Vapor-Liquid Equilibrium Constants of Binary Methane Systems for the Sub-Critical, Critical, and Retrograde Regions

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Several methods are presented in the literature for the prediction of vapor-liquid equilibrium constants of mixtures (*1, 5, 11, 12, 13, 15, 19, 20*) from thermodynamic relationships. Although these methods are valuable, they can be used only for the determination of vapor-liquid equilibrium constants for moderate pressure conditions. Significant deviations result between calculated and experimental values at elevated pressures, particularly for conditions near the critical point.

For a mixture in which the vapor phase behaves as an ideal gas and the liquid phase as an ideal solution, the vapor-liquid equilibrium constant can be expressed as $K = y/x = p^o/\pi$. To account for the effect of pressure on K in a real mixture, Mehra and Thodos (*14*) have introduced the pseudo-vapor pressure of a component, $K\pi$, and have normalized this quantity with the actual critical pressure of the mixture to obtain the reduced pseudo-vapor pressure, $\beta = K\pi/P_c$. For a component in its pure state, this ratio is $\beta^o = P^o/P^o_c$, the reduced vapor pressure of the substance at the reduced temperature of the mixture.

Mehra and Thodos (*14*) utilized the binary systems, ethane—n-butane, n-butane—n-heptane, and ethane—n-heptane, to develop a series of charts which relate the ratio β/β^o to the reduced temperature of the system with composition as a parameter for different values of the ratio of the normal boiling points of the two components

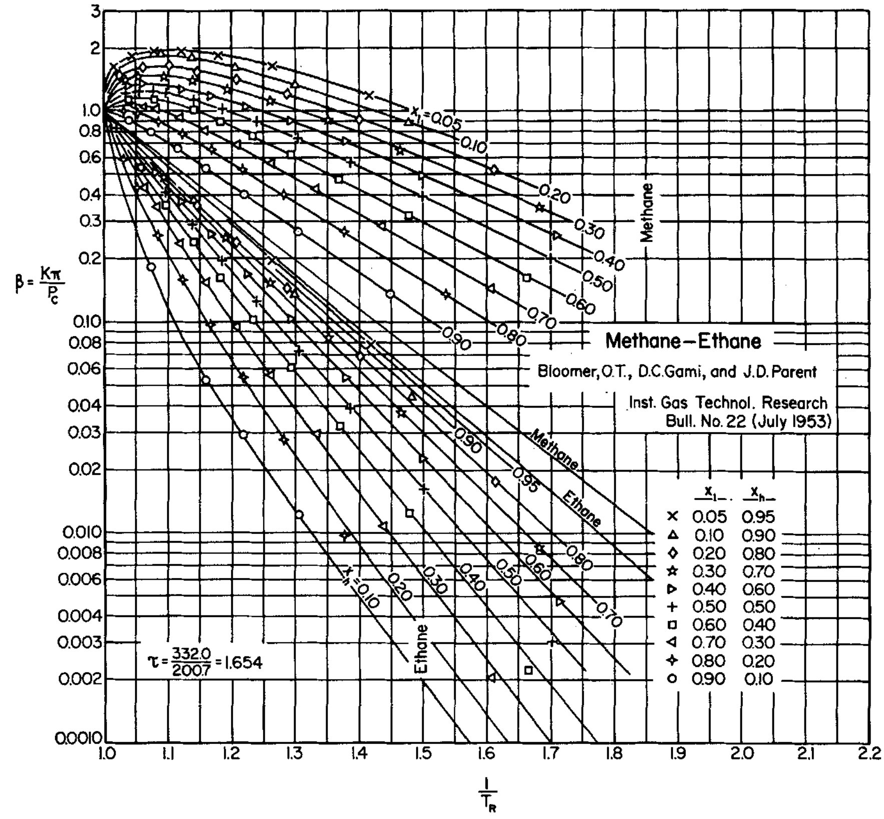

Fig. 1. Relationships between β and $\frac{1}{T_R}$ for the methane-ethane system which exhibits normal behavior.

of the mixture, $\tau = T_{bh}/T_{bl}$. The resulting correlations covered the range $1.00 < \tau < 2.00$ and were found to be applicable to other binary systems.

Because of the industrial importance of binary systems containing methane, the approach utilized by Mehra and Thodos (*14*) has been employed in the present study to develop specific correlations for the prediction of vapor-liquid equilibrium constants for these systems, many of which have values of $\tau > 2.00$. Experimental vapor-liquid equilibrium data for the following systems were utilized in this study:

	τ
Nitrogen—methane (*3*)	1.441
Methane—ethane (*2*)	1.654
Methane—propane (*16*)	2.073
Methane—n-butane (*17*)	2.445
Methane—n-pentane (*18*)	2.773

The nitrogen-methane system was arbitrarily considered because it includes a nonhydrocarbon constituent. It should be noted that in this system methane is the heavy component, whereas in each of the remaining systems it is the light component. The selection of these five systems has permitted the present study to include the range $1.00 < \tau < 2.80$.

CHARACTERISTICS OF SYSTEMS INVESTIGATED

The procedure for the development of the correlations from the experimental data has been presented by Mehra and Thodos (*14*). Values of β for each system were first plotted against $1/T_R$. The relationships obtained for a typical mixture are presented in Figure 1 for the methane-ethane system, $\tau = 1.654$. The general behavior of the β vs. $1/T_R$ relationships for the light component followed a regular pattern below the critical point for all of the five systems investigated as τ increased from a value of 1.441 for the nitrogen-methane system to a value of 2.773 for the methane-n-pentane system. On the other hand, the general trend of the β vs. $1/T_R$ relationships below the critical point for the heavy component was found to approach the reduced vapor pressure curve of the pure component with increasing τ values. For the methane—n-butane system, these relationships for all compositions became essentially coincident to the reduced vapor pressure curve of n-butane; whereas for the methane—n-pentane system they were found to overlap above the reduced vapor pressure curve of n-pentane.

The significant retrograde effects encountered with the methane—n-butane and methane—n-pentane systems were reflected in the presence of β vs. $1/T_R$ relationships for conditions above the critical point of each mixture. These effects were most pronounced for the methane—n-pentane system (Figure 2). These relationships are extensions of the curves for the region below the critical point. It can be seen from Figure 2 that, at the critical point of a system exhibiting retrograde effects, a transition occurs in which the light component becomes the heavy component and the heavy the light for conditions above the critical point. For the two systems which exhibit marked retrograde effects the β vs. $1/T_R$ relationships for the heavy component exhibit curvatures opposite to those encountered for the heavy component of the other systems. This can be seen by a comparison of Figures 1 and 2.

The results of this study indicate that, if the β vs. $1/T_R$ relationships for the heavy component of a binary mixture approach or overlap the corresponding reduced vapor pressure curve of the pure component, the system exhibits significant retrograde effects The retrograde phenomena encountered in this study were found to be insignificant for the systems investigated by Mehra and Thodos (*14*).

FINAL CORRELATIONS

The relationships of β vs. $1/T_R$ for the five systems investigated were cross plotted to produce the final cor-

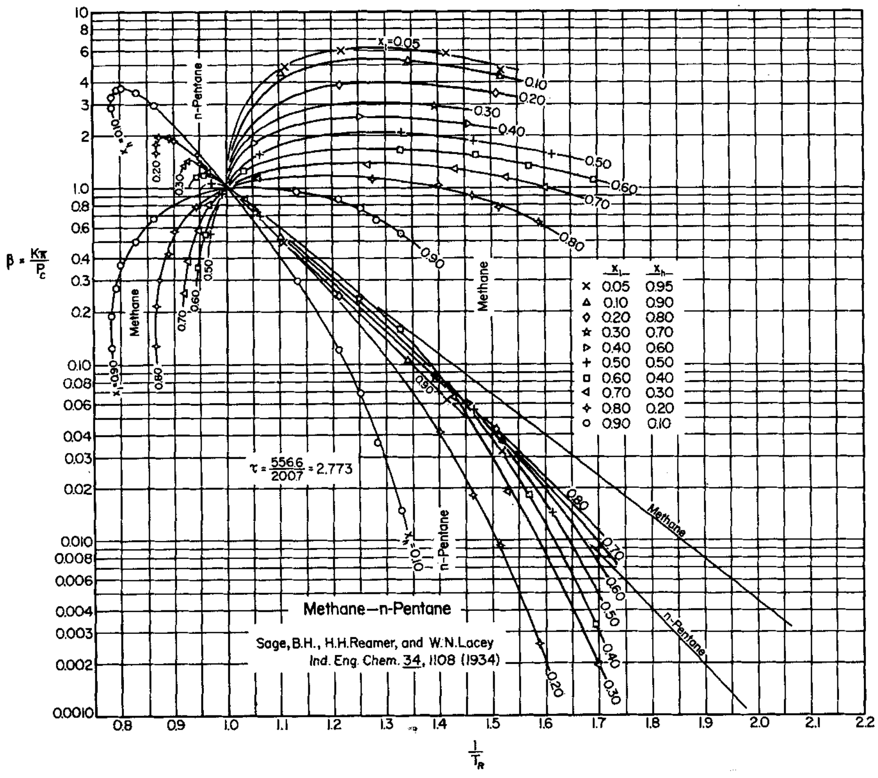

Fig. 2. Relationships between β and $\frac{1}{T_R}$ for the ethane-n-pentane system which exhibits abnormal behavior due to pronounced retrograde phenomena.

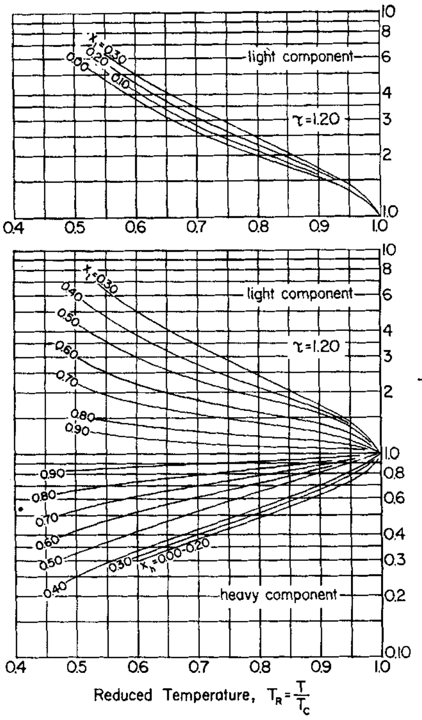

Fig. 3. Reduced state correlation of β/β° vs. T_R ($\tau = 1.20$).

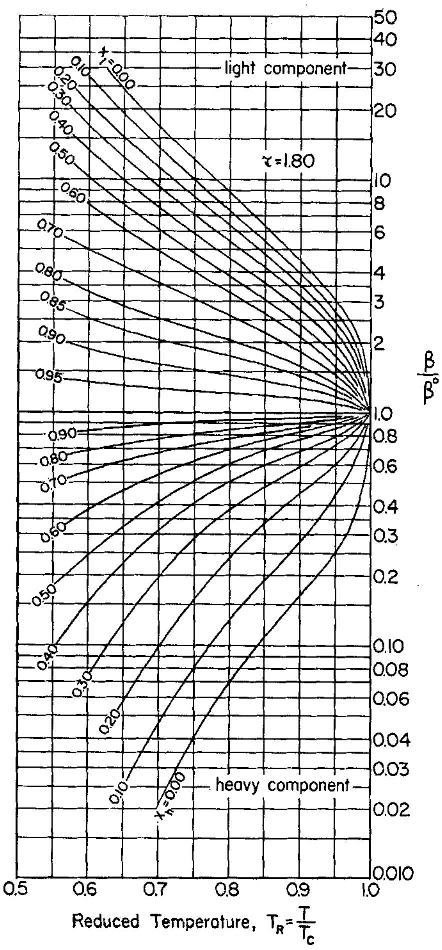

Fig. 4. Reduced state correlation of β/β° vs. T_R ($\tau = 1.80$).

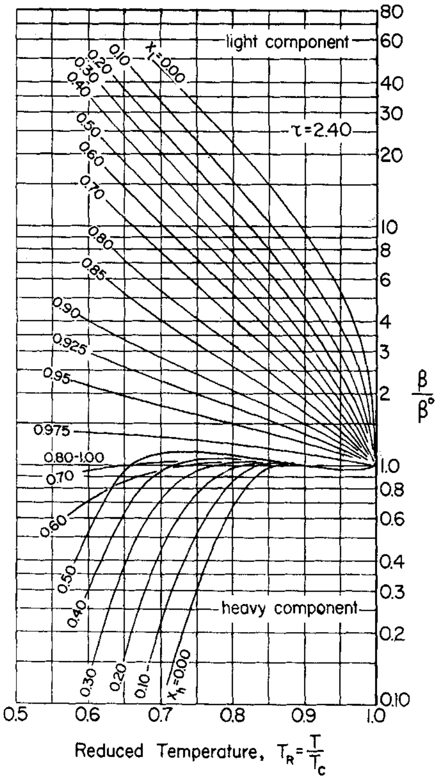

Fig. 5. Reduced state correlation of β/β° vs. T_R ($\tau = 2.40$).

relations of β/β^o against T_R for parameters of composition, x_l and x_h, and for τ values of 1.10, 1.20, 1.40, 1.60, 1.80, 2.00, 2.20, 2.40, 2.60, and 2.80. In Figures 3 to 6 the resulting plots of τ values of 1.20, 1.80, 2.40, and 2.80 are presented.[*] From these figures, values of β/β^o for any value of τ up to 2.80 can be obtained by interpolation. The procedure for the calculation of vapor-liquid equilibrium constants from this information is similar to that presented previously (*14*).

It can be seen from Figures 3 to 6 that the constant composition lines for the light component spread out continuously from the reference line, $\beta/\beta^o = 1.0$. The same type of behavior is exhibited for the heavy component for values of τ up to 1.80. In the range $2.00 < \tau < 2.80$, a progressive trend exists that tends to distort the general pattern until these lines become concave downward and eventually overlap the reference line, $\beta/\beta^o = 1.0$. These results indicate that β/β^o for the heavy component can become greater than one. The retrograde region is represented for both the light and heavy components by the extensions of the β/β^o vs. T_R curves above the critical point.

RESULTS AND CONCLUSIONS

To test the accuracy of these correlations, K values were calculated for the conditions of the experimental data used in this study. An average deviation of 2.33% resulted for 340 points considered indicating that for these five systems good agreement exists between the calculated and reported K values. To test the extension of the correlations of this study to other substances, K values were calculated for five additional systems and compared with experimental values reported in the literature. In the absence of experimental critical values, the method of Grieves and Thodos (*6*) can be used to estimate the critical temperatures and critical pressures of binary mixtures. Equilibrium constants were also calculated for these systems and the methane—ethane and methane—propane systems from the correlations developed by Mehra and Thodos (*14*). The results of these comparisons are summarized as follows:

		Mehra and Thodos (*14*)		Present study	
	τ	Points	Dev. %	Points	Dev. %
Methane—ethane (*2*)	1.654	14	5.65	82	2.29
Methane—propane (*16*)	2.073	16	8.40	48	2.56
n-butane—n-heptane (*9*)	1.363	12	3.10	30	6.42
Ethane—n-butane (*8*)	1.478	24	1.90	34	5.67
Ethane—n-heptane (*7*)	2.014	12	2.36	20	10.11
Nitrogen—oxygen (*4*)	1.166	22	9.40	22	6.63
Ethylene—n-heptane (*10*)	2.193			32	19.5

For the five nonmethane systems an average deviation of 9.83% was obtained for 138 points considered. The larger deviation resulting for the ethylene—n-heptane system may be owing to the fact that considerable distortion of the β/β^o vs T_R relationships exists for the heavy component in the region $2.00 < \tau < 2.80$.

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[*] Additional figures have been deposited as document with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or $1.25 for 35-mm. microfilm.

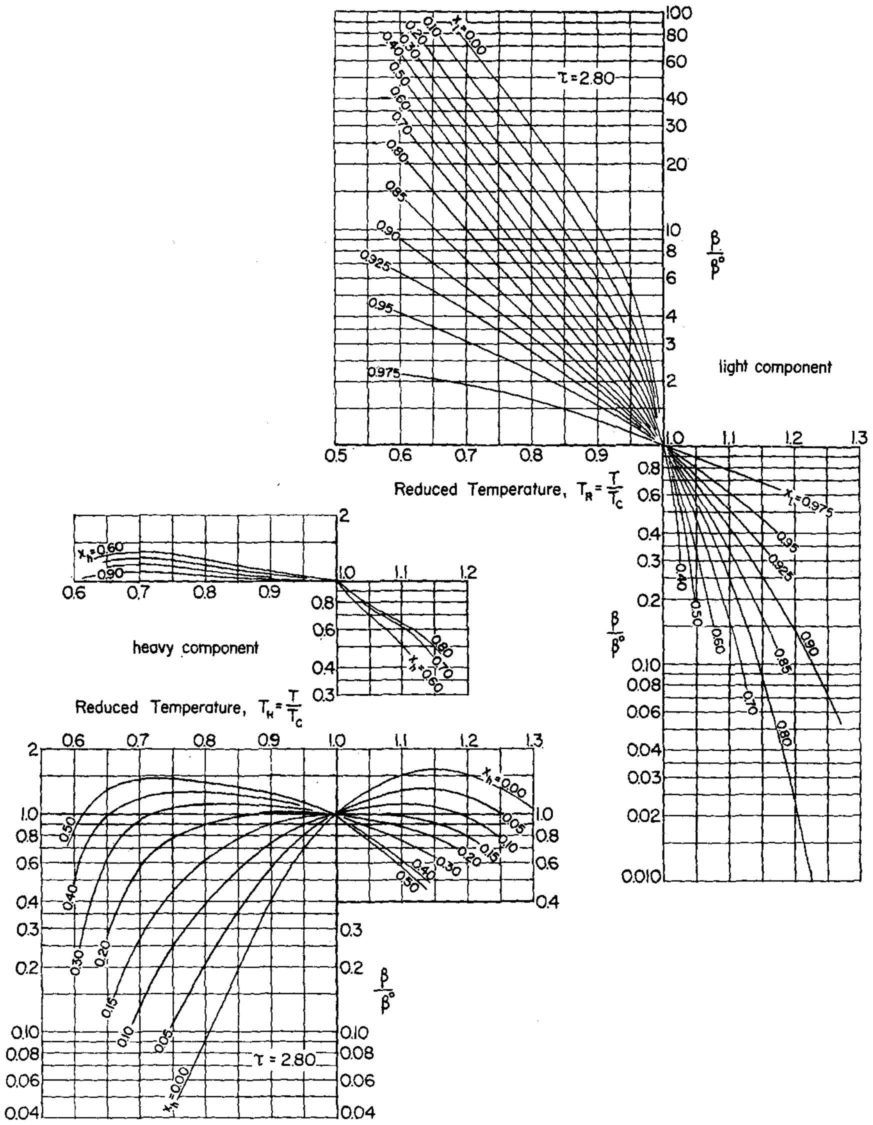

Fig. 6. Reduced state correlation of β/β° vs. T_R (τ = 2.80).

The comparisons indicated that for methane-containing systems better accuracy is obtained from the present study. For the methane-free binary hydrocarbon systems, the correlations of Mehra and Thodos (*14*) produce smaller deviations. For the nitrogen-oxygen system better agreement between calculated and experimental values was obtained with the correlations of the present study. Vapor-liquid equilibrium constants for the ethylene—n-heptane system could not be calculated from the study of Mehra and Thodos (*14*), since for this system $\tau > 2.00$.

Vapor-liquid equilibrium constants calculated for the retrograde region of those systems which exhibit this phenomenon were found to be in good agreement with the corresponding values resulting from the experimental data. Therefore, the approach utilized in the present study can be used to estimate vapor-liquid equilibrium constants for the relatively unexplored retrograde regions of multicomponent systems.

ACKNOWLEDGMENT

A grant from the National Science Foundation (NSF-G14243) supported this project.

NOTATION

K = vapor-liquid equilibrium constant, y/x
P = pressure of the mixture, lb./sq.in.abs.
P^o = vapor pressure of pure component, lb./sq.in.abs.
P_c = critical pressure of mixture, lb./sq.in.abs.
P^o_c = critical pressure of pure component, lb./sq.in.abs.
T = absolute temperature of mixture, °R.
T_{bh} = normal boiling point of heavy component, °R.
T_{bl} = normal boiling point of light component, °R.
T_c = critical temperature of mixture, °R.
T_R = reduced temperature of mixture, T/T_c
x = liquid composition, mole fraction
x_l = liquid composition of light component, mole fraction
x_h = liquid composition of heavy component, mole fraction
y = vapor composition, mole fraction
β = reduced pseudo-vapor pressure, $K\pi/P_c$
β^o = reduced vapor pressure of pure component, P^o/P^o_c
π = total pressure of system, lb./sq.in.abs.
τ = normal boiling point ratio, T_{bh}/T_{bl}

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Forced Convection in Three-Dimensional Flows: I. Asymptotic Solutions for Fixed Interfaces

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In geometrically complicated flows it is seldom feasible to solve the energy or diffusion equation exactly. However, in laminar flows with a sufficiently high Prandtl or Schmidt number, the thermal or diffusional effects become localized in thin boundary layers and can be predicted analytically in some detail. Lighthill (*1*), Levich (*2*), and Acrivos (*3, 4*) have given solutions of this type for systems of arbitrary two-dimensional or axially symmetric form. Here the same basic technique is extended to three-dimensional systems with any number of interfaces. The results may be used either for prediction of transfer behavior a priori, or as guides in correlation of experimental data.

The present treatment is for fixed interfaces, but can also be applied to moving ones under certain conditions. Thus, rigid-body translation and rotation of any interface can be handled without modification of the formulae if the boundary layer is at steady state when viewed from the moving interface. More general types of surface motion will be considered in a subsequent paper.

Only steady, laminar flows are considered here. No attempt is made to treat the flow in a laminar sublayer of a turbulent stream; sublayers exhibit a fluctuating motion to which the present analysis does not apply.

The main assumptions in the present treatment are as follows:

1. The heat-conduction and diffusion fluxes in the fluid are assumed to be directed along the normal to the neighboring interface; the flux components parallel to the interface are neglected.