



Advanced Natural Gas Technology (PGE 516)

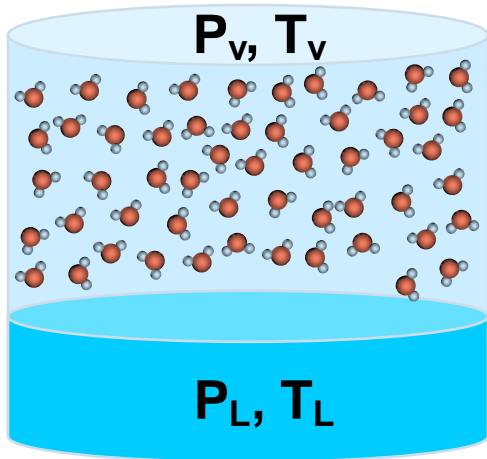
Phase Behavior

BY
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15-9-2015

Vapor Pressure of Pure Substance

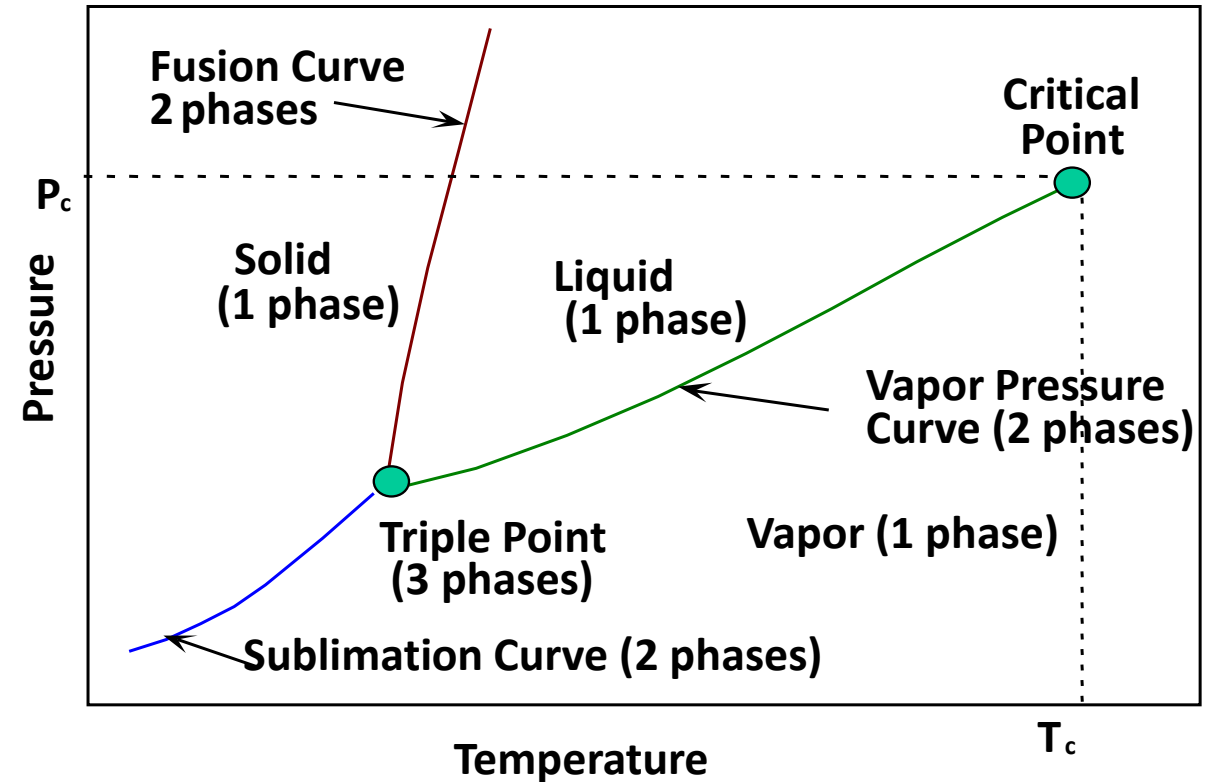
Definition

The pressure exerted by a vapor in equilibrium with its liquid.



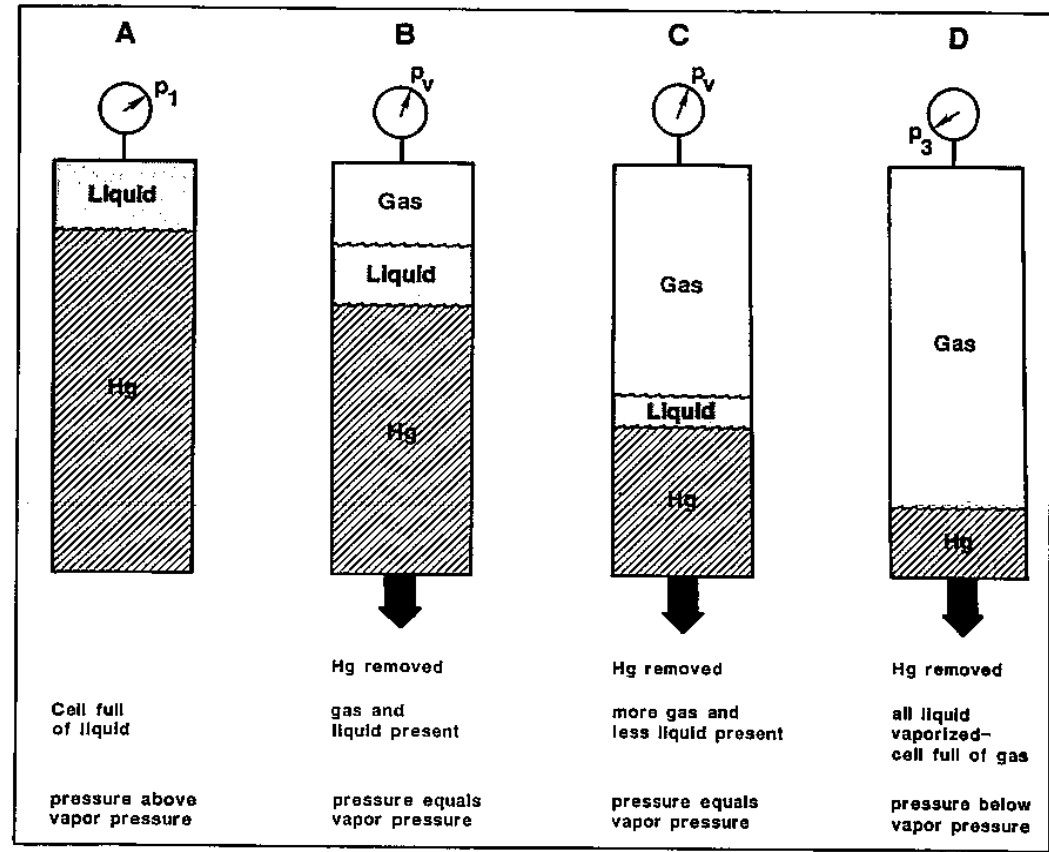
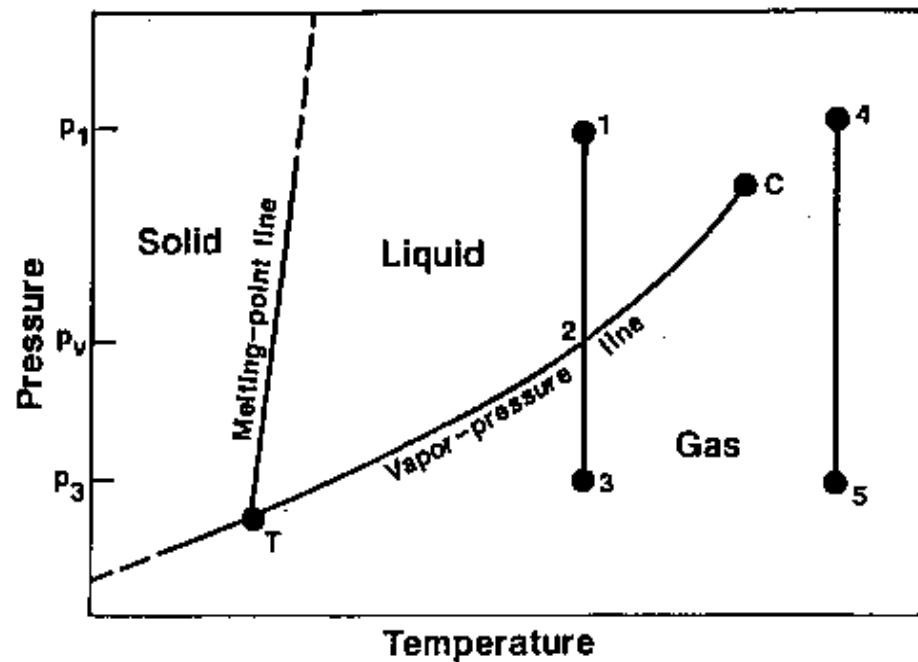
$$P_v = P_L$$

$$T_v = T_L$$



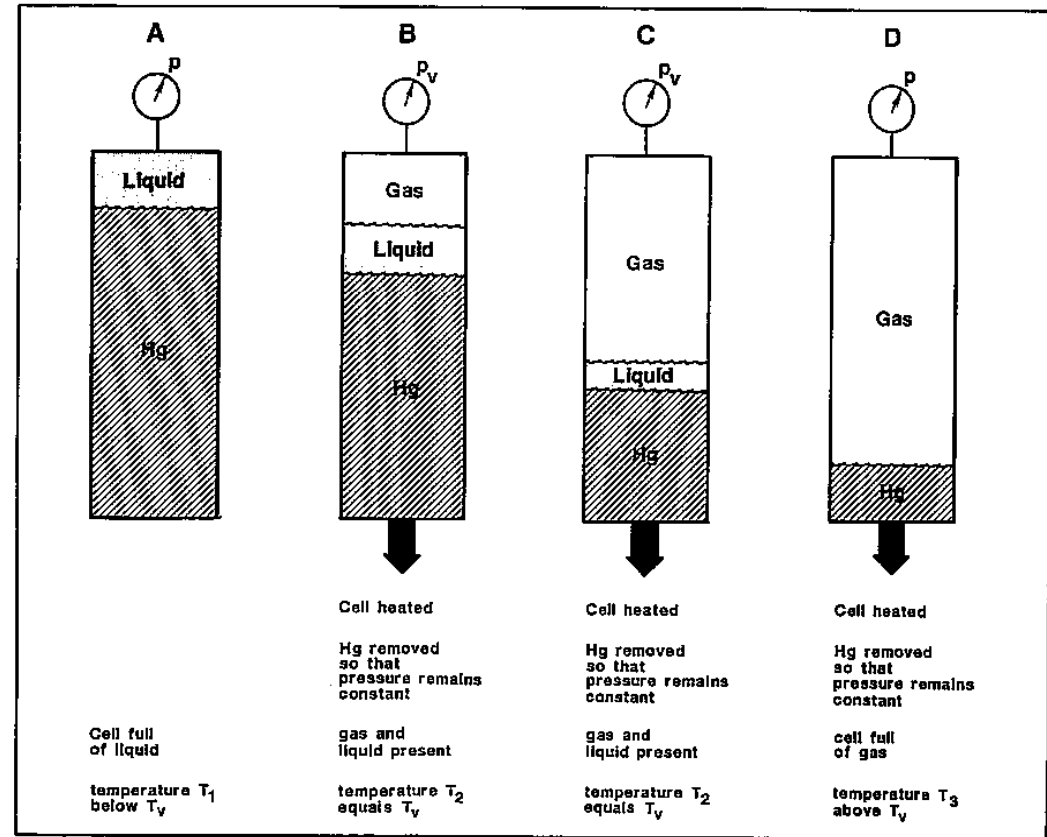
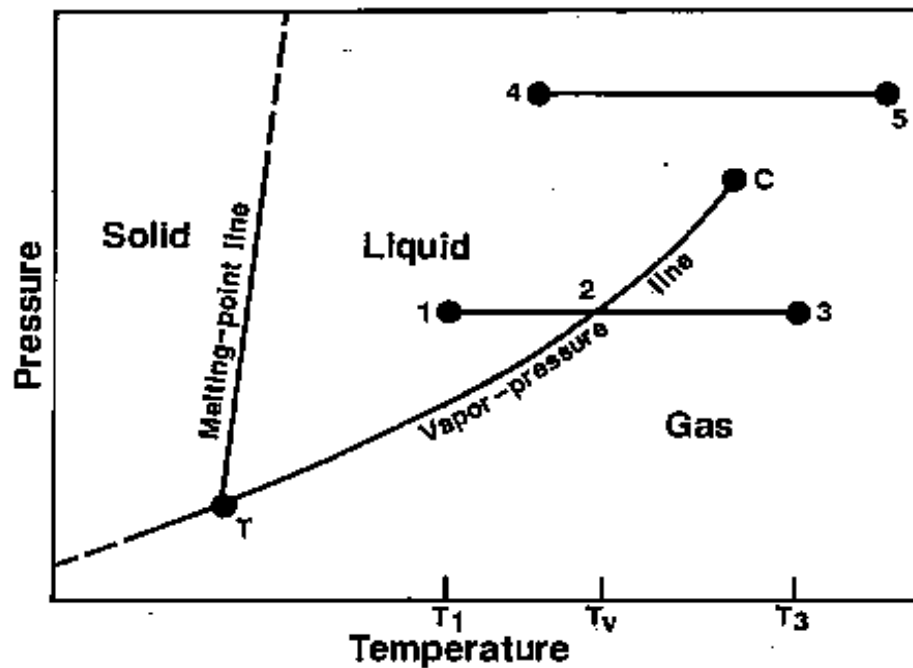
Vapor Pressure of Pure Substance

Vaporization of a pure substance at constant temperature.



Vapor Pressure of Pure Substance

Vaporization of a pure substance at constant pressure.



Vapor Pressure of a Pure Substance

Clausius - Clapeyron Equation

$$\frac{dp_v}{dT} = \frac{L_v}{T(V_{Mg} - V_{ML})}$$

L_v : heat of vaporization of one mole of liquid

$V_{Mg} - V_{ML}$: the change in volume of one mole as it goes from liquid to gas

$$\frac{dp_v}{dT} = \frac{L_v}{TV_{Mg}}$$

Ideal gas

$$P_v V_{Mg} = RT \qquad \frac{dp_v}{dT} = \frac{P_v L_v}{RT^2} \quad (\text{Clausius - Clapeyron Equation})$$

Vapor Pressure of a Pure Substance

Clausius - Clapeyron Equation (CCE)

$$\frac{dp_v}{dT} = \frac{P_v L_v}{RT^2} \quad (\text{Clausius - Clapeyron Equation})$$

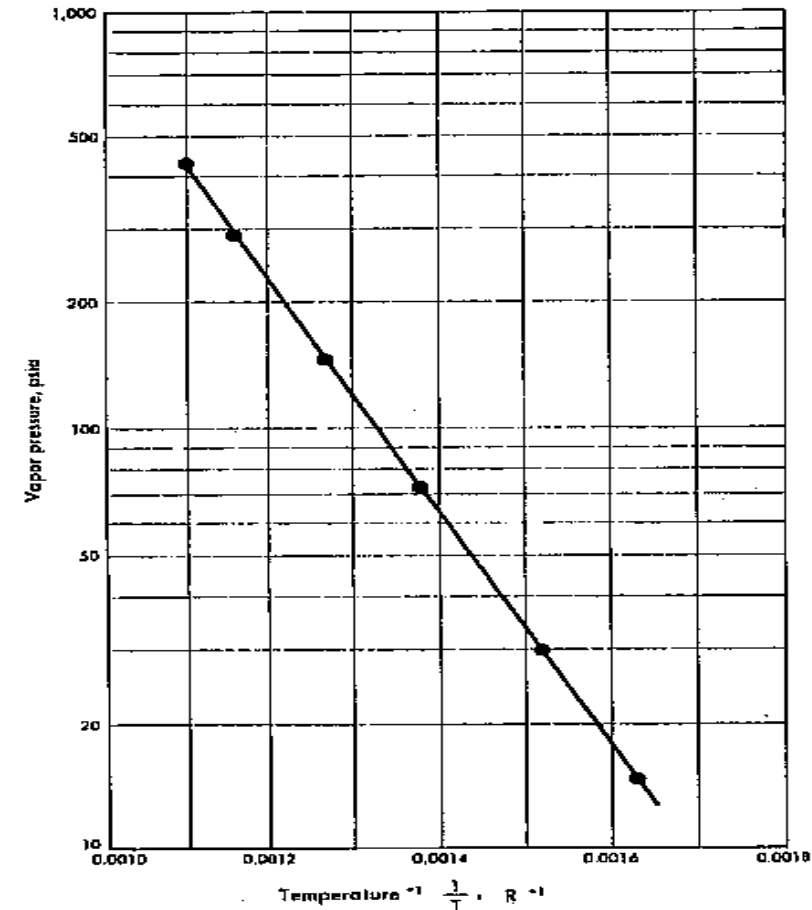
assume that L_v is a constant

$$\int \frac{dP_v}{P_v} = \frac{L_v}{R} \int \frac{dT}{T^2}$$

$$\ln P_v = -\frac{L_v}{R} \left(\frac{1}{T} \right) + C$$

$$\ln \frac{P_{v2}}{P_{v1}} = \frac{L_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$P_{v2} = P_{v1} \cdot \exp \left[\frac{L_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$



Vapor Pressure of a Pure Substance

Example:

A substance has a heat of vaporization of 16.69 kJ/mole. At 254.3 K it has a vapor pressure of 92.44 mm Hg. Calculate its vapor pressure at 275.7 °K.

Solution:

$$P_{v1} = 92.44 \text{ mm Hg} : L_v = 16.69 \text{ kJ/mole} : T_1 = 254.3 \text{ °K} : T_2 = 275.7 \text{ °K} : P_{v2} = ?$$

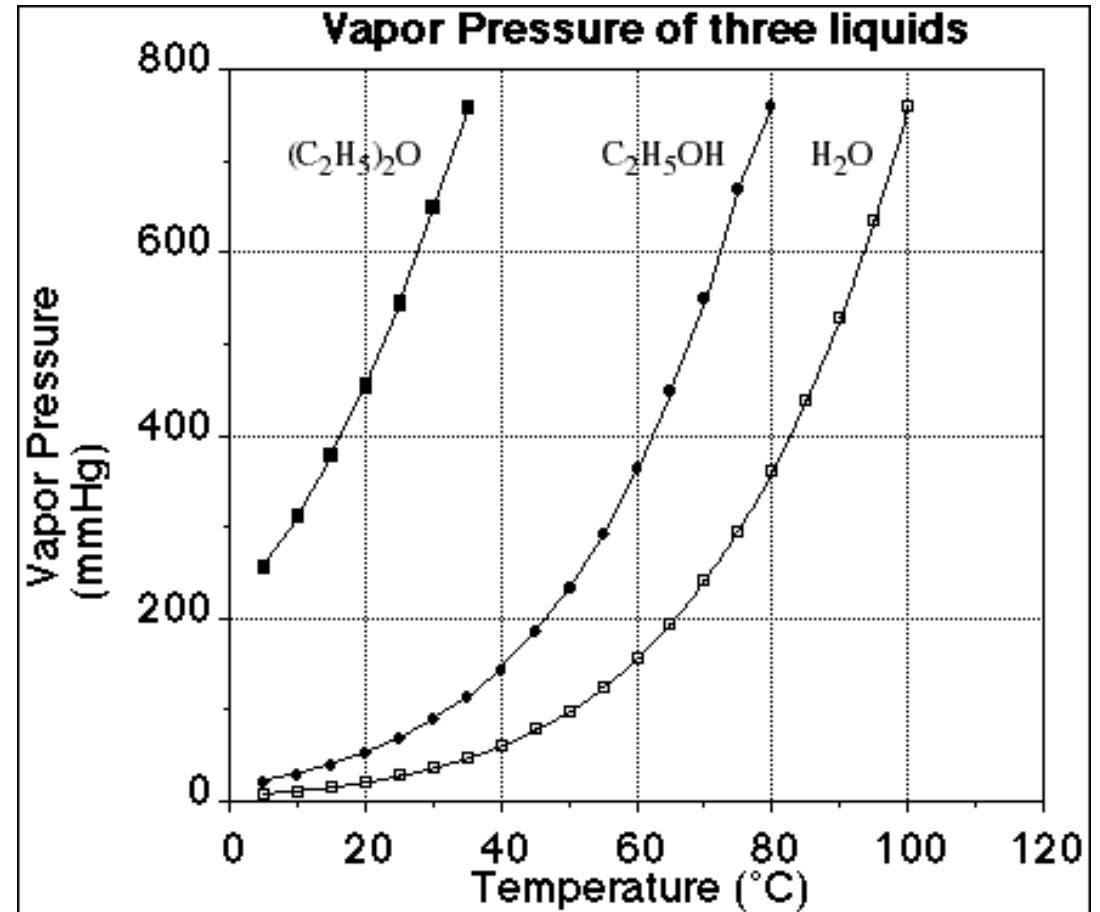
$$P_{v2} = P_{v1} \cdot \exp \left[\frac{L_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] : R = ???$$

$$R = 0.00831443 \text{ kJ/mole.K} \quad : // \text{en.wikipedia.org/wiki/Gas_constant}$$

$$P_{v2} = 92.44 \cdot \exp \left[\frac{16.69}{0.00831443} \left(\frac{1}{254.3} - \frac{1}{275.7} \right) \right]$$

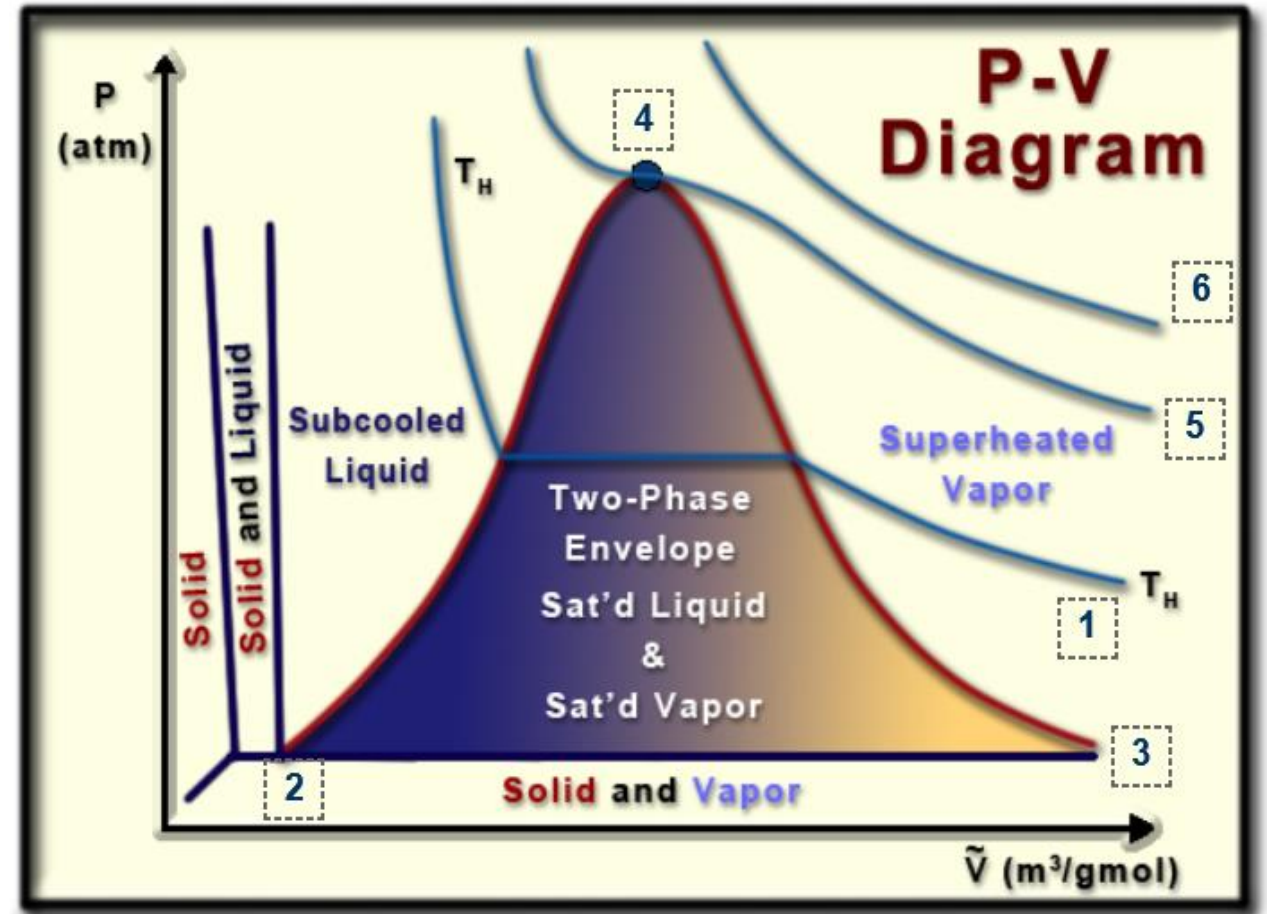
$$P_{v2} = 170.6 \text{ mm Hg.}$$

Vapor Pressure of a Pure Substance



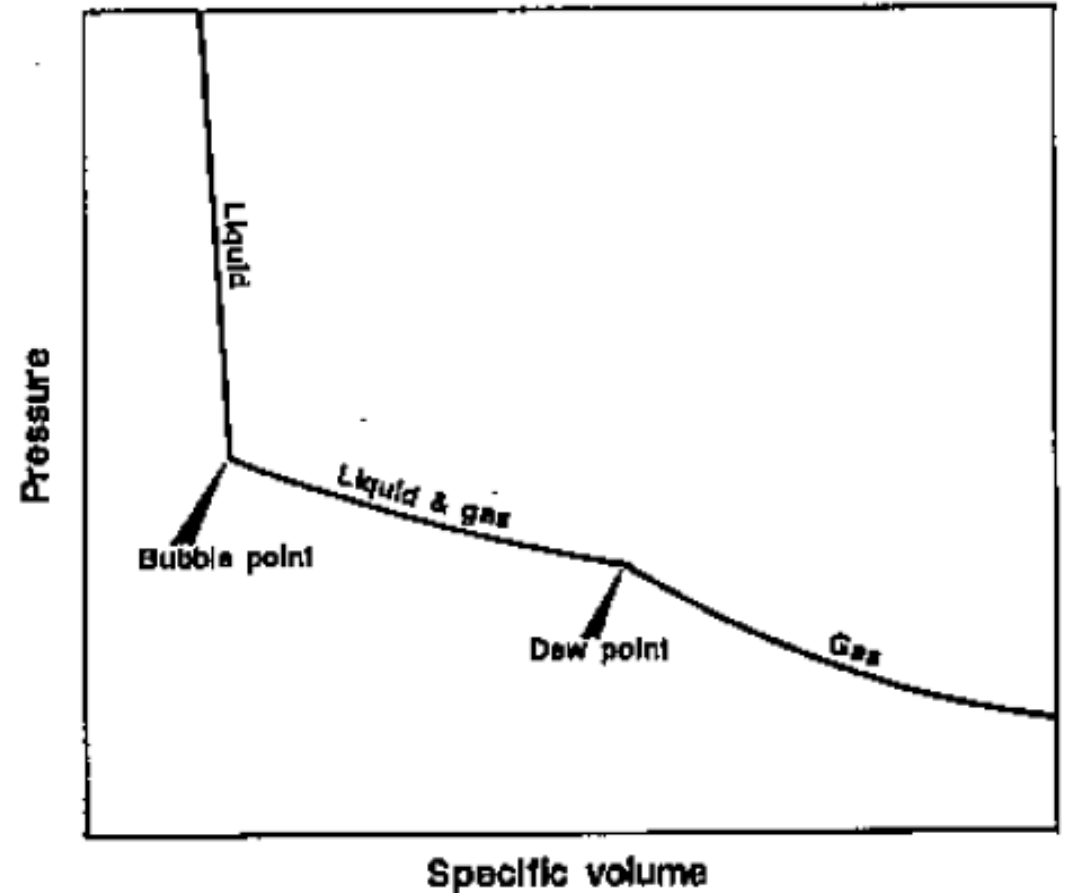
Pressure-Volume diagram of Pure Substance

1. Isotherm curve
 - Constant temp. $< T_c$
2. Saturated liquid curve
3. Saturated vapor curve
4. Critical point
 - Saturated liquid and vapor are identical $T=T_c$
5. Critical isotherm curve
 - $T=T_c$
6. Supercritical isotherm curve
 - $T > T_c$



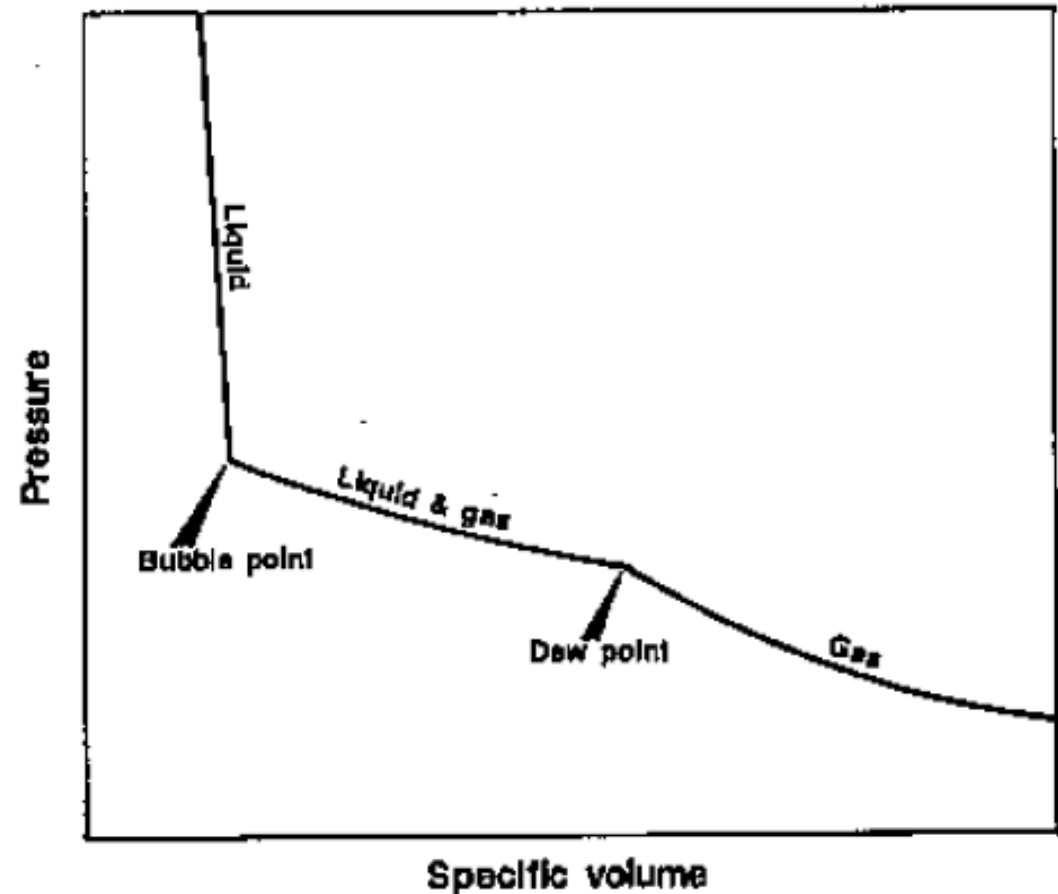
Pressure-Volume diagram of Two Component System

1. Vapor phase
2. Liquid phase
3. Two phase region
 1. Different from “isotherm of pure substance”



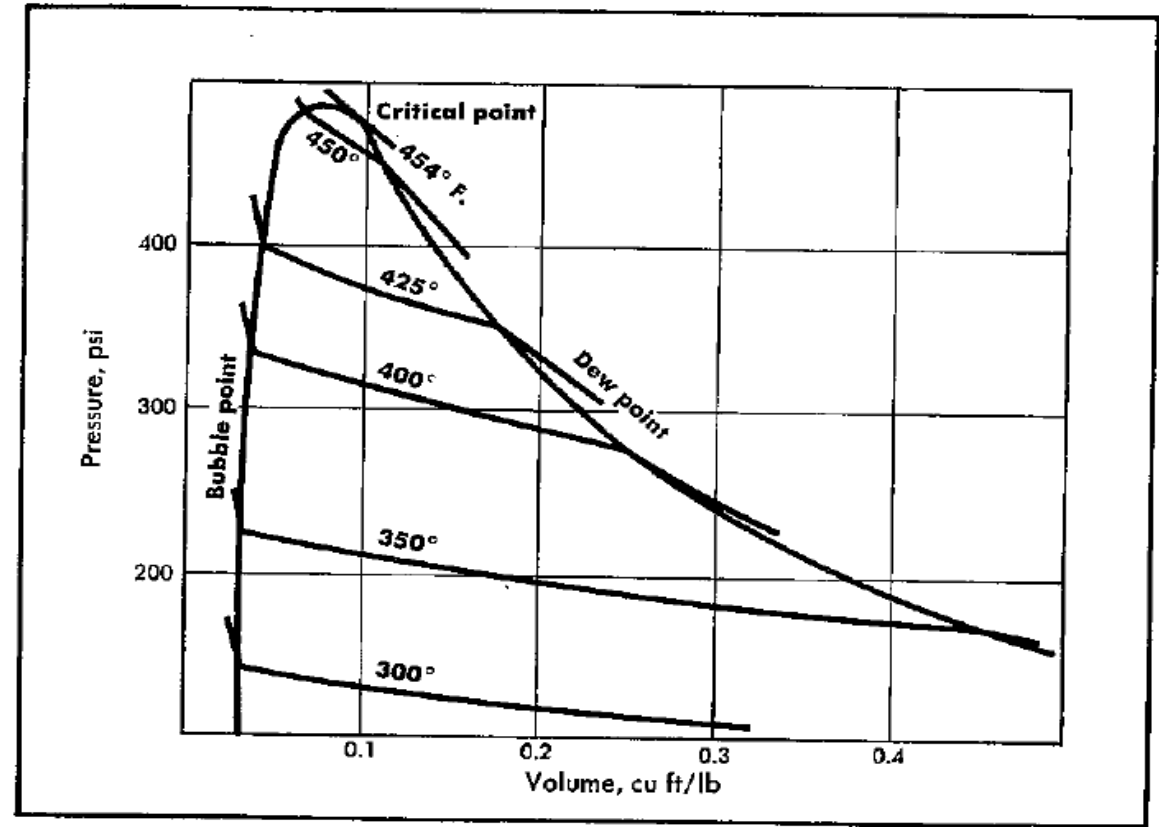
Pressure-Volume diagram of Two Component System

1. At dew point
 - a. Composition of the vapor = composition of the system.
 - b. Infinitesimal (tiny) amount of liquid that condense is richer in the less volatile component.
2. At bubble point
 - a. Infinitesimal amount of vapor remaining is richer in the more volatile component than the system as a whole.

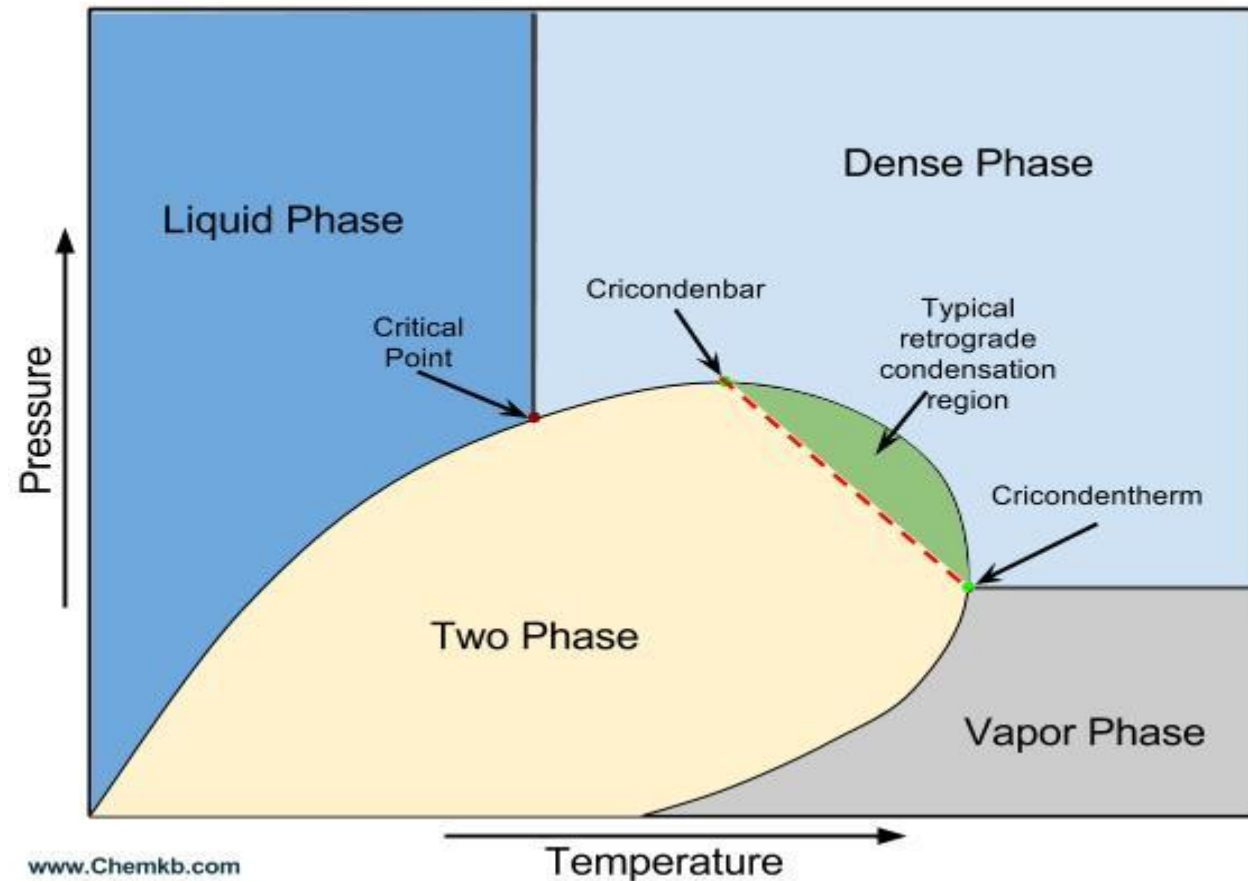


Pressure-Volume diagram of Two Component System

1. Isotherm curves (n-pentane 52 w-% , n-heptane system)
2. Critical point?
 - a. The vapor can exist at $P > P_c$
 - b. Liquid can exist at $T > T_c$.

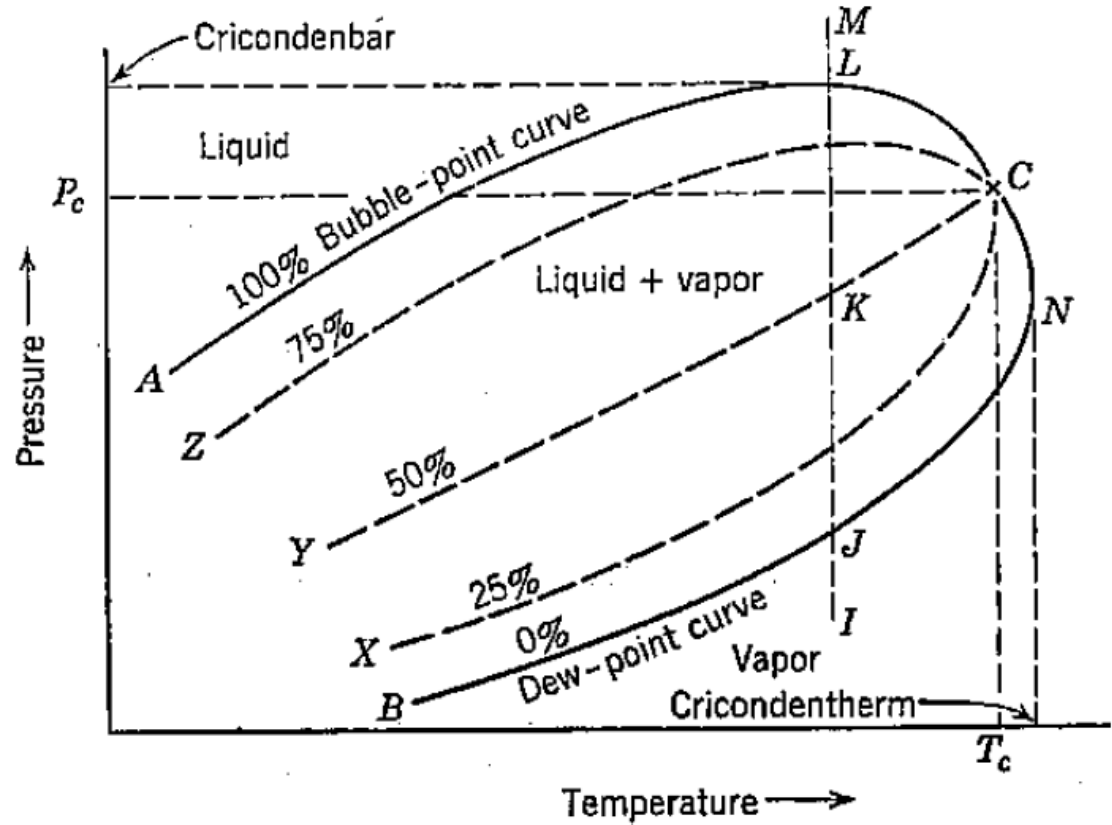


Pressure-Temperature diagram of Two Component System



Pressure-Temperature diagram of Two Component System

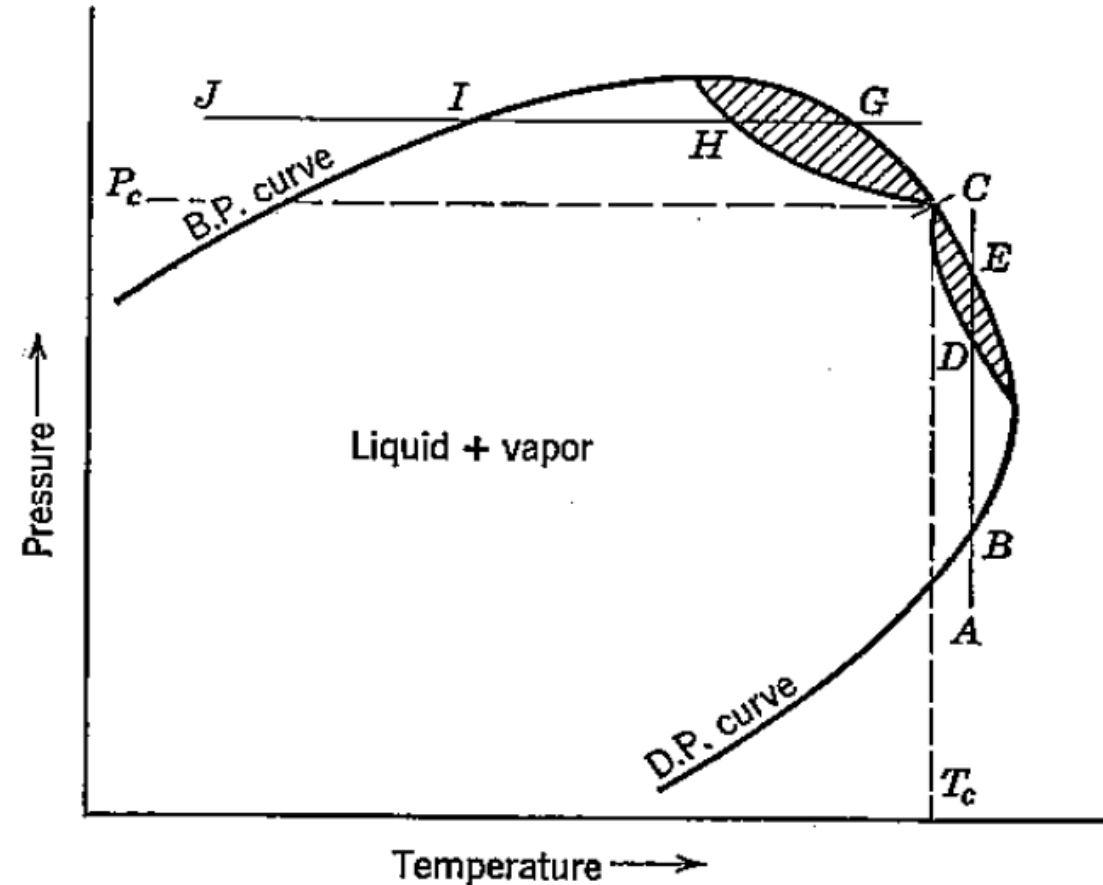
1. AC: Bubble point
2. BC: Dew point
3. C: Critical point
4. L: Cricondenbar (P_{cb})?
 - Cricondertherm pressure (P_{ct}).
5. N: Cricondentherm (T_{ct})?
 1. Cricondenbar temperature (T_{cb}).



Pressure-Temperature diagram of Two Component System

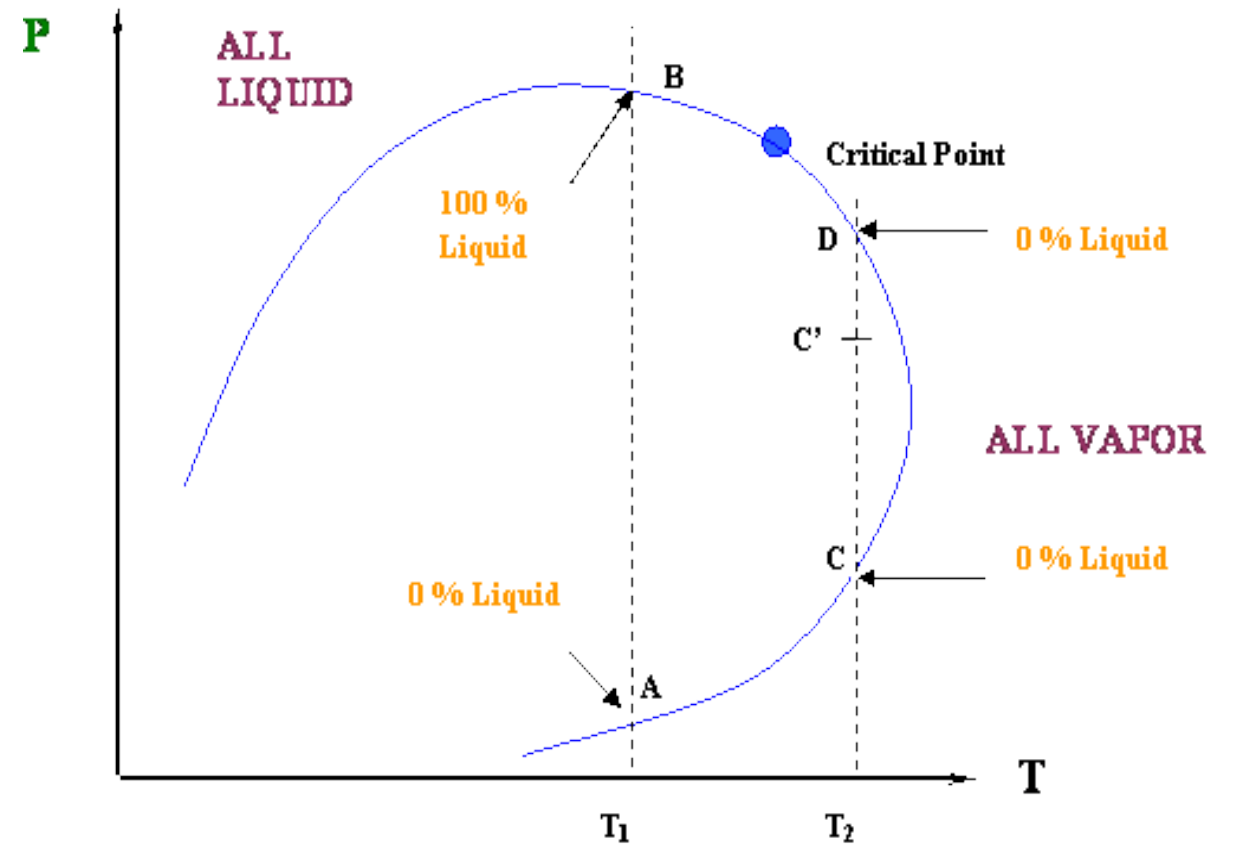
Retrograde phenomenon:

- D-E: isothermal retrograde vaporization.
- E-D: isothermal retrograde condensation
- H-G: isobaric retrograde condensation
- G-H: isobaric retrograde vaporization



Retrograde Phenomenon

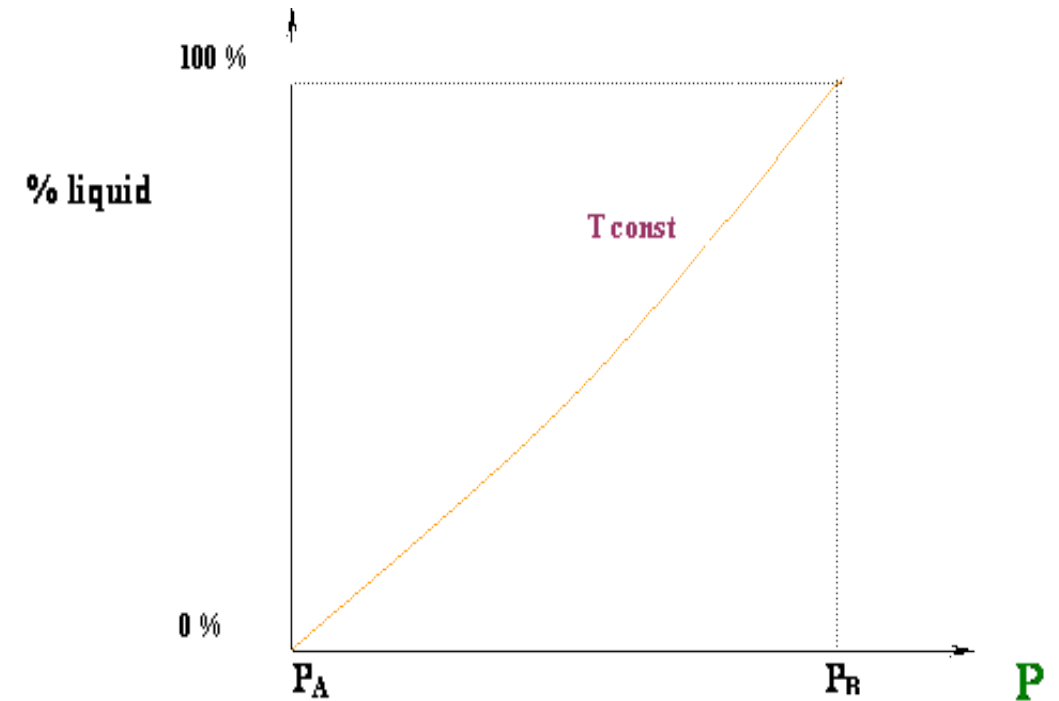
1. Line A-B @ T_1 ($T_1 < T_c$)
2. Line C-C'-D @ T_2 ($T_2 > T_c$)



Retrograde Phenomenon

1. Line A-B

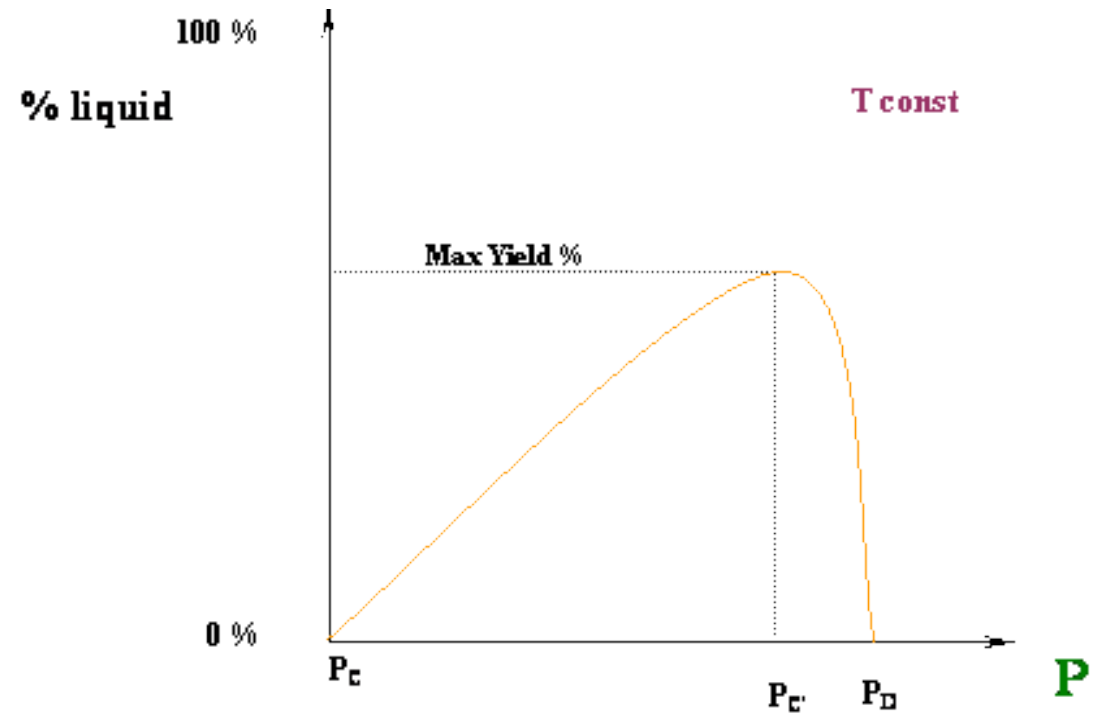
- 0% liquid to 100%



Retrograde Phenomenon

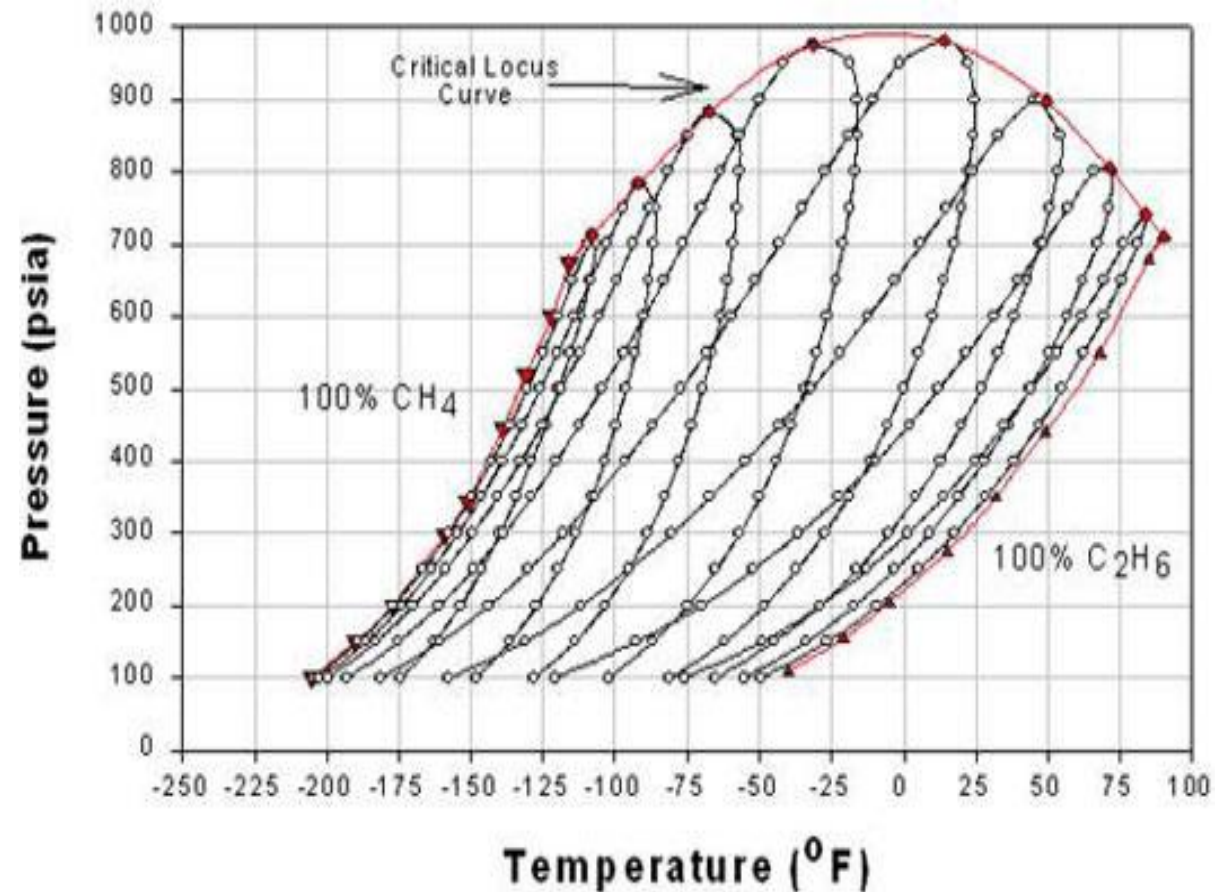
2. Line C-C'-D

- 0% liquid to Max. Yield



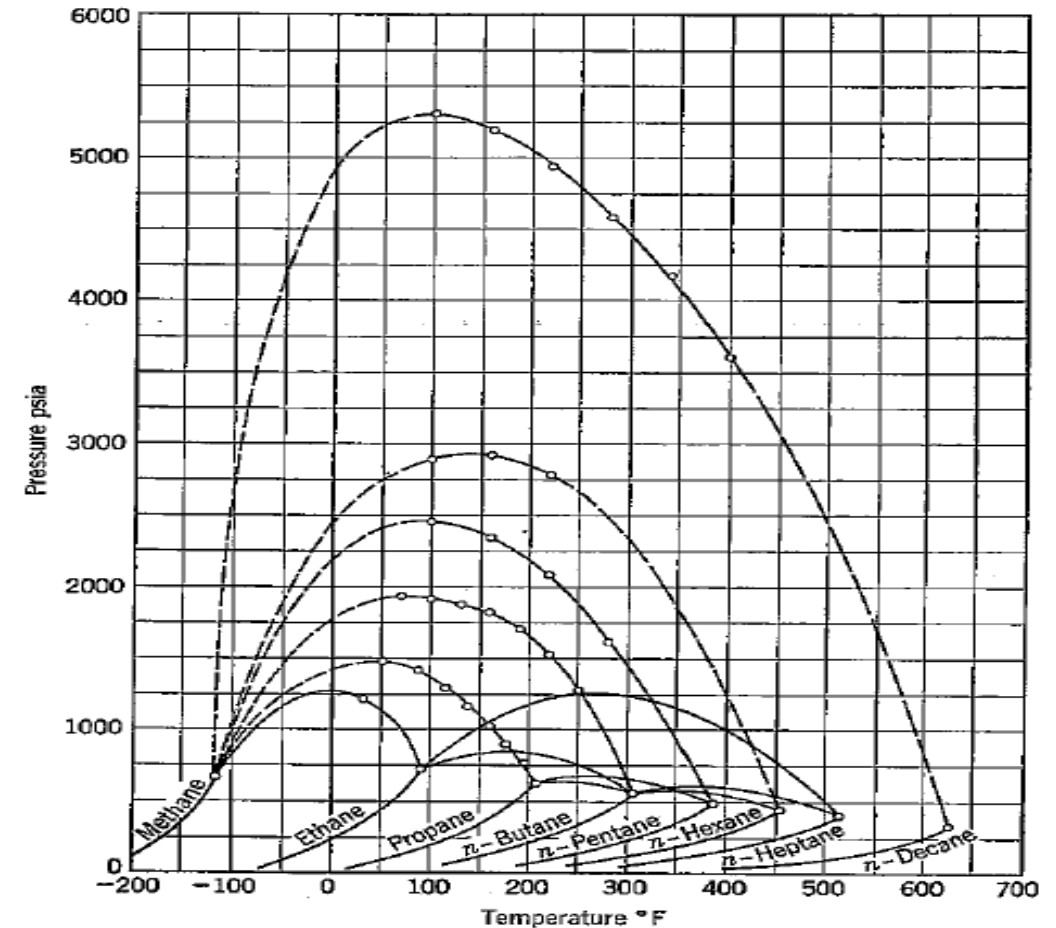
The Composite P-T diagram of methane & ethane

1. Eight mixtures of methane-ethane
2. Vapor pressure lines of pure methane and pure ethane.
3. Critical pressure of the mixtures lie above the critical pressures of the pure components.
4. Critical temperature?
5. The effect of the mixtures similarities or dissimilarities on the critical locus curve?

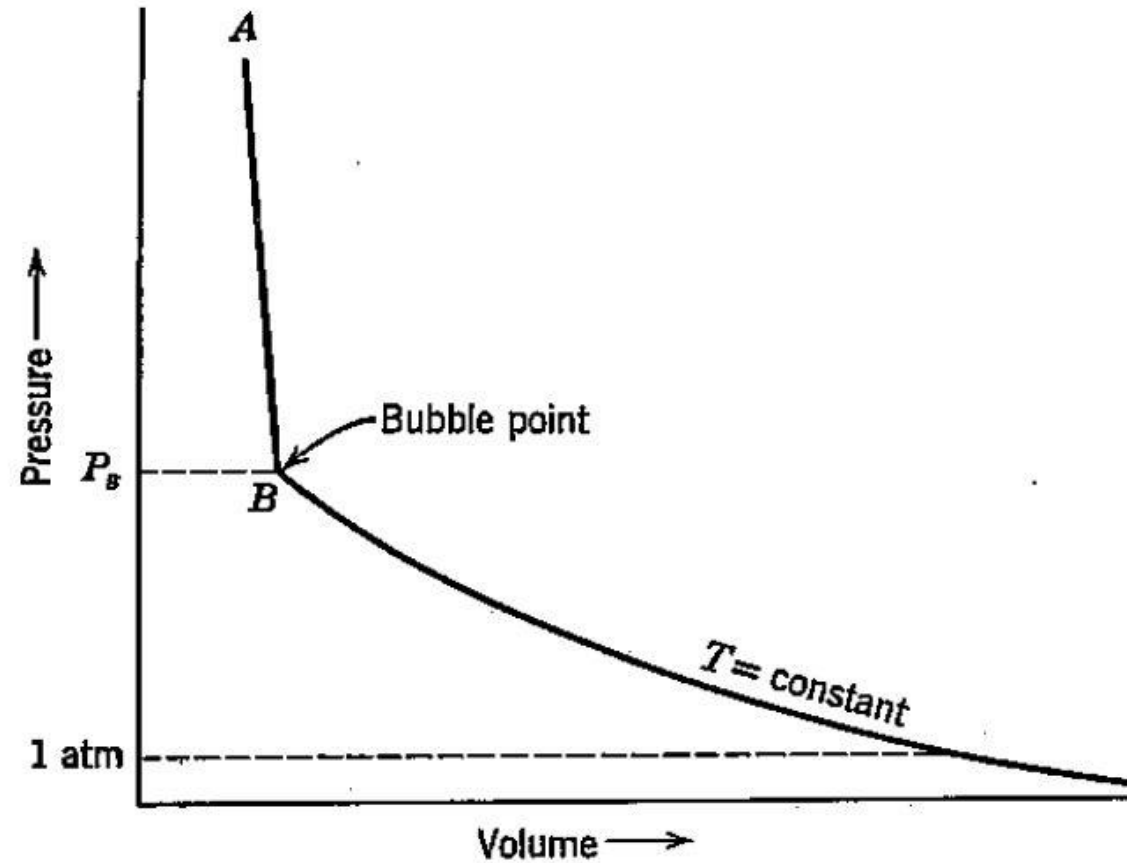


The Composite P-T diagram of n-paraffin mixtures

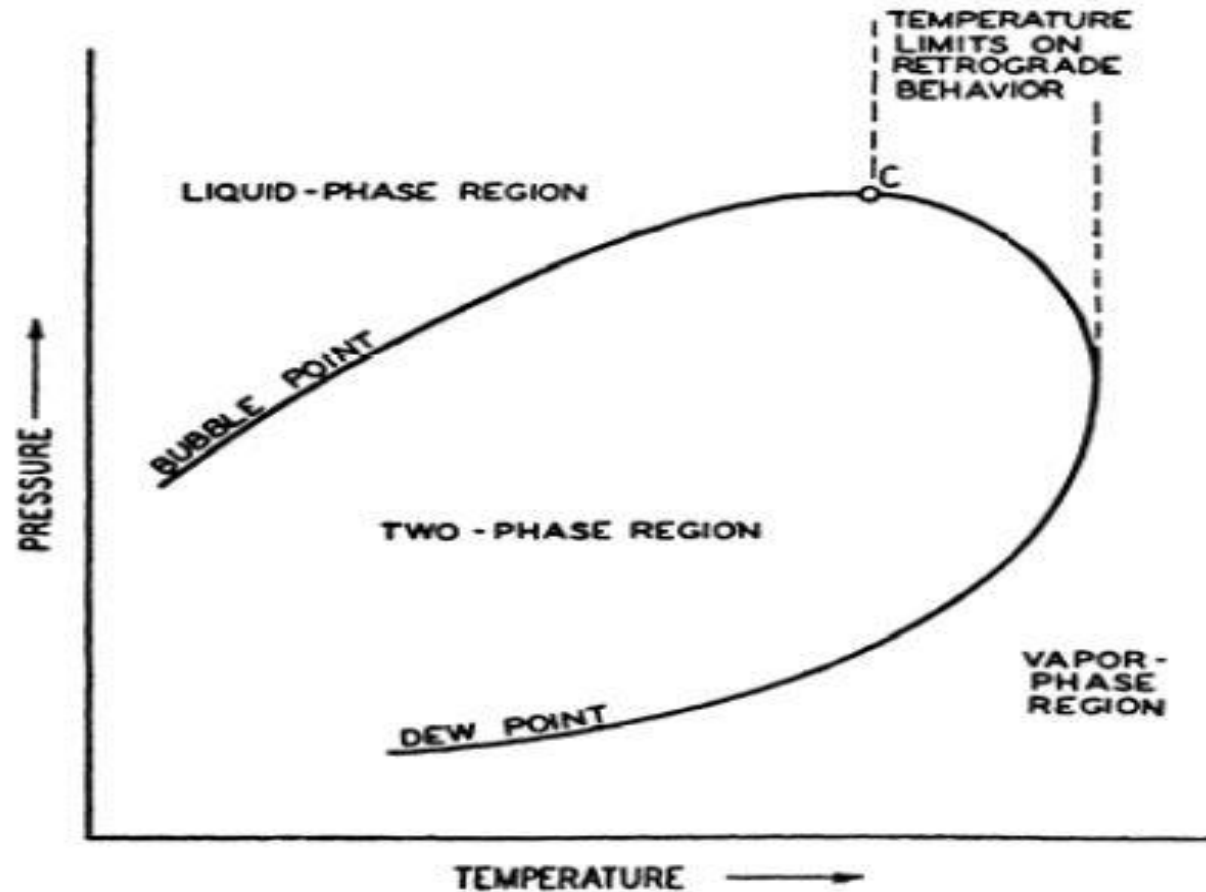
1. The critical pressures of mixtures are higher than those of the components of the mixtures
2. Higher difference in molecular size of the components cause the mixtures to have very large critical pressures.



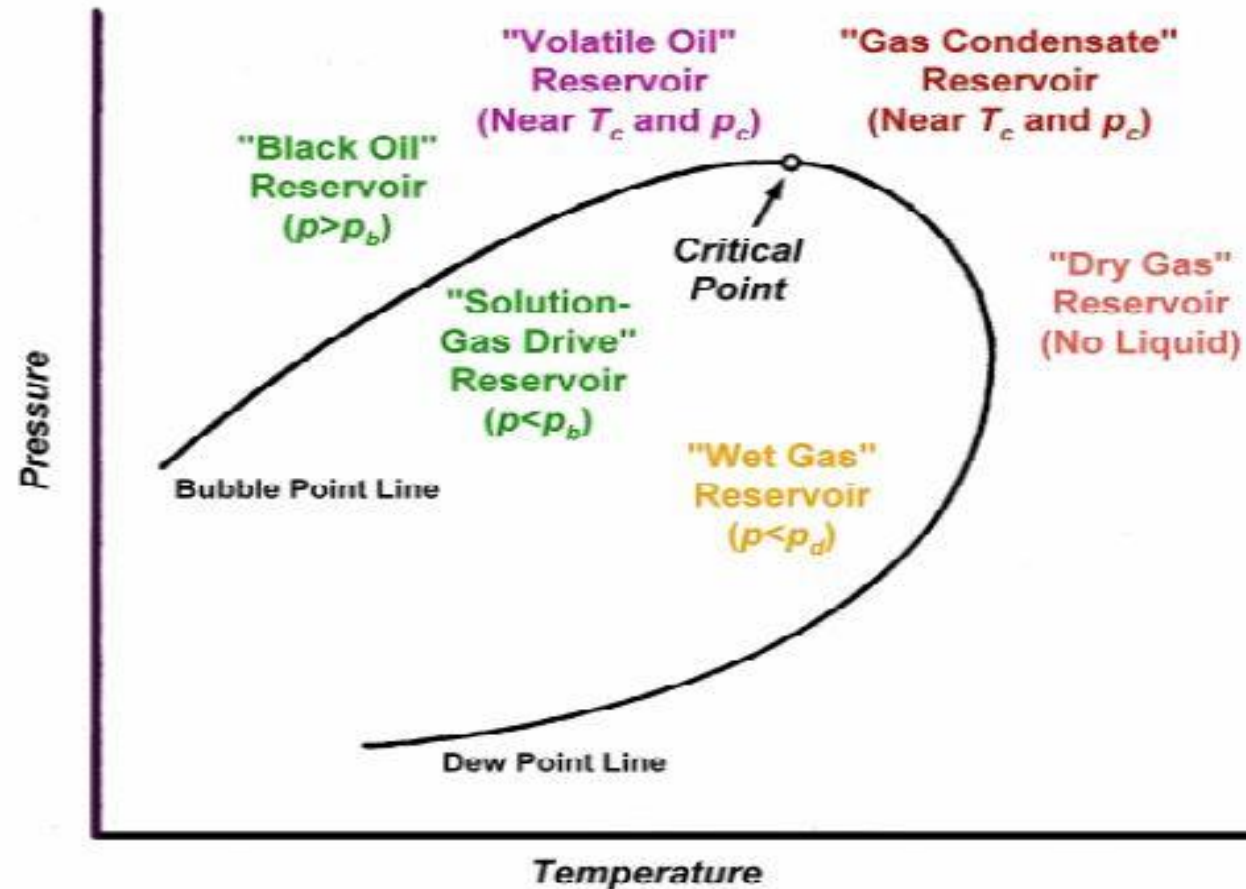
Multicomponent System



Multicomponent System

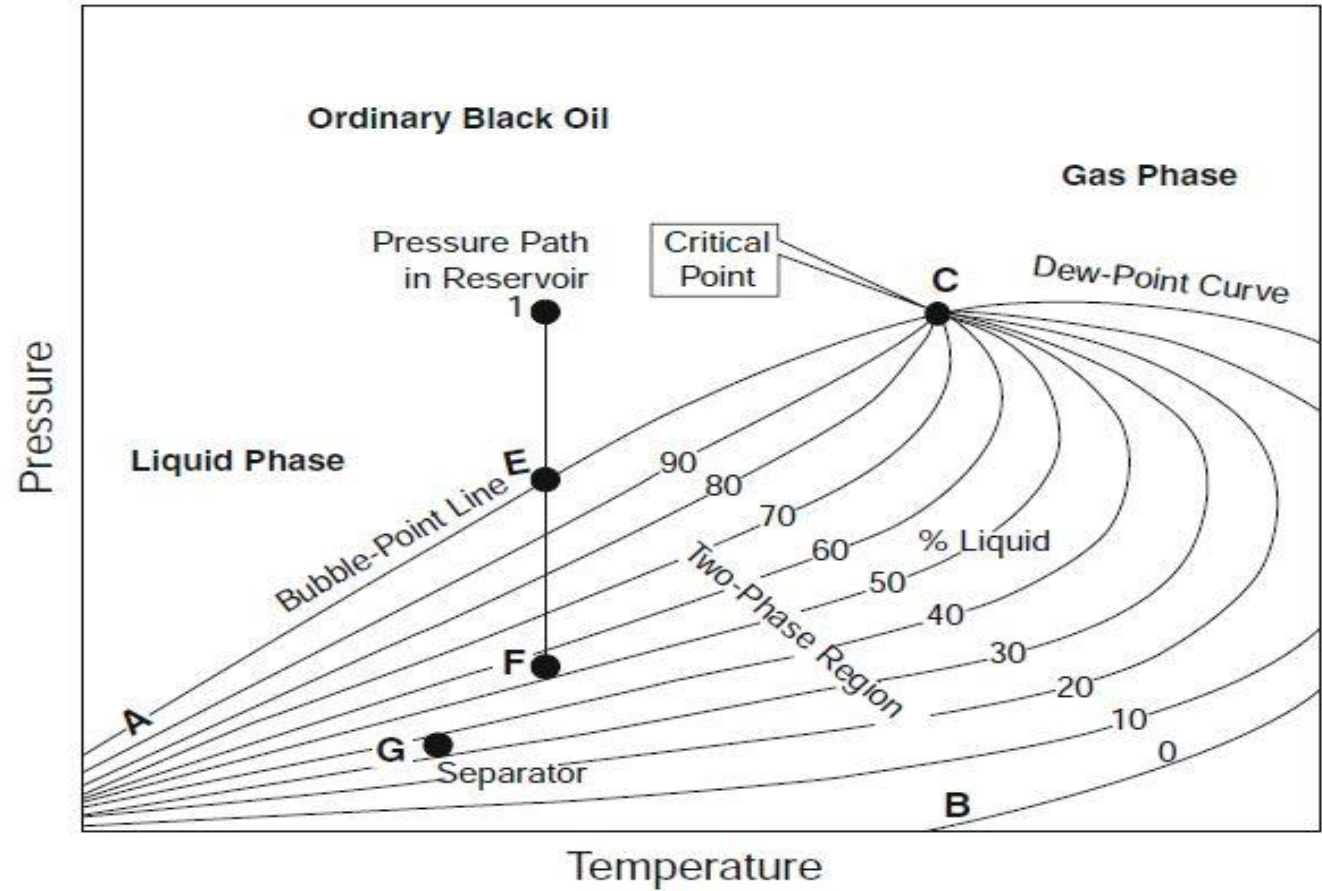


Multicomponent System



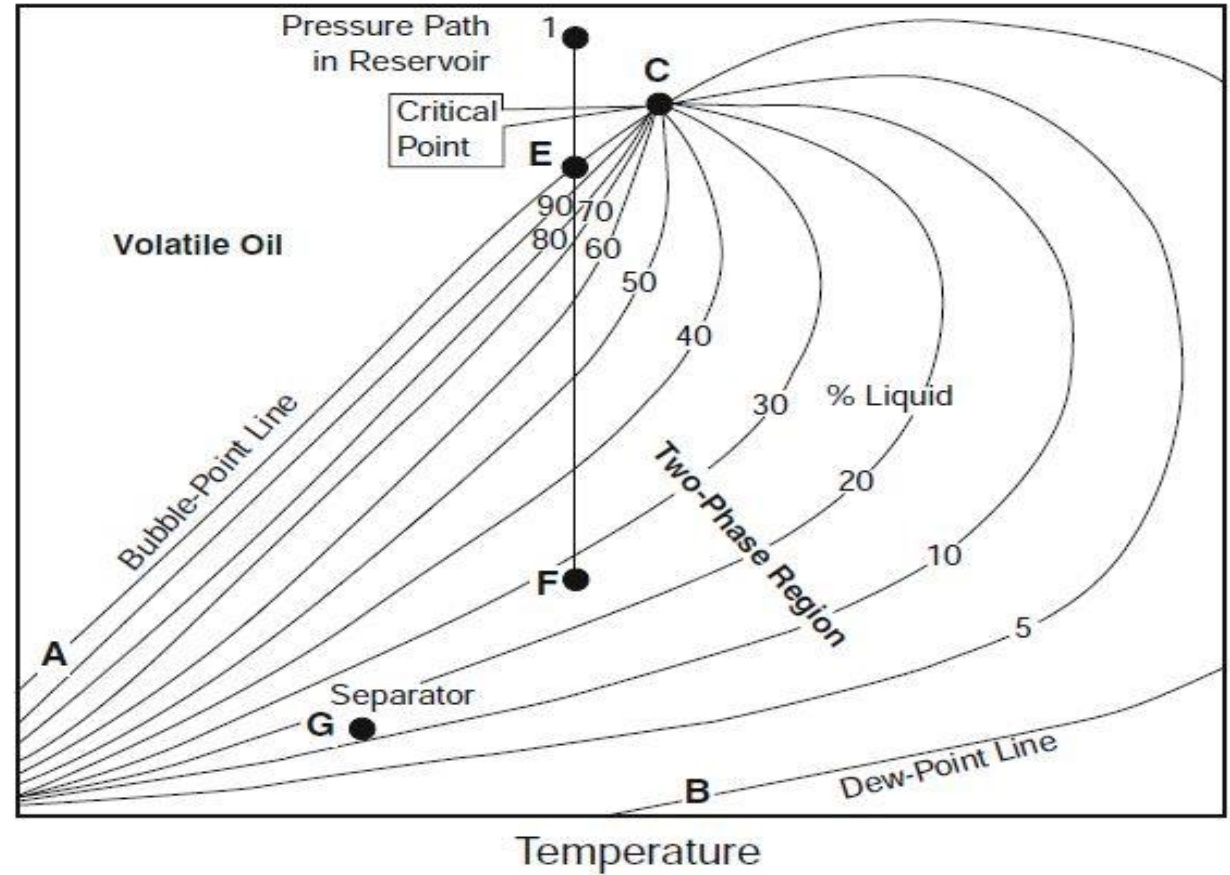
Multicomponent System

Black Oil



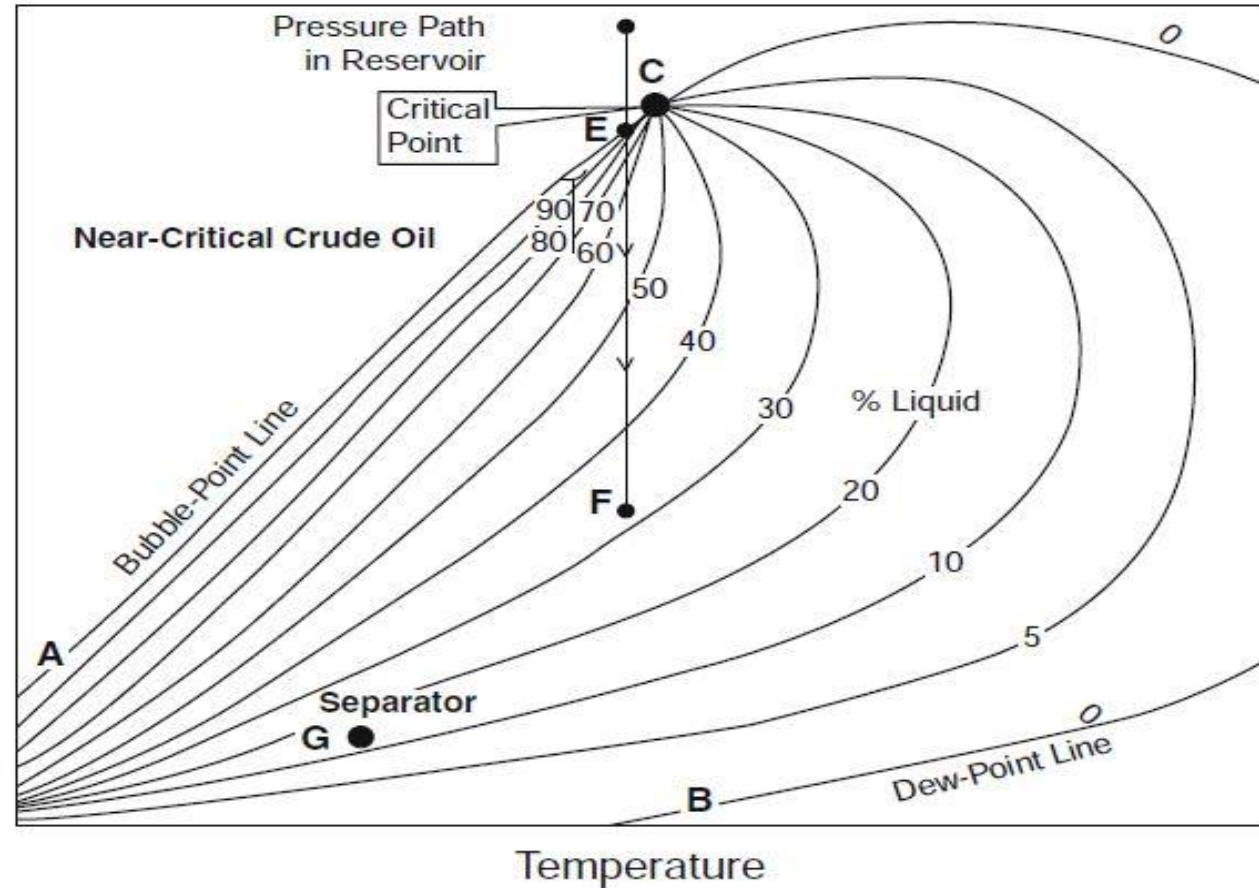
Multicomponent System

Volatile Oil



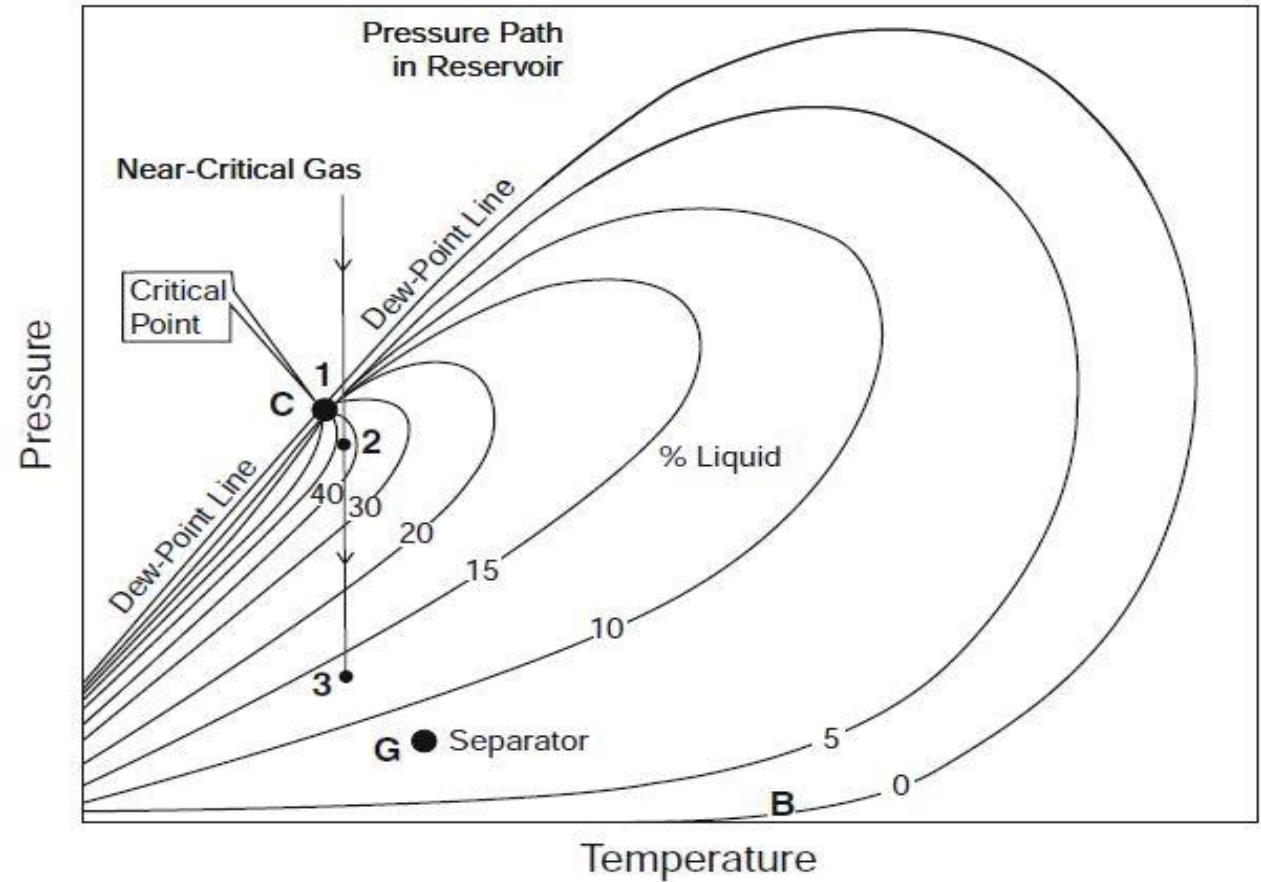
Multicomponent System

Near-Critical Crude Oil



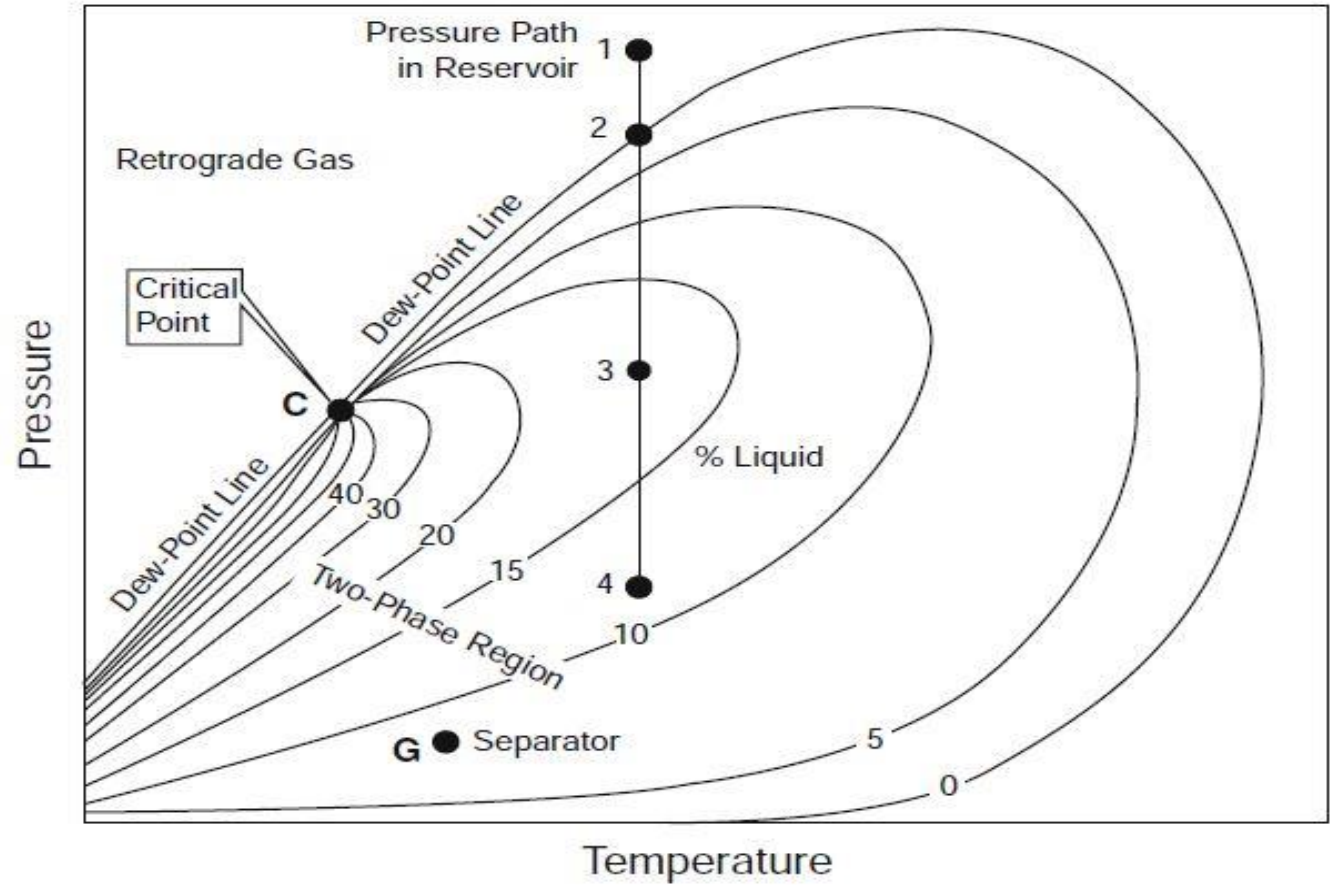
Multicomponent System

Near-Critical Gas



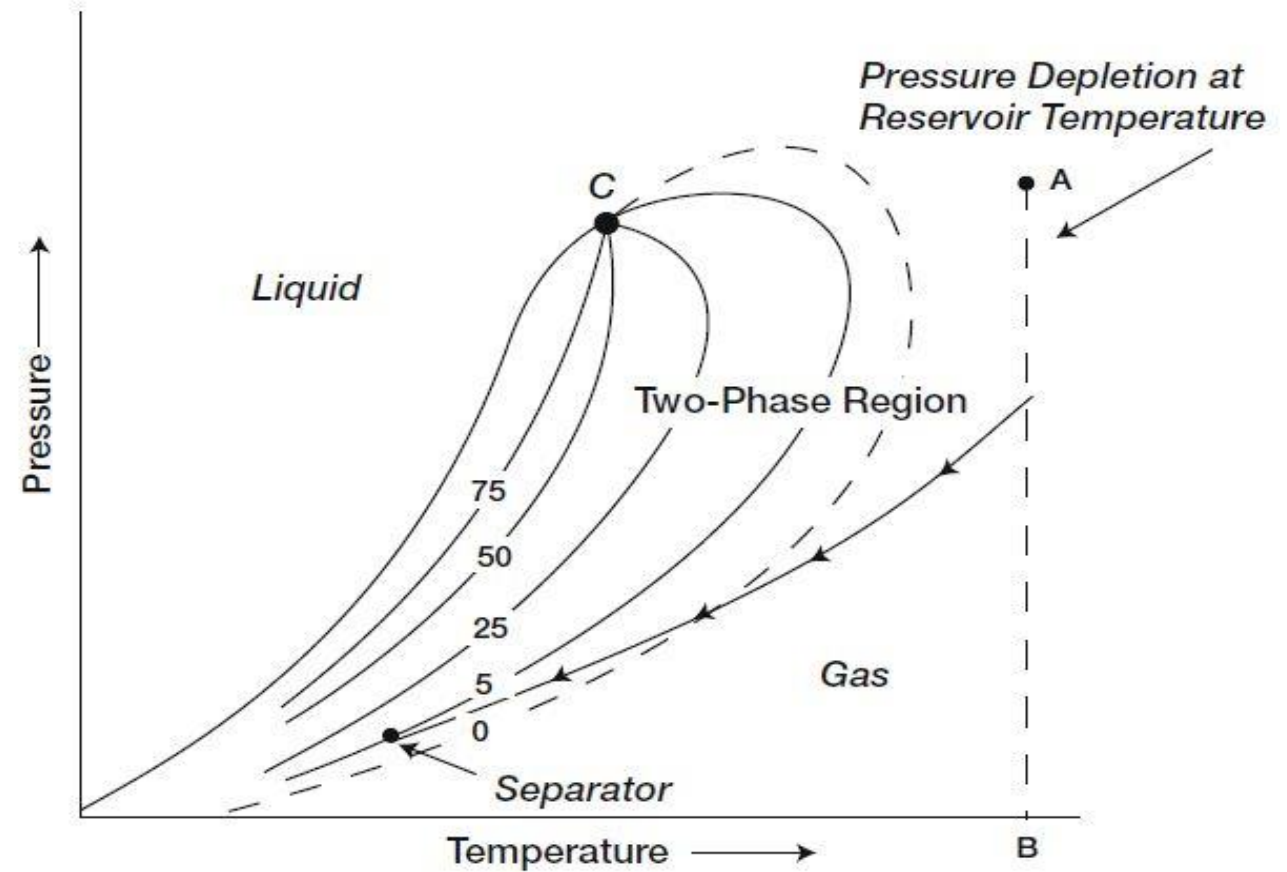
Multicomponent System

Retrograde Gas



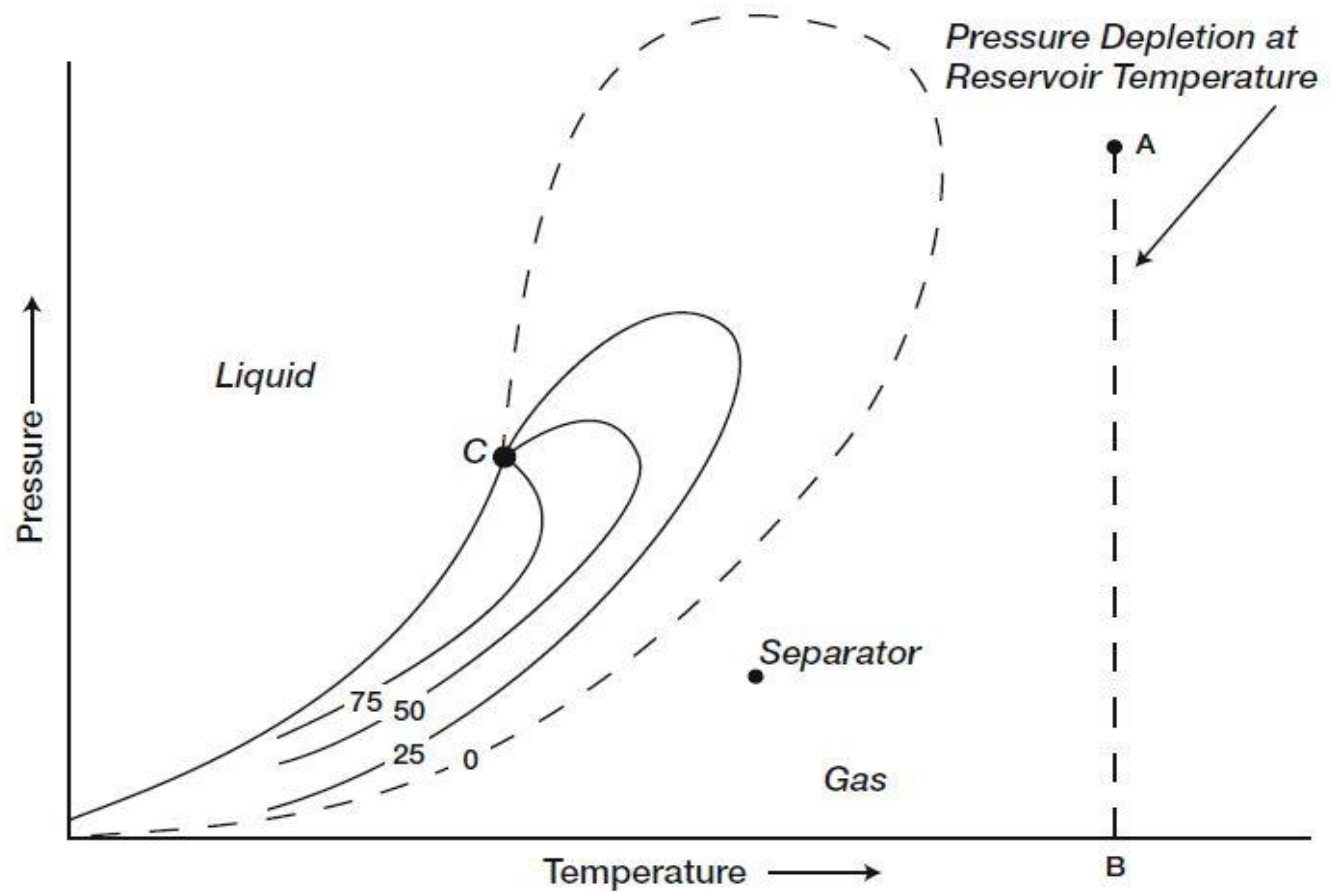
Multicomponent System

Wet Gas



Multicomponent System

Dry Gas



Multicomponent System

The Gibbs' phase rule:

- The number of phases that can coexist in equilibrium for a system under conditions of (T & P).
- $F = C - P + 2$
- F : the variance or the number of degree of freedom.
- C : the min. number of components or chemical compounds required to make up the system.
- P : the number of phases that are present when the system is at equilibrium.

Note: The number of degrees of freedom is the number of independent intensive variable, i. e. the largest number of properties such as temperature or pressure that can be varied simultaneously and arbitrarily without affecting one another.

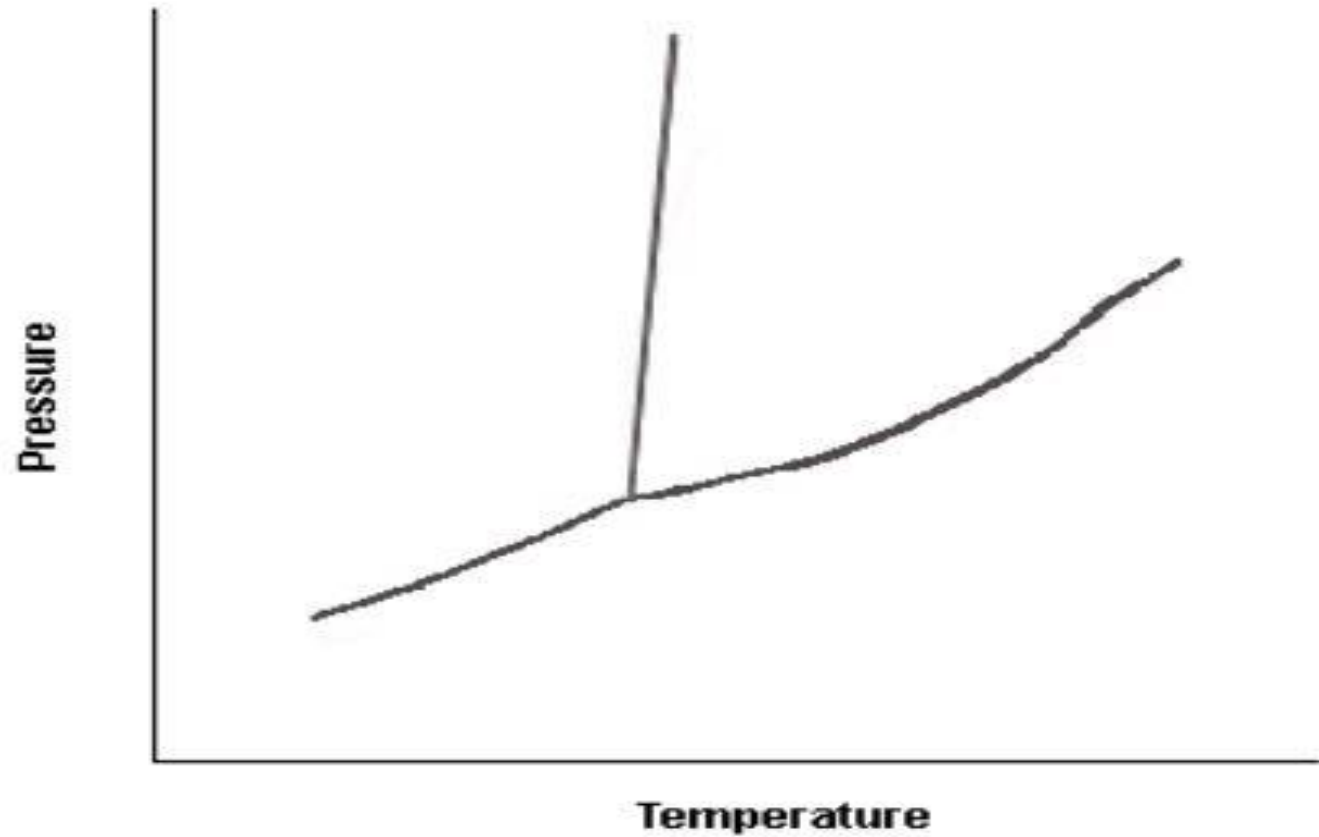
Multicomponent System

The Gibbs' phase rule:

One component

$$F = 1 - P + 2$$

$$F = 3 - P$$

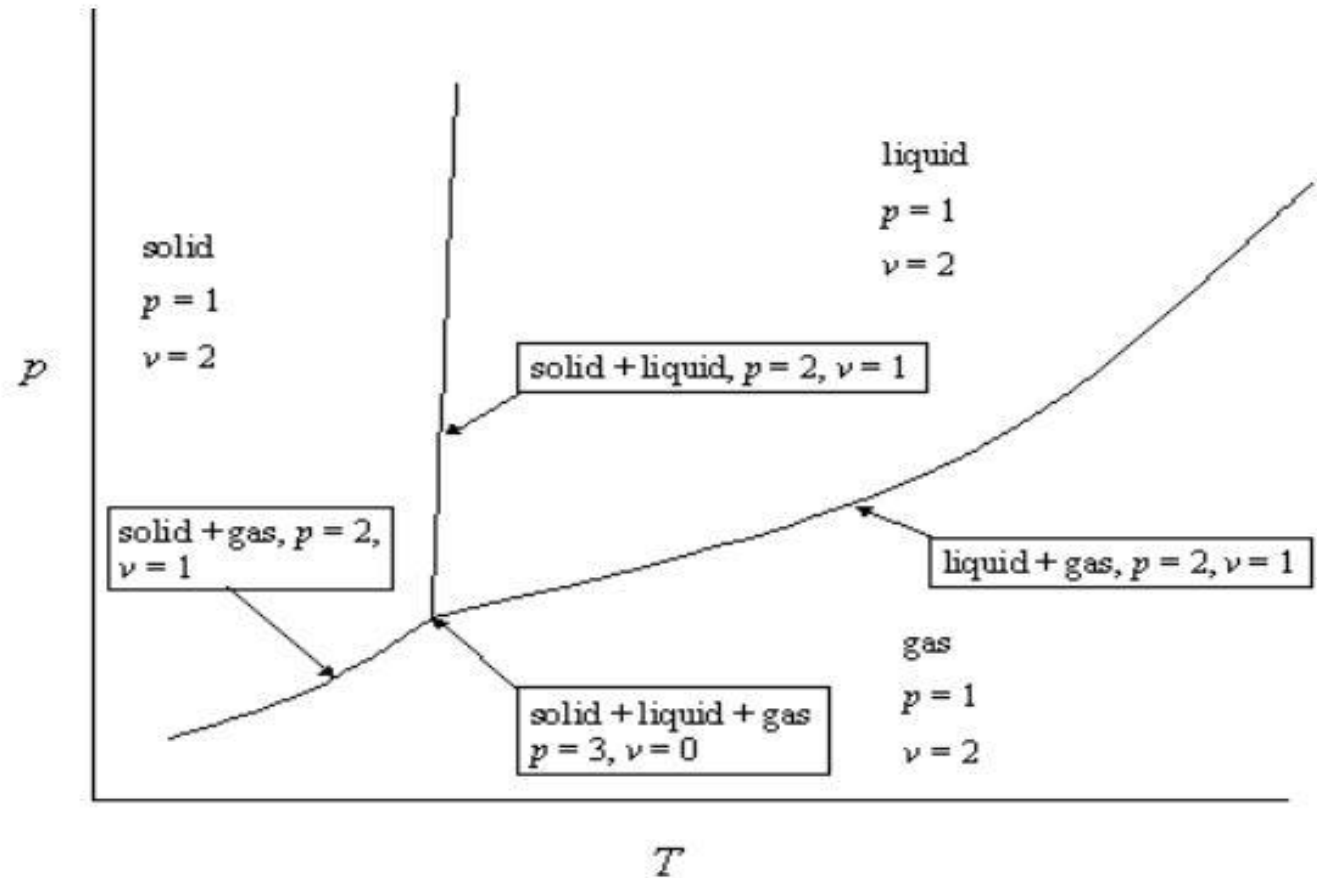


Multicomponent System

The Gibbs' phase rule:

One component

$$F = 3 - P$$



Equilibrium

Ideal solutions:

Raoult's Law and Dalton's Law can be applied.

$$y_i = \frac{x_i P_i^\circ}{P_T}$$

Non-Ideal solutions:

Raoult's Law and Dalton's Law can not be applied.

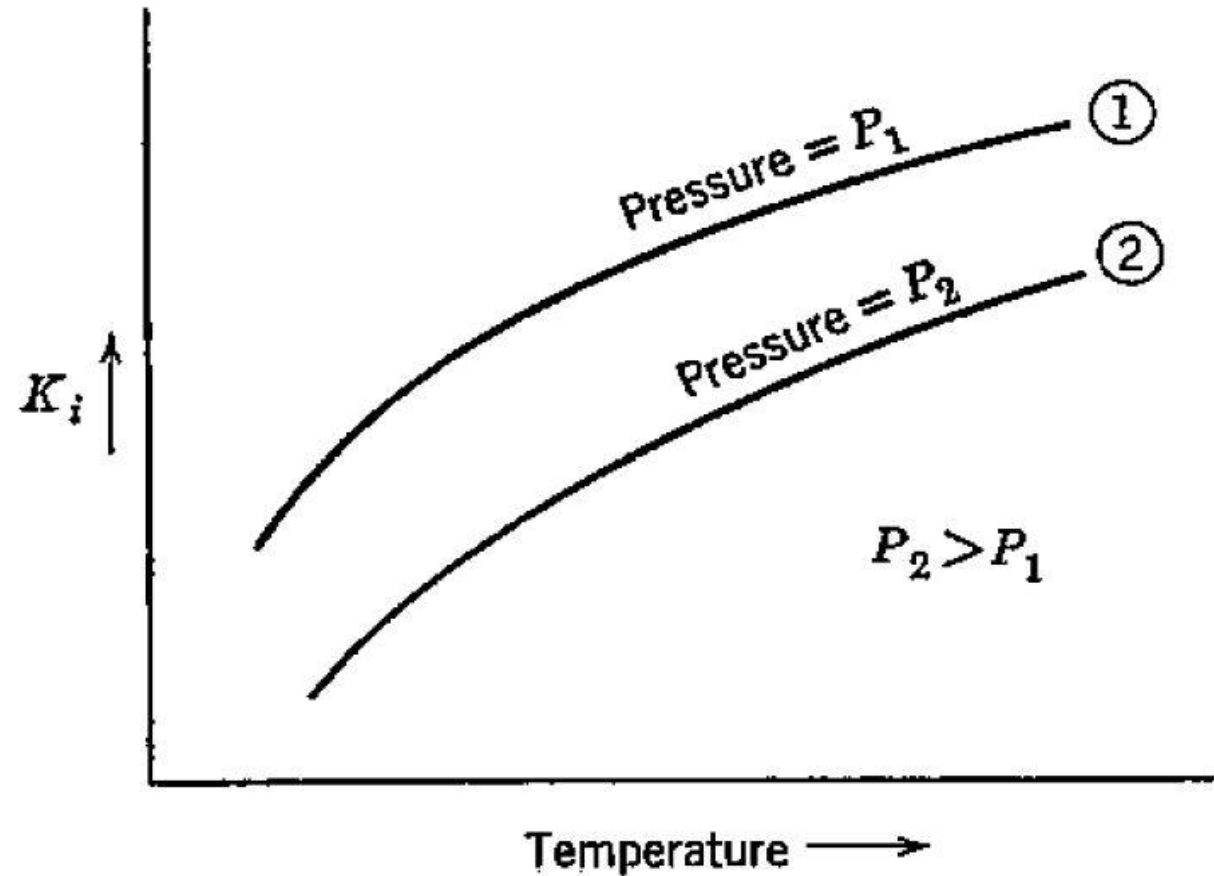
$$y_i = K_i x_i$$

K_i : an experimentally determined constant known as the equilibrium constant. In the case of an ideal solution the value of K_i is a function of temperature and pressure and is equal to the vapor pressure of the pure component divided by the total pressure.

Equilibrium

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

K_i : is a function of pressure, temperature and composition



Equilibrium

EXAMPLE. From the appropriate chart find the equilibrium constants for *n*-butane at 100° F and 25 psia and at 100° F and 400 psia. What would be the value of these constants if the solution containing the *n*-butane were ideal?

Equilibrium

Solution:

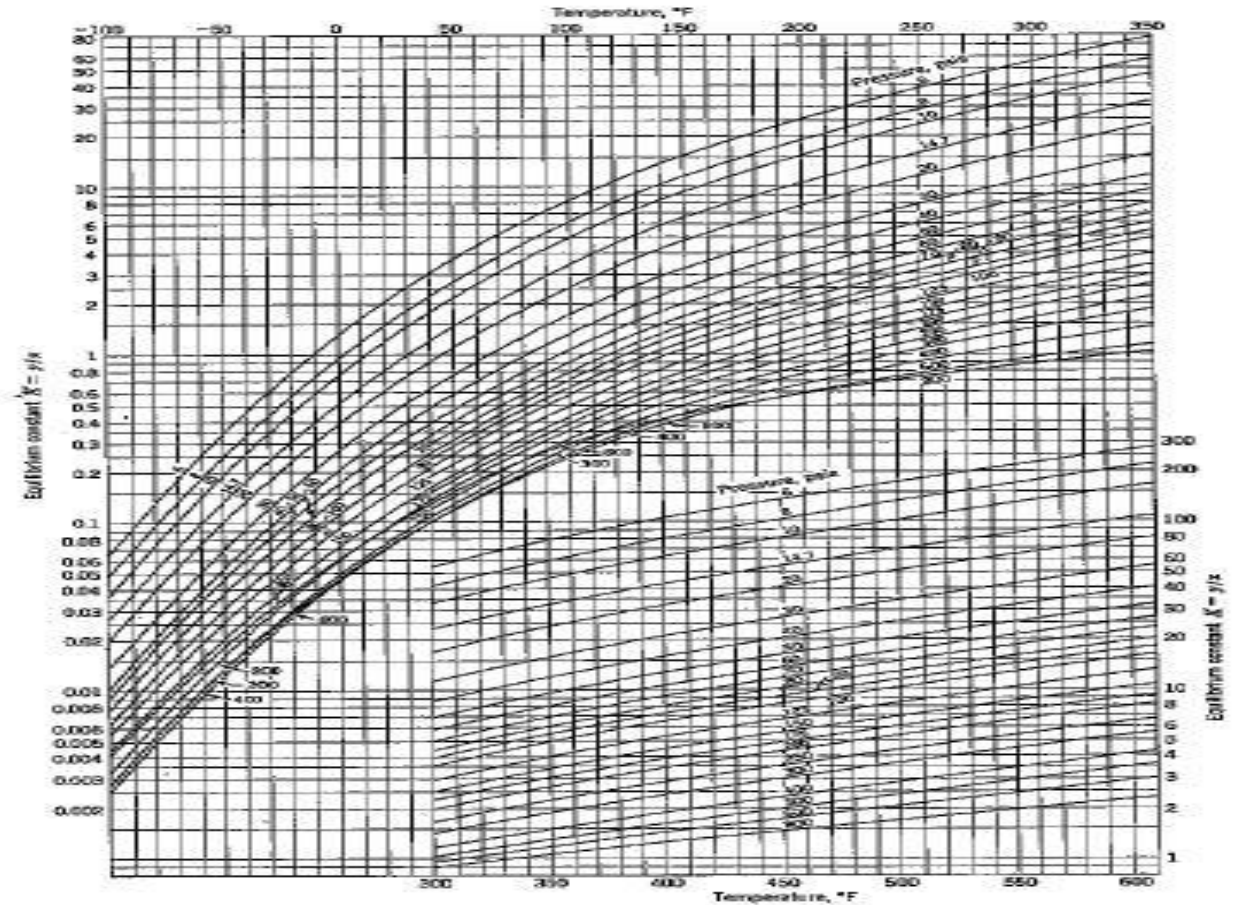


Fig. 45. Equilibrium constants for n-butane. (Natural Gasoline Supply Men's Association, Engineering Data Book, 1961, p. 112.)

Equilibrium

Solution:

From Figure 45 the value of K_i is found by interpolation to be 2.10 at 100° F and 25 psia. At 100° F and 400 psia the value of K_i is 0.25.

Since the vapor pressure of butane is 52.2 psia at 100° F, the values of these constants for an ideal solution are

$$K_i (\text{ideal, 25 psia}) = \frac{P_i^0}{P_T} = \frac{52.2}{25} = 2.09$$

and

$$K_i (\text{ideal, 400 psia}) = \frac{52.2}{400} = 0.13$$

Equilibrium

It is assumed that the K values of a given component are independent of the nature of the other components which constitute the solution. If the solution is ideal this assumption is exact. In the case of actual solutions it has been found that the K values become increasingly dependent on the overall composition as the pressure is increased. The upper limit of the pressure in Figures 41 to 50 is 800 psia but equilibrium constants have been determined at considerably higher pressures and may be found in the literature.

Equilibrium

For two-components systems:

$$K_i = \frac{P_i^\circ}{P_T}$$

$$x_1 = \frac{P_T - P_2^\circ}{P_1^\circ - P_2^\circ}$$

Divide by P_T

$$x_1 = \frac{\frac{P_T - P_2^\circ}{P_T}}{\frac{P_1^\circ - P_2^\circ}{P_T}} = \frac{1 - K_2}{K_1 - K_2}$$

$$y_1 = K_1 x_1$$

$$x_2 = 1 - x_1 = 1 - \frac{1 - K_2}{K_1 - K_2} = \frac{1 - K_1}{K_1 - K_2}$$

$$y_2 = 1 - y_1 = K_2 x_2$$

Equilibrium

EXAMPLE. A two-component system contains one mole of *n*-butane and one mole of *n*-pentane. Calculate the composition of the liquid and the vapor at 180° F and 95 psia. Assume non-ideal solution behavior.

Equilibrium

Solution:

From charts the K values can be obtained.

$$K_{C_4H_{10}} = 1.50, K_{C_5H_{12}} = 0.62$$

$$x_{C_4H_{10}} = \frac{1 - K_{C_5H_{12}}}{K_{C_4H_{10}} - K_{C_5H_{12}}} = \frac{1 - 0.62}{1.50 - 0.62} = 0.431$$

$$x_{C_5H_{12}} = 1 - x_{C_4H_{10}} = 1 - 0.431 = 0.569$$

$$y_{C_4H_{10}} = K_{C_4H_{10}} x_{C_4H_{10}} = 1.50 \times 0.431 = 0.647$$

$$y_{C_5H_{12}} = 1 - y_{C_4H_{10}} = 1 - 0.647 = 0.353$$

Equilibrium

For multi-components systems:

Ideal solution:

$$\sum x_i = \sum \frac{z_i n}{n_l + \frac{P_i^\circ}{P_T} n_v} = 1,$$

$$\sum y_i = \sum \frac{z_i n}{n_v + \frac{P_T}{P_i^\circ} n_l} = 1$$

Non-ideal solution:

$$\sum x_i = \sum \frac{z_i n}{n_l + K_i n_v} = 1,$$

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

Equilibrium

EXAMPLE. A hydrocarbon system has the following composition:

Component	Mole Fraction
CH ₄	0.15
C ₂ H ₆	0.05
C ₃ H ₈	0.25
<i>i</i> -C ₄ H ₁₀	0.05
<i>n</i> -C ₄ H ₁₀	0.15
<i>n</i> -C ₅ H ₁₂	0.25
<i>n</i> -C ₆ H ₁₄	0.10

Calculate the composition of the liquid and the vapor if a separation is conducted at 200 psia and 100° F. Assume non-ideal solution behavior.

Equilibrium

Solution:

For $n = 1$, assume $n_l = 0.77$, $n_v = 0.23$

(1)	(2)	(3)	(4)	(5)
Component	z_i	K_i	$x_i = \frac{z_i}{n_l + K_i n_v} = \frac{z_i}{0.77 + K_i \times 0.23}$	$y_i = K_i x_i$
CH ₄	0.15	14.1	0.037	0.522
C ₂ H ₆	0.05	2.78	0.035	0.097
C ₃ H ₈	0.25	0.97	0.252	0.245
i-C ₄ H ₁₀	0.05	0.46	0.057	0.026
n-C ₄ H ₁₀	0.15	0.35	0.177	0.062
n-C ₅ H ₁₂	0.25	0.116	0.314	0.037
n-C ₆ H ₁₄	0.10	0.041	0.128	0.005
			$\Sigma x_i = 1.000$	

Equilibrium

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.

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

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

Equilibrium

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.

Equilibrium

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

Equilibrium

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

Equilibrium

Solution:

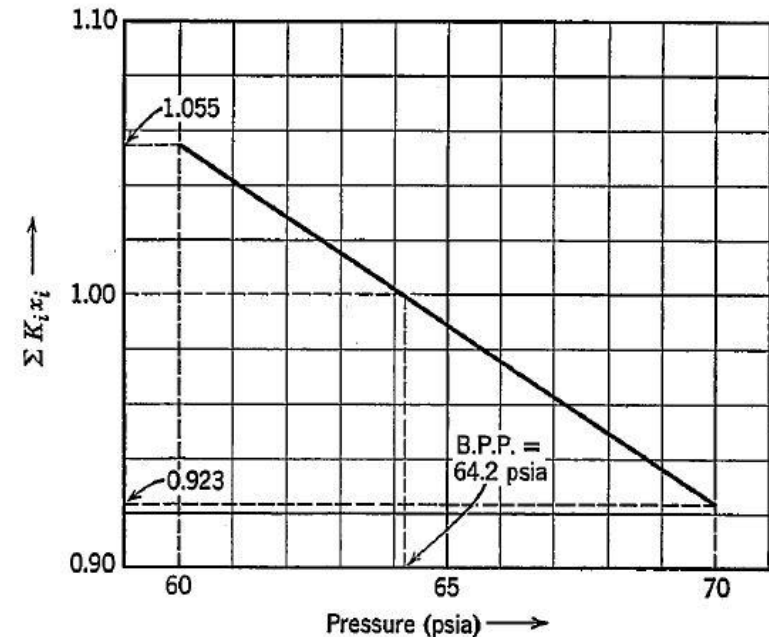
Since the summation is greater than 1 then the bubble point pressure will be between 60-70 psia
The exact value can be obtained either mathematically (interpolation) or graphically.

Interpolation:

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

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

Graphically:



Equilibrium

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

Equilibrium

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

Equilibrium

Solution:

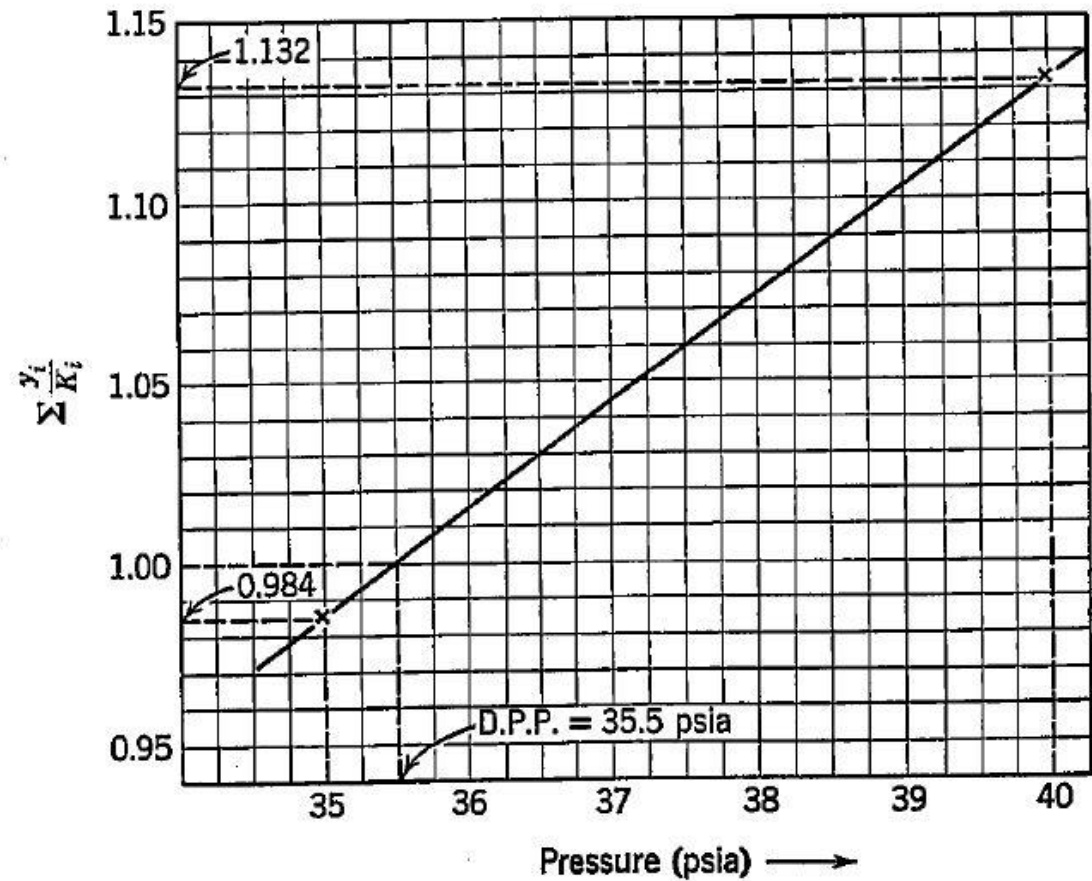
Since the required summation is low the calculation will be repeated at 40 psia

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

Equilibrium

Solution:

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



Equilibrium

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