Partial Derivative Quantities from Phase Equilibria Relationships for Mixtures

James A. Mullins, James B. Rawlings, and Keith P. Johnston
Dept. of Chemical Engineering, University of Texas at Austin, Austin, TX 78712

A systematic formulation of multicomponent/multiphase phase equilibria as a linear algebra problem in the fugacities, mole fractions, partial molar volumes, and partial molar enthalpies is given. The algorithm takes advantage of the Gibbs-Duhem relationships for each phase and a modified Gaussian elimination technique to reduce the system of equations. These algorithmic steps allow current symbolic manipulation packages to generate useful partial derivative relationships in terms of measurable thermodynamic quantities. Features of the algorithm are demonstrated by applying a computer implementation of the method to a simple two-phase/two-component system and to the more complicated examples of a two-phase/three-component supercritical fluid chromatography experiment and a mass-conserving closed system.

Introduction

Expressions relating partial derivatives of intensive process variables with respect to other intensive variables at equilibrium conditions are easily determined for simple cases involving a few degrees of freedom. For example, Modell and Reid (1983) give the relationships for a two-component, two-phase system:

$$\left(\frac{\partial P}{\partial T}\right)_{x_1^2}=\frac{1}{T}\frac{x_1^1\Delta\overline{H}_1^{1,2}+x_2^1\Delta\overline{H}_2^{1,2}}{x_1^1\Delta\overline{V}_1^{1,2}+x_2^1\Delta\overline{V}_2^{1,2}} \qquad (1)$$

$$\left(\frac{\partial P}{\partial x_1^2}\right)_T=RT\frac{\left(\dfrac{x_1^1x_2^2-x_1^2x_2^1}{x_2^2}\right)\left(\dfrac{\partial\ln\hat{f}_1^2}{\partial x_1^2}\right)_{T,P}}{x_1^1\Delta\overline{V}_1^{1,2}+x_2^1\Delta\overline{V}_2^{1,2}} \qquad (2)$$

$$\left(\frac{\partial T}{\partial x_1^2}\right)_P=-RT^2\frac{\left(\dfrac{x_1^1x_2^2-x_1^2x_2^1}{x_2^2}\right)\left(\dfrac{\partial\ln\hat{f}_1^2}{\partial x_1^2}\right)_{T,P}}{x_1^1\Delta\overline{H}_1^{1,2}+x_2^1\Delta\overline{H}_2^{1,2}} \qquad (3)$$

in which

x_i^j = mole fraction of component i in phase j
$\hat{f}_i^j$ = fugacity of component i in phase j
$\Delta\overline{H}_i^{j,k}$ = difference between partial molar enthalpies of component i in phases j and k
$\Delta\overline{V}_i^{j,k}$ = difference between partial molar volumes of component i in phases j and k
T = absolute temperature
P = pressure

Their method in arriving at these results, however, does not generalize well to n components and π phases. This article presents a general formulation of the multicomponent/multiphase equilibrium as a linear system to which the tools of linear algebra and modern symbolic manipulation yield results systematically.

Phase Equilibria Relationships

The equilibrium between n components distributed in π phases is given by equating the chemical potentials, or equivalently the fugacities, of all species in all phases (Modell and Reid, 1983):

$$-\frac{\overline{H}_i^{m-1}-\overline{H}_i^m}{RT^2}dT+\frac{\overline{V}_i^{m-1}-\overline{V}_i^m}{RT}dP+\sum_{j=1}^{n-1}\left[\left(\frac{\partial\ln\hat{f}_i^{m-1}}{\partial x_j^{m-1}}\right)dx_j^{m-1}-\left(\frac{\partial\ln\hat{f}_i^m}{\partial x_j^m}\right)dx_j^m\right]=0 \qquad (4)$$

in which $i=1,\ldots,n$ and $m=2,\ldots,\pi$ and the partial derivatives are understood to be at constant P, T and $x_{i\neq j,n}$. This convention is adopted throughout the article.

Correspondence concerning this article should be addressed to J. B. Rawlings.

Equation 4 may be written concisely as:

$$\begin{bmatrix} \boldsymbol{B}^1 & -\boldsymbol{B}^2 & & & \Delta \boldsymbol{HV}^{1,2} \\ & \boldsymbol{B}^2 & -\boldsymbol{B}^3 & & \Delta \boldsymbol{HV}^{2,3} \\ & & \ddots & \ddots & \vdots \\ & & & \boldsymbol{B}^{\pi-1} \quad -\boldsymbol{B}^{\pi} & \Delta \boldsymbol{HV}^{\pi-1,\pi} \end{bmatrix} \begin{bmatrix} \boldsymbol{dx}^1 \\ \vdots \\ \boldsymbol{dx}^{\pi} \\ dT \\ dP \end{bmatrix} = \boldsymbol{0} \qquad (5)$$

in which

$$\Delta \boldsymbol{HV}^{m-1,m} = \begin{bmatrix} -\dfrac{\Delta \overline{H}_1^{m-1,m}}{RT^2} & \dfrac{\Delta \overline{V}_1^{m-1,m}}{RT} \\ \vdots & \vdots \\ -\dfrac{\Delta \overline{H}_n^{m-1,m}}{RT^2} & \dfrac{\Delta \overline{V}_n^{m-1,m}}{RT} \end{bmatrix}$$

$$\boldsymbol{B}^m = \begin{bmatrix} \dfrac{\partial \ln \hat{f}_1^m}{\partial x_1^m} & \cdots & \dfrac{\partial \ln \hat{f}_1^m}{\partial x_{n-1}^m} \\ \vdots & & \vdots \\ \dfrac{\partial \ln \hat{f}_n^m}{\partial x_1^m} & \cdots & \dfrac{\partial \ln \hat{f}_n^m}{\partial x_{n-1}^m} \end{bmatrix}$$

$$\boldsymbol{dx}^m = \begin{bmatrix} dx_1^m \\ \vdots \\ dx_{n-1}^m \end{bmatrix}$$

and $\Delta \overline{H}_i^{m-1,m}$ and $\Delta \overline{V}_i^{m-1,m}$ are defined by:

$$\Delta \overline{H}_i^{m-1,m} = \overline{H}_i^{m-1} - \overline{H}_i^m$$
$$\Delta \overline{V}_i^{m-1,m} = \overline{V}_i^{m-1} - \overline{V}_i^m$$

The coefficient matrix in Eq. 5 is $[n(\pi-1)] \times [\pi(n-1)+2]$ leaving $n-\pi+2$ degrees of freedom, which agrees with the Gibbs phase rule as expected.

Reduction Algorithm

By taking advantage of the Gibbs-Duhem equations for each phase:

$$\sum_{i=1}^{n} x_i^m \frac{\partial \ln \hat{f}_i^m}{\partial x_j^m} = 0, \quad j = 1, \ldots, n-1 \qquad (6)$$

or in the matrix notation of Eq. 5:

$$[\boldsymbol{x}^m]^T \cdot \boldsymbol{B}^m = \boldsymbol{0}^T \qquad (7)$$

the coefficient matrix of Eq. 5 may be made as upper-triangular as possible prior to beginning elimination. Replacement of the last row of each $\boldsymbol{B}^m$ with the Gibbs-Duhem combination of rows for each phase yields:

$$\begin{bmatrix} \overline{\boldsymbol{B}}_1^1 & -\overline{\boldsymbol{B}}_2^2 & & & \boldsymbol{HV}^{1,2} \\ & \overline{\boldsymbol{B}}_1^2 & -\overline{\boldsymbol{B}}_2^3 & & \boldsymbol{HV}^{2,3} \\ & & \ddots & \ddots & \vdots \\ & & & \overline{\boldsymbol{B}}_1^{\pi-1} \quad -\overline{\boldsymbol{B}}_2^{\pi} & \boldsymbol{HV}^{\pi-1,\pi} \end{bmatrix} \begin{bmatrix} \boldsymbol{dx}^1 \\ \vdots \\ \boldsymbol{dx}^{\pi} \\ dT \\ dP \end{bmatrix} = \boldsymbol{0} \qquad (8)$$

in which

$$\overline{\boldsymbol{B}}_1^m = \begin{bmatrix} \dfrac{\partial \ln \hat{f}_1^m}{\partial x_1^m} & \cdots & \dfrac{\partial \ln \hat{f}_1^m}{\partial x_{n-1}^m} \\ \vdots & & \vdots \\ \dfrac{\partial \ln \hat{f}_{n-1}^m}{\partial x_1^m} & \cdots & \dfrac{\partial \ln \hat{f}_{n-1}^m}{\partial x_{n-1}^m} \\ 0 & \cdots & 0 \end{bmatrix}$$

$$\overline{\boldsymbol{B}}_2^m = \begin{bmatrix} \dfrac{\partial \ln \hat{f}_1^m}{\partial x_1^m} & \cdots & \dfrac{\partial \ln \hat{f}_1^m}{\partial x_{n-1}^m} \\ \vdots & & \vdots \\ \dfrac{\partial \ln \hat{f}_{n-1}^m}{\partial x_1^m} & \cdots & \dfrac{\partial \ln \hat{f}_{n-1}^m}{\partial x_{n-1}^m} \\ \dfrac{1}{x_n^m}\left(x_n^m \displaystyle\sum_{i=1}^{n-1} x_i^{m-1} \dfrac{\partial \ln \hat{f}_i^m}{\partial x_1^m} - x_n^{m-1} \displaystyle\sum_{i=1}^{n-1} x_i^m \dfrac{\partial \ln \hat{f}_i^m}{\partial x_1^m}\right) & \cdots & \dfrac{1}{x_n^m}\left(x_n^m \displaystyle\sum_{i=1}^{n-1} x_i^{m-1} \dfrac{\partial \ln \hat{f}_i^m}{\partial x_{n-1}^m} - x_n^{m-1} \displaystyle\sum_{i=1}^{n-1} x_i^m \dfrac{\partial \ln \hat{f}_i^m}{\partial x_{n-1}^m}\right) \end{bmatrix}$$

$$\boldsymbol{HV}^{m-1,m} = \begin{bmatrix} -\dfrac{\Delta \overline{H}_1^{m-1,m}}{RT^2} & \dfrac{\Delta \overline{V}_1^{m-1,m}}{RT} \\ \vdots & \vdots \\ -\dfrac{\Delta \overline{H}_{n-1}^{m-1,m}}{RT^2} & \dfrac{\Delta \overline{V}_{n-1}^{m-1,m}}{RT} \\ -\dfrac{1}{RT^2} \displaystyle\sum_{i=1}^{n} x_i^{m-1} \Delta \overline{H}_i^{m-1,m} & \dfrac{1}{RT} \displaystyle\sum_{i=1}^{n} x_i^{m-1} \Delta \overline{V}_i^{m-1,m} \end{bmatrix}$$

This step amounts to the selection of the $\partial \ln \hat{f}_n^k / x_i^k$, $k = 1, \ldots, \pi$, $i = 1, \ldots, n-1$, to be eliminated from the experimental data required. Of course, these quantities are often reported independently and then the Gibbs-Duhem equations provide a consistency check of the data. Other choices are possible, but no loss of generality results from the selection of this particular set.

The second step is to select the $n-\pi+3$ variables which are to describe the system and move the columns of the coefficient matrix of Eq. 8 corresponding to those variables into the right-most columns of the coefficient matrix and correspondingly move the selected variables to the bottom-most positions of the unknown vector. This allows the elimination to proceed according to standard Gaussian elimination algorithms leaving zeroes in the left-most positions of the last row of the coefficient matrix when complete.

Gaussian elimination of the coefficient matrix eliminates the dependent variables from the set. The remaining nonzero entries of the last row of the coefficient matrix form the coefficient set of the equation describing the system in terms of the selected variables. Since this equation forms a total differential, the partial derivatives of the intensive variables along equilibrium surfaces are simply the ratios of these final coefficients.

While standard Gaussian elimination provides a result, the limitations of the state-of-the-art in symbolic manipulation software dictate a modified approach. For example, merely solving a three-component, two-phase system using *Mathematica*'s built-in row reduction algorithm produced ten pages of indecipherable output; requested simplification using various combinations of available polynomial manipulation functions consumed over 48 hours of *Mac IIci* CPU time with no conclusion. The problem is that standard Gaussian elimination algorithms, intended for numerical applications, divide by the pivot before subtracting during the forward elimination step. This produces a final result similar in appearance to a lengthy continued fraction which must then be simplified, a notoriously slow operation for current symbolic manipulators. Also, standard elimination routines proceed with the backsubstitution step, further confusing the results. This step is clearly not needed for this application, since we do not seek the solution to the set of equations; all the dT, dP, dx^m are zero at equilibrium. To improve the chance of producing recognizable output in reasonable time, a routine using a slightly modified elimination algorithm relying on products instead of quotients fills the need. The simple idea is illustrated best with an example:

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

The single modified elimination step required for this equation is to subtract ($c\times$ 1st row) from ($a\times$ 2nd row), yielding:

$$0x_1+(ad-cb)x_2=0$$

This is in contrast to the result:

$$0x_1+\left(d-c\frac{b}{a}\right)x_2=0$$

with standard Gaussian elimination. Some symbolic manipulators provide this fraction-free version as an alternative to the standard Gaussian elimination routine (Char et al., 1991). The difference seems trivial, but has a marked effect on the capability of symbolic manipulators to simplify the results. The same three-component, two-phase example cited above took approximately 15 CPU seconds on the *Mac IIci*, as will be discussed later. Applying the Duhem relations prior to elimination reduces the computation burden by reducing the number of symbols involved in the elimination and subsequent simplification. Copies of the *Mathematica* (Wolfram, 1991) notebook to perform this calculation are available upon request.

Examples

Two-component, two-phase system

The two-component, two-phase system provides a convenient example with which to demonstrate the formation of the coefficient matrix, system reduction, and partial derivative formation, in addition to a few subtleties of the method. The equation for the two-component, two-phase system is:

$$\begin{bmatrix} \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1} & -\dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2} & -\dfrac{\Delta \overline{H}_1^{1,2}}{RT^2} & \dfrac{\Delta \overline{V}_1^{1,2}}{RT} \\ \dfrac{\partial \ln \hat{f}_2^1}{\partial x_1^1} & -\dfrac{\partial \ln \hat{f}_2^2}{\partial x_1^2} & -\dfrac{\Delta \overline{H}_2^{1,2}}{RT^2} & \dfrac{\Delta \overline{V}_2^{1,2}}{RT} \end{bmatrix} \begin{bmatrix} dx_1^1 \\ dx_1^2 \\ dT \\ dP \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad (9)$$

In general, at this stage a matrix column reordering is required. For example, if we were to choose to describe the system in terms of the set dx_1^1, dT, dP, the matrix upon rearrangement becomes:

$$\begin{bmatrix} -\dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2} & \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1} & -\dfrac{\Delta \overline{H}_1^{1,2}}{RT^2} & \dfrac{\Delta \overline{V}_1^{1,2}}{RT} \\ -\dfrac{\partial \ln \hat{f}_2^2}{\partial x_1^2} & \dfrac{\partial \ln \hat{f}_2^1}{\partial x_1^1} & -\dfrac{\Delta \overline{H}_2^{1,2}}{RT^2} & \dfrac{\Delta \overline{V}_2^{1,2}}{RT} \end{bmatrix} \begin{bmatrix} dx_1^2 \\ dx_1^1 \\ dT \\ dP \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad (10)$$

However, to compare results directly with those of Eq. 1 we select dx_1^2, dT, dP as the variables with which to describe the system; then, the matrix requires no rearrangement. The Gibbs-Duhem relation is then used to replace the second row in Eq. 9 by summing ($x_1^1\times$ 1st row) and ($x_2^1\times$ 2nd row). The appearance of the $\partial \ln \hat{f}_1^1/\partial x_1^1$ terms in the first column of the coefficient matrix dictates which linear combinations to make in this step. This is automated in the software to perform these manipulations. The resulting system is:

$$\begin{bmatrix} \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1} & -\dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2} & -\Delta \overline{H}_1^{1,2} & \Delta \overline{V}_1^{1,2} \\ 0 & \displaystyle\sum_{i=1}^{2} x_i^1 \frac{\partial \ln \hat{f}_i^2}{\partial x_1^2} & -\dfrac{1}{RT^2}\displaystyle\sum_{i=1}^{2} x_i^1 \Delta \overline{H}_i^{1,2} & \dfrac{1}{RT}\displaystyle\sum_{i=1}^{2} x_i^1 \Delta \overline{V}_i^{1,2} \end{bmatrix} \times \begin{bmatrix} dx_1^1 \\ dx_1^2 \\ dT \\ dP \end{bmatrix} = 0 \qquad (11)$$

The solution for this case is trivial, since the matrix is in row-reduced form after application of the Gibbs-Duhem relations. This, in fact, is generally true for two-phase systems, in which the selected variables include the $n-1$ mole fractions from a single phase. The result is complete with only the application of the Gibbs-Duhem equations, as will be shown later. Use of the Gibbs-Duhem relation for phase 2 reduces the thermodynamic data required from experiments by eliminating $(\partial \ln \hat{f}_2^2)/(\partial x_1^2)$. The system partial derivatives, shown in Eq. 1, are now easily formed using appropriate ratios of the nonzero coefficients.

Supercritical fluid chromatography

A recent publication (Kelley and Chimowitz, 1990) provides a multicomponent phase-equilibrium application in supercritical fluid chromatography. In this process, a mobile phase containing a single solute adsorbs onto the surface of a stationary phase. The solvent and solute from the mobile phase elute at different rates providing a method of separation and analysis of thermodynamic properties using supercritical fluid chromatography. In the analysis of supercritical fluid chromatography data taken at constant pressure in a three-component (solute, solvent, and solid), two-phase system, the temperature derivative of the logarithm of the capacity factor, $(\partial \ln k_i/\partial T)_{P,x_2^1}$, plays an important role. This derivative, written for the solute, is equivalent to:

$$\left(\frac{\partial \ln k_2}{\partial T}\right)_{P,x_2^1} = \left(\frac{\partial \ln x_2^2}{\partial T}\right)_{P,x_2^1} - \left(\frac{\partial \ln x_2^1}{\partial T}\right)_{P,x_2^1} + \left(\frac{\partial \ln \overline{V}^1}{\partial T}\right)_{P,x_2^1} \tag{12}$$

in which $\overline{V}^1$ is the molar volume of the mobile phase. The second term on the righthand side of Eq. 12 is identically zero, and the third term is the volume expansivity, α_m, of the mobile phase. The first term may be related to component fugacities using the phase-equilibrium equations. In their analysis, the authors write these relationships with the solid absent in the mobile phase. More generally, the relationships may be written with all components present in each phase; then the desired quantity results in the limit $x_3^1 \rightarrow 0$.

The desired derivative implies that the differential variables dx_1^1 and dx_1^2 are eliminated from the equilibrium equations. A key point in the interpretation of the temperature derivative of the capacity factor given above is that both P and x_2^1 should be held constant during experiments. Constant pressure conditions are easily maintained, but the condition on x_2^1 requires injection of a sufficiently small pulse that x_2^1 may be considered constant. It is not necessary to be at infinite dilution for the assumption of $dx_2^1 = 0$ to be true; it is the magnitude of the pulse that determines the validity of this assumption. The assumption is equally valid if a sufficiently small pulse is imposed upon a finite, nonzero initial solute concentration in the column, which is far from infinite dilution.

Using the symbolic manipulation package, we calculate:

$$\left(\frac{\partial \ln x_2^2}{\partial T}\right)_{P,x_2^1} = \frac{1}{RT^2}\frac{1}{x_2^2}\frac{A-B}{CDEF} \tag{13}$$

in which

$$A = \left(\frac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\frac{\partial \ln \hat{f}_2^2}{\partial x_1^2} - \frac{\partial \ln \hat{f}_2^1}{\partial x_1^1}\frac{\partial \ln \hat{f}_1^2}{\partial x_1^2}\right)\sum_{i=1}^{3}\Delta\overline{H}_i^{1,2}x_i^1$$

$$B = \left(\frac{\partial \ln \hat{f}_2^1}{\partial x_1^1}\Delta\overline{H}_1^{1,2} - \frac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\Delta\overline{H}_2^{1,2}\right) \times \left(-\frac{\partial \ln \hat{f}_1^2}{\partial x_1^2}x_1^1 - \frac{\partial \ln \hat{f}_2^2}{\partial x_1^2}x_2^1 + \frac{x_3^1}{x_3^2}\left(\frac{\partial \ln \hat{f}_1^2}{\partial x_1^2}x_1^2 + \frac{\partial \ln \hat{f}_2^2}{\partial x_1^2}x_2^2\right)\right)$$

$$C = \frac{\partial \ln \hat{f}_2^1}{\partial x_1^1}\frac{\partial \ln \hat{f}_1^2}{\partial x_2^2} - \frac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\frac{\partial \ln \hat{f}_2^2}{\partial x_2^2}$$

$$D = -\frac{\partial \ln \hat{f}_1^2}{\partial x_1^2}x_1^1 - \frac{\partial \ln \hat{f}_2^2}{\partial x_1^2}x_1^2 + \frac{x_3^1}{x_3^2}\left(\frac{\partial \ln \hat{f}_1^2}{\partial x_1^2}x_1^2 + \frac{\partial \ln \hat{f}_2^2}{\partial x_1^2}x_2^2\right)$$

$$E = \frac{\partial \ln \hat{f}_2^1}{\partial x_1^1}\frac{\partial \ln \hat{f}_1^2}{\partial x_1^2} - \frac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\frac{\partial \ln \hat{f}_2^2}{\partial x_1^2}$$

$$F = -\frac{\partial \ln \hat{f}_1^2}{\partial x_2^2}x_1^1 - \frac{\partial \ln \hat{f}_2^2}{\partial x_2^2}x_2^1 + \frac{x_3^1}{x_3^2}\left(\frac{\partial \ln \hat{f}_1^2}{\partial x_2^2}x_1^2 + \frac{\partial \ln \hat{f}_2^2}{\partial x_2^2}x_2^2\right)$$

which, although cumbersome, is tractable with the automatic algorithm. With $x_3^1 = 0$, $x_2^1 = 1 - x_1^1$, this result reduces to:

$$\left(\frac{\partial \ln x_2^2}{\partial T}\right)_{P,x_2^1} = \frac{1}{RT^2}\frac{1}{x_2^2}\frac{\dfrac{\partial \ln \hat{f}_2^2}{\partial x_1^2}\Delta\overline{H}_1^{1,2} - \dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2}\Delta\overline{H}_2^{1,2}}{\dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2}\dfrac{\partial \ln \hat{f}_2^2}{\partial x_2^2} - \dfrac{\partial \ln \hat{f}_2^2}{\partial x_1^2}\dfrac{\partial \ln \hat{f}_1^2}{\partial x_2^2}} \tag{14}$$

which, except for a sign error in the published article and a change of notation, is identical to the authors' result. Also, under the assumptions of $\hat{f}_2^2 \neq g(x_1^2)$ and Henry's law for $\hat{f}_2^2$, Eq. 13 further reduces to:

$$\left(\frac{\partial \ln x_2^2}{\partial T}\right)_{P,x_2^1} = -\frac{1}{RT^2}\Delta\overline{H}_2^{1,2} \tag{15}$$

in agreement with other approximate expressions used in the analysis of supercritical fluid chromatography experiments (Shim and Johnston, 1991).

Some advantages of the algorithm are apparent from this example:

1. The automated method reduces the possibility for human error.
2. The method obviates the need to reformulate the problem from scratch to get other derivatives.
3. Other limiting solutions, corresponding to alternative experimental conditions are easily obtained from the general solution.

Other kinds of constraints

To demonstrate the advantage of the approach in analyzing alternative system constraints consider the example of the two-component, two-phase system again. In this example, derivatives holding a single intensive variable constant are easily derived using the proposed approach. We could specify explicitly the variable to be held constant at the outset, appending the constraint $dM = 0$, where M is any of the variables x_i^m, T, P, to the set of equations. This precludes finding derivatives with respect to M without reformulating the problem. Similarly, suppose we desire to know a derivative along the equilibrium envelope subject to some nontrivial constraint on the intensive variables. For example, suppose we want:

$$\left(\frac{\partial P}{\partial T}\right)_{\frac{x_1^1}{x_1^2}}$$

This is a well-posed question, and one approach is to merely append $dx_1^1 - c\,dx_1^2 = 0$, in which c is the constant value of x_1^1/x_1^2, to the coefficient matrix of Eq. 11. Like the single-variable constraint this precludes finding derivatives like:

$$\left[\frac{\partial P}{\partial\left(\frac{x_1^1}{x_1^2}\right)}\right]_T$$

without reformulating the problem. The more general approach is to define a new state, $z = x_1^1/x_1^2$, for which

$$dz = \frac{1}{x_1^2}dx_1^1 - \frac{x_1^1}{(x_1^2)^2}dx_1^2 \tag{16}$$

We effect this change of variables by the transformation:

$$C\begin{bmatrix} dx_1^1 \\ dx_1^2 \\ dT \\ dP \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ \frac{1}{x_1^2} & -\frac{x_1^1}{(x_1^2)^2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} dx_1^1 \\ dx_1^2 \\ dT \\ dP \end{bmatrix} = \begin{bmatrix} dx_1^1 \\ dz \\ dT \\ dP \end{bmatrix} \tag{17}$$

The statement of phase equilibrium is then:

$$AC^{-1}C\begin{bmatrix} dx_1^1 \\ dx_1^2 \\ dT \\ dP \end{bmatrix} = AC^{-1}\begin{bmatrix} dx_1^1 \\ dz \\ dT \\ dP \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{18}$$

in which A is the coefficient matrix of Eq. 11 and

$$C^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ \frac{x_1^2}{x_1^1} & -\frac{(x_1^2)^2}{x_1^1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

We then proceed with the elimination as before. Using this approach we find

$$\left(\frac{\partial P}{\partial T}\right)_{\frac{x_1^1}{x_1^2}} = \frac{1}{T}\,\frac{x_2^1 x_1^2 \dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2}\displaystyle\sum_{i=1}^{2}\Delta \overline{H}_i^{1,2} x_i^2 - x_1^1 x_2^2 \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\displaystyle\sum_{i=1}^{2}\Delta \overline{H}_i^{1,2} x_i^1}{x_2^1 x_1^2 \dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2}\displaystyle\sum_{i=1}^{2}\Delta \overline{V}_i^{1,2} x_i^2 - x_1^1 x_2^2 \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\displaystyle\sum_{i=1}^{2}\Delta \overline{V}_i^{1,2} x_i^1} \tag{19}$$

The last row of the matrix after elimination gives other derivatives involving x_1^1/x_1^2 without reformulating the initial problem. For example,

$$\left[\frac{\partial P}{\partial\left(\frac{x_1^1}{x_1^2}\right)}\right]_T = \frac{RT(x_1^2)^2 \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2}(x_1^1 x_2^2 - x_2^1 x_1^2)}{x_2^1 x_1^2 \dfrac{\partial \ln \hat{f}_1^2}{\partial x_1^2}\displaystyle\sum_{i=1}^{2}\Delta \overline{V}_i^{1,2} x_i^2 - x_1^1 x_2^2 \dfrac{\partial \ln \hat{f}_1^1}{\partial x_1^1}\displaystyle\sum_{i=1}^{2}\Delta \overline{V}_i^{1,2} x_i^1} \tag{20}$$

Closed, rigid system

The previous section introduced the idea of incorporating nontrivial constraints when examining system changes. We can extend this idea further using a more realistic example. Thus far, the examples have involved open systems in which mass may be removed to satisfy the constant pressure or other imposed constraints. Consider a two-component, two-phase system, in which the constraint is that mass is conserved and volume is constant. One may desire to know how the compositions and pressure change with a change in temperature for such a system.

To answer this question, we must specify an equation of state for the vapor and liquid phases. For simplicity, we choose the ideal gas equation of state and model the fluid as incompressible with no volume change on mixing. Taking the total differential of the volume from the ideal gas equation gives:

$$dV^1 = \frac{RT}{P}dn_1 + \frac{RT}{P}dn_2 + \frac{(n_1^1 + n_2^1)R}{P}dT - \frac{(n_1^1 + n_2^1)RT}{P^2}dP \tag{21}$$

in which

dV^1 = volume of vapor
n_i^j = mole number of component i in phase j
dn_i = number of moles of component i transferred from phase 2 to phase 1

From our model for the liquid phase, we have:

$$dV^2 = -\overline{V}_1^2 dn_1 - \overline{V}_2^2 dn_2$$

Therefore,

$$0 = \left(\frac{RT}{P} - \overline{V}_1^2\right)dn_1 + \left(\frac{RT}{P} - \overline{V}_2^2\right)dn_2 + \frac{(n_1^1 + n_2^1)R}{P}dT - \frac{(n_1^1 + n_2^1)RT}{P^2}dP \tag{22}$$

From the definition of mole fraction, we have:

$$dx_1^1 = \frac{x_2^1 dn_1 - x_1^1 dn_2}{n_1^1 + n_2^1} \qquad dx_1^2 = \frac{-x_2^2 dn_1 + x_1^2 dn_2}{n_1^2 + n_2^2}$$

Solving these two expressions for dn_1 and dn_2 gives:

$$dn_1 = \frac{x_1^2(n_1^1+n_2^1)}{x_2^1x_1^2 - x_1^1x_2^2}dx_1^1 + \frac{x_1^1(n_1^2+n_2^2)}{x_2^1x_1^2 - x_1^1x_2^2}dx_1^2$$

$$dn_2 = \frac{x_2^2(n_1^1+n_2^1)}{x_2^1x_1^2 - x_1^1x_2^2}dx_1^1 + \frac{x_2^1(n_1^2+n_2^2)}{x_2^1x_1^2 - x_1^1x_2^2}dx_1^2$$

Note that these expressions correctly show that if the starting mole fractions for each component are equal between phases, we are unable to determine the number of moles transferred between phases merely by observing the changes in composition of the two phases. This problem is analogous to the difficulties in choosing an intensive variable set for an azeotropic mixture (Modell and Reid, 1983). With that caveat, substituting these expressions into Eq. 22 and defining $\alpha = (n_1^1+n_2^1)/(n_1^2+n_2^2)$ we have

$$0 = \frac{\alpha\left(\frac{RT}{P} - x_1^2\overline{V}_1^2 - x_2^2\overline{V}_2^2\right)}{x_2^1x_1^2 - x_1^1x_2^2}dx_1^1 + \frac{\frac{RT}{P} - x_1^1\overline{V}_1^2 - x_2^1\overline{V}_2^2}{x_2^1x_1^2 - x_1^1x_2^2}dx_1^2 + \frac{\alpha R}{P}dT - \frac{\alpha RT}{P^2}dP \qquad (23)$$

Equation 23, when appended to the matrix of Eq. 9 allows determination of partial derivatives of intensive variables subject to conservation of mass for this ideal gas system. For example,

General Results

The combinatorial growth in the number of symbols in the general multicomponent, multiphase chemical equilibrium problem as the number of phases increases precludes expression of the final total differential in closed form for all but the simplest cases. In general, including T and P in the total differential provides a much simpler result than excluding one or both of these variables. This observation is obvious from the structure of the coefficient matrix in Eq. 5; the nonzero coefficients of dT and dP appear in each row, reflecting the equilibrium requirement that T and P be equal in all phases at equilibrium. Fortunately, for most applications, T and P are natural variables to include. Even if T and P are included in the total differential, large problems with many components and phases are beyond the capability of current symbolic manipulation software. For any number of components, n, and phases, π, the number of variables that must be eliminated from the set is easily shown to be:

$$n\pi - n - 1 \qquad (25)$$

Equation 25 shows that increasing the number of phases has a greater impact on the problem complexity than adding components. For example, a four-component, four-phase problem exceeds the capability of *Mathematica*'s **Simplify** operation as implemented on an IBM RS6000 workstation. While the elimination proceeds smoothly, subsequent simplifications are limited by machine memory constraints.

$$\left(\frac{\partial P}{\partial T}\right) = -RT\left[\frac{\alpha\frac{\Delta X}{x_1^2x_2^2}\left(\frac{R}{Px_1^1} + \frac{\Delta\overline{H}_1^{1,2}\Delta\overline{V}^2}{RT^2\Delta X}\right) + \frac{\Delta\overline{H}_1^{1,2}x_1^1 + \Delta\overline{H}_2^{1,2}x_2^1}{RT^2\Delta X}\left(\frac{1}{x_1^1}\Delta\overline{V}^1 + \frac{\alpha}{x_1^2}\Delta\overline{V}^2\right)}{\alpha\frac{\Delta X}{x_1^2x_2^2}\left(\frac{1}{x_1^1}\left(\frac{RT}{P}\right)^2 - \left(\frac{RT}{P} - \overline{V}_1^2\right)\frac{\Delta\overline{V}^2}{\Delta X}\right) - \frac{\Delta\overline{V}^1}{\Delta X}\left(\frac{1}{x_1^1}\Delta\overline{V}^1 + \frac{\alpha}{x_1^2}\Delta\overline{V}^2\right)}\right] \qquad (24)$$

in which

$$\Delta X = x_1^2 - x_1^1$$

$$\Delta\overline{V}^1 = \frac{RT}{P} - \overline{V}_1^2x_1^1 - \overline{V}_2^2x_2^1$$

$$\Delta\overline{V}^2 = \frac{RT}{P} - \overline{V}_1^2x_1^2 - \overline{V}_2^2x_2^2$$

It is understood that the partial derivative given by Eq. 24 is at constant total volume, constant total mass, and is subject to the chosen equations of state for the vapor and liquid phases.

Unlike the previous examples, to get other derivatives under this mass constraint requires the selection of a new set of intensive variables to describe the system and repetition of the matrix elimination algorithm, since we appended the constraint to the matrix instead of defining a new state. Equation 24 shows that a hand calculation of this derivative would be extremely tedious, even for the idealized system chosen for demonstration.

However, one useful result with potentially wide application is for a system of n components and two phases with all the mole fractions in one phase eliminated from the total differential; that is, the common equilibrium stage calculation. Many numerical algorithms embedded in distillation design packages require repeated stage equilibrium calculations, and knowledge of the partial derivatives that we calculate are useful for determining gradients of the thermodynamic functions along the equilibrium envelope. Equation 26 provides a closed-form expression to evaluate these derivatives. The result assumes that all derivatives of the nth component fugacity with respect to the mole fractions are eliminated from the required thermodynamic data using Eq. 6.

$$\frac{1}{x_n^1}\sum_{k=1}^{n-1}\left[x_n^1\sum_{j=1}^{n-1}\frac{\partial \ln \hat{f}_j^1}{\partial x_k^1}x_j^2 - x_n^2\sum_{j=1}^{n-1}\frac{\partial \ln \hat{f}_j^1}{\partial x_k^1}x_j^1\right]dx_k^1 - \frac{1}{RT^2}\left(\sum_{j=1}^{n}\Delta\overline{H}_j^{1,2}x_j^2\right)dT + \frac{1}{RT}\left(\sum_{j=1}^{n}\Delta\overline{V}_j^{1,2}x_j^2\right)dP = 0 \qquad (26)$$

Equation 26, similar to a result given by Van Ness and Abbot (1982), allows calculation of the partial derivative of any mole fraction with respect to temperature, pressure, or any other mole fraction along the equilibrium envelope for a two-phase system by simply forming the ratio of the appropriate coefficients.

Conclusion

Exploiting the structure of the phase-equilibrium equations for multicomponent, multiphase systems provides a systematic formulation of a linear algebra problem in the system differential intensive variables. An algorithm using the Gibbs-Duhem relationships available for each phase combined with matrix rearrangement allows the reduction in the number of symbols appearing in the coefficient matrix so that Gaussian elimination may proceed efficiently for many problems of interest. Even so, large problems involving several phases are beyond the reach of the currently available symbolic manipulation software, but this limitation should diminish with improved algorithms and computational capacity. With this algorithm we derive an expression valid for the general n-component, two-phase problem. This result provides analytical formulas for the required derivatives in many equilibrium flash calculations. With further advances in the combined software/hardware capabilities general expressions valid for more phases and more arbitrary selection of the variables included in the total differential should be possible.

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Notation

A = equilibria coefficient matrix
B = submatrix of composition contributions to the chemical potential
$\bar{B}$ = submatrix of composition contributions to the chemical potential after application of the Gibbs-Duhem relation
c = ratio of x_1^1/x_1^2
C = transformation matrix
$\hat{f}$ = fugacity
$\bar{H}$ = partial molar enthalpy
k = capacity factor in supercritical fluid chromatography
n = number of components or mole number if super- and subscripted
P = pressure
R = gas constant
T = absolute temperature
$\underline{V}$ = volume
$\bar{V}$ = partial or total molar volume
x = mole fraction
ΔHV = submatrix of enthalpic and volumetric contributions to the chemical potential
HV = submatrix of enthalpic and volumetric contributions to the chemical potential after application of the Gibbs-Duhem relation

Greek letters

α = ratio of moles in phases 1 and 2
π = number of phases

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