Exploiting the Gibbs-Duhem Equation in Separation Calculations

Various ways of building quasi-Newton matrix approximations that satisfy the special form of the Gibbs-Duhem equation are studied. Partition symmetry, the separability of the functions ln γ and ln ϕ, and the method of iterated projections are used in order to develop thermodynamically consistent matrix approximations with good secant information. Many examples are presented which show that exploiting the special form of the Gibbs-Duhem equation results in improved numerical performance. Ways of exploiting the Gibbs-Helmholtz equation in addition to the special form of Gibbs-Duhem equation, and thus the isobaric form of the Gibbs-Duhem equation, are also discussed.

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SCOPE

In this paper we develop quasi-Newton matrix approximations for separation problems that satisfy the Gibbs-Duhem equation and the zero degree homogeneity of the excess properties ln γ, ln ϕ, H^E, and h^E in conjunction with the traditional secant condition. These matrices are important when solving separation problems such as flash and distillation by Newtonlike methods. There are in fact several ways in which all of this information can be used in updating the Jacobian matrix. Although the resulting algorithms can be shown to have the same theoretical rate of convergence in the limit, their actual problem-solving characteristics such as reliability and computational efficiency can be different. One purpose of this research was to demonstrate that exploiting the Gibbs-Duhem equation is important to the equation solving task. Numerical results obtained prior to this work (Lucia et al., 1985) have been found to be mixed, and failure to satisfy the Gibbs-Duhem equation was cited as one of the causes for this. The second purpose of this work was to uncover the particular combination of secant and thermodynamic information that gave good, consistent numerical results on a wide variety of small problems. We felt that this was an essential step before moving to larger problems such as distillation.

CONCLUSIONS AND SIGNIFICANCE

A strategy for building quasi-Newton approximations that satisfy the special form of Gibbs-Duhem equation as well as a limiting secant condition was developed. These thermodynamically consistent matrix approximations were generated by a combination of iterated projections and the Powell symmetric Broyden (PSB) formula. The need and importance of exploiting partition symmetry and the separability of the functions ln γ and ln ϕ were demonstrated. Numerical support was presented to show that this thermodynamically consistent update improves the equation solving capability of the hybrid method. These numerical results show that it outperforms traditional secant updates such as the Broyden and PSB formulae when used under equivalent conditions and that it is often more reliable than Newton's method, especially on separation problems involving heterogeneous liquid phase behavior. Extensions to the more general isobaric form of the Gibbs-Duhem equation, obtained by simultaneously satisfying the Gibbs-Helmholtz equation and the special form of Gibbs-Duhem equation, were discussed.

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Fundamental Thermodynamic Relationships

In this section, we introduce the basic thermodynamic expressions that are of interest to us in equation solving. From classical thermodynamics it is well known that the intensive properties of a single phase at any temperature T and pressure P are homogeneous functions of degree zero in mole-numbers. Thus, for the partial molar excess free energy of component i in a liquid mixture $\bar{G}_i^E$, application of Euler's theorem gives,

$$\sum_j l_j(\partial \bar{G}_i^E/\partial l_j) = 0, \quad i = 1, 2, \ldots, n_c. \qquad (1)$$

This expression can be restated in terms of the activity coefficient as,

$$\sum_j l_j(\partial \ln \gamma_i/\partial l_j) = 0, \quad i = 1, 2, \ldots, n_c. \qquad (2)$$

Also, the continuity of the second derivatives of the total excess free energy of a liquid mixture gives the following symmetric relationship,

$$(\partial \ln \gamma_i/\partial l_j) = (\partial \ln \gamma_j/\partial l_i), \quad i = 1, 2, \ldots, n_c, j = 1, 2, \ldots, n_c. \qquad (3)$$

Substitution of Eq. 3 in Eq. 2 results in the special form of the Gibbs-Duhem equation.

$$\sum_j l_j(\partial \ln \gamma_j/\partial l_i) = 0, \quad i = 1, 2, \ldots, n_c. \qquad (4)$$

A similar set of expressions can be derived for the fugacity coefficient of any component in the vapor phase. These relationships are summarized below:

$$\sum_j v_j(\partial \ln \phi_i/\partial v_j) = 0, \quad i = 1, 2, \ldots, n_c. \qquad (5)$$

$$(\partial \ln \phi_i/\partial v_j) = (\partial \ln \phi_j/\partial v_i), \quad i = 1, 2, \ldots, n_c, j = 1, 2, \ldots, n_c. \qquad (6)$$

$$\sum_j v_j(\partial \ln \phi_j/\partial v_i) = 0, \quad i = 1, 2, \ldots, n_c. \qquad (7)$$

It is important to note that the above thermodynamic expressions for each phase are not dependent on the equilibrium that exists between the phases.

It is also true that the molar excess enthalpies of the liquid and vapor phases are homogeneous functions of degree zero in mole numbers. Hence,

$$\sum_j l_j(\partial H^E/\partial l_j) = 0. \qquad (8)$$

$$\sum_j v_j(\partial h^E/\partial v_j) = 0. \qquad (9)$$

Modified Hybrid Approach and Thermodynamic Consistency

The original hybrid approach of Lucia and Macchietto (1983) makes use of the following decomposition of the Jacobian matrix:

$$J(x) = C(x) + A(x) \qquad (10)$$

where $C(x)$ is called the computed part and contains the readily available partial derivatives. $A(x)$ is called the approximated part and includes the derivatives that are difficult and/or expensive to obtain.

In order to generate quasi-Newton approximations to the Jacobian matrix that exploit the Gibbs-Duhem equations and the zero degree homogeneity conditions simultaneously, we must use the following decomposition:

$$J(x) = C_1(x) + C_2(x)A(x). \qquad (11)$$

Here $C_1(x)$ corresponds to $C(x)$ in the original decomposition and $C_2(x)$ is a diagonal matrix that is also readily available. $A(x)$ is a modified approximated part with symmetric partitions.

To illustrate the need for this decomposition, consider a single-stage QP flash problem formulated in terms of the component mole-numbers. The set of nonlinear model equations for this problem is,

Component material balances:

$$f_i - l_i - v_i = 0, \quad i = 1, 2, \ldots, n_c. \qquad (12)$$

Equilibrium equations:

$$K_i l_i \Big/ \left(\sum_j l_j\right) - v_i \Big/ \left(\sum_j v_j\right) = 0, \quad i = 1, 2, \ldots, n_c. \qquad (13)$$

Energy balance equation:

$$\left(\sum_i f_i\right) H_f - \left(\sum_i l_i\right) H - \left(\sum_i v_i\right) h + Q = 0. \qquad (14)$$

where f_i, l_i, and v_i denote the component molar flow rates in the feed, liquid, and vapor streams respectively. K_i is the equilibrium ratio of component i, which is a function of the flash temperature T, flash pressure P, and the equilibrium compositions of the exit streams. H_f, H, and h are the molar enthalpies of the feed, liquid and vapor streams respectively. Q denotes the constant heat duty to the flash drum.

The vector of unknown variables is $(l_1, l_2, \ldots, l_{n_c}, v_1, v_2, \ldots, v_{n_c}, T)^T$. The computed part $C_1(x)$ [or $C(x)$ in the original decomposition] for this particular example can be found in the paper by Lucia (1985). The computed part $C_2(x)$ and the approximated part $A(x)$ are given by the following equations.

$$C_2(x) = \begin{bmatrix} 1 & & & & & & \\ & \ddots & & & & & \\ & & 1 & & & & \\ & & & \left(\dfrac{K_1 l_1}{\sum_j l_j}\right) & & & \\ & & & & \ddots & & \\ & & & & & \left(\dfrac{K_{n_c} l_{n_c}}{\sum_j l_j}\right) & \\ & & & & & & 1 \end{bmatrix} \tag{15}$$

In summary, the following information about the modified approximated part is important for building a thermodynamically consistent quasi-Newton update:

1. The overall nonsymmetric matrix $A(x)$ has partitions that are symmetric.
2. The matrix $A(x)$ should satisfy the secant information to a reasonable accuracy, since it is well established that this condition is essential for good numerical performance,
3. The symmetric partitions should satisfy both the zero-degree homogeneity conditions and the Gibbs-Duhem equations.
4. The derivatives of the excess enthalpies should also satisfy certain zero-degree homogeneity conditions.

It is important to note that the thermodynamic constraints are exact and should be satisfied at every iteration, unlike the secant condition, which holds only in the limit.

$$A(x) = \begin{bmatrix} 0 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ \vdots & & \vdots & \vdots & & \vdots & \vdots \\ 0 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ \left(\dfrac{\partial \ln \gamma_1}{\partial l_1}\right) & \cdots & \left(\dfrac{\partial \ln \gamma_1}{\partial l_{n_c}}\right) & -\left(\dfrac{\partial \ln \phi_1}{\partial v_1}\right) & \cdots & -\left(\dfrac{\partial \ln \phi_1}{\partial v_{n_c}}\right) & 0 \\ \vdots & & \vdots & \vdots & & \vdots & \vdots \\ \left(\dfrac{\partial \ln \gamma_{n_c}}{\partial l_1}\right) & \cdots & \left(\dfrac{\partial \ln \gamma_{n_c}}{\partial l_{n_c}}\right) & -\left(\dfrac{\partial \ln \phi_{n_c}}{\partial v_1}\right) & \cdots & -\left(\dfrac{\partial \ln \phi_{n_c}}{\partial v_{n_c}}\right) & 0 \\ -\left(\sum_j l_j\right)\dfrac{\partial H^E}{\partial l_1} & \cdots & -\left(\sum_j l_j\right)\dfrac{\partial H^E}{\partial l_{n_c}} & -\left(\sum_j v_j\right)\dfrac{\partial h^E}{\partial v_1} & \cdots & -\left(\sum_j v_j\right)\dfrac{\partial h^E}{\partial v_{n_c}} & \Delta \end{bmatrix} \tag{16}$$

where $\Delta = -(\Sigma_j l_j)(\partial H^E/\partial T) - (\Sigma_j v_j)(\partial h^E/\partial T)$. Note that the matrix $A(x)$ contains the nonideal derivatives of the functions $\ln \gamma_i$, $\ln \phi_i$, H^E, and h^E. Suppose we define the following two vectors:

$$z_1 = (l_1, l_2, \ldots, l_{n_c}, 0, 0, \ldots, 0, 0)^T \tag{17}$$

and

$$z_2 = (0, 0, \ldots, 0, v_1, v_2, \ldots, v_{n_c}, 0)^T. \tag{18}$$

Then the following conditions are equivalent to Eqs. 2, 5, 8, and 9.

$$Az_1 = \mathbf{0}. \tag{19}$$

$$Az_2 = \mathbf{0}. \tag{20}$$

Therefore, the vectors z_1 and z_2, and similarly any other linear combination of them, lie in the null space of $A(x)$. Also, the $[n_c \times n_c]$ block containing the derivatives of $\ln \gamma$ is symmetric from Eq. 3. A similar symmetry condition holds for the other $[n_c \times n_c]$ block containing the derivatives of $\ln \phi$. Because the null space and partition symmetry conditions imply that the Gibbs-Duhem equation must hold, it follows that this modified decomposition is necessary for exploiting the Gibbs-Duhem equations and zero-degree homogeneity conditions.

Thermodynamically Consistent Quasi-Newton Updates

We developed quasi-Newton formulae that satisfy all four conditions given in the previous section in the following way. Initially, we built partition-symmetric updates that satisfied either the secant condition or the thermodynamic constraints. Then we used the method of iterated projections of Dennis and Schnabel (1979) to generate matrix approximations that satisfied the thermodynamic constraints at each iteration as well as the secant condition toward the limit.

Partition-symmetric secant updates

In this section we briefly discuss the development of updates that satisfy only the secant condition. There are indeed several ways of specifying the secant condition which give rise to algorithms that have the same asymptotic rate of convergence, Q-superlinear. However, their numerical performances are widely different. Here we present some experiments done with different implementations and the relative merits of each update.

Overall Secant Condition. One way of specifying the secant information for $A(x)$ involves the definition of an overall secant condition (by row). Let A and $\bar{A}$ be the successive approximations to $A(x)$; then the overall secant condition is

$$\bar{A}s = y_A \tag{21}$$

where s is the change in the variable vector between two successive iterates. The righthand side of Eq. 21 can be specified by either of the following equations:

$$y_A = \bar{C}_2^{-1}(y - \bar{C}_1 s) \tag{22}$$

$$y_A = [f_A^{k+1} - f_A^k] \tag{23}$$

where y is the change in the function vector corresponding to the model equations between two successive iterates and f_A is the function vector whose derivatives are the elements of the approximated part [e.g., ln (γ_i/ϕ_i) corresponding to the equilibrium equations]. However, note that the secant condition given by Eq. 22 involves the inverse of a diagonal matrix C_2. From Eq. 15, we can see that the diagonal matrix C_2 contains terms that are multiples of component flow rates in one of the streams. During the course of the iterative solution procedure, the component flow rates may assume negative values and it is customary to reset these flow rates to very small positive values. Under these circumstances, the matrix C_2 becomes near-singular and has an inverse that can cause numerical difficulties. This problem can be avoided by using Eq. 23 to define the secant condition. On the other hand, because of the way in which the derivatives of the energy balance are split it is not possible to find a suitable function whose derivatives are the elements in the corresponding row of A. Hence, a combination of Eqs. 22 and 23 is needed. The secant condition corresponding to the equilibrium equations can be specified according to Eq. 23; for the energy balance Eq. 22 can be used.

A least-change secant update that makes use of the partition-symmetric structure and the above modified secant conditions was developed. However, this secant update gave rise to scaling problems that led to the prediction of incorrect null spaces when the thermodynamic constraints were included by the method of iterated projections. For example, in the case of single-stage, two-phase flash calculations, the corrections to the nonideal derivatives of one phase were exactly equal and opposite to the corrections to the other phase, due to the linearity of the component mass balances. Even in multistage liquid-vapor problems, this partition-symmetric secant formula updated the derivatives of activity and fugacity coefficients to the same order of magnitude. (They usually differ by one to two orders of magnitude). These scaling problems in turn gave rise to consistently bad performance of the thermodynamically consistent updates.

Completely Separable Element Functions. The following implementation alleviates the above-mentioned difficulties. In solving liquid-vapor problems, we know that the activity coefficients are not dependent on the change in the vapor phase component mole numbers, and similarly the fugacity coefficients are not dependent on the change in the liquid phase component mole numbers. Thus, the logarithmic values of these two nonideal thermodynamic properties form a set of completely separable element functions whose domains are also completely separable when the temperature dependence of these functions is neglected. Therefore, the secant condition can be specified for each symmetric partition of A independently, based on the iterative change of these element functions.

To exploit this complete separability, we write the overall matrix A as,

$$A = \sum_{m=1}^{n_p} A_m + A_{n_p+1} \tag{24}$$

where n_p is the total number of symmetric partitions in A. A_m is a matrix whose only nonzero block is the mth symmetric partition of A. The subscript $n_p + 1$ corresponds to the remaining nonsymmetric partition of A. In our application it contains the nonideal derivatives of the energy balance equations. Let f_{A_m} denote the function vector whose derivatives are the elements of the matrix A_m. Then the secant condition for this matrix is given by,

$$\bar{A}_m s_m = y_{A_m} = (f_{A_m}^{k+1} - f_{A_m}^k) \tag{25}$$

where s_m is a step vector of the variables whose nonzero entries are the step sizes corresponding to the mth partition. The secant condition for A_{n_p+1} is specified according to Eq. 22.

Although the nonzero block of A_m is symmetric, it is symmetric with respect to the overall framework only when it is a diagonal block. The $n \times n$ matrix A_m with a nonzero diagonal block is updated by the PSB (Powell's symmetric Broyden) formula,

$$\bar{A}_m = A_m + (r_m s_m^T + s_m r_m^T)/(s_m^T s_m) - (r_m^T s_m) s_m s_m^T/(s_m^T s_m)^2 \tag{26}$$

where,

$$r_m = (y_{A_m} - A_m s_m). \tag{27}$$

The matrices with nonzero blocks that are not on the diagonal are handled very easily by proper permutation matrices. The nonsymmetric part of A is updated by the Broyden formula,

$$\bar{A}_{n_p+1} = A_{n_p+1} + r_{n_p+1} s_{n_p+1}^T/(s_{n_p+1}^T s_{n_p+1}) \tag{28}$$

where,

$$r_{n_p+1} = (y_{A_{n_p+1}} - A_{n_p+1} s_{n_p+1}). \tag{29}$$

The updated matrices $\bar{A}_m$, $m = 1, \ldots, n_p + 1$ are added together as in Eq. 23 to form the new matrix $\bar{A}$. Computationally, updating of element matrices and their addition to form the matrix $\bar{A}$ can all be done in place, if the locations of the different partitions are properly identified.

Null space corrections

Updates that satisfy only the thermodynamic constraints are built in a manner very similar to the development of secant updates. Let z_m denote the vector in the null space of $\bar{A}_m$ whose nonzero elements are the component flow rates associated with the mth symmetric partition in $\bar{A}$. The $n \times n$ matrix A_m with a nonzero symmetric block on the diagonal is updated by the following form of the PSB formula:

$$\bar{A}_m = A_m - \{(A_m z_m) z_m^T + z_m (A_m z_m)^T\}/(z_m^T z_m) + \{(A_m z_m)^T z_m\} z_m z_m^T/(z_m^T z_m)^2. \tag{30}$$

Again, permutation matrices and Eq. 30 are used to update matrices with nonzero blocks not on the diagonal. The nonzero row of A_{n_p+1} has sections that have different null space conditions. The null space condition for each section is determined by the phase with which it is associated. This is clear from Eq. 16. The null space vector for the derivatives of H^E is different from that for the derivatives of h^E. Thus, each section is updated with a different null space vector. To do this, the nonsymmetric matrix A_{n_p+1} is expressed as the following sum:

$$A_{n_p+1} = \sum_{m'=1}^{n_s} A^{m'}_{n_p+1} + A^{n_s+1}_{n_p+1} \tag{31}$$

where m' denotes the section with a null space associated with it and n_s denotes the total number of such sections. $A^{n_s+1}_{n_p+1}$ is the rest of A_{n_p+1} that is not included in the above sections. The update that satisfies the null space condition for any section is given by the Broyden (1965) formula:

$$\bar{A}^{m'}_{n_p+1} = A^{m'}_{n_p+1} - \{A^{m'}_{n_p+1} z_{m'}\} z^T_{m'}/(z^T_{m'} z_{m'}). \tag{32}$$

The updated matrices are summed according to Eq. 23 to form $\bar{A}$.

Method of iterated projections

In the previous sections we developed quasi-Newton formulae that use either the secant condition or the thermodynamic constraints. Unfortunately, there is no way of finding a partition symmetric update analytically that satisfies the secant and the null space (thermodynamic) constraints simultaneously because of the symmetry associated with the partitions. Hence, in order to make use of both secant and thermodynamic constraints we used the method of iterated projections of Dennis and Schnabel (1979). The principle behind this approach is explained in Figure 1.

Here, M_1 is the set of partition-symmetric matrices that satisfy the secant condition and M_2 is the set of partition-symmetric matrices that satisfy the thermodynamic constraints. Let A be the approximated part at the current iteration. To find the update for the next iteration we must proceed as follows: We first find a matrix $\hat{A} \in M_1$ closest to A in the Frobenius norm; then we find the matrix $\bar{A} \in M_2$ nearest to $\hat{A}$. That is, we use Eqs. 26 and 28 to estimate $\hat{A}$ from the current update A; then we use Eqs. 30 and 32 to evaluate $\bar{A}$ from $\hat{A}$. This order of projection can also be changed. That is, we could project A on M_2 to find $\hat{A}$ and then project $\hat{A}$ on M_1 to find $\bar{A}$. However, it is physically meaningful to terminate the projections on M_2, since the thermodynamic constraints should be satisfied at every iteration. (In the following section on numerical results we compare both of these implementations to see whether this statement is indeed true.) Either of the above sequences of projections can be continued further. However, we suggest that the successive projections be terminated after projecting once on each of the manifolds M_1 and M_2, regardless of the order of projections. This is because we have observed that the extent to which the update $\hat{A} \in M_1$ (a partition-symmetric secant update) satisfies the constraints corresponding to the manifold M_2 (thermodynamic constraints) does not improve significantly on successive projections. A similar observation was made for the update $\bar{A} \in M_2$.

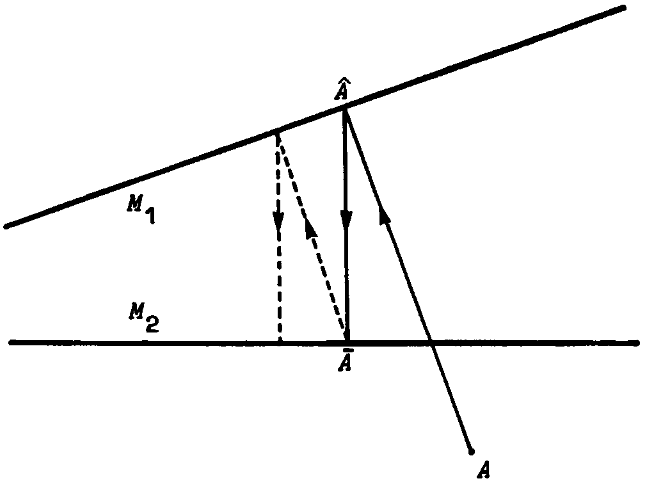

Figure 1. Method of iterated projections.

Dennis and Schnabel (1979) have shown that in the case of two simple affine sets, if the projections are continued infinitely a limit point is reached where the update lies at the intersection of the affine sets and thus satisfies the constraints corresponding to both sets simultaneously. In our case a limit point does exist, but the manifolds M_1 and M_2 do not intersect, due to the symmetry associated with the partitions.

Numerical Results

We studied the numerical performance of various Newton-based fixed-point methods on a variety of single and two-stage problems. What we were looking for was good and consistent performance in solving different types of separation problems rather than the effectiveness in solving isolated cases. The following were the features common to all problems solved.

1. For each problem, the Jacobian was calculated by five different methods.

    N—Newton's method with A calculated by finite difference.

    Hybrid method with A calculated by

    HS—a partition-nonsymmetric secant formula (using Broyden update).

    HPS—a partition-symmetric secant formula (a member of M_1).

    HPST—a sequence of projections, first on M_1 and then on M_2.

    HPTS—a sequence of projections, first on M_2 and then on M_1.

    In building the secant updates, the secant condition was specified partition-wise (even for the update HS). As a consequence of the order of projections used ($\bar{A} \in M_2$), the update HPST satisfies the thermodynamic constraints at every iteration. Hence, it is thermodynamically consistent. On the other hand, the update HPTS satisfies the secant condition at every iteration.

2. The equilibrium pressure was assumed to be 10^5 Pa in all the problems. In liquid-vapor problems, the feed was introduced at its bubble point at a pressure of 5×10^5 Pa.

3. The following ternary mixtures were used in the studies.

    I—benzene, ethanol, and water (335.0 K)
    II—acetic acid, vinyl acetate, and water (270.0 K)
    III—acetone, chloroform, and water (320.0 K)

    The temperatures in parentheses correspond to the stage temperatures used in single-stage liquid-liquid extraction calculations.

4. In our studies we included the nonidealities of both liquid and vapor phases. For estimating the physical properties of the systems, the UNIQUAC model was used for the liquid phase

and the B-truncated virial equation of state was used for the vapor phase (Prausnitz et al., 1980).

5. The Jacobian was initialized by setting $A^0 = 0$. That is, the first step taken was a partial Newton step. This initial step was preferred over the Newton step since it avoided several of the failures for all methods.

6. At every iteration, the correction to the variable vector was a direct prediction step. This step could be modified using Powell's dogleg strategy or by a line-searching procedure. However, we have observed that this modification does not produce any advantage in numerical performance.

7. Convergence was assumed when the Euclidean norm of the function vector fell below a value of 10^{-5}.

8. The maximum number of iterations allowed for convergence was 50.

9. *Resetting Strategy.* During the course of the iteration, if any component flow became negative, it was reset to a small value (10^{-15}) and the step size for this component was reestimated. Sometimes all component flow rates in a stream became negative, thereby wiping out a phase. In such instances, we reevaluated the step vector by resetting $A = 0$. That is, we simply went back to the previous iteration and took a partial Newton step. This resetting was quite effective in avoiding several failures for all methods.

In Table 1 we report the overall numerical performance of all methods in identical environments. NF denotes the number of failures encountered. AI and NPP are, respectively, the average number of iterations and the average number of references to the physical property routines per problem (for the cases when a particular method worked). The references to the thermodynamics models include the calls made to the routines estimating activity and fugacity coefficients, and liquid and vapor enthalpies.

Before giving the details specific to different subproblems, we summarize the overall performance as follows:

Reliability and Efficiency. We consider the numerical results shown in Table 1 to be very encouraging. The thermodynamically consistent update HPST gave good and consistent numerical performance on all problems. It proved to be the most reliable of all of the methods and was also more efficient than all other quasi-Newton formulae.

On all problems, Newton's method converged in the least number of iterations. All the other hybrid methods required more iterations than Newton's method. However, on several examples, during the early iterations, Newton's method took the variables into physically unrealizable regions, which in turn resulted in failure.

Efficiency Related to Thermodynamic Constraints. It can be observed that the update HPS took consistently more iterations to converge in comparison to either the nonsymmetric update HS or the thermodynamically consistent update HPST. This may be attributed to the observation that the error in satisfying the thermodynamic constraints is greater for the update HPS in comparison to the update HS.

Order of Projections. The results reported show that the update HPST failed less often than the update HPTS. This supports the preferred order of projections (i.e., the first projection on M_1 and then on M_2).

Use of Properties of A. Table 1 shows that improvements in reliability are achieved by the inclusion of the partition-symmetric structure and the thermodynamic constraints successively. In going from the nonsymmetric update HS to the thermodynamically constrained update HPST, the number of failures was reduced by about 50%. This supports the conjecture that each piece of information about the approximated part is, in general, useful in improving the performance of the hybrid approach.

Table 1. Numerical Performance for Different Types of Problems

	Problem Type*		
	a	b	c
	No. of Problems		
Method**	150	300	300
	NF (AI, NPP)†	NF (AI, NPP)	NF (AI, NPP)
N	15 (8.50, 44.50)	36 (4.91, 41.28)	6 (6.03, 112.54)
HS	10 (8.32, 18.64)	30 (7.79, 17.58)	0 (9.28, 41.12)
HPS	5 (8.48, 18.96)	29 (8.51, 19.02)	0 (10.93, 47.72)
HPST	3 (8.47, 18.94)	29 (7.31, 16.62)	0 (8.76, 39.04)
HPTS	8 (8.11, 18.22)	30 (7.92, 17.84)	0 (10.22, 44.88)

	Problem Type		
	d	e	f
	No. of Problems		
	300	300	300
	NF (AI, NPP)	NF (AI, NPP)	NF (AI, NPP)
N	92 (8.39, 69.12)	52 (6.19, 103.04)	27 (8.99, 331.64)
HS	45 (12.22, 26.44)	26 (10.34, 45.36)	17 (14.04, 120.32)
HPS	20 (13.25, 28.50)	24 (10.82, 47.28)	18 (15.28, 130.24)
HPST	6 (11.56, 25.12)	15 (10.08, 44.32)	14 (12.50, 108.00)
HPTS	17 (12.13, 26.26)	29 (10.34, 45.36)	18 (14.23, 121.84)

	Overall Comparison	
	No. of Problems	
	1,650	Failures Percent
	NF (AI, NPP)	
N	228 (7.00, 126.91)	13.82
HS	128 (10.49, 47.91)	7.76
HPS	96 (12.32, 51.46)	5.81
HPST	67 (9.92, 44.16)	4.06
HPTS	102 (10.73, 48.42)	6.18

* Problem type:
a Dew Point calculations
b Single-stage TP flash
c Single-stage QP flash
d Single-stage liquid-liquid extraction
e Two-stage TP flash
f Two-stage QP flash
** Defined in text.
† NF No. of failures
AI Avg. no. of iterations
NPP Avg. no. of references to physical property routines per problem

Effect of Nonideality and Complexity of Problems on Numerical Performance. The advantages of using the thermodynamically consistent update HPST are more noticeable when the problems are more nonideal (e.g., liquid-liquid extraction) and/or the model equations are more complex (e.g., two-stage flash problems). Hence, we are encouraged to further apply the thermodynamically consistent hybrid method to multiphase and multistage calculations.

The following sections explain briefly the specific details associated with each subproblem.

Dew point calculations

For each heterogeneous ternary mixture, the dew point temperature and the incipient liquid phase composition were estimated at 50 different random vapor compositions. Care was exercised to avoid regions where the model equations exhibit multiplicity in solution (Van Dongen et al., 1983; Kingsley and Lucia, 1985). At the start of the iterations, the dew point temperature was assumed to be 350.0 K and the incipient liquid composition was set equal to the vapor composition.

The failures reported were due to the temperature getting into unrealistic regions during the course of iteration. We looked for a direct correlation between the material stability of the liquid mixture at the starting point and the failures encountered, but we were unable to find one. However, we do know that the composition iterates wander into materially unstable regions and believe that this may be the cause for the radical jumps in temperature. This belief is partially supported by the observation that dew point problems involving homogeneous mixtures can be solved without failure by any Newton-based fixed point method.

Single-stage TP flash

Fifty different random equilibrium points were generated for each heterogeneous system. Only the problems that resulted in true liquid-vapor solutions were selected (i.e., the liquid-vapor solutions that correspond to global minimum of total Gibbs free energy). This selection was performed with the aid of the algorithm proposed by Kingsley and Lucia (1985) for single-stage *TP* flash problems.

Two different initializations for the component flow rates were used for each feed composition. For one initialization, the composition of the liquid leaving the flash drum was assumed to be equal to the incipient liquid phase composition at the dew point of the feed (at the flash pressure). A random vaporization ratio was also chosen. These estimates and a simple material balance completed the initialization. The second initialization was performed based on the incipient vapor composition at the bubble point of the feed.

Most of the failures reported for these problems were common to all methods. These failures were due to the initial partial Newton step taking the variable vector out of the two-phase region where the usual resetting procedure was of no help.

Single-stage QP flash

The set of equilibrium points described in the previous section was solved as *QP* flash problems. For this, the heat duty to the flash drum for each problem was back-calculated from the solution to the corresponding *TP* flash problem. This way, the equilibrium solution was easily checked.

Again, the incipient vapor/liquid composition at the bubble/dew point of feed (at the flash pressure) was used for the initialization. An arbitrary temperature between the bubble and dew points was assumed to be the flash temperature.

Failures were found to be rare in solving single-stage *QP* flash problems. The few failures that did occur were due to oscillations in the variable vector, which resulted in the failure of Newton's method to reach the convergence tolerance within the iteration limit.

Single-stage liquid-liquid extraction

For these problems, 50 different random compositions of the effective feed (feed plus extraction solvent) were generated for each system. Care was exercised to ensure that all these compositions laid under the binodal curve for each system at the corresponding equilibrium temperature and pressure.

Two different initializations were used for each effective feed. For each initialization, two (random) rich phases, each rich in one of the two components of the immiscible pair, were assumed. The third component was randomly distributed between these two phases.

Newton's method performed poorly on these highly nonideal problems. It failed on approximately one-third of the problems. We attribute this to the highly nonlinear nature of the composition derivatives of the excess Gibbs free energy. It is well known that these derivatives exhibit a change in curvature in heterogeneous liquid mixtures. With this in mind, we again looked for correlation between the material stability of liquid mixtures and failure to find an equilibrium point. First, we observed that even if the initialization gave rise to materially stable liquid phases, these phases did not necessarily remain stable throughout the course of iteration. The iterates often wandered into materially unstable regions. Furthermore, starting with stable liquid phases did not necessarily reduce the number of failures.

During the course of the iterative solution procedure, the step vector corresponding to any one of the two phases (the step sizes are equal and opposite for the two phases) may align with the eigenvector associated with the smallest eigenvalue of the sum of the total Gibbs Hessian matrices of the two phases. This alignment sometimes results in the prediction of very large steps that often wipe out one of the two phases. A succession of such bad steps leads to the failure of the method. For Newton's meth-

Table 2. Alignment of Step Vector with Eigenvector for Newton's Method

Component	Flow Rate Phase 1 kmol/s	Flow Rate Phase 2 kmol/s	$[\nabla^2(nG)^{\text{I}} + \nabla^2(nG)^{\text{II}}]/RT$			Eigenvalues	Eigenvector for smallest Eigenvalue	Newton* Step Phase 2	Normalized Newton Step	Normalized Partial Newton Step
Case 1: Compositions of phases near spinodal curve; phases 1 and 2 are stable										
Ethanol	12.965	20.263	0.04535	−0.06521	−0.05882	0.00354	0.8585	31.780	0.8560	0.8753
Benzene	14.781	1.593	−0.06521	0.45922	0.02430	0.12794	0.0960	5.198	0.1400	0.4787
Water	4.915	45.483	−0.05882	0.02430	0.09913	0.47221	0.5038	18.470	0.4975	−0.0678
Case 2: Compositions of phases away from spinodal curve; phase 1 is unstable, phase 2 is stable										
Ethanol	22.343	10.885	0.05348	−0.10998	−0.02392	−0.00071	0.4998	143.762	0.5119	0.2924
Benzene	15.190	1.184	−0.10998	0.55681	0.02602	0.04096	0.0583	18.023	0.0642	0.0990
Water	19.430	30.968	−0.02392	0.02602	0.01137	0.58141	0.8642	240.562	0.8566	0.9511

*Step vector for phase 1 is equal to and opposite that for phase 2.
Temp., 335.0 K; pressure, 10^5 Pa.

od, these alignments of vectors occur under the following circumstances: (i) when the compositions of the two phases fall near the spinodal curve (here the stability of the individual phases does not matter), or (ii) when the compositions of the two phases are away from the spinodal curve with one phase being stable while the other phase is unstable. In the first case, the alignment always leads to very large step sizes irrespective of the sign of the eigenvalue. The latter results in large steps only when the smallest eigenvalue is negative. Also, the smaller the eigenvalue, the more pronounced is the alignment. To combat these difficulties we use a partial Newton step. The partial Newton step is usually small and avoids any alignment completely. Table 2 illustrates these difficulties and the effectiveness of our resetting strategy for the two different cases of alignment described above. These alignments occurred during the course of the iterative solution procedure when the same equilibrium point was solved using two different initializations. It can be seen that normalized Newton correction is nearly equal to the appropriate eigenvector, whereas the normalized partial Newton correction is quite different.

To illustrate the superiority of the thermodynamically consistent update HPST over Newton's method, we present the iteration history of these two methods in Figures 2 and 3 for a particular example of system I. The (effective) component feed rates and the initialization for the two phases are given in Table 3. The binary interaction parameters were taken from Prausnitz et al. (1980). For this example, the calculations were started with the same stable liquid phases for each of the methods compared. On subsequent iterations, one of the phases wandered into a materially unstable region. Newton's method wiped out the unstable liquid phase at every step upon entry into this materially unstable region. The resetting strategy helped to avoid early failure by replacing these wild steps with partial Newton steps. Hence, initially the progress was made only with the help of partial Newton steps. However, in the long run failure became unavoidable when the Newton step selectively wiped out two of the three components in the unstable phase. If partial Newton steps were used throughout the solution procedure, convergence would have been achieved in 95 iterations. The thermodynamically consistent update HPST was unaffected by this migration across the spinodal curve and easily converged to the solution in 13 iterations.

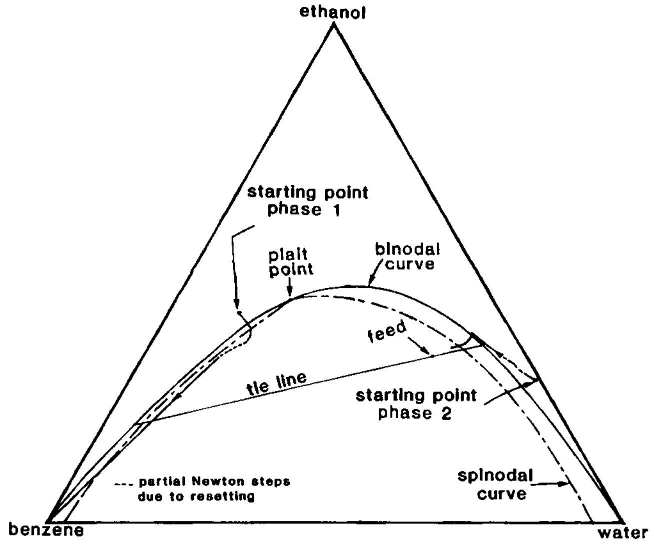

Figure 2. Iteration history for Newton's method.
System: ethanol-benzene-water; 335.0 K, 10^5 Pa.

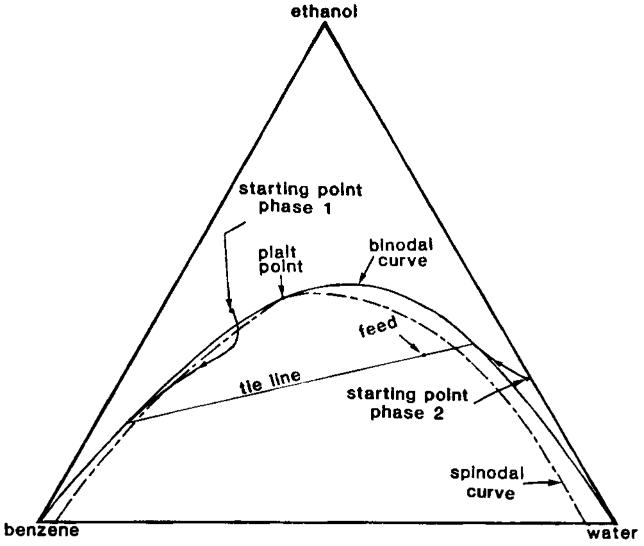

Figure 3. Iteration history for the thermodynamically consistent update, HPST.
System: ethanol-benzene-water; 335.0 K, 10^5 Pa.

Two-stage TP flash

This two-stage liquid-vapor problem is essentially a small distillation unit consisting of a reboiler and a partial condenser. The partial condenser is the first stage and the reboiler is the second stage. The feed is introduced into the reboiler. The vapor and liquid products are withdrawn from the first and second stages, respectively.

Fifty different random equilibrium points were generated for each system. Again, only the equilibrium points that resulted in true liquid-vapor solutions at each stage were selected. Two different initializations were used for each feed mixture. For one initialization the lightest component was chosen as the reference component. The split for this component was arbitrarily selected, with a considerable percentage going in the distillate. The splits for the other components were fixed using Fenske's equation. The total flow rates of all streams were initiated using Underwood's correlation. The composition of the liquid recycled to the second stage was assumed to be equal to the composition of the liquid stream leaving the second stage. Finally, a simple material balance fixed the values of all remaining unknown vari-

Table 3. Initialization for Single-stage Liquid-liquid Extraction Problem

	Flow Rate, kmol/s		
Component	Effective Feed	Phase 1	Phase 2
Ethanol	33.228	14.198	19.030
Benzene	16.374	15.787	0.587
Water	50.398	4.392	46.006

Temperature, 335.0 K; pressure, 10^5 Pa.

ables. A similar initialization was performed using the heaviest component as the reference component.

There were two major causes that led to failures in these problems. One cause was the oscillation of the variables and hence failure to reach convergence tolerance within the iteration limit. The second kind of failure was due to wiping out a phase during the iterative solution procedure, for which the usual resetting procedure was of no help.

Two-stage QP flash

The set of equilibrium points described in the previous section was solved as two-stage *QP* flash problems. For this, the heat duties for the drums for each problem were back-calculated from the solution to the corresponding two-stage *TP* flash problem. The same procedure described in the previous section was used to initialize the component flow rates. The equilibrium temperature in the second stage was arbitrarily assumed to be between the bubble point and the dew point of the feed mixture (at the flash pressure). The equilibrium temperature in the first stage was set randomly between the second stage temperature and the bubble point of the feed. The nature of failures encountered here was the same as described in the previous section.

Exploiting the Gibbs-Helmholtz Equation

The use of thermodynamic constraints to build quasi-Newton matrix approximations is not limited to the Gibbs-Duhem equation. For example, up to this point, we have omitted the temperature derivatives of $\ln \gamma$ and $\ln \phi$ in A when the equilibrium temperature was one of the unknown variables (see the last column of A in Eq. 16). This was done to avoid the numerical difficulties caused by the differences in scale between the temperature and composition derivatives of the equilibrium equation (Miller and Lucia, 1985). However, these temperature derivatives can be introduced in A without scaling problems by exploiting the Gibbs-Helmholtz equation, which is given by

$$(\partial \ln \gamma_i/\partial T) = -(\bar{H}_i^E/RT^2), \quad i = 1, 2, \ldots, n_c \tag{33}$$

and

$$(\partial \ln \phi_i/\partial T) = -(\bar{h}_i^E/RT^2), \quad i = 1, 2, \ldots, n_c \tag{34}$$

The temperature derivatives of $\ln \gamma$ and $\ln \phi$ are updated using the linear constraint given by,

$$\sum_i l_i \bar{H}_i^E = \left(\sum_i l_i\right) H^E \tag{35}$$

or

$$\sum_i v_i \bar{h}_i^E = \left(\sum_i v_i\right) h^E \tag{36}$$

in conjunction with the Gibbs-Helmholtz equation, provided the partial derivatives of the energy balance equation are expressed as partial molar enthalpies (both ideal and excess parts). Note that satisfying the special form of the Gibbs-Duhem equation and the Gibbs-Helmholtz equation for each elemental matrix is equivalent to satisfying the isobaric form of the Gibbs-Duhem equation.

Preliminary experiments done with this alternate implementation show that the temperature derivatives of $\ln \gamma$ and $\ln \phi$ can be updated to the right order of magnitude. Work is continuing toward determining whether it is better to use the null space condition of the molar excess enthalpies and forget about the temperature derivatives of $\ln \gamma$ and $\ln \phi$, or to use the Gibbs-Helmholtz equation.

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Notation

A = part/whole of the approximated part of the Jacobian
$\bar{A}$ = updated approximated part of the Jacobian
C, C_1, C_2 = computed parts of the Jacobian
f = function vector
f = component feed flow rate
G = molar Gibbs free energy
$\bar{G}$ = partial molar Gibbs free energy
H = molar enthalpy of liquid mixture
$\bar{H}$ = partial molar liquid enthalpy
h = molar enthalpy of vapor mixture
$\bar{h}$ = partial molar vapor enthalpy
J = Jacobian matrix
K = equilibrium ratio
l = component liquid flow rate
M = matrix with special properties
n = dimension of the domain/range of a matrix
n_c = total number of components
n_p = total number of symmetric partitions
n_s = total number of sections of the row in the approximated part corresponding to the energy balance equation that have null spaces associated with them
P = pressure
Q = heat duty
r = error in the secant condition
s = step vector of the variables
T = temperature
v = component vapor flow rate
x = variable vector
y = iterative change in the function vector
z = the null space vector
γ = activity coefficient
ϕ = fugacity coefficient

Subscripts

A = corresponding to A
A_m = corresponding to A_m
i, j = component indices in a phase
m = index for a symmetric partition of the approximated part
m' = index for a section with a null space condition in the nonsymmetric partition of the approximated part
$n_p + 1$ = index for the nonsymmetric partition of the approximated part

Superscripts

E = excess part
I = ideal part
I = corresponding to phase 1
II = corresponding to phase 2
k = iteration counter
m' = index for a section with a null space condition in the nonsymmetric partition of the approximated part
$n_s + 1$ = index for the portion not included in the sections with null space conditions in the nonsymmetric partition of the approximated part
T = transpose

Literature Cited

Broyden, C. G., "A Class of Methods for Solving Nonlinear Simultaneous Equations," *Math. Comp.*, **19**, 577 (1965).

Dennis, J. E., and R. B. Schnabel, "Least-Change Secant Updates for Quasi-Newton Methods," *SIAM Rev.*, **21**, 443 (1979).

Kingsley, J. P., and A. Lucia, "Using the Structure of Solutions to Multiphase Equilibrium Problems as a Computational Tool," submitted to *AIChE J.* (1985).

Lucia, A., "Partial Molar Excess Properties, Null Spaces, and the New Update for the Hybrid Method of Chemical Process Design," *AIChE J.*, **31**, 558 (1985).

Lucia, A., and S. Macchietto, "New Approach to Approximation of Quantities Involving Physical Property Derivatives in Equation-Oriented Process Design," *AIChE J.*, **29**, 705 (1983).

Lucia, A., D. C. Miller, and A. Kumar, "Thermodynamically Consistent Quasi-Newton Formulae," *AIChE J.*, **31**, 1,381 (1985).

Miller, D. C., and A. Lucia, "The Behavior of a Hybrid Fixed-Point Method in a Chemical Process Design Environment," *AIChE J.*, **31**, 329 (1985).

Prausnitz, J., et al., *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria,* Prentice-Hall, Englewood Cliffs, NJ (1980).

Van Dongen, D. B., M. F. Doherty, and J. R. Haight, "Material Stability of Multicomponent Mixtures and the Multiplicity of Solutions to Phase Equilibrium Equations. 1: Nonreacting Mixtures," *Ind. Eng. Chem. Fund.*, **22**, 472 (1983).

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