A Non-Ideal Multiphase Chemical Equilibrium Algorithm

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Abstract

Two non-ideal, multiphase chemical reaction equilibrium algorithms are presented. An approach to multiphase equilibrium calculations due to Abdel-Ghani *et al*. [1, 2] was modified to include reaction equilibrium, exploiting two proposals by Michelsen [3,4]. In both algorithms, nested processes are used with an inner loop treating the phases as ideal solutions and an outer loop updating non-ideal parts of the models. Both of the algorithms were initiated with a number of phases which was reduced in the outer loop by combining phases as they approach the same composition and density. Initiation strategies for phase amounts and compositions are presented.

Introduction

There is an extensive literature on phase and chemical equilibria calculations, most of which concentrates on ideal gas systems with a possibility of pure condensed, or solid, phases. Non-ideal systems have been a concern, but not a focus, in the computational aspects of chemical equilibria until recently. Zeleznik and Gordon [5] reviewed methods available prior to 1968, van Zeggeren and Storey [6] published the first monograph dedicated to this area, and Smith [7] wrote an additional review of the material just prior to Smith and Missen's [8] publication of a second monograph dedicated to chemical and phase equilibria calculations. Additional reviews include those by Seider *et al.* [9], Mather [10].and Seider and Widagdo [11].

The two papers closest to ours in intent are by Castier *et al*. [12] and Gupta *et al*. [13]. Both present methods for computing reaction equilibrium in non-ideal multiphase systems with more than one phase described by the same model. Determining a correct equilibrium when phases can split due to internal instability is a significant problem [14]. Both Castier *et al*. and Gupta *et al*. make use of a test of the stability of equilibrium that was proposed by Michelsen [15]. Castier *et al*. begin with a small number of phases, compute the reaction and phase equilibrium, test stability with respect to the addition of a new phase, then recalculate the equilibrium with an increased number of phases if an additional phase is

required. The process continues until a stable solution is reached. The steps during which stability is tested require iterative computations, with a number of trial phases covering the composition space as starting points in searching for alternative equilibrium phases. Gupta *et al*. begin with the maximum number of phases anticipated at equilibrium. Michelsen's test is used during the solution process in determining which of the phases initiated remains in the solution.

Basic issues in structuring calculation methods arise in the handling of the stoichiometry or mass conservation equations, the way the equilibrium criteria are posed, the form used for the chemical potential models and the choice of independent variables in the computations themselves. The C species in a reacting mixture are possibly distributed through π phases with molar amounts n_{ij} ; $i = 1, \cdots C$: $j = 1, \cdots \pi$. The jth phase has mole fractions x_{ij} and total amount β_j. The total moles of species i in all the phases is denoted by N_i, which can be calculated in two ways; i.e.,

$$N_i \equiv \sum_{j=1}^{\pi} n_{ij} = \sum_{j=1}^{\pi} \beta_j x_{ij} \tag{1}$$

Any chemical reactions can cause the total moles of the individual species to change but linear constraints (typically the equations representing conservation of the elements) must be obeyed. These constraints are written;

$$\mathbf{AN} - \mathbf{b} = \mathbf{0} \tag{2}$$

or,

$$\mathbf{A}\Delta\mathbf{N} = \mathbf{0} \tag{3}$$

where $\Delta\mathbf{N}$ is the difference between any two set of mole numbers that satisfy the constraints or, more particularly, $\Delta\mathbf{N} = \mathbf{N} - \mathbf{N^o}$, where $\mathbf{N^o}$ is a reference or initial set. The k components of vector **b** are constants determined by the content of the equilibrium system: i.e., $\mathbf{b} = \mathbf{AN^o}$. There are M linear constraint equations and the matrix **A** has elements a_{kj} ; $k = 1, \cdots M$: $i = 1, \cdots C$. We assume that any redundant equations have been eliminated

from equation (2) and that the number of species is at least equal to the number of constraint equations; i.e., $C \geq M$.

An alternative way to represent mass conservation is through chemical reactions and reaction extents. In this approach the mole numbers are tracked through a parametric solution of equation (3) in the form;

$$\Delta \mathbf{N} = \mathbf{N} - \mathbf{N^0} = \boldsymbol{\nu\xi} \tag{4}$$

where $\nu_{ik}; i = 1, \cdots, C: k = 1, \cdots, R$ is a matrix of stoichiometric coefficients and $\xi_k; k = 1, \cdots, R$ is a vector of reaction extents. The number of linearly independent reactions, *R*, is equal to $C - M$ given the assumption that there are no redundant equations in (2). The reaction coefficients can be found as solutions of:

$$\mathbf{A}\nu = \mathbf{0} \tag{5}$$

Smith and Missen [8] provide further analysis of these approaches to stoichiometry.

The equilibrium criteria are well known but must be stated carefully in calculations on multiphase systems where the number of equilibrium phases must be determined in the computations. At equilibrium, the chemical potential of a species *i* must have the same value in every phase actually present. In multiphase computations, some phases postulated may not actually be present at equilibrium. Michelsen [15] developed a "stability" test for phases not present at equilibrium based on the Gibbs tangent plane criterion. Equilibrium and stability can be expressed compactly by the relation:

$$\mu_{ij} - D_j = \hat{\mu}_i \tag{6}$$

where $D_j \geq 0$ and is zero for phases present. When these equations are satisfied, the variable, D_j, has a geometric interpretation as the minimum distance that the jth free energy surface lies above the common tangent plane that defines the equilibrium.

Reaction equilibrium criteria are super-imposed on the phase equilibrium and stability criteria in equation (6). These can be expressed in two equivalent ways. The first involves a

set of Lagrangian multipliers $\lambda_k\,;\, k = 1,\cdots,M$ that are introduced when the Gibbs free energy is minized under the constraints of equation (2). That is;

$$\hat{\mu} = RT\mathbf{A}^{\mathbf{T}}\lambda\,,\ \text{or,}\ \hat{\mu}_i = RT\sum_{k=1}^{M} a_{ki}\lambda_k \tag{7}$$

The alternative expression uses the stoichiometric coefficients in the reaction equations;

$$\boldsymbol{\nu}^{\mathbf{T}}\hat{\mu} = \mathbf{0}\,;\ \text{or,}\ \sum_{i=1}^{C} \nu_{ik}\hat{\mu}_i = 0 \tag{8}$$

In the calculations reported here, all the phase models are based on the same equation of state. Furthermore, all the phases are mixed phases and all components are constituents of every potential phase. The chemical potential of the ith component in phase j is written in terms of the fugacity, then the mole fraction and fugacity coefficient;

$$\mu_{ij} = \mu_i^0 + RT\ln f_{ij} = \mu_i^0 + RT\ln\left(x_{ij}\phi_{ij}P\right) \tag{9}$$

where μ_i^0 is the standard state chemical potential of i and is the same in all the phases. The computation of equilibrium and stability together is facilitated by introducing a composition variable equivalent to a mole fraction before normalizing, X_{ij}. In terms of this variable, equation (9) can be written;

$$\mu_{ij} + RT\ln\sum_{i=1}^{C} X_{ij} = \mu_i^0 + RT\ln X_{ij} + RT\ln\left(\phi_{ij}P\right) \tag{10}$$

$$\text{or,}\qquad \mu_{ij} - D_j = \mu_i^0 + RT\ln X_{ij} + RT\ln\left(\phi_{ij}P\right);\quad \text{with,}\ D_j \equiv -RT\ln\sum_{i=1}^{C} X_{ij} \tag{11}$$

and serves the purpose of the "minimum tangent plane distance" in the Michelsen [15] stability test. All the necessary equilibrium and stability criteria are met when X_{ij} and phase amounts are found that satisfy the mass balance constraints of equation (2), the phase equilibrium criteria in equation (6), and the reaction equilibria criteria in equation (7) or equation (8).

Computational Algorithms

Reaction equilibrium computational methods are routinely classified as "Stoichiometric" if reaction extents and equation (8) are employed to keep track of the stoichiometry and "Non-Stoichiometric" if Lagrangian multipliers and equation (7) are employed (Smith and Missen [8]). In this paper, we present adaptations of two algorithms recently proposed by Michelsen [3,4] for systems potentially containing many ideal phases. One of the Michelsen algorithms [3] is "Non-Stoichiometric" and the other [4] is "Stoichiometric". The adaptations are in the methods for dealing with non-ideal phases described by equations of state and in details of handling the equilibrium equations.

We use a nested approach in both algorithms described here. In an inner loop, the compositional dependence of fugacity coefficients is ignored and phase amounts and compositions that satisfy all the equations are found. Then the fugacity coefficients are updated in an outer loop and the process is repeated until outer loop convergence is obtained.

<u>Stoichiometric Algorithm.</u> The approach to mulitphase equilibrium computations of Abdel-Ghani *et al*. [1, 2] is used. The common chemical potential (hence, fugacity) for substance *i* in the coexisting phases is taken as a weighted average; i.e.,

$$\hat{\mu}_i = \left(\sum_{j=1}^{\pi} \beta_j \mu_{ij} \right) \Big/ \sum_{j=1}^{\pi} \beta_j \; ; \qquad \text{or, } \ln \hat{f}_i = \left(\sum_{j=1}^{\pi} \beta_j \ln f_{ij} \right) \Big/ \sum_{j=1}^{\pi} \beta_j \tag{12}$$

There is no particular composition associated with this average chemical potential and fugacity, but in these calculations of phase and reaction equilibria we have found it convenient to to write;

$$\hat{f}_i = \hat{x}_i \hat{\phi}_i P \tag{13}$$

Note that the product $\hat{x}_i \hat{\phi}_i$ is defined through this equation. Note also that phases present in zero amount (and in which the chemical potentials need not equal the chemical potentials in the other phases) do not contribute to the weighted sums. Also, the phase amounts do not

necessarily sum to unity and their sum may change as chemical reactions proceed and alter the total number of moles in the system.

Phase equilibrium K factors are defined using the average fugacity rather than the fugacity in any one of the coexisting phases. This definition yields;

$$X_{ij} = \left(\hat{\phi}_i / \phi_{ij}\right)\hat{x}_i = K_{ij}\hat{x}_i \tag{14}$$

The usual mass balances permit solution for the X_{ij} in terms of the phase amounts, giving;

$$X_{ij} = K_{ij}N_i / E_i\,; \qquad \text{where,} \qquad E_i \equiv \sum_{k=1}^{\pi} K_{ik}\beta_k \tag{15}$$

The $\hat{x}_i$ variables have dropped out of these equations and could have been fixed arbitrarily, however the choice $\hat{x}_i = N_i$ is one way to provide a convenient scaling for the equations.

<u>*Inner Loop Calculations*</u>. With a similar formulation (but differing in several details), Michelsen [4] showed that the stability, phase equilibrium and reaction equilibrium criteria are obtained as the minimum point of a convex function. The convexity of the function is a crucial property since it assures uniqueness of the minimum and serves as a guide in the development of solution procedures. The comparable function in our formulation is;

$$Q = \sum_{j=1}^{\pi}\beta_j + \sum_{i=1}^{C} N_i\left(\mu_i^0 / RT + \ln N_i\hat{\phi}_i P - \ln E_i - 1\right) \tag{16}$$

The function Q is minimized with respect to the phase amounts (which must be non-negative) and the reaction extents. The minimum point is characterized by

$$h_j \equiv \left(\partial Q / \partial\beta_j\right) = 1 - \sum_{i=1}^{C} N_i K_{ij} / E_i = 1 - \sum_{i=1}^{C} X_{ij} \begin{cases} = 0; \beta_j > 0 \\ > 0; \beta_j = 0 \end{cases} \tag{17}$$

and,

$$l_k \equiv \left(\partial Q / \partial\xi_k\right) = \sum_{i=1}^{C} \nu_{ik}\left(\mu_i^0 / RT + \ln\left[N_i\hat{\phi}_i P / E_i\right]\right) = \sum_{i=1}^{C} \nu_{ik}\hat{\mu}_i = 0 \tag{18}$$

Equation (17) with equations (12) and (14) assures that the chemical potentials within a phase present in a non-zero amount are equal to the equilibrium values. The inequality for

phases in zero amount assures that the missing phase should not form. Equation (18) is the equation for reaction equilibrium using the stoichiometric formulation.

Equations (17) and (18) can be solved efficiently and safely by Newton-Raphson iteration so long as precautions specified by Abdel-Ghani *et al*. [1,2] are observed. When a phase amount j is zero, ($\beta_j = 0$), it is not included as a variable in any equation other than $h_j = 0$. The Newton step size is controlled to permit only one β_j to move from positive to zero in a given iteration. Negative values are never permitted.

The Jacobian elements in the Newton-Raphson process are;

$$\partial^2 Q / \partial\beta_m \partial\beta_j = \sum_{i=1}^{C} X_{ij} X_{im} / N_i \; ; \qquad \partial^2 Q / \partial\xi_k \partial\xi_s = \sum_{i=1}^{C} \nu_{ik} \nu_{is} / N_i$$

$$\partial^2 Q / \partial\beta_j \partial\xi_k = -\sum_{i=1}^{C} \nu_{ik} X_{ij} / N_i \tag{19}$$

<u>*Outer Loop Calculations*</u>. In the outer loop, the mole fractions are normalized, the fugacities are all recalculated at the new compositions, then the K_{ij} are updated in the outer loop through the successive substitution relationship;

$$\ln K_{ij}^{(k+1)} = \ln K_{ij}^{(k)} - \left(\ln f_{ij} - \ln \hat{f}_i - \theta_j \right) \tag{20}$$

with

$$\theta_j \equiv -D_j / RT = -\ln \sum_{i=1}^{C} X_{ij} \tag{21}$$

Converged solutions from this process can include compositions of incipient phases, missing from the equilibrium mixture, which can enter if the temperature, pressure or overall composition is altered. The variables $\theta_j > 0$ and $\sum_{i=1}^{C} X_{ij} < 1$ indicate a kind of "distance" the conditions must be moved before the phase would appear.

<u>Non-Stoichiometric Algorithm</u>. In an extension of Michelsen's non-stoichiometric algorithms for ideal phases [3], we treat non-normalized mole fractions as dependent

variables determined by the Lagrangian multipliers. Equations (6), (7) and (10) are combined to give;

$$\mu_{ij} - D_j = \mu_i^0 + RT \ln X_{ij} + RT \ln\left(\phi_{ij} P\right) = \hat{\mu}_i = RT \sum_{k=1}^{M} a_{ki} \lambda_k \tag{22}$$

then solved for,

$$\ln X_{ij} = \sum_{k=1}^{M} a_{ki} \lambda_k - \mu_i^0 / RT - \ln\left(\phi_{ij} P\right) \tag{23}$$

<u>*Inner Loop Calculations*</u>. In the inner loop of these nested calculations, the fugacity coefficients are regarded as independent of the phase compositions. The independent variables are the phase amounts (the β_j) and the Lagrangian multipliers (the λ_k). The equations that must be satisfied are;

$$h_j = \left[\sum_{i=1}^{C} X_{ij} - 1 \right] \begin{cases} = 0; \beta_j > 0 \\ < 0; \beta_j = 0 \end{cases} \tag{24}$$

and the M linear mass balance constraints, written here as;

$$l_k = -b_k + \sum_{i=1}^{C} a_{ki} \left(\sum_{j=1}^{\pi} \beta_j X_{ij} \right) = 0 \tag{25}$$

These equations are used to solve for M Lagrangian multipliers and π phase amounts by Newton-Raphson iteration. Care in handling phase amounts at the zero constraint is necessary here, as in the "Stoichiometric" algorithm. Also, no more than M phases can be included in any one iteration to avoid having a singular Jacobian matrix.

The derivatives in the Jacobian matrix are;

$$\partial l_k / \partial \lambda_m = \sum_{i=1}^{C} a_{ki} a_{mi} N_i \; ; \;\; \partial l_k / \partial \beta_j = \partial h_j / \partial \lambda_k = \sum_{i=1}^{C} a_{ki} X_{ij} \; ; \;\; \partial h_j / \partial \beta_n = 0 \tag{26}$$

<u>*Outer Loop Calculations.*</u> The purpose of the outer loop is simply to update the fugacity coefficients to reflect the new phase compositions returned from the inner loop. The convergence criteria are the same as are used in the stoichiometric technique.

Initiation. A key step in the initiation is to determine which species are likely to be most abundant at equilibrium. In the stoichiometric procedure, linear programming is used to find the minimum of the function;

$$G = \sum_{i=1}^{C} N_i \left(\mu_i^0 / RT + \ln P \right) \tag{27}$$

subject to the constraints that $\mathbf{AN} = \mathbf{b}$ and all of the N_i are non-negative. The Simplex Method described in Chapter 10 of Fraleigh and Beauregard [16] is used. The method results in a solution with $C - M$ of the mole numbers zero, a reordering of the species and a modified constraint equation;

$$\mathbf{A}^* \mathbf{N}^* = \begin{bmatrix} \mathbf{I} & \mathbf{A_2} \end{bmatrix} \begin{bmatrix} \mathbf{N_{reactant}} \\ \xi \end{bmatrix} = \mathbf{b}^* \tag{28}$$

In equation (28), the vector of mole numbers has been partitioned demonstrating that a set of chemical reactions can be written immediately. Those reactions are:

$$\mathbf{N} = \begin{bmatrix} \mathbf{N_{reactants}} \\ \mathbf{N_{products}} \end{bmatrix} = \mathbf{N^o} + \nu\xi = \begin{bmatrix} \mathbf{b}^* \\ \mathbf{0} \end{bmatrix} + \begin{bmatrix} -\mathbf{A_2} \\ \mathbf{I} \end{bmatrix} \xi \tag{29}$$

These equations identify the mole numbers of $C - M$ "product" species as identical with the reaction extents and provide numerical values for the N_i^o. This process for constructing the chemical reactions taking place and the feed molar amounts reduces the likelihood of catastrophic cancellation in calculating mole numbers of trace species.

Positive reaction extents are required in order for computations to proceed. Initial values, ξ_k^0, are obtained from the reaction equilibrium equations (8), which, with the reactions in equation (29), can be rewritten;

$$\mu_{M+k}^0 / RT + \ln\left(\xi_k^0 P / \sum b^* \right) = -\sum_{i=1}^{M} \nu_{ik} \left[\mu_i^0 / RT + \ln\left(b_i^* P / \sum b^* \right) \right] \tag{30}$$

This initialization uses the feed molar amounts of the first M (reactant) species to compute mole fractions and treats the mixture as an ideal gas. Given the initial ξ_k values, all C of the mole numbers are calculated from equation (29). There is a possibility at this point that some of the mole numbers of "reactant" species may become negative. This can be avoided by dividing all the initial ξ_k by a constant factor. Positive feed mole fractions for all species are computed from $z_i^0 = N_i^0 \,/\, \sum_{k=1}^{C} N_k^0$.

Initial phase amounts and compositions that satisfy conservation of mass for $C+1$ phases are computed from;

$$\beta_j = \begin{cases} 1/C+1 & ;\ j=1 \\ z_{j-1}^0 C/(C+1) & ;\ 2 \le j \le C+1 \end{cases} \tag{31}$$

$$x_{ij} = \begin{cases} z_i^0 & ;\ j=1\,;\ 1 \le i \le C \\ 0.99 + 0.01 z_i^0 & ;\ 2 \le j \le C+1\,;\ i = j-1 \\ 0.01 z_i^0 & ;\ 2 \le j \le C+1\,;\ i \ne j-1 \end{cases} \tag{32}$$

The first of the phases is treated as a vapor, the others as liquids.

The non-stoichiometric procedure requires initial values for the M Lagrangian multipliers and the π phase amounts. The initial number of phases is set equal to the number of constituents plus one and the compositions of each of these phases is found from equation (32), using the feed composition for z_i^0. Fugacity coefficients, ϕ_{ij}^0, are evaluated. Then linear programming is employed to minimize the function;

$$G = \sum_{j=1}^{C+1} \sum_{i=1}^{C} n_{ij} \left[\mu_i^0 \,/\, RT + \ln \phi_{ij}^0 P \right] \tag{33}$$

subject to the linear constraints in equation (2), but treating each of the n_{ij} as independent. The **A** matrix, in this case, has dimension M by $C(C+1)$. The linear program returns only M positive mole numbers containing all the mass, distributed through as many as M phases.

These numbers are used as the phase amounts in the active phases at the start of the calculations. In addition, a reduced and reordered **A** matrix is obtained with a leading *M*-dimensional identity matrix. From this large **A** matrix, an $\mathbf{A}^*$ matrix with the dimensions as in equation (28) can be set up. The initial values of the *M* Lagrangian multipliers are found from;

$$\lambda_i = \mu_i^0 / RT + \ln \phi_{ij}^0 x_{ij}^0 P \; ; \; i = 1, \cdots, M \tag{34}$$

where mole fractions x_{ij}^0 are included in case an initial phase contains more than one species.

Once the phase amounts and the Lagrangian multipliers have been initiated, all the functions needed for updating and convergence of the inner loop can be evaluated.

Example

Space permits documenting the performance of the two algorithms in only one example, a system that was examined by Castier *et al*. [12] and Gupta *et al*. [13]. Methanol is produced from a mixture containing carbon monoxide, hydrogen, carbon dioxide and water. Also present are methane and normal octadecane as inert species. Potential reactions involving methane or octadecane conversion, such as steam reforming to carbon monoxide and hydrogen, are prevented by adding equations to the linear constraints showing that the two mole numbers are constants. The total number of constraint equations is $M = 5$ and the species count gives $C = 7$. The composition of the initial feed stream is shown in Table 1. The SRK equation with conventional mixing rules is used as the thermodynamic model, with ideal gas chemical potentials taken from [17]. The parameters used in the SRK model are the same as in [12] and [13].

The computations, as we carried them out, required initiation of 8 phases with chemical reactions that were dealt with through 2 reaction extents in the stoichiometric method or 5 Lagrangian multipliers in the non-stoichiometric method.

P (MPa)	Iterations St.	Iterations NSt.	Methanol Produced	Reaction Extent 1	Reaction Extent 2	Vapour Phase	Aqueous Phase	HC Phase
0.1[a]	6	7	0.0000	3.86E-03	3.82E-05	0.9654	(0.0079)[c]	0.0347
0.5	7	7	0.0010	3.82E-03	1.02E-03	0.9346	(0.0410)	0.0654
1	8	11	0.0040	3.64E-03	4.00E-03	0.9292	(0.0840)	0.0708
2	10	13	0.0138	3.08E-03	1.38E-02	0.9223	(0.1824)	0.0777
4	12	14	0.0376	2.03E-03	3.76E-02	0.9068	(0.4348)	0.0932
6	13	15	0.0599	1.36E-03	5.99E-02	0.8858	(0.7367)	0.1142
8	18	17	0.0867	9.24E-04	8.67E-02	0.8111	0.0415	0.1474
10	25	22	0.1381	4.05E-04	1.38E-01	0.4899	0.2957	0.2145
10.13	25	21	0.1402	3.79E-04	1.40E-01	0.4740	0.3082	0.2178
12[b]	20	21	0.1553	1.64E-04	8.72E-03	0.3374	0.4133	0.2493
14	21	23	0.1601	8.51E-05	3.98E-03	0.2760	0.4552	0.2688
16	21	24	0.1620	5.07E-05	2.14E-03	0.2397	0.4755	0.2848
18	21	24	0.1629	3.28E-05	1.28E-03	0.2128	0.4876	0.2996
20	21	25	0.1634	2.25E-05	8.18E-04	0.1903	0.4956	0.3141
25	21	24	0.1639	1.04E-05	3.31E-04	0.1421	0.5078	0.3501
30	22	26	0.1640	5.65E-06	1.63E-04	0.0982	0.5147	0.3871
35	23	26	0.1641	3.40E-06	9.05E-05	0.0552	0.5194	0.4254
40	22	28	0.1641	2.20E-06	5.51E-05	0.0120	0.5227	0.4653
45	23	35	0.1642	1.64E-06	3.87E-05	(0.9794)	0.5295	0.4705
50	31	33	0.1642	1.29E-06	2.90E-05	(0.9554)	0.5370	0.4630
55	43	57	0.1642	1.05E-06	2.23E-05	(0.9358)	0.5437	0.4563
60	24	34	0.1642	8.58E-07	1.75E-05		0.5496	0.4504
65	23	28	0.1642	7.14E-07	1.39E-05		0.5550	0.4450

Feed - CH_4: 0.0214 CO: 0.1071 H_2: 0.5286 CO_2: 0.0571
CH_3OH: 0.0000 H_2O: 0.2143 $C_{18}H_{38}$: 0.0715

Temperature is 473.15 K and methane is inert in all runs.

[a] Subsequent Reactions are: $H_2+CO_2 \rightleftharpoons CO+H_2O$ $3H_2+CO_2 \rightleftharpoons CH_3OH+H_2O$

[b] Subsequent Reactions are: $CH_3OH \rightleftharpoons CO+2H_2$ $CH_3OH+H_2O \rightleftharpoons 3H_2+CO_2$

[c] Parenthesis indicate an incipient phase, the number being the sum of the mole fractions.

Table 1 - Methanol Synthesis Example.

Table 1 summarizes the results of the computations at a temperature of 200 ^{o}C and over a pressure range from 0.1 MPa to 65 MPa. Pressure favors conversion of CO and CO_2 to methanol and virtually complete conversion is obtained at pressures above 30 MPa (which is a typical pressure at which methanol manufacture has been carried out).

The model used shows that three phases persist over the pressure range between roughly 8 MPa and 40 MPa. The liquid splitting is largely due to the presence of both water and octadecane in the mixture. At lower pressures, the water-rich liquid does not appear and at higher pressures, the lighter compounds such as hydrogen and methane dissolve in the two liquids and the light phase (which we refer to as a vapor) is absorbed.

The number of phases, which is initiated in this example at 8, is reduced by combining phases as they become identical. However, phases in zero amount but with mole fractions different from the coexisting phases are not deleted. The quantity $\sum X_{ij}$, which is less than 1 for these "incipient" phases, is given in parentheses in Table 1 in place of the phase amount.

The initiation schemes described permitted the two algorithms to arrive at the same result at all the pressures in the table.

In general, the non-stoichiometric technique was more difficult to control than the stoichiometric technique, at least in completing this example. In some cases, the inner-loop Newton-Raphson routine did not converge or produced large changes in the Lagrangian multipliers between iterations, sometimes on a scale that caused numerical overflow. These difficulties, and others, were easily avoided by using two separate damping factors: one factor to ensure that the Lagrangian multipliers did not change by more than 10% per iteration and another factor to ensure that, at most, only one of the phase fractions became zero during a single iteration. Phases that were not active at the start of the Newton-Raphson procedure were added if $\sum_{i}^{C} X_{ij}$ became greater than unity. The addition of a phase was permitted only after the third iteration, only one phase was added at a time,

according to which $\sum_{i}^{C} X_{ij}$ was larger, and the phase was introduced with an amount $\beta_j = 10^{-6}$.

The stoichiometric technique, once initialized as described with reaction extents that produced positive mole numbers for all species, was relatively trouble free. The chemical reactions that resulted from the linear programming step, depended on the specified pressure, and are indicated in Table 1.

Iteration counts in the outer loops of the two algorithms are shown in the Table. Inner loop iterations were typically 10-15 in the early stages, dropping to 3 later. The initial 8 phases were reduced to 3 in the outer loop of the algorithms in relatively few iterations and the total iteration count was not prohibitive at any pressure. The temperature of 200 ^{o}C is apparently not particularly close to any critical condition in these mixtures, or larger iteration counts could be expected. The maximum number of outer loop iterations occured at 55 MPa, near the pressure where it became impossible to locate an incipient phase rich in the light components. The disappearance of an "incipient" phase occurs when the phase becomes locally unstable, and this property is responsible for the high iteration count.

Conclusions

The two new algorithms proposed for phase and reaction equilibrium in non-ideal systems make use of Michelsen's techniques for ideal phases [3,4] in nested successive-substitution approaches. The possibility of several mixed phases being present at equilibrium is dealt with using the approach of Abdel-Ghani et al. [1, 2] which involves initiating the calculations with a large number of phases rather than adding phases if indicated by stability tests on converged solutions with fewer stages.

Iteration counts in the cases examined were not excessive.

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