

Equal Area Rule and Algorithm for Determining Phase Compositions

Philip T. Eubank and Kenneth R. Hall

Chemical Engineering Dept., Texas A&M University, College Station, TX 77843

The Maxwell equal area rule is a basic construct for determining saturated phase volumes from equations of state. The fundamental idea is that for a pure substance a horizontal line drawn through the trace of an isotherm, which equalizes the van der Waals loops area above and below the line, intersects the isotherm at the saturated volumes.

Another basic construct exists for determining the phase compositions in a binary mixture by establishing the tangent line to the total Gibbs energy curve plotted against composition. We demonstrate that finding the tangent also reduces to an equal area construction for the derivative of the total Gibbs energy plotted against composition. An efficient algorithm suggested effects such equal area determinations. The trial-and-error procedure normally converges in one to three steps to the correct solution given any reasonable starting guess. Implementation using modern calculators with graphics capabilities is simple and straightforward.

Introduction

The technique to determine from an equation of state the saturated volumes for pure compounds is learned early by one who studies thermodynamics. The Maxwell equal area rule construct can be found in any thermodynamics textbook. Later, one learns how to determine the phase compositions for a binary mixture splitting into multiple phases by drawing a tangent to the Gibbs energy function plotted against composition.

Both of these problems can be reduced to an equal area determination. The only alteration is to utilize the derivative of the Gibbs energy as a function of composition. Modern calculators, which easily plot functions, reduce these trial and error determinations to simple, routine procedures.

Using the equal area technique for phase composition determinations simplifies and speeds the procedure significantly. This is of considerable practical importance.

Derivations

For completeness, we present the derivations to prove the equal area rule for standard volumes and the tangent line for phase compositions. We then present the derivation which illustrates the equal area rule for phase compositions.

Calculation of the saturated volumes results from the fundamental equation for the Gibbs energy:

$$d(nG) = -(nS)dT + (nV)dP + \sum_{i=1}^N \mu_i dn_i \quad (1)$$

Equation 1 is the general expression for any number of components, and for a pure fluid, the final term is zero. For any system of constant total moles, the mole number n cancels. We now integrate from the saturated liquid state to the saturated vapor state at constant temperature and composition using an equation of state to obtain:

$$\begin{aligned} G(v) - G(l) &= \int_{\text{sat liq}}^{\text{sat vap}} VdP = 0 \\ &= P^{\text{sat}}[V(v) + V(l)] - \int_{V(l)}^{V(v)} PdV \quad (2) \end{aligned}$$

Since this is an equilibrium situation, the Gibbs energies are equal in the separate phases. Since equations of state exhibit van der Waals loops inside the two-phase regions, Eq. 2 proves that the areas U and L in Figure 1 are equal, thus the equal area rule.

To determine the phase compositions for a binary mixture at constant temperature and pressure, we return to Eq. 1:

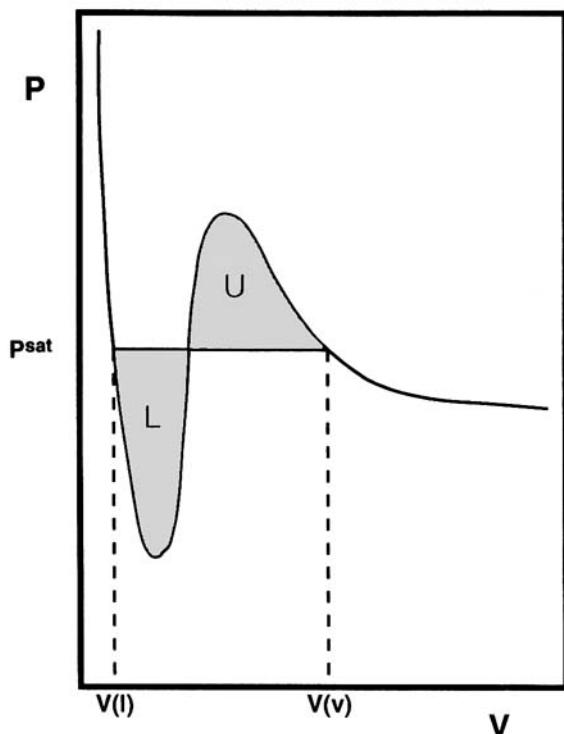


Figure 1. Pressure-volume plot showing the van der Waals loops.

$$dG = \mu_1 dx_1 + \mu_2 dx_2 \quad (3)$$

$$\left(\frac{\partial G}{\partial x_1} \right)_{T,P} = \mu_1 + \mu_2 \frac{dx_2}{dx_1} = \mu_1 - \mu_2 \quad (4)$$

$$\begin{aligned} x_1 \left(\frac{\partial G}{\partial x_1} \right)_{T,P} &= x_1 \mu_1 - x_1 \mu_2 = x_1 \mu_1 - (1 - x_2) \mu_2 \\ &= x_1 \mu_1 + x_2 \mu_2 - \mu_2 = G - \mu_2 \end{aligned} \quad (5)$$

and similarly

$$x_2 \left(\frac{\partial G}{\partial x_1} \right)_{T,P} = \mu_1 - G \quad (6)$$

Under phase equilibrium conditions, the chemical potential of each component is equal in each phase and either Eq. 5 or Eq. 6 reduces to:

$$G^\alpha - G^\beta = x_1^\alpha \left(\frac{\partial G}{\partial x_1} \right)_{T,P}^\alpha - x_1^\beta \left(\frac{\partial G}{\partial x_1} \right)_{T,P}^\beta \quad (7)$$

If the line is tangent to the G curve at x_1^α and at x_1^β as shown in Figure 2, then

$$\left(\frac{\partial G}{\partial x_1} \right)_{T,P}^\alpha = \left(\frac{\partial G}{\partial x_1} \right)_{T,P}^\beta = \frac{G^\alpha - G^\beta}{x_1^\alpha - x_1^\beta} \equiv g'_1 \quad (8)$$

and the tangent line establishes the equilibrium compositions as x_1^α and x_1^β .

Figure 3 illustrates a typical plot of $(\partial G/\partial x_1)_{T,P}$ vs. x_1 . The question is if area U equals area L . The proof is deceptively simple:

$$\int_{x_1^\beta}^{x_1^\alpha} \left(\frac{\partial G}{\partial x_1} \right)_{T,P} dx = G^\alpha - G^\beta = g'_1 (x_1^\alpha - x_1^\beta) \quad (9)$$

Thus, the equal area rule works for binary phase compositions, as well as for pure component saturated volumes.

Algorithm

An algorithm exists normally converging in one to three iterations for equal area problems (assuming a reasonable, if not accurate, initial guess). Since Eqs. 2 and 8 are mathematically identical, the same algorithm works for each. The procedure estimates a vapor pressure or slope, then calculates the saturated volumes or phase compositions and finally adjusts the vapor pressure or slope using:

$$P_{k+1}^{\text{sat}} = \frac{\left[\int_{V(l)}^{V(v)} P dV \right]_k}{[V(v) - V(l)]_k} \quad (10)$$

or

$$(g'_1)_{k+1} = \frac{\left[\int_{x_1^\beta}^{x_1^\alpha} \left(\frac{\partial G}{\partial x_1} \right)_{T,P} dx \right]_k}{[x_1^\alpha - x_1^\beta]_k} \quad (11)$$

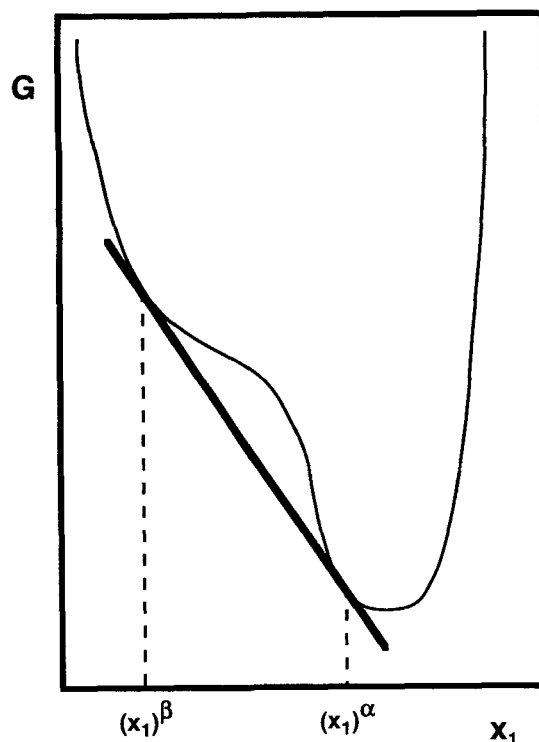


Figure 2. Gibbs Energy-composition plot showing the tangent line concept.

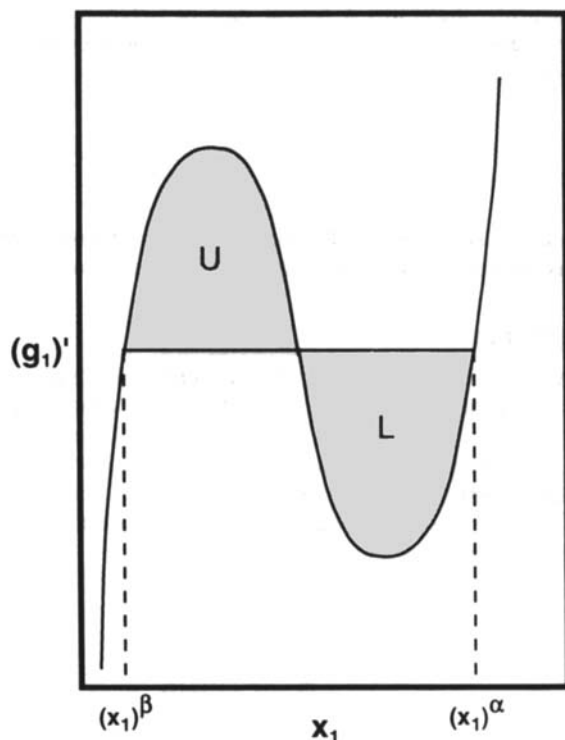


Figure 3. $(\partial G/\partial x_1)_{T,P} - x_1$ plot showing loops similar to those of Figure 1.

A "reasonable" initial guess for the property appears to be any value lying between the extremes of the curves plotted in Figures 1 or 3 and a logical choice is the average value. Termination of the algorithm occurs when successive iterations produce values within a predetermined difference. This is an efficient, "blind" procedure. Earlier techniques for finding equal areas involve plotting the curves and guessing the vapor pressure, then integrating and iterating. In our experience, this procedure is slower than the one suggested here.

Examples

The examples we have selected to illustrate determination of saturated volumes and phase compositions are amenable to solution using modern, hand-held calculators. The capabilities required are numerical integration (area under curves) and graphics. Tangent line construction and automatic functional differentiation are desirable but not essential.

For our first example, we calculate the saturated volumes for a Peng-Robinson fluid:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (12)$$

Let us assume a fluid which has the properties: $T_c = 500$ K, $P_c = 50$ bar and $\omega = 0.2$. This fluid would then have adjustable parameters:

$$a = 0.45724 \left[(RT_c)^2 / P_c \right] \times \left[1 + (0.37464 + 1.54226\omega - 0.2699\omega^2) \left(1 - \sqrt{T/T_c} \right) \right]^2 \quad (13)$$

$$b = 0.0778(RT_c/P_c) \quad (14)$$

At 450 K, $a = 1.6912(10^7)$ bar \cdot cm³ \cdot mol⁻¹ and $b = 64.6829$ cm³ \cdot mol⁻¹. The van der Waals loops resembling Figure 1 with the loop minimum would be at 450 K, -10 bar and the loop maximum would be at 450 K, 31.48 bar. The vapor pressure is 24.242 bar. Using our algorithm, we select the average of the extrema pressures as our initial guess: $P^* = 10.74$ bar. After three iterations using Eq. 9, the resulting pressure is 24.208 bar. If we select a visual initial guess instead of the average pressure, the algorithm would converge in one fewer iteration. Barrufet and Eubank (1989) provide correct reduced vapor pressures for van der Waals, Redlich-Kwong, SRK and Peng-Robinson equations of state should the reader wish to test the algorithm further.

For the second example, we model binary, two-phase, liquid-liquid equilibrium using the Margules equation:

$$\frac{G^E}{x_1 x_2 RT} = Ax_2 + Bx_1 \quad (15)$$

which yields the Gibbs energy of mixing as:

$$\frac{\Delta_m G}{RT} = x_1 x_2 (Ax_2 + Bx_1) + x_1 \ln x_1 + x_2 \ln x_2 \quad (16)$$

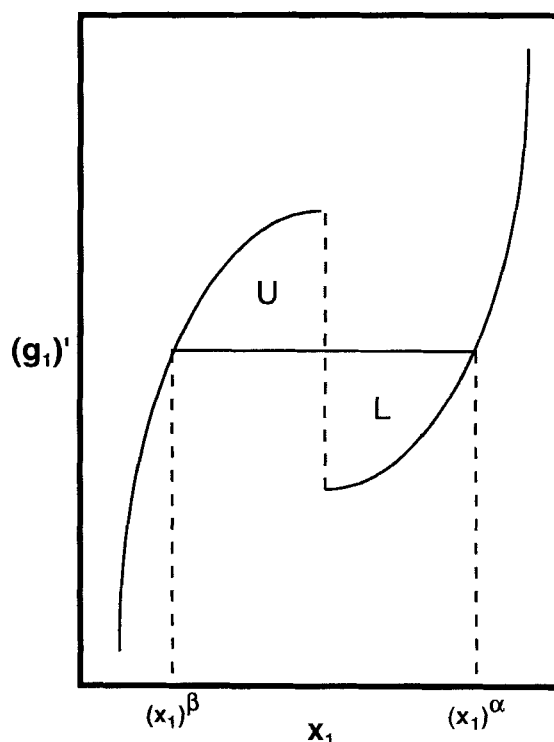


Figure 4. Example of Figure 3 with discontinuous slope.

The Gibbs energy (but not excess Gibbs energy) of mixing can substitute for G in Eqs. 3–8 and Eq. 10. Using $A = 3$ and $B = 1$ produces representation of $\Delta_m G$ similar to those shown in Figures 2 and 3. The correct value of the slope required by Eq. 10 is $g'_1 = -0.3325$. The extrema slopes in Figure 3 would be: $(g'_1)_{\min} = -0.5$ at $x_1 = 0.5$ and $(g'_1)_{\max} = -0.098$ at $x_1 = 0.140$ so the algorithm indicates a starting guess of $s = -0.3$. After two iterations the slope is $g'_1 = -0.3325$ with phase compositions of $x_1^\alpha = 0.060$ and $x_1^\beta = 0.656$.

The phase composition derivation and algorithm also apply to the situation in which $\Delta_m G$ is generated from an equation of state with mixture combining rules. Radzysinski and Whiting (1987) have noted that the different volume roots of the equation of state cause a cusp in $\Delta_m G$ for vapor/liquid equilibria. The cusp then creates a discontinuity in the derivative of $\Delta_m G$, as shown qualitatively in Figure 4. The discontinuity presents no problems for the derivation or the algorithm presented here. Equation 8 remains valid because $\Delta_m G$ is continuous at the cusp.

Conclusions

Only recently (Smith, 1994), we have been informed that two previous articles have published Figure 3. Hicks and Young (1977) first used this construct as a graphical aid in locating critical loci of binary mixtures. Later, Smith et al. (1989) were the first to use it in phase equilibria calculations, working on a molecular model for dipolar hard spheres. Neither publication provided a derivation nor the present algorithm. Both applications were to binary mixtures using molecular models rather than cubic equations of state that provide the discontinuities of Figure 4.

To our knowledge, the equal area rule for phase compositions has not been advanced previously. The current equal area rule and algorithm is completely different from the similarly named "area rule" proposed by Eubank et al. (1992), which uses the area under the Gibbs energy curve to determine phase equilibrium for mixtures. The algorithm makes possible much more efficient determinations of saturated volumes and phase compositions in iterative computer codes. Therefore, this article has much the same characteristics as our earlier theoretical works (Rowlinson et al., 1986; Barrufet and Eubank, 1987) dealing with the continuous slope of the isochore passing through the maximum temperature of the phase loop for mixtures.

While the currently proposed procedure applies only to binary mixtures for phase compositions, we have begun working on an extension to multicomponent mixtures. However, many practical applications utilize binary mixtures, and it is often possible to lump multicomponents into pseudo binaries (such as in petroleum reservoir and natural gas calculations).

Acknowledgments

We gratefully acknowledge support from the National Science

Foundation (CTS-9021129), the Dept. of Energy (32525-4357ACH) and the Texas Engineering Experiment Station.

Notation

a, b = cubic EOS attraction and repulsion constants, respectively
 A, B = Margules constant
 c = critical property
 E = excess property
 g'_1 = partial derivative of G wrt to mole fraction at constant T and P
 G = Gibbs energy per mole
 $\Delta_m G$ = Gibbs energy change on mixing
 l = liquid phase
 n = number of moles
 N = number of components
 P = pressure
 R = gas constant
 sat = saturated property
 S = entropy per mole
 T = temperature
 v = vapor phase
 V = volume per mole
 x = mole fraction

Greek letters

α = identifiable phase
 β = identifiable phase in equilibrium with α
 μ = chemical potential
 ω = acentric factor

Literature Cited

- Barrufet, M. A., and P. T. Eubank, "The General Conditions of Collinearity at the Phase Boundaries of Fluid Mixtures," *AIChE J.*, **33**, 1882 (1987).
- Barrufet, M. A., and P. T. Eubank, "Generalized Saturation Properties of Pure Fluids via Cubic Equations of State," *J. Chem. Eng. Ed.*, 168 (1989).
- Eubank, P. T., A. E. Elhassan, M. A. Barrufet, and W. B. Whiting, "Area Method for Prediction of Fluid Phase Equilibria," *I&EC Res.*, **31**, 942 (1992).
- Hicks, C. P., and C. L. Young, "Theoretical Prediction of Phase Behavior at High Temperatures and Pressures for Non-Polar Mixtures: I. Computer Solution Techniques and Stability Tests," *J. Chem. Soc. Farad. Trans.*, **2**(73), 597 (1977).
- Radzysinski, I. F., and W. B. Whiting, "Fluid Phase Stability and Equations of State," *J. Fluid Phase Equilib.*, **34**, 101 (1987).
- Rowlinson, J. S., G. J. Esper, J. C. Holste, K. R. Hall, M. A. Barrufet, and P. T. Eubank, "The Collinearity of Isochores at Single- and Two-Phase Boundaries for Fluid Mixtures," in *Equations of State: Theories and Applications*, Chap. 2, *ACS Symp. Ser.*, K.-C. Chao and R. L. Robinson, Jr., eds., **300**, 42 (1986).
- Smith, W. R., personal communication (Dec. 29, 1994).
- Smith, W. R., O. H. Scalise, and T. W. Melnyk, "Phase Equilibria in Model Binary Mixtures: I. Dipolar Hard Spheres of Equal Size," *J. Fluid Phase Equilib.*, **44**, 237 (1989).

Manuscript received Mar. 7, 1994, and revision received May 16, 1994.