

FIGURE 1—Representation of Equation (2) for ethane-propane system.

# New Relative Volatility Method for Distillation Calculations

This new relation holds accurately for many systems at constant pressure even though the temperatures may vary several hundred degrees.

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THE USUAL METHOD of relating the vapor-liquid equilibrium  $K$  ratio of one component to that of another is by the equation

$$K = \alpha K' \quad (1)$$

This equation is a very simple one, but the  $\alpha$  varies considerably with temperature. An average  $\alpha$  must be used for many problems, and as a result doubts about accuracy arise.

A new equation has been found which relates the  $K$  of one component to that of another:

$$K = \beta (K')^b \quad (2)$$

where  $\beta$  and  $b$  are constants at a fixed pressure. This equation does not apply to mixtures forming azeotropes or at conditions near the critical.

The equation accurately represents the relation between isobaric  $K$ 's at ordinary conditions for many systems. A simple test of applicability is obtained by plotting  $\log K$  of one component at several temperatures against that of another component at corresponding temperatures, with pressure held constant. The relation holds if a straight line can be drawn. As an example, Figure 1 shows a plot

$K$  ethane against  $\log K$  propane from DePriesters' experimental data<sup>2</sup> at 200 psia. The  $N_2-CH_4$  data of C.C. et al.<sup>1</sup> also are well represented by the equation in the critical region. The equation can be derived from the following type vapor-pressure equation:

$$\log P = A + B/T \quad (3a)$$

$$\log P' = A' + B'/T \quad (3b)$$

On the assumption that Raoult's and Dalton's laws hold,

$$\log P/\pi + \log \pi - A = B/T \quad (4a)$$

$$\log P'/\pi + \log \pi - A' = B'/T \quad (4b)$$

Using (4a) by (4b) to eliminate temperature and substituting  $K$  for  $P/\pi$  gives.

$$\frac{\log K\pi - A}{\log K'\pi - A'} = \frac{B}{B'} = b \quad (5)$$

$$\text{from which } K = \beta (K')^b \quad (6)$$

$$\text{where } \beta = \pi^{b-1} 10^{A-bA'} \quad (7)$$

Although the constants of Equation (2) may be evaluated by means of vapor-pressure data, a more accurate representation is obtained by use of experimental  $K$  data or  $K$  correlations.

**Minimum Theoretical Trays.** Minimum trays are conventionally determined by tray-to-tray calculations, by stepping off stages on a McCabe-Thiele diagram, or by the Fenske equations.<sup>3</sup> The McCabe-Thiele method is accurate if large-scale plots are used but it requires the preparation of an x-y plot. The Fenske equations do not give reliable results if the relative volatility varies appreciably, as in the case of widely differing top and bottom temperatures.

Because Equation (2) does accurately represent  $K$  data over the temperature ranges ordinarily encountered in commercial practice, its use will yield an accurate value for minimum theoretical trays.

An equation for minimum theoretical trays can be derived by procedures similar to that used by Fenske. For the case of all vapor overhead product,

$$\frac{y_D}{x_B} = K_B K_1 K_2 \dots K_n K_D \quad (8)$$

$$\frac{y'_D}{x'_B} = K'_B K'_1 K'_2 \dots K'_n K'_D \quad (9)$$

Dividing each side of Equation (8) by the  $b$  power of Equation (9), and combining with Equation (2), one obtains

$$\beta^{n+1} = \left(\frac{y_D}{x_B}\right) \left(\frac{x'_B}{y'_D}\right)^b \quad \text{for vapor overhead product} \quad (10)$$

Similarly,

$$\beta^{n+1} = \left(\frac{x_D}{x_B}\right) \left(\frac{x'_B}{x'_D}\right)^b \quad \text{for liquid overhead product} \quad (11)$$

The relation here can be used conveniently to store  $K$  data in both digital and analog computers. . . . Potential applications of the relation include the calculation of minimum reflux and the number of equilibrium stages at finite reflux ratios.

Equations (10) and (11) may also be written in terms of product rates:

$$\beta^{n+1} = \left(\frac{V_D}{W}\right) \left(\frac{W'}{V'_D}\right)^b \left(\frac{B}{D}\right)^{1-b} \quad \text{for vapor overhead product} \quad (12)$$

$$\beta^{n+1} = \left(\frac{L_D}{W}\right) \left(\frac{W'}{L'_D}\right)^b \left(\frac{B}{D}\right)^{1-b} \quad \text{for liquid overhead product} \quad (13)$$

For the case where the overhead product is part liquid and part vapor, either Equation (10) or Equation (11) may be used, or in terms of product rates

$$\beta^{n+1} = \left(\frac{d}{w}\right) \left(\frac{w'}{d'}\right)^b \left(\frac{W}{K_D V_D + L_D}\right) \left(\frac{K' + L_D}{W'}\right)^b \quad (14)$$

Equation (14) applies for the general case. It can be reduced to Equations (10) to (13).

### Distribution of Other Than Key Components

The foregoing equations apply to any pair of components in a multicomponent system. The key components having been used to establish the number of trays, the distribution of other components at total reflux is fixed.

**Example:** The minimum number of trays necessary to deisobutanize the effluent from an alkylation reactor will be calculated. The feed, products, and vapor-liquid equilibrium constants of the key components at conditions of temperature and pressure corresponding to the top tray and reboiler are shown in Table 1. The tower has a total condenser.

The constants  $\beta$  and  $b$  are evaluated using Equation (6) as follows:

$$0.94 = \beta (0.70)^b$$

$$3.55 = \beta (3.00)^b$$

TABLE 1—Alkylation Deisobutanizer

Component	Feed, moles	Overhead, moles	Bottoms, moles	Equilibrium $K$ 's	
				Top tray	Re-boiler
Ethylene	1	1	.....	.....	.....
Ethane	2	2	.....	.....	.....
Propane	48	48	.....	.....	.....
Isobutane	863	848	15	0.94	3.55
Normal butane	132	71	61	0.70	3.00
Isopentane	33	.....	33	.....	.....
Normal pentane	5	.....	5	.....	.....
Alkylate	277	.....	277	.....	.....
	1361	970	391	.....	.....

$$3.78 = (4.29)^b$$

$$b = 0.913$$

$$\beta = 1.301$$

By use of Equation (13) the minimum number of theoretical stages is calculated as follows:

$$(1.301)^{n+1} = (848/15) (61/71)^{0.913} (391/970)^{0.087}$$

$$(1.301)^{n+1} = 45.5$$

$$n + 1 = 14.5$$

This is exactly the number of stages obtained by tray-to-tray calculations with the  $K$  correlation of Winn.<sup>4</sup> The minimum number of stages by the Fenske equation, with a geometric average  $\alpha$  of 1.261, is 16.8. The Fenske equation gives an answer which is too high by 2.3 stages, or 16 percent.

### Other Applications

**Computers:** The relation also can be used as a convenient means for storage of  $K$  data in digital and analog computers. In this application the following, more versatile, form of Equation (2) may be used:

$$K_{\pi} = \beta [f(T)]^b \quad (15)$$

$$f(T) = K'_{\pi} \quad (16)$$

where  $\beta$  and  $b$  are functions of component identities and pressure  $\pi_1$  and  $\pi_2$ . This equation also applies to many systems except in the critical region. A test of applicability is obtained by plotting at corresponding temperatures  $\log K$  of any component at constant pressure against  $\log K$  of a base component at another pressure. Figure 2 shows a plot of the nitrogen-methane data of Cines, et al.,<sup>1</sup> on this basis. It will be noted that a straight-line relation is obtained even though this system is far from being ideal.

**Finite Reflux Ratios:** Potential applications of the relation include the calculation of minimum reflux and the number of equilibrium stages at finite reflux ratios.

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### NOTATION

- $A, B$  = constants in vapor-pressure equation
- $b$  = exponent in equation (2)
- $d$  = moles of a component in overhead product
- $D$  = total moles of overhead product
- $n$  = minimum number of equilibrium trays in tower
- $K = y/x$  = vapor-liquid equilibrium ratio for a component
- $L$  = moles of a component in liquid phase
- $P$  = vapor pressure, psia
- $T$  = absolute temperature, °R
- $V$  = moles of a component in vapor phase
- $w$  = moles of a component in bottoms product
- $W$  = total moles of bottom product
- $x$  = mole fraction of a component in liquid phase
- $y$  = mole fraction of a component in vapor phase
- $\alpha$  = relative volatility
- $\beta$  = constant in Equation (2)
- $\pi$  = total pressure, psia
- $L$  = total moles in liquid phase
- $V$  = total moles in vapor phase

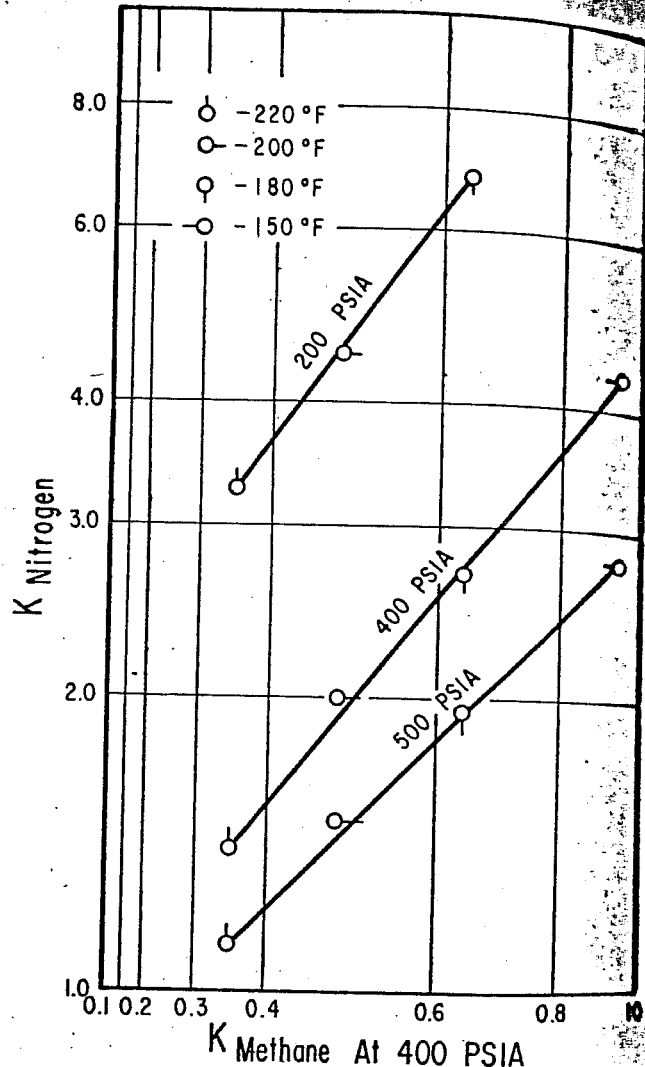


FIGURE 2—Representation of Equation (15) for the nitrogen-methane system.

### SUBSCRIPTS AND SUPERSSCRIPTS

- $D$  = distillate
- $B$  = bottoms
- 1, 2 . . . = tray number
- (\*) heavy key component

### LITERATURE CITED

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### About the Author

Francis W. Winn is technical director in charge of research for Fractionation Research Inc., Alhambra, Calif. A chemical engineering graduate from the University of Oklahoma, he joined the company in 1951, following an assignment as assistant chief engineer with Catalytic Construction Corp. He also has been associated with a number of major oil companies and once served with the Petroleum Administration for War. In past years Winn has contributed many excellent articles to *PETROLEUM REFINER*.



