A New Method to Calculate Phase Coexistence

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Introduction

A classic problem in thermodynamics is the evaluation of phase equilibria from equations of state (EOS). The development and solution of said problems is normally presented during the undergraduate chemical engineering thermodynamics course, with the problems solved either through an iterative procedure [1-3] or using a root-finding algorithm. However, we have recently developed a new method [4] for solving these types of problems that uses a differential form of the phase equilibria constraints that are solved through numerical integration. This second approach, in the example presented in this work, has a computational speed up relative to a root-finding algorithm of about 30. We also revisit a combined approach [5, 6] which allows for larger steps to be taken in the independent variable.

This paper sets up as follows. First we provide a typical example problem that a chemical engineering student might be required to solve. Next, we develop the solution to this problem using a root-finding algorithm (here, Newton-Raphson). Third, we introduce and solve the example problem using our proposed method. Fourth, we demonstrate the benefit of using a
combined approach, which is nothing more than a merging of the second and third ideas above. After that, we discuss pedagogical benefits of the proposed approaches in terms of their incorporation into the classroom. We close with some concluding remarks. Please note some of the more technical details of this study are provided elsewhere. [4]

Example Problem

Sandler [2] illustrates the use of an equation of state (Peng-Robinson) to calculate, among other quantities, the vapor pressure of Oxygen from a low temperature to its critical point. For this example, we have chosen a similar-type problem, namely to trace out the coexistence curve for propane from \( T = 200K \) to the predicted critical point using the Redlich-Kwong equation of state. [7]

Direct Method

The solution methodology using a root-finding algorithm is here given the name “Direct method” since it provides the solution at each point directly from the equilibrium conditions. Specifically, we arrive at the three constraints of equilibrium [8], namely

\[
\begin{align*}
T^l (P^l, \rho^l) &= T^v (P^v, \rho^v) \\
P^l (T^l, \rho^l) &= P^v (T^v, \rho^v) \\
\mu^l (T^l, \rho^l) &= \mu^v (T^v, \rho^v)
\end{align*}
\]

where \( T \) is the temperature, \( P \) is the pressure, \( \rho \) is the density and \( \mu \) is the chemical potential while the superscript “\( l \)” refers to liquid and “\( v \)” refers to vapor.

According to the Gibbs phase rule [3] for this one-component, two-phase system, one
independent intensive variable must be fixed in order to establish the intensive state of the system. Since the Redlich-Kwong equation of state is explicit in pressure, we fix the temperature (i.e.: $T^l = T^v$), as we will be solving the equilibrium conditions at given temperatures. From these specifications, we are left with two coupled, non-linear equations (equations 2-3 above) and two unknowns ($\rho^l$ and $\rho^v$). Here, the Newton-Raphson method\textsuperscript{[9]} is used to solve for the two unknowns at the system specifications. To reach the critical point, steps in the temperature are taken starting from 200 K. The maximal step size in temperature that could be used for convergence (re: before the method generates candidate solutions that diverge) was found to be 0.02 K. For this step size the Direct method took $\sim$1.5 seconds to run on a Dell Dimension (600 MHz, 256Kb RAM, DIGITAL Visual Fortran).

**Integrate Method**

The solution methodology using a differential form of the equilibrium constraints is here given the name “Integrate method” since it provides the solution via numerically integrating the resulting differential equations. Though the problem specification is for a two-phase, one-component mixture, we will present the Integrate method for a two-phase, $n$-component mixture (keeping in mind that what follows is applicable for three-phase or higher equilibrium) to show how the equations would look for mixtures.

The chemical potential and pressure for each component is given as

$$\mu_i^l = \mu_i^l(T^l, \rho_i^l, \ldots, \rho_n^l)$$  \hspace{1cm} (4)
\( P^l = P^l(T^l, \rho^l_1, \ldots, \rho^l_n) \) \hspace{1cm} (5)

\( \mu^v_i = \mu^v_i(T^v, \rho^v_1, \ldots, \rho^v_n) \) \hspace{1cm} (6)

\( P^v = P^v(T^v, \rho^v_1, \ldots, \rho^v_n) \) \hspace{1cm} (7)

where \( \rho_i \) indicates a component density of species i (the product of the mole fraction of component i and the molar density of that phase), while the differentials are:

\[
d\mu^l_i = \left( \frac{\partial \mu^l_i}{\partial T^l} \right)_{\rho^l_i} \, dT^l + \sum_{j=1}^{n} \left( \frac{\partial \mu^l_i}{\partial \rho^l_j} \right)_{T^l, \rho^l_i} \, d\rho^l_j \quad (8)
\]

\[
dP^l = \left( \frac{\partial P^l}{\partial T^l} \right)_{\rho^l_i} \, dT^l + \sum_{j=1}^{n} \left( \frac{\partial P^l}{\partial \rho^l_j} \right)_{T^l, \rho^l_i} \, d\rho^l_j \quad (9)
\]

\[
d\mu^v_i = \left( \frac{\partial \mu^v_i}{\partial T^v} \right)_{\rho^v_i} \, dT^v + \sum_{j=1}^{n} \left( \frac{\partial \mu^v_i}{\partial \rho^v_j} \right)_{T^v, \rho^v_i} \, d\rho^v_j \quad (10)
\]

\[
dP^v = \left( \frac{\partial P^v}{\partial T^v} \right)_{\rho^v_i} \, dT^v + \sum_{j=1}^{n} \left( \frac{\partial P^v}{\partial \rho^v_j} \right)_{T^v, \rho^v_i} \, d\rho^v_j \quad (11)
\]

For a system at equilibrium, the following constraints exist regarding the chemical potential and pressure of the system, respectively \(^{[10]}\).

\[
d\mu^l_i = d\mu^v_i \quad (12)
\]

\[
dP^l = dP^v \quad (13)
\]

We next divide each differential by an infinitesimal change in the temperature and take these partial derivatives constrained to a path that satisfies the equilibrium of chemical potential and
pressure (the symbol $\sigma$ represents this path).

\[
\left( \frac{\partial \mu}{\partial T} \right)_\sigma = \left( \frac{\partial \mu}{\partial T} \right)_\sigma
\]

\[
\left( \frac{\partial P}{\partial T} \right)_\sigma = \left( \frac{\partial P}{\partial T} \right)_\sigma
\]

(14) \hspace{10cm} (15)

From the Gibbs phase rule we can specify $n$ independent variables in our system – here we fix the temperature and the $n - 1$ independent mole fractions of the liquid phase. Doing this, we can write the differential equations for the liquid as follows:

\[
\left( \frac{\partial \mu}{\partial T} \right)_\sigma = \left( \frac{\partial \mu}{\partial T} \right)_\sigma \rho \left( \frac{\partial T}{\partial T} \right)_\sigma + \sum_{j=1}^{n} \left( \frac{\partial \mu}{\partial \rho_j} \right)_{T, \rho_j} x_j \left( \frac{\partial \rho}{\partial T} \right)_\sigma
\]

(16)

\[
\left( \frac{\partial P}{\partial T} \right)_\sigma = \left( \frac{\partial P}{\partial T} \right)_\sigma \rho \left( \frac{\partial T}{\partial T} \right)_\sigma + \sum_{j=1}^{n} \left( \frac{\partial P}{\partial \rho_j} \right)_{T, \rho_j} x_j \left( \frac{\partial \rho}{\partial T} \right)_\sigma
\]

(17)

For the vapor, we arrive at

\[
\left( \frac{\partial \mu}{\partial T} \right)_\sigma = \left( \frac{\partial \mu}{\partial T} \right)_\sigma \rho \left( \frac{\partial T}{\partial T} \right)_\sigma + \sum_{j=1}^{n} \left( \frac{\partial \mu}{\partial \rho_j} \right)_{T, \rho_j} \left( \frac{\partial \rho}{\partial T} \right)_\sigma
\]

(18)

\[
\left( \frac{\partial P}{\partial T} \right)_\sigma = \left( \frac{\partial P}{\partial T} \right)_\sigma \rho \left( \frac{\partial T}{\partial T} \right)_\sigma + \sum_{j=1}^{n} \left( \frac{\partial P}{\partial \rho_j} \right)_{T, \rho_j} \left( \frac{\partial \rho}{\partial T} \right)_\sigma
\]

(19)

where $x_i$ are the mole fractions of component $i$ in the liquid phase.

Substituting (16) and (18) into (14) and noting that...
\[
\left( \frac{\partial T}{\partial T} \right)_\sigma = 1
\]  

(20)
yields the following result:

\[
\left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} + \sum_{j=1}^{n} \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} x_j \left( \frac{\partial \rho_j^I}{\partial T} \right)_\sigma = \left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} + \sum_{j=1}^{n} \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} x_j \left( \frac{\partial \rho_j^I}{\partial T} \right)_\sigma
\]

or

\[
\left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} - \left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} = \sum_{j=1}^{n} \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} x_j \left( \frac{\partial \rho_j^I}{\partial T} \right)_\sigma
\]

Similarly for the pressure:

\[
\left( \frac{\partial P_i^l}{\partial T_i^l} \right)_{\rho^I} - \left( \frac{\partial P_i^l}{\partial T_i^l} \right)_{\rho^I} = \sum_{j=1}^{n} \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I} x_j \left( \frac{\partial \rho_j^I}{\partial T_i^l} \right)_\sigma
\]

(23)

Recognizing that (22) and (23) can be written in linear form, we can use matrix notation to compactly represent the system of equations in terms of a coefficient matrix \((A)\), a solution vector \((b)\) and an unknown vector \((x)\); \(Ax = b\).

\[
\begin{bmatrix}
-\sum_{j=1}^{n} x_j \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} & \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} & \cdots & \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} \\
-\sum_{j=1}^{n} x_j \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I} & \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I} & \cdots & \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I} \\
-\sum_{j=1}^{n} x_j \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} & \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} & \cdots & \left( \frac{\partial \mu_i^v}{\partial \rho_j^I} \right)_{T^I, \rho_i^I} \\
-\sum_{j=1}^{n} x_j \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I} & \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I} & \cdots & \left( \frac{\partial P_i^l}{\partial \rho_j^I} \right)_{T_i^l, \rho_i^I}
\end{bmatrix}
\begin{bmatrix}
\left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} \\
\left( \frac{\partial P_i^l}{\partial T_i^l} \right)_{\rho^I} \\
\left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} \\
\left( \frac{\partial P_i^l}{\partial T_i^l} \right)_{\rho^I}
\end{bmatrix}
= \begin{bmatrix}
\left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} \\
\left( \frac{\partial P_i^l}{\partial T_i^l} \right)_{\rho^I} \\
\left( \frac{\partial \mu_i^v}{\partial T} \right)_{\rho^I} \\
\left( \frac{\partial P_i^l}{\partial T_i^l} \right)_{\rho^I}
\end{bmatrix}
\]

(24)

In order to start the Integrate method, a converged point must be used as an initial condition.
Such a point is easily provided by the Direct method. For an equation of state that has the mole fraction, density and temperature as independent variables, all of the elements of the matrix $A$ and the solution vector $b$ can be solved from the equation of state. Thus, the unknown vector $x$ is given as $x = A^{-1}b$. The $n + 1$ coupled differential equations are then numerically integrated to yield the overall liquid phase density and the component densities of the vapor phase. The mole fractions can be determined from the overall density and the individual component densities. A step in the temperature is taken next and the process is repeated until the critical point is reached. A block diagram (Figure 1) may be helpful in illustrating the technique.
Figure 1: A flowchart illustrating the Integrate method algorithm.

Fix $T_{start}$ and $\{x_i\}$.

Calculate $\rho_i, \rho_1', \ldots, \rho_n'$ at $T_{start}$ using Direct or an iterative method.

Fill the $A$ matrix and $b$ vector.

Perform matrix inversion and solve for $x$.

Calculate $\rho_i, \rho_1', \ldots, \rho_n'$ by taking one integration step in $T$.

Print $T, \rho_i, \rho_1', \ldots, \rho_n'$.

Is the specified exit criteria met, for example, is $T \leq T_{final}$?

No
For the solution of this problem we use a 4th order Runge-Kutta method \([11]\) to numerically integrate the coupled pair of differential equations. We find that for the same step size used in the Direct method (0.02 K), we achieve reliable results for the phase densities in about the same amount of time using the Integrate method, as seen in Figure 2 and Table 1, respectively.

Table 1: The CPU time required for each method at various step sizes to provide a solution to the problem.

<table>
<thead>
<tr>
<th>Method</th>
<th>Step Size (K)</th>
<th>CPU Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>0.02</td>
<td>1.5</td>
</tr>
<tr>
<td>Integrate</td>
<td>0.02</td>
<td>1.5</td>
</tr>
<tr>
<td>Integrate</td>
<td>1.0</td>
<td>0.05</td>
</tr>
<tr>
<td>Integrate</td>
<td>10.0</td>
<td>0.02</td>
</tr>
<tr>
<td>Integrate + Direct</td>
<td>10.0</td>
<td>0.02</td>
</tr>
</tbody>
</table>

However, if we increase the integration step size to 1 K, the Integrate method provides reliable results for the coexistence densities with a computational speedup of around 30 compared to the Direct method. At a step size of 10 K, the Integrate method starts to fail (ie: produce inaccurate coexistence densities) as seen in Figure 2.
Figure 2: The saturated liquid volume (top) and saturated vapor volume (bottom) predicted from the Direct method compared to that predicted from the Integrate method at various step sizes.

**Integrate + Direct Method**

The Direct Method can be extended (ie: a larger step size can be used) by utilizing good “guesses” for input into the Newton-Raphson algorithm. The Integrate method is properly designed to provide these better guess solutions and, thus, a combination of the Integrate and
Direct methods can solve the problem quicker (and accurately) than either of the methods individually. In fact for the example problem used in this study, a combined Integrate + Direct method provided equilibrium densities for a step size of 10 K with a computational speed of 75 as compared to the Direct method alone. Note that such a combined approach has been suggested before. [5, 6, 12]

**Pedagogical Benefits**

The solution technique presented in this work, known as Integrate, was shown for the problem at hand to be more efficient than the Direct method. Thus, the presentation of such an approach in the classroom has merit from this standpoint. However, does the Integrate method offer any pedagogical advantage over the Direct method with regards to equilibrium thermodynamics or numerical methods? Certainly the Direct method is easier to conceptualize, thermodynamically, as the equations can attest. However, the Integrate method offers the opportunity to discuss/review many important concepts, both thermodynamic and mathematical in nature, during its derivation, such as: Gibbs phase rule, intensive variables, the differential, partial derivatives, selection of a convenient path, linear algebra, numerical integration, and truncation error. The latter two concepts also allow the Integrate method to fit nicely into a section on numerical integration during a Numerical Methods course since the results from the Integrate method in this work are a function of the order of the numerical integration method used for solution. Since the method developed is new, it has not been presented during any course yet. However, we are preparing to present the Integrate method in a Junior level Thermodynamics course in the Spring of 2002 as well as in a Senior level Applied Mathematics class in the Fall of 2002.
Concluding Remarks

A novel integration technique called Integrate has been presented to solve phase equilibrium problems using equations of state. This method was shown to result in a computational speedup of ~30 relative to the Direct method owing to the larger step size the Integrate method allows. Also, a combined Integrate + Direct method proved most useful in utilizing the best features of both approaches. Possible pedagogical benefits of using the Integrate method, owing to the number of concepts it touches upon during its development, is discussed.

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