ , psia

$p$  = system pressure, psia

# Equilibrium Ratio for Ideal Solutions

Liq.

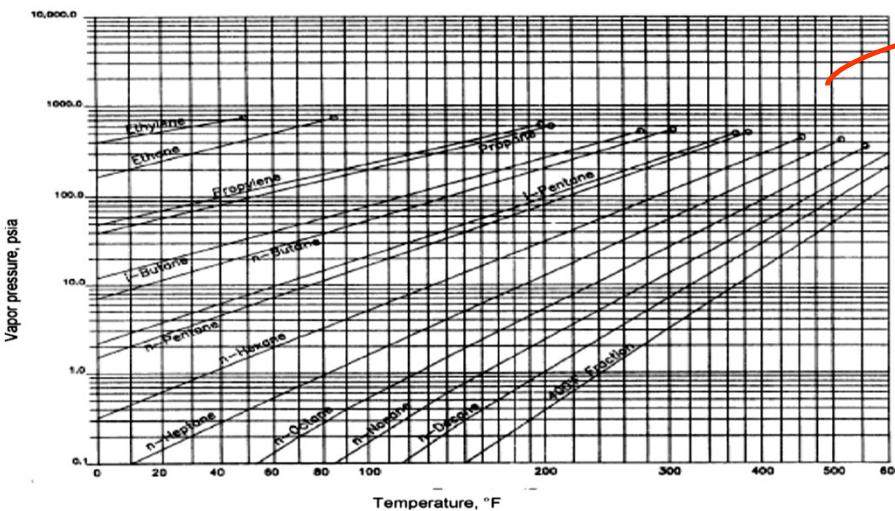
$$p_i = x_i p_{vi}$$

Vap.

$$p_i = y_i p$$

@ Equilibrium: the partial pressure exerted by a component in the vapor must be equal to the partial pressure exerted by the same component in the liquid phase.

Cox Chart



$$x_i p_{vi} = y_i p \Rightarrow \frac{p_{vi}}{p} = \frac{y_i}{x_i} = K_i$$

$K_i$  is independent of overall position



# Flash Calculations (I)

$$n_t = n_L + n_v$$

The **total number of moles ( $n$ )** in the system is equal to the **total number of moles in the liquid phase ( $n_L$ )** plus the **total number of moles in the vapor ( $n_v$ )** phase.

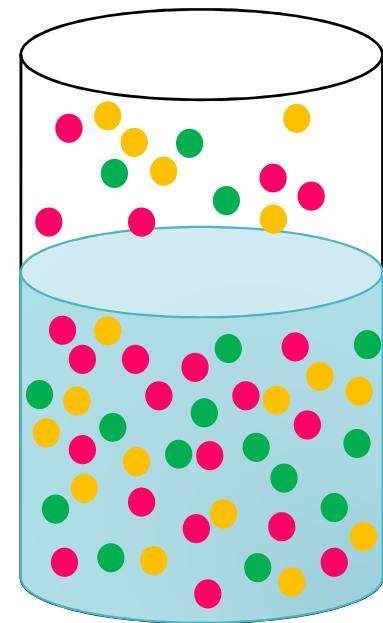
A material balance on the  $i^{\text{th}}$  component results in:

$$z_i n_t = x_i n_L + y_i n_v$$

$z_i$  = **mole fraction** of component in the entire hydrocarbon mixture

$$z_{\bullet} = \frac{\text{mole}_{\bullet}}{\text{mole}_{\bullet} + \text{mole}_{\bullet} + \text{mole}_{\bullet}}$$

Hydrocarbon Mixture  
@ Equilibrium



# Flash Calculations (II)

$$\xrightarrow{\text{If } n_t=1} x_i n_L + y_i n_v = z_i \xrightarrow{K_i = \frac{y_i}{x_i}} x_i n_L + (K_i x_i) n_v = z_i \Rightarrow x_i = \frac{z_i}{n_L + n_v K_i} \xrightarrow{\sum_i x_i = 1}$$

$$\sum_i x_i = \sum_i \frac{z_i}{n_L + n_v K_i} = 1 \quad (\textbf{a})$$

$$\xrightarrow{\text{If } n_t=1} x_i n_L + y_i n_v = z_i \xrightarrow{K_i = \frac{y_i}{x_i}} \left( \frac{y_i}{K_i} \right) n_L + y_i n_v = z_i \Rightarrow y_i = \frac{z_i K_i}{n_L + n_v K_i} \xrightarrow{\sum_i y_i = 1}$$

$$\sum_i y_i = \sum_i \frac{z_i K_i}{n_L + n_v K_i} = 1 \quad (\textbf{b})$$

# Flash Calculations (III)

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Since  $\sum_i y_i - \sum_i x_i = 0$

$$\xrightarrow{\quad} (a) - (b) = \sum_i \frac{z_i K_i}{n_L + n_v K_i} - \sum_i \frac{z_i}{n_L + n_v K_i} = 0 \Rightarrow$$

$$\sum_i \frac{z_i(K_i - 1)}{n_L + n_v K_i} = 0 \xrightarrow{n_L = 1 - n_v} f(\mathbf{n}_v) = \sum_i \frac{z_i(K_i - 1)}{\mathbf{n}_v(K_i - 1) + 1} = 0$$

**Target:** Finding an appropriate  $n_v$  which *satisfies the equation*, and then *determine the  $x_i$  and  $y_i$*  for each component at equilibrium conditions

# The Algorithm

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1. Assume *any arbitrary* value of  $\mathbf{n}_v$  between 0 and 1.

- A *good assumed* value:

$$\mathbf{n}_v = \mathbf{A}/(\mathbf{A} + \mathbf{B})$$

$$\mathbf{A} = \sum_i [\mathbf{z}_i(K_i - 1)]$$

$$\mathbf{B} = \sum_i \left[ \mathbf{z}_i \left( \frac{1}{K_i} - 1 \right) \right]$$

2. Calculate the  $f(n_v) \rightarrow$  Is it less than a preset tolerance?

- *Yes* → Calculate the  $y_i$  and  $x_i$
- *No* → Correcting the  $n_v$

$$(\mathbf{n}_v)_{new} = \mathbf{n}_v - \frac{\mathbf{f}(\mathbf{n}_v)}{\mathbf{f}'(\mathbf{n}_v)} \quad \text{where} \quad \mathbf{f}'(\mathbf{n}_v) = - \sum_i \left\{ \frac{\mathbf{z}_i(K_i - 1)^2}{[\mathbf{n}_v(K_i - 1) + 1]^2} \right\}$$

# Example 2

A hydrocarbon mixture with the following overall composition is flashed in a separator at **50 psia** and **100°F**. Perform flash calculations.

Cox Chart



Comp.	$z_i$	$p_{vi}$ at 100°F	$K_i = p_{vi}/p$
C <sub>3</sub>	0.2	190	3.8
i-C <sub>4</sub>	0.1	72.2	1.444
n-C <sub>4</sub>	0.1	51.6	1.032
i-C <sub>5</sub>	0.2	20.44	0.4088
n-C <sub>5</sub>	0.2	15.57	0.3114
C <sub>6</sub>	0.2	4.956	0.09912

$$f(n_v) = \sum_i \frac{z_i(K_i - 1)}{n_v(K_i - 1) + 1} = 0 \Leftarrow K_i = \frac{p_{vi}}{p}$$

Iteration	$n_v$	$f(n_v)$
0	0.08196579	$3.073(10^{-2})$
1	0.1079687	$8.894(10^{-4})$
2	0.1086363	$7.60(10^{-7})$
3	0.1086368	$1.49(10^{-8})$
4	0.1086368	0.0

$x_i$	$y_i$
0.1534	0.5829
0.0954	0.1378
0.0997	0.1029
0.2137	0.0874
0.2162	0.0673
0.2216	0.0220

# Reminder: Assumptions

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- The vapor phase is an *ideal gas* as described by Dalton's law.
- The liquid phase is an *ideal solution* as described by Raoult's law.

Therefore:

The **combination** of the above two assumptions is *unrealistic* and results in  
inaccurate predictions of equilibrium ratios at high pressures.

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS

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In ideal solutions:

$$K_i = f(p, T)$$

In real solutions:

$$K_i = f(p, T, \mathbf{z}_i)$$

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Wilson (1968)

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$$K_i = \frac{p_{ci}}{p} e^{[5.37(1+\omega_i)\left(1 - \frac{T_{ci}}{T}\right)]}$$

$p_{ci}$ =critical pressure of component  $i$ , psia

$p$ =system pressure, psia

$T_{ci}$ =critical temperature of component  $i$ , °R

$T$ =system temperature, °R

**It provides a consistent set of K-values at a specified pressure and temperature; that is,  $K_{C1} > K_{C2} > K_{C3} >$ , and so on.**

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Standing (1968)

$$K_i = \frac{1}{p} 10^{(a+cF_i)}$$

$$a = 1.2 + 0.00045p + 15(10^{-8})p^2$$

$$c = 0.89 - 0.00017p - 3.5(10^{-8})p^2$$

$$F_i = b_i [1/T_{bi} - 1/T]$$

$$b_i = \frac{\log(p_{ci}/14.7)}{[1/T_{bi} - 1/T_{ci}]}$$

It should be pointed out that Standing's proposed correlations are valid for pressures and temperatures that are less than 1000 psia and 200°F, respectively.

Component	$b_i$	$T_{bi}$ (°R)
N <sub>2</sub>	470	109
CO <sub>2</sub>	652	194
H <sub>2</sub> S	1136	331
C <sub>1</sub>	300	94
C <sub>2</sub>	1145	303
C <sub>3</sub>	1799	416
i-C <sub>4</sub>	2037	471
n-C <sub>4</sub>	2153	491
i-C <sub>5</sub>	2368	542
n-C <sub>5</sub>	2480	557
C <sub>6</sub>	2738	610
n-C <sub>6</sub>	2780	616
n-C <sub>7</sub>	3068	616
n-C <sub>8</sub>	3335	718
n-C <sub>9</sub>	3590	763
n-C <sub>10</sub>	3828	805

The offered optimized values

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example 3

A hydrocarbon mixture with the following composition is flashed at **1000 psia** and **150°F**. If the **molecular weight** and **specific gravity** of  $C_{7+}$  are **150.0** and **0.78**, respectively, calculate the equilibrium ratios.

Component	$z_i$
$CO_2$	0.009
$N_2$	0.003
$C_1$	0.535
$C_2$	0.115
$C_3$	0.088
$i\text{-}C_4$	0.023
$n\text{-}C_4$	0.023
$i\text{-}C_5$	0.015
$n\text{-}C_5$	0.015
$C_6$	0.015
$C_{7+}$	0.159



# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example 3 – Cont.

Wilson's method:

$$K_i = \frac{p_{ci}}{p} e^{\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right]}$$

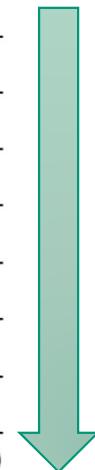
*p<sub>c</sub>* & *T<sub>c</sub>* of C<sub>7+</sub>: ? → Riazi and Daubert     $\theta = a(M)^b \gamma^c \exp [dM + e\gamma + f\gamma M]$

*ω<sub>i</sub>* for C7+: ? → Edmister     $\omega = \frac{3[\log(p_c/14.70)]}{7[T_c/T_b - 1]} - 1$

<i>θ</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
<i>M</i>	581.96000	-0.97476	6.51274	$5.43076 \times 10^{-4}$	9.53384	$1.11056 \times 10^{-3}$
<i>T<sub>c</sub></i> (°R)	10.6443	0.81067	0.53691	$-5.17470 \times 10^{-4}$	-0.54444	$3.59950 \times 10^{-4}$
<i>p<sub>c</sub></i> (psia)	$6.16200 \times 10^6$	-0.48440	4.08460	$-4.72500 \times 10^{-3}$	-4.80140	$3.19390 \times 10^{-3}$
<i>V<sub>c</sub></i> (ft <sup>3</sup> /lb)	$6.23300 \times 10^{-4}$	0.75060	-1.20280	$-1.46790 \times 10^{-3}$	-0.26404	$1.09500 \times 10^{-3}$

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example 3 – Cont.

Component	$P'_c$ (psia)	$T'_c$ ( $^{\circ}$ R)	$\omega$	$K_i$
CO <sub>2</sub>	1071	547.9	0.225	2.0923
N <sub>2</sub>	493	227.6	0.040	16.343
C <sub>1</sub>	667.8	343.37	0.0104	7.155
C <sub>2</sub>	707.8	550.09	0.0986	1.263
C <sub>3</sub>	616.3	666.01	0.1524	0.349
i-C <sub>4</sub>	529.1	734.98	0.1848	0.144
n-C <sub>4</sub>	550.7	765.65	0.2010	0.106
i-C <sub>5</sub>	490.4	829.1	0.2223	0.046
n-C <sub>5</sub>	488.6	845.7	0.2539	0.036
C <sub>6</sub>	436.9	913.7	0.3007	0.013
C <sub>7+</sub>	320.3	1139.4	0.5069	0.00029



# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example 3 – Cont.

Standing's method:

$$K_i = \frac{1}{p} 10^{(a+cF_i)}$$

**Reminder:**  $a$  and  $c$  are pressure dependent parameters.

$T_{bi}$  &  $b_i$  of C<sub>7+</sub>: ?

1. Calculate the number of carbon atoms, n.

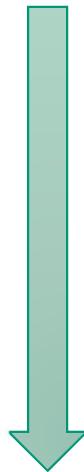
$$n = 7.30 + 0.0075(T - 460) + 0.0016p$$

2. Determine the parameter b and the boiling point, Tb.

$$b = 1013 + 324n - 4.256n^2 \quad T_b = 301 + 59.85n - 0.971n^2$$

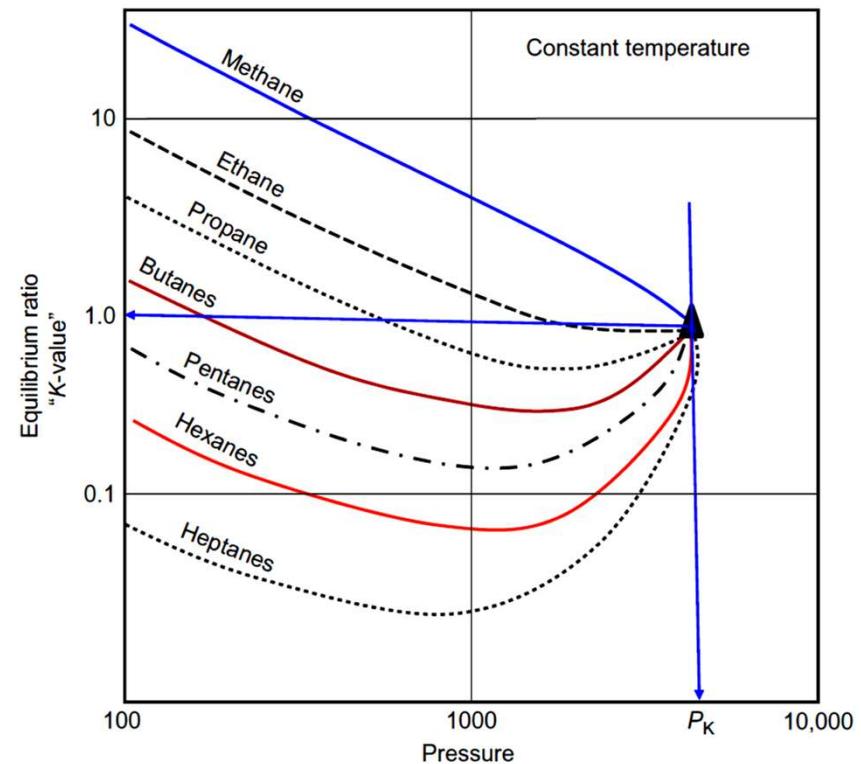
# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example – Cont.

Component	$b_i$	$T_{b_i}$	$F_i$	$K_i$
CO <sub>2</sub>	652	194	2.292	2.344
N <sub>2</sub>	470	109	3.541	16.811
C <sub>1</sub>	300	94	2.700	4.462
C <sub>2</sub>	1145	303	1.902	1.267
C <sub>3</sub>	1799	416	1.375	0.552
i-C <sub>4</sub>	2037	471	0.985	0.298
n-C <sub>4</sub>	2153	491	0.855	0.243
i-C <sub>5</sub>	2368	542	0.487	0.136
n-C <sub>5</sub>	2480	557	0.387	0.116
C <sub>6</sub>	2738	610	0	0.063
C <sub>7+</sub>	3833.369	803.41	-1.513	0.0058



# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Convergence Pressure

when a hydrocarbon mixture of a fixed overall composition is held **at a constant temperature** as the **pressure increases**, the equilibrium values of all components **converge toward a common value of unity at certain pressure**. This pressure is termed the **convergence pressure**,  $p_k$ , of the hydrocarbon mixture.



# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Whitson and Torp

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$$K_i = \left( \frac{p_{ci}}{p_k} \right)^{A-1} \left( \frac{p_{ci}}{p} \right) \exp \left[ 5.37A(1 + \omega_i) \left( 1 - \frac{T_{ci}}{T} \right) \right]$$

$$A = 1 - \left( \frac{p}{p_k} \right)^{0.7}$$

$$p_k = 60M_{C_{7+}} - 4200$$

$p$  = system pressure, psig

$p_k$  = convergence pressure, psig

$T$  = system temperature, °R

$\omega_i$  = acentric factor of component  $i$

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example 4

A hydrocarbon mixture with the following composition is flashed at **1000 psia** and **150°F**. If the **molecular weight** and **specific gravity** of C<sub>7+</sub> are **150.0** and **0.78**, respectively, calculate the equilibrium ratios. (Whitson and Torp)

Component	p <sub>c</sub>	T' <sub>c</sub> (°R)	ω
CO <sub>2</sub>	1071	547.9	0.225
N <sub>2</sub>	493	227.6	0.040
C <sub>1</sub>	667.8	343.37	0.0104
C <sub>2</sub>	707.8	550.09	0.0986
C <sub>3</sub>	616.3	666.01	0.1524
i-C <sub>4</sub>	529.1	734.98	0.1848
n-C <sub>4</sub>	550.7	765.65	0.2010
i-C <sub>5</sub>	490.4	829.1	0.2223
n-C <sub>5</sub>	488.6	845.7	0.2539
C <sub>6</sub>	436.9	913.7	0.3007
 C <sub>7+</sub>	320.3	1139.4	0.5069

# EQUILIBRIUM RATIOS FOR REAL SOLUTIONS – Example 4 – Cont.

$$p_k = 60M_{C7+} - 4200 \xrightarrow{M_{C7+}=150} p_k = 947 \text{ psi}$$

$$A = 1 - \left(\frac{p}{p_k}\right)^{0.7} \xrightarrow{p_k = 947 \text{ psi} \text{ & } p = 1000 \text{ psi}} A = 0.793$$

$$K_i = \left(\frac{p_{ci}}{9474}\right)^{0.793-1} \frac{p_{ci}}{1000} e^{0.793*5.37*(1+\omega_i)\left(1-\frac{T_{ci}}{610}\right)}$$

Component	$p_c$	$T'_c$ ( $^{\circ}$ R)	$\omega$	$K_i$
CO <sub>2</sub>	1071	547.9	0.225	2.9
N <sub>2</sub>	493	227.6	0.040	14.6
C <sub>1</sub>	667.8	343.37	0.0104	7.6
C <sub>2</sub>	707.8	550.09	0.0986	2.1
C <sub>3</sub>	616.3	666.01	0.1524	0.7
i-C <sub>4</sub>	529.1	734.98	0.1848	0.42
n-C <sub>4</sub>	550.7	765.65	0.2010	0.332
i-C <sub>5</sub>	490.4	829.1	0.2223	0.1794
n-C <sub>5</sub>	488.6	845.7	0.2539	0.150
C <sub>6</sub>	436.9	913.7	0.3007	0.0719
C <sub>7+</sub>	320.3	1139.4	0.5069	0.683( $10^{-3}$ )

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

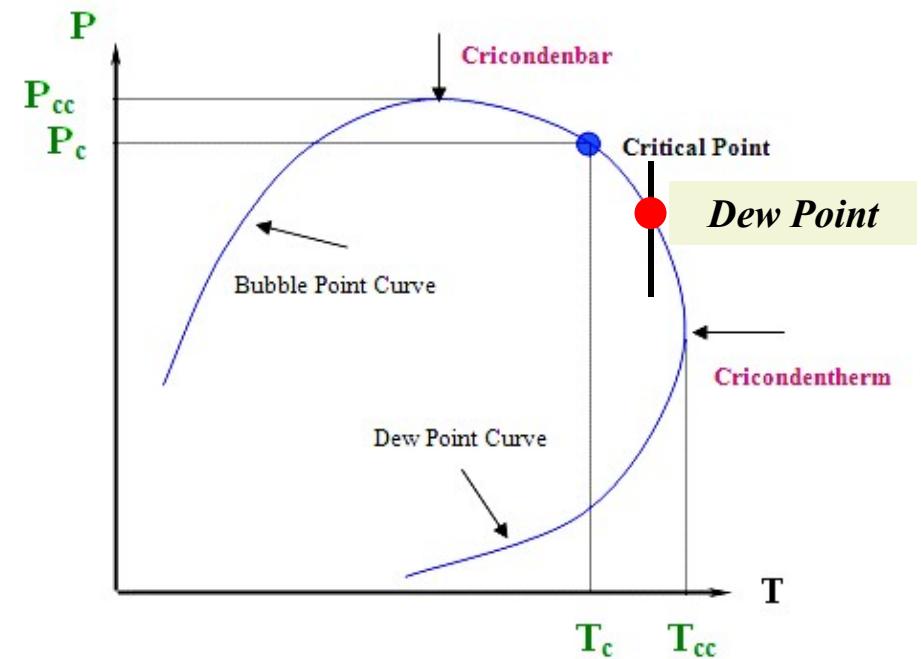
The dew point pressure,  $p_d$ , of a hydrocarbon system is defined as the pressure at which *an infinitesimal quantity of liquid is in equilibrium with a large quantity of gas.*

$$n_L \approx 0$$

$$n_v \approx 1$$

$$\Rightarrow y_i = z_i$$

$$\sum_i x_i = \sum_i \frac{z_i}{n_L + n_v K_i} = 1 \xrightarrow{n_L \approx 0} \sum_i \frac{z_i}{K_i} = 1$$



# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 5

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***Estimate*** the dew point pressure of the gas mixture:

Component	$z_i$
C <sub>1</sub>	0.7778
C <sub>2</sub>	0.0858
C <sub>3</sub>	0.0394
i-C <sub>4</sub>	0.0083
n-C <sub>4</sub>	0.016
i-C <sub>5</sub>	0.0064
n-C <sub>5</sub>	0.0068
C <sub>6</sub>	0.0078
C <sub>7+</sub>	0.0517

The heptane-plus fraction is characterized by a **molecular weight and specific gravity of 150 and 0.78**, respectively. The reservoir exists at **250°F**.

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 5 – Cont.

$$\sum_i \frac{z_i}{K_i} = 1 \xrightarrow{K_i = \frac{p_{ci}}{p} e^{[5.37(1+\omega_i)(1-\frac{T_{ci}}{T})]}, \text{ Wilson's Eq.}} \sum_i \frac{z_i}{K_i} = \sum_i \left\{ \frac{z_i}{\frac{p_{ci}}{p_d} \exp \left[ 5.37(1+\omega_i) \left( 1 - \frac{T_{ci}}{T} \right) \right]} \right\} = 1$$

Solving for  $p_d$   $\Rightarrow p_d = \frac{1}{\sum_i \left\{ \frac{z_i}{p_{ci} \exp \left[ 5.37(1+\omega_i) \left( 1 - \frac{T_{ci}}{T} \right) \right]} \right\}}$

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 5 – Cont.

C<sub>7+</sub> properties  $\otimes$  ( $p_{ci}$ ,  $T_{ci}$ ,  $\omega_i$ )

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$$\theta = a(M)^b \gamma^c \exp[dM + e\gamma + f\gamma M]$$

$$T_c = 544.2(150)^{0.2998}(0.78)^{1.0555} \exp[-1.3478 \times 10^{-4}(150) - 0.61641(0.78) + 0] \\ = 1139.4^\circ\text{R}$$

$$p_c = 4.5203 \times 10^4 (150)^{-0.8063} (0.78)^{1.6015} \exp[-1.8078 \times 10^{-3}(150) - 0.3084(0.78) + 0] \\ = 320.3 \text{ psia}$$

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$$\omega = \frac{3[\log(320.3/14.7)]}{7[1139.4/825.26 - 1]} - 1 = 0.5067$$

$$T_b = 6.77857(150)^{0.401673}(0.78)^{-1.58262} \exp[3.77409 \times 10^{-3}(150) - 2.984036(0.78) \\ - 4.25288 \times 10^{-3}(150)(0.78)] = 825.26^\circ\text{R}$$

FLASH CALCULATIONS

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 5 – Cont.

Component	$z_i$	$P_{ci}$	$T_{ci}$	$\omega_i$	Sum
C <sub>1</sub>	0.7778	667.8	343.37	0.0104	7.0699E-05
C <sub>2</sub>	0.0858	707.8	550.09	0.0986	3.2101E-05
C <sub>3</sub>	0.0394	616.3	666.01	0.1524	4.357E-05
i-C <sub>4</sub>	0.0083	529.1	734.98	0.1848	1.9623E-05
n-C <sub>4</sub>	0.016	550.7	765.65	0.201	4.8166E-05
i-C <sub>5</sub>	0.0064	490.4	829.1	0.2223	3.9247E-05
n-C <sub>5</sub>	0.0068	488.6	845.7	0.2539	5.0404E-05
C <sub>6</sub>	0.0078	436.9	913.7	0.3007	0.00013244
→ C <sub>7+</sub>	0.0517	320.3	1139.4	0.5067	0.02153184

Total sum of the last column = 0.02197 to give a dew point pressure = **1/0.02197 = 45 psi**

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

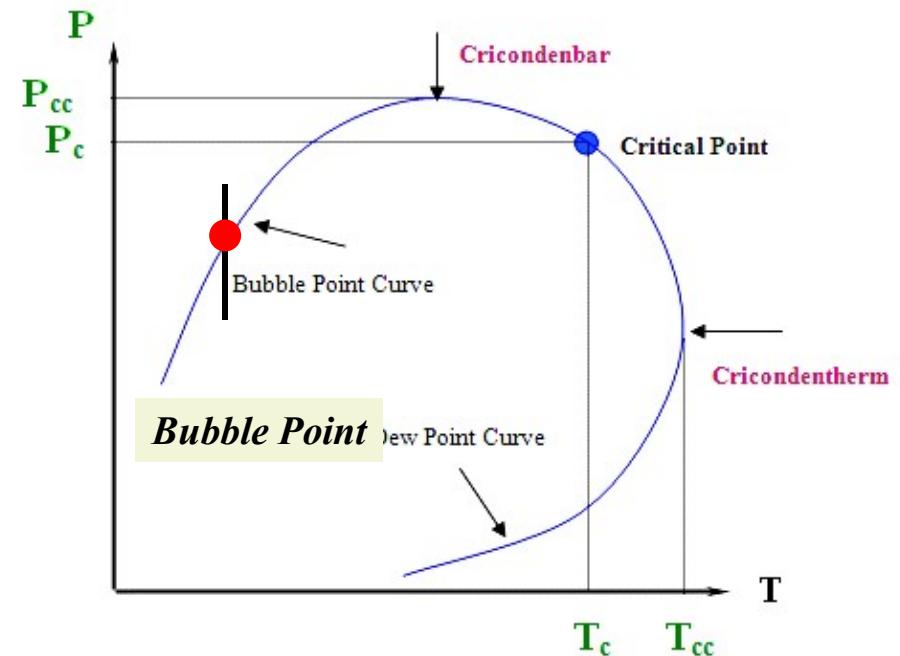
At the bubble point  $p_b$ , the hydrocarbon system **is essentially liquid**, except for **an infinitesimal amount of vapor**.

$$n_L \approx 1$$

$$n_v \approx 0$$

$$\Rightarrow x_i = z_i$$

$$\sum_i y_i = \sum_i \frac{z_i K_i}{n_L + n_v K_i} = 1 \xrightarrow{n_v \approx 0} \sum_i z_i K_i = 1$$



# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 6

***Estimate*** the bubble point pressure of the crude oil:

<b>Component</b>	<b><i>z<sub>i</sub></i></b>
C <sub>1</sub>	0.42
C <sub>2</sub>	0.05
C <sub>3</sub>	0.05
<i>i</i> -C <sub>4</sub>	0.03
<i>n</i> -C <sub>4</sub>	0.02
<i>i</i> -C <sub>5</sub>	0.01
<i>n</i> -C <sub>5</sub>	0.01
C <sub>6</sub>	0.01
C <sub>7+</sub>	0.40

Where:

$$(M)_{C_{7+}} = 216.0$$

$$(\gamma)_{C_{7+}} = 0.8605$$

$$(T_b)_{C_{7+}} = 977^\circ R$$

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 6 – Cont.

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$$\sum_i z_i K_i = 1 \xrightarrow{\text{Wilson's Eq.}} \sum_i \left\{ z_i \frac{p_{ci}}{p_b} \exp \left[ 5.37(1+\omega) \left( 1 - \frac{T_{ci}}{T} \right) \right] \right\} = 1$$

*Solving for  $p_b$*   $\Rightarrow p_b \approx \sum_i \left\{ z_i p_{ci} \exp \left[ 5.37(1+\omega) \left( 1 - \frac{T_{ci}}{T} \right) \right] \right\}$

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS – Example 6 – Cont.

<b>Component</b>	$z_i$	$P_{ci}$	$T_{ci}$	$\omega_i$	
C <sub>1</sub>	0.42	667.8	343.37	0.0104	4620.64266
C <sub>2</sub>	0.05	707.8	550.09	0.0986	133.639009
C <sub>3</sub>	0.05	616.3	666.01	0.1524	45.2146052
i-C <sub>4</sub>	0.03	529.1	734.98	0.1848	12.6894565
n-C <sub>4</sub>	0.02	550.7	765.65	0.201	6.6436649
i-C <sub>5</sub>	0.01	490.4	829.1	0.2223	1.630693
n-C <sub>5</sub>	0.01	488.6	845.7	0.2539	1.34909342
C <sub>6</sub>	0.01	436.9	913.7	0.3007	0.58895645
C <sub>7+</sub>	0.4	320.3	1279.8	1.0633	0.01761403
$\sum$					4822.41575

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