The Calculation of Density by the BWRS Equation of State In Process Simulation Contexts

The requirements of thermodynamic data predictors in process simulation applications are especially rigorous. The calculation of vapor and liquid density by the Benedict, Webb, Rubin, Starling equation of state has been reformulated to better satisfy these requirements; the necessary mathematical and programming techniques have been developed and are presented here. The resulting algorithm is believed superior for process simulation purposes.

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SCOPE

During the development of subroutines for predicting thermodynamic properties by the BWRS equation of state for use in a process simulation application, published methods for the calculation of density were examined. Each exhibited one or more inadequacies for the purpose, such as: excessive computer time consumption, occasional failure to reach convergence, occasional selection of an improper solution and prediction of density values which may be discontinuous with respect to continuous change in one or more of the independent variables.

A new strategy has been devised which does not exhibit the last three inadequacies, and methods which implement it efficiently have been developed.

The resulting subroutine has been tested with complete success on mixtures and at conditions which were known to be problematical for previously published algorithms. Incorporated in a process simulation program, the subroutine has been used for simulations of natural gas purification and liquefaction systems and for various ethylene plant applications. In all cases, it has proven to be efficient and reliable.

While development and verification have been limited to the BWRS equation of state, we believe that the proposed strategy and methods are applicable to all situations where any single equation of state is used for density of both phases, and its pressure-density isotherms have the same general form.

CONCLUSIONS AND SIGNIFICANCE

For single-phase mixtures which are at equilibrium, or are superheated or subcooled, the newly proposed algorithm converges to the proper BWRS density within given accuracy in fewer iterations than most methods proposed previously. For mixtures which are two-phase according to the equation of state, alternate values of density which are more appropriate to the process simulation context are produced. In all cases, the algorithm is essentially certain to converge to the prescribed density value.

Replacement of present subroutines for BWRS density in existing process simulation programs is advocated. This should markedly reduce the time necessary for calculation of equilibrium constants, enthalpies and entropies from this equation of state and effect a significant improvement in performance for any programs which utilize it.

Starling (1973) proposed modifications to the well-known equation of state developed by Benedict et al. (1940, 1942, 1951). In his work, three constants and a binary interaction parameter were added to the original eight-constant equation, and multiproperty regression was used on pure component data to obtain values for the required constants.The resulting equation, now generally known as the BWRS equation of state, was a substantial improvement on its already successful forerunner. Starling's work was extended by methods for regression utilizing equilibrium constant and enthalpy data for mixtures by Lin and Hopke (1973). Hopke and Lin (1974) then demonstrated successful applications of the BWRS equation of state with their resulting values for the required constants to natural gas processing, etc. Subsequently, a package of computer programs incorporating algorithms and values for the required constants (and predictors thereof) as developed by Hopke and Lin has been made available commercially (1974).

In an authoritative review of uses of equations of state, Adler (1977) reported that the BWR equation, and developments thereof, give excellent predictions of thermodynamic properties for light hydrocarbons over a broad range of conditions, and that the main problems with the equation have been the generation of values of the required constants and in computational difficulties imposed by the complexity of the equation. Since the authors had available to them the prediction algorithms developed by Lin and Hopke, the latter seemed the more serious problem for them.

Before any properties of use in process simulation such as equilibrium constants (K values), enthalpies, etc., can

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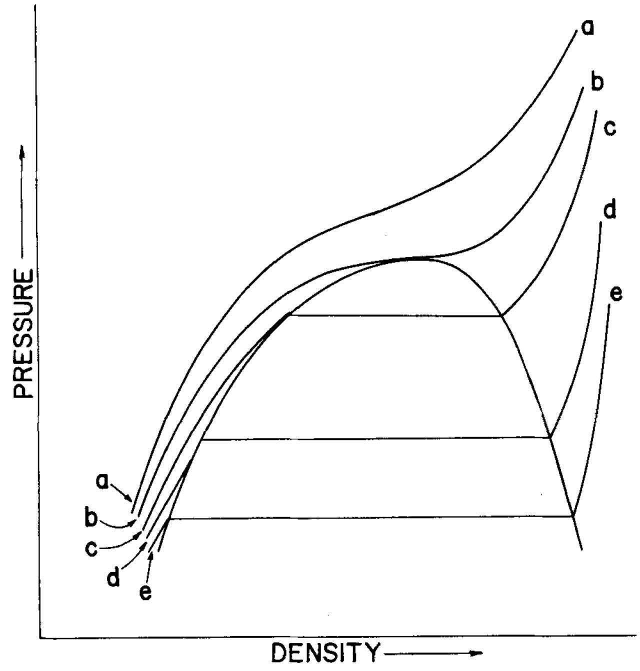

Fig. 1. Pressure-density behavior of a pure compound.

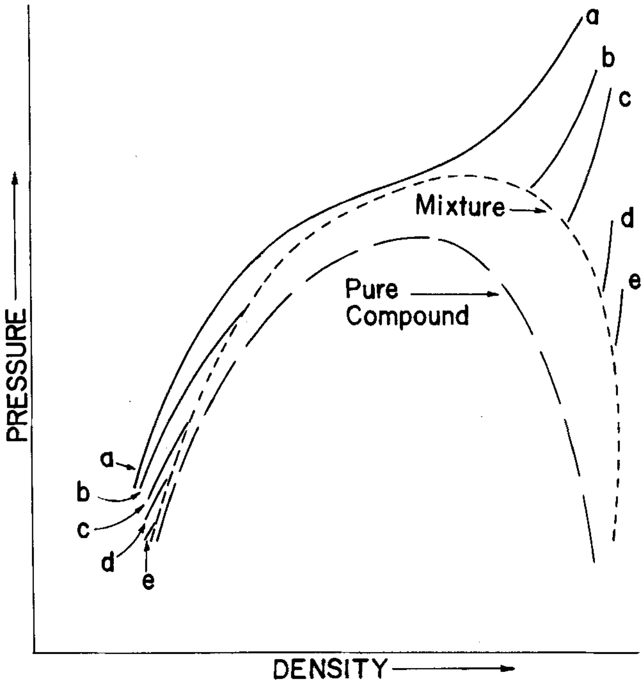

Fig. 2. Pressure-density behavior of a mixture of fixed composition.

be generated from the BWRS equation of state, it must first be solved for density. Figure 1 shows the density behavior of a pure compound. The area at the left is the vapor regime and at the right is the liquid regime. Between these two regions the familiar two-phase dome can be recognized. Isotherms at five decreasing temperatures are denoted *a*, b, c, d and e. Isotherm *a* is above the critical temperature of the compound, and isotherm b is at the critical temperature and therefore passes through the critical point at the peak of the dome, at which point the first and second derivatives of pressure with respect to density are zero. Isotherms c, d and e are at lower temperatures and enter the dome, emerging into the other regime at the same pressure level. Conventionally, dew point and bubble point pressures on these isotherms are connected by a horizontal line.

If other compounds are now added to the first, creating a mixture, the behavior changes, as has been described by Rowlinson (1969). The two-phase dome becomes larger and may change shape considerably. The critical point may no longer be at the peak of the dome, and since bubble point pressures for a normal mixture are higher than dew point pressures, the impingement of an isotherm on the liquid side of the dome occurs at a higher pressure than on the vapor side. There is still an isotherm on which the first and second derivatives become simultaneously zero (the quasicritical isotherm), but this point now occurs inside the two-phase dome. This situation for mixtures has been portrayed diagramatically in Figure 2 on which isotherms analogous to the previous *a*, b, etc., are shown. Notice that the outline of the mixture dome is for illustration purposes only and cannot be deduced from density behavior alone; its location can only be determined by means of equilibrium calculations.The dome from Figure 1 has no meaning for this mixture and is included only as a comparison to show the increased size of the mixture dome.

Since the BWRS equation has been devised as an analogue of this behavior, a resemblance between Figures 2 and 3, which shows the BWRS density predictions for the same isotherms, is not surprising. Notice, however, that the BWRS equation typically connects the isotherms through the two-phase region by sigmoid sections as shown for isotherms c and d. When the temperature is low enough, as in isotherm e, the simple sigmoid is replaced by more complex behavior with multiple maxima and minima.

Note that these isotherms can be intersected one, three or five times by a horizontal line, depending on the elevation of the line and the particular isotherm. The leftmost intersection is to be construed as representing the vapor density and the rightmost intersection as representing the liquid density. The other solutions have no physical significance, and their presence is a source of difficulty in obtaining the desired solutions.

The BWRS equation is explicit in pressure, not density, and therefore an iterative technique is necessary to com-

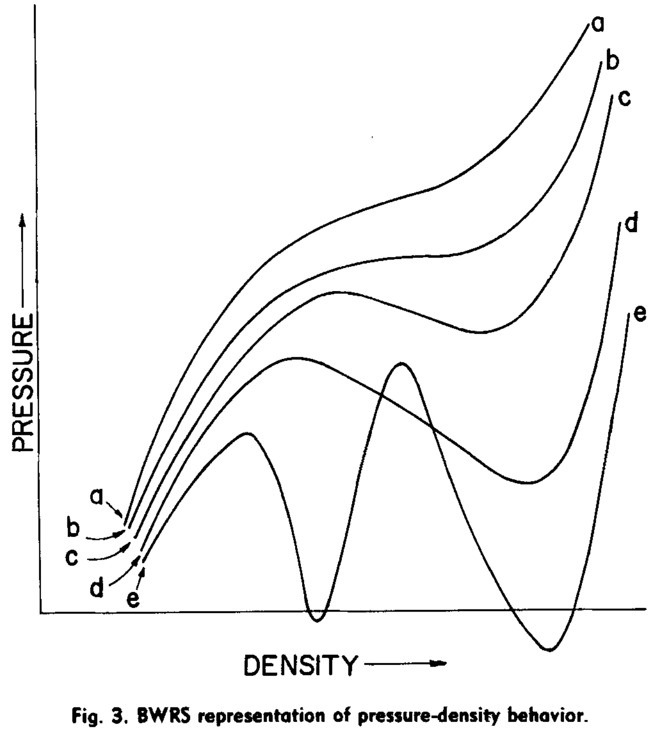

Fig. 3. BWRS representation of pressure-density behavior.

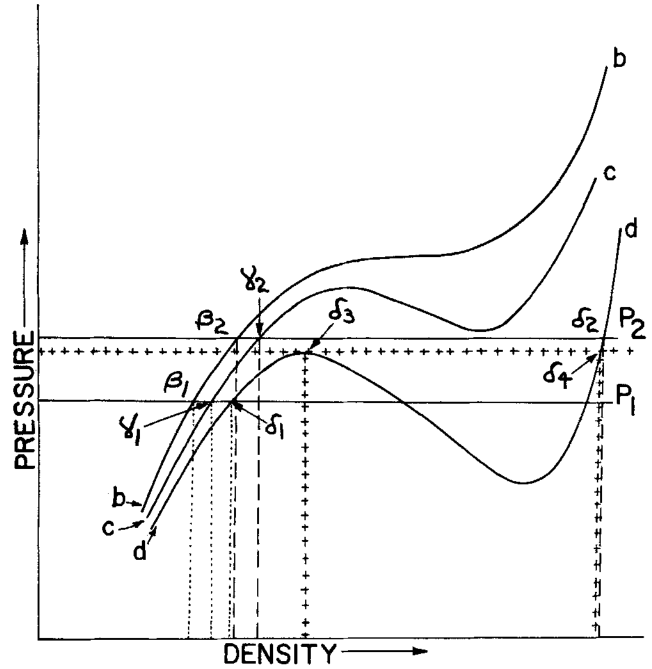

Fig. 4. Density predictions by the BWRS equation.

pute the density of a mixture. Several methods have been proposed. The well-known Newton-Raphson technique converges rapidly when only one root exists, that is, for all pressures on isotherms like *a* and for certain pressure ranges on most other isotherms. Whenever inflections or multiple roots exist, the Newton-Raphson technique may fail to converge, and, if it converges, the solution obtained will depend on the initial guess. Johnson and Colver (1968) proposed an incremental technique (that is, a stepping procedure). This method is reliable but usually needs a large number of iterations and thus consumes excessive computer time. Starling (1973) proposed using a Regula-Falsi method and following this by an incremental method whenever the Regula-Falsi failed to converge. This technique simply shifts the time penalty to those cases which initially fail and which are not necessarily unusual or infrequent cases. Plocker and Knapp (1976) recast the equation so as to eliminate some of the possible solutions and proposed a Newton-Raphson technique. Their method is fast, but it can provide results which are discontinuous when any two of temperature, pressure and composition are held constant and the third is varied continuously. This method may also yield undesired results when confronted with some of the more bizarre forms of BWRS density behavior, for example, isotherm e.

It was the intention of the authors to include data predictors using the BWRS equation of state into a process simulation program described by Schorsch and Newman (1974). It is everyday practice with this program to simulate complete refinery units, substantial sections of petrochemical plants, etc., as single problems requiring some tens of seconds on a CDC 7600 computer. The program has a high success rate and is considered resilient and reasonably tolerant of poor estimates, occasional data prediction failures, etc.; however, there is no doubt that traumatic events of more than a certain magnitude and frequency would cause serious deterioration in its performance. The density subroutine is the cornerstone of any package predicting thermodynamic properties from an equation of state. In view of the inadequacies of the published methods, the authors believed that development of a new algorithm would be justified if it could efficiently calculate values which were continuous throughout pressure-temperature-composition space.

COMPUTATIONAL STRATEGY

In Figure 4 three isotherms from Figure 3 are sketched, intersected by two horizontal lines representing system pressures P_1 and P_2. The densities at these two pressures are given by the perpendiculars dropped from points β_1, γ_1, δ_1 and β_2, γ_2, δ_2 (alternate solutions from isotherm d being ignored for the moment). It can be seen that the three densities at pressure P_1 are all close together, whereas at pressure P_2 the density on isotherm d is considerably displaced from the other two.

Suppose that the three isotherms correspond to vapor products from two modules operating at pressures P_1 and P_2 on three successive iterations of some simulation, the compositions having remained the same. The sequence of three densities calculated for the first module is quite natural, but the third iteration result for the module at pressure P_2 is likely to create a major disturbance to the simulation.

These discontinuities become even more apparent on a differential basis than on the finite difference basis used to represent module operation. At a pressure intermediate between P_1 and P_2, such that the horizontal (pressure) line is tangential to d at δ_3, the vapor density will flip flop between that at δ_3 and that at δ_4 for the smallest possible change in pressure, temperature or composition.

Consideration of Figures 1, 2, 3 and 4 reveals that the densities from points β_1, β_2, γ_1, γ_2 and δ_1 are vapor densities, but that δ_2 yields a liquid density, giving rise to the discontinuities. Such instances are not real world effects but artifacts of the sigmoid shape within the dome which occurs because the equation of state must provide two solutions for density in the two-phase region.

At the beginning of any simulation and for a substantial part of the computation, the compositions and conditions of the streams thereof may be radically at odds with the final converged values. During these initial iterations, the equation of state may very well be reflecting the real world accurately when it reports that no vapor density solution exists for a stream that the simulation program has computed as the vapor leaving some module, and that the stream must be a liquid at the purported module conditions. Nevertheless, a strategy will be proposed which has the effect of allowing the viewpoint of the simulation program to prevail when they disagree.

When the product of a module which has been assigned a vapor density on previous iterations is assigned a liquid density on the next iteration, the consequences for the enthalpy of the stream, and thus for other modules dependent on that enthalpy, are essentially analogous to a switch by the module from vapor to liquid in a single iteration. Module calculators in most simulation programs are prohibited from making such drastic changes in a single iteration because they are known to be destabilizing. The data generators must be similarly curbed if consistent success in process simulation is the objective.

We will now postulate that the maxima and minima associated with the sigmoid patterns occur only within the two-phase dome. While not absolutely correct, this assumption will hold whenever the equation of state constants for the mixture reasonably reflect the behavior of the real world, and this, after all, is the situation of greatest interest. It can then be held that, for any isotherm, the maximum that occurs at lowest density marks the upper limit of the isotherm for calculation of vapor density, and therefore no higher density can be predicted at any pressure for the mixture at that temperature. Likewise for liquids, the minimum that occurs at highest density on any isotherm marks the lower limit of the isotherm for calculation of liquid density. These tenets can be expressed in the form of a strategy for density, as follows:

Vapors: starting below the lowest possible density ($\rho = 0$), and moving towards higher density, report the density at whichever occurs first: an intersection by system pressure, or a maximum.

Liquids: starting above the highest possible density ($\rho = 32.0$ kg mole/m^3, has proved satisfactory), and moving to lower density, report density at whichever occurs first on the isotherm: an intersection by system pressure, or a minimum.

With reference to Figure 4, it can be seen that this strategy will produce densities for vapors at pressure P_2 represented by the verticals at β_2, γ_2 and δ_3, a result clearly superior to the one obtained previously in the absence of the strategy, when compared to the common results at pressure P_1, as denoted by the verticals at β_1, γ_1 and δ_1.

The behavior resulting from the strategy given above is depicted graphically in Figure 5, which shows the BWRS isotherms *a*, b, etc., from Figure 3. A dashed line connects the locus of leftmost maxima and terminates at the quasicritical point. A dotted line connects the locus of rightmost minima, terminating at the same point. Vapor density calculations are restricted to areas left of the dashed line or above the quasicritical isotherm b. Liquid density calculations are restricted to the areas right of the dotted line or above the quasicritical isotherm b. The dashed line thus delineates the maximum densities for vapors and the dotted line the minimum densities for liquids, which can be predicted for the isotherms of lower temperature.

For convenience, the leftmost maxima and the rightmost minima will hereafter be denoted collectively as L points. An L point is defined as the first occurrence of $\partial P/\partial p = 0$, when moving from $\rho = 0$ toward higher density, or from $\rho = 32$ toward lower density.

Provided that the assumption that sigmoid behavior is confined to the interior of the two-phase dome remains valid, the BWRS densities that are predicted will be genuine (BWRS densities) for vapor mixtures (both equilibrium and superheated) and for liquid mixtures (both equilibrium and subcooled. For two-phase mixtures, densities may or may not be genuine, but they will always be consistent with adjacent vapor densities when a vapor density is requested, or consistent with adjacent liquid densities when a liquid density is requested. The densities predicted will be continuous throughout, apart from the limited exceptions noted below.

The behavior of the density predicted by our strategy with changing pressure should already be apparent from Figure 5 and the preceding discussion. When this behavior is cross plotted against temperature, for vapors, Figure 6 results. It can be seen that a discontinuity of derivative occurs at the point where each isobar intersects the locus of densities at the L points because the density predictions are then forced to follow the L point locus (down and to the left). It could also be held that the trend while following the locus, for vapor density to decrease as temperature decreases, is contrary to the usual expectation. There remains, also, a residual discontinuity of value at the quasicritical temperature, between an isobar above the quasicritical pressure and isobars below that pressure.

The discontinuity of value, occurring at a known condition, can be circumvented by appropriate strategies in higher level algorithms computing further properties. The discontinuities of derivative, and subsequent reverse slope, occur well within the two-phase dome (provided the constants for the equation of state have the proper values). The way vapor density should behave, when vapor alone cannot exist, would appear open to a degree of arbitrary interpretation.

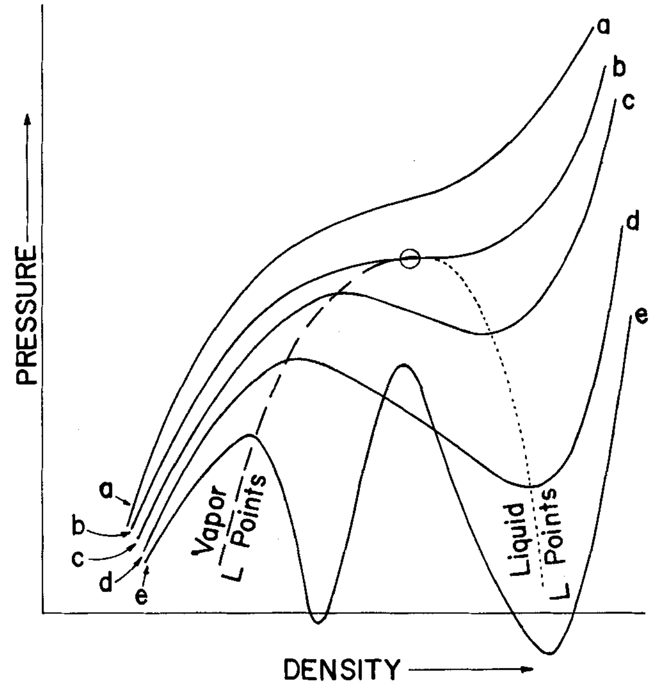

Fig. 5. BWRS representation of pressure-density behavior.

If the behavior of density, as predicted by a subroutine, with respect to the independent variables (temperature, pressure and composition) is known, and if the effects of this behavior on other variables which it may be used to predict (enthalpy, entropy, K values) are understood, then the subroutine for, say, calculating enthalpies can be programmed to accept L point densities or to reject them in favor of some other course, depending on the particular circumstances for that property. The density subroutine has merely to report the density resulting from the strategy, together with a flag to indicate whether this density is an L point density or a genuine BWRS density.

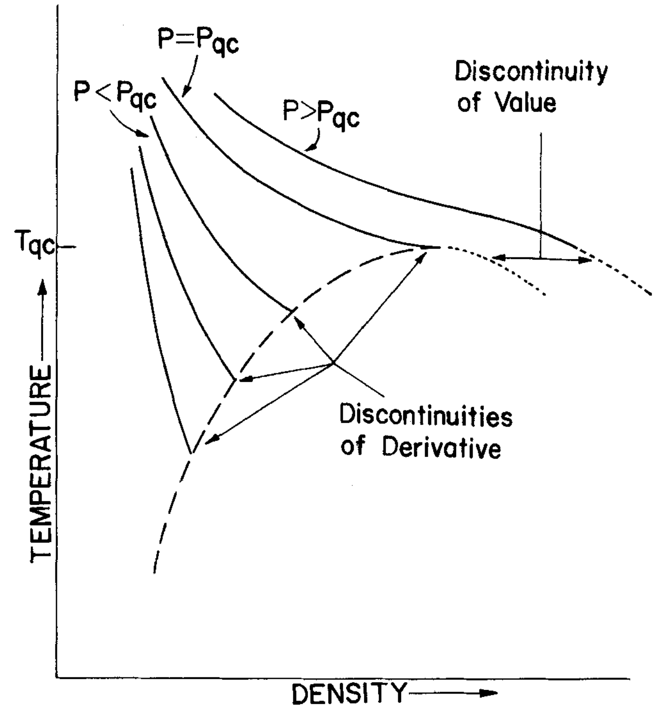

Fig. 6. Predicted behavior in temperature-density space for several isobars.

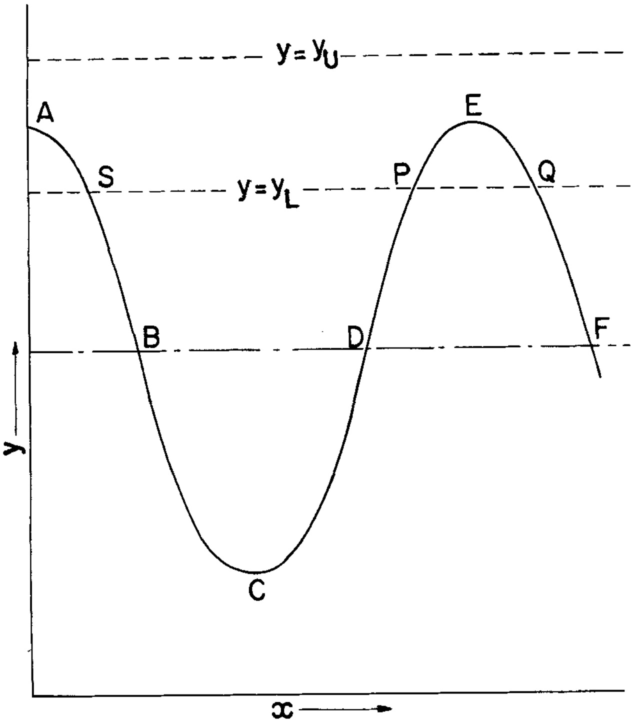

Fig. 7. A general periodic (sinelike) curve.

MATHEMATICAL METHODS AND PROGRAMMING TECHNIQUES

The strategy formulated in the previous section requires the computation of density at the first occurring of either L point or system pressure intersection. Any implementation which evaluates the density separately at both points is bound to be inefficient, particularly since an L point does not exist on all isotherms. Efficiency demands tactics whereby a simultaneous search can be made in a single convergence loop for the first occurring point. These tactics will be discussed in this section in terms of vapor density only, for reasons of clarity.Since the liquid case is essentially a mirror analogue, the minor modifications necessary should be self-evident.

Consider the general curve sketched as Figure 7. Regions A-B-C and E-F will be arbitrarily defined as having incorrect slope. Our strategy calls for the location of point P when the intersection of $y=y_L$ is required, and for the location of point E when the intersection of $y=y_u$ is required. It is assumed that a starting point within the region of correct slope C-D-E can always be found, and the direction of the initial move will be toward the right in Figure 7. It can therefore be stated that if a region of incorrect slope is encountered, this has happened because the convergence procedure has overstepped a maximum, and appropriate backtracking measures can be instituted.

When in the region of correct slope C-D-E, a prediction can be made of the point of intersection by the (second-order) Newton-Raphson method as

$$y^* = f(x) + f'(x)\,\Delta x + \tfrac{1}{2} f''(x)\,\Delta x^2 \qquad (1)$$

and thus

$$\Delta x = \frac{-f'(x) + \sqrt{f'(x)^2 - 2[f(x) - y^*]\,f''(x)}}{f''(x)} \qquad (2a)$$

$$\Delta x = \frac{-f'(x) - \sqrt{f'(x)^2 - 2[f(x) - y^*]\,f''(x)}}{f''(x)} \qquad (2b)$$

If we refer back to Figure 7, it is apparent that from the region D-E the dual prediction refers to the two points P and Q; from region C-D, the prediction is of the pair S and P. Note that in both cases the desired intersection by $y=y_L$, that is, point P, is included.

At this point the equations for a (first-order) Newton-Raphson prediction of the L point (maximum) can be stated. At the L point $f'(x)=0$, and thus

$$0 = f'(x) + f''(x)\,\Delta x \qquad (3)$$

Therefore

$$\Delta x = -\frac{f'(x)}{f''(x)} \qquad (4)$$

Equations (2) can be recast as

$$\Delta x = -\frac{f'(x)}{f''(x)} + \frac{\sqrt{f'(x)^2 - 2\,[f(x) - y^*]f''(x)}}{f''(x)} \qquad (5a)$$

$$\Delta x = -\frac{f'(x)}{f''(x)} - \frac{\sqrt{f'(x)^2 - 2\,[f(x) - y^*]f''(x)}}{f''(x)} \qquad (5b)$$

And thus it is apparent that the second-order Newton-Raphson prediction, in effect, combines a first-order prediction of an L point (that is, maximum or minimum) with consequent predictions of the intersections as parabolic deviations from this L point.

Now consider the intersection of the curve by $y=y_u$. In the region C-D all is as before, but in the region D-E Equations (5) are not usable because the term within the square root becomes negative. The solution thus includes an imaginary term, and this happens because the predicted parabola does not intersect the line $y=y_u$. If the imaginary term is dropped by setting it to zero, the prediction then becomes

$$\Delta x = \frac{-f'(x)}{f''(x)} \qquad (6)$$

which will be recognized as the first-order prediction of the maximum, and this is precisely the prediction which is called for by the proposed strategy under these circumstances.

A consideration of the signs in Equations (5) leads to the simple, five-step procedure below, the following equivalences being first noted:

$$x = \rho,\; y = P,\; y^* = P_{sys},\; f'(x) = \frac{\partial P}{\partial \rho},\; f''(x) = \frac{\partial^2 P}{\partial \rho^2}$$

1. Calculate $f'(x)^2 - 2[f(x) - y^*]\,f''(x)$.
2. Take the maximum of the above and zero.
3. Take the square root of the result from the above.
4. Subtract $f'(x)$ from the above.
5. Divide the above by $f''(x)$.

The result from step 5 can be used as the change in density predicted for the first occurring of either intersection or L point, from any region analogous to C-D-E (that is, which has correct slope). Obviously, the BWRS equation of state is too complex for this procedure to suffice in a single move; however, the position following the move will be closer to the desired point than the previous one, and the five-step procedure can be applied again at the new position, provided it too is within the region of correct slope.

With the BWRS equation, for isotherms close to the quasicritical temperature, a flat region is encountered in the environs of the quasicritical point. Because $f'(x)$ is essentially zero, predictions using the procedure outlined in the previous paragraph are often radically incorrect in

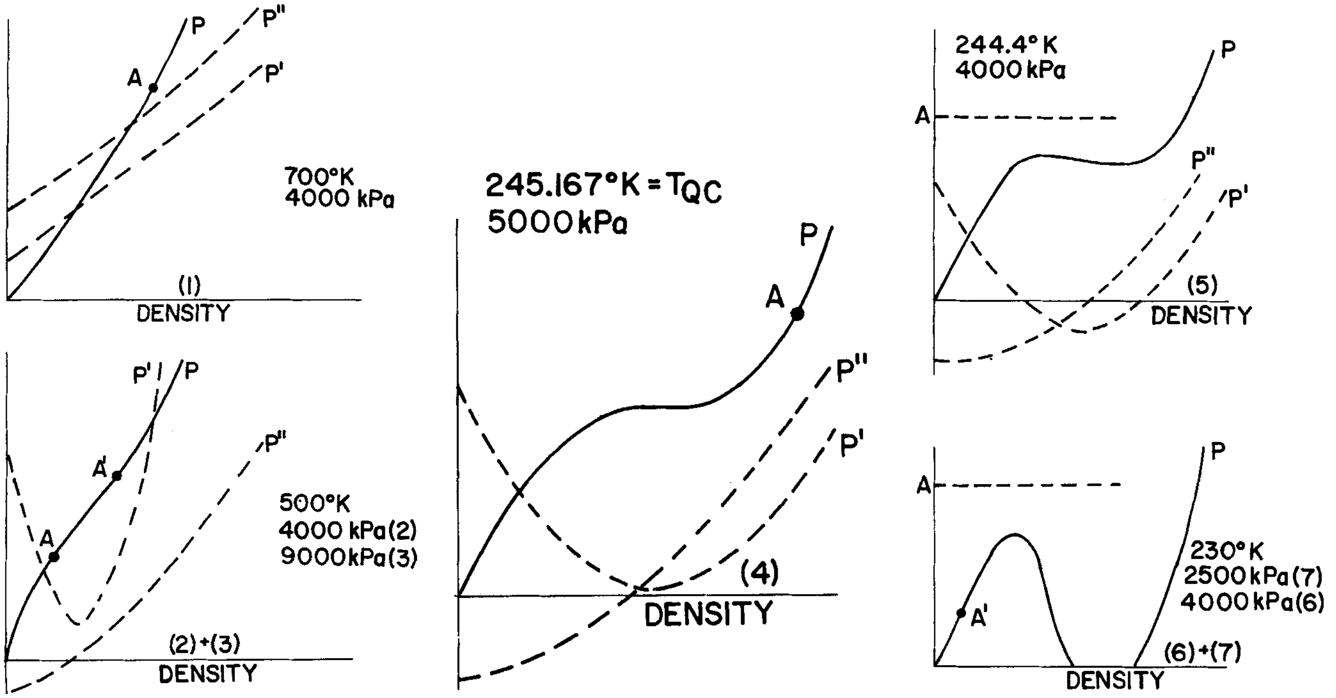

Fig. 8. Numerical results.

this region. The authors were concerned by this and especially by the effect that numerical imprecisions inherent in machine computation might have in this situation. Therefore, after some experimentation, we decided to replace the usual prediction by a fixed step of 0.4 kg mole/m^3 whenever the region was encountered. The region was defined arbitrarily by the magnitude of $f'(x)$ being less than 40, simultaneously with the magnitude of $f''(x)$ being less than 135 (units of kPa, kg mole/m^3). While this stepping procedure does reduce efficiency, cases involving this region do not occur frequently in most process simulation applications.

A convergence loop utilizing the procedure above is incorporated in our density subroutine. This loop can terminate when the desired solution is obtained within the specified tolerance, or (since unidirectionality is enforced) when it is overstepped. The latter case is quite likely to occur, because an equation with terms to the sixth power can exhibit behavior which will usually be more complex than a second-order prediction will allow for. It has been arranged that, on an overstep, exit is made from the first loop to one of two further, separate, convergence loops. The first of these loops uses a first-order Newton-Raphson convergence method to locate an L point which has been overstepped. On convergence to L point, the pressure is checked to ensure that it is below the system pressure, and, if not, exit is made from the second convergence loop to the third so as to locate an overlooked intersection which must precede the L point (this may happen when intersection and L point are essentially coincident). This third loop uses a Regula-Falsi technique to locate an intersection which has been overstepped. Both of these convergence loops are limited to a range defined by the last two steps of the initial loop and commence by utilizing the derivatives established in the initial loop. While the above logic could be replaced by a single loop, considerations of coding clarity prevailed in this instance over the efficiency increment that could thereby be attained.

The subroutine incorporating these procedures has proved to be quite fast and completely reliable in process simulation use. If we refer again to Figure 7, the chief danger would appear to be that the initial convergence loop might jump from the region C-D-E into a further region similar to B-C-D-E lying beyond F (for example, on an isotherm similar to e in Figure 3). This would require a predicted change being too large by a factor of three or more. It is believed that this is unlikely, and in all test cases that have been tried, no such behavior has been observed.

It is known that utilizing a previously calculated result as the initial estimate for a new case usually improves efficiency in trial and error calculations. However, a unidirectional strategy has been chosen which is equivalent to always requiring initial estimates of zero for vapors and 32 kg mole/m^3 for liquids, which must appear nonoptimal. However, the process simulation program for which the density subroutine was designed differs from the usual style. Modules are not required to achieve convergence when they are called for calculation; it is required only that they make one or more moves for each independent variable toward the predicted convergence values. As a result, stream compositions and conditions usually change between successive calls on the density subroutine to an extent that the previous density result is not a particularly accurate estimate for a new calculation. A technique for utilizing initial estimates has, nevertheless, been included in the subroutine and is described below, because the authors foresee uses for it in other applications, where different convergence methods are used and the benefits in efficiency may thus be more readily attainable.

If, before the subroutine is called, the argument representing density is assigned a value which lies between 0 and 32 (kg mole/m^3), this value is taken to be an initial estimate of density. Pressure, and derivatives thereof, are computed at perturbations 1% above and below this density. If an L point or an intersection is included between these perturbation points, it is taken to be the solution, and the subroutines jumps directly to the second or third convergence loop, as indicated, to locate it exactly. Otherwise, the initial density is changed to 0 (vapors) or 32 (liquids), and the subroutine proceeds just as described previously.

NUMERICAL RESULTS

CASE	T k	P kPa	Loop	Iter. No.	ρ kg. moles/m^3	$F(\rho) = P_{calc} - P$ kPa	$F'(\rho)$	$F''(\rho)$	$\Delta\rho$	ρ min	ρ max
1)	700,000	4000,0	1	1	0,	-,400000E+04	,582117E+04	-,233254E+02	,688096E+00		
				2	,688096E+00	,938489E+01	,584604E+04	,956205E+02	-,160536E-02		
			3	0	,688096E+00	,938489E+01			-,160536E-02	0,	,688096E+00
				1	,686490E+00	-,121577E-06	,584596E+04		,207968E-10	,686490E+00	,688096E+00
2)	500,000	4000,0	1	1	0,	-,400000E+04	,415798E+04	-,245130E+03	,990952E+00		
				2	,990952E+00	,189830E+02	,397254E+04	-,129069E+03	-,477819E-02		
			3	0	,990952E+00	,189830E+02			-,477819E-02	0,	,990952E+00
				1	,986174E+00	-,213383E-05	,397285E+04		,537104E-09	,986174E+00	,990952E+00
3)	500,000	9000,0	1	1	0,	-,900000E+04	,415798E+04	-,245130E+03	,232367E+01		
				2	,232367E+01	,245178E+03	,390547E+04	,291607E+02	-,627928E-01		
			3	0	,232367E+01	,245178E+03			-,627928E-01	0,	,232367E+01
				1	,226088E+01	-,498152E-02	,390463E+04		,127580E-05	,226088E+01	,232367E+01
				2	,226088E+01	-,965695E-06	,390388E+04		,247368E-09	,226088E+01	,232367E+01
4)	245,167	5000,0	1	1	0,	-,500000E+04	,203880E+04	-,746948E+03	,272950E+01		
				2	,272950E+01	-,173306E+04	,532311E+03	-,357898E+03	,148733E+01		
				3	,421683E+01	-,126300E+04	,147692E+03	-,165305E+03	,893446E+00		
				4	,511028E+01	-,118414E+04	,423559E+02	-,747976E+02	,566273E+00		
				5	,567655E+01	-,116971E+04	,126214E+02	-,323495E+02	,390158E+00		
				6	,607655E+01	-,116661E+04	,431734E+01	-,102878E+02	,419655E+00		
				7	,647655E+01	-,116525E+04	,350101E+01	,511106E+01	,206795E+02		
				8	,687655E+01	-,116316E+04	,756143E+01	,141896E+02	,122823E+02		
				9	,727655E+01	-,115887E+04	,141146E+02	,177493E+02	,106597E+02		
				10	,767655E+01	-,115180E+04	,211968E+02	,170960E+02	,104341E+02		
				11	,807655E+01	-,114203E+04	,274723E+02	,140674E+02	,109381E+02		
				12	,847655E+01	-,113000E+04	,324488E+02	,110419E+02	,116665E+02		
				13	,887655E+01	-,111617E+04	,366916E+02	,109265E+02	,113246E+02		
				14	,927655E+01	-,110051E+04	,420299E+02	,171251E+02	,914525E+01		
				15	,132766E+02	,761629E+03	,175355E+04	,139205E+04	-,557864E+00		
			3	0	,132766E+02	,761629E+03			-,557864E+00	,927655E+01	,132766E+02
				1	,127187E+02	-,233426E+02	,140710E+04		,165891E-01	,127187E+02	,132766E+02
				2	,127353E+02	-,495911E+01	,110816E+04		,447507E-02	,127353E+02	,132766E+02
				3	,127398E+02	,460023E-01	,111844E+04		-,411306E-04	,127353E+02	,127398E+02
				4	,127397E+02	-,894318E-04	,112062E+04		,798057E-07	,127397E+02	,127398E+02

The use of this window technique, where the estimate is only acceptable if the desired result lies within a small region around the estimate, is essential with a multiple root equation, such as the BWRS equation of state, if the occasional selection of a wrong root is to be kept to a tolerable, minimal frequency. The two initial perturbations, essentially two extra iterations, represent the penalty exacted for an insufficiently accurate estimate. However, when the estimate is successful, convergence will be obtained in one or two iterations following the perturbations. This compares with an average of about seven iterations when no estimate is provided. It is thus possible to roughly evaluate whether (or at what point to commence) to use the window technique in any program of known characteristics.

NUMERICAL RESULTS AND DISCUSSION

Seven instances of vapor density calculation for a mixture will be presented and discussed. The mixture has the same composition in each case (mole fraction, C_1=0.698, C_2=0.297, nC_{10}=0.005) and is known to present various difficulties in computation of density, depending on system conditions. The particular system conditions chosen have been selected to demonstrate the convergence characteristics of the implementation of our method in several disparate situations, rather than to reflect normal usage in process simulation. The seven cases are depicted graphically in Figure 8, which shows for each case the isotherm at system temperature, intersected (or otherwise) by a horizontal line at system pressure. Also shown are the curves of the first and second derivatives for each isotherm. The convergence behavior of the subroutine is reported in Table 1. In this table, iterations are reported separately for the three loops required in this implementation, which was described in the previous sections.

In order for an intersection solution to be accepted as converged, system pressure must be matched within 0.0007 kPa, and the predicted change in density must be less than 0.00001 times the current value. For L point solutions, the second criterion is applied in conjunction with a requirement that the magnitude of the first derivative must be less than 4 × 10^{-6} (units of kPa and kg mole/m^3).

Our comments on the system conditions for each case, and on the performance of the subroutine as shown in Table 1, are given separately below.

Case 1 (700°K, 4 000 kPa). The system temperature is above the Boyle temperature, and therefore the isotherm is almost linear. The second density estimate in the first loop proves to be a slight overstep, and recourse to the third (Regula-Falsi) loop obtains a solution within tolerance in one further iteration (since it uses the change predicted by the first loop). Three iterations is a good performance, but any method would do well in this case because the curve so closely approximates linearity.

Case 2 (500°K, 4 000 kPa). The system temperature is below the Boyle temperature but above the quasicritical temperature. The isotherm thus exhibits a point of inflection; the intersection with system pressure occurs at lower density than the inflection. Once again, two iterations in the first loop and one in the third loop are sufficient. Second-order predictions are especially suited to the shape of this isotherm. Notice, however, that the closer the system pressure comes to the pressure at the inflection, the more iterations will be required by first-order Newton-Raphson and Regula-Falsi methods, etc. If the two pressures were coincident, such methods would never converge.

Case 3 (500°K, 9 000 kPa). The system pressure has been raised, compared with case 2, so as to intersect at higher density than the point of inflection. The subroutine converges after two iterations in the first loop and two in the third loop. Note that if the subroutine had landed exactly on the point of inflection while moving to the intersection, a first-order prediction would have been

TABLE 1 - (Cont'd)

CASE	T k	P kPa	Loop	Iter. No.	ρ kg. moles/m^3	F(ρ) = P$_{calc}$ -P kPa	F' (ρ)	F" (ρ)	Δρ	ρ min	ρ max
5)	244.400	4000.0	1	1	0.	-.400000E+04	.203242E+04	-.749792E+03	.271064E+01		
				2	.271064E+01	-.768528E+03	.527617E+03	-.361466E+03	.145966E+01		
				3	.417030E+01	-.312854E+03	.143275E+03	-.170858E+03	.838563E+00		
				4	.500887E+01	-.241921E+03	.380995E+02	-.837174E+02	.455097E+00		
				5	.540887E+01	-.232461E+03	.113947E+02	-.508433E+02	.224115E+00		
				6	.580887E+01	-.231222E+03	-.343767E+01	-.244293E+02	-.140719E+00		
			2	0	.540887E+01				.224115E+00		
				1	.563298E+01		.178913E+01	-.352221E+02	.507956E-01		
				2	.568378E+01		.830186E-01	-.319714E+02	.259665E-02		
				3	.568637E+01		.212035E-03	-.318082E+02	.666605E-05		
				4	.568638E+01		.137797E-08	-.318077E+02	.433220E-10		
6)	230.000	4000.0	1	1	0.	-.400000E+04	.191267E+04	-.806918E+03	.237034E+01		
				2	.237034E+01	-.138015E+04	.446697E+03	-.430591E+03	.103740E+01		
				3	.340774E+01	-.111971E+04	.826043E+02	-.273492E+03	.302039E+00		
				4	.370978E+01	-.110658E+04	.647298E+01	-.230962E+03	.280261E-01		
				5	.373781E+01	-.110649E+04	.538658E-01	-.227121E+03	.237167E-03		
				6	.373804E+01	-.110649E+04	.384438E-05	-.227089E+03	.169290E-07		
7)	230.000	2500.0	1	1	0.	-.250000E+04	.191267E+04	-.806918E+03	.237034E+01		
				2	.237034E+01	.119853E+03	.446697E+03	-.430591E+03	-.240444E+00		
			3	0	.237034E+01	.119853E+03			-.240444E+00	0.	.237034E+01
				1	.212990E+01	-.363499E+00	.499976E+03		.727033E-03	.212990E+01	.237034E+01
				2	.213062E+01	.397126E-01	.554599E+03		-.716061E-04	.212990E+01	.213062E+01
				3	.213055E+01	.109896E-04	.554445E+03		-.198209E-07	.212990E+01	.213055E+01

substituted, rather than allowing an overflow to result from the second-order method.

Case 4 (245.167°K, 5 000 kPa). The system temperature has been set equal to the quasicritical temperature and the system pressure to be above the quasicritical pressure. The unidirectional steps of the first loop must, therefore, pass through the region where the isotherm is essentially horizontal, where it is required to make steps of a fixed, small, size. As a consequence, fifteen iterations are required in the first loop, followed by four more in the third loop. This is excessive, but the alternative, on this isotherm, would be wild leaps to ridiculously high density and frequent failures to converge.

Case 5 (244.4°K, 4 000 kPa). The system temperature is now very slightly below the quasicritical temperature, and the system pressure remains above the quasicritical pressure. This isotherm therefore exhibits a maximum located between the steeply rising section at low density and the later, almost horizontal, section. The strategy requires that this maximum is to be located to obtain the solution at this pressure. The subroutine does this, using six iterations in the first loop and then four iterations in the second loop. Note that the fixed step size pre-empts the normal change for each of the last several iterations of the first loop.

Case 6 (230°K, 4 000 kPa). The system temperature has been reduced further below the quasicritical temperature, and the isotherm consequently possesses a sharply defined maximum. System pressure exceeds the pressure at this maximum. Again, the strategy requires that the maximum be located so as to report the density at this point as the result. The subroutine achieves this in six iterations of the first loop alone.

Case 7 (230°K, 2 500 kPa). The system pressure has been lowered, relative to the previous case, so that the intersection with the isotherm occurs at lower density than the maximum. The first loop slightly oversteps the intersection on its second iteration, and then the third loop makes three further iterations to achieve convergence. Both this and the previous case are reasonably typical of frequent situations in process simulation work, and the convergence performance is acceptably fast.

It must be emphasized again that these results were selected to show the performance of the subroutine in differing situations, not to demonstrate the speed of the method. In particular, cases like 4 and 5 occur infrequently because an almost flat region is only encountered when the temperature is quite close to the quasicritical temperature. As was discussed in the preceding sections, case 7 is typical of vapor mixtures at dew point, and this is therefore the case that will occur most often in process simulation calculations. Such reasoning confirms our experience that the average number of iterations required for vapor density calculation with this subroutine in these contexts is slightly less than six. For liquid density calculations in these contexts, we have found that about eight iterations are usually needed. The initial guess for liquids (32.0 kg mole/m^3) is normally further from the result, and the rate of change of curvature on the liquid side of the isotherm is usually more pronounced than on the vapor side. These two factors combine to consume the extra two iterations.

When initial guesses were used in conjunction with the window technique, and the guesses were actually the correct results, the computation time for a large mix of cases was reduced by over 60%, reflecting convergence in three iterations almost invariably.

We foresee possibilities that the algorithm could be further improved in two ways. The value 32.0 kg mole/m^3 is used as the starting estimate of liquid density because it is known to be larger than any density of interest, and therefore the unidirectional search is certain to find the required solution. However, 32.0 kg mole/m^3 is so much larger than most normal liquid densities that extra iterations are needed to traverse the interval. A simple expression that would always predict an initial estimate that was larger than the desired solution, but by a smaller amount, would improve the efficiency of the subroutine. It is also possible that the stepping logic used for the flat regions of isotherms passing near the quasicritical point could be improved if better information were available. It may be possible to reduce the region in which stepping is enforced, to pick a more optimal size for the steps, etc. However, the rewards here are not as great as they are for a better starting point for liquids, because the flat sections are not encountered very often.

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NOTATION

f = general function

F = pressure deviation function = $P_{calc} - P$
P = pressure
T = temperature
x = independent variable
y = dependent variable
Δ = deviation
ρ = density

Subscripts

calc = calculated quantity
min = minimum quantity
max = maximum quantity

Superscripts

$*$ = special variation of the dependent variable, y
$'$ = first derivative
$''$ = second derivative

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Optimal Sensor Location with an Application to a Packed Bed Tubular Reactor

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A number of approaches to the optimal selection of sensor locations are presented, and some of these are applied to determine optimal thermocouple positions in a packed bed tubular reactor. As expected, the optimal locations were found to be those surrounding the hot spot location. The theory also revealed that for good state estimation and for goodlinear quadratic control of the reactor, only one or two well located temperature measurements are necessary rather than the entire temperature profile.

SCOPE

In most processes, it is not feasible to measure all the process variables of interest. This may be due to economic constraints, lack of on-line detectors, or the hostile environment in which the sensors are located. Therefore, only a certain subset of these variables, or variables related to these process or state variables are measured. If all the states are to be inferred from such measurements, the precision of the state estimates will depend on which subset of the states, or auxiliary variables are measured, and on the precision of the measurements. Assum-

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