Convergence Pressures for Close-boiling Nonideal Systems

J. M. LENOIR

C. F. Braun and Company, Alhambra, California

The unconventional behavior of equilibrium ratios and convergence pressures is illustrated for close-boiling systems with activity coefficients exceeding 1 throughout the two-phase region. Also presented is a correlation to predict convergence pressure, or the critical locus, of nonideal binary systems.

The behavior and correlation of convergence pressure for hydrocarbon mixtures (*1, 7, 15*) and the relation of equilibrium-ratios to convergence pressure have been presented in several articles (*9, 10, 13, 15*). Such methods do not apply to narrow-boiling mixtures that are nonideal throughout the two-phase region, and the convergence-pressure loci for such mixtures differ markedly from the conventional shape. In addition, the relationships between equilibrium-ratios and convergence pressure are often unusual. This paper presents an empirical procedure to evaluate convergence-pressure loci, and a qualitative analysis of the behavior of equilibrium ratios for nonideal close-boiling systems. Nonideal experimental phase equilibria form the basis of the studies (*2, 3, 4, 5, 8, 11, 14*).

The pressure-temperature diagram shown in Figure 1 typifies the phase areas for binary mixtures that behave ideally at low pressures. The curved arc, M to N, is the critical locus connecting the critical points of pure component M and pure component N. The projection at constant composition to the critical locus gives the critical pressure Pc for a two-phase condition, O. The isothermal projection to the critical locus produces the convergence pressure P_G. The identity of the components and the temperature define the convergence pressure for a binary system. Temperature, pressure, convergence pressure, and component identity determine equilibrium ratios. Typical equilibrium-ratio isotherms shown in Figure 2, illustrate the merging of the equilibrium-ratio curves at the convergence pressure. Two-phase mixtures exist at temperatures less than the minimum critical temperature. The isothermal projection to the curve CM on Figure 1 results in the point QP_G, the convergence pressure that correctly correlates equilibrium ratios at temperatures less than the minimum critical temperature. The point QP_G has been termed the quasiconvergence pressure (*1*). The curve CM represents the locus of quasiconvergence pressures (*7*). Figure 3 shows the behavior of equilibrium ratios under conditions where QP_G correlates the equilibrium ratios. The quasiconvergence pressure may be thought of as the pressure where convergence of the equilibrium ratios would occur if total condensation did not occur first when the pressure is raised. Quasiconvergence pressures are obtained by extrapolation of the equilibrium-ratio isotherms, and it is difficult to ascertain their exact numerical value.

The general phase behavior of close-boiling nonideal mixtures was first studied in the last part of the nineteenth century (*5, 14*) and the results were summarized by Kuenen (*6*) and Roozeboom (*12*). It is now desired to determine the convergence-pressure and equilibrium-ratio behavior. As a means of analysis, component M is defined as the component of a binary system with the higher critical pressure. Component N is the component with lower critical pressure. Figure 4 illustrates the behavior of convergence-pressure loci as the critical temperature of M increases relative to the critical temperature of N. Figure 4–1 shows the situation with the critical temperature of M roughly 100°F. less than the critical temperature of N. Region A, the two-phase area to the right of the critical temperature of M, represents conditions where the isothermal projection to the critical locus results in a real convergence pressure. Region B, to the left of M and below the vapor-pressure curve of M, represents conditions where the isothermal projection results in a quasiconvergence pressure.

In Figure 4–2, the critical temperature of M and N are closer together, with a smaller area A and a larger area B. With continued rise of critical temperature M, Figure 4–3 shows region A still smaller and some additional peculiarities. The convergence-pressure locus has folded over in such a way that two convergence pressures are possible at the same temperature. A minimum temperature exists on the critical locus that is not the critical temperature of either component. A quasiconvergence-pressure locus exists in a real two-phase zone, and a two-phase zone exists at higher pressures than the quasiconvergence pressure, a zone termed *region C*. Region C is bounded by the critical locus, the quasiconvergence pressure line, and either the vapor-pressure curve for component M or an azeotrope line, whichever is higher in pressure.

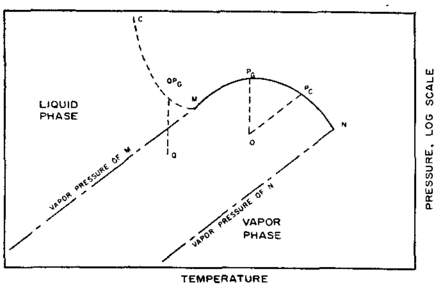

Fig. 1. Typical phase behavior.

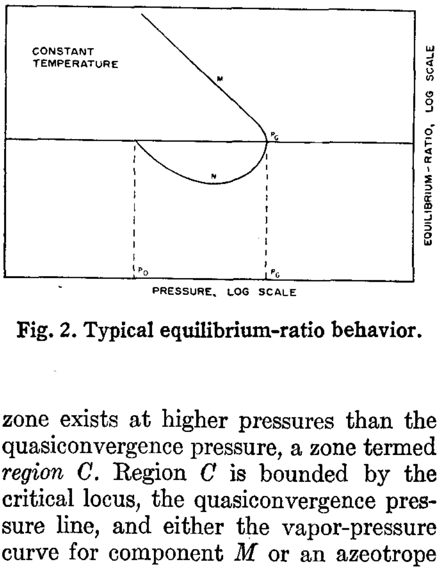

Fig. 2. Typical equilibrium-ratio behavior.

In Figure 4–4 a continuation of the folding process occurs. A new region A, denoted A_2, has appeared. The volatility relations in regions A and A_2 are reversed. In area A component M is more volatile. In area A_2 component N is more volatile. Azeotrope compositions can exist because the phase-boundary curves can lie outside the area bounded by the vapor-pressure curves (*2, 5, 6*). With Figure 4–5 the original A region has almost disappeared, and with Figure 4–6 has disappeared. Figures 4–4 and 4–5 show azeotropes. A locus of the type of Figure 4–6 may also show an azeotrope, as illustrated by Kay and Brice (*3*).

The curves of Figure 4 are not intended to represent quantitatively actual binary mixtures. Figure 4–1 approximates the acetylene-propane system (*8*). Figure 4–4 is similar to the propane-H_2S system (*4*), or the nitrous oxide-ethane system (*5*). Figure 4–6 is like the H_2S-ethane system (*3*) or the H_2S-pentane system (*11*).

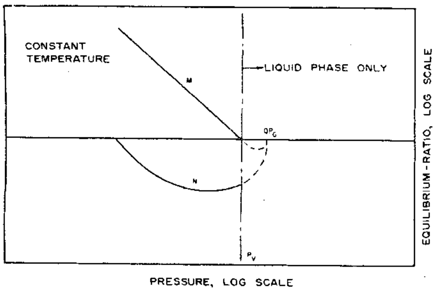

Fig. 3. Equilibrium-ratio behavior where quasi-convergence pressure applies.

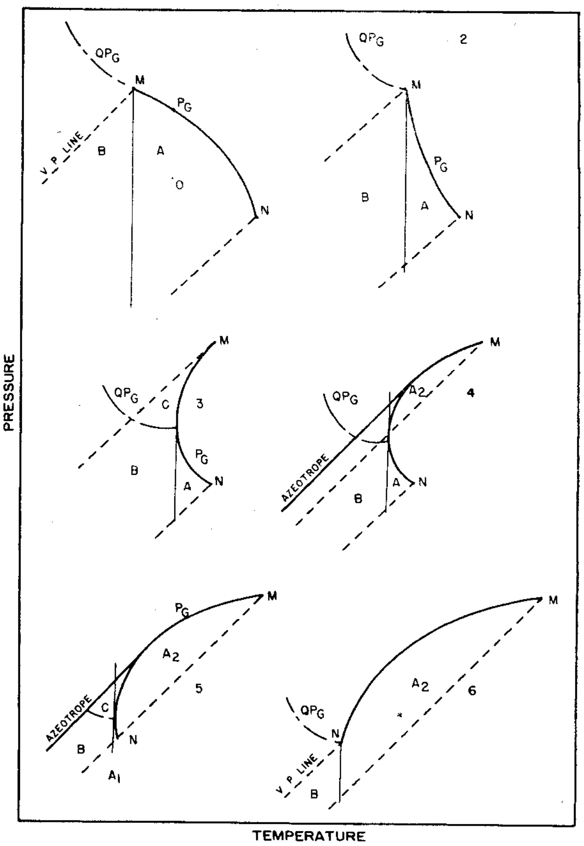

Fig. 4. Behavior of convergence-pressure loci for close-boiling mixtures.

The locus of the quasiconvergence pressure curves results from extrapolation of the isothermal equilibrium-ratio curves to the line where $K = 1$. Figure 5 shows the equilibrium ratios of H_2S and propane at a temperature of 178°F. where a real convergence pressure does not exist. Below 800 lb./sq. in. abs. the behavior of the equilibrium ratios is conventional, appearing to converge at some pressure between 800 and 900 lb./sq. in. abs. Extrapolation of the isotherms of Figure 5 with similitude to the shape of the equilibrium ratios for temperatures where a real convergence pressure exists gives the dashed line converging at 860 lb./sq. in. abs. This pressure is considered to be the quasiconvergence pressure. A study of the H_2S-propane system in this manner resulted in quasiconvergence pressures of 850 lb./sq. in. abs. at 170°F., 850 lb./sq. in. abs. at 175°F., and a real convergence pressure of 880 lb./sq. in. abs. at 184.2°F., the minimum critical temperature. The quasiconvergence pressure appears to be essentially constant in the two-phase area for the H_2S-propane system.

At pressures below the lower pressure convergence pressure and at pressures a reasonable pressure below the quasiconvergence pressure, the pattern of the isothermal-equilibrium-ratio curves appears conventional, permitting the development of a rational correlation of activity coefficients. At higher pressures the situation is more complex.

Figure 6 presents an empirical correlation to predict convergence pressures for close-boiling nonideal mixtures, dependent upon the measured values of the ethane-acetylene (*5*, *8*), propane-acetylene (*8*), propylene-acetylene (*8*), ethylene-acetylene (*8*), ethane-H_2S (*3*), propane-H_2S (*4*), pentane-H_2S (*11*), ethane-nitrous oxide (*5*), ethane-CO_2 (*5*), acetylene-CO_2 (*5*), and ethane-HCl (*14*) systems. The abscissa of Figure 6 is the operating temperature less the critical temperature of component N. The parameter is the difference in critical temperatures, $T_M - T_N$. The ordinate is $(P_G - P_N)/(P_M - P_N)$. It is possible to predict two convergence pressures for the same temperature. Composition considerations dictate the correct choice. Where quasiconvergence pressures are needed, a horizontal projection to the left from the minimum temperature point on the critical locus is suggested as the quasiconvergence-pressure line. Figure 6 is based on nonideal systems for the range of temperature between 50° and 213°F. and from 700 to 1,300 lb./sq. in. abs. convergence pressure, with mixtures having activity coefficients greater than 1.0. The correlation predicts the measured values of convergence pressure with an arithmetic deviation of 2.3% and a statistical deviation of 3.3%.

The unconventional behavior of equilibrium ratios is pictured by the curves of Figure 7 for a locus similar to that of Figure 4–4. Figure 7–1 shows the behavior for the case of an operating temperature above the minimum critical temperature. The customary behavior is shown for the equilibrium ratios in region A. For the A_2 region the volatility is reversed, and the equilibrium ratios converge at the azeotrope composition. As the pressure is reduced beyond the azeotrope, the equilibrium ratios spread apart and then converge again at the upper convergence pressure as the pressure is decreasing. Convergence takes place at three pressures, at the two convergence pressures and at the azeotrope pressure. Figure 7–2 shows equilibrium ratios where the temperature is the minimum critical temperature, resulting in a merging of the two convergence pressures. Figure 7–3 shows the situation just below the minimum critical temperature. As the pressure increases, the equilibrium ratios approach the quasiconvergence pressure but never quite converge to $K = 1$. Rather, with increasing pressure the equilibrium ratios tend to spread apart and then to converge at the azeotrope pressure.

It is not presumed that a knowledge of the convergence pressure for nonideal systems is all that is required to predict the equilibrium ratios. But the convergence-pressure locus outlines the two-phase area and indicates how the equilibrium ratios will behave. And this gives a degree of confidence in the prediction of activity coefficients in the high-pressure range, through the knowledge of the termination points of the equilibrium-ratio isotherms.

Example: It is desired to find the convergence pressure of an H_2S-propane mixture at 188°F. The critical conditions are 213°F. and 1,306 lb./sq. in. abs. for H_2S, and 206°F. and 616 lb./sq. in. abs. for propane. Because propane has the lower critical pressure, it is component N.

$$T - T_N = 188° - 206° = -18°\text{F.}$$

$$T_M - T_N = 213° - 206° = 7°\text{F.}$$

From Figure 2 $(P_G - 616)/(1{,}306 - 616) = 0.25$ and 0.53.

$$P_G = 788 \text{ or } 982 \text{ lb./sq. in. abs.}$$

Kay and Rambosek (*4*) show values of 797 and 1,021 lb./sq. in. abs. The lower

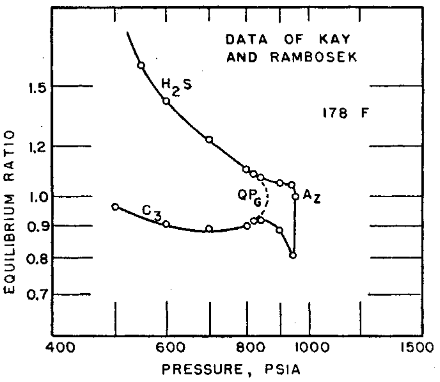

Fig. 5. Equilibrium-ratio behavior, quasiconvergence pressure in two-phase region.

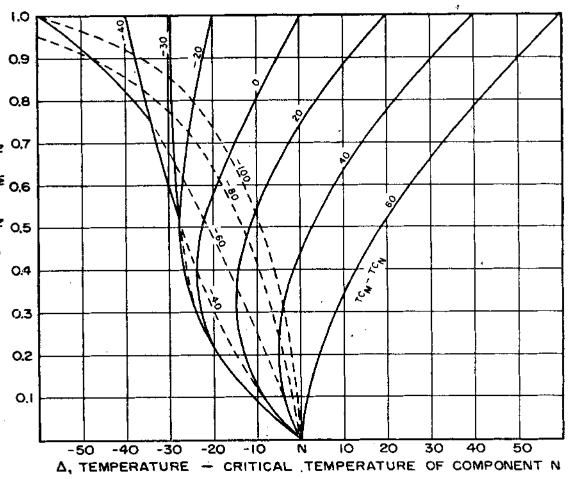

Fig. 6. Prediction of convergence pressure for close-boiling nonideal mixtures.

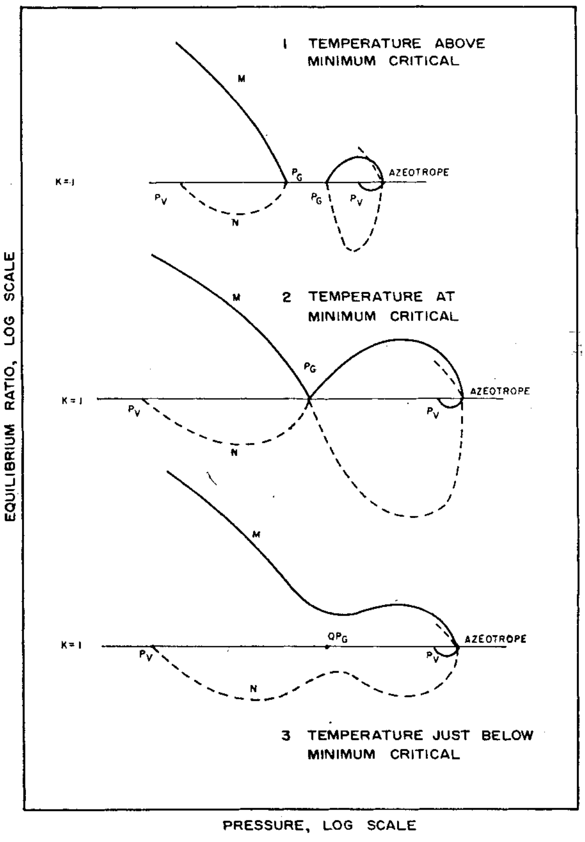

Fig. 7. Equilibrium ratios in the critical region for close-boiling nonideal mixtures.

pressure applies to the propane-rich mixture.

NOTATION

Az = azeotrope pressure, lb./sq. in. abs.
K = equilibrium ratio
M = component with higher critical pressure
N = component with lower critical pressure
Pc = critical pressure, lb./sq. in. abs.
P_G = convergence pressure, lb./sq. in. abs.
P_M = critical pressure of component M, lb./sq. in. abs.
P_N = critical pressure of component N, lb./sq. in. abs.
P_v = vapor pressure, lb./sq. in. abs.
QP_G = quasiconvergence pressure, lb./sq. in. abs.
T = temperature, °F.
T_M = critical temperature of component M, °F.
T_N = critical temperature of component N, °F.
Δ = temperature minus the critical temperature of component N, °F.

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