

An Iterative Sequence for Phase-Equilibria Calculations Incorporating the Redlich-Kwong Equation of State

D. D. FUSSELL
J. L. YANOSIK
MEMBERS SPE-AIME

AMOCO PRODUCTION CO.
TULSA, OKLA.

ABSTRACT

Phase equilibria equations that incorporate the Redlich-Kwong equation of state are nonlinear and, therefore, must be solved by an iterative method. The method of successive substitutions commonly is used. This method, however, almost always diverges near the critical region for bubble point, dew point, and two-phase calculations. Iterative methods that converge for these calculations are presented. These iterative methods are called "minimum variable Newton-Raphson" (MVNR) methods because they try to minimize the number of variables for which simultaneous iteration is required and use the Newton-Raphson method for the correction step. Procedures are given for obtaining starting values for the first iteration and several example problems are discussed.

INTRODUCTION

Reservoir performance predictions for gas condensate and volatile oil reservoirs require a knowledge of the vapor-liquid phase equilibria of the reservoir fluids. A similar knowledge also is required when studying multiple-contact, miscible oil recovery methods that involve injection of hydrocarbons and/or carbon dioxide. Such knowledge is obtained experimentally or calculated from physical properties of the components of the reservoir fluid system. Calculation is desirable because experimental determination is both laborious and expensive.

A common basis for calculation of vapor-liquid phase equilibria is the single-stage separation unit. This unit represents a PVT cell in which a fluid mixture of known over-all composition is equilibrated at the temperature and pressure of interest. Liquid and vapor compositions and moles of liquid and vapor per mole of fluid mixture are determined. Reliable estimates of other fluid properties (such

as phase densities and viscosities) are obtained readily with these properties.

The Redlich-Kwong¹ equation of state is used widely in the petroleum industry for phase equilibria calculations. The phase equilibria equations that incorporate this equation of state are nonlinear. As a result, they must be solved by an iterative method. The method of successive substitutions commonly is used. This method, however, almost always diverges for bubble point, dew point, and two-phase calculations near the critical region. This region is extremely important when studying multiple-contact, miscible oil recovery methods involving CO₂ or rich-gas injection because the path of the over-all fluid mixture passes through this region. The method of successive substitutions also will diverge for some fluid mixtures near their saturation (bubble point or dew point) pressure at conditions removed from the critical region.

This paper presents a reliable iterative sequence that can be used to predict phase equilibria of multiple-contact, miscible oil recovery methods. The method includes sequences for calculation of the saturation pressure and phase equilibria in the two-phase region.

These MVNR methods rely on minimization of the number of unknowns for which simultaneous iteration is required and use the Newton-Raphson method for the correction step. Minimization is subject to the constraint that all additional unknowns can be calculated by using simple linear equations or, at most, an iteration method applied to one equation in one unknown.

MVNR is compared with the method of successive substitutions for a two-phase fluid mixture at various pressures for a fixed temperature. MVNR also is compared with the method of successive substitutions for saturation-envelope calculations near the critical region.

DESCRIPTION OF PHYSICAL SYSTEM

The single-stage separation unit is the basis for the phase equilibria calculations discussed in this study. This unit represents a PVT cell in which a fluid mixture of known over-all composition is equilibrated at the temperature and pressure of interest. Liquid and vapor compositions and moles

Original manuscript received in Society of Petroleum Engineers office Aug. 2, 1976. Paper accepted for publication July 12, 1977. Revised manuscript received March 22, 1978. Paper (SPE 6050) first presented at the SPE-AIME 51st Annual Fall Technical Conference and Exhibition, held in New Orleans, Oct. 3-6, 1976.

0037-9999/78/0005-6050\$00.25
© 1978 Society of Petroleum Engineers of AIME

of liquid and moles of vapor per mole of fluid mixture are determined.

Fluid mixtures considered are either single-phase and saturated or two-phase (liquid and vapor) at the system temperature and pressure. Fig. 1 presents a simplified phase diagram for a given fluid mixture as a function of temperature and pressure. The bubble-point and dew-point loci are shown and their intersection is the critical region. The curve described by these loci is called the saturation envelope. The region encompassed by the saturation envelope is the two-phase region. Phase equilibria of fluid mixtures that are within the envelope are described by the equations for a single-stage separation unit. The saturation pressure equations that are simplifications of the single-stage, separation equations describe the phase equilibria of fluid mixtures on the saturation envelope.

The single-stage, separation and saturation-pressure equations are presented and then followed by presentation of MVNR for calculation of phase equilibria described by these equations.

SINGLE-STAGE SEPARATION EQUATIONS

The single-stage separation unit can be described with four types of equations, an *over-all material balance*, *component material balances*, a *restrictive equation* on the phase compositions, and *thermodynamic phase equilibria equations*. The *over-all material balance* can be written as

$$L + V = 1, \dots \dots \dots (1)$$

where L is the moles of liquid per mole of fluid mixture and V is the moles of vapor per mole of fluid mixture. The *component material balance* for each component within the fluid mixture can be written as

$$Lx_i + Vy_i = z_i; 1 \leq i \leq n, \dots \dots \dots (2)$$

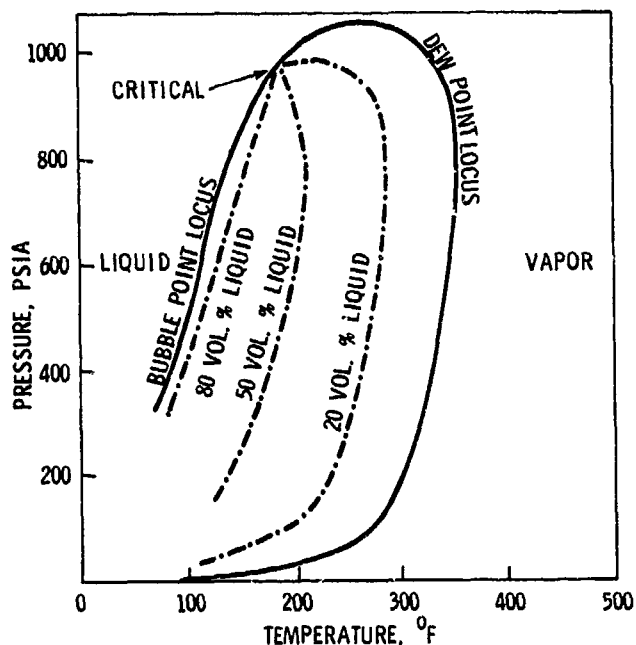


FIG. 1 — EXAMPLE PHASE DIAGRAM.

which shows that z_i moles of component i , when equilibrated, will be distributed as Lx_i moles of component i in the liquid phase and Vy_i moles of component i in the vapor phase. From Eqs. 1 and 2, x_i , y_i , and z_i are mole fractions and, by definition, $\left(\sum_{i=1}^n z_i \right)$, must be unity.

These equations also require a *restrictive equation* on the liquid phase compositions of

$$\sum_{i=1}^n x_i = 1, \dots \dots \dots (3a)$$

or a *restrictive equation* on the vapor phase compositions,

$$\sum_{i=1}^n y_i = 1, \dots \dots \dots (3b)$$

Both Eqs. 3a and 3b cannot be used because, given one, the second may be derived by combining the given equation with Eqs. 1 and 2.

The component fugacity in each phase is introduced to develop a criterion for thermodynamic equilibria. Physically, the fugacity of a component in one phase, with respect to the fugacity of that component in a second phase, is a measure of the potential for transfer of that component between phases. The phase with the lower component fugacity accepts the component from the second phase. Equal fugacities of a component in the two phases results in a zero net transfer. A zero transfer for all components implies a fluid system that is in thermodynamic equilibrium. Therefore, the *thermodynamic phase equilibria equation* can be expressed by

$$f_{iL} = f_{iV}; 1 \leq i \leq n, \dots \dots \dots (4)$$

REDLICH-KWONG EQUATION OF STATE

The component fugacity is a function of the partial molal volume of the component. Because the partial molal volume is difficult to establish experimentally, it is necessary to relate the partial molal volume and the component fugacity to easily determined quantities — for example, temperature, pressure, phase composition, and the components in the fluid system. This is accomplished with a combination of the thermodynamic definition of fugacity and an equation of state — in this case, the Redlich-Kwong equation of state as presented by Zudkevitch and Joffe.² Expressed in terms of the liquid phase compressibility factor, this equation of state is

$$Z_L^3 - Z_L^2 + Z_L [A_L - B_L (B_L + 1)] - A_L B_L = 0, \dots \dots \dots (5)$$

and the equation of state, expressed in terms of the vapor-phase compressibility factor, is

$$Z_V^3 - Z_V^2 + Z_V [A_V - B_V(B_V + 1)] - A_V B_V = 0 \dots \dots \dots (6)$$

The derivations of Eqs. 5 and 6 incorporate the actual gas law, $pv = ZRT$, which is valid for the liquid and vapor phases.

Following the work of Zudkevitch and Joffe, the component fugacity in the liquid phase now can be expressed as

$$f_{iL} = \frac{px_i \exp[b_{iL}(Z_L - 1)]}{(Z_L - B_L) \left(1 + \frac{B_{iL}}{Z_L}\right)^{u_i}} ; 1 \leq i \leq n \dots \dots \dots (7)$$

Similarly, the component fugacity in the vapor phase is given by the relation

$$f_{iV} = \frac{py_i \exp[b_{iV}(Z_V - 1)]}{(Z_V - B_V) \left(1 + \frac{B_{iV}}{Z_V}\right)^{w_i}} ; 1 \leq i \leq n \dots \dots \dots (8)$$

The equation parameters are defined in Appendix A and the Nomenclature. These are functions of pressure, temperature, phase composition, and the component parameters, Ω_{ai} and Ω_{bi} . The component parameters are assumed independent of composition and pressure. MVNR methods presented in this paper can be adapted readily to any equation of state.

SATURATION PRESSURE EQUATIONS

A saturated fluid state may be described mathematically by Eqs. 4 through 8, a *saturation pressure equation*, and simplifications of the *over-all* and *component material balances*.

SATURATED LIQUID

A saturated liquid exists, for a given temperature, at the pressure at which an infinitesimal amount of vapor first appears. This pressure is referred to as the bubble-point pressure. Based on this definition, the *over-all material balance* for a saturated liquid is simply

$$L = 1, \dots \dots \dots (9)$$

and the *component material balances* are

$$x_i = z_i ; 1 \leq i \leq n \dots \dots \dots (10)$$

The *restrictive equation* on the liquid-phase compositions is redundant because, by definition, the fluid mixture compositions, z_i , add up to unity. The saturation (bubble-point) pressure is related to the *component fugacities* in the liquid phase and the *component fugacity coefficients* in the vapor phase by

$$p_s = \sum_{i=1}^n \frac{f_{iL}}{\psi_{iV}} \dots \dots \dots (11)$$

where the component fugacity coefficient in the vapor phase is defined as

$$\psi_{iV} = \frac{f_{iV}}{py_i} ; 1 \leq i \leq n \dots \dots \dots (12)$$

The *thermodynamic phase-equilibria equation* (Eq. 4) states that, for all components, the fugacity of each component in the liquid phase is equal to the fugacity of that component in the vapor phase when equilibrium is attained. Using these equations with Eqs. 11 and 12 shows that the vapor-phase compositions must equal unity at equilibrium for the system pressure, p , to equal the saturation pressure, p_s . During the iteration sequence for calculation of the saturation pressure, however, the vapor-phase compositions are not forced to equal unity. In general, the sum of these compositions is less than unity if the estimated pressure is low, and greater than unity if the pressure is high. Consequently, the *restrictive equation* on the vapor-phase compositions is not included in the set of saturation pressure equations.

SATURATED VAPOR

A saturated vapor exists for a given temperature at the pressure at which an infinitesimal amount of liquid first appears. This pressure is referred to as the dew-point pressure. Using logic similar to that for developing the saturated liquid equations, equations can be developed for a saturated vapor.

DESCRIPTION OF MVNR METHODS

To introduce MVNR methods, consider the single-stage separation equations, Eqs. 1 through 4, 7, and 8. These equations constitute a set of $(4n + 2)$ equations that are to be solved simultaneously to determine L , V , and n liquid-phase compositions, x_i , n vapor-phase compositions, y_i , n liquid-phase fugacities, f_{iL} , and n vapor-phase fugacities, f_{iV} . The solution must be iterative because the equations are nonlinear.

There are numerous methods for organizing the iterative sequence. At one extreme, it would be possible to correct all $(4n + 2)$ unknowns at each iteration. A more efficient method, however, is called minimum variable Newton-Raphson (MVNR), which reduces the size of the correction step by eliminating as many unknowns as possible from the correction step.³ This is done by dividing the unknown variables into two groups. The first group contains the *iteration* (independent) variables that are the unknowns to be corrected. The second group contains the *dependent* variables. One equation must be used to define each dependent variable, and the collection of these equations is referred to as the *defining equations*. The remaining equations (equal in number to the number of iteration variables)

are called the *error equations*. The iteration sequence for MVNR then will be a four-step process. The four steps are (1) select the *iteration variables* and assume values for these variables. (2) use the *defining equations* to calculate the *dependent variables*, (3) use the *error equations* to calculate the error, and (4) use the Newton-Raphson method to correct the *iteration variables*. This process is repeated until the error calculated in Step 3 is less than a small error tolerance, ϵ , which corresponds to a converged solution.

The methods have been defined as a four-step process. The development of MVNR is presented step-by-step for two-phase calculations and for saturation pressure determination.

SELECTION OF ITERATION VARIABLES

Two-Phase Fluids

Two sets of iteration variables that satisfy the MVNR criteria are (1) L and $(n - 1)$ liquid-phase compositions, x_j , and (2) V and $(n - 1)$ vapor-phase compositions, y_j . MVNR that uses the first set will be referred to as the L - X iteration, and MVNR that uses the second set will be referred to as the V - Y iteration. The L - X iteration is used for a fluid system that is predominantly vapor and the V - Y iteration is used for a fluid system that is predominantly liquid. The section entitled "Example Problems" demonstrates the necessity and mechanics for using two iterations — that is, L - X and V - Y iterations.

Initial estimates of the iteration variables are required. Generally, the phase distribution as a function of pressure between the saturation pressure, p_s , and a given pressure, p , must be calculated. Therefore, the procedure is to calculate the saturation pressure followed by two-phase calculations for the given pressure range. Assuming the saturation pressure is known, the following method is used to obtain initial estimates for the L - X and V - Y iterations. For the first two-phase calculation using an L - X iteration (dew-point fluid), the initial values are $L = 0$ and the $n-1$ liquid-phase compositions, x_j , determined by the dew-point calculation. For the V - Y iteration (bubble-point fluid), the initial values of the iteration variables are $V = 0$ and the $n - 1$ vapor-phase compositions, y_j , determined by the bubble-point calculation. For each successive pressure, the initial estimates of the iteration variables are the values of these variables calculated at the previous pressure.

Saturation Pressure

Bubble-Point Liquid. Eqs. 4, 7, 8, and 11 constitute a set of $(3n + 1)$ equations that are to be solved simultaneously to determine the bubble-point pressure, p_s , n vapor-phase compositions, y_i , n liquid-phase fugacities, f_{iL} , and n vapor-phase fugacities, f_{iV} . The number of iteration variables required by MVNR is $n + 1$; the pressure is p ; and n vapor-phase compositions is y_i . MVNR using this set of iteration variables is called the p - Y

iteration.

Dew-Point Vapor. The saturation pressure equations for a dew-point fluid also constitute a set of $(3n + 1)$ equations that are to be solved simultaneously to determine the dew-point pressure, p_s ; n liquid-phase compositions, x_i ; n liquid-phase fugacities, f_{iL} ; and n vapor-phase fugacities, f_{iV} . Similar to MVNR for bubble-point liquids, the number of iteration variables is $n + 1$; the pressure is p , and n liquid-phase compositions is x_i . MVNR using this set of iteration variables is called the p - X iteration.

Initial Estimates of Iteration Variables. Initial estimates of p and y_i for the p - Y iteration and of p and x_i for the p - X iteration are required. Our experience has shown that component K values calculated by the empirical relation⁴

$$K_i = \frac{\exp\{5.37(1+\omega_i)(1-1/T_{ri})\}}{p_{ri}}; \quad 1 \leq i \leq n, \quad (13)$$

can be used to flash the over-all fluid mixture at the system temperature and an estimated saturation pressure. The flash calculations result in liquid and vapor compositions. Depending on the iteration used (p - X or p - Y), the appropriate phase compositions are used as initial estimates of the iteration variables, x_i or y_i . The other phase composition is equal to the composition of the fluid mixture (Eq. 10).

DEFINING EQUATIONS

The second step of MVNR is to solve the defining equations for the dependent variables.

V - Y Iteration Steps

1. Values for the iteration variables V , y_2 , y_3, \dots, y_n , are available.
2. The *total hydrocarbon mole balance* (Eq. 1) is used to calculate L .
3. The *restrictive equation* on the vapor-phase compositions (Eq. 3b) is used to calculate the composition of the first component in the vapor phase, y_1 .
4. The *component mole balance* (Eq. 2) is used n times to calculate x_1, x_2, \dots, x_n .
5. The hydrocarbon-phase compressibility factors, Z_L and Z_V , are calculated by solving the Redlich-Kwong equation of state (Eqs. 5 and 6).
6. Eq. 7 is used n times to calculate the component fugacities, f_{iL} , in the liquid phase. Eq. 8 is used n times to calculate the component fugacities, f_{iV} , in the vapor phase.

L - X Iteration

The steps outlined for the V - Y iteration are applicable to the L - X iteration if L , V , x_i , and y_i are interchanged. In addition, Eq. 3b is replaced with Eq. 3a.

p-Y and p-X Iterations

Steps 5 and 6 of the V-Y iteration outline the defining equations for these iterations. Fewer defining equations are required by these iterations than required by the L-X and V-Y iterations because of the lesser total number of unknowns.

ERROR DETERMINATION

The error equations are the equations remaining after selection of the defining equations.

L-X and V-Y Iterations

A review of Paragraphs 1 and 2 in Section 3 (V-Y and L-X iterations), and Eqs. 1 through 8 shows that Eq. 4 has not been included as a defining equation. There are n of these equations and there are n iteration variables.

The error equations, which represent the residual of the thermodynamic phase equilibria equation (Eq. 4) can be written as

$$\phi_i = f_{iL} - f_{iV} ; 1 \leq i \leq n \quad (14)$$

These equations are evaluated. If the Euclidean norm of the ϕ_i 's,

$$\sqrt{\sum_{i=1}^n \phi_i^2},$$

is less than the error tolerance, the iterative sequence ends. If not, the iteration variables are corrected by the methods outlined in Section D.

p-Y and p-X Iterations

For the p-Y iteration, there are $n + 1$ iteration variables. Eq. 14 represents n error equations, and the remaining error equation is the residual of Eq. 11, which can be written as

$$\phi_{n+1} = p_s - \sum_{i=1}^n \frac{f_{iL}}{\psi_{iV}} \quad (15)$$

Similarly, the additional error equation for the p-X iteration is

$$\phi_{n+1} = p_s - \sum_{i=1}^n \frac{f_{iV}}{\psi_{iL}} \quad (16)$$

THE CORRECTION STEP

The purpose of the correction step is to obtain improved estimates of the iteration variables that, in turn, will reduce the residuals calculated by the appropriate error equations. The correction step reduces to a matrix problem with an order directly proportional to the number of components, n , for the L-X and V-Y iterations and proportional to $n + 1$ for the p-X and p-Y iterations.

V-Y Iteration

Consider the V-Y iteration for a two-phase fluid that is predominantly vapor. If \vec{R} is defined as a vector, $(V, y_2, y_3, \dots, y_n)^T$ and $\vec{\Phi}$ as the error vector, $(\phi_1, \phi_2, \dots, \phi_n)^T$, then a linear correction algorithm can be written as

$$J^q \{\vec{R}^{q+1} - \vec{R}^q\} = -\vec{\Phi}^q, \dots \quad (17)$$

where the superscript q indicates the quantity is evaluated using known values from iteration q . This set of simultaneous linear equations is solved for the elements of \vec{R}^{q+1} , which are the values of the iteration variables used in the next iteration. Quadratic convergence of Eq. 17 near the solution is obtained when J is the Jacobian matrix, defined as the matrix in which each element is the partial derivative of one of the errors with respect to one iteration variable when all other iteration variables are constant.

The elements of J for the V-Y iteration are defined by the following equations.

$$j_{i1} = \frac{\partial \phi_i}{\partial V} ; 1 \leq i \leq n, \dots \quad (18)$$

$$j_{ij} = \frac{\partial \phi_i}{\partial y_j} ; 1 \leq i \leq n, 2 \leq j \leq n \dots \quad (19)$$

The analytical expressions for the derivatives in Eqs. 18 and 19 can be obtained by differentiating the defining equations (Eqs. 1, 2, and 3) with respect to the iteration variables (see Appendix B). The resulting equations then are used during the implicit differentiation of the error equations. The elements of J are

$$j_{i1} = \frac{\partial \phi_i}{\partial V} = -\frac{1}{L} \sum_{j=2}^n \frac{\partial f_{iL}}{\partial x_j} (y_j - x_j) ; 1 \leq i \leq n \quad (20)$$

$$j_{ij} = \frac{\partial \phi_i}{\partial y_j} = -\frac{V}{L} \frac{\partial f_{iL}}{\partial x_j} - \frac{\partial f_{iV}}{\partial y_j} ; 1 \leq i \leq n, 2 \leq j \leq n \quad (21)$$

Analytical expressions for $\partial f_{iL}/\partial x_j$ and $\partial f_{iV}/\partial y_j$ can be developed by differentiating Eqs. 7 and 8 with respect to x_j and y_j , respectively.

The elements of the Jacobian matrix, J , for L-X, p-Y, and p-X iterations are given in Appendix C.

EXAMPLE PROBLEMS

CO₂-HYDROCARBON SYSTEM

The prediction of reservoir performance of

multiple-contact, miscible oil recovery methods with either CO_2 or rich-gas injection requires an understanding of the transition zone that exists between the in-place oil and the injected gas. It commonly is accepted that near-critical fluid mixtures exist within a small region of this transition zone. The experimental program required to obtain phase-equilibria data for this region is laborious and expensive. The alternate approach is to minimize the experimental program and adjust the parameters of an equation of state so that it can be used for the phase-equilibria calculations.

The first problem considers the calculation of the saturation envelope for the CO_2 - $n\text{C}_4$ - C_{10} fluid system at 1,600 psia and 160°F using the Redlich-Kwong equation of state. Comparison of the envelopes calculated by MVNR methods with the method of successive substitutions is made.

Fig. 2 presents the saturation envelope as calculated by the method of successive substitutions. The saturated (bubble-point) liquid and the saturated (dew-point) vapor curves should continue to close on each other as the over-all mixture becomes richer in $n\text{C}_4$ and the intersection should be the critical mixture at these conditions. Instead, the curves move away from each other near the critical region. This implies that in this region, either the equation of state errs or the method of successive substitutions fails to converge. The investigation of this behavior was the principal reason for developing MVNR methods.

Fig. 3 presents the saturation envelope for this simple fluid system at 1,600 psi and 160°F as calculated by MVNR methods. For comparison, the calculated saturation curves presented in Fig. 2 also are included in Fig. 3. The saturation curves calculated by MVNR methods continue to close on each other as the over-all mixture becomes richer in $n\text{C}_4$. In other words, MVNR converged for near-critical mixtures. The Euclidean norms for Point A of Fig. 3 are given in Table 1. These norms show that MVNR converged quadratically near the solution.

TABLE 1 — EUCLIDEAN NORMS FOR MIXTURE A USING MVNR

Iteration Number	Euclidean Norm
0	5.94
1	1.45
2	0.283
3	0.110
4	0.0651
5	0.0359
6	0.0022
7	8×10^{-8}

TABLE 2 — RESERVOIR OIL COMPOSITION

Component	Mole Fraction
N_2	0.00808
C_1	0.5699
CO_2	0.01501
C_2	0.12714
C_3	0.07596
$i\text{C}_4$	0.01075
$n\text{C}_4$	0.03055
$i\text{C}_5$	0.00849
$n\text{C}_5$	0.01074
C_6	0.01272
180 BP*	0.01716
230 BP	0.01764
280 BP	0.01416
330 BP	0.01115
380 BP	0.07055

*BP represents boiling-point fractions of the C_7+ .

The results clearly demonstrate that phase equilibria as calculated by the equation of state are physically realistic, which lends confidence to adjusting the parameters so that the equation of state matches experimental data.

MULTICOMPONENT RESERVOIR OIL

Saturation-pressure and phase-equilibria calculations in the two-phase region using MVNR are demonstrated in the second example problem. Reservoir fluid composition is given in Table 2 and the temperature is 235°F.

Fig. 4 presents the calculated phase distribution between the calculated saturation pressure (4,952 psia) and 4,500 psia. The program required 10

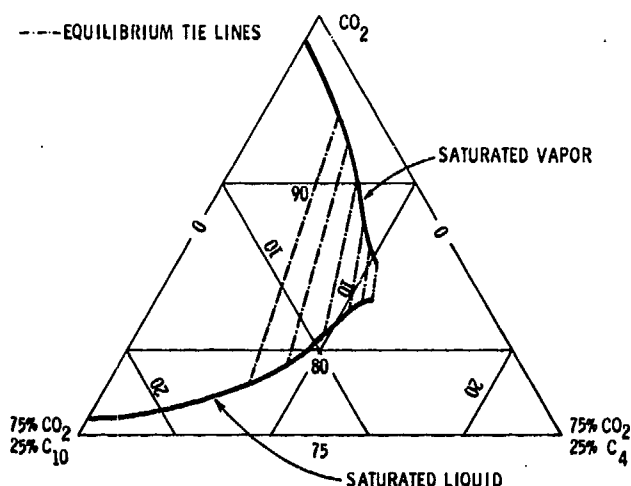


FIG. 2 — CALCULATED PHASE EQUILIBRIA BY SUCCESSIVE SUBSTITUTION, CO_2 - $n\text{C}_4$ - C_{10} FLUID SYSTEM AT 1,600 PSIA AND 160°F.

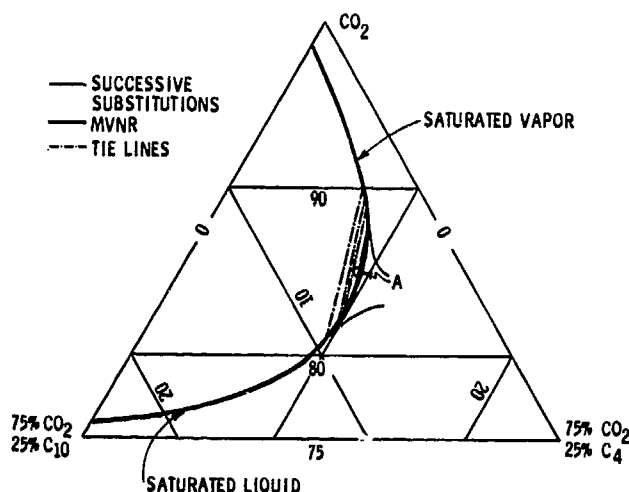


FIG. 3 — COMPARISON OF SOLUTION METHODS AND CALCULATED PHASE-EQUILIBRIA FOR CO_2 - $n\text{C}_4$ - C_{10} FLUID SYSTEM AT 1,600 PSIA AND 160°F.

iterations to calculate the saturation pressure. The Euclidean norm as a function of the iteration number is presented in Table 3. Quadratic convergence was obtained near the solution. Two-phase calculations for the results presented in Fig. 4 each required four or five iterations. The Euclidean norm as a function of iteration number for the calculations at 4,950 psia is presented in Table 3. Quadratic convergence was obtained near the solution. MVNR methods required a total of 52 iterations to calculate the saturation pressure and the phase equilibria at 10 pressures (Fig. 4).

The method of successive substitutions also was used to calculate the phase equilibria presented in Fig. 4. The program allowed 100 iterations per solution. At all pressures, the Euclidean norm exceeded the specified tolerance of 10^{-6} after 100 iterations. However, the calculated mole fraction of liquid, L , as a function of pressure, agreed within 0.001 of the values calculated by MVNR methods. Table 3 presents the Euclidean norm for the first 10 iterations of the method of successive substitutions at 4,950 psia and the error norm after 100 iterations. Note that the norm was reduced to only 0.07. The method of successive substitutions required a total of 1,000 iterations to calculate the phase equilibria presented in Fig. 4. This did not include a saturation-pressure calculation.

For this example, MVNR methods required approximately 10^{-5} CPU second/component/iteration and the total CPU time, compared with the time required by the method of successive substitutions, was reduced by a factor of seven. MVNR methods actually performed more calculations because the saturation pressure and the two-phase calculations were calculated. This clearly demonstrates the computational advantage of MVNR methods.

The convergence of MVNR methods depends on the proper choice of iteration variables as discussed in the section entitled, "Description of

MVNR Methods." For two-phase fluids, either the L - X or V - Y iteration is used. The L - X iteration is used for a fluid that is predominantly vapor ($L < V$), while the V - Y iteration is used for a fluid mixture that is predominantly liquid ($L > V$). Therefore, the V - Y iteration was used to calculate the results in Fig. 4. To demonstrate the effect of improper selection of iteration variables, the phase equilibria in Fig. 4 was calculated using only the L - X iteration. (The calculations began at 4,500 psia, not at the saturation pressure.) The results were identical to those in Fig. 4, up to and including 4,850 psia. The L - X iteration required two additional iterations at 4,900 psia, but did converge. At 4,950 psia, the L - X iteration diverged. The decision to switch iteration variables based on the "predominant phase" is arbitrary as demonstrated by these results because L was much larger than V before convergence occurred. However, this method of selecting iteration variables is successful.

CONCLUSIONS

Iteration sequences, referred to as minimum variable Newton-Raphson (MVNR) methods, were developed for calculating the phase equilibria in the two-phase region and the saturation pressure of a multicomponent fluid mixture. The phase-equilibria equations used for these calculations incorporate the Redlich-Kwong equation of state. This study presents results for a multicomponent fluid mixture that demonstrate the following conclusions.

1. MVNR methods can be used to calculate phase equilibria of CO_2 and rich-gas, multiple-contact, miscible oil recovery methods because these methods converge for near-critical fluid mixtures. The method of successive substitutions diverges for these mixtures.

2. MVNR methods exhibit quadratic convergence for phase-equilibria calculations in the two-phase region. The success of these calculations depends on the proper selection of iteration variables. A successful selection procedure is given.

3. MVNR methods converge quadratically for

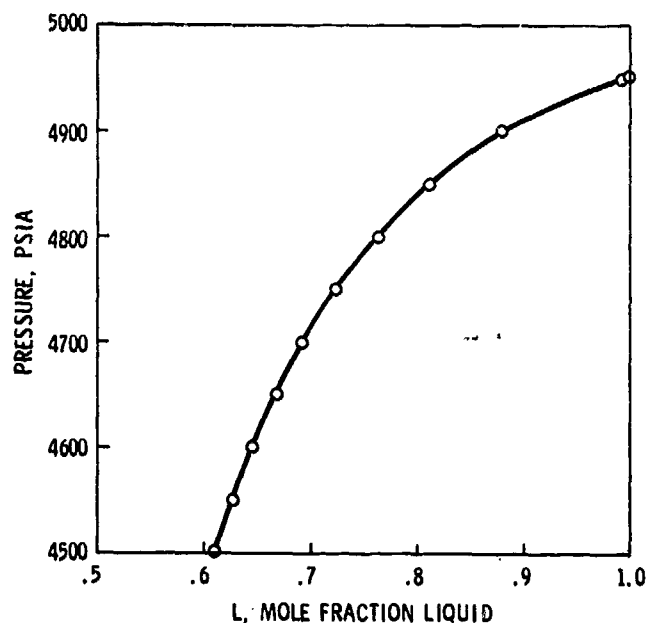


FIG. 4 — LIQUID MOLE FRACTION VS PRESSURE/RESERVOIR-OIL SYSTEM.

TABLE 3 — EUCLIDEAN NORMS, RESERVOIR OIL PHASE-EQUILIBRIA CALCULATIONS

Iteration Number	MVNR Methods		Method of Successive Substitutions
	Saturation Pressure	Two-Phase at 4,950 psia	Two-Phase at 4,950 psia
0	240.6	3.28	3.3
1	48.3	0.99	3.08
2	5.67	0.13	2.91
3	1.71	0.0025	2.78
4	1.32	$6. \times 10^{-7}$	2.62
5	0.81		2.48
6	0.43		2.36
7	0.136		2.24
8	0.0126		2.14
9	$9. \times 10^{-5}$		2.03
10	$4. \times 10^{-9}$		1.94
.	.	.	.
.	.	.	.
.	.	.	.
100			0.07

saturation-pressure calculations.

4. MVNR methods are more economical, based on computer cost, than the method of successive substitutions.

NOMENCLATURE

- a = temperature, pressure, and composition-dependent component parameter
 A = temperature, pressure, and composition-dependent phase parameter
 b = temperature, pressure, and composition-dependent component parameter
 B = temperature, pressure, and composition-dependent phase parameter
 C_{ij} = interaction parameter for component i with component j
 f_{iL} = fugacity of component i in the liquid phase, psia
 f_{iV} = fugacity of component i in the vapor phase, psia
 j = elements of Jacobian correction matrix, \mathcal{J}
 \mathcal{J} = Jacobian correction matrix
 K_i = equilibrium ratio, $K_i = y_i/x_i$
 L = mole fraction of liquid phase, mol liquid/mol fluid
 n = number of components in the fluid system
 p = pressure, psia
 p_r = reduced pressure
 R = gas constant
 \vec{R} = iteration variable vector
 T = system temperature, °R
 T_r = reduced temperature
 u_i = exponent in Eq. 7, $A_L(2a_{iL} - b_{iL})/B_L$
 v = phase molar volume
 V = mole fraction of vapor phase, mol vapor/mol fluid
 w_i = exponent in Eq. 8, $A_V(2a_{iV} - b_{iV})/B_V$
 x_i = mole fraction of component i in the liquid phase, mol i /mol liquid
 y_i = mole fraction of component i in the vapor phase, mol i /mol vapor
 z_i = mole fraction of component i in the fluid, mol i /mol fluid
 Z = phase compressibility factor
 a_{ij} = temperature and pressure-dependent component parameter
 β_i = temperature and pressure-dependent component parameter
 δ_{ij} = Kronecher δ function; $\delta_{ij} = 0$ for $i \neq j$, $\delta_{ij} = 1$ for $i = j$
 ϵ = error tolerance for the Euclidean norm
 ϕ = error equation for MVNR
 $\vec{\phi}$ = error vector for MVNR
 ψ = component fugacity coefficient
 ω = Pitzer acentric factor

Ω_a, Ω_b = generalized component parameters — function of the reduced temperature and Pitzer acentric factor for a component

SUBSCRIPTS

- i = component number
 j = component number
 L = liquid phase
 s = saturation pressure
 V = vapor phase

SUPERSCRIPTS

- q = iteration number
 T = transpose of a vector

REFERENCES

1. Redlich, O. and Kwong, J. N. S.: *Chem. Rev.* 44 (1949) 233.
2. Zudkevitch, David and Joffe, Joseph: "Correlation and Prediction of Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State," *AIChE Joun.* (Jan. 1970) Vol. 16, No. 1, 112-119.
3. Soave, Giorgio: "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.* (1972) Vol. 27, 1197-1203.
4. Bruno, J. A., Yanosik, J. L., and Tierney, J. W.: "Distillation Calculations with Nonideal Mixtures," *Extractive and Azeotropic Distillation*, Advances in Chemistry Series 115, ACS, Washington, D. C. (1972).
5. Wilson, Grant, M.: "A Modified Redlich-Kwong Equation of State, Application to General Physical Data Calculations," paper No. 15C presented at the AIChE 65th National Meeting, Cleveland, Ohio, May 4-7, 1969.

APPENDIX A

REDLICH-KWONG EQUATION OF STATE

The Redlich-Kwong equation of state (Eqs. 5 and 6) and the parameters for this equation are presented as follows.

The liquid phase,

$$Z_L^3 - Z_L^2 + Z_L[A_L - B_L(B_L + 1)] - A_L B_L = 0, \dots \dots \dots (A-1)$$

Vapor phase,

$$Z_V^3 - Z_V^2 + Z_V[A_V - B_V(B_V + 1)] - A_V B_V = 0, \dots \dots \dots (A-2)$$

and parameters are

$$A_L = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}, \dots \dots \dots (A-3)$$

$$A_V = \sum_{i=1}^n \sum_{j=1}^n y_i y_j a_{ij}, \dots \dots \dots (A-4)$$

$$a_{iL} = \frac{1}{A_L} \sum_{j=1}^n x_j \alpha_{ij} \quad \dots \dots \dots (A-5)$$

$$a_{iV} = \frac{1}{A_V} \sum_{j=1}^n y_j \alpha_{ij} \quad \dots \dots \dots (A-6)$$

$$B_\Omega = \sum_{i=1}^n x_i \beta_i \quad \dots \dots \dots (A-7)$$

$$B_V = \sum_{i=1}^n y_i \beta_i \quad \dots \dots \dots (A-8)$$

$$b_{iL} = \frac{\beta_i}{B_L} \quad \dots \dots \dots (A-9)$$

$$b_{iV} = \frac{\beta_i}{B_V} \quad \dots \dots \dots (A-10)$$

$$\alpha_{ij} = \alpha_{ji}$$

$$= (1 - C_{ij}) \left\{ \frac{\Omega_{ai}^{pr} r_i}{T_{ri}^{2.5}} \frac{\Omega_{aj}^{pr} r_j}{T_{rj}^{2.5}} \right\}^{1/2}$$

$$\dots \dots \dots (A-11)$$

$$\beta_i = \frac{\Omega_{bi}^{pr} r_i}{T_{ri}} \quad \dots \dots \dots (A-12)$$

The parameters α_{ij} and β_i are independent of composition so derivatives of these parameters with respect to x_j and y_j are zero. The component parameters Ω_{ai} and Ω_{bi} are independent of pressure and composition so derivatives of these parameters with respect to x_j , y_j , or p are zero. The component interaction parameters, C_{ij} , are constant.

APPENDIX B

DERIVATIVES OF DEFINING EQUATIONS

From the over-all material balance,

$$\frac{\partial L}{\partial V} = -1 \quad \dots \dots \dots (B-1)$$

Because y_2, y_3, \dots, y_n are iteration variables, the restrictive equation on the liquid-phase composition is used to obtain derivatives of y_i with respect to y_j as

$$\frac{\partial y_i}{\partial y_j} = \delta_{ij} \quad ; \quad 2 \leq i, j \leq n, \quad \dots \dots \dots (B-2)$$

and

$$\frac{\partial y_1}{\partial y_j} = -1 \quad ; \quad 2 \leq j \leq n \quad \dots \dots \dots (B-3)$$

Differentiating the component material balances with respect to the independent liquid-phase compositions gives

$$\frac{\partial x_i}{\partial y_j} = -\frac{V}{L} \delta_{ij} \quad ; \quad 2 \leq i, j \leq n \quad \dots \dots \dots (B-4)$$

Differentiating these equations with respect to L gives

$$\frac{\partial x_i}{\partial V} = \frac{x_i - y_i}{L} \quad ; \quad 1 \leq i \leq n \quad \dots \dots \dots (B-5)$$

APPENDIX C

ELEMENTS OF J : L - X , p - Y , AND p - X ITERATIONS

L - X ITERATION

$$j_{i1} = \frac{\partial \phi_i}{\partial L} = -\frac{1}{V} \sum_{j=2}^n \frac{\partial f_{iV}}{\partial y_j} (y_j - x_j) \quad ;$$

$$1 \leq i \leq n \quad \dots \dots \dots (C-1)$$

$$j_{ij} = \frac{\partial \phi_i}{\partial x_j} = \frac{\partial f_{iL}}{\partial x} + \frac{L}{V} \frac{\partial f_{iV}}{\partial y_j} \quad ;$$

$$1 \leq i \leq n, \quad 2 \leq j \leq n \quad \dots \dots \dots (C-2)$$

p - Y ITERATION

$$j_{1,j} = \frac{\partial \phi_1}{\partial y_j} = -\frac{\partial f_{1V}}{\partial y_j} \quad ; \quad 1 \leq i, j \leq n, \quad \dots \dots \dots (C-3)$$

$$j_{1,n+1} = \frac{\partial \phi_1}{\partial p} = \frac{\partial f_{1L}}{\partial p} - \frac{\partial f_{1V}}{\partial p} \quad ; \quad 1 \leq i \leq n$$

$$\dots \dots \dots (C-4)$$

$$j_{n+1,j} = \frac{\partial \phi_{n+1}}{\partial y_j}$$

$$= -\frac{f_{jL}^p}{f_{jV}^p} + \sum_{i=1}^n \left\{ \frac{f_{iL}^{py} y_i}{f_{iV}^2} \frac{\partial f_{iV}}{\partial y_j} \right\} \quad ; \quad 1 \leq j \leq n,$$

$$\dots \dots \dots (C-5)$$

$$j_{n+1,n+1} = \frac{\partial \phi_{n+1}}{\partial p}$$

$$= 1 - \sum_{i=1}^n \left\{ \frac{p y_i}{f_{iV}} \left| \frac{\partial f_{iL}}{\partial p} + \frac{f_{iL}}{p} - \frac{f_{iL}}{f_{iV}} \frac{\partial f_{iV}}{\partial p} \right| \right\}$$

..... (C-6)

p-X ITERATION

$$j_{i,j} = \frac{\partial \phi_i}{\partial x_j} = \frac{\partial f_{iL}}{\partial x_j} ; 1 \leq i, j \leq n, \dots (C-7)$$

$$j_{i,n+1} = \frac{\partial \phi_i}{\partial p} = \frac{\partial f_{iL}}{\partial p} - \frac{\partial f_{iV}}{\partial p} ; 1 \leq i \leq n,$$

..... (C-8)

$$j_{n+1,j} = \frac{\partial \phi_{n+1}}{\partial x_j}$$

$$= - \frac{f_{jV} p}{f_{jL}} + \sum_{i=1}^n \left\{ \frac{f_{iV} p x_i}{f_{iL}^2} \frac{\partial f_{iL}}{\partial x_j} \right\} ; 1 \leq j \leq n,$$

..... (C-9)

$$j_{n+1,n+1} = \frac{\partial \phi_{n+1}}{\partial p}$$

$$= 1 - \sum_{i=1}^n \left\{ \frac{p x_i}{f_{iV}} \left| \frac{\partial f_{iV}}{\partial p} + \frac{f_{iV}}{p} - \frac{f_{iV}}{f_{iL}} \frac{\partial f_{iL}}{\partial p} \right| \right\}$$

..... (C-10)
