



Properties of Reservoir Fluids (PGE 362)

Quantitative Phase Behavior

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Non-Ideal Solutions

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.

$$y_i = K_i x_i$$

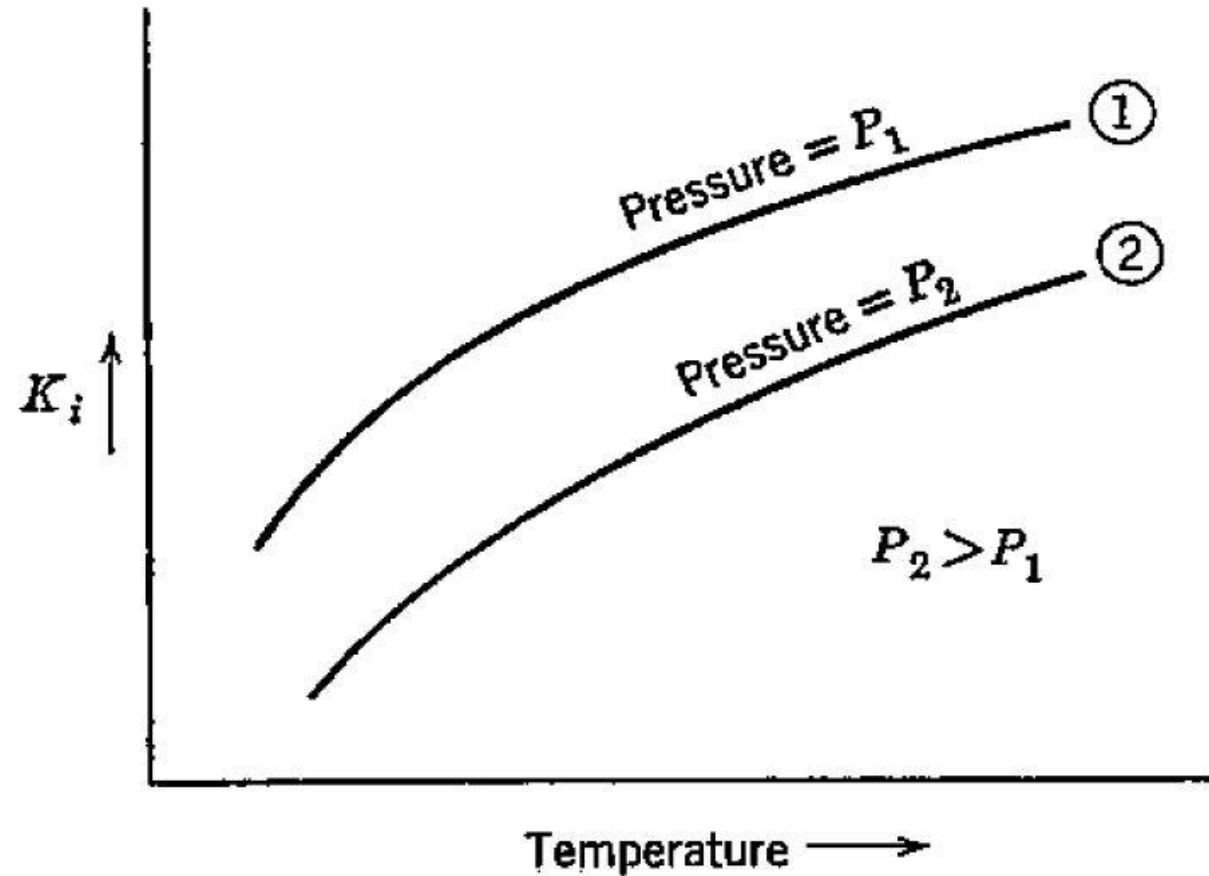
K_i : An experimentally determined constant known as the equilibrium constant.

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.

Non-Ideal Solutions

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

K_i : is a function of pressure, temperature and composition



Non-Ideal Solutions

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?

Non-Ideal Solutions

Solution:

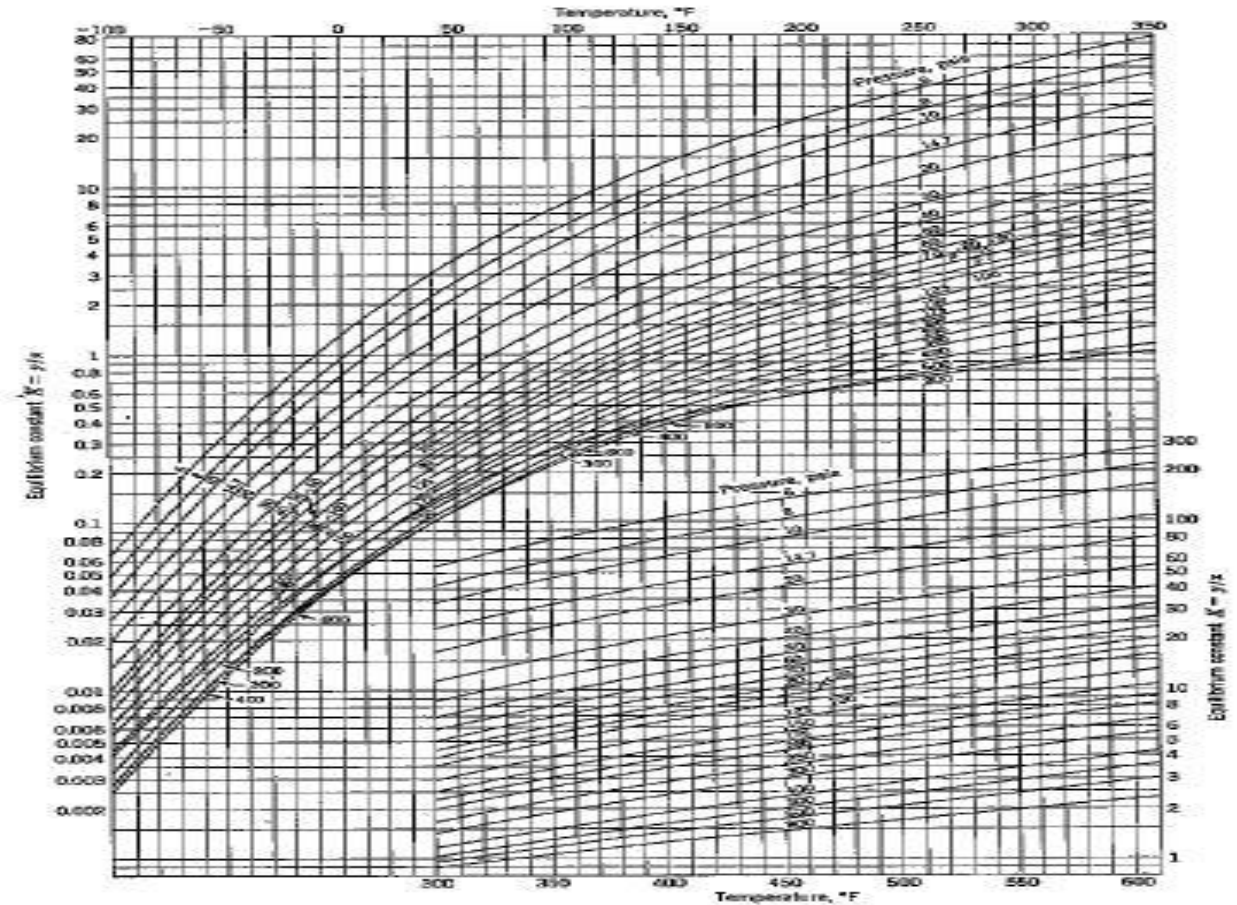


Fig. 45. Equilibrium constants for *n*-butane. (Natural Gasoline Supply Men's Association, Engineering Data Book, 1961, p. 110.)

Non-Ideal Solutions

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

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

Non-Ideal Solutions

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.

Non-Ideal Solutions

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

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

$$y_1 = K_1 x_1$$

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

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

Non-Ideal Solutions

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.

Non-Ideal Solutions

Solution:

From charts the K values can be obtained.

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

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

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

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

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

Non-Ideal Solutions

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:

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

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

Non-Ideal Solutions

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.

Non-Ideal Solutions

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
			$\Sigma x_i = 1.000$	