Uniqueness of Solutions to Single-Stage Isobaric Flash Processes Involving Homogeneous Mixtures

All single-stage isobaric flash processes involving multicomponent homogeneous mixtures are shown to have unique two-phase solutions. No simplifications with regard to nonideal phase behavior are made. The main result for the isothermal, isobaric (*TP*) case is established with the aid of a different characterization of material stability, the Gibbs-Duhem equation, and the Cauchy interlace theorem. Results for the other traditional specifications of heat duty and pressure (*QP*), and total vapor flow rate and pressure (*VP*) are proved by establishing a one-to-one correspondence between the solution sets for *TP* and *QP* and the solution sets for *TP* and *VP* flash problems, respectively. Construction of these one-to-one mappings results in some interesting analysis associated with the appropriate plane curves in the *TQ* and *TV* planes. Some new properties of the underlying matrices involved in the phase equilibrium of homogeneous mixtures are presented.

Angelo Lucia
Department of Chemical Engineering
Clarkson University
Potsdam, NY 13676

Introduction

The separation literature contains a large number of papers that deal with the modeling and subsequent computer solution of separation processes involving homogeneous mixtures, ideal and nonideal. A very good and recent survey of the field is given by Wang and Wang (1981). In spite of the vast amount of literature, there are very few articles concerned with the question of the uniqueness of real solutions for even simple processes like single-stage flash calculations, let alone distillation.

The question of uniqueness arises because the set of model equations that describe separation processes is nonlinear and the equations in the set are quite often large in number. Furthermore, the answer to this question is important because:

- It is of theoretical interest in its own right.
- It is important to the process design and control system design tasks.
- It would possibly assist in the development and/or numerical analysis of computer tools or algorithms for solving separation process problems involving homogeneous mixtures, provided constructive proofs of uniqueness (or nonuniqueness) could be found.

The purpose of this paper is to study the question of uniqueness of solutions to single-stage isobaric flash processes involving homogeneous multicomponent mixtures. The long-range goal is the multistage case, with emphasis on distillation. To our knowledge, Doherty and Perkins (1982) are the only other workers who have investigated this problem. They did so by studying the stability of the dynamic model equations and restricting their attention to constant molar overflow. We make no such restriction here. Instead, we consider energy balance effects and analyze the steady state model directly.

Our analysis shows that the solution to any single-stage isobaric flash problem involving a multicomponent homogeneous mixture is unique. In all cases uniqueness rests on the assumption of the metastability of the single liquid and single vapor solutions. Solution curves for the energy balance equation (for the *QP* case) and the vapor specification equation (for the *VP* case) are studied and shown to be monotonic. This analysis has also led to the discovery of new properties of the matrices involved in phase equilibrium. These new properties include the interlocking eigenvalue relationship between the Gibbs Hessian matrix for any homogeneous fluid and its projection onto the mass balance constraint for that closed phase, and the inverse nonnegativity of the projected Jacobian matrix of the phase equilibrium equations.

A second, closely related objective is to provide constructive proofs that may aid in the development of new computer tools or may contribute to the numerical analysis and understanding of existing algorithms for solving these and other types of separation problems. The monotonicity of the various solution curves used in our analysis implies that numerical solution to these flash problems can be guaranteed by certain homotopy methods. Other implications of the analysis with regard to the computer solution of these problems and extensions to the multistage case are also discussed.

Problem Statement

Consider the flash drum shown in Figure 1. The nonlinear equations that model the steady state operation of the flash drum, assuming that it is an equilibrium stage, are

$$f_i - l_i - v_i = 0, \quad i = 1, 2, \dots, n_c \tag{1}$$

$$K_i l_i/\Sigma l_j - v_i/\Sigma v_j = 0, \quad i = 1, 2, \dots, n_c \tag{2}$$

$$H_f(\Sigma f_j) - H^L(\Sigma l_j) - H^V(\Sigma v_j) + Q = 0 \tag{3}$$

where f_i, l_i, and v_i are the ith component molar flow rates in the feed, liquid product, and vapor product streams, respectively. K_i is the ith component equilibrium ratio or K value, and H denotes the enthalpy of the appropriate stream. T and p are the temperature and pressure, Q is the heat duty, and n_c is the number of components in the homogeneous mixture.

Simple analysis shows that there are $n_c + 4$ degrees of freedom, which are usually fixed by specifying the $n_c + 2$ feed conditions (i.e., the f_i's, T_f, and p_f) and any two variables from the set $\{T, p, Q, V\}$. Assuming that the specifications are chosen below the critical state of the mixture (to avoid retrograde effects) and so as to define at least one real vapor-liquid solution (positive amounts of material in each phase), we seek an answer to the question: Is this solution unique? The answer is yes, and the rest of this paper is devoted to proving that fact.

Outline of Some Uniqueness Proofs

The proofs that follow are done in the following way. We use the classification of the single-stage flash problem due to Boston and Britt (1978) and consider the *TP* flash problem first. This allows us to remove the energy balance from the analysis and pose the problem as a Gibbs free energy minimization problem.

Having posed the *TP* flash problem as a Gibbs free energy minimization subject to the linear mass balance constraints, we then use convexity arguments and some standard affine projections to show that the Gibbs function is a convex function on the convex set defined by the mass balance constraints, provided that the mixtures are homogeneous and stable. This produces the result that the equilibrium solutions (i.e., phase equilibrium points) also form a convex set. Finally, some simple null space arguments, which are necessary because of the Gibbs-Duhem equation, show that there is only one member in the solution set, even for homogeneous mixtures that form azeotropes. The energy balance is then used to produce a unique heat duty and the uniqueness proof for the *TP* flash problem is complete.

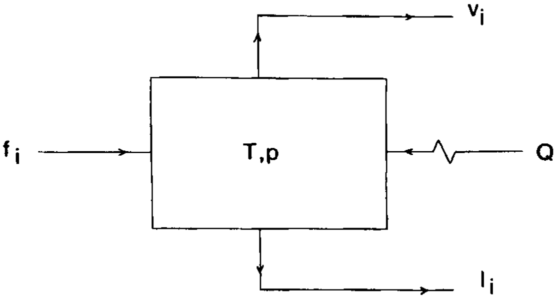

Figure 1. Two-phase flash process

Solutions of the remaining isobaric flash types (i.e., *QP* and *VP*) are proved to be unique for multicomponent homogeneous mixtures by producing injective (or one-or-one) mappings from the solutions to *TP* flash problems to the solutions for these other pairs of specifications.

Stable Homogeneous Mixtures

Most of what we can actually prove rests on the assumption that the multicomponent mixtures (vapor and liquid) under consideration are homogeneous for all physically meaningful compositions over the temperature and pressure range of interest. That is, we require that both the single-liquid and single-vapor-phase solutions be stable with respect to phase splitting for all compositions over the temperatures and pressures of interest and are therefore metastable solutions in the true two-phase region (see Van Dongen et al., 1983, for a good treatment of material stability). While this may seem to be an unreasonable assumption, it is not. In fact, it is precisely in line with any intuitive concept of a homogeneous fluid. To make this more rigorous we need the following definition.

Definition. Let T and p be fixed. A fluid is said to be a stable homogeneous fluid at the composition of interest if the matrix $P^T\nabla^2GP$, the projection of the Hessian matrix onto the mass balance constraint, is positive definite.

This requires some interpretation. Suppose n_i denotes the number of moles of component i in this single homogeneous fluid phase and let n_T, the total number of moles of mixture, be fixed (the system is closed). Classical thermodynamics tell us that if this mixture has the potential to exist in a single phase at this composition at the given T and p, then the Gibbs free energy of the system must be a minimum with respect to all changes in composition. Furthermore, this phase is stable at the given composition if any $(n_c - 1) \times (n_c - 1)$ block of the Hessian matrix of the Gibbs free energy is positive definite (Van Dongen et al.). This condition of stability can be stated in its equivalent form:

$$\nabla^2 G \tag{4}$$

is positive definite when projected onto the tangent subspace defined by the constraint

$$\Sigma n_i - n_T = 0. \tag{5}$$

We will treat these projections in a manner similar to that given in Luenberger (1973).

We denote the tangent subspace defined by the mass balance constraint (i.e., Eq. 5) by M and define it in the following way:

$$M = \{\Delta n \in R^{n_c} : J\Delta n = 0\}, \tag{6}$$

where J is the $1 \times n_c$ Jacobian matrix of the constraint, which is normal to the constraint surface and given by

$$J = (1, 1, \ldots, 1) \tag{7}$$

The important thing to note about the definition of the tangent subspace is that for any vector in M, $n + \Delta n$ will satisfy the mass balance constraint provided that the point n did.

To project $\nabla^2 G = \nabla^2 G(n)$ onto the tangent subspace we must construct an orthonormal basis for M. To do this, we can simply use a technique such as Gram-Schmidt orthogonalization to build a new basis for R^{n_c} from the standard (or canonical) basis. If we let J^T be the first vector in this new basis, then the $n_c - 1$ remaining vectors generated by the Gram-Schmidt process will form an orthogonal basis for M because J is orthogonal to M. Furthermore, if we normalize each vector and simply reorder them, we can produce a new orthonormal basis, say B, for R^{n_c}. This basis is given by

$$B = \{p_1, p_2, \ldots, p_{n_c-1}, p_{n_c}\} \tag{8}$$

where p_i, $i = 1, 2, \ldots, n_c - 1$ are the vectors formed from the orthogonalization and normalization process and are an orthonormal basis for M, and $p_{n_c} = (1/\sqrt{n_c})\, J^T$. Finally, if we form the $n_c \times (n_c - 1)$ matrix

$$P = [p_1 p_2 \cdots p_{n_c-1}], \tag{9}$$

then $P^T \nabla^2 G P$ is the projection of $\nabla^2 G$ onto the tangent subspace defined by the mass balance constraint. Note that it is an $(n_c - 1) \times (n_c - 1)$ symmetric matrix, which reflects the fact that not all n_i, $i = 1, 2, \ldots, n_c$, can vary independently in a closed system.

If $P^T \nabla^2 G P$ is positive definite, then it follows that the homogeneous fluid phase is stable at that composition. This is the characterization of material stability that we will use throughout this manuscript. It is different from but completely equivalent to the criteria given in Van Dongen et al. Also, note that the fact that $P^T \nabla^2 G P$ is positive definite does not imply that $\nabla^2 G$ is positive definite.

For fixed T and p, if $P^T \nabla^2 G P$ is positive definite for all physically meaningful n (i.e., n such that $n_i > 0$ for $i = 1, 2, \ldots, n_c$), then we say that the homogeneous fluid is globally stable with respect to composition.

Finally, if this homogeneous fluid is globally stable with respect to composition for all temperatures and pressures of interest, then we simply say that it is globally stable. Note this implies that $P^T \nabla^2 G P$ is positive definite independent of composition, temperature, and pressure.

We end this section with a proof that for any stable homogeneous fluid, $\nabla^2 G$, the Hessian matrix of the Gibbs free energy function is positive semidefinite in the full space of the variables. It is not a particularly difficult proof; however, we can not find it anywhere in the literature. It relies on the above characterization of material stability, the Gibbs-Duhem equation, a simple change of basis, and eigenvalue analysis.

Lemma 1. Let T and p be fixed and let $n \neq 0$ denote the composition of interest of any stable homogeneous fluid. Then $\nabla^2 G$ is positive semidefinite.

Proof. The special form of the Gibbs-Duhem equation at constant T and p implies that

$$n^T \nabla^2 G n = 0. \tag{10}$$

This means that $\nabla^2 G$ is singular or that the Hessian matrix of the Gibbs function has at least one zero eigenvalue at the given composition. The question is, what are the other $n_c - 1$ eigenvalues?

$\nabla^2 G$ is the standard matrix representation of the second derivatives of the Gibbs function. Thus, the basis for the domain and range spaces, which are the same, is the standard or canonical basis. We denote this standard basis by B_s, and it is given by

$$B_s = \{e_1, e_2, \ldots, e_{n_c}\}, \tag{11}$$

where e_i is the usual unit vector in R^{n_c}.

The key to the proof is the change of basis from B_s to B given by Eq. 8. We define P_B by

$$P_B = [p_1 p_2 \cdots p_{n_c}]. \tag{12}$$

Note that P_B is the $n_c \times n_c$ matrix formed by adjoining p_{n_c} with the $n_c \times (n_c - 1)$ matrix P. Furthermore P_B is an orthogonal matrix.

Because P_B is orthogonal $P_B^T \nabla^2 G P_B$ and $\nabla^2 G$ have the same eigenvalues. Thus, the matrix $P_B^T \nabla^2 G P_B$ has at least one zero eigenvalue. However, observe that the $P_B^T \nabla^2 G P_B$ matrix can be partitioned as follows:

$$P_B^T \nabla^2 G P_B = \left[\begin{array}{c|c} P^T \nabla^2 G P & P^T \nabla^2 G p_{n_c} \\ \hline p_{n_c}^T \nabla^2 G P & p_{n_c}^T \nabla^2 G p_{n_c} \end{array}\right]. \tag{13}$$

The upper left $(n_c - 1) \times (n_c - 1)$ partition is positive definite because the homogeneous fluid is stable by hypothesis. Consequently, $P_B^T \nabla^2 G P_B$ has $(n_c - 1)$ positive eigenvalues and one zero eigenvalue by Cauchy's interlace theorem (Parlett, 1980, p. 186). Because $\nabla^2 G$ and $P_B^T \nabla^2 G P_B$ have the same eigenvalues, $\nabla^2 G$ has $(n_c - 1)$ positive eigenvalues and one zero eigenvalue. Thus, $\nabla^2 G$ is positive semidefinite at the given composition of a stable homogeneous fluid.

The following are also true; the proofs are unnecessary.

1. For any homogeneous fluid that is globally stable with respect to composition at a specified temperature and pressure, $\nabla^2 G$ is globally positive semidefinite with respect to composition.
2. For any globally stable homogeneous fluid, $\nabla^2 G$ is globally positive semidefinite.

The foregoing proof and the related results are very useful in establishing the uniqueness of any solution to the single-stage *TP* flash problem for stable homogeneous mixtures. They do so because they provide us with the fact that the Gibbs function for a stable homogeneous mixture is globally convex.

Uniqueness Proofs

It seems logical to start the proofs of the uniqueness of solutions to single-stage flash processes involving homogeneous mixtures with the isothermal, isobaric (*TP*) case because of the equivalence between Eqs. 1 and 2 and an appropriately posed minimum Gibbs free energy problem.

TP flash process

At constant temperature and pressure, the Gibbs free energy of any closed system takes on its minimum value (consistent with material balance) at a point of equilibrium. The second law of thermodynamics for reversible processes guarantees this. For the steady state operation of an isothermal, isobaric flash process, the system is open but this has no consequence on the condition of phase equilibrium because the material balances ensure that the amount of mass in the system (the vessel) is constant. Thus, the flash process can be taken as a closed system with regard to the phase equilibrium. This enables us to pose Eqs. 1 and 2 in the convenient form

$$\min G \tag{14}$$

$$\text{subject to} \quad f_i - l_i - v_i = 0, \quad i = 1, 2, \ldots, n_c \tag{15}$$

assuming that we are in the true two-phase region.

In order to prove a uniqueness result for the single-stage *TP* flash we use the following, which can be found in Hestenes (1975).

Definition 2. A set S in R^n is convex if, given two points x_1 and x_2 in S,

$$x = \alpha x_1 + (1 - \alpha)x_2$$

is in S for all α, $0 \le \alpha \le 1$.

Lemma 2. (Theorem 5.1, Hestenes, p. 28) Let f be a convex function on a convex set S. If a point x^* in S affords a local minimum to f on S, then x^* minimizes f on S. The set of minimum points on S is convex. If f is strictly convex, it has at most one minimum point on S.

We also need the following characterization of a convex function on a convex set.

Lemma 3. (Corollary, Hestenes, p. 33) Let f be class C^2 (twice continuously differentiable) on an open convex set S. Then f is convex on S if and only if at each point x in S we have

$$h^T \nabla^2 f(x) h \ge 0 \tag{16}$$

for all h such that $x + h$ is in S. If at each x in S we have

$$h^T \nabla^2 f(x) h > 0 \tag{17}$$

for all nonzero h such that $x + h$ is in S, then f is strictly convex on S.

This lemma simply means that f is convex on S if and only if $\nabla^2 f$ is positive semidefinite on S, and is strictly convex on S if and only if $\nabla^2 f$ is positive definite on S.

We now state and prove the uniqueness result for the isothermal, isobaric flash.

Theorem 1. Let T and p be given. Let the mixture under consideration be any multicomponent mixture that is globally stable with respect to composition in both the liquid and vapor phases. Let the specifications of temperature and pressure define a two-phase solution that does not lie at an azeotropic point. Then this solution is unique.

Proof. We want to use lemma 2 to prove uniqueness, so the first thing that we show is that the set of points that satisfy the component mass balance constraints, say C, is a convex set.

The tangent subspace defined by the constraints is given by

$$M = \{\Delta x \text{ in } R^{2n_c} : J\Delta x = 0\}, \tag{18}$$

where the $n_c \times 2n_c$ Jacobian matrix of the constraints is

$$J = -[I \mid I] \tag{19}$$

The identity matrices in Eq. 19 are both of order n_c.

This tangent subspace is a convex set. To see this, simply choose any Δx_1 and Δx_2 in M and use the definition of a convex set. Direct computation gives:

$$J\Delta x = J[\alpha\Delta x_1 + (1 - \alpha)\Delta x_2] = \alpha J\Delta x_1 + (1 - \alpha)J\Delta x_2 = 0.$$

The set of points that satisfy the mass balance constraints can be written as

$$C = \{r \text{ in } R^{2n_c} : Jr + f = 0\}, \tag{20}$$

where f is the vector of fixed-feed molar flow rates. Observe that this set C is an affine set because it is simply a linear translation of the vector space M. The tangent subspace M is also called the parallel subspace of C. Because M is a convex set and C is parallel to M, the set of points that satisfy the component mass balances is also convex.

Next we show that the Gibbs function is a convex function on the convex set C.

The matrix that projects onto M has the form

$$P = (1/\sqrt{2})\left[\begin{array}{c} I \\ \hline -I \end{array}\right] \tag{21}$$

and the columns of P constitute an orthonormal basis for M. Furthermore, because C is parallel to M, the matrix P can be used to project onto C.

Observe that any Δx in M can be written as

$$\Delta x = Py \tag{22}$$

for some y in R^{n_c}. Also observe that, if we agree on a variable ordering, the Hessian matrix of the Gibbs function is given by

$$\nabla^2 G = \left[\begin{array}{c|c} \nabla^2 G^L & 0 \\ \hline 0 & \nabla^2 G^V \end{array}\right]. \tag{23}$$

This matrix is $2n_c \times 2n_c$, block diagonal and symmetric. $\nabla^2 G^L$ and $\nabla^2 G^V$ are full, $n_c \times n_c$ symmetric matrices that denote the Hessian of the liquid and vapor phases, respectively.

Let $x = (l_1, l_2, \ldots, l_{n_c}, v_1, v_2, \ldots, v_{n_c})^T$ be any physically meaningful point in C. Also, define $h = \Delta x = Py$ and $\nabla^2 f(x) = \nabla^2 G(x)$ in lemma 3. It follows that $x + h$ is in C and that $h^T \nabla^2 f(x) h = \frac{1}{2} y^T P^T \nabla^2 G P y$. Furthermore, direct calculation shows that

$$P^T \nabla^2 G P = \nabla^2 G^L + \nabla^2 G^V. \tag{24}$$

Consequently, $h^T \nabla^2 f(x) h = \frac{1}{2} y^T (\nabla^2 G^L + \nabla^2 G^V) y$.

Finally, because the liquid and vapor phases are stable with respect to phase splitting, $\nabla^2 G^L$ and $\nabla^2 G^V$ are positive semidefinite at x by lemma 1. Thus, $h^T \nabla^2 f(x) h = \frac{1}{2} y^T (\nabla^2 G^L + \nabla^2 G^V) y \ge 0$. This means that the Gibbs function is convex on C, the set of points that satisfy the mass balances. Unfortunately, we cannot make the stronger statement that the Gibbs free energy function is strictly convex on C because the matrix $P^T\nabla^2 GP$ can have a null space. This null space arises when the kernels of the matrices $\nabla^2 G^L$ and $\nabla^2 G^V$ (which are a consequence of the Gibbs-Duhem equation) align at points of equal composition in both phases.

The fact that the Gibbs free energy function is convex on the convex set of points which satisfy the material balances allows us to invoke lemma 2 and conclude that the set of minimizers of G that are consistent with the conservation of mass form a convex set. Let X denote this convex solution set.

Because the specifications of temperature and pressure define a two-phase solution, the set X is not empty. Let $x^* = (l_1^*, l_2^*, \ldots, l_{n_c}^*, v_1^*, v_2^*, \ldots, v_{n_c}^*)^T$ be any member of X. We must prove that X contains only one element. To do this, we use the standard ploy of assuming there is more than one solution and producing a contradiction. We also use some null space arguments.

Let x_1^* and x_2^* be any two arbitrary members of X. Also let $N(x^*)$ denote the null space of $\nabla^2 G$ at x^* in X. This null space is defined by $N(x^*) = \{z \text{ in } R^{2n_c}\colon \nabla^2 G(x^*)z = 0\}$.

Because the set X is convex,

$$x^* = \alpha x_1^* + (1 - \alpha)x_2^* = x_1^* + (\alpha - 1)(x_1^* - x_2^*)$$
$$= x_1^* + (\alpha - 1)\Delta x$$

is also a minimizer of G on C for any α such that $0 \le \alpha \le 1$. This implies that $\Delta x = x_1^* - x_2^*$ is in $N(x_1^*) \cap M$ because any other perturbation in M causes an increase in G.

Certainly, $\Delta x = 0$ is in $N(x_1^*) \cap M$. The only way that $\Delta x \neq 0$ can be in $N(x_1^*) \cap M$ is if the Hessian matrices of the liquid and vapor phases share the same null space because of the form of Eq. 24. That is, for $\Delta x \neq 0$

$$0 = \Delta x^T \nabla^2 G \Delta x = \tfrac{1}{2} y^T P^T \nabla^2 G P y$$
$$= \tfrac{1}{2} y^T (\nabla^2 G^L + \nabla^2 G^V) y$$

if and only if $\nabla^2 G^L y = \nabla^2 G^V y = 0$. Note that $\Delta x \neq 0$ implies $y \neq 0$.

If x_1^* is not an azeotropic point, the condition just described cannot occur because the Gibbs-Duhem equation for each phase tells us the null spaces of $\nabla^2 G^L$ and $\nabla^2 G^V$ are different if the compositions of the two phases are different. So immediately we see that if x_1^* is not an azeotropic point, $N(x_1^*) \cap M = \{0\}$ and the two-phase solution to the problem defined by Eqs. 14 and 15 must be unique.

Because x^* is the unique solution to the Gibbs free energy minimization problem, it is also the unique solution to Eqs. 1 and 2 at the same temperature and pressure. This follows from the opening remarks on the TP flash process. Also, the energy balance is explicit in Q. Let Q^* be the value of the heat duty associated with x^*. It follows that (x^*, Q^*) is the unique solution to Eqs. 1, 2, and 3 at constant T and p. This completes the proof.

Unfortunately, if the solution to the minimum Gibbs free energy problem lies at an azeotropic point (which means the feed is an azeotropic mixture), then the solution is not unique. An azeotropic mixture behaves like a pure component in that it changes phase completely (or boils) at constant temperature. Therefore, in this case the heat duty must also be specified in order to fix the total amount of liquid and vapor. This is the meaning of the singularity of the projected Gibbs Hessian at any azeotropic composition, as shown in the proof of theorem 1.

We end this section by noting that many of the mathematical properties used in the foregoing proof (e.g., global material stability and Cauchy's interlace theorem as it applies to the Hessian matrix of the Gibbs function) have been verified by numerical computation for a variety of homogeneous, nonideal multicomponent mixtures.

QP flash process

Recall that for the TP flash problem the heat duty, Q^*, is most conveniently calculated from the energy balance equation after the phase equilibrium point is determined. For any fixed feed composition, suppose we follow the solution of the phase equilibrium equations, say x^*, and the energy balance equation, Q^*, parameterized in T between the bubble and dew point temperatures of that feed. Remember that $x^* = (l_1^*, l_2^*, \ldots, l_{n_c}^*, v_1^*, v_2^*, \ldots, v_{n_c}^*)^T$. Theorem 1 guarantees that for each temperature in this range x^* is unique; but what about Q^*? That is, for two different temperature specifications, say T_1 and T_2, are the corresponding heat duties Q_1^* and Q_2^* different?

Intuitively, one would think that the answer to the above question is yes for homogeneous mixtures. In fact, the solution curve for the energy balance equation in the TQ plane should look qualitatively like the one shown in Figure 2a. However because of nonlinear effects (such as enthalpies of mixing), it is not entirely obvious that this is the case. If the solution curve to the energy balance equation is like the one shown in Figure 2a, then this fact implies that solutions to QP flash problems are unique. It does so because it establishes a one-to-one correspondence between the set of solutions to TP flash problems and the solution set for QP flash problems. If, on the other hand, the solution curve to the energy balance equation behaves like the one shown in Figure 2b, then solutions to QP flash problems may exhibit multiplicity.

Mathematically, the proof of uniqueness to QP flash problems involving homogeneous mixtures is equivalent to showing that there are no turning points in the solution curve of the energy balance equation in the TQ plane. Let the energy balance equation for a single-stage flash drum (i.e., Eq. 3) be denoted by

$$E(Q, x, T) = 0. \tag{25}$$

For convenience, we have dropped the * superscript. It is understood that all points (Q, x, T) satisfy the mass and energy balance and equilibrium equations.

To follow the solution curve of the energy balance equation (for fixed feed conditions) parameterized in T, we use the implicit function theorem (see, e.g., Taylor and Mann, 1972). This is rather standard nonlinear analysis, which is the common starting point for classical stability and bifurcation theory as well as homotopy theory and perturbation analysis. In our case we must be careful to account for both the explicit and implicit effects of temperature on the solution curve of the energy balance equation. Note that changing T changes x through the phase equilibrium conditions and that Eq. 25 is a function of x as well as temperature.

We establish the effect of T on the phase equilibrium point for homogeneous mixtures.

Lemma 4. Let the multicomponent mixture under consideration be a homogeneous mixture. For any nonazeotropic but fixed feed conditions, let $x = (l_1, l_2, \ldots, l_{n_c}, v_1, v_2, \ldots, v_{n_c})^T$

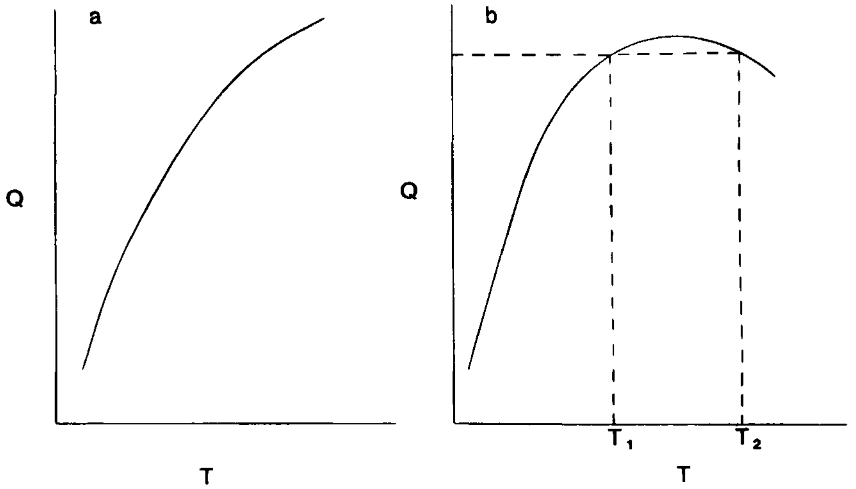

Figure 2. Qualitative behavior of energy balance equation solution curves

denote the two-phase equilibrium point for a specified temperature T and pressure p. The change in x with respect to T at isobaric conditions is given by $\Delta x = \sqrt{2}P(\nabla^2 G^L + \nabla^2 G^V)^{-1}(\overline{H}^L \overline{H}^V)\Delta T/T$.

Proof. The Kuhn-Tucker conditions for the minimization problem defined by Eqs. 14 and 15 are

$$\mu - J\lambda = 0 \tag{26}$$

$$c(x) = 0 \tag{27}$$

where $\mu = [(\mu^L)^T \,\vdots\, (\mu^V)^T]^T$, J is defined by Eq. 19; Eq. 27 is the compact representation of the component mass balances (i.e., Eq. 15); and λ is a vector of Lagrange multipliers associated with the mass balance constraints. μ^L and μ^V are vectors of chemical potentials for the liquid and vapor phases, respectively. Note that each is a function of temperature and the composition of the appropriate phase at isobaric conditions. The vectors μ^L, μ^V, and λ are all of length n_c.

It is easy to show that the Kuhn-Tucker conditions are equivalent to the set of equations

$$\mu^L - \mu^V = 0 \tag{28}$$

$$c(x) = 0. \tag{29}$$

Also, note that Eqs. 28 and 29 are equivalent to Eqs. 1 and 2.

Theorem 1 guarantees that for fixed T and p the solution to Eqs. 28 and 29 is unique. It also guarantees that there are no turning or bifurcation points on the solution curve for the collection of phase equilibrium and mass balance equations parameterized in temperature. Thus we can use the implicit function theorem to establish the relationship between x and T at isobaric conditions. Equation 28 can be written compactly as $f(x, T) = 0$. Application of the implicit function theorem gives $f(\overline{x}, \overline{T}) = f(x, T) + J_x\Delta x + J_T\Delta T$ to first order, where ΔT is an arbitrary small perturbation in temperature and $\overline{T} = T + \Delta T$. This small perturbation in temperature results in a change in the equilibrium point, Δx, and $\overline{x} = x + \Delta x$. J_x and J_T are matrices of first partial derivatives of Eq. 28 with respect to x and T, respectively. J_x is an $n_c \times 2n_c$ matrix and J_T is an $n_c \times 1$ matrix. They are given by

$$J_x = [\nabla^2 G^L \,\vdots\, -\nabla^2 G^V] \tag{30}$$

$$J_T = -(\overline{S}^L - \overline{S}^V) = -(\overline{H}^L - \overline{H}^V)/T \tag{31}$$

where $\overline{S}^L$ and $\overline{S}^V$ are the vectors of partial molar entropies for the liquid and vapor phases, respectively.

Because we are following solutions to the phase equilibrium equations in temperature, $f(\overline{x}, \overline{T}) = f(x, T) = 0$. This yields

$$J_x\Delta x = -J_T\Delta T. \tag{32}$$

To ensure that we follow the part of the solution curve to the phase equilibrium equations that is consistent with the conservation of mass, we project onto the tangent subspace defined by the mass balance equations. This reduces the dimension of the space of the solution curve due to the linearity of the component mass balances.

Recall that $\Delta x = Py$, where P is defined by Eq. 21. This together with Eq. 32 gives

$$\begin{aligned} y &= -(J_xP)^{-1}J_T\Delta T \\ &= \sqrt{2}(\nabla^2 G^L + \nabla^2 G^V)^{-1}(\overline{H}^L - \overline{H}^V)\Delta T/T. \end{aligned} \tag{33}$$

The null space arguments used in the proof of theorem 1 guarantee that $J_xP = (1/\sqrt{2})(\nabla^2 G^L + \nabla^2 G^V)$ is invertible provided that x is not an azeotropic point, which it is not by hypothesis. Thus,

$$\Delta x = \sqrt{2}P(\nabla^2 G^L + \nabla^2 G^V)^{-1}(\overline{H}^L - \overline{H}^V)\Delta T/T \tag{34}$$

which gives the local temperature dependence of the phase equilibrium point consistent with the conservation of mass.

Note that Eq. 34 can be written as

$$\begin{bmatrix} \Delta l \\ \hdashline \Delta v \end{bmatrix} = \begin{bmatrix} (\nabla^2 G^L + \nabla^2 G^V)^{-1}(\overline{H}^L - \overline{H}^V) \\ \hdashline -(\nabla^2 G^L + \nabla^2 G^V)^{-1}(\overline{H}^L - \overline{H}^V) \end{bmatrix}(\Delta T/T)$$

where $\Delta l = (\Delta l_1, \Delta l_2, \ldots, \Delta l_{n_c})^T$ and $\Delta v = (\Delta v_1, \Delta v_2, \ldots, \Delta v_{n_c})^T$, and that $\Delta v = -\Delta l$, which is required by mass balance.

It now becomes a simple matter to show that the solution curve to the energy balance equation cannot have any turning points, or equivalently that solutions to QP flash problems involving homogeneous mixtures are unique. We state this result in the following theorem.

Theorem 2. Let Q and p be given. Let the mixture under consideration be any multicomponent mixture that is globally stable in both the liquid and vapor phases. Let the specifications of heat duty and pressure define a two-phase solution that does not lie at an azeotropic point. Then the solution is unique.

Proof. Let x denote the phase equilibrium point and T denote the corresponding equilibrium temperature. By the implicit function theorem

$$E(\overline{Q}, \overline{x}, \overline{T}) = E(Q, x, T) + J_Q \Delta Q + J_x \Delta x + J_T \Delta T, \quad (35)$$

where J_Q, J_x, and J_T are the parts of the Jacobian matrix of the energy balance equation associated with the heat duty, the molar flow rates of the equilibrium phases, and temperature, respectively. They are

$$J_Q = 1 \quad (36)$$

$$J_x = -[\overline{H}_1^L, \overline{H}_2^L, \ldots \overline{H}_{n_c}^L \,|\, \overline{H}_1^V, \overline{H}_2^V, \ldots, \overline{H}_{n_c}^V] \quad (37)$$

$$J_T = -\Sigma l_j (\partial H^L / \partial T) - \Sigma v_j (\partial H^V / \partial T). \quad (38)$$

Note that J_Q and J_T are scalar quantities and that J_x is a $1 \times 2n_c$ matrix of partial molar enthalpies.

The fact that $E(\overline{Q}, \overline{x}, \overline{T}) = E(Q, x, T) = 0$ and Eqs. 35 and 36 imply the relationship

$$\Delta Q = -(J_x \Delta x + J_T \Delta T). \quad (39)$$

This condition, lemma 4, and the fact that $J_x P = (1/\sqrt{2})(\overline{H}^L - \overline{H}^V)^T$ give

$$\Delta Q = [(1/T)(\overline{H}^L - \overline{H}^V)^T (\nabla^2 G^L + \nabla^2 G^V)^{-1} (\overline{H}^L - \overline{H}^V) - J_T] \Delta T. \quad (40)$$

Observe that the first term on the righthand side of Eq. 40 is positive because T is positive and that $(\nabla^2 G^L + \nabla^2 G^V)^{-1}$ is positive definite because the liquid and vapor phases are globally stable. The temperature derivative of any molar enthalpy function is also positive and thus so is the term in brackets. This precludes the occurrence of any turning points in the solution curve of the energy balance equation. Consequently, for any fixed but nonazeotropic feed conditions there is a one-to-one correspondence between the solution set for TP flash problems and the set of solutions for QP flash problems. This fact and theorem 1 imply that solutions to QP flash problems involving homogeneous mixtures are unique.

We have conducted numerical experiments on a variety of homogeneous multicomponent mixtures in order to verify that Eq. 40 is correct. For example, for the ternary mixture of methanol, benzene, and n-hexane we computed phase equilibrium points at 0.2 K intervals between the bubble and dew point temperatures of the feed by solving Gibbs free energy minimization problems. For this system the UNIQUAC equation was used to model the excess Gibbs free energy of the liquid phase and the vapor phase was assumed to be ideal. For each equilibrium temperature the corresponding heat duty was calculated *a posteriori* by solving the energy balance equation. We then computed the heat duty as predicted by Eq. 40 for a 0.2 K perturbation in T for each equilibrium temperature (and corresponding phase equilibrium point) and compared these values with the actual heat duties obtained from the energy balance calculations. The results of this comparison are the plane curves shown in Figure 3.

Very little in the way of discussion is needed. The energy balance solution curve behaved exactly as expected, monotonic in temperature. We note that for the methanol, benzene, n-hexane system the solution curve is concave; for other homogeneous mixtures (for example, ethanol, acetone, water) the solution curve is convex. However, regardless of curvature the curves are always monotonic. One thing that did come as a surprise was the excellent agreement between the actual heat duty and that predicted by Eq. 40, which is only a first-order perturbation. We did not expect it to be that good. Finally, we note that the actual and predicted local temperature dependence of the phase equilibrium point also showed very good agreement.

VP flash process

In order to produce the one-to-one correspondence between the solutions to TP and VP flash problems, we again use lemma 4 and the implicit function theorem, this time on the vapor specification equation

$$S(V, x) = V - \Sigma v_i = 0. \quad (41)$$

However, unlike the QP flash, there is no fortuitous symmetric term associated with the operator $(\nabla^2 G^L + \nabla^2 G^V)^{-1}$ (see Eq. 40). Rather the slope of the solution curve takes the form

$$-J(\nabla^2 G^L + \nabla^2 G^V)^{-1} (\overline{H}^L - \overline{H}^V)/T, \quad (42)$$

where J is defined by Eq. 7. This asymmetry forces us to use some additional matrix analysis in order to show that the solution curve in the TV plane behaves monotonically, and thus prove uniqueness.

To do the proof we must sharpen our characterization of the matrix $(\nabla^2 G^L + \nabla^2 G^V)$. Up to this point, we have characterized it as a positive definite matrix. However, it is more than that; its

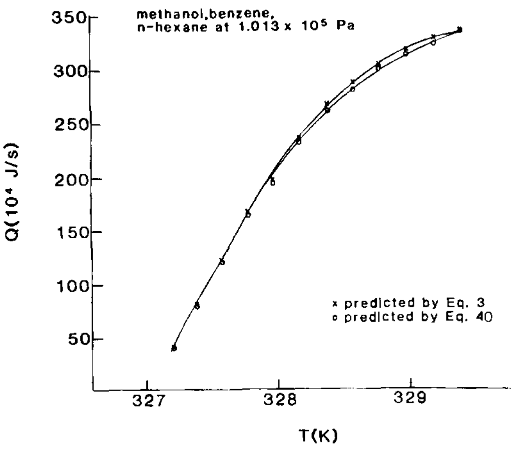

Figure 3. Energy balance solution curve

inverse is a nonnegative matrix. This, in turn, implies that $(\nabla^2 G^L + \nabla^2 G^V)^{-1}$ is an isotone operator.

We need the following definitions from the Perron-Frobenius theory of nonnegative matrices. These definitions can be found in Varga (1962) or the more recent text by Berman and Plemmons (1979).

Definition. Let A be an $n \times n$ real matrix. Then A is a nonnegative matrix (written $A \geq 0$) if $a_{ij} \geq 0, \quad i, j = 1, 2, \ldots, n$.

Definition. An $n \times n$ real matrix A is a Stieltjes matrix if it satisfies each of the following conditions:

- A is symmetric,
- $a_{ij} \leq 0$, for all $i \neq j$
- A is positive definite.

A Stieltjes matrix is also called a symmetric M-matrix.

At this point, it is instructive to consider three different cases:

1. Binary mixtures in which either phase can have ideal or nonideal solution behavior.
2. Multicomponent ideal mixtures.
3. Multicomponent mixtures in which at least one of the equilibrium phases is nonideal.

For cases 1 and 2 it is easy to show that the matrix $(\nabla^2 G^L + \nabla^2 G^V)$ is a Stieltjes matrix when the phases are homogeneous. For example, for any binary mixture, the Gibbs-Duhem equations for $\nabla^2 G^L$ and $\nabla^2 G^V$ together with the condition of positive semidefiniteness of $\nabla^2 G^L$ and $\nabla^2 G^V$ guarantee that $(\nabla^2 G^L + \nabla^2 G^V)$ is a Stieltjes matrix, whether the phases are ideal or nonideal. For the multicomponent ideal case, straightforward differentiation of $nG = \Sigma n_i[\mu_i + RT \ln (n_i/\Sigma n_j)]$, the Gibbs-Duhem equation and the positive definiteness of $(\nabla^2 G^L + \nabla^2 G^V)$ show that $(\nabla^2 G^L + \nabla^2 G^V)$ is a Stieltjes matrix. Thus for cases 1 and 2 we can use the following theorem from Graybill (1983) to establish the inverse nonnegativity of $(\nabla^2 G^L + \nabla^2 G^V)$.

Lemma 5. Let A be an $n \times n$ Stieltjes matrix. Then every element in A^{-1} is nonnegative.

The proof of lemma 5 is given in Graybill (p. 402). It involves a simple induction on the Gauss-Jordan elimination process.

For multicomponent mixtures in which either phase (or both) can exhibit nonideality, the situation is a bit different. For many multicomponent mixtures the matrix $(\nabla^2 G^L + \nabla^2 G^V)$ is a symmetric M-matrix over the temperature and pressure range of interest. Thus, $(\nabla^2 G^L + \nabla^2 G^V)$ is inverse nonnegative by lemma 5. On the other hand, for some mixtures, the matrix $(\nabla^2 G^L + \nabla^2 G^V)$ is not a Stieltjes matrix. Nevertheless it is inverse nonnegative; for an illustration of this see Table 1.

Table 1. Illustration of Inverse Nonnegativity

Mixture	Methanol, benzene, *n*-hexane
Pressure	1×10^5 Pa
Equilb. pt.	
Liquid*	(1.374, 3.534, 1.124)
Vapor**	(44.830, 30.171, 18.967)
Temperature	328.98 K
$(\nabla^2 G^L + \nabla^2 G^V) =$	$\begin{bmatrix} 179.54 & -106.36 & 33.31 \\ -106.36 & 251.98 & -533.42 \\ 33.31 & -533.42 & 1{,}624.40 \end{bmatrix}$
$(\nabla^2 G^L + \nabla^2 G^V)^{-1} =$	$\begin{bmatrix} 0.0166 & 0.0206 & 0.0064 \\ 0.0206 & 0.0386 & 0.0122 \\ 0.0064 & 0.0122 & 0.0045 \end{bmatrix}$

*Nonideal, UNIQUAC equation used for lnγ

**Ideal

In order to establish inverse nonnegativity in this case we need the following results from Perron-Frobenius theory. They can be found in Ortega and Rheinboldt (1970) and in Berman and Plemmons (1979).

Definition. Let A, B, and C be real $n \times n$ matrices. $A = B - C$ is a regular splitting of A if $B^{-1} \geq 0$ and $C \geq 0$.

Definition. The spectral radius of an $n \times n$ real matrix A, denoted by $\rho(A)$, is $\rho(A) = \max_{1 \leq i \leq n} |\lambda_i|$ where λ_i is an eigenvalue of A.

Lemma 6. (Ortega and Rheinboldt, p. 56) Let A be an $n \times n$ real matrix and let $A = B - C$ be a regular splitting of A. Then $A^{-1} \geq 0$ if and only if $\rho(B^{-1}C) < 1$.

Lemma 7. Let the multicomponent mixture under consideration be homogeneous. At any two-phase equilibrium point the matrix $(\nabla^2 G^L + \nabla^2 G^V)$ is inverse nonnegative.

Proof. The key to the proof is to split the matrix $(\nabla^2 G^L + \nabla^2 G^V) = A - LL^T$, where A is a symmetric M-matrix and L is at least a positive semidefinite lower triangular M-matrix satisfying the following conditions:

- $L^T A^{-1} L \geq 0$
- $I - L^T A^{-1} L$ is symmetric and positive definite
- $L^T A^{-1} \geq 0$.

Such a split, while not unique, is guaranteed by the form of the excess parts of $\nabla^2 G^L$ and $\nabla^2 G^V$, the Gibbs-Duhem equation for each phase, and the positive definiteness of $(\nabla^2 G^L + \nabla^2 G^V)$.

Application of the Sherman-Morrison-Woodbury formula (Ortega and Rheinboldt, p. 50) gives $(A - LL^T)^{-1} = A^{-1} + A^{-1}L(I - L^T A^{-1} L)^{-1} L^T A^{-1}$, where $A^{-1} \geq 0$ since A is a symmetric M-matrix.

Define $B = I - L^T A^{-1} L$. Then $I - L^T A^{-1} L$ is a regular splitting of B since $I^{-1} > 0$, $L^T A^{-1} L \geq 0$ and $\rho(L^T A^{-1} L) < 1$ because B and $I + L^T A^{-1} L$ are symmetric and positive definite (Berman and Plemmons, p. 192). Consequently $(I - L^T A^{-1} L)^{-1} \geq 0$, and this together with the fact that $A^{-1} \geq 0$ and $L^T A^{-1} \geq 0$ show that $(A - LL^T)^{-1} \geq A^{-1} \geq 0$.

Note that lemma 7 is trivially true for the case where $(\nabla^2 G^L + \nabla^2 G^V)$ is a symmetric M-matrix because in this case a positive definite or semidefinite diagonal matrix can be chosen for L.

Theorem 3. Let V and p be given. Let the mixture under consideration be any multicomponent mixture that is globally stable in both the liquid and vapor phase. Let the specifications of vapor flow and pressure define a two-phase solution that does not lie at an azeotropic point. Then the solution is unique.

Proof. Let x denote the phase equilibrium point and T denote the corresponding equilibrium temperature. By the implicit function theorem

$$S(\overline{V}, \overline{x}) = S(V, x) + J_V \Delta V + J_x \Delta x, \tag{43}$$

where $S(V, x)$ is defined by Eq. 41 and where

$$J_V = 1 \tag{44}$$

$$J_x = -[0, 0, \ldots, 0, 1, 1, \ldots, 1]. \tag{45}$$

Note that the temperature dependence of $S(V, x) = 0$ is implicit through the phase equilibrium point. The fact that $S(\overline{V}, \overline{x}) = S(V, x) = 0$ and Eqs. 44 and 45 imply that $\Delta V = -J_x \Delta x$. Furthermore, the form of J_x and Eq. 34 give the relationship

$$\Delta V = -J(\nabla^2 G^L + \nabla^2 G^V)^{-1}(\bar{H}^L - \bar{H}^V)\Delta T/T, \qquad (46)$$

where J is defined by Eq. 7.

Note that $(\bar{H}^L - \bar{H}^V)$ is a vector of length n_c and that each element of that vector is negative. Furthermore, $J = (1, 1, \ldots, 1)$ and $(\nabla^2 G^L + \nabla^2 G^V)^{-1}$ is a nonnegative matrix either by lemma 5 or lemma 7. This means that the inner product $J(\nabla^2 G^L + \nabla^2 G^V)^{-1}(\bar{H}^L - \bar{H}^V)$ is always negative. (In fact, each term is the inner product is negative.) Since T is positive, the slope of the solution curve of the vapor specification equation is always positive. This precludes the occurrence of any turning points in the solution curve and establishes a one-to-one correspondence between the solution sets to *TP* and *VP* flash problems. Finally, this and theorem 1 combine to establish the uniqueness of solutions to *VP* flash problems involving homogeneous mixtures. This completes the proof.

We have verified the monotonicity of the solution curve for the vapor specification equation (i.e., Eq. 41) for many homogeneous multicomponent mixtures, using numerical computation. Actual solution cuves and those predicted by Eq. 46 show very good agreement. In fact, the solution curves in the *TV* plane are qualitatively similar to those for the energy balance equation and therefore have been omitted here. Finally, note that the arguments used to prove that the vapor specification equation is monotonic in temperature can also be used to show that the solution curves for Δv and Δl are monotonic (see Eq. 34).

Concluding Remarks

The uniqueness proofs for single-stage isobaric flash problems involving homogeneous mixtures are valuable in their own right. They of course show that these systems admit only one solution when properly specified. Thus when an engineer faced with such a problem computes a solution, he or she can be assured that the problem is truly solved. However, the proofs do more than that. They also point the way to future research.

Perhaps the most natural extension of this work is to multistage separation processes involving homogeneous mixtures, such as ordinary distillation. It is our conjecture that the results for the single-stage *QP* flash problem can be extended and combined with the contraction mapping principle (Ortega and Rheinboldt, 1970) to prove uniqueness results for distillation processes involving homogeneous mixtures under a wide variety of specifications.

Second, the results on the monotonicity of the plane curves for systems involving homogeneous mixtures imply that numerical solutions to those flash problems can be guaranteed by homotopy methods. These problems can be started at bubble point feed conditions, naturally parameterized in either T, Q, or V, and continued to the desired specification. The monotonicity of the plane curves guarantees that this homotopy admits a well-defined problem at each stage of the path-following procedure.

Finally, in our opinion, the single biggest contribution of this paper is the discovery of certain new properties of the various underlying Hessian matrices of problems involving the phase equilibrium of homogeneous mixtures. These include the interlocking eigenvalue relationship between the matrices $\nabla^2 G$ and $P^T \nabla^2 G P$ for any homogeneous fluid and the fact that the matrix $(\nabla^2 G^L + \nabla^2 G^V)$ has a nonnegative inverse. To our knowledge, these properties have not been reported in the open literature before.

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Notation

B = set of basis vectors
$c(x)$ = vector of mass balance constraints
C = mass balance constraint manifold
$E(x, T, Q)$ = energy balance
f = ith component molar feed rate
G, G^L, G^V = total Gibbs free energy, for the liquid phase, for the vapor phase
$H, \bar{H}$ = molar enthalpy, partial molar enthalpy
I = identity matrix
J, J_Q, J_x, J_T, J_V = Jacobian matrix, with respect to heat duty, phase equilibrium point, temperature, total vapor flow rate, respectively
K = equilibrium ratio
l = vector of liquid molar flow rates
M = tangent subspace for mass balance constraints
n, n_c = vector of mole numbers, number of components
$N(x)$ = null space at phase equilibrium point
p, p = pressure, ith basis vector
P = projection matrix
Q = heat duty
R = real vector space of dimension n
$S(V, x), S$ = total vapor specification equation, molar entropy
T = temperature
v = vector of vapor molar flow rates
V = total molar vapor flow rate
x, x^* = vector of liquid and vapor molar flow, at the phase equilibrium point
X = convex solution set
z = vector in null space

Subscripts and superscripts

i = component index
f = feed
L = liquid phase
V = vapor phase
T = transpose
$*$ = phase equilibrium point

Greek letters

$\Delta, \Delta T$ = perturbation, in temperature
λ = vector of Lagrange multipliers
μ = vector of chemical potentials
∇ = differential operator

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