ON THE MIN-MAX FORMULATION OF MULTIPHASE CHEMICAL EQUILIBRIUM PROBLEM AND STABILITY ANALYSIS

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In previous works (Geană, 1980, 1981, 1984, 1987), the computation of phase and/or chemical equilibrium has been formulated as a min-max nonlinear primal geometric program with constraints, using the duality theorem. A reformulation of the nonlinear min-max program is suggested, that restates the problem in terms of mole fractions in a reference phase. The potential function, called tangent plan intersection (TPI), is the set of intersections, at the global mixture composition, of tangent plan to the Gibbs free energy of mixing. Based on this tangent plan intersection function, a new approach for the stability analysis is advanced, allowing to obtain the number and the identity of phases, as well as good approximates of the phase compositions. Numerical algorithms are advanced for solving the min-max program, with constraints corresponding to a system that include all the phases considered coexisting at equilibrium.

Key words: Multiphase Equilibria; Chemical Equilibrium; Stability analysis, Tangent plan intersection criterion.

INTRODUCTION

The calculation of the equilibrium of complex multiphase mixtures with chemical reactions is an important problem in chemical engineering, especially in modern process simulation. The problem is of considerable interest, from both the theoretical and computational points of view. Rigorous or unique solutions of phase equilibrium problem in chemically reacting systems are not easily attainable, and rarely is any particular method of solving the problem overwhelmingly superior. Accordingly, many papers in the literature have presented theoretical viewpoints and procedures for calculating multiphase chemical equilibrium problems. The literature of the field and the principal approaches have been reviewed by Smith and Missen[1], Geană[2], Seider et al.[3] and Seider and Widagdo[4].

In some recent papers, the authors (Smith et al.[5], Mc Donald and Floudas[6,7], Sun and Seider[8], Jiang et al.[9], Wasylkiewicz et al.[10]) reviewed the difficulties that arise in computing equilibrium in a multiphase and/or multireaction system and suggested general optimality criteria for the phase stability problem, on the basis of the Gibbs tangent-plane criterion (Baker et al.[11], Michelsen[12]). Important new contributions have been provided by Smith et al.[5] and Jiang et al.[9] who introduced the so-called reaction tangent-plane criterion.

In a series of previous papers (Geană[13-16,2]), an alternative approach was presented based on the theory of geometric programming. The computation of phase and/or chemical equilibrium has been formulated as a min-max nonlinear primal geometric program with constraints, using the duality theorem. This note presents a reformulation of the nonlinear min-max program, restating the problem in terms of mole fractions in a reference phase. The potential function, called tangent plan intersection (TPI), is the set of intersections, at the global mixture composition, of tangent plan to the Gibbs free energy of mixing. Based on this tangent plan intersection function, a new approach for the stability analysis is advanced, allowing to obtain the number and the identity of phases, as well as good approximates of the phase compositions.

Then a nonlinear program with constraints corresponding to a system that include all the phases considered to coexist at equilibrium can be solved. Numerical algorithms are advanced for solving the min-max program.

FORMULATION OF THE MIN-MAX PROBLEM IN THE PRIOR WORKS

Based on the duality theory of geometric programming, the following min-max program was obtained for a chemical system with *N* components (chemical compounds), *F* phases and *R* chemical reactions, at specified temperature, *T*, pressure, *P*, and initial mole numbers of components, n_i^0 ,(Geană[14,16]):

$$\min_{z_i} - \max_{\xi_k} Y = -\sum_i \left(n_i^0 + \sum_k \nu_{ki} \xi_k \right) \ln z_i \qquad (1)$$

with the constraints

$$c_{11} z_1 + c_{12} z_2 + \ldots + c_{1N} z_N \le 1 \qquad (2)$$

$$c_{21} z_1 + c_{22} z_2 + \ldots + c_{2N} z_N \le 1 \qquad (3)$$

$$\ldots$$

$$c_{F1} z_1 + c_{F2} z_2 + \ldots + c_{FN} z_N \le 1 \qquad (4)$$

$$z_i > 0; \qquad i = 1, 2, \ldots N \qquad (5)$$

$$n_i^0 + \sum_k \nu_{ki} \xi_k \ge 0; \qquad k = 1, 2, \ldots R \qquad (6)$$

Y is the corresponding potential function to be considered for optimality, z_i are the primal geometric variables, ξ_k are the extents of chemical reactions, and n_i^0 are the initial mole numbers of components in the system. ν_{ki} are the elements (negative for reactants and positive for products), of a stoichiometric matrix assumed of rank *R*. The first *F* inequality constraints are called posinomials and the matrix of their coefficients is:

$$c_{\phi i} = \exp(-g_{\phi i}) \qquad \phi = 1, 2, \ldots F \qquad (7)$$

$$g_{\phi i} = \frac{\mu_i^0(T)}{RT} + \ln C_{\phi i} \qquad (8)$$

where $\mu_i^0(T)$ is the ideal gas standard chemical potential, and $C_{\phi i}$ is a function dependent of *T, P* and the composition of phase ϕ, as explained in textbooks on chemical thermodynamics (see, for example, Sandler[17]).

Applications of the program (1-6) were presented by Geană[13-16], and by Mrema[18]. The coefficients

$$c_{\phi i} = \frac{1}{C_{\phi i}} \exp\left(-\frac{\mu_i^0(T)}{RT} \right) \qquad (9)$$

may have very low or high values (for example, in the range of $e^{-100} - e^{100}$), leading to computational problems. A change of variable was suggested to scale the problem (Geană[2]):

$$f_i = z_i \exp\left(-\frac{\mu_i^0(T)}{RT} \right) \qquad (10)$$

The program (1-6) becomes:

$$\min_{f_i} - \max_{\xi_k} Y = -\sum_i n_i^0 \ln f_i - \sum_k \xi_k \left(\sum_i \nu_{ki} \ln f_i + \frac{\Delta G_k^0(T)}{RT} \right) \qquad (11)$$

with the constraints

$$\frac{1}{C_{11}} f_1 + \frac{1}{C_{12}} f_2 + \ldots + \frac{1}{C_{1N}} f_N \le 1 \qquad (12)$$

$$\frac{1}{C_{21}} f_1 + \frac{1}{C_{22}} f_2 + \ldots + \frac{1}{C_{2N}} f_N \le 1 \qquad (13)$$

$$\ldots.$$

$$\frac{1}{C_{F1}} f_1 + \frac{1}{C_{F2}} f_2 + \ldots + \frac{1}{C_{FN}} f_N \le 1 \qquad (14)$$

$$f_i > 0; \qquad i = 1, 2, \ldots N \qquad (15)$$

$$n_i^0 + \sum_k \nu_{ki} \xi_k \ge 0; \qquad k = 1, 2, \ldots R \qquad (16)$$

The ideal gas standard Gibbs free energy of reaction is given by:

$$\frac{\Delta G_k^0}{RT} = \sum_i \nu_{ki} \frac{\mu_i^0(T)}{RT} \tag{17}$$

including the constant term $\sum_i n_i^0 \frac{\mu_i^0(T)}{RT}$ in *Y.*

It was shown (Geană[16,2]) that the terms in the constraints have the physical meaning of mole fractions of a component in a phase:

$$X_{\phi i} = \frac{1}{C_{\phi i}} f_i \tag{18}$$

Then the constraints give normalization conditions of mole fractions in a phase:

$$\sum_i X_{\phi i} \le 1 \tag{19}$$

Moreover, the inequality corresponds to the case when a phase cannot exist in the system under given conditions.

NEW FORMULATION OF THE MIN-MAX PROBLEM

We arrive to a new formulation of the multiphase multicomponent chemical equilibrium problem by using the change of variable (Geană[19]):

$$f_i = C_{\phi i}^{ref} X_i \tag{20}$$

The program (11-16) becomes, by taking the phase 1 as reference phase:

$$\min_{X_i} - \max_{\xi_k} Y = -\sum_i n_i^0 \, ln(C_{1i}^{ref} X_i) - \\ -\sum_k \xi_k \left(\sum_i \nu_{ki} ln(C_{1i}^{ref} X_i) + \frac{\Delta G_k^0(T)}{RT} \right) \tag{21}$$

with the constraints

$$X_1 + X_2 + ... + X_N \le 1 \tag{22}$$

$$K_{21} X_1 + K_{22} X_2 + ... + K_{2N} X_N \le 1 \tag{23}$$

….

$$K_{F1} X_1 + K_{F2} X_2 + ... + K_{FN} X_N \le 1 \tag{24}$$

$$X_i > 0 \qquad i = 1, 2, \ldots N \tag{25}$$

$$n_i^0 + \sum_k \nu_{ki} \xi_k \ge 0 \qquad k = 1, 2, \ldots R \tag{26}$$

The phase equilibrium constants are given by:

$$K_{\phi i} = \frac{C_{\phi i}}{C_{1i}^{ref}} \tag{27}$$

An important case is that of phase equilibrium without chemical reactions ($\xi_k = 0$, $k = 1, 2, \ldots R$), when the program (21-26) becomes (Geană[13,16]):

$$\min_{X_i} Y = -\sum_i n_i^0 \, ln(C_{1i}^{ref} X_i) \tag{28}$$

with the constraints (22-25).

The constraints (22-24) give physical conditions for phase splitting, thus:

- for the phases that coexist at the fixed conditions (T, P, n_i^0), the constraints are satisfied with the sign "=";
- for the phases that does not coexist at the fixed conditions (T, P, n_i^0), the constraints are satisfied with the sign "<".

Some general algorithms for solving optimum problems with constraints use the Kuhn-Tucker stationarity conditions (Sima and Varga[20]). At optimum, the values of Kuhn-Tucker multipliers, corresponding to the constraints verified with equal sign, give directly the phase amounts (in mole number) that coexist in equilibrium.

STABILITY AND GLOBAL OPTIMALITY

Similarly to other equivalent formulations of multiphase chemical equilibrium problem, the solution technique is complicated by the facts:

- the number of phases at equilibrium, *F*, is unknown a priory;
- the existence of many solutions, only one being the global optimum.

Several approaches have been proposed in the literature to solve the phase uncertainty problem and to achieve global solutions (see the recent reviews of Sun and Seider[8], and of Seider and Widagdo[4]).

This work advances a new approach for stability analysis and global optimality, based on the restriction to phase equilibrium problem, equation

(28), of the min-max formulation[19]. An initial estimate for locating the optimum of the potential function Y is thus provided. Firstly, for phase equilibrium problem (28), we consider, without restricting the analysis, that the amounts n_i^0 are normalized, $\sum_i n_i^0 = 1$, $i = 1\ldots N$, having the meaning of mole fractions in the global mixture. Then we get the significance of potential function Y: starting with a single phase of mole fractions n_i^0, the Y function is the set of intersections at n_i^0, with changed sign, of the tangent plan to the Gibbs free energy of mixing (G_m/RT) at each composition X_i.

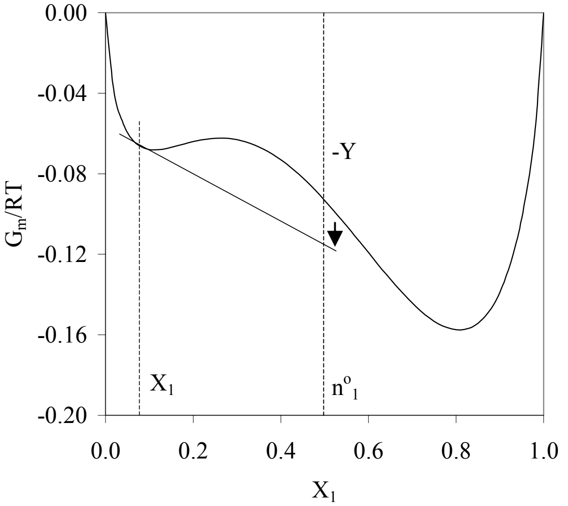

Fig. 1. The Y function as the intersection of tangent plan (TPI) to the Gibbs free energy of mixing, at the global mixture composition n_i^0.

This is illustrated in Fig.1, for a two-component system described by a symmetric free energy (G^E) model, showing phase instability.

It must be observed that this tangent plan is different of that usually traced in the point n_i^0 and giving the intersections at different X_i compositions (Baker et al.[11], and Michelsen[12]).

We call $Y(X_i;\ n_i^0)$ the tangent plan intersection (TPI) function. Fig.2 illustrates the TPI for the mixture having the Gibbs free energy of mixing of fig.1, for three initial compositions n_1^0=0.5, 0.05 and 0.9. For this mixture G_m/RT is a non-convex function, and then the TPI is non-convex too, showing several stationary points (minima, maxima and saddle points).

The following observations are important for the application of the TPI as stability criterion:

- the Y functions have stationary points at the corresponding inflection points (spinodal points) of the Gibbs free energy of mixing (G_m/RT), and at the global mixture composition n_i^0 point;
- the Y functions corresponding to different n_i^0 points cross all at compositions that are the stationary points of G_m/RT function.

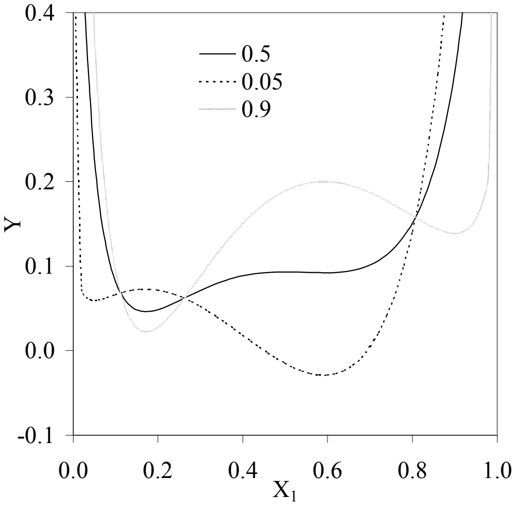

Fig.2. Three tangent plan intersection (TPI) functions for the Gibbs free energy of mixing of fig.1, at initial mole fraction n_1^0= 0.5, 0.05 and 0.9. Spinodal compositions are the stationary points of all Y functions at X_1= 0.18 and 0.6.

The rigorous mathematical proofs of these assertions were given in a previous work (Crişciu and Geană[21]). Stationary points of the TPI, corresponding to spinodal points of G_m/RT can be used as starting approximations in solving the minimization program for phase equilibrium (28) with the constraints (22-25). For binary mixtures the crossing points of any two Y functions can be used as initial starting compositions too. A homotopy-continuation method as that proposed by Sun and Seider[8], or the trajectory method of Wasylkiewicz et al.[10] can be implemented for obtaining of stationary points of TPI function in this work.

ALGORITHMS

Two procedures can be applied to solve the *min-max* program:

- The first method is to solve the min-max program directly, with linear phase constraints (inequalities) at an iteration step[16]. At each iteration, for generated feasible values of reaction extents, a phase equilibrium problem is solved (*min Y*). The search is for a set of reaction extents that gives the *max* (*min Y*). The global minimum of phase equilibrium program (28) is obtained based on the finding of stationary points of the TPI function *Y*.

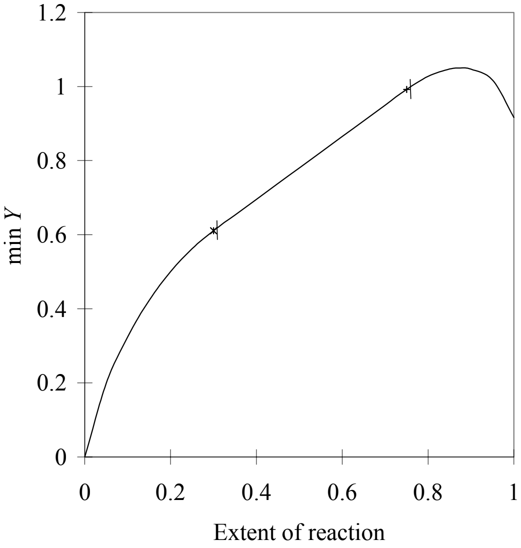

Fig. 3. The dependence min *Y*–ξ for vapor-liquid equilibrium with reaction $A_1 = A_2$.

An example is the vapor(V)-liquid(L) equilibrium with a chemical reaction ($A_1 = A_2$). Then N=2, R=1 and F=2, and assuming ideal behavior in both phases (Geană[14,16]): $C_{11} = P_1^0(T)$; $C_{12} = P_2^0(T)$; $C_{21} = C_{22} = P$. $P_1^0(T)$, $P_2^0(T)$ are the vapor pressures at temperature *T*, and *P* is the total pressure. Considering the vapor phase as reference, the program (21-26) becomes:

$$\underset{X_i}{min}\text{-}\underset{\xi}{max}\, Y = -n_1^0\ ln(PX_1) - n_2^0\ ln(PX_2) - \\ - \xi\left(ln(PX_2) - ln(PX_1) + \frac{\Delta G^0}{RT} \right) \qquad (29)$$

with the constraints

$$X_1 + X_2 \le 1;\quad \frac{1}{K_1}X_1 + \frac{1}{K_2}X_2 \le 1 \qquad (30)$$

where $X_1 > 0$, $X_2 > 0$ and the phase equilibrium constants are:

$$K_1 = \frac{P_1^0(T)}{P};\quad K_2 = \frac{P_2^0(T)}{P} \qquad (31)$$

The first constraint corresponds to the vapor phase, and then the variables X_1, X_2 are the mole fractions in vapor. The terms in the second constraint are the mole fractions in liquid phase.

For given *T, P* the program (29-31) can be solved by choosing a series of values $\xi \in [0, 1]$ and for each case in turn a phase equilibrium problem is solved ($\underset{X_{1,2}}{min} Y$ for given ξ). Fig.3 presents the calculated curve *min* Y(ξ) for $\Delta G^0 = 0$, $P = 1$ atm, $K_1 = 2.8$ and $K_2 = 0.4$ and $n_1^0 = 1$, $n_2^0 = 0$ moles. The maximum lies at $\xi = 0.875$ corresponding to an equilibrium in the liquid phase, for which $X_1 = X_2 = 0.35$. The mole fractions in liquid phase are 0.125 and 0.875 respectively. On the curve in fig.3 it was marked the dew point at $\xi = 0.3$, and the bubble point at $\xi = 0.75$.

- The second method is the application of Kuhn-Tucker multipliers theory that transforms the program in a nonlinear equation system with *N*+*R*+*F* variables (Geană[13,16], Geană and Danes[22]). The lagrangean function of the *min-max* problem is:

$$L = Y - \sum_{\phi} \lambda_{\phi}(1 - \sum_{i} K_{\phi i} X_i) \qquad (32)$$

with multipliers $\lambda_{\phi} \ge 0$. Then:

$$L = -\sum_i n_i^0\ ln(C_{1i}^{ref} X_i) - \\ -\sum_k \xi_k \left(\sum_i \nu_{ki} ln(C_{1i}^{ref} X_i) + \frac{\Delta G_k^0(T)}{RT} \right) - \\ -\sum_{\phi} \lambda_{\phi}(1 - \sum_i K_{\phi i} X_i) \qquad (33)$$

with $i = 1 \ldots N$, $k = 1 \ldots R$ and $\phi = 1 \ldots F$. The phase equilibrium constants $K_{\phi i} = 1$, in the reference phase.

An important observation is that the extents of reactions play the role of Kuhn-Tucker multipliers for chemical equilibrium constraints. The stationarity conditions for the lagrangean function are:

$$\nabla L(\mathbf{X}, \xi, \lambda) = 0 \qquad (34)$$

with the vectors $\mathbf{X} = (X_1, X_2 \ldots X_N)^t$, $\xi = (\xi_1, \xi_2 \ldots \xi_R)^t$, $\lambda = (\lambda_1, \lambda_2 \ldots \lambda_F)^t$. It results:

$$\frac{n_i^0 + \sum_k \nu_{ki}\xi_k}{X_i} = \sum_\phi \lambda_\phi K_{\phi i} \tag{35}$$

$$\sum_i \nu_{ki} ln(C_{1i}^{ref} X_i) + \frac{\Delta G_k^0(T)}{RT} = 0 \tag{36}$$

with multipliers $\xi_k \neq 0$, and

$$\sum_i K_{\phi i} X_i \leq 1 \tag{37}$$

with multipliers $\lambda_\phi \geq 0$. Thus, $\lambda_\phi > 0$ for phases that exist at equilibrium (constraints fulfilled with "=" sign), and respectively $\lambda_\phi = 0$ for phases that do not exist at equilibrium (constraints fulfilled with "<" sign).

The second important observation is that the Kuhn-Tucker multipliers of the phase equilibrium constraints give the amounts (mole numbers) of phases at equilibrium.

A consequence of the above equations (35, 36) is the balance of mole numbers:

$$\sum_\phi \lambda_\phi = \sum_i (n_i^0 + \sum_k \nu_{ki}\xi_k) \tag{38}$$

which reduces to

$$\sum_\phi \lambda_\phi = \sum_i n_i^0 \tag{39}$$

for the case of phase equilibrium without chemical reactions (Geană[16]).

The non-linear system of equations (35-37) can be solved to find the mole fractions in the reference phase, the extents of reactions and the phase amounts ($N + R + F$ unknowns). Rearrangement to equivalent equation systems leads to different algorithms for solving the problem, and allows the connection to the methods appeared in the literature and based on the classical equilibrium conditions.

Good starting approximations of phase compositions are obtained based on the finding of stationary points of the TPI function *Y*.

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