

Calculation of Pressure-Temperature Phase Envelopes of Multicomponent Systems

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ABSTRACT

K-factor data for hydrocarbon systems have been correlated as a function of temperature, pressure and convergence pressure. Recently, a very precise technique was developed to predict accurate convergence pressures, even in the area of the critical state.¹ It is the object of this paper to demonstrate how this convergence pressure calculation can be used to determine the p - T envelopes of multicomponent systems, including the retrograde region.

INTRODUCTION

The petroleum engineer is interested in the p - T envelope that describes the fluid existing in a given reservoir. If the reservoir temperature and pressure are sufficiently high, relative to this phase envelope, it may be economically feasible to miscibly displace the reservoir fluid with a drier, less expensive gas (Fig. 1). These phase envelopes are normally established by laboratory measurements involving expensive PVT equipment. By the use of a computer program that utilizes some of the latest correlations of hydrocarbon property data, these envelopes can be generated in seconds from composition analysis data including the molecular weight of the C_7^+ fraction.

It is the purpose of this paper to show how convergence pressures can be used to predict the p - T envelopes of multicomponent systems. Convergence pressure is shown to be a phase-rule variable for the two-phase, three-component system at equilibrium. Ternary phase diagrams are presented for three-component systems that define the convergence pressure for a given temperature, pressure, and system composition.

PREDICTION OF THE PRESSURE-TEMPERATURE ENVELOPE OF A TWO-COMPONENT SYSTEM

The data for the two-component system will be used to demonstrate how convergence pressure calculations can be used to predict p - T envelopes for multicomponent systems. Figs. 2 and 3 show experimental p - T - Z data for a system such as the ethane-heptane system.² $(p-Z)_T = C_1$ data has been used to establish convergence pressure K -factor correlations such as those published in the 1957 NGSMA Data Book.³ These K -factors are plotted as functions of T , p , p_{cv} .

These data, in turn, can be used to predict the $(p-T)_Z = C_1$ envelope. Suppose we wish to calculate the p - T envelope of Mixture Z of Fig. 3. To use the convergence pressure correlations to establish such a p - T envelope, the following three methods (A, B and C) were developed to predict dewpoint and/or bubble-point states. The method depends on whether the temperature was equal to, greater, or less than the critical temperature. Methods B and C depend on the

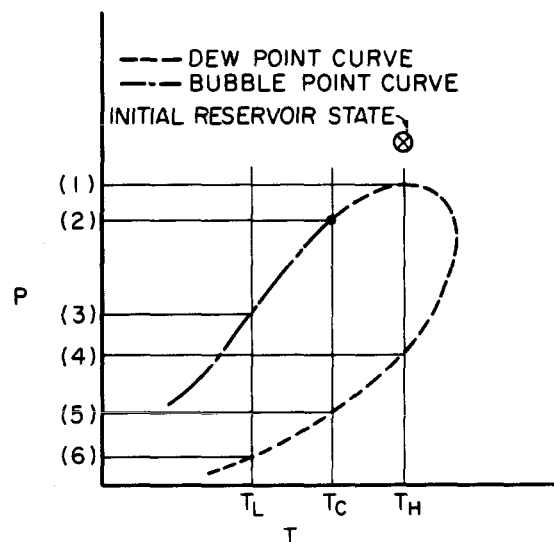


FIG. 1 — THE PRESSURE-TEMPERATURE PHASE ENVELOPE OF A SYSTEM OF FIXED OVER-ALL COMPOSITION.

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¹References given at end of paper.

results of Method A; thus it is important to first perform the Method A calculation.

METHOD A — STEPS FOR CALCULATING THE PHASE ENVELOPE AT THE CRITICAL STATE

At the critical state, the calculating procedure is quite simple, since there are no trial-and-error calculations involved with respect to convergence pressure. The critical pressure and critical temperature at the critical state can be directly calculated since the composition, z , of the system is known. These calculations can be made using suitable empirical correlations.⁴

For this particular state, which is a critical state, the convergence pressure of the dewpoint mixture equals the calculated critical pressure, and no iteration on convergence pressure is required.

Thus the steps to be followed in calculating the phase envelope boundaries for the critical isotherm are as follows.

1. From the known over-all composition of the system, calculate the critical temperature of the mixture. This defines the critical isotherm.

2. From the over-all system composition, next calculate the critical pressure from suitable correlations. Steps 1 and 2 define state $[p(2), T_c]$, the critical state, of the phase diagrams of either Fig. 1 or Fig. 3.

3. Let the calculated critical pressure of Step 2 be the convergence pressure of the system. Using this convergence pressure, assume various pressures such that $p < p_{cvC}$, and calculate $\sum z_i/K_i$. The pressure for which this sum equals 1 is the dew point. State $[p(5), T_c]$ of Figs. 1 and 3 represents this state.

These three steps complete the calculations required to define the phase envelope along the critical isotherm.

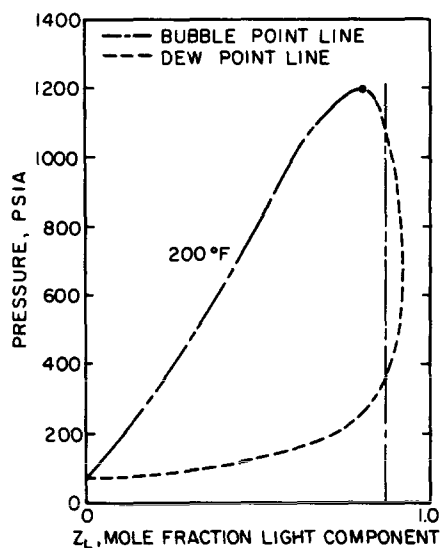


FIG. 2 — PRESSURE-COMPOSITION PHASE ENVELOPE OF A TWO-COMPONENT SYSTEM AT FIXED TEMPERATURE.

METHOD B — STEPS FOR CALCULATING THE PHASE ENVELOPE IN THE RETROGRADE REGION

For temperatures above the critical temperature, the bubble-point line does not exist. There will thus be no point for which $\sum K_i z_i = 1$, but two points for which $\sum z_i/K_i = 1$. These two points will define the phase envelope boundary of the dewpoint curve in the retrograde region along a given isotherm.

The steps to be followed for the envelope calculations in the retrograde region are:

1. Assume a value for the independent variable, T .

2. Assume values of the convergence pressure for the two dewpoint pressures to be determined.

3. For the now defined values of T and p_{cv} , next assume a value of p .

4. Use the convergence pressure correlations to determine the K -factors to be applied to the fluid components.

5. Calculate $\sum z_i/K_i$ for both the high-pressure and low-pressure case. Vary the two pressures (and thus the K -factors) until $\sum z_i/K_i = 1$ for both cases.

6. Next calculate the convergence pressure for the two cases using the Critical Composition Method outlined in the Appendix.

7. Compare the assumed convergence pressures of Step 2 to those calculated in Step 6. If the assumed and calculated values are equal, the two dewpoint pressures have been accurately defined. If not, assume new values for the convergence pressures and repeat Steps 3 through 7.

METHOD C — STEPS FOR CALCULATING THE BUBBLE-POINT AND DEWPOINT PRESSURES FOR OPERATING TEMPERATURES LESS THAN THE CRITICAL TEMPERATURE

Convergence pressure calculations can be used to establish the bubble-point curve for this region. However, the tie-lines that define the K -factors along the dewpoint curve do not intersect the critical temperature locus, and a convergence

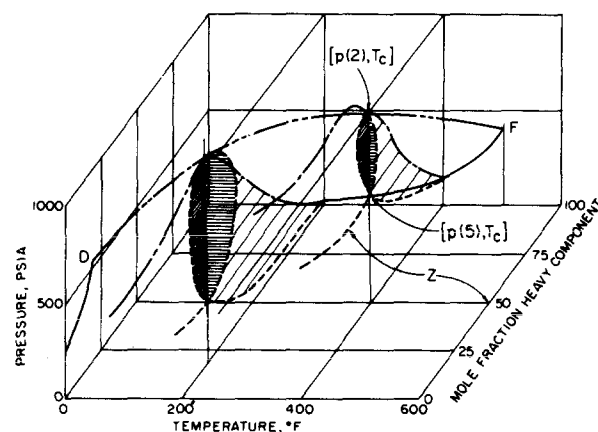


FIG. 3 — PRESSURE-TEMPERATURE-COMPOSITION PHASE DIAGRAM OF A TWO-COMPONENT SYSTEM.

pressure calculation cannot be made for these lower pressure cases. It was assumed that the convergence pressure used for the bubble-point calculation may also be used to determine the dewpoint state. The implications of this assumption are discussed in the section describing the three-component calculation.

The following steps outline the procedure to be followed for predictions involving temperatures less than the critical temperature.

1. Select a value for the independent variable, T .
2. Assume a value of the convergence pressure for the bubble-point state.
3. For the values of T and p_{cva} , next assume a value of p .
4. Use the convergence pressure correlations to determine the appropriate K -factors for the respective components.
5. Calculate $\sum K_i z_i$ and $\sum z_i/K_i$ until two pressures are defined such that $\sum K_i z_i = 1$ and $\sum z_i/K_i = 1$.
6. Next use the critical composition method to calculate the convergence pressure at the bubble-point pressure state.
7. If the assumed value of p_{cva} of Step 2 equals the calculated value of Step 6, the dewpoint and bubble-point pressures have been accurately defined for the selected value of the independent variable, T , and the calculation is complete for this isotherm. If not, repeat Steps 2 through 7.

This procedure is repeated for other isotherms until the p - T envelope is adequately defined.

In applying this technique to a two-component system, Gibbs phase rule tells us that only two intensive properties need be specified; in this study, pressure and temperature were two such properties. The convergence pressure calculation thus becomes redundant since $p_{cv} = p_{cv}(T)$ for a two-component system, and convergence pressure is not an independent phase-rule variable. This means that, given the temperature, the convergence pressure can readily be determined from an appropriate correlation that will predict a curve such as DF of Fig. 3.

THREE-COMPONENT SYSTEM

The calculation procedure consisting of the three methods just outlined is general and, according to the convergence pressure postulate,⁵ can be used to predict the phase envelopes of multicomponent systems containing three or more components. For a three-component, two-phase system Gibbs phase rule ($F = C - P + 2$) states that F , the degrees of freedom, is 3. It will now be shown that, for such a system, convergence pressure is a third independent phase-rule variable that can be used to define the intensive properties at an equilibrium state.

First consider Fig. 4. The convergence pressure to be applied to Mixture Z is the critical pressure of Mixture G, defined by the intersection of tie-line x - y and the critical temperature locus A - A^1 . Thus,

$$p_{cvC} = p_{cvC}(G) \dots \dots \dots (4)$$

On the other hand,

$$G = G[T, y_i, x_i, i = 1, 3] \dots \dots \dots (5)$$

However, the relation $\sum_{i=1}^3 y_i = \sum_{i=1}^3 x_i = 1$ reduces the number of independent variables in Eq. 5 to five. Thus,

$$G = G[T, y_1, y_2, x_1, x_2] \dots \dots \dots (6)$$

Now applying the phase rule in a conventional manner, $F = 3$. Specification of T and p defines a specific phase envelope such as that shown in Fig. 4. Specification of $x_2 = C$ completely defines the intensive states of the system, including x_1 , x_2 , x_3 and y_1 , y_2 , y_3 . Thus the K -factors are also uniquely determined by specifying three of the phase-rule variables. Thus if $F = 3$, K_1 , K_2 , K_3 can be determined.

$$\begin{aligned} K_1 &= K_1(T, p, x_2) = \frac{y_1}{x_1} \\ K_2 &= K_2(T, p, x_2) = \frac{y_2}{x_2} \dots \dots \dots (7) \\ K_3 &= K_3(T, p, x_2) = \frac{y_3}{x_3} \end{aligned}$$

Substituting into Eq. 6, we obtain

$$G = G[T, x_1 K_1(T, p, x_2), x_2 K_2(T, p, x_2), x_1, x_2] \dots \dots \dots (8)$$

or

$$G = G[T, p, x_1, x_2] \dots \dots \dots (9)$$

As stated before, specifying x_2 a constant, in addition to p and T , completely defines the system including x_1 . Thus x_1 can no longer be considered an independent variable and Eq. 9 becomes:

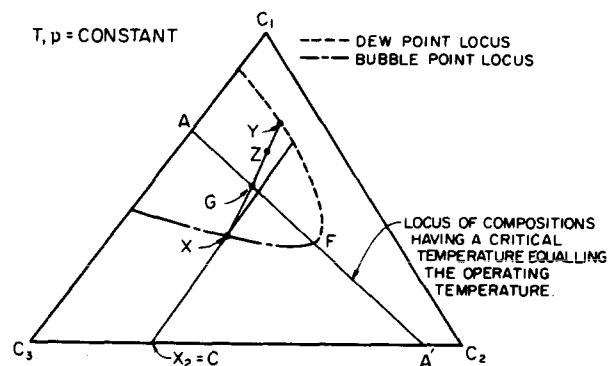


FIG. 4 — TERNARY PHASE DIAGRAM OF A THREE-COMPONENT SYSTEM.

$$G = G[T, p, x_2] \dots \dots \dots (10)$$

Substituting Eq. 10 into Eq. 4, we obtain:

$$P_{cvC} = P_{cvC} [T, p, x_2] \cdot$$

Thus convergence pressure is a variable that, in itself, is a function of the commonly used phase-rule variables.

This implies that, if we correlate $K_i = K_i(T, p, p_{cv})$ for a three-component system, we have in fact correlated $K_i = K_i(T, p, x_2)$ and have a thermodynamically rigorous correlation for a three-component system.

To extend convergence pressure predictions to systems containing four or more components violates Gibbs phase rule, and thus empirical trends must be relied upon for any such extension. Such a trend has been noted in correlating PVT data and has been stated as the law of corresponding states as applied to mixtures. Similarly, a law based on experimental data has been stated that postulates convergence pressure as a correlating parameter for K -factors along with temperature and pressure for multicomponent systems.⁵

THREE-COMPONENT PHASE DIAGRAMS

The p - T envelope for a three-component system and its dependence on the convergence pressure calculation can be demonstrated with ternary diagrams coupled with the $(p$ - $T)$ $Z = C_1$ phase envelope.

Fig. 1 shows the p - T envelope of a three-component system of fixed Composition Z . On this diagram are three isotherms; one is the critical isotherm that passes through the critical state, one isotherm represents a temperature greater than the critical temperature, and the other one, a temperature less than the critical temperature. The intersection of three isotherms

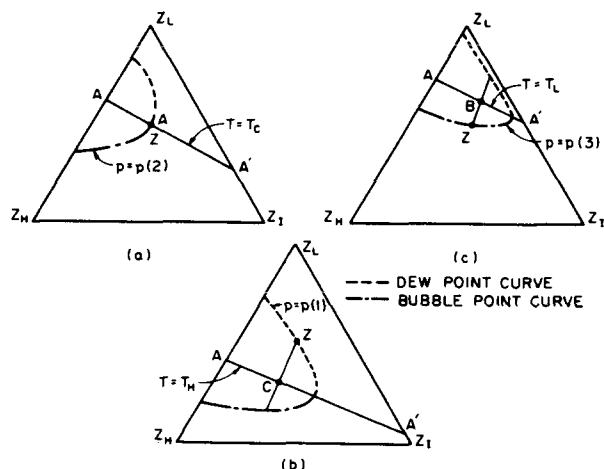


FIG. 5 — DEFINITION OF MIXTURES FOR DETERMINING CONVERGENCE PRESSURES OF HIGH-PRESSURE STATES.

with the p - T envelope define six states.

The convergence pressures used to define these six states are shown on the six accompanying ternary phase diagrams of Figs. 5 and 6. Mixture Z is a fixed, common composition on all six of these diagrams. Each diagram has a temperature and pressure equivalent to one of the state points on the p - T envelope. Also on each

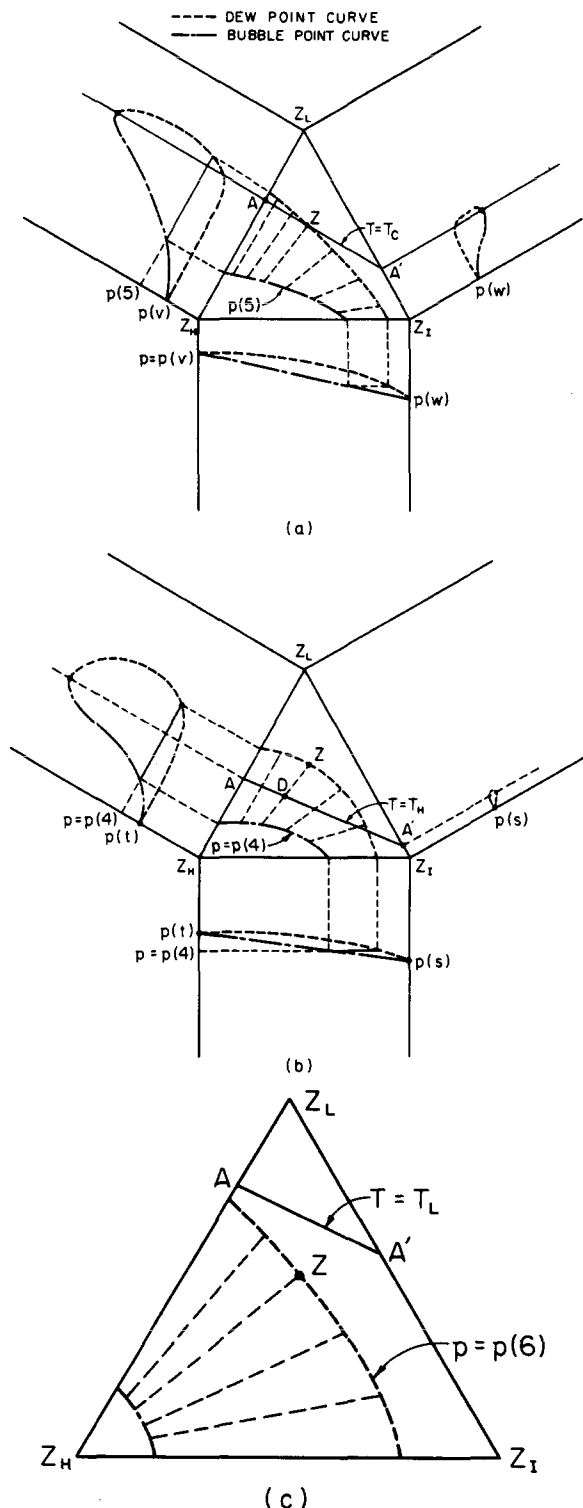


FIG. 6 — DEFINITION OF MIXTURES FOR DETERMINING CONVERGENCE PRESSURES OF LOW-PRESSURE STATES.

diagram are shown the bubble-point and dewpoint lines that exist for compositions other than Z, but for the same temperature and pressure. Note that Z is located on either the bubble-point lines or the dewpoint lines as indicated by the p - T envelope.

Consider state $[p(2), T_c]$ of Fig. 1. This is a critical state and corresponds to Point A of Fig. 5a. The critical pressure of Point A can be directly calculated from empirical correlations as outlined by Method A for the two-component system calculation. Pressure $p(2)$ is also the convergence pressure to be used in determining state $[p(5), T_c]$. The composition envelope of Fig. 6a also shows this state at this lower pressure. Also shown on this figure are $(p-Z)_{T=T_c}$ envelopes for the two-component systems that exist at $T=T_c$. At the apexes of this figure are shown the vapor pressures of the pure components. $p(v)$ represents the vapor pressure of the heavy component and $p(w)$, the vapor pressure of the intermediate component. These two pressures are also shown on the vapor-pressure chart of Fig. 7. The phase envelopes cannot intersect the light component axis since the operating temperature, T_c , is greater than the critical temperature of the light component (as shown by Fig. 7). The bubble-point curve between $p(v)$ and $p(w)$ was drawn as a straight line to comply with Raoult's law.

Next consider the isotherm T_H . The intersection of this isotherm with the p - T envelope defines states $[p(1), T_H]$ and $[p(4), T_H]$ on the dewpoint curve in the retrograde region. Method B, to be followed in calculating these state points, was previously outlined. The convergence pressure to be used to calculate state $[p(1), T_H]$ is the critical pressure of Mixture C of Fig. 5b. The Mixture Z necessarily lies on the dewpoint locus. Fig. 6b shows the composition envelope at the lower pressure, $p(4)$. Again Mixture Z lies on the dewpoint locus. The convergence pressure associated with Mixture Z at state $[p(4), T_H]$ is the critical pressure of Mixture D. Vapor pressures $p(t)$ and $p(s)$ are shown on Fig. 7 and Fig. 6b. Note that $p(s)$ is very close to the critical pressure of the intermediate component and hence the light-intermediate phase envelope is very small.

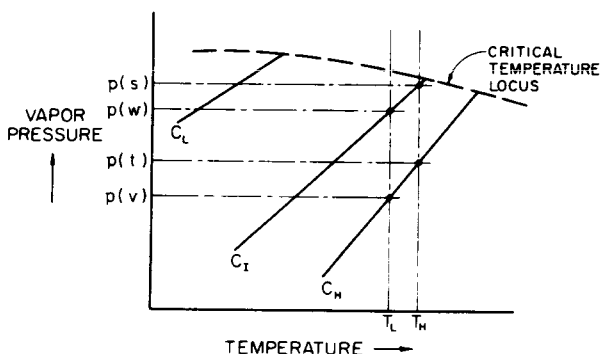


FIG. 7 — ONE-COMPONENT VAPOR PRESSURES.

Finally, consider the isotherm T_L of Fig. 1. The intersection of this isotherm with the p - T phase envelope defines states $[p(3), T_L]$ and $[p(6), T_L]$. The state $[p(3), T_L]$ of fluid of Composition Z is also shown on Fig. 5c. The convergence pressure used in determining the bubble-point pressure $p(3)$ is equal to the critical pressure of Mixture B.

In general, the dewpoint pressure $p(6)$ cannot be determined with a convergence pressure calculation since the tie-line that terminates at State Z does not intersect the critical temperature locus (Fig. 6c). In this study, the convergence pressure used in determining state $[p(3), T_L]$ was also used to determine the state $[p(6), T_L]$. The rationale for this assumption was that the pressure $p(6)$ is far removed from the convergence pressure, where the K -factors are still strongly dependent on temperature and pressure but relatively independent of fluid composition. Thus some error can be made in determining convergence pressure without introducing much of an error in the K -factors applicable to the state $[p(6), T_L]$. This assumption is justified graphically by Fig. 8, which is similar to the one presented by Katz *et al.*¹⁵

SYSTEMS CONTAINING MORE THAN THREE COMPONENTS

The methods outlined in this paper were shown to be thermodynamically rigorous for two- and three-component systems. The convergence

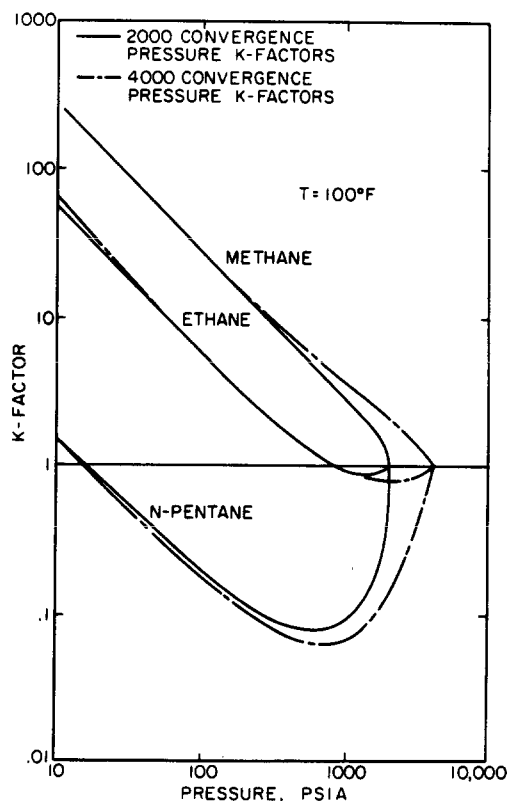


FIG. 8 — EFFECT OF CONVERGENCE PRESSURE ERROR ON LOW PRESSURE K -FACTORS.

pressure postulate extends these methods to systems containing more than three components. Assuming the empirical correlations (the K -factor correlations, and the critical temperature and pressure correlations) are exact, the accuracy of the envelope calculation will depend on the validity of the convergence pressure postulate. The system must satisfy the criterion set forth by this postulate. For instance, the components of a given system must be of the same homologous series. If the system contains significant portions of aromatics, or nonhydrocarbon molecules such as H_2S or CO_2 , failure to predict system phase behavior would not be surprising.

COMPUTATIONAL PROCEDURE

Fig. 9 is a flow diagram of the computer program written to calculate the pressure-temperature phase envelopes. The data required are the system

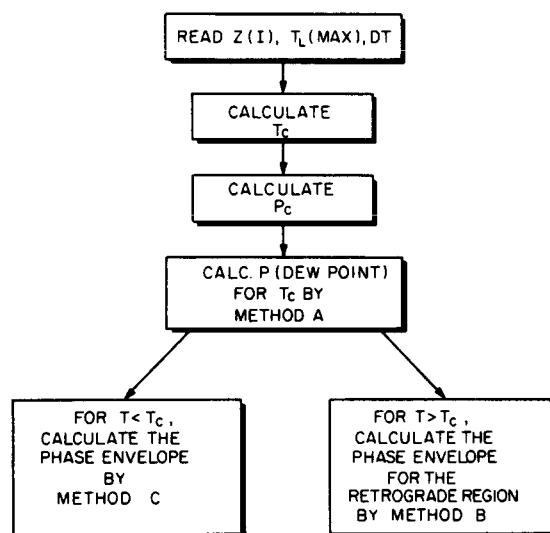


FIG. 9 — COMPUTER PROGRAM FLOW CHART.

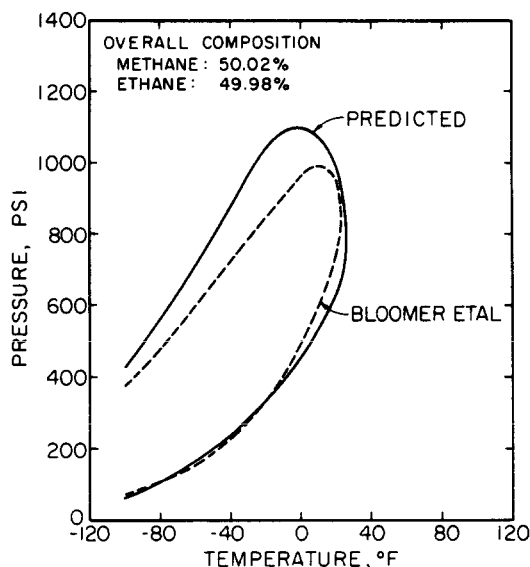


FIG. 10 — PHASE ENVELOPE FOR A METHANE-ETHANE SYSTEM.

composition, the lower temperature limit to the phase envelope calculations $(T_L)_{max}$, and ΔT , the spacing between adjacent isotherms and the molecular weight of the C_{7+} .

The program first calculates T_c and p_c using the basic correlations developed by Etter and Kay.⁶ These correlations had to be modified somewhat to give sufficient accuracy to predict the phase envelopes.¹⁶ The dewpoint pressure at the critical temperature was then calculated using the convergence pressure K -factor correlations developed by NGSMA to fit their 1957 data. An extrapolation subroutine was written to determine K -factors for convergence pressures other than those tabulated in 1957. Method A outlines the steps to this calculation.

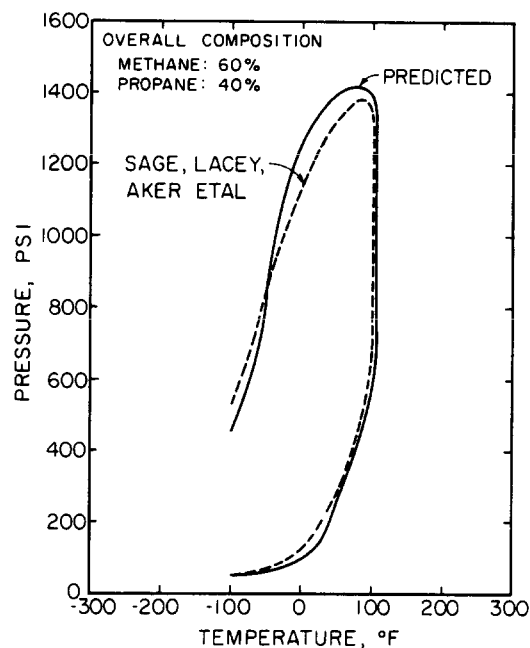


FIG. 11 — PHASE ENVELOPE FOR A METHANE, PROPANE SYSTEM.

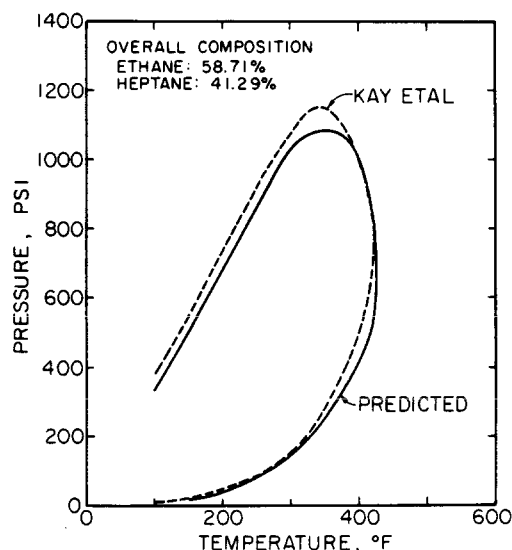


FIG. 12 — PHASE ENVELOPE FOR AN ETHANE, HEPTANE SYSTEM.

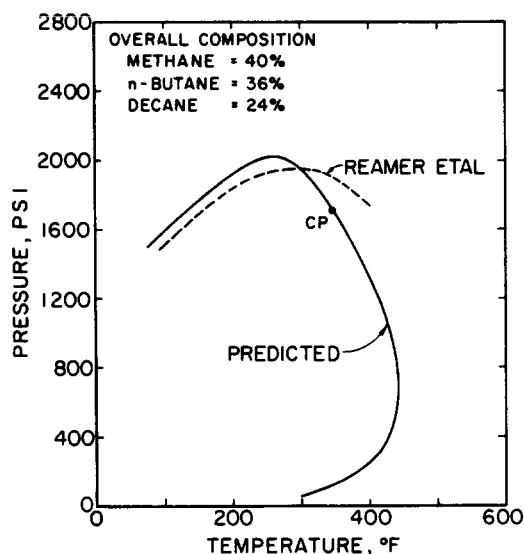


FIG. 13 — PHASE ENVELOPE FOR A METHANE, N-BUTANE, DECANE SYSTEM.

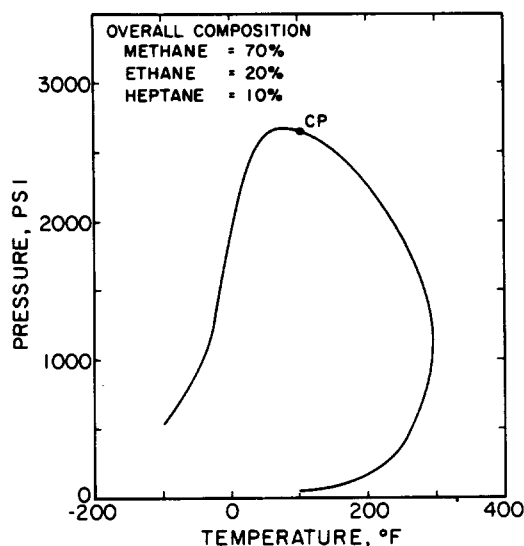


FIG. 14 — PHASE ENVELOPE FOR A METHANE, ETHANE, HEPTANE SYSTEM.

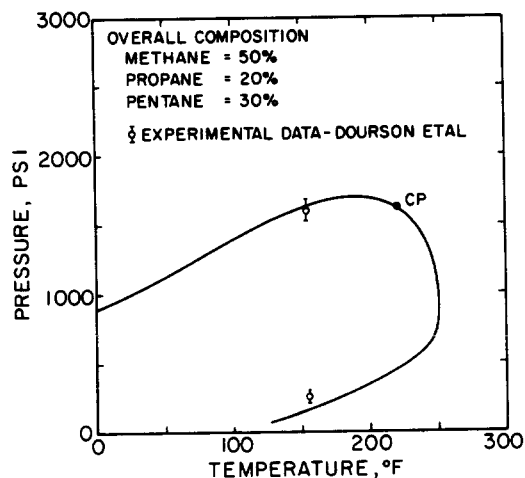


FIG. 15 — PHASE ENVELOPE FOR A METHANE, PROPANE, PENTANE SYSTEM.

The method for the calculation of the retrograde region is outlined under Method B of this paper. Again, Etter and Kay's critical temperature and critical pressure correlations were used to calculate the convergence pressures,^{4,6} while the 1957 NGSMA correlations were used to determine the K -factors. Method C was followed in calculating the remainder of the envelope.

RESULTS

Pressure-temperature phase envelopes were calculated for a total of seven hydrocarbon systems on which some published experimental data were available.⁸⁻¹⁴ The calculated and experimental results are presented in Figs. 10 through 16.

Figs. 10 through 12 present the results for two-component systems. The maximum error in the cricondenthem temperature was approximately 5°F, while the maximum error in the cricondenbar pressure was 100 psi. Figs. 13 through 15 compare calculated and experimental results for the three-component systems. Here the maximum temperature error was 80°F, while the maximum pressure error was 100 psi. Fig. 16 shows the phase envelope calculated for a multicomponent system containing more than three components. The cricondenbar pressure error for this system was 200 psi, while the cricondenthem temperature error was 25°F. The molecular weight of the C_{6+} fraction was determined by trial and error from the critical pressure of the mixture. Different values of the molecular weight of the C_{6+} fraction were assumed, and critical pressures calculated until the calculated critical pressure equaled the published experimental value. The resultant molecular weight was then used to extrapolate NGSMA K -factor data.⁴

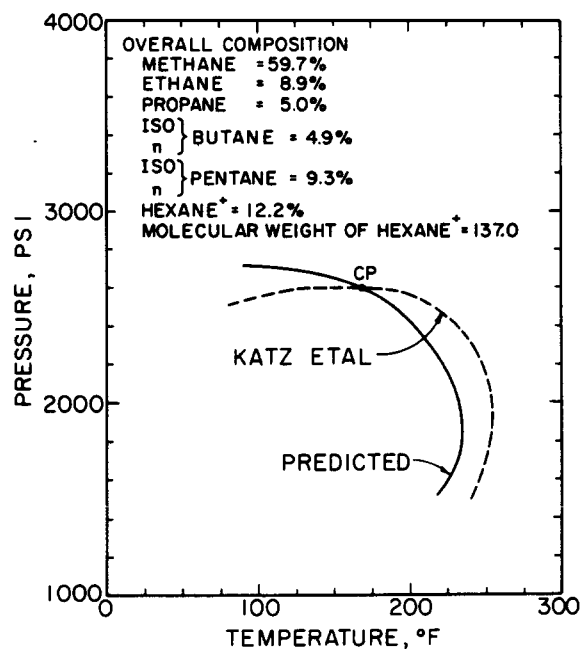


FIG. 16 — PHASE ENVELOPE FOR A MULTI-COMPONENT SYSTEM.

CONCLUSIONS

K -factors correlated as a function of temperature, pressure and convergence pressure, were successfully used to calculate the pressure-temperature phase envelopes of multicomponent systems of fixed over-all composition, including the retrograde region. It was shown that convergence pressure is a phase-rule variable for a three-component system. This implies that any error made in calculating the pressure-temperature phase envelopes of the two- and three-component systems can be attributed to imprecise correlations of critical pressures, critical temperatures and/or K -factors.

A literature survey indicated that very little pressure-temperature composition data that includes the molecular weight of the C_{7+} fraction has been published on multicomponent systems that defines the complete retrograde region.¹⁷⁻²⁴ Such data would be quite useful for improving available correlations and further evaluation of the convergence pressure postulate. Improved correlations would permit the engineer to quickly determine the feasibility of the pressure-maintenance program. Should such a program prove feasible, the calculated phase envelope would be useful in designing PVT experiments to verify the phase behavior of the reservoir fluid.

NOMENCLATURE

- C_1 = constant
 C = number of independent chemical species in a mixture
 F = number of independent phase rule variables
 K = equilibrium ratio
 n = total number of components in a mixture
 p = system pressure
 p_c = critical pressure
 p_{cv} = convergence pressure
 p_{cva} = assumed convergence pressure
 p_{cvC} = calculated convergence pressure
 P = number of equilibrium phases
 T = temperature
 T_c = critical temperature
 x = mole fraction of a component in the liquid phase
 y = mole fraction of a component in the vapor phase
 z = mole fraction of a component in a mixture
 Z = composition designator for systems of two or more components.

SUBSCRIPTS

- H = supercritical temperature index
 i = component identity index
 L = subcritical temperature index

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APPENDIX

CONVERGENCE PRESSURE THEORY

K-factors have been correlated as a function of temperature, pressure and convergence pressure. These correlations led to the following postulate: "The equilibrium vaporization constant for one component in a complex system is the same as the equilibrium constant at the same temperature and pressure for the same component in another system whether or not composed of the same number or kind of components, providing only that the convergence pressures of the two systems are exactly the same at the same temperature and that the components are of the same homologous series".⁵

Convergence pressure, in turn, was recently defined as the critical pressure of a mixture in the critical state that, when flashed to the operating pressure, results in a tie-line that passes through the mixture of fixed over-all composition that is being flashed. The critical temperature of the critical mixture is equal to the operating temperature.¹ Based on this definition,

the following method was developed to determine the convergence pressure of a mixture Z (Fig. 4) that exists in the two-phase region.

1. Assume a value for the convergence pressure, p_{cva} .
2. For this value of p_{cva} and known equilibrium temperature and pressure, look up the corresponding K-factors from suitable correlations.
3. Perform a flash calculation to determine the compositions of the coexisting phases into which Mixture Z will separate. This establishes tie-line X-Y.
4. Establish Mixture G, defined by the intersection of tie-line X-Y with the true critical temperature locus A-A¹. This can be done by writing a computer program that calculates the critical temperature along tie-line X-Y until a value is calculated that equals the operating temperature.
5. Calculate the true critical pressure of Mixture G, using an accurate correlation. This is the calculated convergence pressure p_{cvC} .
6. If the assumed value p_{cva} of Step 1 equals the calculated value, p_{cvC} of Step 5, the calculation is complete.
7. If the assumed and calculated values are not equal, a new value of p_{cva} must be assumed and Steps 1 through 6 repeated. Experience has shown that a solution is quickly reached if the new assumed convergence pressure is set equal to the one just calculated.

Recent work has shown that this method can be used to predict composition phase envelopes such as that shown in Fig. 4 up to and through the critical state.⁷ This method was used to calculate the convergence pressures of this study.
