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## NOTATION

$A_n$ = dimensional constants
$A$ = cross-sectional area
$C_n$ = dimensionless constants, Table 1
$D_h$ = hydraulic diameter, $4\ A/P$
$f$ = friction factor, $2\bar{\tau}/\rho\bar{u}^2$
$I_n$ = integrals, Equation (12*a*) and Table 2
$k$ = summation index
$n$ = summation index
$N$ = inward-drawn normal
$N_{Re}$ = Reynolds number, $\bar{u}\ D_h/\nu$
$p$ = static pressure
$P$ = perimeter
$R$ = radius of circular sector
$r$ = radial coordinate
$s$ = height of isosceles duct
$u$ = axial velocity
$\bar{u}$ = average axial velocity
$x$ = axial coordinate
$w$ = mass rate of flow

### Greek Letters

$\alpha$ = half opening angle of duct
$\theta$ = angular coordinate
$\mu$ = absolute viscosity
$\nu$ = kinematic viscosity
$\rho$ = density
$\tau$ = local wall shear stress
$\bar{\tau}$ = average wall shear stress

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# The Prediction of Vapor-Liquid Equilibrium Constants for Binary Hydrocarbon Systems in the Critical Region

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**A series of reduced state correlations for the prediction of equilibrium constants for the components of binary hydrocarbon systems have been developed utilizing experimental vapor-liquid equilibrium data reported by Kay (*7, 8, 9*) for the enthane-*n*-heptane, ethane-*n*-butane, and *n*-butane-*n*-heptane systems. Each correlation applies for a specific value of $\tau = T_{bh}/T_{b1}$, the ratio of the normal boiling points of the two components. Plots of $\beta/\beta^\circ$ vs. $T_R$ covering the complete *range of liquid compositions are presented for values of* $\tau$ *= 1.10, 1.20, 1.40, 1.60, 1.80, and 2.00.* The term $\beta^\circ$ represents the reduced vapor pressure of the pure substance, while $\beta$ is the ratio *of the pseudo vapor pressure of this substance in the mixture,* $K\pi$, to the critical pressure of the mixture.**

**The correlations presented *in this study* reproduce the *experimental data* used in their development with an average deviation of 2.3% for forty-eight points, with the experimental critical constants reported *by Kay. The reliability of these correlations has been tested with the propane*-isopentane, methane-ethane, and ethane-cyclohexane systems which have $\tau$ values in the range *included in this study and for which experimental critical constants are available. An average de*viation of 5.1% was produced for thirty-six points. In addition the systems methane-propane, propane-benzene, nitrogen-oxygen, and carbon dioxide-*n*-butane were tested with calculated values for their critical constants and produced average deviations of 8.4, 8.2, 9.4, and 20%, respectively.**

The concept of the vapor-liquid equilibrium constant as the ratio of vapor and liquid compositions at equilibrium $K = y/x$ was introduced in 1932 by Souders, Selheimer, and Brown (*19*). If both phases behave as ideal solutions, and the vapor is an ideal gas, the equilibrium constant is equal to the ratio of the vapor pressure of the pure component to the total pressure of the system $K = P^\circ/\pi$.

At elevated pressures the vapor is no longer an ideal gas. When one assumes continued ideal solution behavior for both phases, the equilibrium constant can be expressed as the ratio of the fugacities of the pure component in the vapor and liquid phases $K = f_l^\circ/f_v$. In order to obtain the fugacity of the light component in the liquid phase it becomes necessary to extrapolate the vapor pressure of the pure component past its critical temperature. On the other hand the fugacity of the heavy component in the vapor phase can not be obtained ordinarily at pressures greater than its vapor pressure.

Various methods are presented in the literature for the estimation of equilibrium constants, particularly for hydrocarbon systems. Of notable interest are the methods presented by Gamson and Watson (*4*), Smith and Watson (*20*), Organick and Brown (*16*), Prausnitz, Edmister, and Chao (*17*), and the M. W. Kellogg Com-

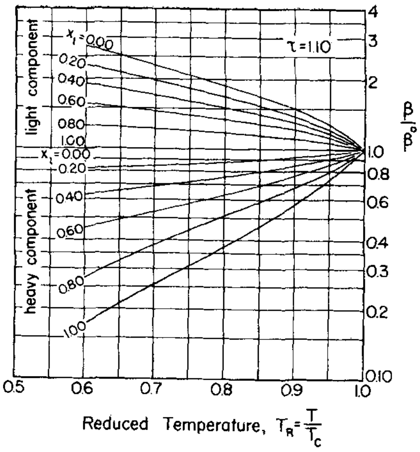

**Fig. 1. Reduced state correlation of $\beta/\beta^{\circ}$ vs. $T_R$ ($\tau = 1.10$).**

pany (*11, 12*). The Gamson-Watson and Smith-Watson methods utilize the pseudo reduced temperature and pressure of both phases in order to obtain activity coefficients. The Organick-Brown method is based on methane binary systems and utilizes as parameters the average molar boiling point of the vapor phase, the equivalent molecular weight of the liquid, and the liquid composition. Prausnitz, Edmister, and Chao (*17*) introduce the solubility parameter concept to calculate vapor-liquid equilibrium constants for hydrocarbons. The Kellogg charts (*11, 12*) are used to obtain fugacities resulting from the Benedict-Webb-Rubin equation of state, and the equilibrium constants are calculated with the average molar boiling points of both phases.

Although these are the most reliable methods available for the estimation of equilibrium constants, the accuracy of the values is uncertain at elevated pressures, particularly in the vicinity of the critical point of the mixture. These deviations justify a re-examination of this area with an approach which differs fundamentally from existing methods for the development of correlations from available experimental data.

## REDUCED STATE CORRELATIONS

The vapor pressure of a component of a mixture which exhibits ideal behavior can be expressed as $P^{\circ} = K\pi$. For a nonideal mixture the product $K\pi$ will be defined as the *pseudo vapor pressure* of a component. As the mole fraction of either of the components of this mixture approaches unity, its pseudo vapor pressure becomes identical to its vapor pressure. The pseudo vapor pressure takes into account both the nonideal gas behavior and the nonideal solution behavior of the mixture and depends only on temperature and composition. To determine pseudo-vapor pressures experimental values of the equilibrium constants are required.

The vapor-liquid equilibrium data presented by W. B. Kay (*7, 8, 9*) for the binary systems ethane–*n*-heptane, ethane–*n*-butane, and *n*-butane–*n*-heptane constitute the experimental information utilized in this study. Values of the equilibrium constants of each mixture were calculated from the data for pressures from 100 lb./sq.in.abs. up to the critical point. The corresponding pseudo vapor pressures were then calculated. For each system the ratio $\beta/\beta^{\circ}$ was plotted vs. $T_R$, the reduced temperature of the mixture for varying liquid compositions $x_l$. The term $\beta$ represents the ratio of the pseudo vapor pressure to the critical pressure of the mixture $\beta = K\pi/P_c$, while $\beta^{\circ}$ is the reduced vapor pressure of the component in its pure state, at the same reduced temperature as that of the mixture $\beta^{\circ} = P^{\circ}/P_c$. The information supplied by these plots for the three systems was utilized to prepare reduced state correlations of $\beta/\beta^{\circ}$ vs. $T_R$ with liquid composition as a parameter for different values of $\tau$, the ratio of the normal boiling points of the two components $\tau = T_{bh}/T_{bl}$. For the systems included in this study the following information was used:

| | $T_{bl}$, °K | $T_{bh}$, °K | $\tau$ |
|---|---|---|---|
| *n*-Butane–*n*-heptane | 272.7 | 371.6 | 1.36 |
| Ethane–*n*-butane | 184.5 | 272.7 | 1.48 |
| Ethane–*n*-heptane | 184.5 | 371.6 | 2.02 |

The correlations are presented in Figures 1 to 6 for $\tau$ = 1.10, 1.20, 1.40, 1.60, 1.80, and 2.00. The curves of these figures converge to the critical point of the mixture, $\beta/\beta^{\circ} = 1$ and $T_R = 1$.

In the correlation of the three systems reported by Kay it was found that the curves for $\beta/\beta^{\circ}$ greater than 1 apply to the light component of the mixture, while the other curves are for the heavy component. Thus in the system ethane–*n*-butane the values of $\beta/\beta^{\circ}$ less than 1 apply to *n*-butane, but in the system *n*-butane–*n*-heptane the values of $\beta/\beta^{\circ}$ for *n*-butane are greater than 1. Therefore in using these correlations the curves for $\beta/\beta^{\circ}$ greater than 1 should be used for the light component.

## APPLICATION OF METHOD

In order to use Figures 1 to 6 it becomes necessary to obtain first the critical temperature and the critical pressure of the binary system. Several methods have been reported in the literature for the estimation of critical temperatures and pressures of hydrocarbon systems (*3, 6, 13, 14, 16*), the most recent being that of Grieves and Thodos (*6*). This method introduces two dimensionless temperature parameters which account for the composition of the mixture and the nature of the components involved. These parameters are defined from the molar average boiling point, the boiling point, and the dew point, all calculated at atmospheric pressure. Relationship are presented graphically and permit the direct calculation of the critical temperature and critical pressure of the mixture from their corresponding pseudo critical temperatures and pressures and the dimensionless temperature parameters.

Once the critical temperatures and pressures are established, the equilibrium constants of the light and heavy components of the binary mixture are readily calculated from Figures 1 to 6 for systems having values of $\tau$ = 2.0. In order to expedite such calculations it is convenient to use a reduced vapor-pressure plot. The procedure adopted for the calculation of equilibrium constants is illustrated through the following example:

### Example

For the propane-isopentane system containing 0.204 mole fraction of propane in the liquid phase, calculate values of the equilibrium constants of the components, at 443°K. (797°R.) and 37 atm. (544 lb./sq.in.abs. using the following data:

| | $T_b$,°R. | $T_c$,°R. | $P_c$, lb./sq.in.abs. |
|---|---|---|---|
| Propane | 416 | 666 | 617 |
| Isopentane | 542 | 830 | 484 |

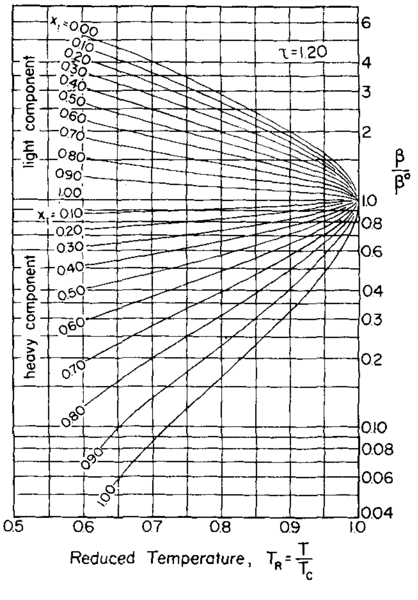

**Fig. 2. Reduced state correlation of $\beta/\beta^{\circ}$ vs. $T_R$ ($\tau = 1.20$).**

*Calculation of Critical Temperature and Pressure of Mixture.* The boiling point of the mixture at atmospheric pressure is calculated from the relationship $P_3 x_3 + P_5 x_5 = 14.7$, where $P_3$ and $P_5$ represent the vapor pressures of propane and isopentane, respectively. By trial-and-error, using vapor pressure data one can find $T_b$ to be 480°R.

The dew point of the mixture at atmospheric pressure is calculated from the relationship $y_3/P_3 + y_5/P_5 = 1/14.7$. Again, by trial-and-error, the vapor pressures at $T_d$ = 541°R. satisfy this condition.

The pseudocritical temperature, the pseudocritical pressure, and the pseudonormal boiling point for this mixture are calculated as follows:

$$T_c' = 666\ (0.204) + 830\ (0.796) = 797°\text{R.}$$

$$P_c' = 617\ (0.204) + 484\ (0.796) = 511\ \text{lb./sq.in.abs.}$$

$$T_b' = 416\ (0.204) + 542\ (0.796) = 515°\text{R.}$$

When one uses the method of Grieves and Thodos (*6*), from these values, the dimensionless temperature parameters $\gamma$ and $\vartheta$ are calculated to be:

$$\gamma = \frac{T_d}{T_b} = \frac{541}{480} = 1.13$$

and

$$\vartheta = \frac{T_b' - T_b}{T_d - T_b} = \frac{515 - 480}{541 - 480} = 0.574$$

These temperature parameters produce values of $T_c/T_c'$ = 1.018 and $P_c/P_c'$ = 1.115. Therefore for this mixture $T_c$ = 1.018 × 797 = 811°R. (450°K.) and $P_c$ = 1.115 × 511 = 570 lb./sq.in.abs. (38.8 atm.). Vaughan and Collins (*21*) report critical constants for this mixture of $T_c$ = 448°K. and $P_c$ = 38.3 atm.

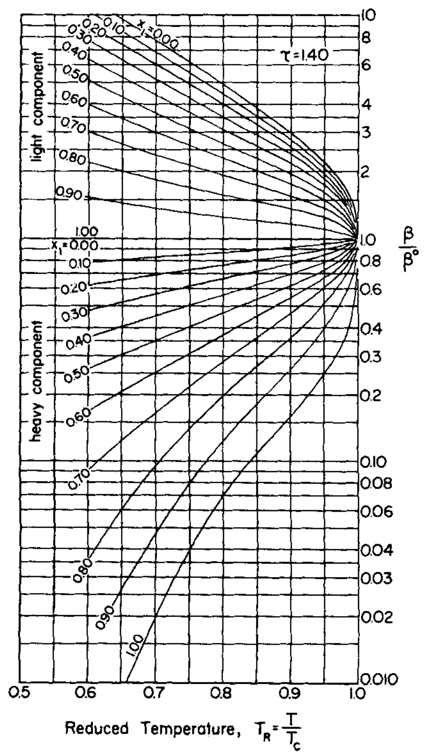

**Fig. 3. Reduced state correlation of $\beta/\beta^\circ$ vs. $T_R$ ($\tau$ = 1.40).**

*Calculation of $\tau$ and $T_R$ of Mixture.*

$$\tau = \frac{T_{bh}}{T_{bl}} = \frac{542}{416} = 1.30$$

$$T_R = \frac{797}{811} = 0.983$$

As already mentioned this reduced temperature applies to both components in their pure state.

*Calculation of Equilibrium Constants.* From a plot of log $P_R$ vs. $1/T_R$ the reduced vapor pressures of propane and isopentane were obtained to be 0.897 and 0.890, respectively.

Light component (propane)

$$\beta^\circ = 0.897$$

$$\beta/\beta^\circ = 1.32\ \text{(Figures 2 and 3)}$$

$$\beta = \frac{K_3 \pi}{P_c} = 1.184$$

$$K_3 = 1.184 \times \frac{570}{544} = 1.241$$

Heavy component (isopentane)

$$\beta^\circ = 0.890$$

$$\beta/\beta^\circ = 0.97$$

$$\beta = \frac{K_5 \pi}{P_c} = 0.863$$

$$K_5 = 0.863 \times \frac{570}{544} = 0.904$$

For these conditions Vaughan and Collins (*21*) report equilibrium constants of $K_3$ = 1.282 and $K_5$ = 0.928.

## CONCLUSIONS

The correlations in Figures 1 to 6 reproduce the experimental data used in their development with an average deviation of 2.3% for forty-eight points with the experimental critical constants reported by Kay (*7, 8, 9*). The validity of these correlations has also been tested on three other systems which have values of $\tau < 2.0$ and for which experimental critical constants are available. These systems and their average deviation are:

| System | Source | $\tau$ | Points | Average deviation, % |
|---|---|---|---|---|
| Propane-isopentane | (*21*) | 1.30 | 8 | 3.55 |
| Methane-ethane | ( *1*) | 1.66 | 14 | 5.65 |
| Ethane-cyclohexane | (*10*) | 1.92 | 14 | 5.32 |

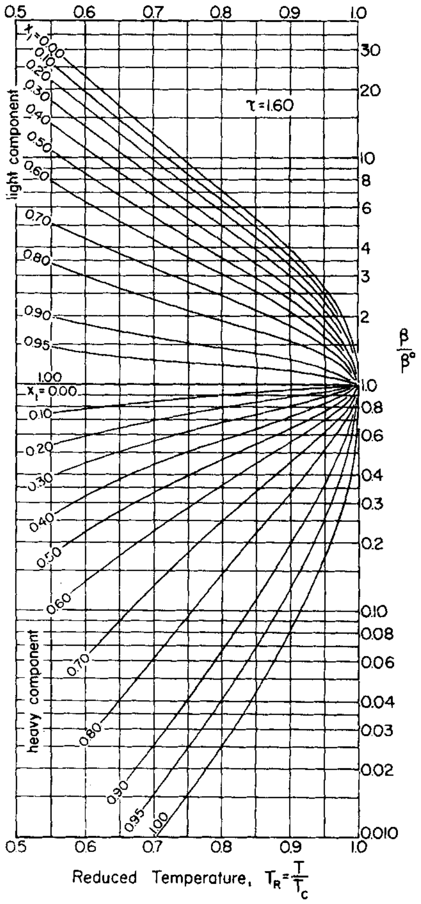

**Fig. 4. Reduced state correlation of $\beta/\beta^\circ$ vs. $T_R$ ($\tau$ = 1.60).**

An overall average deviation of 5.1% resulted for thirty-six experimental points for these three systems.

Four additional systems were tested with calculated values of their critical constants. These systems were of varying complexity and included some nonhydrocarbon components. The results for these systems were:

| System | Source | $\tau$ | Points | Average deviation, % |
|---|---|---|---|---|
| Methane-propane | (*18*) | 2.07 | 16 | 8.4 |
| Propane-benzene | ( *5*) | 1.53 | 16 | 8.2 |
| Nitrogen-oxygen | ( *2*) | 1.17 | 22 | 9.4 |
| Carbon dioxide—*n*-butane | (*15*) | 1.48 | 16 | 20.3 |

Although this method has been restricted to binary hydrocarbon systems, the results of the comparisons indicate

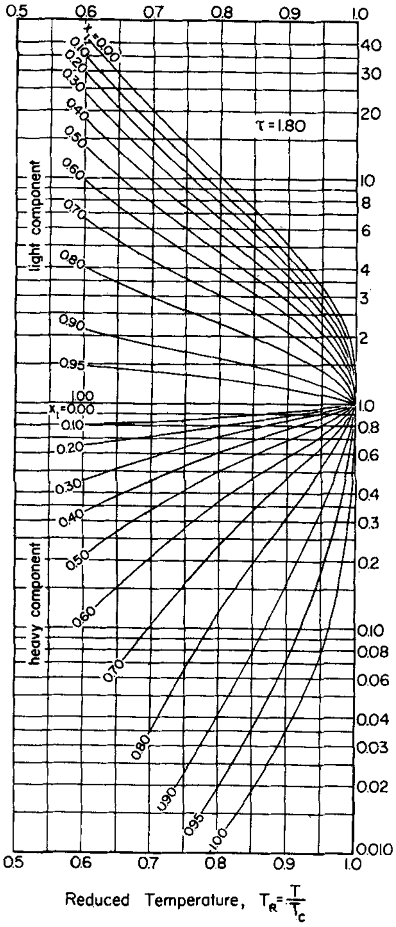

**Fig. 5. Reduced state correlation of $\beta/\beta^\circ$ vs. $T_R$ ($\tau = 1.80$).**

that this approach can be extended to nonhydrocarbon systems whose components are chemically simple and similar in nature. Thus the nitrogen-oxygen system produces an average deviation similar to those of the methane-propane and propane-benzene systems, but the carbon dioxide–*n*-butane system shows a considerably greater deviation using this approach.

The approach presented in this study differs from other existing methods aiming to produce $K$ values in the critical region. This method is relatively simple, directly applicable, and readily enables the calculation of $K$ values. Through the application of this method difficulties are eliminated by avoiding extrapolation of vapor-pressure curves required for the calculation of fugacities. The present study should not be considered as limited, but rather as the beginning of this type of approach which is capable of reproducing closely experimental $K$ values for binary systems.

## NOTATION

$f^\circ_l$ = fugacity of pure component in liquid phase
$f^\circ_v$ = fugacity of pure component in vapor phase

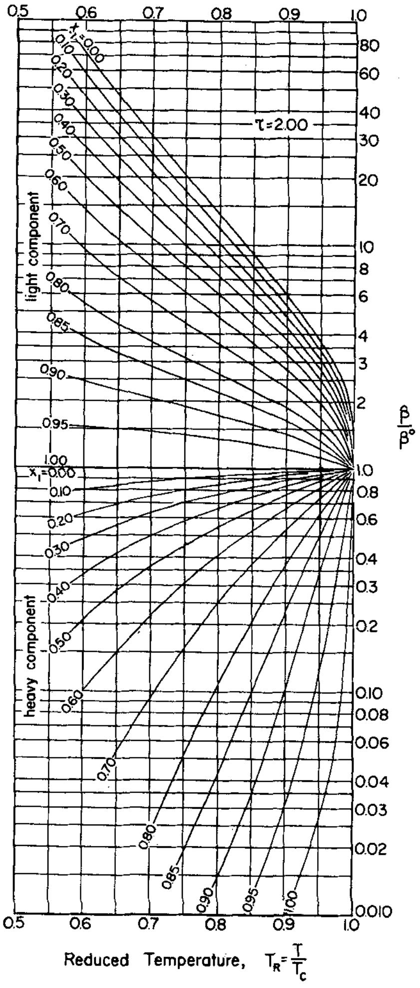

**Fig. 6. Reduced state correlation of $\beta/\beta^\circ$ vs. $T_R$ ($\tau = 2.00$).**

$K$ = vapor-liquid equilibrium constant, $y/x$
$P^\circ$ = vapor pressure of pure component
$P_c$ = critical pressure of mixture
$P_c'$ = pseudocritical pressure of mixture
$P^\circ_c$ = critical pressure of pure component
$t$ = temperature of system, °F.
$t_c$ = critical temperature of mixture, °F.
$T$ = absolute temperature of system, deg. abs.
$T_b$ = normal boiling point of mixture, deg. abs.
$T_b'$ = pseudonormal boiling point of mixture, deg. abs.
$T_{bh}$ = normal boiling point of heavy component, deg. abs.
$T_{bl}$ = normal boiling point of light component, deg. abs.
$T_c$ = critical temperature of mixture, deg. abs.
$T_c'$ = pseudocritical temperature of mixture, deg. abs.
$T_d$ = dew point of mixture at atmospheric pressure, deg. abs.
$T_R$ = reduced temperature, $T/T_c$
$x$ = liquid composition, mole fraction
$x_l$ = composition of light component in liquid phase, mole fraction
$y$ = vapor composition, mole fraction

### Greek Letters

$\beta$ = reduced pseudo vapor pressure, $K\pi/P_c$
$\beta^\circ$ = reduced vapor pressure, $P^\circ/P^\circ_c$
$\gamma$ = temperature parameter, $T_d/T_b$
$\vartheta$ = temperature parameter $(T'_b - T_b)/(T_d - T_b)$
$\pi$ = total pressure of system
$\tau$ = normal boiling point ratio of system, $T_{bh}/T_{bl}$

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