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Thermodynamic Properties from a Cubic Equation of State: Avoiding Trivial Roots and Spurious Derivatives

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A simple method is presented to find and avoid trivial roots and spurious derivatives for a cubic equation of state. The method's utility is demonstrated with some illustrative distillation calculations.

Introduction

When an equation of state for a mixture represents the P - V - T - x behavior of the liquid as well as the vapor phase, the equation can be used to calculate thermodynamic properties for both phases. This calculation has the advantage of avoiding activity coefficients and their associated standard states, which in some cases are hypothetical. Equations of state that are cubic in volume can represent both liquid and vapor phase behavior. Although cubic equations cannot represent the P - V - T behavior over a wide density range (Martin, 1979), their simplicity has led to their widespread use for calculation of vapor-liquid equilibria at high pressures. This simplicity results because no iterative procedures are required to calculate mixture or derivative properties; all calculations can be done analytically. However, application of a cubic equation of state to iterative distillation calculations may introduce computational problems. This work discusses two such problems and suggests a useful technique for their solution.

In this study, the Soave modification (1972) of the Redlich-Kwong equation is used to generate equilibrium ratios, K_i , mixture enthalpies, and appropriate derivative properties. The Soave equation may be written as

$$f(z) = z^3 - z^2 + (A - B - B^2)z - AB = 0 \quad (1)$$

where z is the compressibility factor and A and B are given by

$$A = 0.42747 \frac{P}{T^2} \left(\sum_i x_i \frac{T_{ci} \alpha_i^{1/2}}{P_{ci}^{1/2}} \right)^2$$

$$B = 0.08664 \frac{P}{T} \left(\sum_i x_i T_{ci} / P_{ci} \right)$$

Here x_i is the mole fraction in either the liquid or vapor phase. For hydrocarbons, according to Graboski and Daubert (1978)

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$$\alpha_i^{1/2} = 1 + (0.48508 + 1.55171\omega_i - 0.15613\omega_i^2)(1 - T_{ri}^{1/2})$$

and for hydrogen, according to Graboski and Daubert (1979)

$$\alpha_i^{1/2} = 1.096 \exp(-0.15114T_{ri})$$

where ω is the acentric factor and T_r is the reduced temperature.

To obtain values of thermodynamic properties, eq 1 is first solved analytically for z . When eq 1 has three real roots at a fixed composition and temperature, the largest represents the vapor phase and the smallest represents the liquid phase. The corresponding values of z are then used to calculate a fugacity coefficient and enthalpy departure function for each phase by the equations listed, for example, in Reid et al. (1977). Equilibrium ratios, K_i , are then given by $K_i = \phi_i^{liq} / \phi_i^{vap}$ where ϕ_i is the fugacity coefficient of i in either the liquid or vapor phase. Equations for the desired derivative properties (dK_i/dT , partial molar enthalpies, and $(\partial H/\partial T)_P$ for both phases) can be obtained by techniques described by Shah and Bishnoi (1978).

Below the pseudocritical point, there is a range of temperatures for a given pressure and composition over which there are three real roots to eq 1. Over this temperature range, eq 1 can adequately represent both vapor and liquid properties. Outside this range, there is only one real root. In the course of iterative distillation calculations, where only rough estimates of temperatures and phase compositions are available during early iterations, this root may not correspond to the desired phase. This situation is illustrated in Figure 1 for an equimolar methane-ethylene-ethane mixture at 30 atm. The three-root region occurs between 232 and 250 K. Below 232 K, vapor-phase properties are not predicted and above 250 K liquid-phase properties are not predicted. Thus, for a flash or distillation calculation with an early estimate of an equimolar vapor phase at 230 K, the equation of state would give liquid-like rather than vapor-like thermodynamic properties. The case when eq 1 has a single root has been

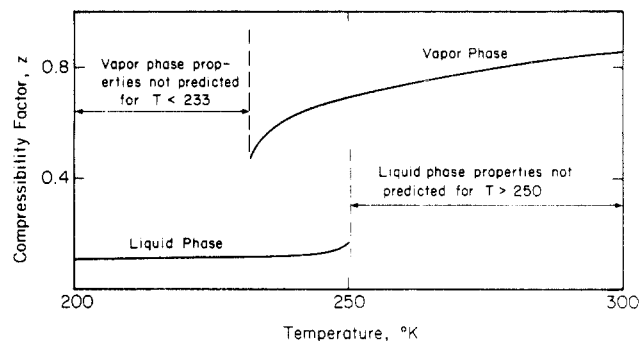


Figure 1. Compressibility factors predicted by Soave equation for an equimolar mixture of methane-ethylene-ethane at 30 atm.

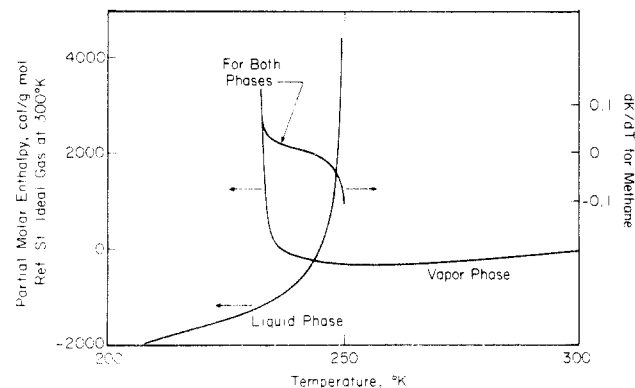


Figure 2. Typical derivative property predictions of Soave equation. Partial molar enthalpy and dK/dT for methane in an equimolar mixture of methane-ethylene-ethane at 30 atm. Both phases are equimolar.

discussed in detail by Asselineau et al. (1979); they demonstrate that when below the pseudocritical point, a root to eq 1 can be unequivocally assigned to either the liquid or vapor phase by comparing the calculated volume to the pseudocritical volume, V_{pc} , where $V_{pc} = R(\sum_i x_i T_{ci}/P_{ci})/3$ and $V = zRT/P$. The root gives liquid-like properties when $V < V_{pc}$ and vapor-like properties when $V > V_{pc}$.

A second difficulty associated with eq 1 is that spurious derivative values are predicted when roots lie within, but near the edge of, the three-root region. Figure 2 shows partial molar enthalpies and values of dK/dT for methane in an equimolar mixture of methane-ethylene-ethane at 30 atm. Between 244 and 250 K, negative values are predicted for dK/dT and for the heat of vaporization. Also, as T decreases to 232 K, the lower limit of the three-root region, dK/dT approaches infinity. The reason for these results, which are physically unrealistic, can be seen in Figure 3, which shows several isotherms predicted by eq 1 for an equimolar methane-ethylene-ethane mixture at 30 atm. At 232.2 K, the function, $f(z)$, as well as its derivative, df/dz , is zero at the predicted vapor z of 0.445. Because the evaluation of derivatives of thermodynamic properties involves division by df/dz , these derivatives for the vapor will necessarily be unbounded at the edge of the three-root region. Similar behavior occurs for liquid phase properties at 249.8 K at the predicted liquid phase z of 0.150. This behavior, although observed here only for the Soave equation, seems characteristic of any equation of state capable of predicting continuous behavior between the liquid and vapor phase. The bubble and dew points for the mixture in Figure 3 occur at 229 and 251 K, respectively. However, the three-root region does not coincide with this temperature range; it may be wider or narrower. The problem arises in using eq 1 to generate properties for a phase at conditions, especially

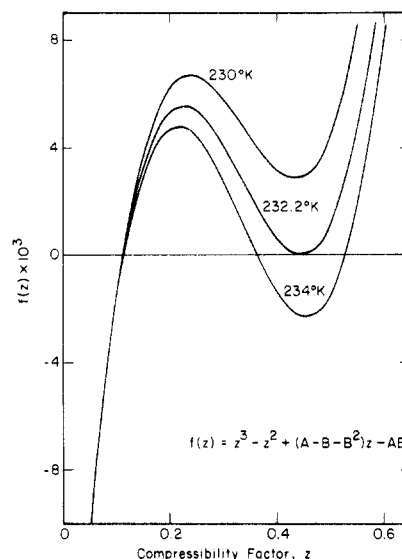


Figure 3. Plots of $f(z)$ vs. z for an equimolar methane-ethylene-ethane mixture at 30 atm. At 232.2 K, $f(z)$ and its derivative are zero at the same value of z .

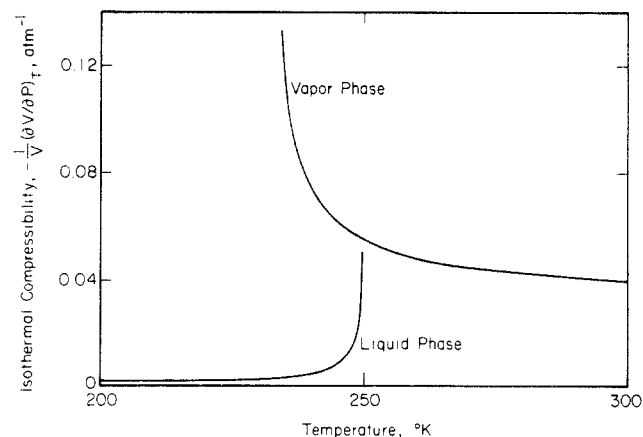


Figure 4. Isothermal compressibility predicted by the Soave equation for an equimolar mixture of methane-ethylene-ethane at 30 atm. One root and spurious derivative regions are identified by isothermal compressibility.

composition, where that phase does not exist, a situation that may arise in an iterative vapor-liquid equilibrium calculation.

Diagnosis of Undesired Roots and Spurious Derivatives

Comparison of the molal volume to the pseudocritical volume calculated with the equation of state successfully assigns a root to the liquid or vapor phase but does not indicate when spurious derivatives will be obtained. It is desirable to be able to identify single-root problems and spurious derivatives by a single criterion. This is accomplished with the isothermal compressibility, β . Using the definition, $\beta = -(\partial V/\partial P)_T/V$, along with eq 1, gives

$$\beta = \frac{1}{P} \left(1 - \frac{2AB + zB + 2B^2z - Az}{z(3z^2 - 2z + A - B - B^2)} \right) \quad (2)$$

Figure 4 shows the isothermal compressibility predicted by eq 2 for an equimolar mixture of methane-ethylene-ethane at 30 atm at various temperatures. Note that liquid and vapor roots are easily identified because the isothermal compressibility of the liquid phase is about an order of magnitude smaller than that of the vapor phase. The compressibility factor, z , for liquids need not be smaller

Table I. Application to Distillation—Examples

component	example			
	A	B mol % in feed	C	D
H ₂				17.7
CH ₄			36.2	29.8
C ₂ H ₄			37.4	30.8
C ₂ H ₆			9.0	7.4
C ₃ H ₆			15.7	12.9
C ₃ H ₈		6	1.7	1.4
<i>i</i> -C ₄ H ₁₀	6			
<i>n</i> -C ₄ H ₁₀	17	17		
<i>i</i> -C ₅ H ₁₂	32			
<i>n</i> -C ₅ H ₁₂	45	32		
<i>n</i> -C ₆ H ₁₄		45		
pressure, atm	5.0	5.0	30.0	30.0
feed rate, mol/h	100	100	100	100
distillate flow, mol/h	23.2	23.2	37.5	47.5
reflux flow, mol/h	98.9	98.9	33.0	41.8
number of stages	27	27	16	16
feed stage	18	18	5	5
feed condition	bubble point liquid	bubble point liquid	30% vapor	62% vapor
condenser type	total	total	partial	partial

than for vapors when the true values of x and y are used for the two phases.

The isothermal compressibility also indicates the regions of spurious derivatives. In Figure 4, the β values for liquid and vapor go to infinity in the region where spurious derivative properties would be predicted for those phases. This is expected, since the isothermal compressibility is itself a derivative property. Further, the term $3z^2 - 2z + A - B - B^2$, which appears in the denominator in eq 2, is the derivative of $f(z)$ in eq 1 with respect to z . This derivative necessarily goes to zero as a phase "disappears" at the transition between the one-root and three-root regions.

For an ideal gas, the isothermal compressibility is $1/P$. This fact, plus information similar to that shown in Figure 4, leads to the criteria below for identification of the nature of a root. A value of z is considered satisfactory for determining liquid-phase properties if the condition

$$\beta < 0.005 \text{ atm}^{-1} \quad (3)$$

is satisfied. The corresponding criterion for the vapor phase is

$$0.9/P < \beta < 3/P \quad (4)$$

There is no theoretical significance to eq 3 and 4, but real liquid and vapor phases satisfy the conditions as stated for wide ranges of temperature and pressure.

Generation of Required Roots

When, in the course of a vapor-liquid equilibrium calculation, estimates of the variables P , T , x , and y do not yield two values of z such that eq 3 and 4 are respectively satisfied, continuation of the calculations will not lead to a correct solution. There are two approaches one can take to ensure that conditions (3) and (4) are satisfied. The first is to make better initial estimates of P , T , x , and y . This approach generally relies on using ideal K_i values for the initial estimates and has been used successfully by Huron et al. (1978) and Asselineau et al. (1979) for flash calculations, and by Shah and Bishnoi (1978) for distillation calculations. The second approach, which is the one used in this study, forces compressibility factors, z , to be generated by eq 1 so that both (3) and (4) are satisfied. This is accomplished by changes in P , T , x , or y until conditions are found where (3) and (4) are both satisfied. Thermodynamic properties are then generated at these "artificial"

values of P , T , x , and y , but the original values of P , T , x , and y are retained for use in the phase equilibrium computation.

Two criteria necessary for selection of which variable(s) to adjust are that: (a) the adjustment should be a change that will reliably lead to satisfaction of whichever of (3) or (4) is not satisfied, and (b) the variable chosen for adjustment should not have a strong effect on the thermodynamic properties to be calculated. Temperature adjustments do not satisfy criterion (b). Thus, pressure and composition remain as candidates for adjustment. When it is necessary to generate vapor-phase properties, that is, to satisfy (4), reduction of the pressure is most effective. A sufficient decrease of the pressure always produces a vapor phase. Moreover, pressure has a small effect on vapor-phase fugacity coefficients and vapor-phase enthalpies. Also, pressure adjustments are computationally more efficient than composition adjustments. When it is necessary to generate liquid-phase properties, that is, to satisfy (3), adjustment of compositions is recommended. Increases in the pressure can lead to near-critical or supercritical conditions where acceptable properties are not generated. When the composition is adjusted to generate a liquid phase, the mole fraction of the heaviest component is raised at the expense of the lighter components until eq 3 is satisfied.

It should be emphasized that the adjustment procedures described above are used only to obtain initial estimates and estimates for use in early iterations of a computation procedure. At some point in the calculations, when T , P , x , and y become sufficiently close to their true values, criteria (3) and (4) will be met and adjustments will not be necessary. Diagnosis of the existence of spurious derivatives is made with the β values found in the course of the adjustment procedure. This is important, since in moving from the one-root to the three-root region, the spurious-derivative region is necessarily encountered. The success of criteria (3) and (4) is not strongly dependent on the specific limits placed on β . When 0.005 in eq 3 is replaced by 0.03, the method is still successful for the examples described below.

Application to Distillation Calculations

The techniques discussed above were applied to several distillation problems for the systems shown in Table I. The calculation method employed was a simultaneous correction procedure similar to that described by Naphtali

Table II. Results of Distillation Calculations

	A	B	C	D
no. of iterations for convergence	5	9	9	12
no. of mixtures adjusted to obtain initial estimates	0	0	17	7
total number of mixtures adjusted to generate liquid-like properties	0	0	6	15
total number of mixtures adjusted to generate vapor-like properties	0	0	36	2
total number of mixtures adjusted	0	0	42	17

and Sandholm (1971). The examples are operating problems in which the number of stages, overhead flow rate, reflux rate, feed condition, and feed composition are specified. The usual procedure for conduct of the iterative calculations is to establish initial estimates of all system variables (T , P , x , y) on all stages of the distillation column. In this work, the initial composition profile is the profile at total reflux, except that hydrogen, when present, is initially assumed to be entirely in the vapor phase. The initial temperature profile is obtained by linear interpolation between the bubble-point temperatures on the top stage, feed stage, and bottom stage. Thermodynamic properties for each stage are calculated at the estimated conditions obtained at each successive iteration.

The calculations were converged so that material and enthalpy balances had a relative error of less than 0.1%. The results are shown in Table II. The four examples taken as a group provide an indication of when trivial-root and spurious-derivative problems are likely to be encountered. Examples A and B, which were at 5 atm, required no adjustments; i.e., eq 3 and 4 were satisfied in all cases. This suggests that at conditions far removed from critical, spurious derivatives and single-root problems are not likely to be encountered.

Table II shows that composition and pressure adjustments were required for examples C and D. In example C, for instance, 17 mixtures had to be adjusted during the course of establishing initial estimates of temperature and composition on each stage. Twenty-five more mixtures had to be adjusted during the first and second iterations for a total of 42 adjustments. Of these 42, 6 were to obtain liquid-like properties and 36 were to obtain vapor-like properties. When these adjustments were not made, convergence was not obtained in either example. Either the trivial solution would result (identical vapor and liquid phases) or the computation would diverge. The cause of the failure was often not apparent; distillation calculation procedures are not well suited to diagnose bad thermodynamic properties.

The temperature profiles, initially and at convergence, are given for examples C and D in Figures 5 and 6. A comparison of these figures indicates that example C provided a more severe test of the adjustment methods than example D. In example D, because of the presence of hydrogen, a vapor phase was predicted for almost all conditions encountered. Most of those points that are solid in Figure 5, but not in Figure 6, represent stages for which vapor-phase properties were not predicted unless hydrogen was present. This suggests that spurious derivatives and single-root problems are more likely to be encountered for narrow-boiling mixtures.

The methods described in this paper for avoidance of spurious derivatives and trivial roots are not exact. Above the pseudocritical point, more robust, but also more time-consuming methods are likely to be necessary.

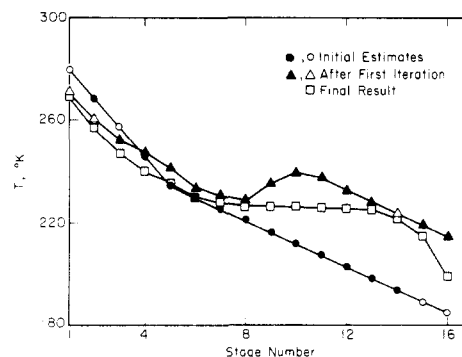


Figure 5. Temperature profiles from example C. Solid points required composition or pressure adjustment for Soave equation to predict acceptable liquid or vapor root.

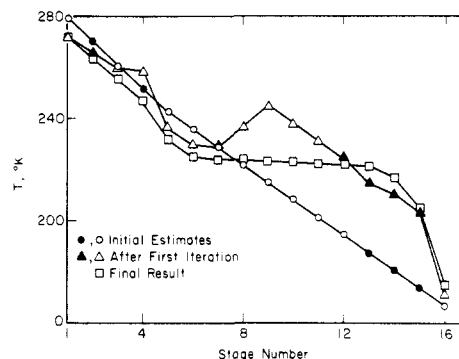


Figure 6. Temperature profiles from example D. Solid points required composition or pressure adjustment for Soave equation to predict acceptable liquid or vapor root.

Nevertheless, for examples C and D, the methods presented led to the solutions shown; without them, these solutions could not have been obtained.

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Nomenclature

- $A, B, \alpha_i^{1/2}$ = parameters in Soave equation of state
- K_i = equilibrium ratio of component i ; $K_i = y_i/x_i$
- P = pressure, atm
- P_{ci} = critical pressure of i , atm
- T = temperature, K
- T_{ci} = critical temperature of i , K
- T_{ri} = reduced temperature of i
- V = volume, $\text{cm}^3/\text{g-mol}$
- V_{pc} = pseudocritical volume, $\text{cm}^3/\text{g-mol}$
- x_i = mole fraction of i in either phase or in the liquid
- y_i = mole fraction of i in the vapor
- z = compressibility factor
- β = isothermal compressibility, atm^{-1}
- ϕ_i^{liq} = fugacity coefficient of i in the liquid
- ϕ_i^{vap} = fugacity coefficient of i in the vapor
- ω_i = acentric factor of i

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